# Silicone Wristbands as Personal Passive Samplers

*Kim A. Anderson, Steven G. O'Connell, Laurel D. Kincl* ‡
Environmental and Molecular Toxicology, Oregon State University, Corvallis, OR
‡College of Public Health and Human Sciences, Oregon State University

fses.oregonstate.edu
citizen.science.oregonstate.edu

## Introduction

**Active-sampling approaches are commonly used for personal monitoring, but are limited by energy usage and data that may not represent bioavailable concentrations. Current passive techniques are popular, but often involve extensive preparation, or are developed for only a small number of targeted compounds. We present a novel application for measuring environmental, bioavailable exposure with silicone wristbands as personal passive samplers.**


Examples of passive wristband samplers (PWSs)

## Approach and Study Design

Laboratory methodology affecting pre-cleaning, infusion, and extraction were developed using commercially available silicone, and chromatographic background interference was reduced after solvent cleanup with good extraction efficiency (>96%).

In a 30-day ambient deployment with volunteers, 49 compounds were sequestered 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) (See Table).

In two occupational settings where hot asphalt was being applied, the PWS sequestered 25 PAHs during 8- and 40-hour exposures, as well as 2 oxygenated-PAHs (benzofluorenone and fluorenone) suggesting sensitivity of the devices 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 evidence of spatial sensitivity and diverse applications.

Configurations of PWSs during deployment and transport

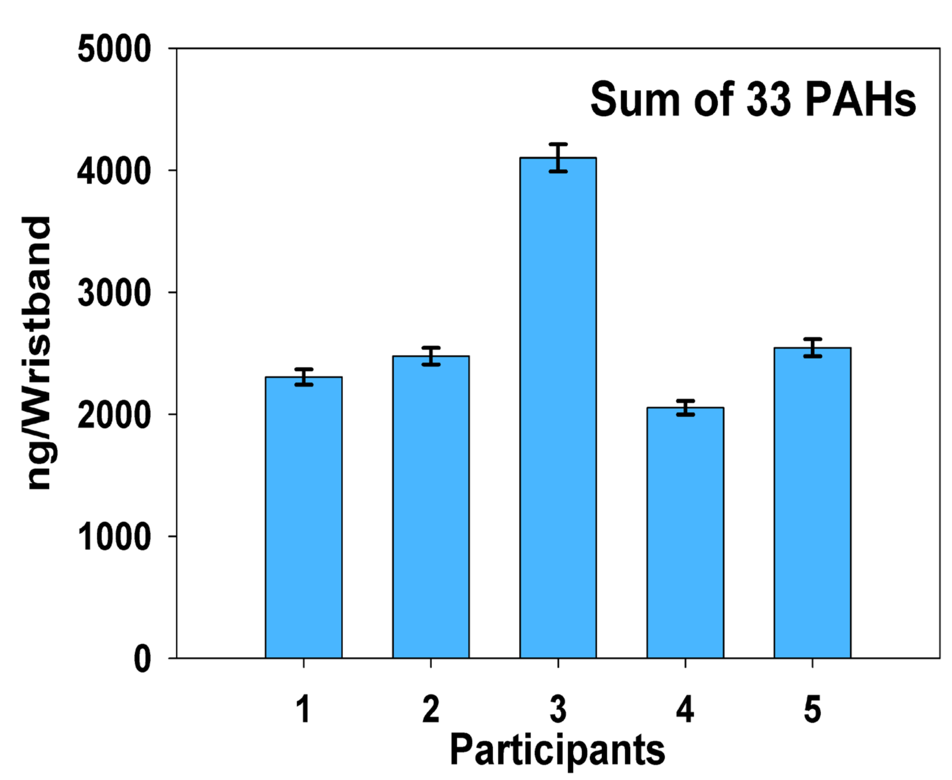
## Ambient Results: Compounds identified in volunteers after 30 days

| Groups | Compounds | CAS | log $K_{ow}$ | # 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 | 5 | Compounds from petrogenic and pyrogenic sources |
| | 1,6-Dimethylnaphthalene | 575-43-9 | 4.26 | 4 | Compounds from petrogenic and pyrogenic sources |
| | 1-Methylphenanthrene | 832-69-9 | 5.08 | 3 | Compounds from petrogenic and pyrogenic sources |
| | 1,2-Dimethylnaphthalene | 573-98-8 | 4.31 | 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 |
| | Retene | 483-65-8 | 6.35 | 1 | Compounds from petrogenic and pyrogenic sources |
| Consumer Products | Tonalide | 1506-02-1 | 5.70 | 20 | Fragrance in cosmetics, or household cleaning products |
| | Carvone | 99-49-0 | 3.07 | 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 | 2 | Musk fragrance in cosmetics or perfumes[a] |
| | Musk Ketone | 81-14-1 | 4.30 | 1 | Fragrance in cosmetics, perfumes |
| | Phantolide | 15323-35-0 | 5.85 | 1 | Musk fragrance[a] |
| | Phthalimide | 85-41-6 | 1.15 | 1 | Used in dyes, fungicide |
| Pesticides | Benzyl benzoate | 120-51-4 | 3.97 | 18 | Acaricide and Insecticide |
| | N,N-Diethyl-m-toluamide | 134-62-3 | 2.02 | 11 | Insect and acarid repellant (DEET) |
| | Promecarb artifact | 3228-03-3 | 3.52 | 6 | Possible metabolite of a non-systemic 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 |
| | Fipronil-sulfone | 120068-36-2 | 4.42 | 2 | Metabolite of fipronil |
| | Fipronil, Desulfinyl- | 111246-15-2 | 4.22 | 1 | Photodegredate of fipronil |
| | Trifluralin | 1582-09-8 | 5.34 | 1 | Pre-emergent herbicide |
| Phthalates | 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-n-octyl phthalate | 117-84-0 | 8.10 | 11 | Plasticizer for cellulose and vinyl resins |
| | Di-n-hexyl phthalate | 84-75-3 | 6.82 | 9 | Used for dip-molded plastics and automobile parts |
| | Dicyclohexyl phthalate | 84-61-7 | 6.20 | 6 | Plasticizer for cellulose, chlorinated rubber, and other polymers |
| | Dimethylphthalate | 131-11-3 | 1.60 | 5 | Plasticizer for cellulose and vinyl resins |
| Industrial Compounds | Benzophenone | 119-61-9 | 3.18 | 19 | Used in paints, cosmetics, pesticides, pharmaceuticals |
| | Triphenyl phosphate | 115-86-6 | 4.59 | 15 | Fire retardant and plasticizer |
| | 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 |
| | 2-Methylphenol | 95-48-7 | 1.95 | 4 | A solvent, disinfectant, and/or chemical intermediate |
| | Tris(2-chloroethyl) phosphate | 115-96-8 | 1.44 | 3 | Flame-retardant plasticizer used in carpet backing or upholstery |
| | Tris(2-ethylhexyl) phosphate | 78-42-2 | 9.49 | 3 | Flame-retardant plasticizer and antifoaming agent |
| | o-Tricresylphosphate | 78-30-8 | 6.34 | 2 | Flame-retardant plasticizer in lacquers, varnishes, and adhesives |
| | Triethylphosphate | 78-40-0 | 0.80 | 2 | As a solvent/plasticizer in cellulose gums |
| | 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 resins, disinfectants, fumigants, photographic developers, explosives |
| | p-Tricresylphosphate | 78-32-0 | 6.34 | 1 | In cellulose, vinyl and rubber products, also a sterilizing agent |
| | 2,4-Dimethylphenol | 105-67-9 | 2.30 | 1 | Used as an disinfectant, fungicide, sanitizer, and virucide |
| | 4-Methylphenol | 106-44-5 | 1.94 | 1 | Used in resins, petroleum, photography, paints, and fumigant |

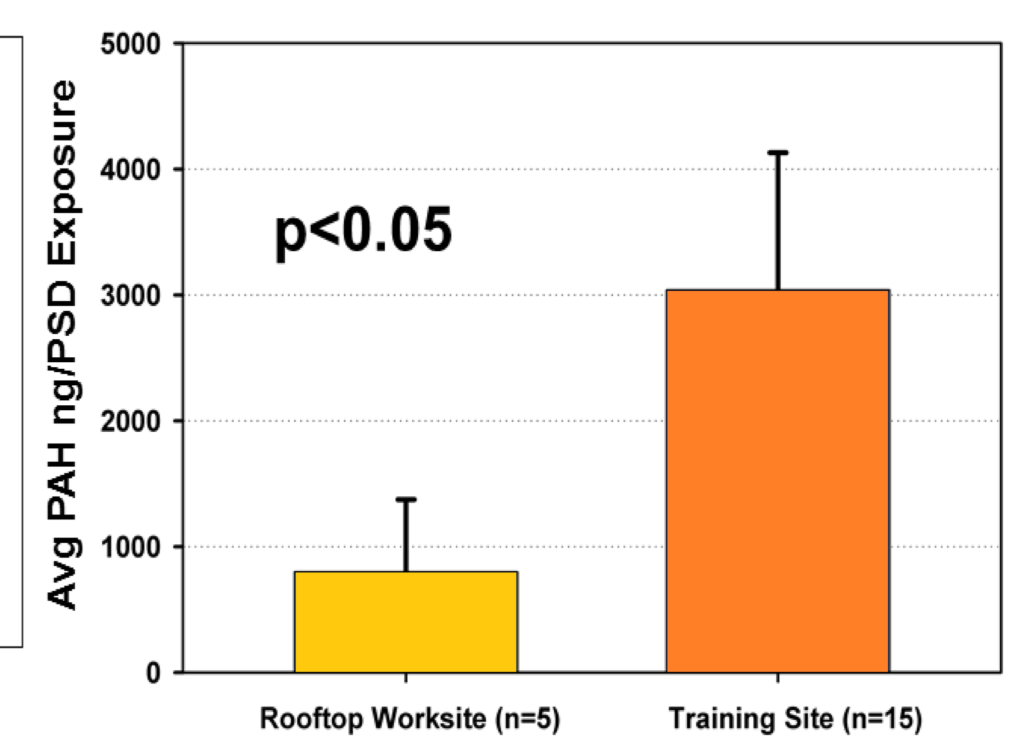
## Occupational Results: PAHs from roofers over 8-hour shifts at two sites

**Data collected with roofers confirm several important points**:

- Significant and quantifiable PAHs exist in the vapor phase
- Passive samplers worn by roofers can sequester substantial quantities of PAHs (and OPAHs, data not shown) during an 8-hour work shift
- We can extract PAHs and OPAHs from the samplers and identify and quantify them via GC-MS




<u>Temporal Sensitivity</u>: PAH exposures for five roofers

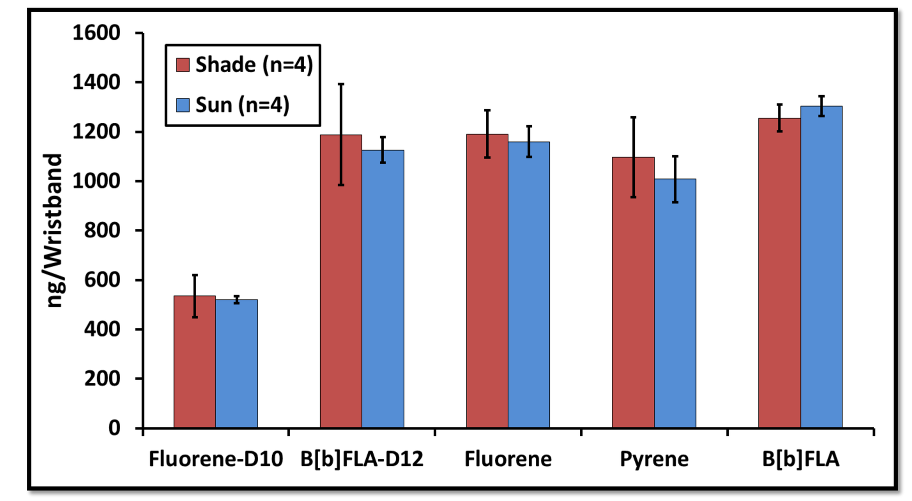



<u>Spatial Sensitivity</u>: Average PAH exposure for workers at different worksites.

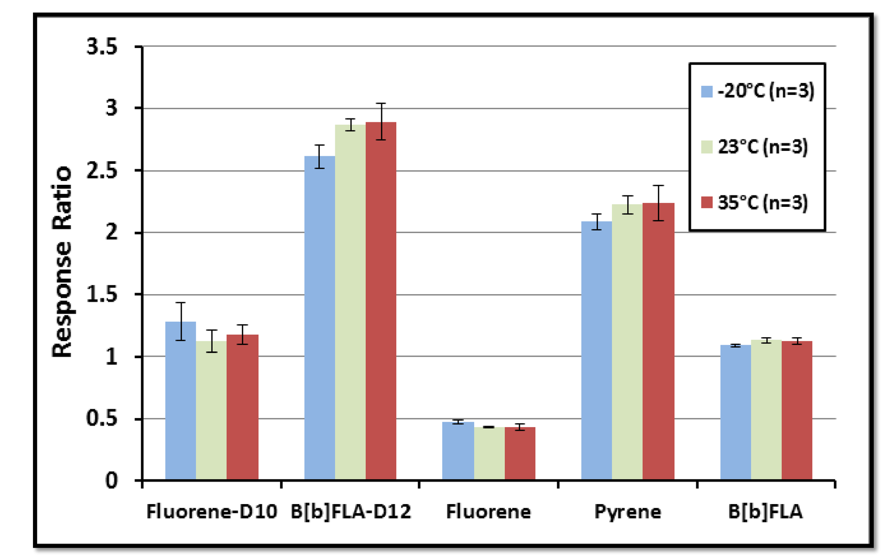
## Robustness Testing

**Data in figures below confirm several important points:**

- PAHs are stable in the wristbands
- wristbands can be transported to the laboratory under ambient conditions
- wristbands are chemically secure in the PFTE bags.




**PAHs in PWS AND UV Stability:** PAHs in Wristbands Exposed to UV. <u>No statistical difference</u> between shade or UV exposed wristbands (n=4), Photo: wristbands on Al-roof. Benzo[b]fluoranthene (B[b]FLA




**PAHs in PWS and Transport Robustness:** PAHs wristbands simulated transport at -20, 23, and +35C, 72 hrs, n=4, <u>No statistical difference</u> between transport conditions

## Conclusion

**Personal Wristband Samplers present an innovative sampling technology platform producing relevant, quantifiable data. By using these passive samplers, an atmospheric, time-weighted average concentration 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.**

**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.**

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