

Silicone Wristbands as Personal Passive Samplers

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Supporting Information

ABSTRACT: Active-sampling approaches are commonly used for personal monitoring, but are limited by energy usage and data that may not represent an individual's exposure or bioavailable concentrations. Current passive techniques often involve extensive preparation, or are developed for only a small number of targeted compounds. In this work, we present a novel application for measuring bioavailable exposure with silicone wristbands as personal passive samplers. Laboratory methodology affecting precleaning, infusion, and extraction were developed from commercially available silicone, and chromatographic background interference was reduced after solvent cleanup with good extraction efficiency (>96%). After finalizing laboratory methods, 49 compounds were sequestered during an ambient deployment which encompassed a diverse set of compounds including polycyclic aromatic hydrocarbons (PAHs), consumer products, personal care products, pesticides, phthalates, and other industrial compounds ranging in log K_{ow} from -0.07 (caffeine) to 9.49 (tris(2-ethylhexyl) phosphate). In two hot asphalt occupational settings, silicone personal samplers sequestered 25 PAHs during 8- and 40-h exposures, as well as 2 oxygenated-PAHs (benzofluorenone and fluorenone) suggesting temporal sensitivity over a single work day or week ($p < 0.05$, power = 0.85). Additionally, the amount of PAH sequestered differed between worksites ($p < 0.05$, power = 0.99), suggesting spatial sensitivity using this novel application.



■ INTRODUCTION

Whether through work-related exposure, or interactions with the ambient environment, people are exposed to a complex mixture of natural and man-made chemicals. Chemical exposure may occur through dermal, oral, or inhalation pathways, and compounds such as polycyclic aromatic hydrocarbons (PAHs), pesticides, dioxins, and polychlorinated biphenyls have been studied for decades.¹ However, linking mixed chemical exposures to health effects is often difficult given the diversity of compounds and often low levels of exposure.^{2,3} Even in occupational circumstances where many chemicals of concern are identified, linking exposure to biological end points is challenging given the long latency of some diseases, the magnitude of the potential doses or interactions, and other confounders with exposure such as life behaviors and genetic variability.^{3,4} Because of this complexity, there is now a push to capture life-course environmental exposures from before birth onward recognized as the "exposome".⁵ To understand linkages between the exposome and resulting toxicity, researchers are developing new technologies and methods to characterize exposure to an ever larger range of compounds. Often however, environmental data are gathered from single time points which may not reflect average exposures in profile or magnitude. In contrast to single time point samples, active and passive sampling has been used to monitor PAHs and other organic chemicals with stationary and personal samplers.^{6–9} Although stationary samplers are

used in several occupational studies, personal samplers have the advantage of being more relevant to an individual.⁶ The most common personal samplers are active devices that pump air through filters that are extracted for target compounds. However, active personal devices are relatively expensive, require energy, and ultimately limited to implement on a wide scale.⁶ An alternative to active monitoring is passive sampling.

A report of a personal passive sampler was first published in 1973,⁸ but most growth in passive sampling and personal monitoring has occurred within the past decade.¹⁰ Passive sampling devices (PSDs) are used to sequester organic molecules through passive diffusion from water or air, and provide time-weighted averages of chemical concentrations.¹¹ Because chemicals continually accumulate in PSDs, the sensitivity of analytical detection is increased, and samplers represent time-averaged concentrations rather than episodic contamination.¹¹ PSDs have been used for personal monitoring starting with water vapor and SO₂ measurements,⁸ and have expanded to include organic contaminant classes like PAHs and PCBs in recent years.⁶ Materials used in passive sampling vary widely, and have included simple matrices like activated

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carbon,¹² as well as complex polymers like polyethylene and silicone.¹⁰

Historically, most personal monitoring samplers measure only one or a few compounds,¹³ but recently the applications of PSDs have expanded to entire compound classes in order to assess chemical mixtures. One recent example includes polyurethane foam (PUF) used as personalized passive samplers.¹⁴ While this material successfully sequesters hydrophobic PAHs, PCBs, and certain pesticides,⁶ it is unclear whether these samplers would be able to target less hydrophobic compounds and more volatile pesticides.¹⁵ In addition, it is unclear if future work will be able to exclude nontarget particulate sizes with a protective surface.¹⁴ In contrast, compounds reported in silicone PSDs represent only the vapor phase, which may encompass 34–86% of the toxicological dose of PAHs in industrial exposures.¹⁶ We wanted to demonstrate a PSD that can be used to measure PAHs and volatile organic compounds, but also one that captures personal care products, pesticides, and other compounds of emerging concern with a wide range of physicochemistry. Silicone is known to absorb a wide range of compounds in field applications from volatile benzene, toluene, ethylbenzene, and xylene compounds to more hydrophilic contaminants containing hydroxyl, ketone, or carboxyl groups.^{17,18}

We hypothesized that silicone material in commercial wristbands could be modified for use as a personal passive sampler in much of the same way silicone is used and demonstrated in environmental studies. By using wristbands as a personal passive sampler, it would have advantages as compared with active samplers mentioned previously, and result in data that represents time-weighted, vapor-phase concentrations. Our objectives were 3-fold: modify commercially available wristbands for analytical extraction, identification, and quantitation of target compounds; demonstrate sequestration of a wide physiochemical range to broaden potential usage of the personal PSD; and finally, present quantitated data in real-world occupational settings to examine if samplers provide useful sensitivity and selectivity in this novel application.

EXPERIMENTAL SECTION

Wristband and Precleaning Experiments. All solvents were Optima-grade (Fisher Scientific, Pittsburgh, PA) or equivalent, and all laboratory glassware or other tools were solvent-rinsed before use. Any water used in postdeployment cleaning or initial washes of commercial silicone was filtered through a Barnstead D7389 purifier (Dubuque, IA). Commercially available silicone bracelets were purchased in two sizes (width: 1.3 and 2.5 cm; inner diameter: 6.4 and 6.7 cm respectively; 24hourwristbands.com, Houston, TX), and were used in several configurations throughout the study (Figure 1). Weights of smaller width wristbands were similar regardless of pigmentation (orange: 5.67 ± 0.02 g; clear: 5.68 ± 0.02 g; orange/white: 5.71 ± 0.02 g; $n = 15$ for each color). Larger 2.5 cm wristbands weighed 10.38 ± 0.02 g, but only the smaller sized wristbands were used in quantitative work described below. Before deployment, oligomers and other material that might interfere with future chemical analyses were reduced with various solvents in material/solvent ratios similar to other published work.^{19–23} After several experiments to optimize the process with less solvents or cleaning time, the final procedure used nominally ≤ 65 g of silicone in 800 mL of

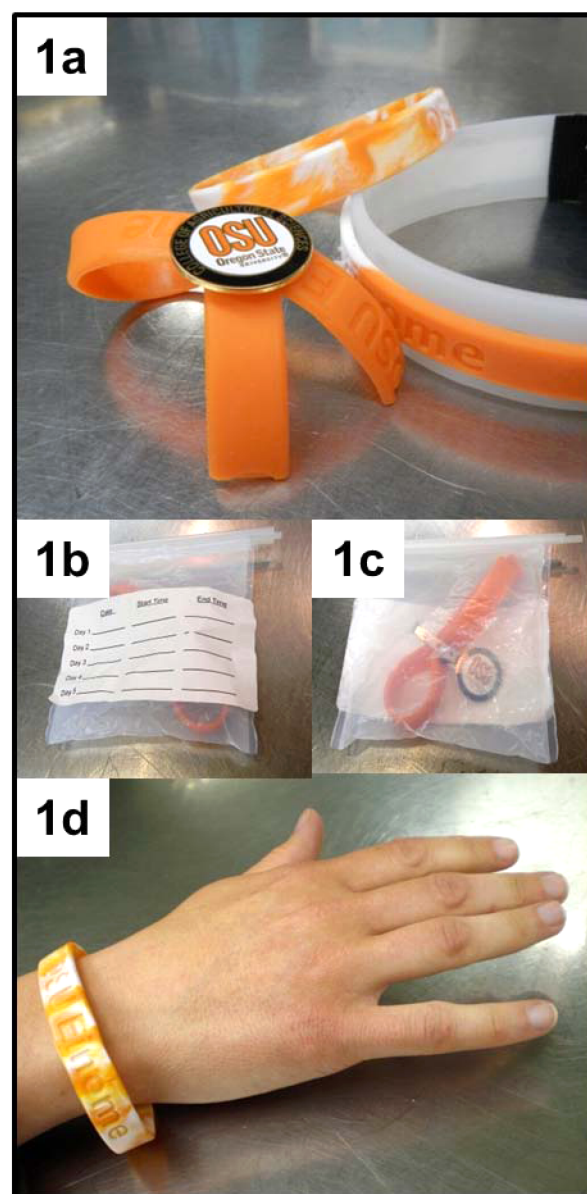


Figure 1. Examples of silicone personal sampling samplers. (a) Configurations of wristbands used in the study including a “single” wristband, one cut and worn as a “lapel”, and as a “stacked” wristband in which only the outer band was analyzed; (b–c) bags used for transport that were attached to track participant ID and exposure time in the occupational deployments; (d) single wristband deployment (debossed writing as pictured: “OSU EINOME”, Oregon State University Environmental Integrated Organic Monitor of Exposure).

mixed solvent for 5 exchanges. A mixture of ethyl acetate/hexane (1:1, v:v) was used for the first three exchanges, and ethyl acetate/methanol (1:1, v:v) was used for the last two exchanges. Each exchange occurred after a minimum of 2.5 h at 60 rotations per minute (VWR orbital shaker, Radnor, PA). Afterward, solvent-cleaned wristbands were placed in stainless steel canisters (AEB Kegs, Delebio SO, Italy) and dried under PUF filtered vacuum (≤ 3 days). Dried wristbands throughout the study were stored in either amber glass jars or in polytetrafluoroethylene (PTFE) airtight bags (Figure 1b–c) at 4 °C until needed. Prior to occupational field deployment, two wristbands from a batch of precleaned silicone were assessed to ensure cleaning processes were adequate for

quantitative analyses. Specifically, if the highest background peak had an area less than 15-fold of a spiked internal standard of 500 ng/mL, then that background level was considered adequate for deployment and quantitative analysis.

Extraction and Exposure Optimization. Reports of extraction of silicone vary widely from single soaking periods, to extended Soxhlet extraction over 90 h.^{22,24} To determine an adequate extraction method, precleaned silicone wristbands were infused with four deuterated PAHs similar to a previous method.²³ Briefly, acenaphthylene-D8, fluorene-D10, phenanthrene-D10, and pyrene-D10 were pipetted into a 1 L jar filled with approximately 50–100 g of silicone and a methanol/water (1:1, v:v) solution. Compounds were allowed to equilibrate for three days since the ratio of methanol/water used was 1:1 rather than 4:1 as originally described.²³ Using a 1:1 ratio requires less deuterated compounds in the infusing solution since more will partition to the silicone. Wristbands were dried as previously described, and then three rounds of extraction at two time periods of either 2 or 24 h were used to examine efficiency (Supporting Information (SI) Figure S1).

Postdeployment cleaning consisted of two rinses with purified water, and one rinse with isopropyl alcohol to reduce any water residue and further remove surface particulates (SI Figure S2). Field samplers were extracted twice with 100 mL of ethyl acetate on an orbital shaker at 60 rotations per minute (VWR) for nominally 2 h each time. Both rounds of extraction were combined and reduced to 1 mL (measured with premarked glassware) with closed-cell evaporators (Biotage LLC, Charlotte, NC). Samples were transferred and stored in amber chromatography vials at 4 °C.

To examine whether PAHs would degrade after sorption to the wristband, or if field/handling conditions would influence exposure concentrations, we again infused wristbands with several PAHs (fluorene-d10, benzo[b]fluoranthene-d12, fluorene, pyrene, and benzo[b]fluoranthene) and either exposed outdoors (in sun or shade) or within PTFE storage bags at approximately −20 °C, 23 and 35 °C. Additional details are described in the SI. Silicone PSDs were extracted and stored as described above.

Instrumental Analysis. Samples screened for 1182 chemicals of concern were analyzed using retention time locking automatic mass spectral deconvolution and identification software (AMDIS) on an Agilent 5975B gas chromatograph–mass spectrometer (GC-MS) with a DB-5MS column (Agilent) at an electron impact mode of 70 eV. The spectra were compared against in-house and purchased libraries of compounds that included pesticides, polychlorinated biphenyls (PCBs), parent and substituted PAHs, pharmaceuticals, phthalates, as well as other compounds. Prior to PAH and OPAH instrumental analyses, perylene-d12, and fluorofluorene-C¹³ were spiked at 500 ng mL^{−1} as internal standards, respectively. Instrument parameters to analyze PSD extracts for 33 PAH compounds and 22 OPAHs have been described previously.^{25,26} Analyses were performed on the same GC-MS and column described above but in selective ion mode rather than full scan. In addition, deuterated homologues of PAHs (7) and OPAHs (2) were used during the extraction process to monitor potential losses in the laboratory.^{25,26} For PAHs, sample concentrations were determined by the relative response of deuterated surrogates to target analytes in a 9-point calibration curve with correlation coefficients for each analyte greater than 0.98. OPAHs were also quantitated with a 9-point calibration curve with correlation coefficients >0.99, but

were not recovery corrected due to the availability of appropriate surrogates.²⁶

Ambient Demonstration. To determine if silicone wristbands could sequester a wide range of organic compounds, a public query was made to collect volunteers. Participants were instructed to wear a wristband continuously for 30 days including bathing, sleeping, or other activities. A total of 30 precleaned and dried wristbands were placed inside three amber jars, and metal tongs were used by participants as they took one or two wristbands to wear. A sign-out sheet was used to track the number of wristbands a participant took (1 or 2), but no surnames or personal information was asked or collected during this initial demonstration. At the end of the 30 day period, small (250 mL) amber jars were used to collect each individual wristband and were stored at −20 °C until postdeployment cleaning and extraction. In addition, three nondeployed wristbands were placed inside amber jars at room temperature to serve as controls for potential laboratory or processing contamination.

Occupational Application. To meet our final objective, we deployed silicone PSDs to roofers using hot asphalt since occupational environments represent relevant exposures, and we focused on PAH quantitation since this compound class is of toxicological concern for this occupation.^{3,4} Our occupational study was approved by the institutional review board (IRB) of Oregon State University, and roofers were recruited to wear the silicone personal samplers while working with hot asphalt. To see if reduced skin contact would improve chemical analyses, each roofer wore three designs of silicone personal samplers simultaneously: a single wristband like the initial ambient study, a cut wristband pinned as a lapel on a shirt collar, and a stacked wristband in which an inner silicone band protected the outer band from sweat and oils (Figure 1a). Hereafter, each configuration will be referred to as either single, lapel, or stacked, respectively. In the first setting, three workers wore PSDs for both a single day (approximately 8 h), and for a representative workweek (32–39 h) while refurbishing a roof at an active worksite. Due to availability, only the single and lapel configurations were worn for 8 h while all three configurations were worn for the representative workweek. Both the single and multiday deployments began on the same day. At the second site, five preapprentice roofers wore all three silicone PSD configurations throughout an 8-h shift at a training facility. Before either deployment, each sampler was placed into prelabeled PTFE bags (Figure 1b–c). Nitrile gloves were used before and after each shift by nonparticipants when handling PSDs. In the case of the multiday deployment, PSDs were returned at the beginning of the next available shift after overnight storage at 4 °C. Travel blanks consisting of precleaned silicone PSDs in PTFE bags were used at each setting and type of deployment (single or multiday). Additional roofing information is available in SI.

Quality Control and Statistics. Over 40% of instrumental samples were for quality control (QC) purposes. QC samples not already mentioned included instrument check standards run before and after each set of samples (every 10 or less) as well as laboratory solvent blanks. PAHs and OPAHs in check standards had to be within 20% of the true value before samples would be allowed to proceed with analysis. Nondeployed wristbands were used during postdeployment cleaning to ensure there was no contamination or compound carryover between samples. For AMDIS analysis, only compounds above a 60% mass spectral match were considered

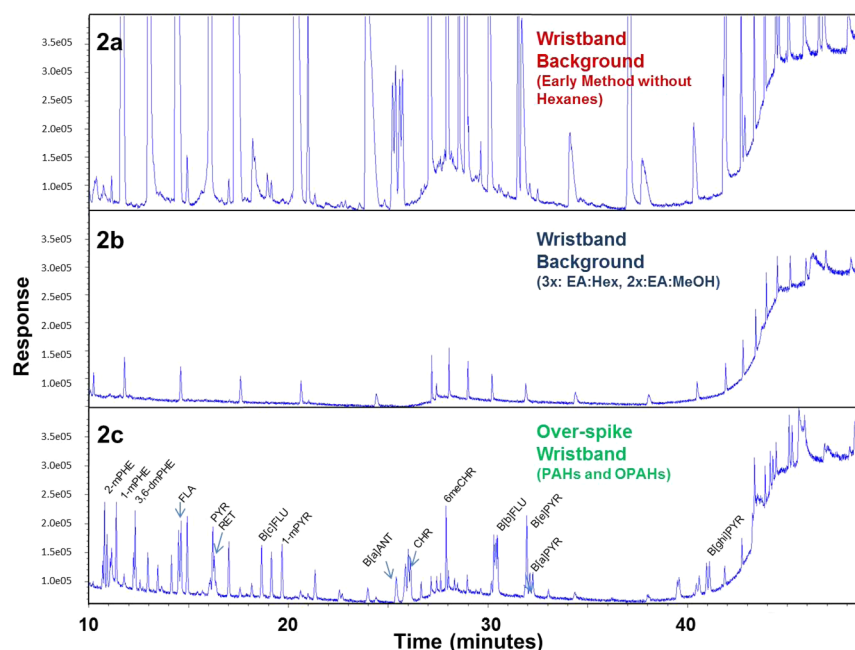


Figure 2. Total ion chromatograms of wristband extracts through stages of cleaning and overspike on the GC-MS. All chromatograms are scaled equally to easily show differences in chromatograms. (a) A wristband background with five rounds of ethyl acetate/methanol. (b) The addition of hexane to solvent precleaning drastically reduced total background interferences. Peaks here were identified as forms of siloxanes from mass spectral comparisons to NIST libraries. (c) Notable peaks of the overspike chromatogram are labeled with corresponding PAH abbreviations.

for chemist review. Deconvoluted results are compared against reference spectra for each target analyte, and if multiple lines of evidence (ex: correct ratios of ions, larger ions more representative of the parent ion, and retention time match) are present, then an analyte is considered as identified in the sample. Any compounds identified in controls or laboratory blanks were removed from the initial ambient demonstration since AMDIS results are descriptive as presented. Any quantitated compounds in blanks from PAH or OPAH methods are described in the Results section.

Multivariate statistics were performed on ambient data using R statistical software (R development core team, Vienna, Austria). Identification data was converted into binary values, and a nonmetric multidimensional scaling model was used to graphically represent the data with Jaccard distance. For occupational comparisons, after normality and equal variance tests passed criteria, parametric *t* tests were performed in Sigmaplot (Systat Software Inc., San Jose, CA) with an assumed alpha value of 0.05. The power and *p*-value for the *t* tests are listed for each result described below. In this demonstration, PAHs were not back-calculated to atmospheric concentrations since meaningful comparisons could already be made and address our original objectives of sensitivity and selectivity in a real-world exposure.

RESULTS AND DISCUSSION

Laboratory Method Development. Initially, silicone background was reduced similar to other methods in either solvents used or extraction times.^{19–21,23} While this initial methodology allowed compounds to be identified without postextraction silica cleanup used in other work,^{19,23,24} improvements were sought to further reduce cleanup time and siloxane background (Figure 2a). After optimization experiments, cleanup was improved by incorporating hexanes in addition to ethyl acetate and methanol. Additionally, a

reduction of precleaning time was achieved in under two days versus five (Figure 2b). After the cleanup method was finalized, all compounds reported in this work (PAHs and OPAHs) were spiked with silicone wristbands, extracted through the laboratory procedure, and quantitated within 26% of the true value (Figure 2c).

In extraction efficiency experiments, over 90% of the total amount of acenaphthalene-D8, fluorene-D10, phenanthrene-D10, and pyrene-D10 were extracted with the first round of ethyl acetate (SI Figure S1). Less than 6% and 5% were extracted with a second and third round, respectively. Variability of infused wristbands used for these extraction experiments had less than 13% relative standard deviation across all time points and compounds. PAHs with lower hydrophobicity had lower extraction efficiency over the first round of solvent, but all four compounds were $\geq 96\%$ of the final extracted amount after two rounds of extraction. The total amount of compounds did not differ whether treatments were 2 or 24 h (892 ± 60 ng/mL or 878 ± 47 ng/mL, respectively).

In the sun/shade experiment, we did not observe any statistical difference between PAHs over a four-hour period (SI Figure S4). This preliminary evidence suggests there was no photodegradation of 5 PAHs once sequestered into the PSD, which is consistent with a previous observation that PAHs sorbed to fly ash have reduced photo-oxidation.²⁷ Further study would be needed to examine PAH stability of longer time periods and varied irradiance, but for the purposes of this initial paper, potential degradation of sorbed analytes was not of concern. Additionally, no difference was observed among transport temperatures in PTFE bags (SI Figure S5). Our data suggests that transportation in PTFE bags with temperatures as high as 35 °C and transport times up to 72 h does not affect target analyte recovery. Stability during PTFE transport is consistent with similar work with PAHs and pesticides in polyethylene passive samplers (manuscript submitted).

Table 1. Compounds Identified from AMDIS Spectra against Chemical Libraries during Ambient Exposures^a

groups	compounds	CAS	log K_{ow}	no. of WBs	possible use or occurrence
PAHs	1-methylnaphthalene	90–12–0	3.87	16	compounds from petrogenic and pyrogenic sources
	anthracene	120–12–7	4.45	6	compounds from petrogenic and pyrogenic sources
	fluorene	86–73–7	4.18 ^a	5	compounds from petrogenic and pyrogenic sources
	1,6-dimethylnaphthalene	575–43–9	4.26 ^a	4	compounds from petrogenic and pyrogenic sources
	1-methylphenanthrene	832–69–9	5.08 ^a	3	compounds from petrogenic and pyrogenic sources
	1,2-dimethylnaphthalene	573–98–8	4.31 ^a	2	compounds from petrogenic and pyrogenic sources
	acenaphthylene	208–96–8	4.07	1	compounds from petrogenic and pyrogenic sources
	pyrene	129–00–0	4.88	1	compounds from petrogenic and pyrogenic sources
consumer products	retene	483–65–8	6.35 ^a	1	compounds from petrogenic and pyrogenic sources
	tonalide	1506–02–1	5.70	20	fragrance in cosmetics, detergents, fabric softeners, household cleaning products
	carvone	99–49–0	3.07 ^a	14	oil of caraway seeds, used in perfumes, soaps
	triclosan	3380–34–5	4.76	9	active agent in deodorants and antiseptic products
	caffeine	58–08–2	–0.07	6	common component of coffee, sodas, and other beverages
	nicotine	54–11–5	1.17	4	active ingredient in tobacco products
	eugenol	97–53–0	2.49	4	clove perfumes, essential oils, dental medicine (analgesic)
	celestolide	13171–00–1	5.93(est) ^b	2	musk fragrance in cosmetics or perfumes ^a
pesticides	musk ketone	81–14–1	4.30	1	fragrance in cosmetics, perfumes
	phthalide	15323–35–0	5.85(est) ^b	1	musk fragrance ^a
	phthalimide	85–41–6	1.15	1	used in dyes, fungicide
	benzyl benzoate	120–51–4	3.97	18	acaricide and Insecticide
	<i>N,N</i> -diethyl- <i>m</i> -toluamide	134–62–3	2.02	11	insect and acarid repellent used for households and domestic purposes (DEET)
	promecarb artifact	3228–03–3	3.52(est) ^b	6	possible metabolite of a nonsystemic contact insecticide
	methoprene	40596–69–8	5.50	5	broad spectrum insecticide
	fipronil	120068–37–3	4.00	3	insecticide designed for pet use targeting fleas and ticks
phthalates	fipronil-sulfone	120068–36–2	4.42(est) ^b	2	metabolite of fipronil ^c
	fipronil, desulfinyl-	111246–15–2	4.22(est) ^b	1	photodegradeate of fipronil ^c
	trifluralin	1582–09–8	5.34	1	pre-emergent herbicide
	diethyl phthalate	84–66–2	2.47	23	vehicle for fragrances and cosmetics
	butyl benzyl phthalate	85–68–7	4.73	19	plasticizer for floor tile, foams, carpet backing
	di- <i>n</i> -octyl phthalate	117–84–0	8.10	11	plasticizer for cellulose and vinyl resins
	di- <i>n</i> -hexyl phthalate	84–75–3	6.82	9	used in making plastisols, which are used for dip-molded plastics and automobile parts
	dicyclohexyl phthalate	84–61–7	6.20 (est)	6	plasticizer for cellulose, chlorinated rubber, and other polymers
industrial compounds	dimethylphthalate	131–11–3	1.60	5	plasticizer for cellulose and vinyl resins
	benzophenone	119–61–9	3.18	19	used in paints, cosmetics, pesticides, pharmaceuticals, and as a fragrance enhancer
	triphenyl phosphate	115–86–6	4.59	15	fire retardant in cellulose products, roofing paper, plasticizer in lacquers and varnishes
	tris(2-butoxyethyl) phosphate	78–51–3	3.75	4	plasticizer in rubber gaskets and floor care products
	tributyl phosphate	126–73–8	4.00	5	a fire retardant, plasticizer, antifoaming agent, also found in hydraulic fluid
	2-methylphenol	95–48–7	1.95	4	a solvent, disinfectant, and/or chemical intermediate in several industries
	tris(2-chloroethyl) phosphate	115–96–8	1.44	3	flame-retardant plasticizer in vinyl resins, used in carpet backing or upholstery
	tris(2-ethylhexyl) phosphate	78–42–2	9.49 ^a	3	flame-retardant plasticizer in vinyl resins, and antifoaming agent
	o-tricresylphosphate	78–30–8	6.34	2	flame-retardant plasticizer in lacquers, varnishes, vinyl resins, coatings, and adhesives
	triethylphosphate	78–40–0	0.80	2	as a solvent/plasticizer in cellulose gums, a component of resins and plastics
	o-phenylphenol	90–43–7	3.09	2	a citrus fungicide, lumber disinfectant, preservative and sanitizing agent
	m-cresol	108–39–4	1.96	2	in synthetic resins, disinfectants, fumigants, photographic developers, explosives
	p-tricresylphosphate	78–32–0	6.34	1	in cellulose, vinyl and rubber products, also a sterilizing agent for surgical instruments

Table 1. continued

groups	compounds	CAS	log K_{ow}	no. of WBs	possible use or occurrence
	2,4-dimethylphenol	105–67–9	2.30	1	used as an disinfectant, fungicide, sanitizer, and virucide in agriculture and/or hospitals
	4-methylphenol	106–44–5	1.94	1	used in resins, petroleum, photography, paints, and as a disinfectant and fumigant

^aUnless otherwise noted, log K_{ow} and compound occurrence information was acquired from the Hazardous Substances Data Bank by the National Library of Medicine. Abbreviations: WBs, wristbands; est, estimated values. ^aNational Library of Medicine, (NLM 1993). ^bEstimated from EpiSuite EPA (EPIWEB 4.1). ^cNational Pesticide Information Center, (NPIC 2009).

Ambient Demonstration. A wide range of compounds were identified from the ambient wristband extracts from 22 participants, with log K_{ow} properties ranging from -0.07 (caffeine) to 9.49 (tris(2-ethylhexyl) phosphate) listed in Table 1. In contrast, a recent publication required that two PSDs materials together in an environmental deployment were needed to obtain a similar range of chemistry (K_{ow} : caffeine -0.07 to DDT 6.91).²⁸ In total, 49 different compounds were identified in our study, including PAHs, consumer and personal care products, pesticides, phthalates, and other industrial compounds (Table 1). Most individual compounds were PAHs, or consisted of industrial compounds typically used as flame retardants, plasticizers, or used in synthetic material manufacturing (Table 1).²⁹ The two most detected compounds are diethyl phthalate (all samples) and tonalide (20 of 23), both of which are used in personal care products like fragrances or cosmetics.²⁹ Home-use pesticides like *N,N*-diethyl-*m*-toluamide (DEET) and fipronil (pet flea medicine) were identified in several samples as well as consumer product ingredients like caffeine and nicotine. Many of the individual compounds listed in Table 1 have been previously sequestered in environmental studies using silicone,^{18,30} and all of the compound classes have been associated with human exposures through previous research.^{2,31,32} Overall, results from these personal silicone samplers represent a wide diversity of bioavailable compounds, and appear to be different among individual participants using the nonmetric multidimensional scaling model (SI Figure S3). Further enhancements and separation of unique profiles of exposure should be possible once squalene and free fatty acids detected from full scan analysis are reduced by minimizing skin contact (in placement or duration as demonstrated in the occupational study).

Along with prominent skin components, caffeine and other relatively nonvolatile compounds in Table 1 were likely taken up through direct contact, and wristband passive samplers may be beneficial in cases where less volatile metabolites or unchanged parent compounds are targeted in human exposure estimates. However, further evidence of this route of exposure is needed before studies may exploit this potential sampling attribute while separating out interferences from skin components. For the purposes of the occupational study discussed below, several silicone configurations (single, lapel, and stacked) were used to evaluate changes, if any, with skin contact during these shorter exposure periods.

Occupational PAH Results. A total of eight roofers were silicone passive samplers, with three at an active worksite (nos. 1–3, Figure 3a), and five at the training center (nos. 4–8, Figure 3a). No discomfort or work interference was reported from the samplers regardless of configuration. All extracted samplers contained measurable levels of PAHs, 12 of which are on the EPA priority list.³³ In addition, two OPAHs (benzofluorenone and fluorenone) were detected and quantified

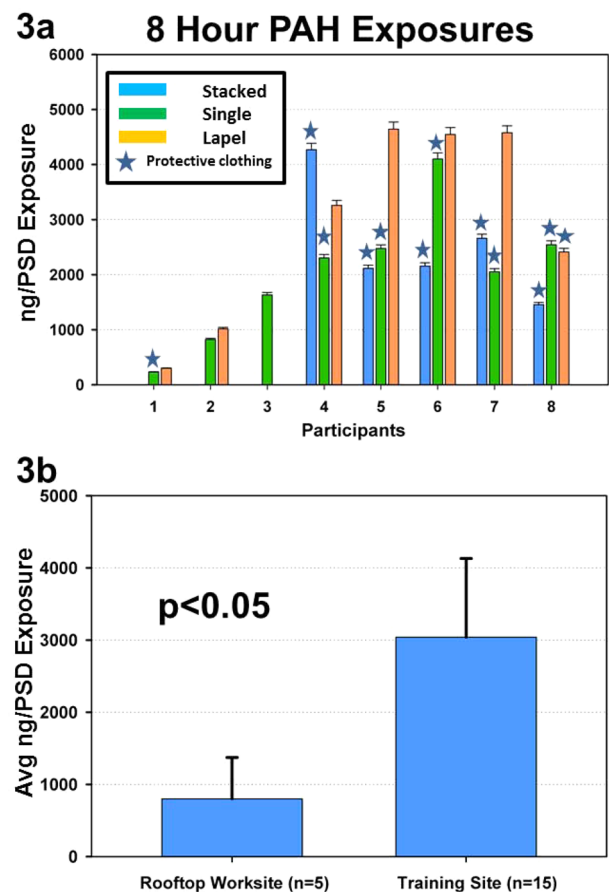


Figure 3. Three silicone passive sampler designs sequestering PAHs in a single work day. (a) All samplers from both occupational settings are pictured including those from nos. 1–3 at a rooftop worksite, and nos. 4–8 at the training facility. The lapel corresponding to no. 3 was lost during the field deployment. Standard deviations here are derived from nondeployed wristbands ($n = 5$) representing laboratory and instrumental variability spiked with all target PAHs (average RSD: 2.30%). Blue stars represent silicone passive samplers that were reported as covered with protective clothing during exposure. (b) Overall exposures between sites differed significantly over an 8 h work period ($p < 0.05$). Standard deviations here are the result of all samplers pooled together from each participant.

able in both occupational settings. OPAHs are not typically monitored in asphalt exposures, so this represents some of the first evidence of a potential data gap in occupational exposure. Total PAHs ranged from 230 to 4600 ng/PSD (Figure 3a) and trip blank PAH concentrations were all below 11 ng/PSD. Therefore, wristbands were extremely sensitive even after only 8 h of exposure, and individual PAH concentrations from silicone PSDs exceeded instrument detection limits from 2 to over 1400 fold. In addition, blanks had PAHs below

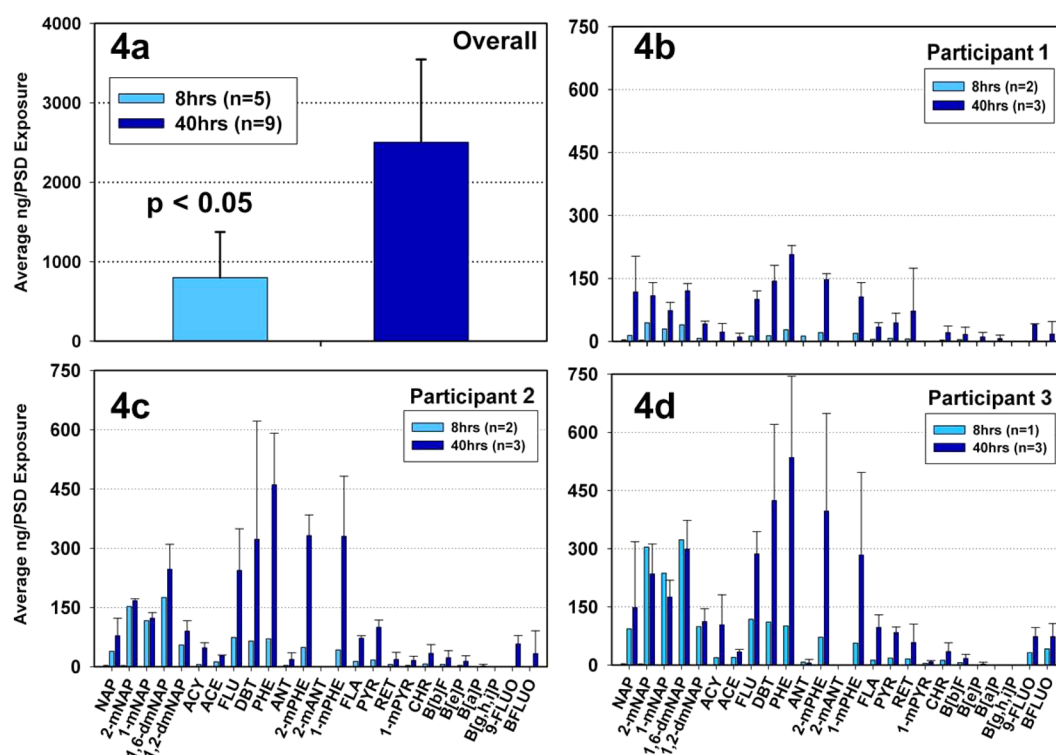


Figure 4. Worksite PSDs (all configurations) with sum (4a) and individual PAH exposure (4b–d) for a single (8 h) or multiday period (40 h). Individual profiles are scaled equally to observe differences in magnitude and profile between silicone samplers. Standard deviations are the result of PSDs pooled together from each participant.

detection for 31 of the 33 PAHs measured, with only naphthalene or 2-methylnaphthalene as background PAHs. However, levels of these two PAHs in blanks were negligible, considering average background from either PAH was nominally 3-fold lower or more than any individual's deployed sample. There were no detectable OPAHs in any blank. Individual PAH surrogate recoveries ranged from 53 to 122% (average = 91%, median = 94%) while OPAH surrogate recoveries ranged 64–120% (average = 83%; median = 82%).

While the chromatography was easier to interpret for lapel and stacked designs, all PAHs and OPAHs were able to be identified and accurately quantified in all three configurations at all exposure durations. Although sample sizes are small at either site, there is no statistical difference between configurations ($p > 0.05$, power < 0.8, SI Figure S6). However, in some cases both single and stacked designs had lower concentrations than lapels for some roofers (participants nos. 5, and 7, Figure 3a), and after reviewing participant questionnaires it was determined that these wristbands (either in stacked or single configurations) were worn underneath protective clothing. In the case of participant 8, who had a lower value for the lapel than other roofers, the survey data indicated that this lapel was covered as well. Not all discrepancies can be explained with protective clothing information (participant 4's stacked wristband was reportedly covered yet is the highest value for that individual), but in future occupational applications, it would be important to indicate how the sampler should be worn with respect to personal protection equipment. Even though PSDs are sequestering the vapor phase, it is likely that personal protection equipment impacts the level of exposures seen by restricting air flow with respect to a noncovered PSD. Further study would be needed to explore this idea, and this potential

application of evaluating the effectiveness of protective clothing. Ultimately however, designs did not significantly differ, and all PSDs from each individual were pooled together to observe the trends described below.

Regarding temporal sensitivity, there was a significant difference between single day or multiday exposures ($p < 0.05$, power = 0.85, Figure 4a). Interestingly, 22 out of 23 PAHs and OPAHs detected in the 40 h deployment were also detected in the 8 h deployment, further illustrating the capability of the sampler for typical 8 or 10 h time-weighted averages. Benzo[a]pyrene was not detected in the 8 h deployment, but benzo[e]pyrene was quantitated, refuting the inference that larger PAHs would not be able to be detected in a shorter exposure period. Additionally, because benzo[a]pyrene was just above reporting limits after nominally 40 h of exposure, it is likely that this compound was too low for our methods to quantitate at 8 h, rather than a failure of the sampler itself. Phenanthrene and alkylated phenanthrenes were the most common and most abundant individual PAHs (Figure 4b–d). Other atmospheric PAH profiles report the prominence of phenanthrene in hot asphalt exposure,³⁴ and it has the highest emission rate out of 14 PAHs measured in working asphalt.⁴ Unexpectedly, naphthalene and alkylated homologues (Figure 4c–d) were higher in 8-h over 40-h deployments. Differences in compound equilibrium between silicone and the atmosphere could explain naphthalene concentrations over time, and it is known that naphthalene is difficult to interpret with work-related exposure due to confounders such as cigarette smoking.³⁵ In fact, participants 2 and 3 did report cigarette use, while participant 1 did not. However, due to the small sample size, we are reluctant to over interpret the results here.

At both occupational sites personal silicone samplers were worn for approximately one 8 h work day. While this small study cannot examine specific differences between worksites, we make the following casual observation about spatial sensitivity as detected by our passive sampler. Individuals at the rooftop site had similar profiles of PAH exposure, but differed in magnitude between participant 1 and participants 2–3 (Figure 4b–d). Survey information indicated participant 1 was a safety monitor at the worksite, while the other two participants were journeymen roofing professionals that reported directly handling hot asphalt. In another example, exposures were compared between occupational settings, and a significant difference was seen between study sites ($p < 0.05$, power = 0.99, Figure 3b). The training center had a higher average PAH concentration than at the worksite (training center: 3040 ± 1090 ng/PSD; worksite: 800 ± 570 ng/PSD). Survey reports indicated that while hot asphalt was used in a similar manner at both sites, there was a difference between work enclosures. At the training center, hot asphalt is used to build a simulated roof at ground level in a semienclosed outdoor space. In contrast, hot asphalt was used on the rooftop only after the old roofing material was taken out, reducing some of the asphalt exposure. Taken together, spatial evidence supports the use of silicone wristbands as sensitive personal monitoring PSDs for exposures in a real world application. However, since we did not expect this level of sensitivity, additional work should be carried out to explore more specific differences between individual exposures.

Silicone personal samplers present an innovative sampling technology platform producing relevant, quantifiable data. By using these passive samplers, an atmospheric, time-weighted average concentration over an exposure period can be compared with exposure limits and compliance measurements through in situ calibration. Future work using isotope-labeled performance reference compounds to obtain in situ sampling rates will be done by infusing these compounds into PSDs prior to use.^{23,36–38} Studies utilizing this sampler are currently underway, and we hope this easy-to-wear and dynamic application of silicone may become a valuable tool to address challenges of the exposome and mixture toxicity.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional roofing information; extraction efficiency under two time treatments with four labeled PAHs (Figure S1); photographic demonstration of postdeployment cleaning (Figure S2); graphical representation of nonmetric multidimensional scaling of binary ambient wristband data (Figure S3); sun and shade 4 h exposures of infused silicone samplers (Figure S4); simulated transport conditions at three temperatures (Figure S5); and sample configurations from eight hour training PSD exposure (Figure S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

NAP:	naphthalene
2-mNAP:	2-methylnaphthalene
1-mNAP:	1-methylnaphthalene
1,6-dmNAP:	1,6-dimethylnaphthalene
1,2-dmNAP:	1,2-dimethylnaphthalene
ACY:	acenaphthylene
ACE:	acenaphthene
FLU:	fluorene
DBT:	dibenzothiophene
PHE:	phenanthrene
ANT:	anthracene
2-mPHE:	2-methylphenanthrene
2-mANT:	2-methylanthracene
1-mPHE:	1-methylphenanthrene
3,6-dmPHE:	3,6-dimethylphenanthrene
FLA:	fluoranthene
PYR:	pyrene
RET:	retene
B[c]FLU:	benzo[c]fluorene
1-mPYR:	1-methylpyrene
B[a]ANT:	benzo[a]anthracene
CHR:	chrysene
B[b]FLA:	benzo[b]fluoranthene
B[e]PYR:	benzo[e]pyrene
B[a]PYR:	benzo[a]pyrene
B[g,h,i]PYR:	benzo[g,h,i]pyrene
9-FLUO:	9-fluorenone
BFLUO:	benzofluorenone

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