

# ***Using Silicone Wristbands to Assess the Personal Chemical Exposome: Strengths and Limitations***

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NICHOLAS SCHOOL  
OF THE ENVIRONMENT  
DUKE UNIVERSITY

*forging a sustainable future*

# ***Conflicts of Interest***

- Serve as a Science Advisor for the San Francisco Estuary Institute Regional Monitoring Plan Emerging Contaminants Workgroup
- Research funded by:
  - National Institutes of Health
  - Environmental Protection Agency
  - Housing & Urban Development
  - North Carolina Collaboratory Program
  - Michael & Annie Falk Foundation, V Foundation, Thyca
  - Duke University Cancer Institute

# The Exposome

- Research on the exposome seeks to assess the totality of **exposures over the life course** and understand how these combined stressors impact health.
- Can we use wristbands and wearables to assess **patterns of exposure**, particularly based on:
  - Behaviors
  - Housing characteristics/consumer products
  - Occupation
  - Temporal changes

## Ecosystems

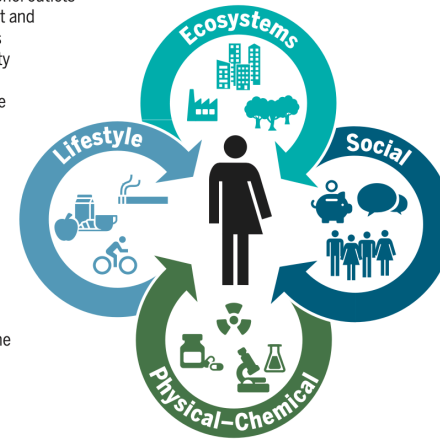
Food outlets, alcohol outlets  
Built environment and urban land uses  
Population density  
Walkability  
Green/blue space

## Lifestyle

Physical activity  
Sleep behavior  
Diet  
Drug use  
Smoking  
Alcohol use

## Social

Household income  
Inequality  
Social capital  
Social networks  
Cultural norms  
Cultural capital  
Psychological and mental stress



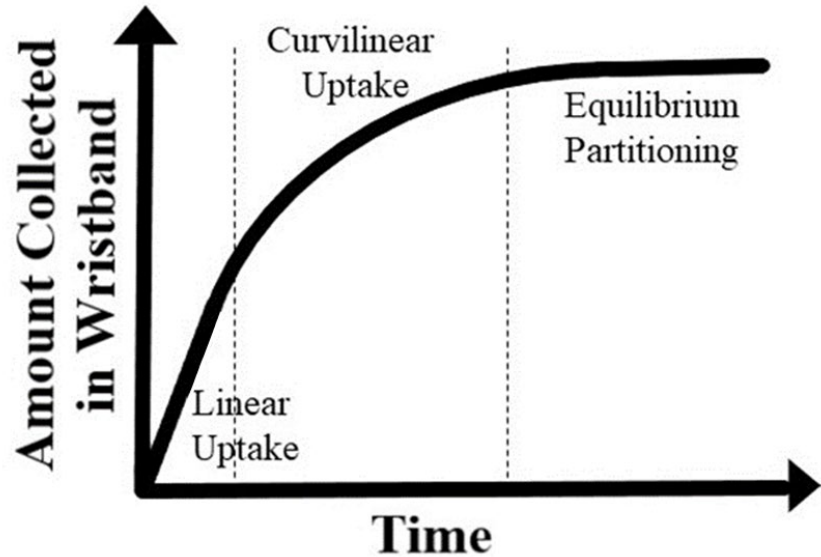
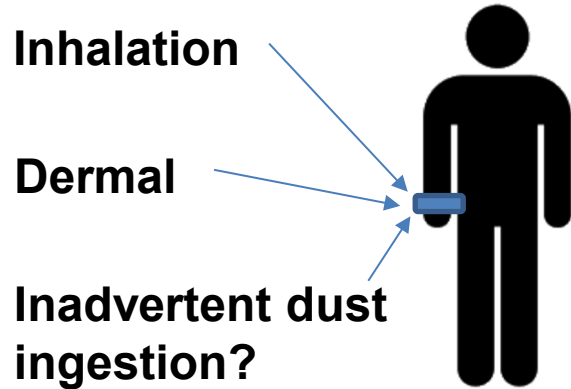
## Physical-Chemical

Temperature/humidity  
Electromagnetic fields  
Ambient light  
Odor and noise  
Point, line sources, e.g. factories, ports  
Outdoor and indoor air pollution  
Agricultural activities, livestock  
Pollen/mold/fungus  
Pesticides  
Fragrance products  
Flame retardants (PBDEs)  
Persistent organic pollutants  
Plastic and plasticizers  
Food contaminants  
Soil contaminants  
Drinking water contamination  
Groundwater contamination  
Surface water contamination  
Occupational exposures

**Fig. 1. The exposome concept.** The exposome is an integrated function of exposure on our body, including what we eat and do, our experiences, and where we live and work. The chemical exposome is an important and integral part of the exposome concept. Examples of external stressors are adapted from (39). These stressors are reflected in internal biological perturbations (Fig. 3); therefore, exposures are not restricted to chemicals (toxicants) entering the body, but also include chemicals produced by biological and other natural processes.

# ***Wearable Samplers: The Silicone Wristband***

## **Exposure Routes**

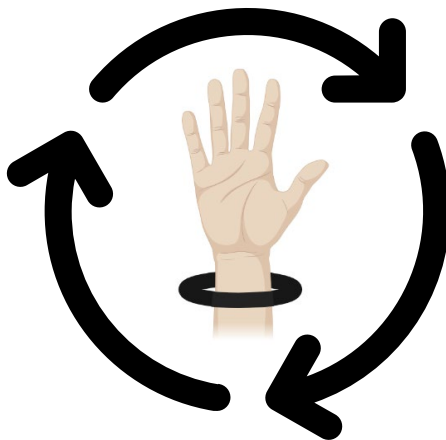
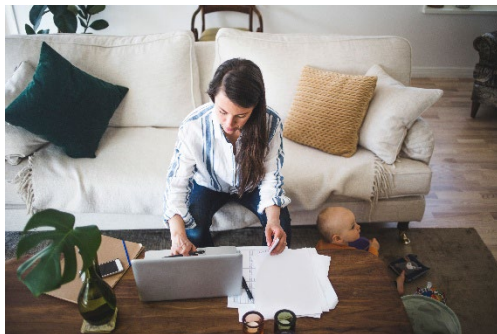


# ***Integrates Exposure Measures Across Different Micro-environments & Over Time***



**Commuting**

**Home**



**Work**



# ***Or Focus on One Micro-Environment***

**Occupational**



# Overview



## Wristband Analyses

### Questions

- How well do wristband measurements correlate with internal dose?
- How long should you wear a wristband?
- Can children wear them?
- Do wristbands predict internal dose better than house dust?
- Is there variability in chemical levels around the wristband?

### Wristband Studies

- Chemical exposures in firefighters

### Strengths & Limitations

# ***Wristband Analyses***

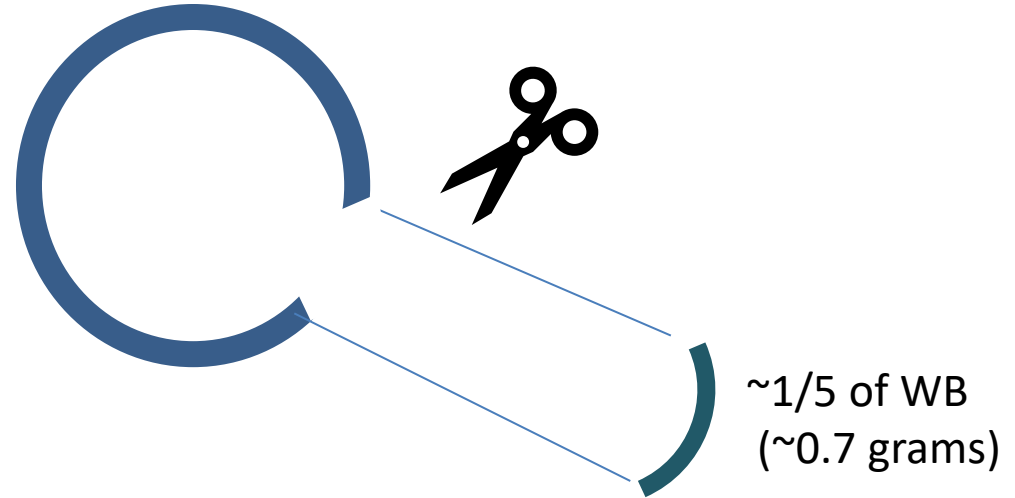




# *Analytical Details*



Wristband (WB)



# Current Wristband Analysis Overview

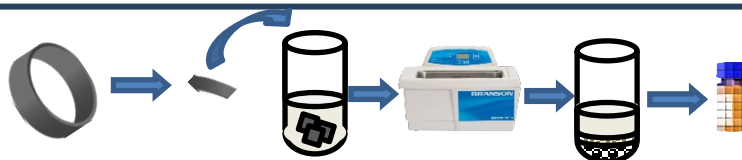
Sample  
Preclean  
Treatment



Sample  
Deployment  
& Collection



Laboratory  
Analysis



Methanol  
Extract



GC-HRMS EI



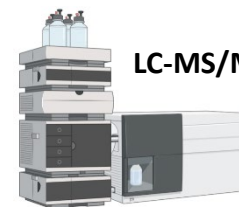
GC-MS ECNI



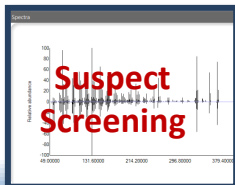
GC-HRMS PCI



LC-MS/MS



9 Brominated Flame Retardants (BFRs)  
30 Organophosphate Esters (OPEs)  
25 Polycyclic Aromatic Hydrocarbons  
21 Pesticides  
12 Phthalates  
13 Polychlorinated Biphenyls (PCBs)  
3 industrial and personal care chemicals



9 High Molecular Weight BFRs  
e.g. BEHTBP  
BDE 209  
DBDPE  
17 dioxins/furans

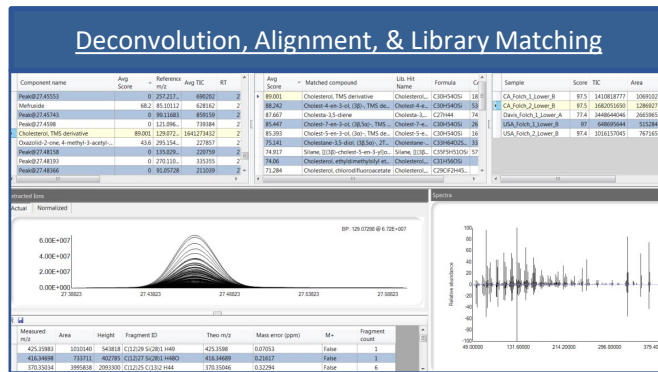
13 Volatile PFAS:  
n:2 Fluorotelomer Alcohols,  
n:2 Fluorotelomer Acrylate &  
Methacrylates  
Sulfonamidoethanols (i.e. MeFOSE)

LC Amenable targets:  
48 PFAS: PFAAs, FTS, PAPs, FOSAA,  
Gen X, etc.  
Parabens (Methyl, Ethyl, Propyl)  
Triclosan, Triclocarban

# Suspect Screening: Workflow Summary



Nicholas Herkert, PhD



## Libraries

- NIST
- Thermo Hi-Res
- In-house

## Feature QA/QC

- Blank Subtraction
- Standard Normalization



## PubchemLite

- Patent counts
- PubMed Entries

## Product Uses

- Current CPCAT
- Soon to be ChemExpo

## Feature Annotation

- Patent Counts
- Product Uses

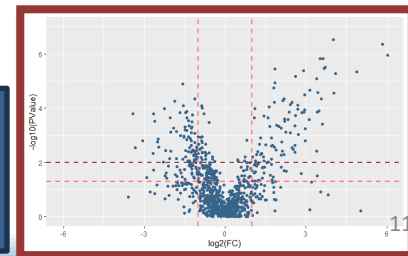
## Rank Matches

- Return top Match

## Output

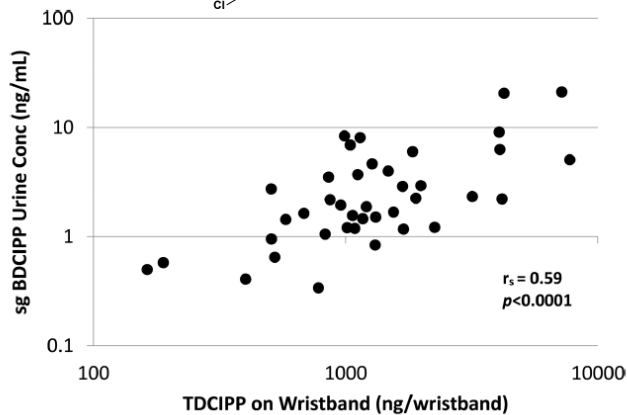
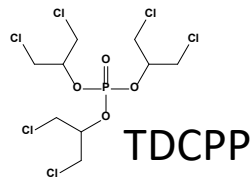
## Feature Analysis

- Volcano Plots
- Summary Stats
- Correlations

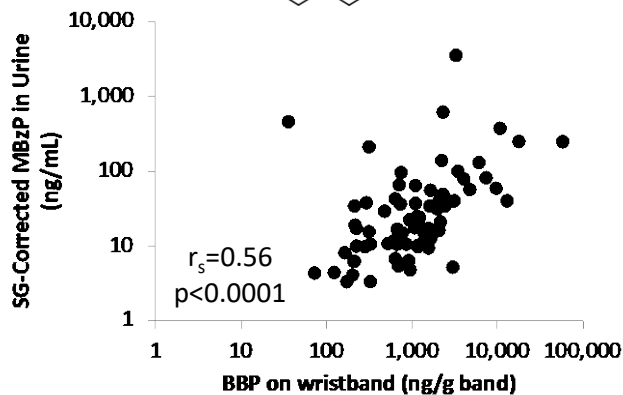
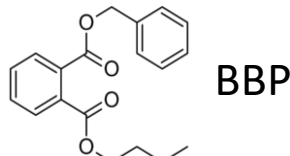


***Are measurements of chemicals on  
wristbands correlated with internal dose?***

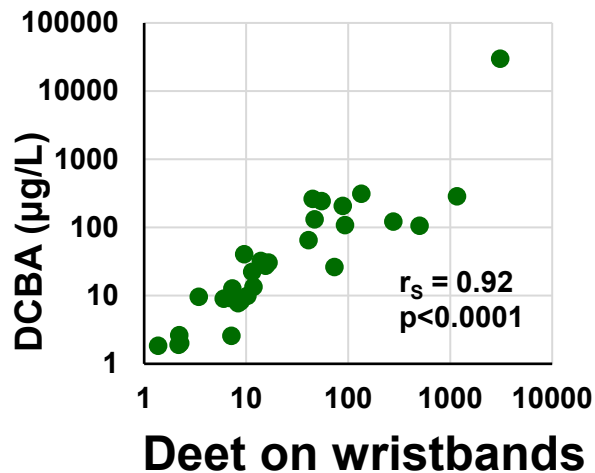
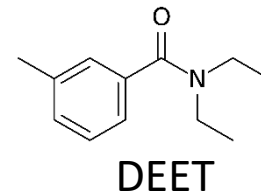
# Wristbands correlated with urinary metabolites



Hammel et al. 2016



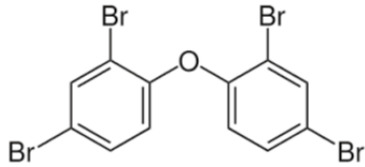
Hammel et al. 2020



Wise et al. 2022

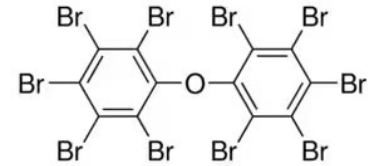
\* All urine samples are pooled from three 1st morning voids

# Wristband measurements correlated with blood

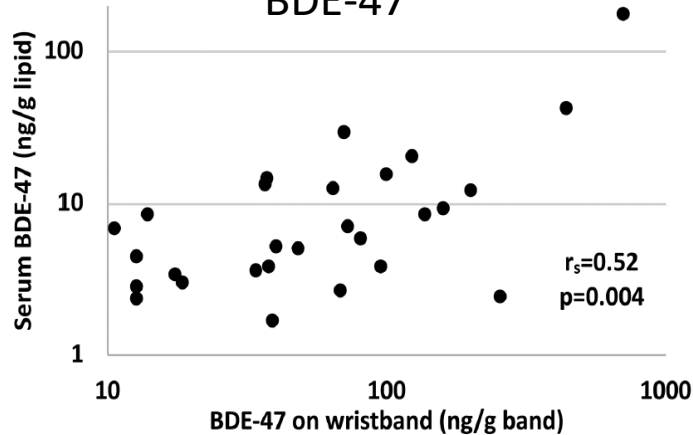


BDE-47

**Brominated Flame Retardants**

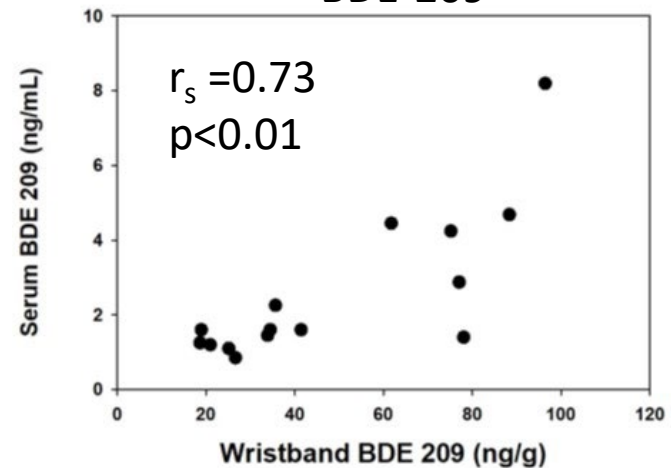


BDE-209



Hammel et al. 2018

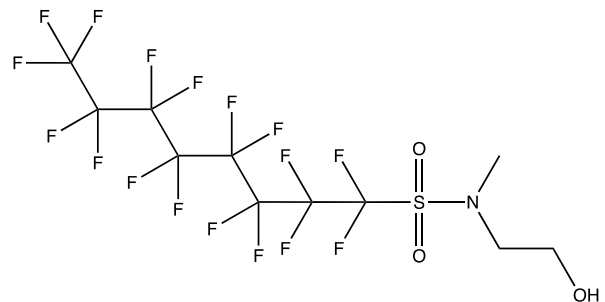
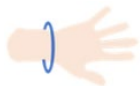
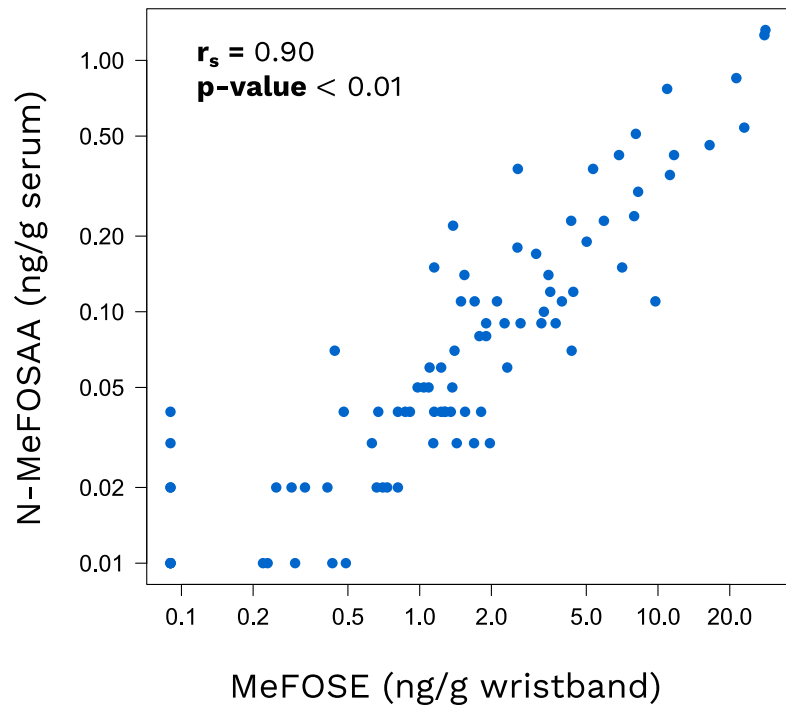
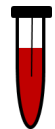
**Half-life ~ 1.8 years**



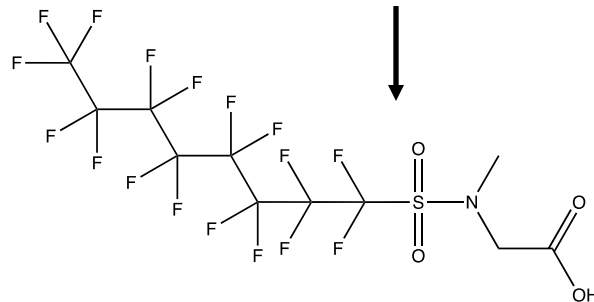
Hoffman et al. 2024

**Half-life ~ 2 weeks**

# Volatile PFAS



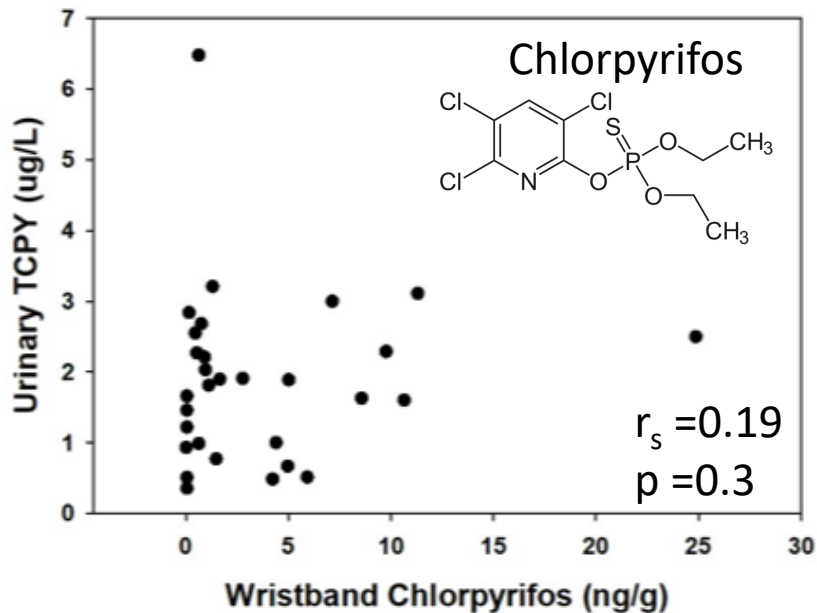
MeFOSE



N-MeFOSAA

Hoxie et al. 2024

# *Not all chemicals are correlated*



- Detection frequencies
  - Wristband = 83%
  - Urine = 100%
- Suggests diet is likely more important exposure route in NC
- **However, a significant & positive correlation was identified in Central America agricultural area (Tore, et al. In Draft)**



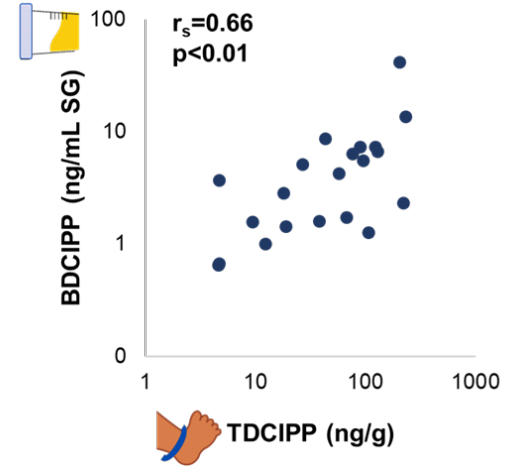
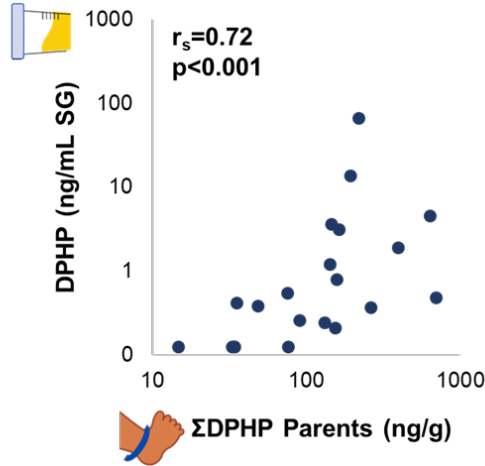
# Use in Infants- Ankle Band



n = 21  
6-18 months



3 days



Wise et al., Accepted

***Do wristband levels correlate with internal dose  
better than house dust & hand wipes?***

# Spearman correlation coefficients

(with urine or serum biomarker; n=77) \* - statistically significant

Analyte Pair		Wristband	Handwipe	House Dust
Organophosphate Flame retardants/ plasticizers	TDCPP - BDCIPP	0.52*	0.48*	0.13
	4tBDPP- tbPPP	0.35*	0.16	0.05
Phenols	Ethyl paraben	0.66*	0.48*	0.34*
	Triclosan	0.51*	0.50*	0.16
Phthalate Plasticizers	Diethyl phthalate- MEP	0.41*	NA	0.17
	Benzyl butyl phthalate- MBzP	0.56*	0.56*	0.23*
Brominated Flame Retardant	BDE-47 (n=19)	0.73*	0.71*	0.57*

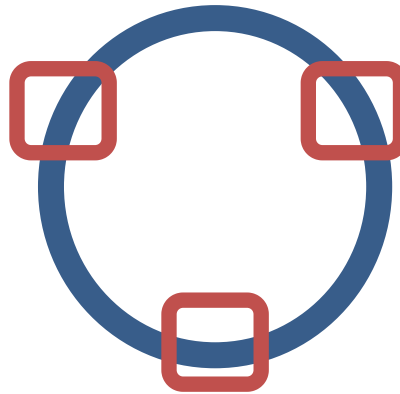
Urine  
Correlations

Serum  
Correlations

Phillips et al., 2018; Hammel et al., 2020; et al., 2021; Hoffman et al., 2024

# ***How variable are chemical measurements around the wristband?***

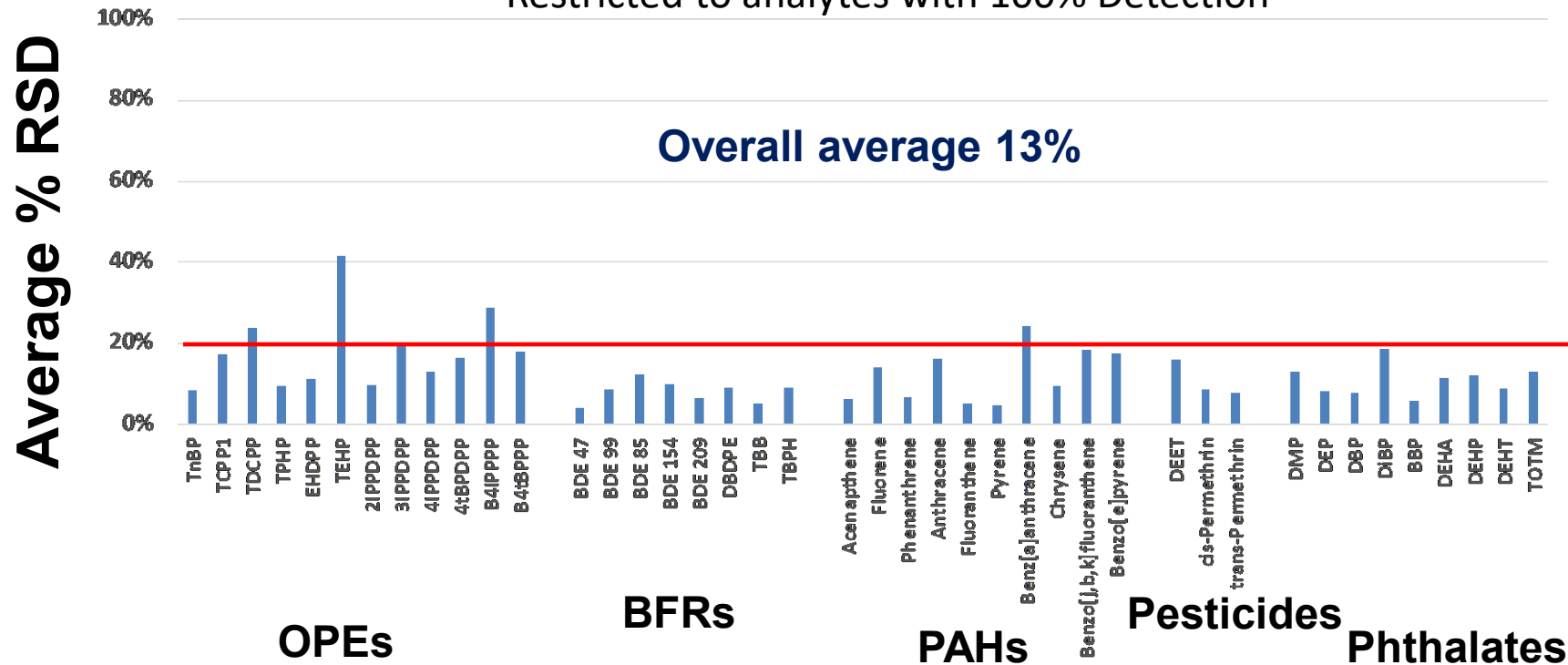
Wristband (WB)



# Measurement precision around the wristband

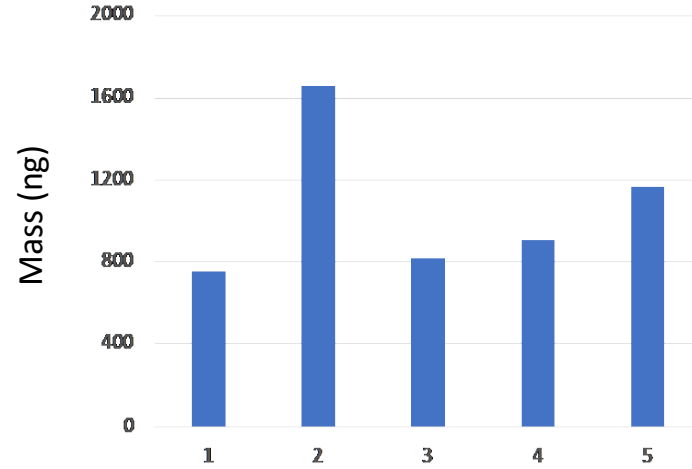
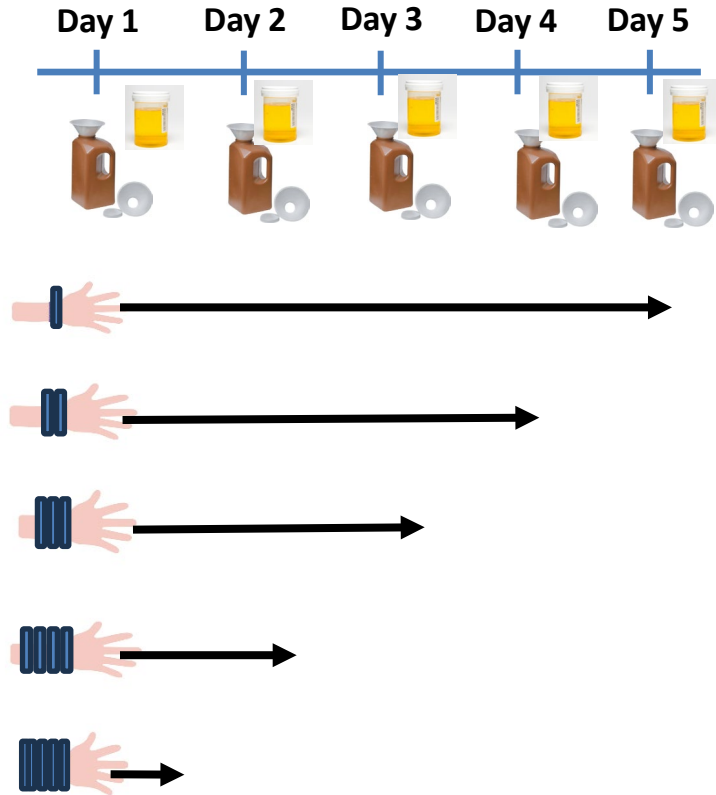
N= 10 wristbands

\* Restricted to analytes with 100% Detection

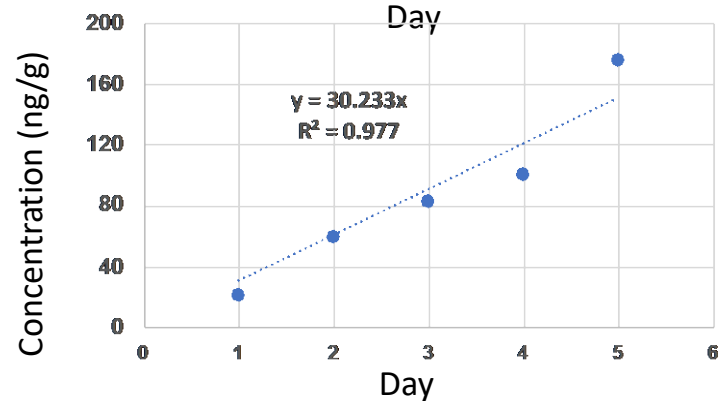


***How do wristband levels compare to spot urine?***

# Experimental Design

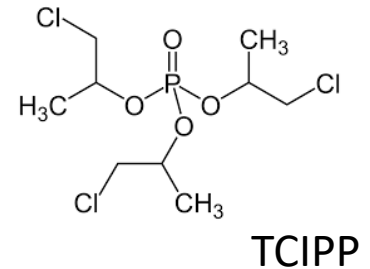
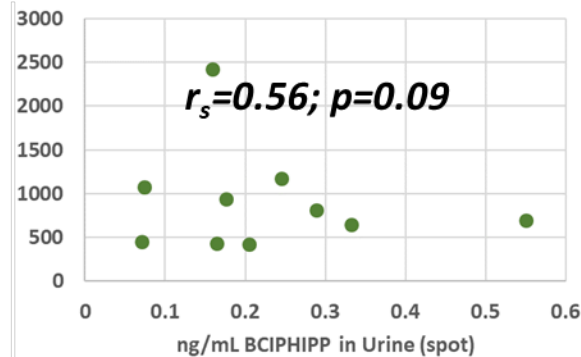
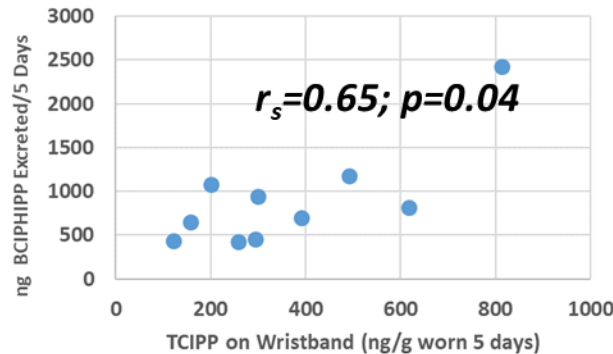
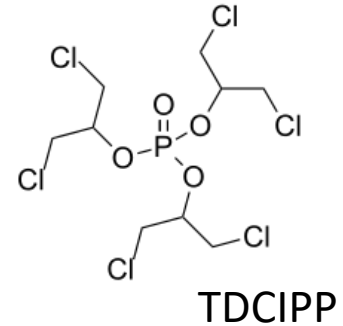
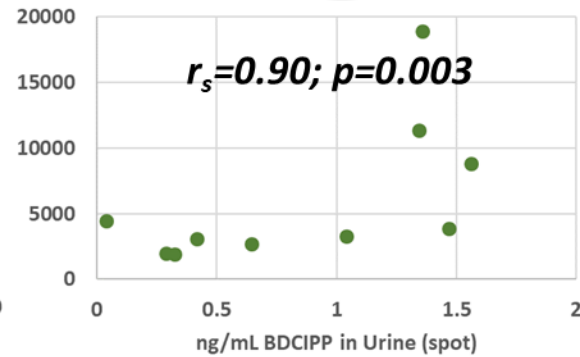
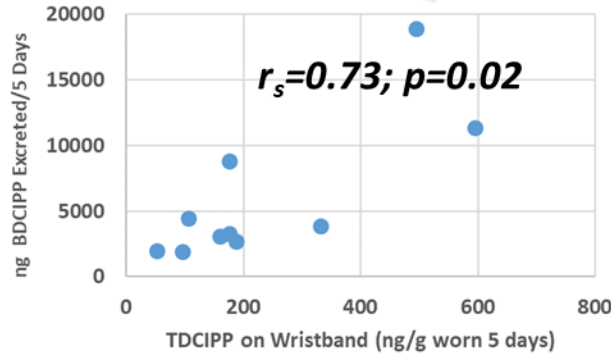
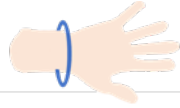


**Urinary  
Metabolite**



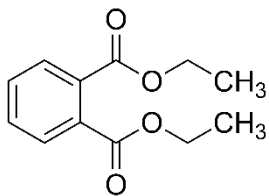
**Parent  
Chemical**

# Wristbands or Spot Urine?

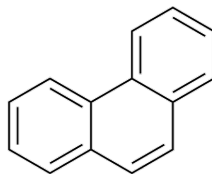




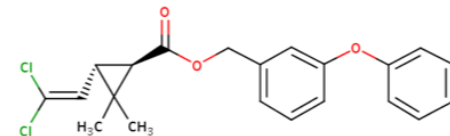
# Chemical Accumulation Over 5 Days



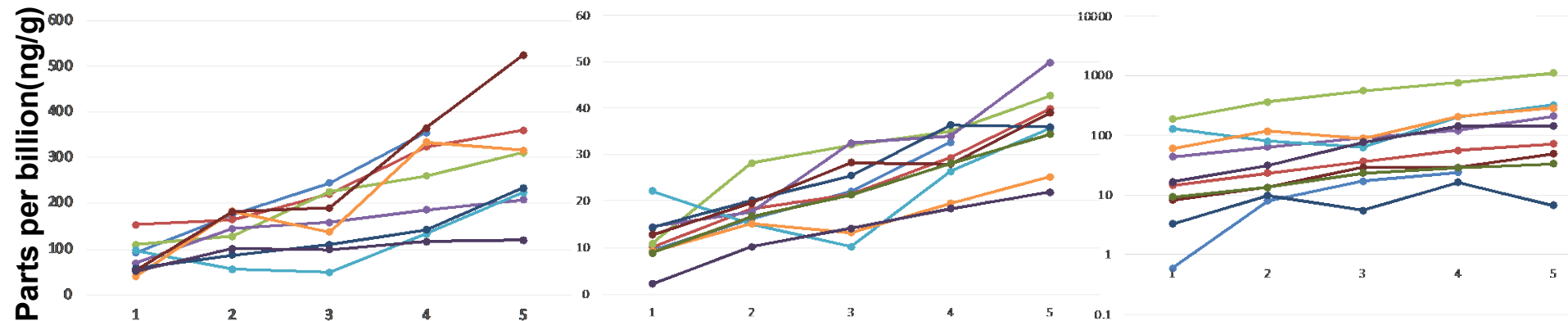
Diethyl phthalate



Phenanthrene



Trans-Permethrin



**Sampling Days**

Wristbands worn for 1, 2, 3, 4 or 5 days



# ***Using Wristbands to Assess Firefighters Exposures***

---



# Characterizing Exposures in Firefighters

- Research collaboration with firefighters in Durham, NC
- Each firefighter was asked to wear silicone wristbands for 6 days while during the following three periods:



Home



Work  
(no fire event)



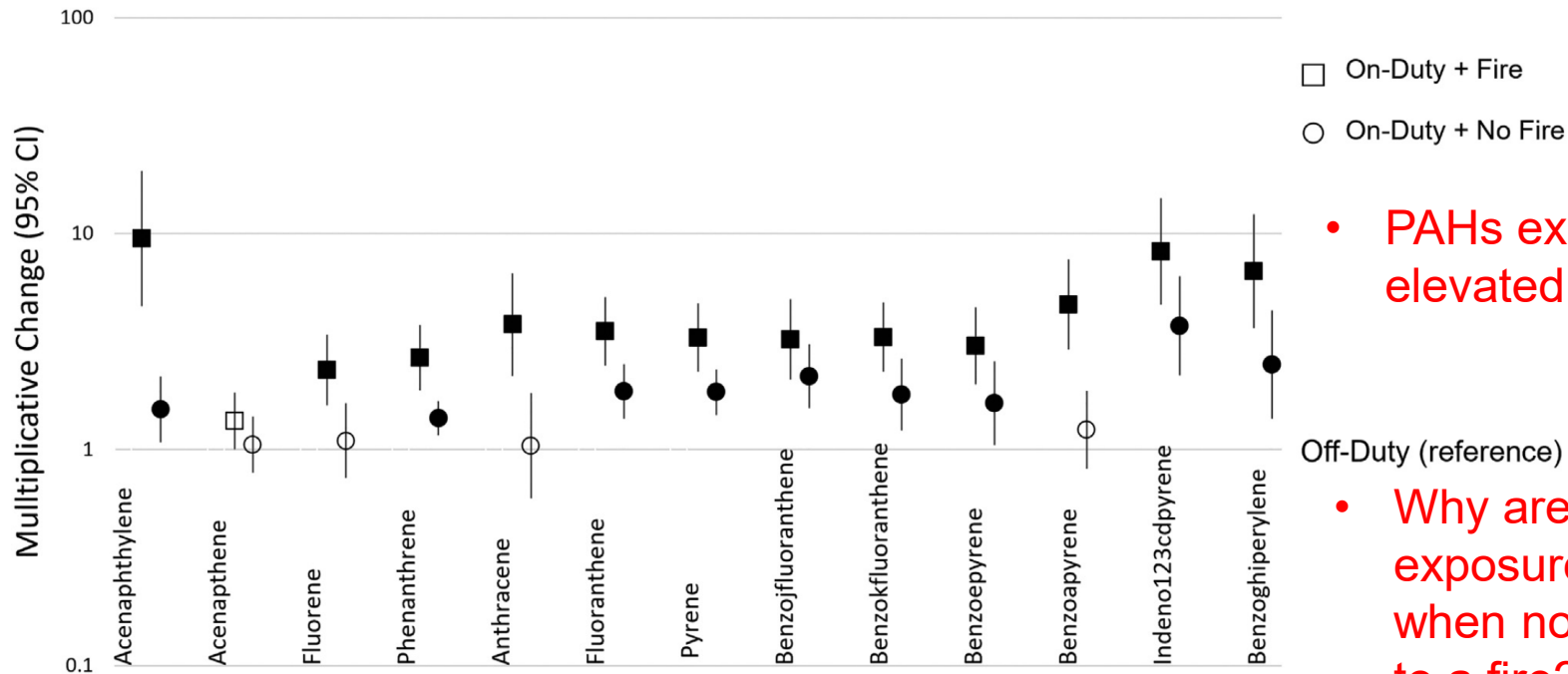
Work  
(fire event)



Jessica  
Levasseur  
PhD student

Question: How do chemical exposures change on-duty vs off-duty? When responding to a fire?

# PAH Exposures in Firefighters

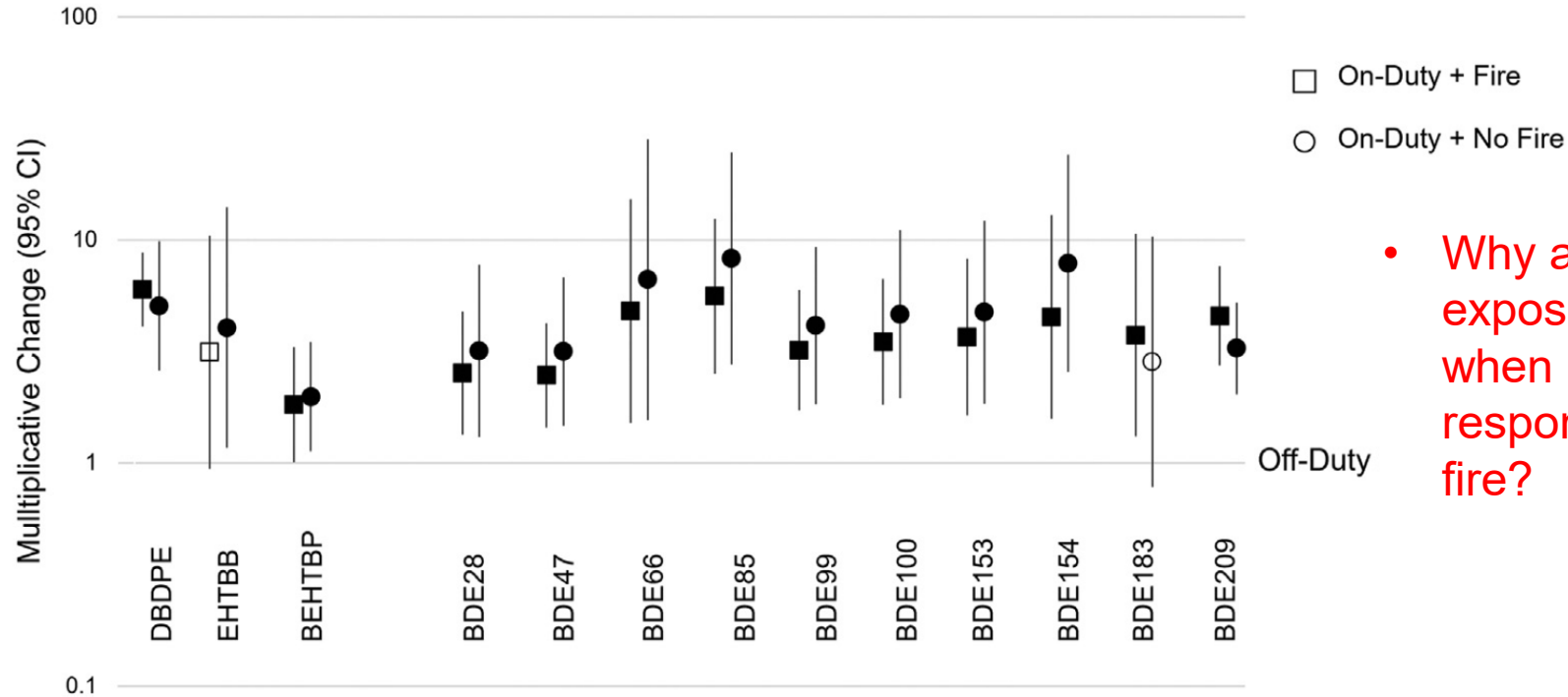


- PAHs exposure elevated during fires

- Why are PAH exposures higher when not responding to a fire?

\* Filled symbols are statistically significant ( $p < 0.05$ )

# BFR Exposures in Firefighters

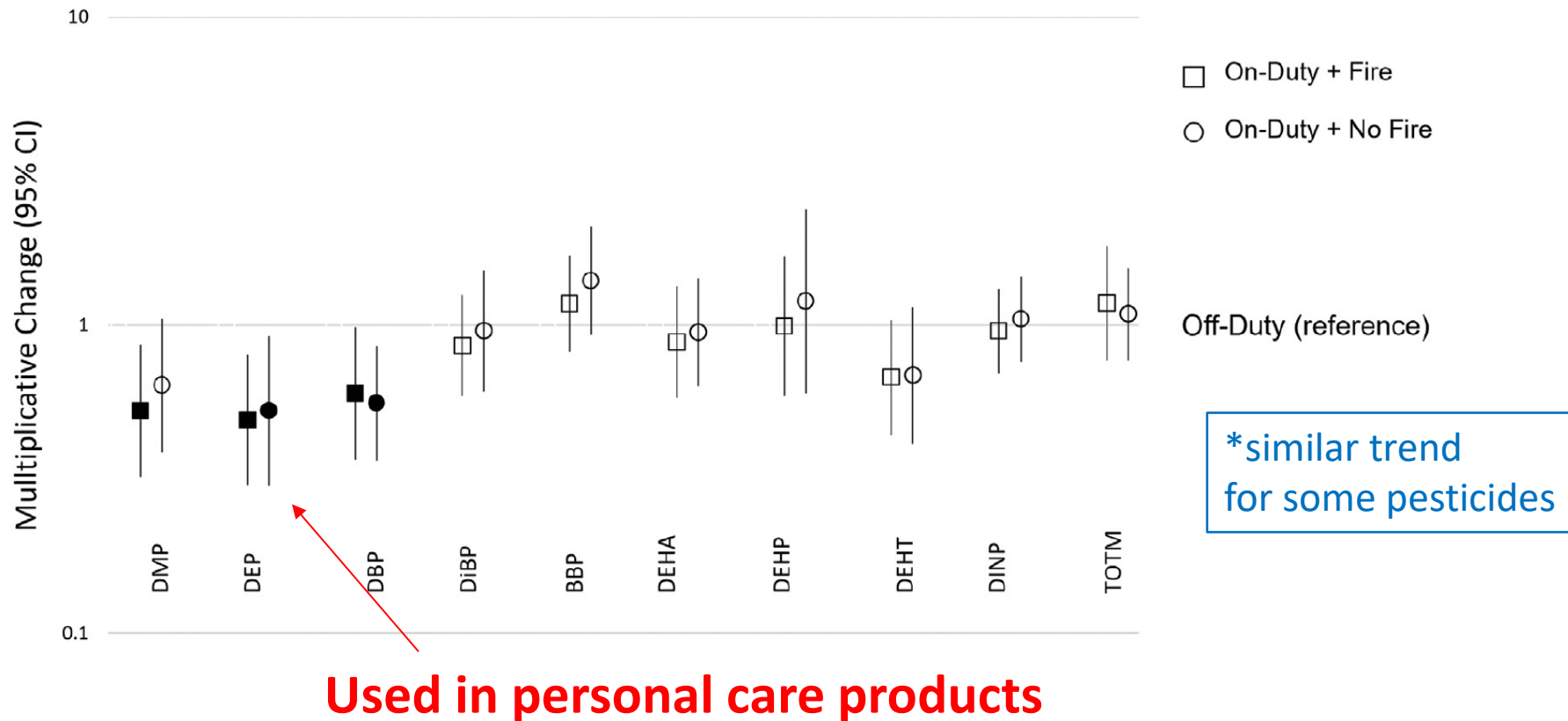


- Why are BFR exposures higher when not responding to a fire?

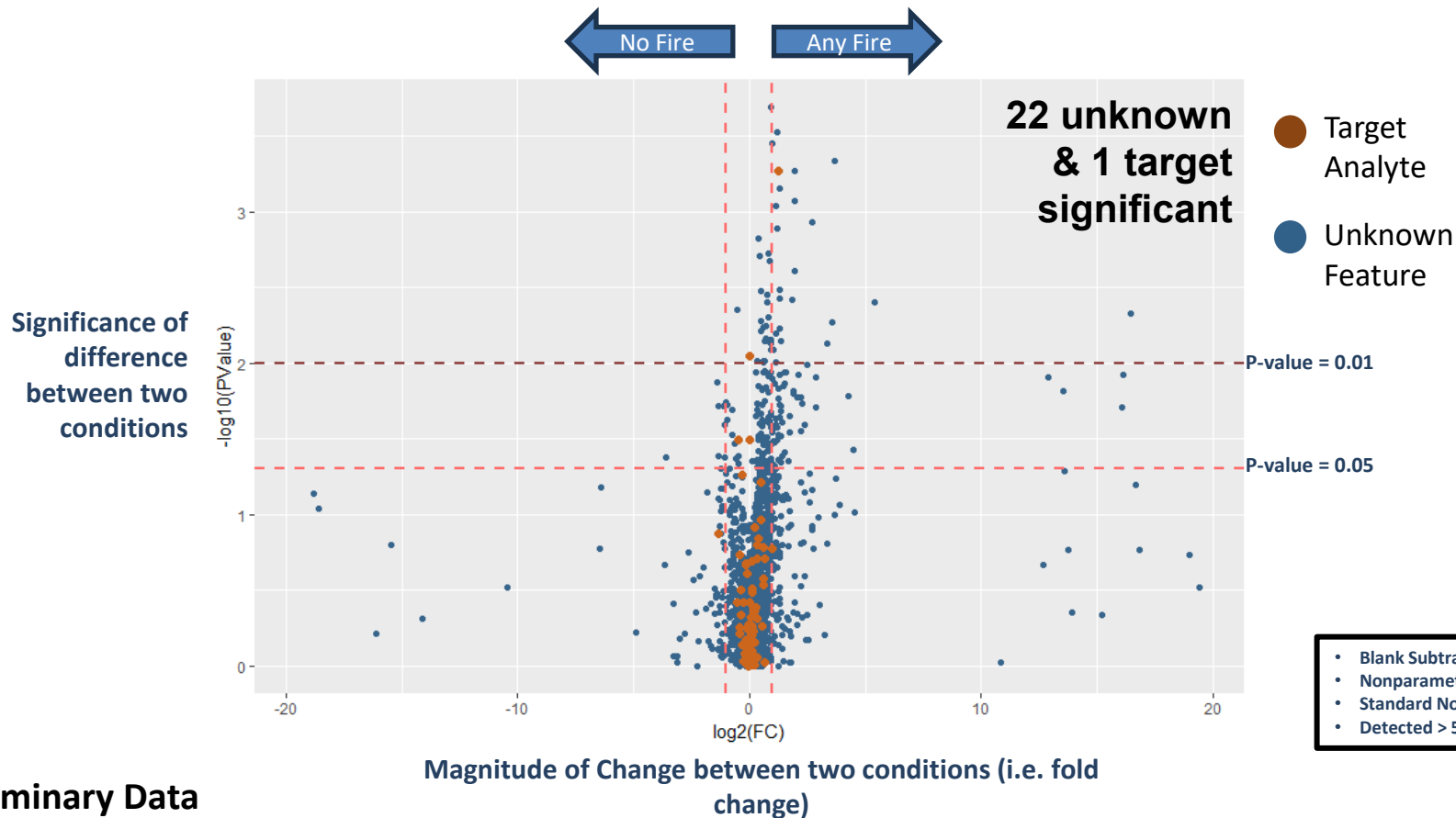
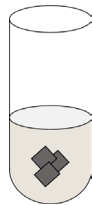
\* Filled symbols are statistically significant ( $p < 0.05$ )

Levasseur et al., 2022

# Phthalate Exposures in Firefighters

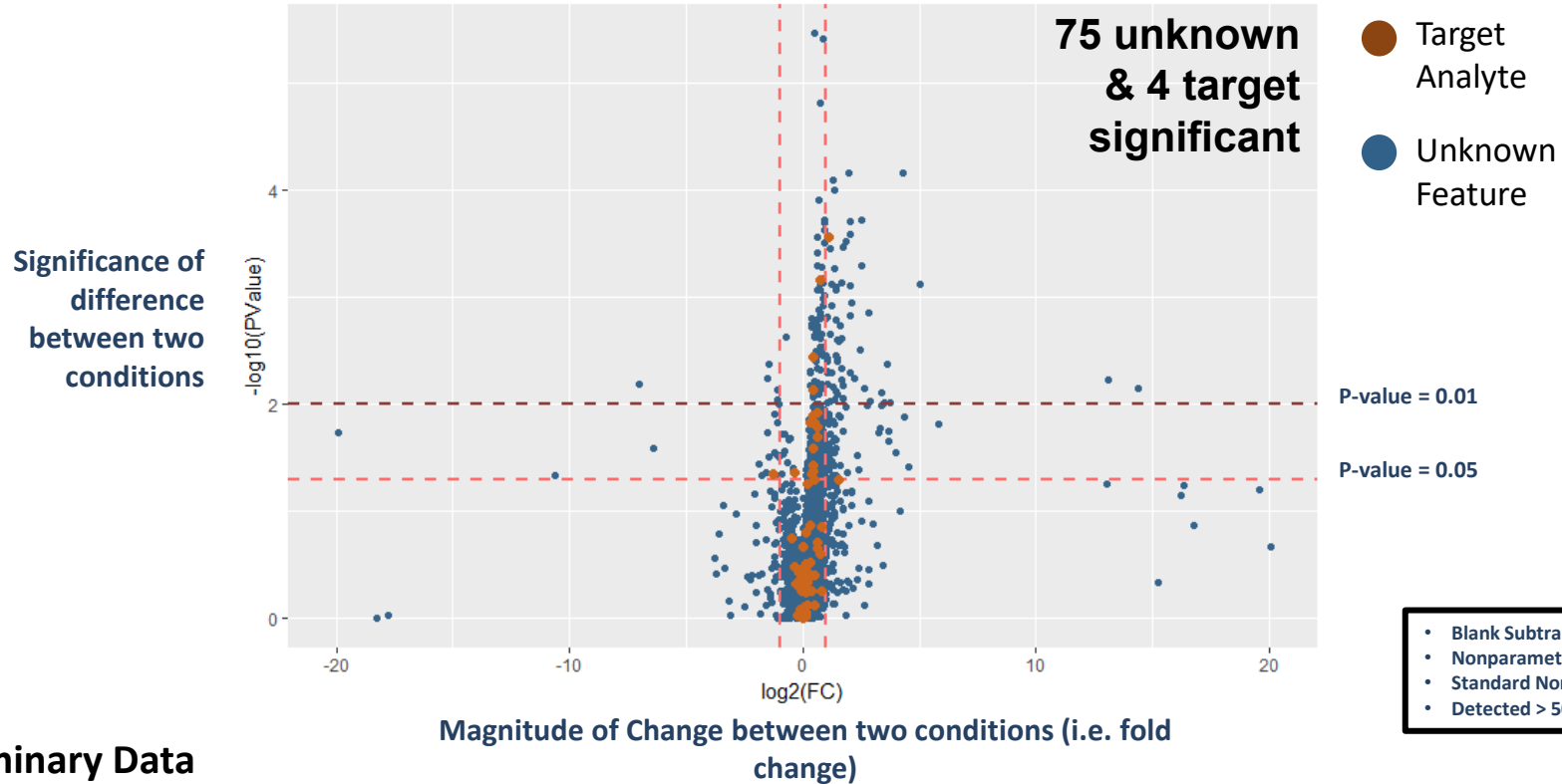
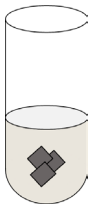


# Bands with Any Fire Event



Preliminary Data

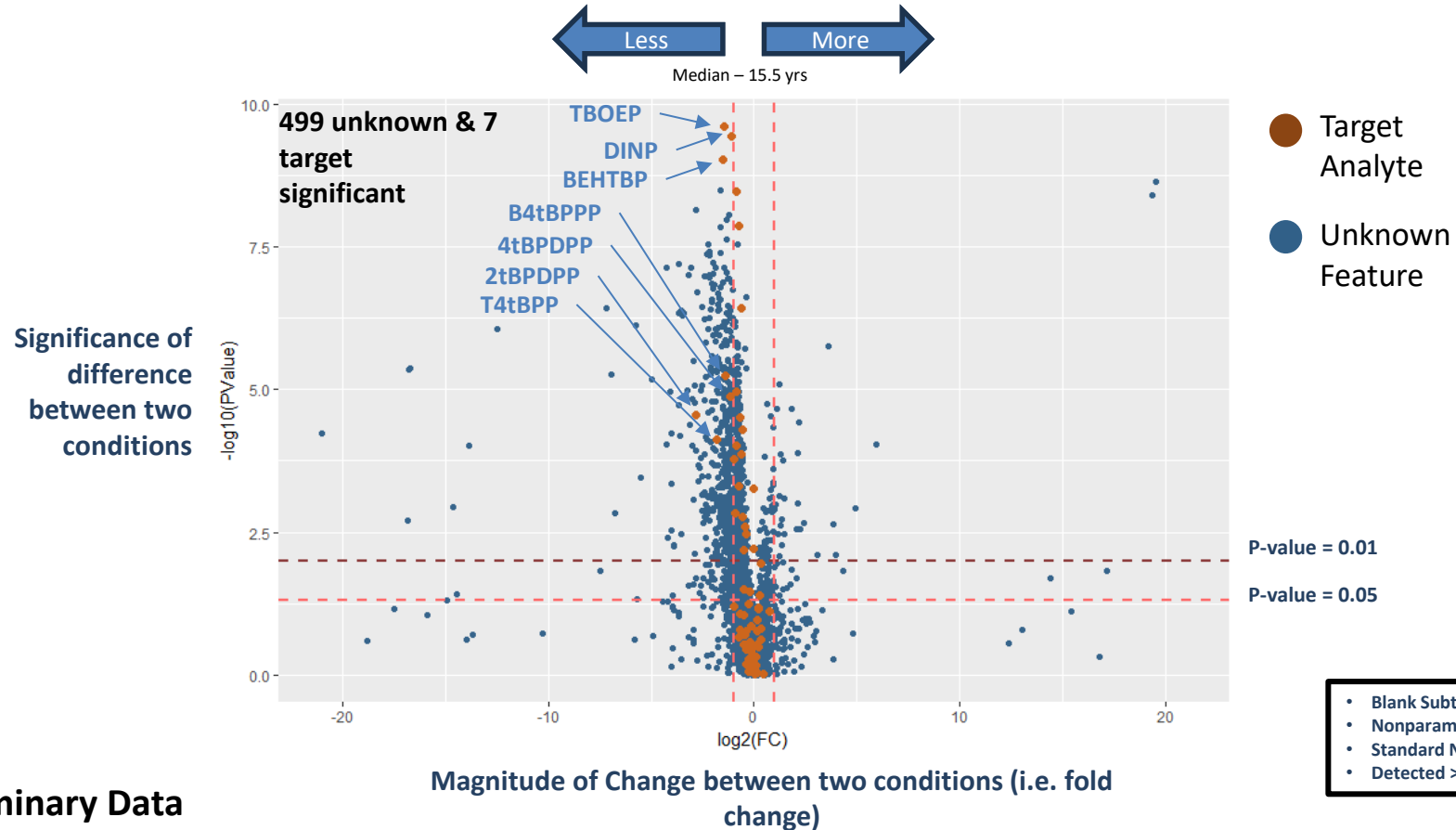
# Time Spent at Fire



Preliminary Data



# # Years as a Firefighter



# ***Wristband Measurements: Using them in an Exposure Framework***



**Estimate Indoor Air Concentrations?**

**Estimate Internal Dose?**

# ***Are wristband measurements influenced by movement?***



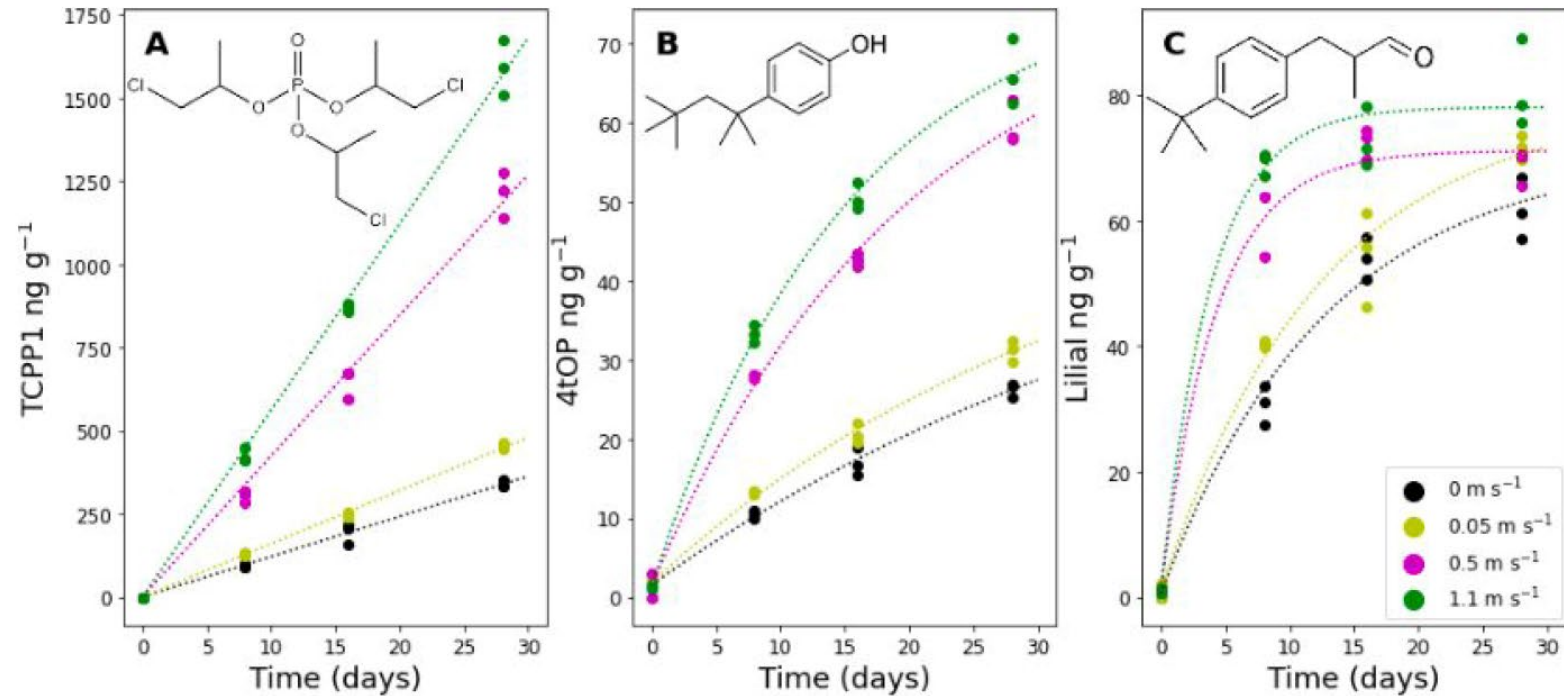
Heileen Hsu-Kim  
Professor



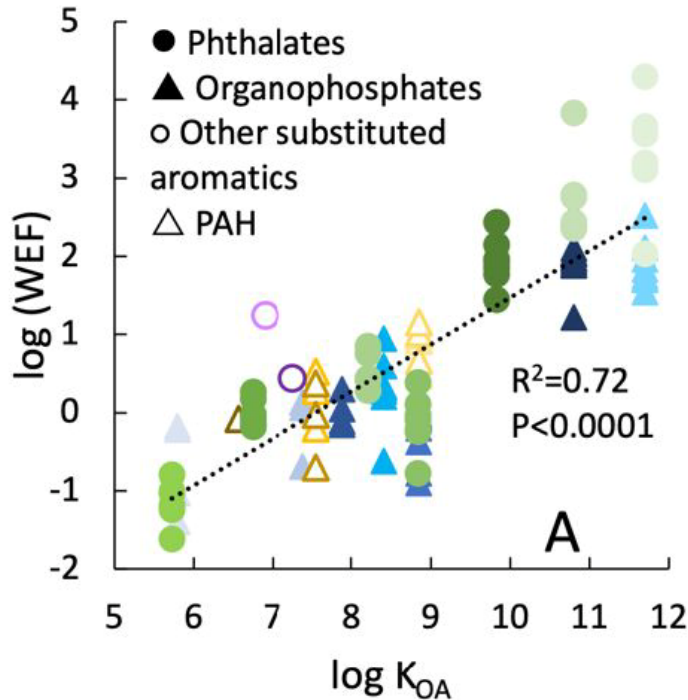
Josh Miller  
PhD Student



# *Chemical accumulation as a function of movement*



# Implications



- Graph depicts enrichment of chemicals in worn wristbands compared to wristbands rotating at 1.1 m/sec
- Enrichment is a function of the  $\log K_{OA}$
- Suggests that uptake on wristbands is a complex process, not driven solely by gas phase partitioning

# *Advantages of Using Silicone Samplers*

- ✓ Non-invasive tool for measuring exposure to hundreds of chemicals using targeted & nontargeted approaches
- ✓ Integrate exposure to hundreds of chemicals **over time**
- ✓ Can be easily mailed back and forth (no clinic visit!)
- ✓ Can help us understand patterns of exposure over space and time
- ✓ Wristbands can help reach & engage isolated communities



**Behavior**



**Built  
Environment**

# ***Limitations of Using Silicone Samplers***

- Not applicable for measuring metals
- Applicability may be limited for:
  - Very water soluble/ionic chemicals (e.g. glyphosate, PFBS)
  - Very volatile chemicals (e.g. toluene, MTBE)
- Unclear whether confounding occurs based on:
  - Hand dominance
  - Clothing (long sleeves vs short sleeves)
  - Physical activity
- Need more studies to determine at what point chemicals are no longer in the linear range of uptake

# *Ongoing Wristband Studies*

CKDu CURE 





# Acknowledgements

## Stapleton Lab:

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Elizabeth Boxer  
Jess Levasseur  
Taylor Hoxie  
Shaza Gaballah  
Emina Hodzic  
Michelle Misselwitz



Rachel Smith  
Amelia Kane  
Mackenzie Laney  
Daniel Ehrlich  
Candance Van Vleet  
Eve Marion  
Alex Beste



CENTER FOR  
ENVIRONMENTAL  
EXPOSOMICS

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- Andreas Sjodin

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- Bryan Ormond
- Jane Hoppin

## Durham County firefighters

Corey Miller  
Chief Wayne Cheek



## Colorado School of Mines

- Chris Higgins

## Michigan State University

- Courtney Carignan



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Victory Over Cancer



U2C ES030851



R01 ES016099  
P42 ES010356



CR-83948201

Michael & Annie Falk Foundation