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Tracking Semivolatile Organic Compounds Indoors: Merging Models and Field Sampling to Assess Concentrations, Emissions, and Exposures

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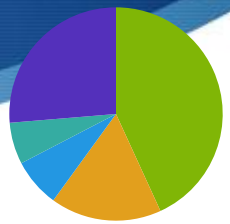
Population-based human exposure



Direct consumer product use

Inhalation, dermal, non-dietary ingestion from home environment

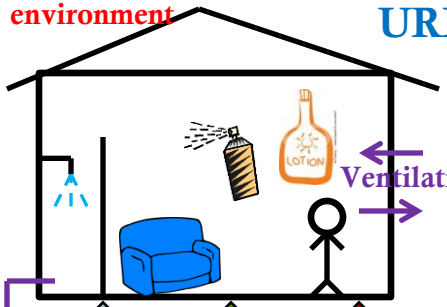
Inhalation from outdoor environment

Ingestion of crops & food-producing animals

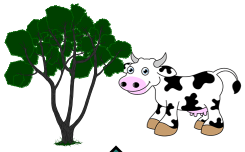
Ingestion of fish & drinking water

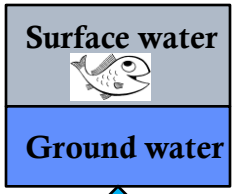
URBAN

RURAL



Ventilation





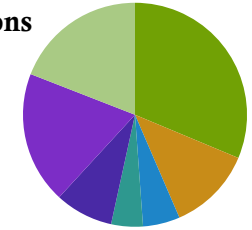
Urban/mobile air emissions

Pesticide applications

Water emissions

Outdoor emissions

Introduction to environment from commerce



Down-the-drain to wastewater & surface water

Direct consumer use (food packaging & personal care products)

Indoor releases (active product use & diffusion from materials)

Indoor releases to down-the-drain (personal care products & cleaning products)

Residential Indoor Sources of Organic Compounds

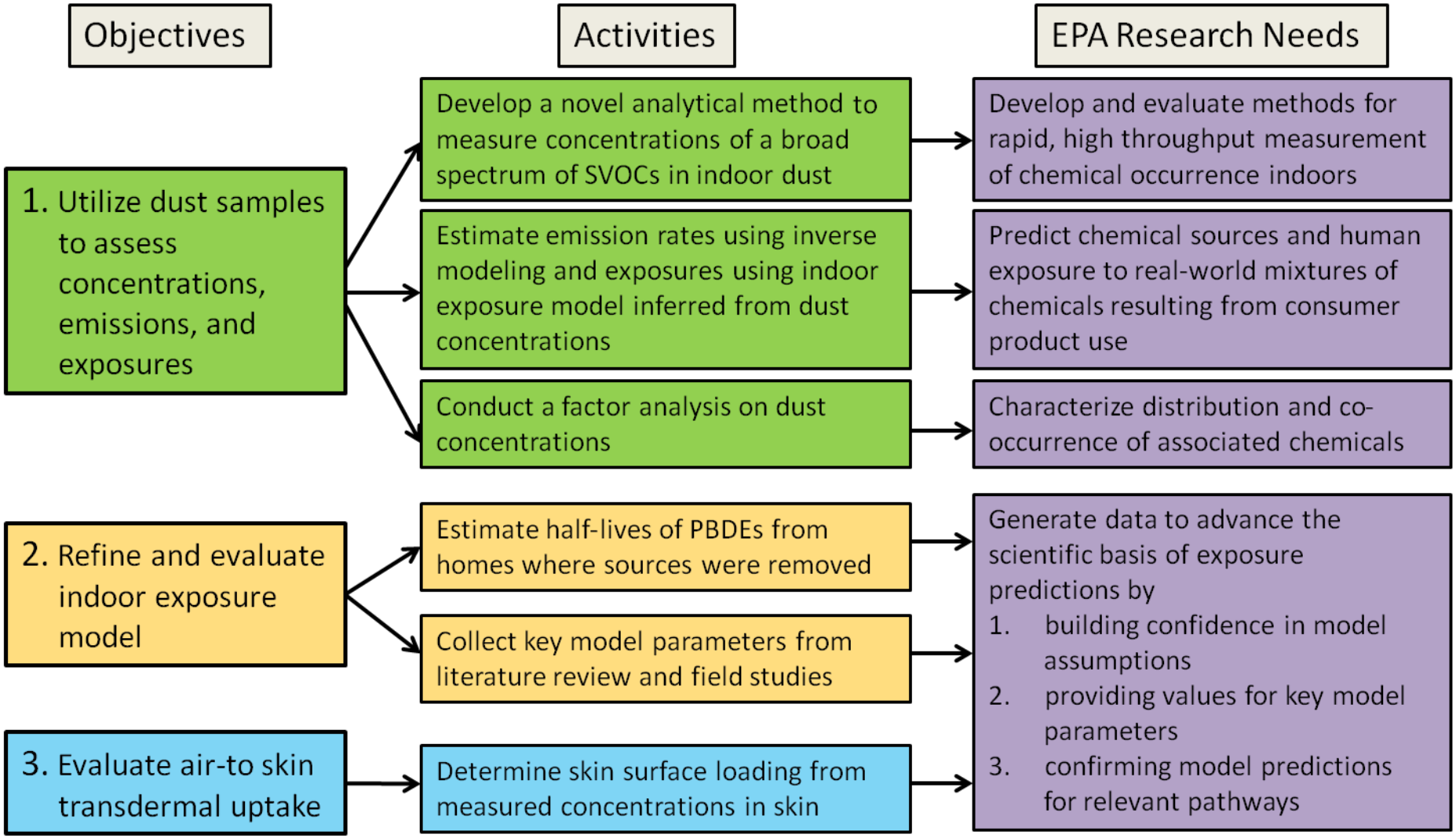
What is in our home?

- Very little data on chemicals used in commerce
  - Composition
  - Product formulation
  - Distribution of total production volumes
  - Exposure
  - Toxicity

Objectives

- Measure concentrations of a broad spectrum of target and non-target SVOCs in indoor dust
- Estimate emission rates from dust levels and predict resulting exposures
- Refine and evaluate a multi-compartment indoor fate, transport, and exposure model
- Evaluate air-to-skin transdermal uptake models

Overview


Objectives
Activities
EPA Research Needs
1. Utilize dust samples to assess concentrations, emissions, and exposures
Develop a novel analytical method to measure concentrations of a broad spectrum of SVOCs in indoor dust
Develop and evaluate methods for rapid, high throughput measurement of chemical occurrence indoors
Estimate emission rates using inverse modeling and exposures using indoor exposure model inferred from dust concentrations
Predict chemical sources and human exposure to real-world mixtures of chemicals resulting from consumer product use
Conduct a factor analysis on dust concentrations
Characterize distribution and co-occurrence of associated chemicals
2. Refine and evaluate indoor exposure model
Estimate half-lives of PBDEs from homes where sources were removed
Collect key model parameters from literature review and field studies
Generate data to advance the scientific basis of exposure predictions by
1. building confidence in model assumptions
2. providing values for key model parameters
3. confirming model predictions for relevant pathways
3. Evaluate air-to skin transdermal uptake
Determine skin surface loading from measured concentrations in skin

Why Dust?

- Correlated with blood/urine samples
  - Pyrethroid pesticides
  - Flame retardants
  - PFCs
- More practical (compared to air samples)
  - Can be collected in a single visit
  - Compounds with low VP are likely to have levels that exceed LOD in dust
- Chemical reservoirs
  - Potentially reflecting chemical loading in the home over a long period
  - Indicator of source strength as it integrates emissions from all sources

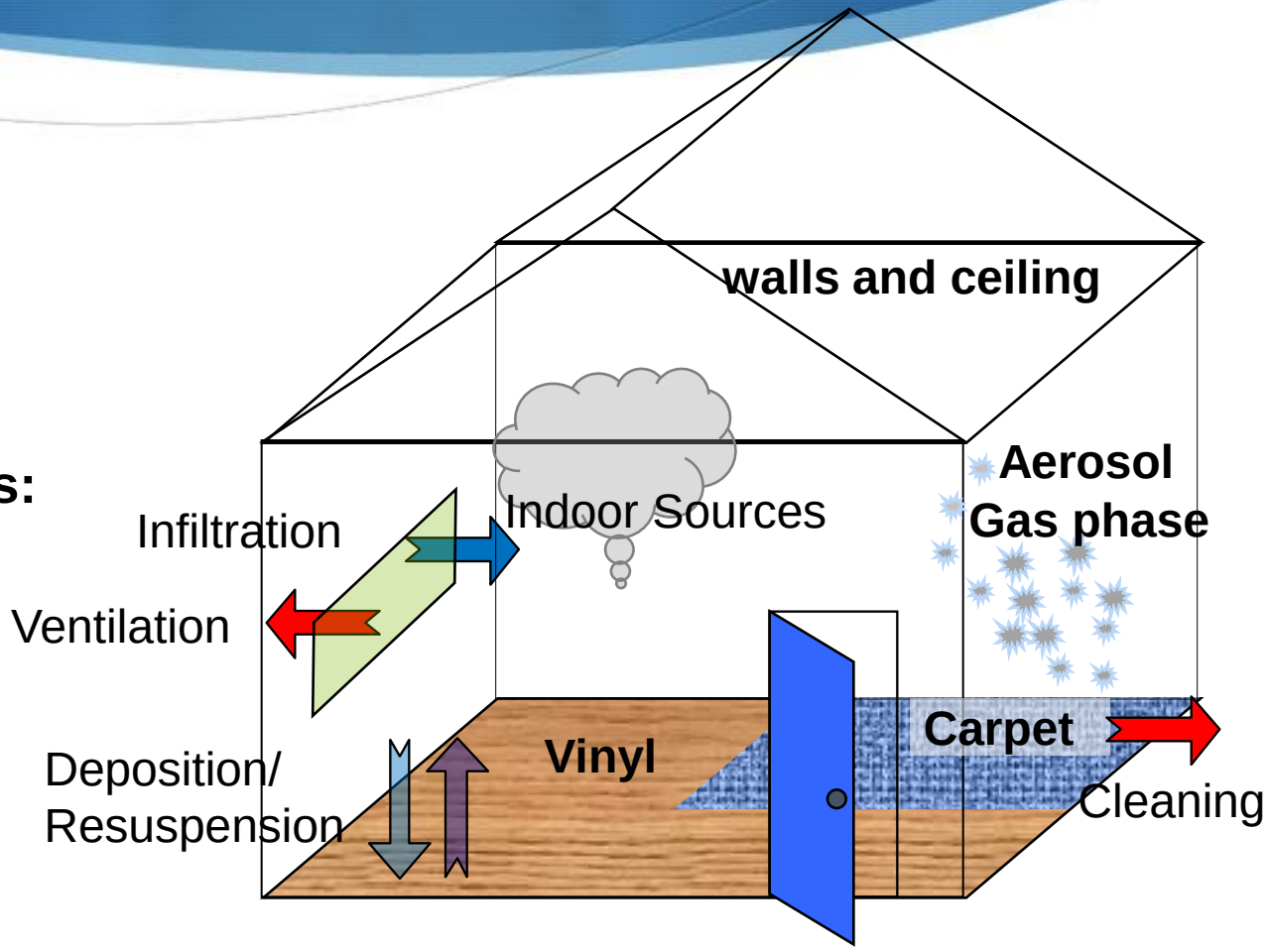
Fugacity-Based Indoor Model

Compartments:

- air (gas + particles)
- carpet
- vinyl flooring
- walls and ceiling

Mass transfer factors:

- diffusive
- advective



Indoor SVOCs Removal Processes

- Degradation → Minor
  - Chemical transformation, biological and microbial degradation, photochemical degradation, oxidation, hydrolysis
- **Ventilation**
  - Volatile organic compounds
- **Surface cleaning**
  - Semi-volatile organic compounds
    - Strong tendency to bind to organic carbon in dust or indoor surface materials → Consider removal by cleaning

Residence Times of SVOCs

Decreasing volatility →

Property name	diazinon	chlorpyrifos	pbde-47	pbde-99	permethrin
Log VP (Pa)	-2.0	-2.7	-3.3	-4.5	-6.0
Log Koa	8.0	8.7	10.0	11.2	13.0
Mass (%)					
air (gas +particles)	**0.01**	**0.03**	0.001	0.0001	0.00001
dust on carpet	0.1	0.2	1.3	**2.0**	**6.6**
carpet	98.7	98.8	97.8	97.4	93.0
Removal (%)					
ventilation	**99.1**	**96.0**	57.5	24.3	19.9
carpet cleaning	0.9	3.9	40.9	**72.8**	**76.9**
Equilibrium Residence time (years)	**2.2**	**6.9**	**10.5**	**12.5**	**3.8**
Steady-state Residence time (years)	**6.7**	**19.0**	**16.2**	**13.7**	**3.9**

- **Lower residence times for home with less carpet**

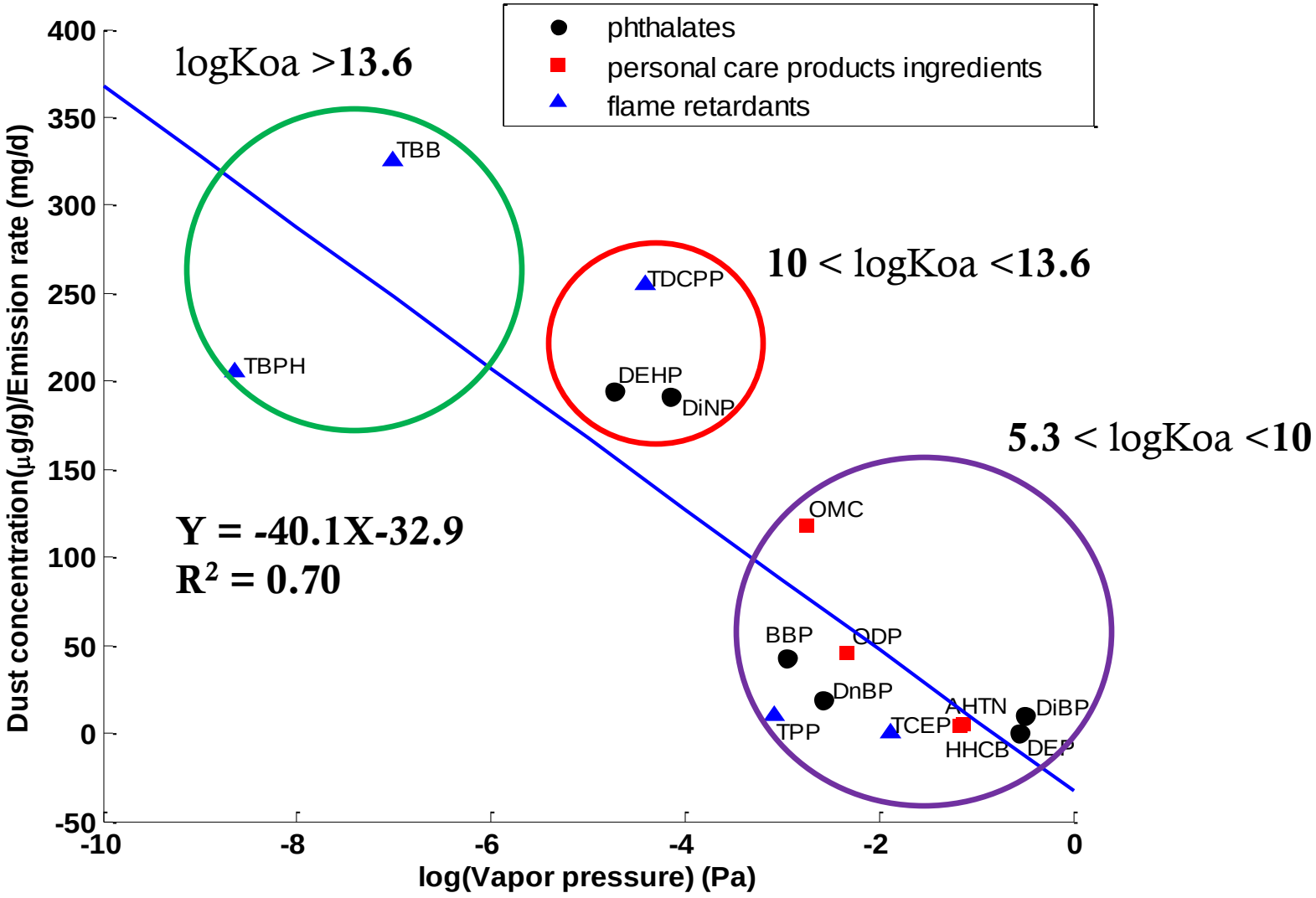
Chlorpyrifos Field Air Samples

- Sampling Design
  - Collected using passive air sampler 1 year apart in California in **2008** and **2009** from 38 homes
  - Chlorpyrifos has not been sold for indoor use since **2001**
    - Assumed that no chlorpyrifos was applied in the home between two measurement periods
    - Some homes were removed as concentrations went up
    - For the homes that either went down or stayed the same, the residence time based on measurements was almost exactly the same as the value predicted with the equilibrium model

Estimate Source Strength from Fugacity-Based Indoor Model

- Set up mass balance equation for each compartment
- Assumptions
  - The mass in each compartment is at steady state (e.g., $dMa/dt = 0$)
  - Each phase in a given compartment is in chemical equilibrium (e.g., fugacity in the carpet fiber = fugacity in the carpet dust)
- Solve for S (emission rate) in the air compartment

Log (VP) vs. the ratio of the measured dust concentration to the estimated emission rate

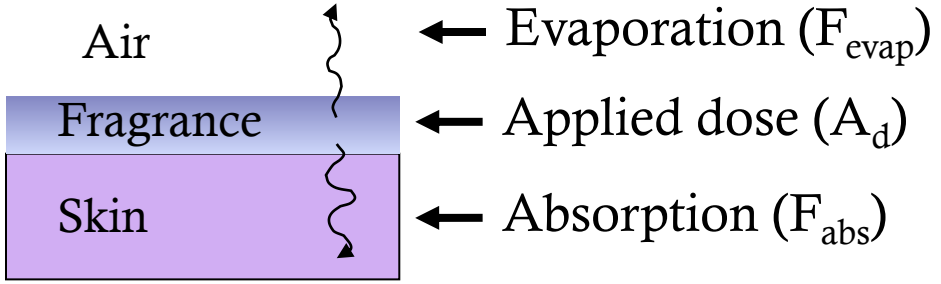


Alternate Approaches to Estimate Source Strength

- Evaporation from Personal Care Product Use

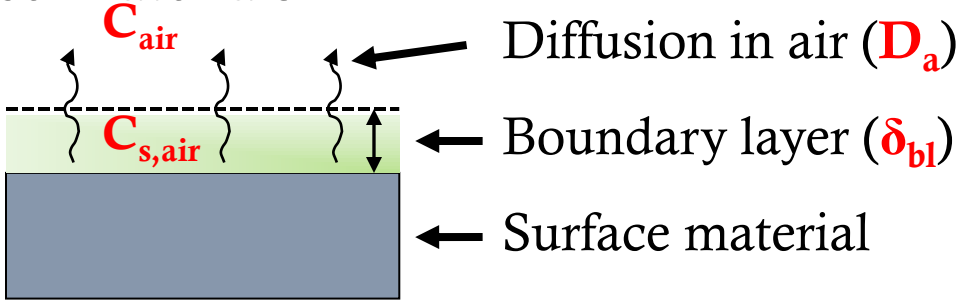
$$S_{pcp} = A_d \cdot F_{evap} \cdot f_{retention}$$

$f_{retention}$ = 1.00 for body lotion
0.05 for body wash



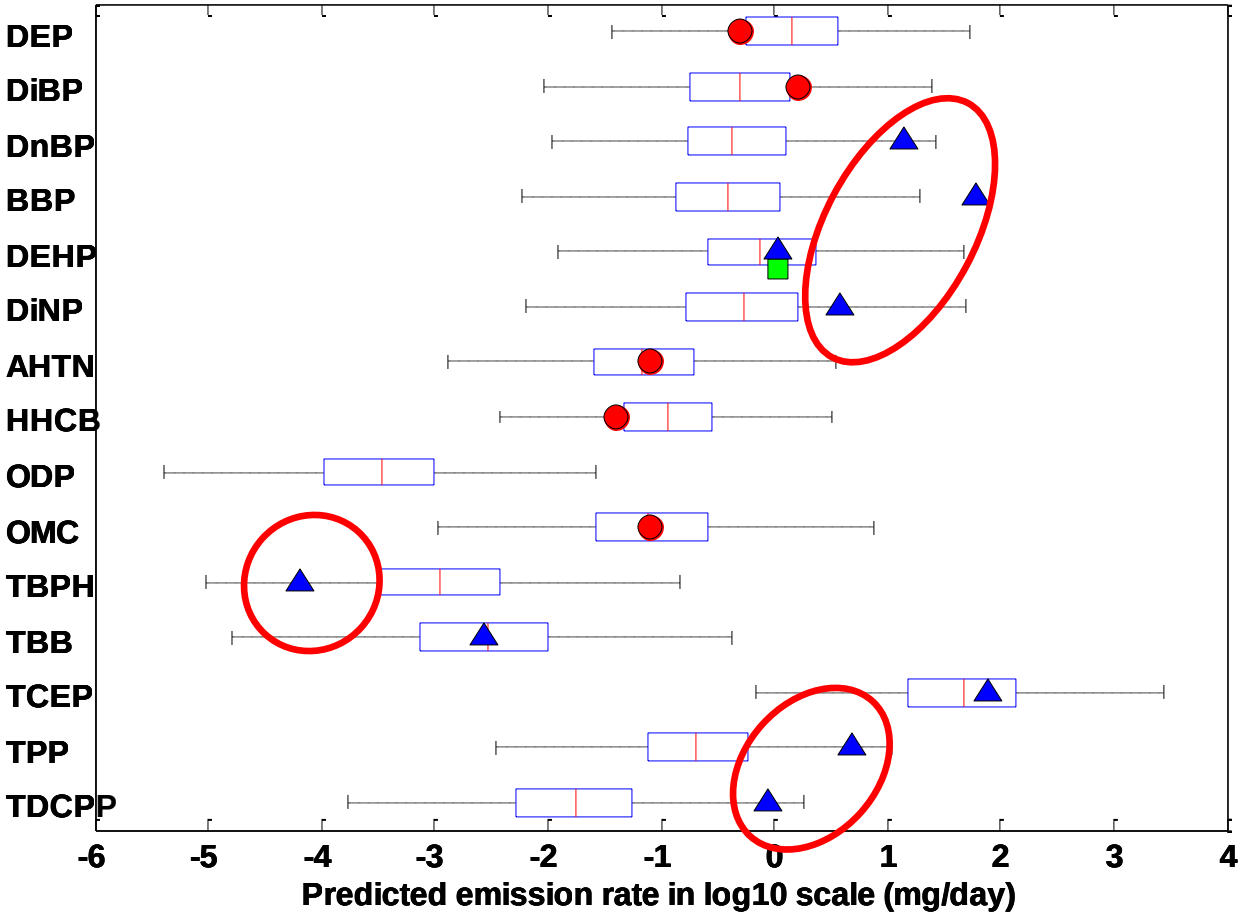
- Diffusive Transfers from Surface Materials

$$S_{surf,i} = J_i \cdot A_i = D_a \frac{(C_{s,air} - C_{air})}{\delta_{bl}} \cdot A_i$$



$C_{s,air}$ = VP·MW/(R·T)

Predicted Emission Rate (mg/day)



- Monte Carlo simulation
- ■ Reported value from experiments (Xu et al. 2009)
- ● Predicted from personal care product use behaviors
- ▲ Predicted from diffusive transfers of surface materials

Field Studies

- Study 1
  - 100 participants from existing studies
  - collect a one-time dust sample for rapid assessment of a broad spectrum of SVOCs in indoor dust
- Study 2
  - 10 participants who recently purchased new couches/replaced the foam in their coach
  - Collect dust removal rates and total dust loading over a 2-month period
  - collect dust samples over an 18-month period to determine the half-life of penta-BDEs

Existing Population

- CHARGE study (PI: Hertz-Picciotto)
  - ***CH***ildhood ***A***utism ***R***isk from ***G***enetics and ***E***nvironment
  - A population-based autism case-control study that has enrolled over 1600 index children and their families
  - Autism can be reliably diagnosed by 2 years of age, with some signs recognizable in the first year of life
  - Cases (autism and developmental delay w/o autism) - California Department of Developmental Services (DDS)
  - Controls (typical development) - randomly selected from California births, age, sex and geographically matched to cases
  - Provides a large number of cases and controls along with other samples and endpoints when their child is 2 to 4 years old

Collected Dust Samples

- These will be used for targeted and non-targeted analysis to determine what compounds are in home
- Field sampling + modeling
  - Calculate the source rate into the home
  - Provide information on distribution and co-occurrence of chemicals in the indoor environment
  - Improve understanding of what chemicals and which pathways result in current exposures to the U.S. populations
  - Limited questionnaire data

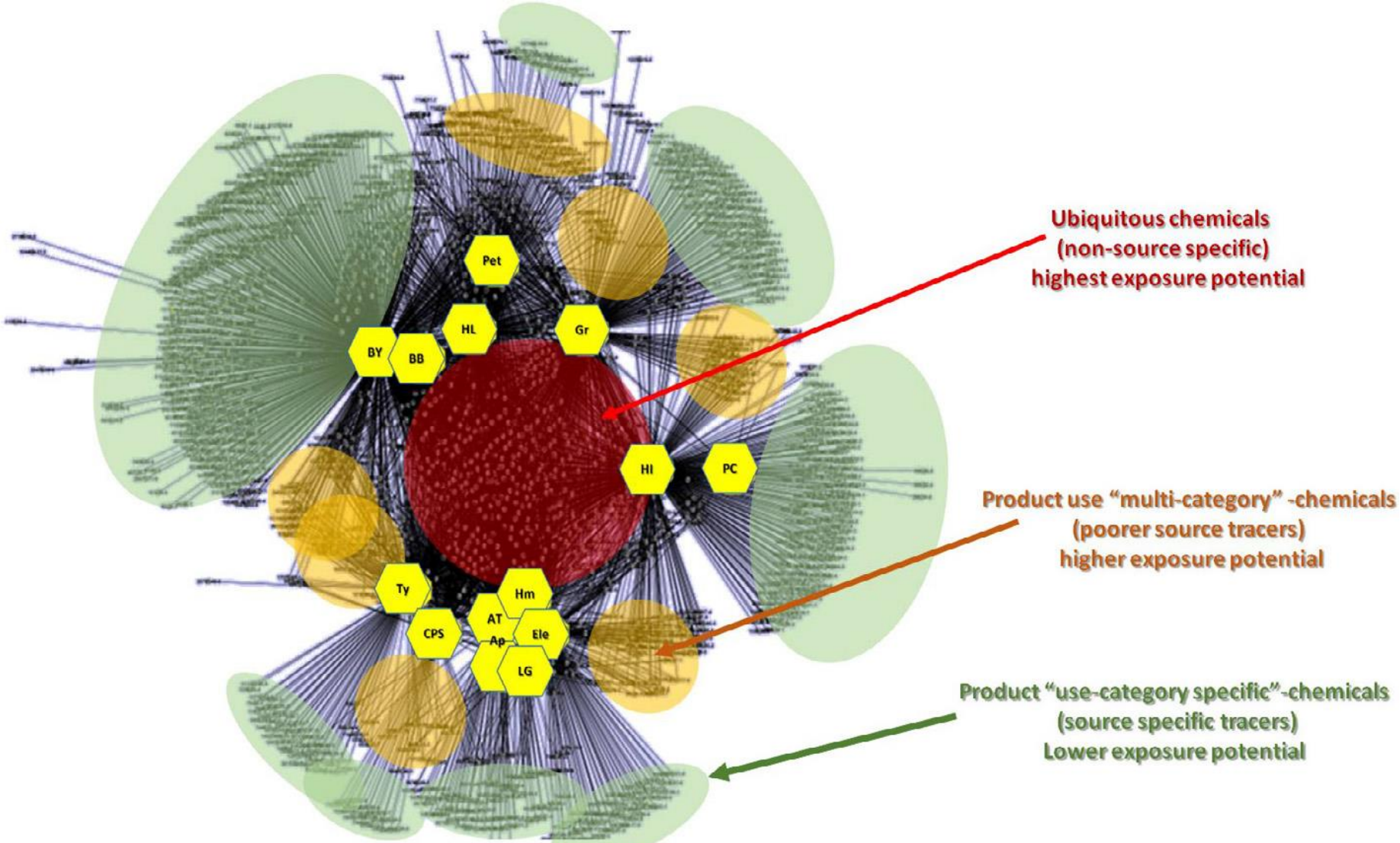
General Approach for Chemical Analysis

- Perform organic extractions of dust samples from participating homes
- Analyze extracts on two HRMS platforms
  - LC-QTOF-MS: Agilent 6530
  - GC-QTOF-MS: Agilent 7200
- Quantify concentrations of 50 target chemicals
- Identify non-target chemicals present at high abundance
- Identify transformation products or unexpected compounds

Selecting Targeted Compounds

- A number of “traditional” compounds
- Flame retardants, both those we expect to decrease and newer compounds
- Less studied compounds that we anticipate being able to find in dust
- Select tracer compounds found in a limited number of product categories
- Compounds highlighted in error recent ExpoDat comparison of exposure and biological activity levels

Selecting Target Chemicals: Consumer Products



Goldsmith et al., *Food and Chem. Toxicol.*, 65, 269 (2014)

Compounds Measured in Dust

- "Typical" compounds
  - Phthalates (DEP, BBP, DEHP, DBP)
  - PBDEs (47, 99, 100)
  - PAHs (anthrecene, pyrene)
  - Pesticides (cis- and trans-permethrin, chlorpyrifos, fipronil, imidacloprid, cyfluthrin)
  - PFCs (PFOA, PFOS)
- New Flame Retardants
  - Firemaster 550 (TBB, TBPH, TPP)
  - Other flame retardants (TCEP, TDCPP, TPPA)

Compounds Measured in Dust

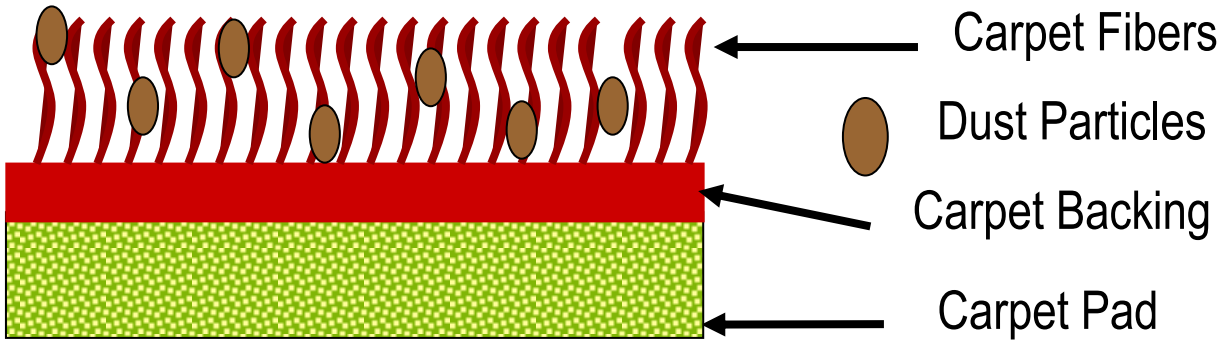
- Personal care product ingredients
  - Musks (AHTN, HHCB)
  - Parabens (methyl paraben, ethyl paraben, propylparaben)
  - Preservatives (phenoxyethanol)
- Surfactants (represents cleaning intensity)
  - 4-nonylphenol
  - nonylphenol monoethoxylate [2-(2-Nonylphenoxy)ethanol]
  - nonylphenol diethoxylate [2-[2-(4-nonylphenoxy)ethoxy]ethanol]
  - Alcohols, C12-16, ethoxylated
  - Didecyldimethyl ammonium chloride
  - dimethyldioctadecylammonium chloride
- Plasticizers
  - Tributyl phosphate, DEHA [Di(2-ethylhexyl) adipate], bisphenol A

Databases for Chemical Identification

- 1,500 Environmental contaminants
  - Typically measured in environmental samples
  - 610 persistent and bioaccumulative organic chemicals used in commerce, pharmaceuticals, and 320 byproducts, impurities, and transformation products (Howard and Muir)
- 1,800 organic compounds in Walmart Database
- Stock databases for pesticides, pharmaceuticals, drugs, explosives
- Would like to identify more databases

Refine Model Parameters

- Dust loading
  - Surface dust (easily removable dust from standard vacuuming)
  - Deeply embedded dust
- Dust removal rates (from vacuum cleaners)
  - Collect all dust removed over two 1-month periods from all 20 homes
  - Determine how much dust is typically removed from homes during cleaning
- Further evaluation of air-dust partitioning models



Studying Residence Time

- Eligibility
  - People who have purchased a new couch/foam within the last year
    - No other sources of penta-BDE in home
- Objectives
  - Determine how chemicals from old couch get change over time (half-life indoors)
  - Provide a model validation data set to compare to modeled half-life
  - Provide dust removal rates

Importance of Skin

- Weschler and Nazaroff recently published a model for estimating exposure from air to skin
- Two components, loading to skin and transfer through skin
- Model was confirmed experimentally for diethyl phthalate and di-n-butyl phthalate
- Based on median dust concentrations, skin concentrations were calculated

Air-to-Skin Transdermal Uptake

- Measure concentrations of chemicals in skin obtained as surgical waste
  - Skin will be collected from patients who undergo plastic surgery from the UCDMC Plastic Surgery Department
  - Ideally skin from face
- Evaluate air-to-skin transdermal uptake models
  - Compare measured concentrations to model predictions

Thank you for your attention!

Target Compound Selection Criteria

- Ubiquitous indoor exposure known or suspected
  - Central "node" on previous diagram (e.g., methyl 4-hydroxybenzoate, propyl 4-hydroxybenzoate)
  - On EPA high production volume chemical list
  - Likely precursor of widely detected biomarker
- Chemicals likely to be good source tracers
  - Ethofenprox (pets: flea and tick control)
  - 5-tert-butyl-1,3-benzoxazole (toys: drawing and coloring)