Migration of Organophosphorus Flame Retardants from Sources to Settled Dust

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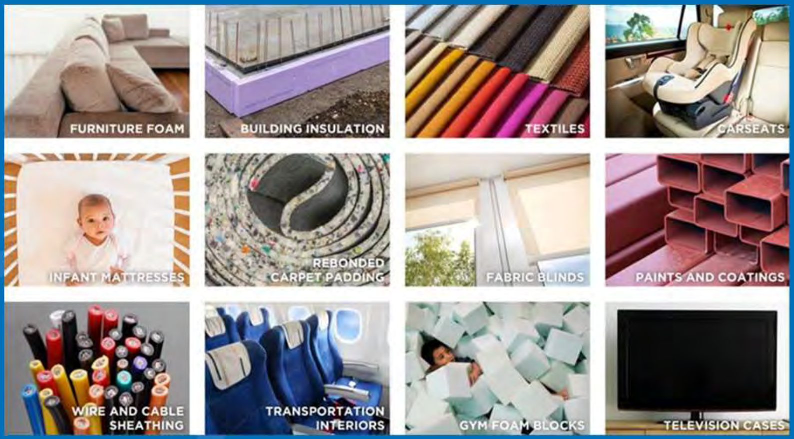
Why is it important?

- EPA ORD's research goal is to protect human health through improved risk assessments and strategies to prevent pollution and minimize exposures
- This research will contribute to
  - Filling critical knowledge gaps – lack of standard or reliable methods to characterize semi-volatile organic compounds (SVOCs) sources and sinks
  - Filling critical data gaps to predict the SVOC emissions and transport in indoor environments (experimental data and model parameters)

Organophosphorus Flame Retardants (OPFRs)

- SVOCs
- In building materials and consumer products
- Product concentrations range from 5-30%
- Not chemically bonded in materials
- Occurrence in indoor air, house dust, water, sediments, etc.
- Adverse health effects



(Van der Veen and De Boer, 2012; Wei et al., 2015; Wensing et al., 2005; Stapleton et al., 2009)

Mass Transfer Mechanisms

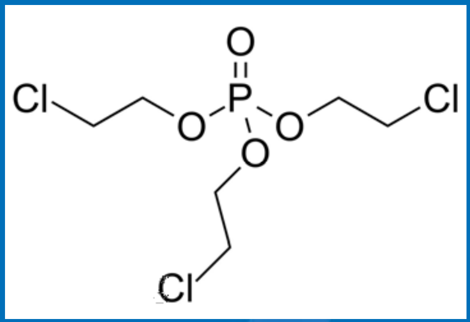
- Pollutant transport from sources to indoor air, surfaces and dust
- Sorption and desorption
- Partition

Material	⟷	Air	Material	⟷	Material
Dust	⟷	Air	Dust	⟷	Material

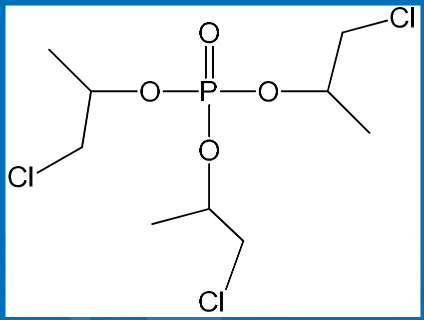
- Particle formation

OPFRs

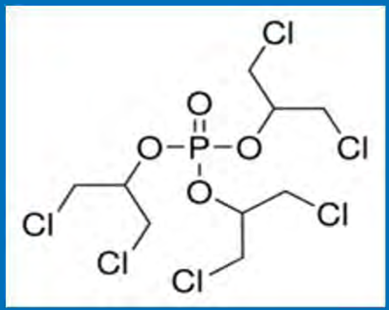
CAS RN	Chemical Name	Synonyms
115-96-8	Ethanol, 2-chloro-, phosphate	TCEP
13674-84-5	2-Propanol, 1-chloro-, 2,2',2''-phosphate	TCPP
13674-87-8	2-Propanol, 1,3-dichloro-, phosphate	TDCPP



TCEP



TCPP



TDCPP

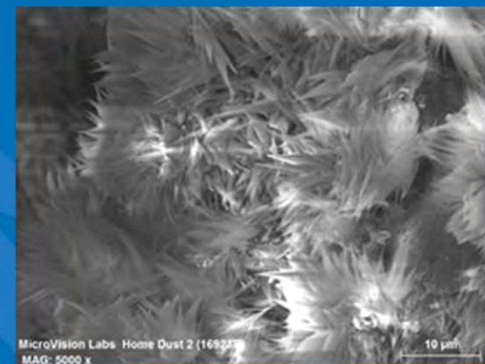
Objectives

- Study migration of OPFRs from sources to settled dust on the source surfaces through direct contact
  - OPFR in Polyisocyanurate Rigid Foam (PIR-foam) vs. in Dry Alkyl Paint
  - House Dust (HD) vs. Arizona Test Dust (ATD)
  - Different dust loadings (0.5, 0.1, 0.2, 0.3 g)
  - Different air change rates (ACR, 0.25, 0.5, 1 h^{-1})

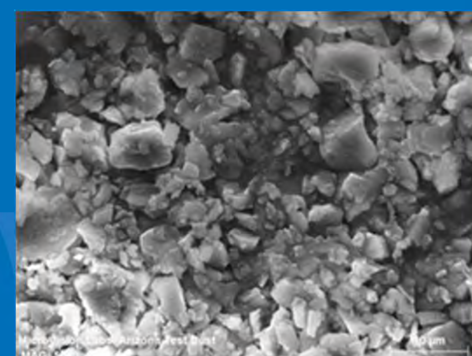
Experimental Approaches

- Small Chamber Tests

- PIR foam
- Dry alkyl paint on release paper



HD2



ATD

Experimental Approaches

Table 1. Summary of Tests (23°C, 50% RH) [a]

Test ID	Test Conditions
T1	HD, $1h^{-1}$ ACR, 0.1% OPFR foam duration 479 h
T2 [b]	ATD, $1h^{-1}$ ACR, 15% OPFR foam, duration 913 h, different dust loading at the end
T3 [b]	HD, $1h^{-1}$ ACR, 16% OPFR foam, duration 917 h, different dust loading at the end
T4	HD, $0.5h^{-1}$ ACR, 16% OPFR foam, duration 888 h
T5	HD, $0.25h^{-1}$ ACR, 16% OPFR foam, duration 888 h
T6 [b]	HD, $1h^{-1}$ ACR, 0.5% OPFR alky paint on release paper, duration 864 h, different dust loading at the end

a. For each test, OPFR-free material pieces were loaded with dust for investigation of sorption. T1 and T3 were designed as duplicate tests except the % wt of OPFR in foam was different.
b. Extra dust samples with 0.2 - 0.5 g dust on material strips were prepared.

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Experimental Approaches

- Analytical Methods
  - Collected Air samples using polyurethane foams (PUFs)
  - Extracted Dust, PUFs and test materials with 1:1 methylene chloride/ethyl acetate
  - Analyzed by gas chromatography/mass spectrometry (GC/MS)
  - Analyzed organic carbon and elemental carbon (OC/EC) contents and particle properties

Results

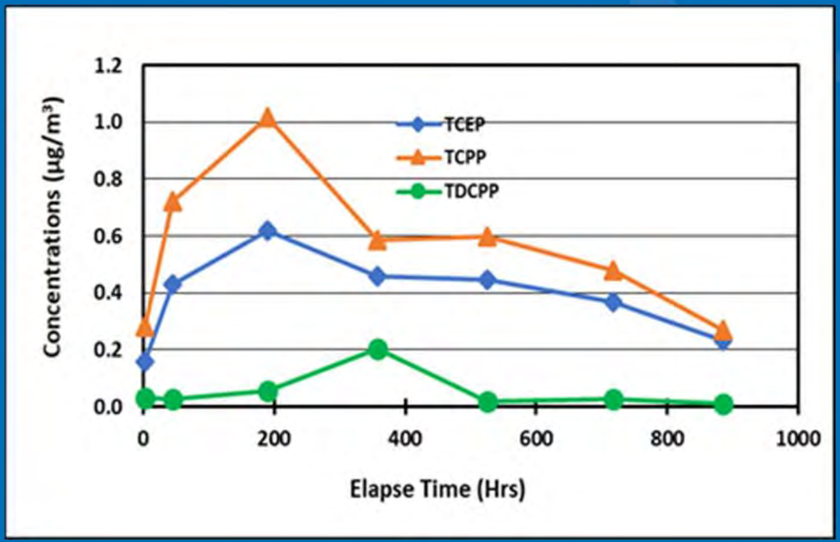
Table 2. Dust Properties

Property	Dust Type	
	HD2	ATD
Weight by volume, g/mL [a]	0.938 ± 0.008	0.723 ± 0.016
Surface area, m^2/g [b, c]	3.599 ± 0.017	10.323 ± 0.025
Particle size ─ mean, μm [b, d]	67.882 ± 0.209	4.346 ± 0.008
Particle size ─ range, μm [b, e]	0.922 to 260	0.291 to 103
Total carbon, % (w/w) [f]	20.83 ± 0.48 [f]	1.03 ± 0.13 [f]
Organic carbon, % (w/w) [f]	20.11 ± 0.56 [f]	1.03 ± 0.13 [f]

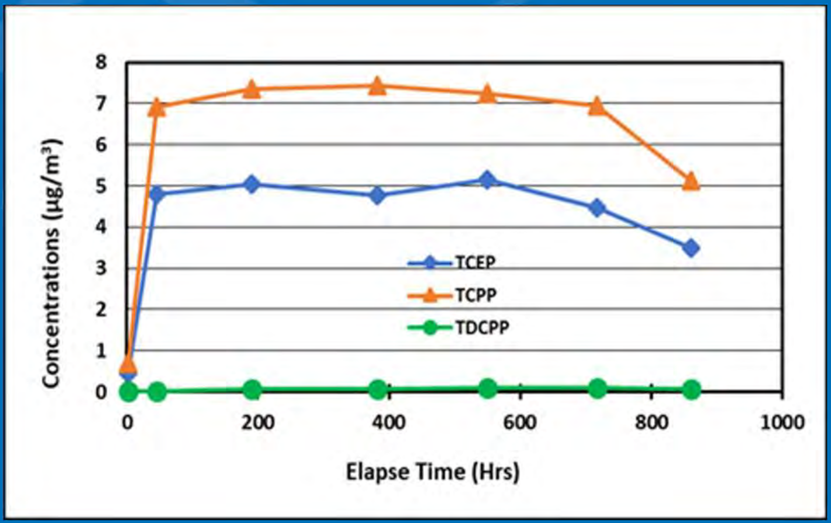
a Arithmetic mean ± standard deviation (SD) (n = 2); measured at room temperature by gravimetric method.
b Analyzed by Micromeritics Analytical Services.
c Arithmetic mean ± SD (n = 2); method: Brunauer-Emmett-Teller (BET) method with N2.
d Weighted mean value ± SD (n = 2); method: light scattering (ISO 13320).
e Method: light scattering (ISO 13320).
f Arithmetic mean ± SD (n = 4); method: NIOSH 5040.

Results

Source Emissions to the Air



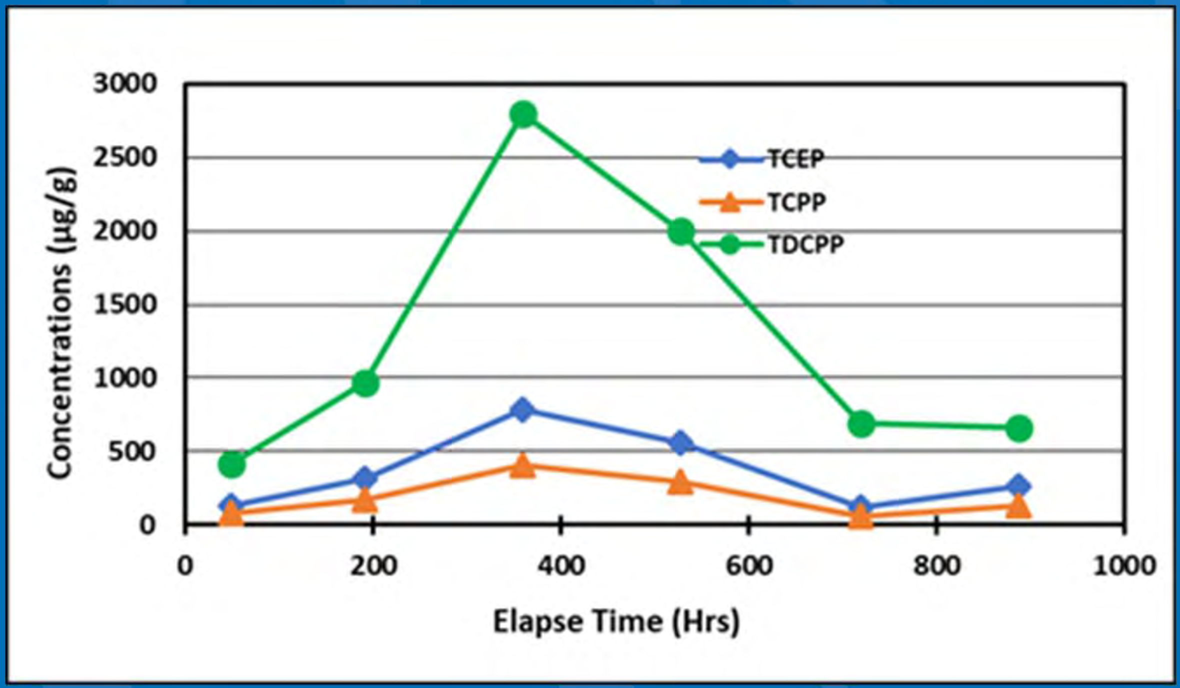
16% OPFRs in PIR Foam (T4)



0.5% OPFRs in Dry Alkyl Paint (T6)

Results

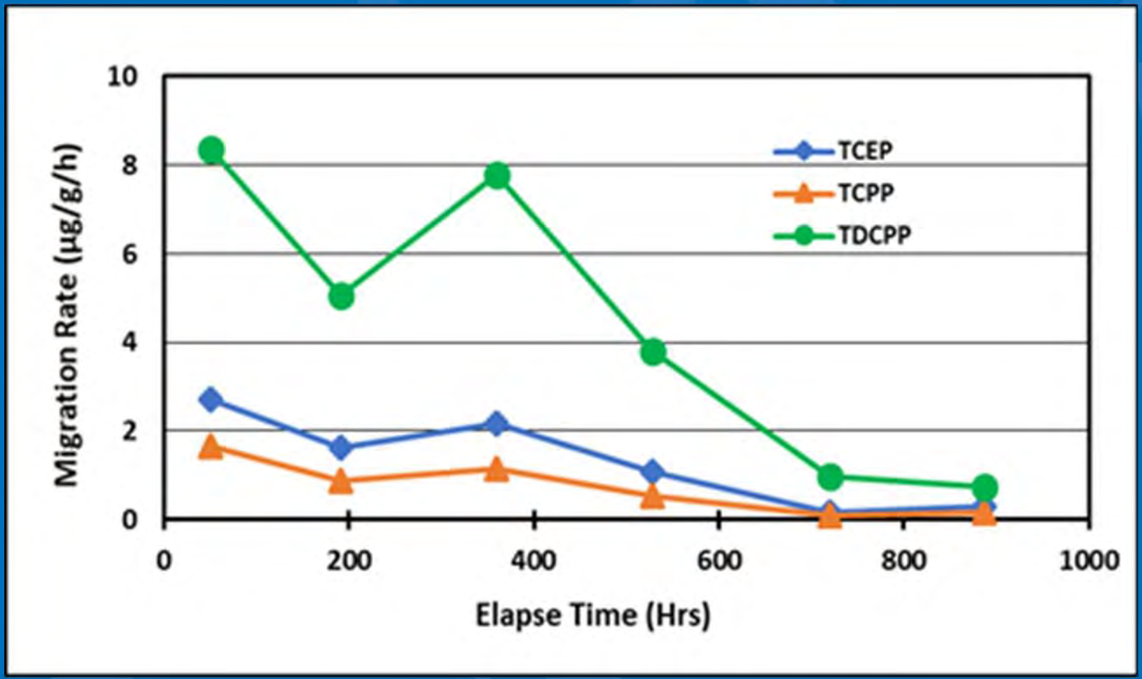
Migration Concentrations Measured in House Dust on PIR Foam



T4

Results

Migration Rates Measured in House Dust on PIR Foam

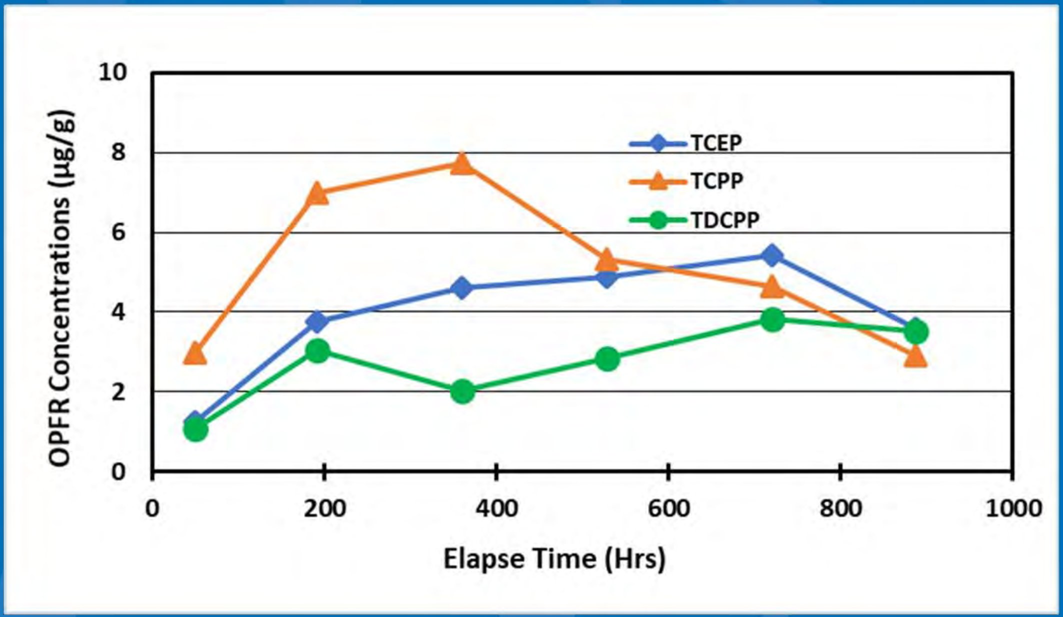


T4

Time-averaged migration rate (µg/g/h) is the experimentally determined migration concentration divided by the exposure time, t (h).

Results

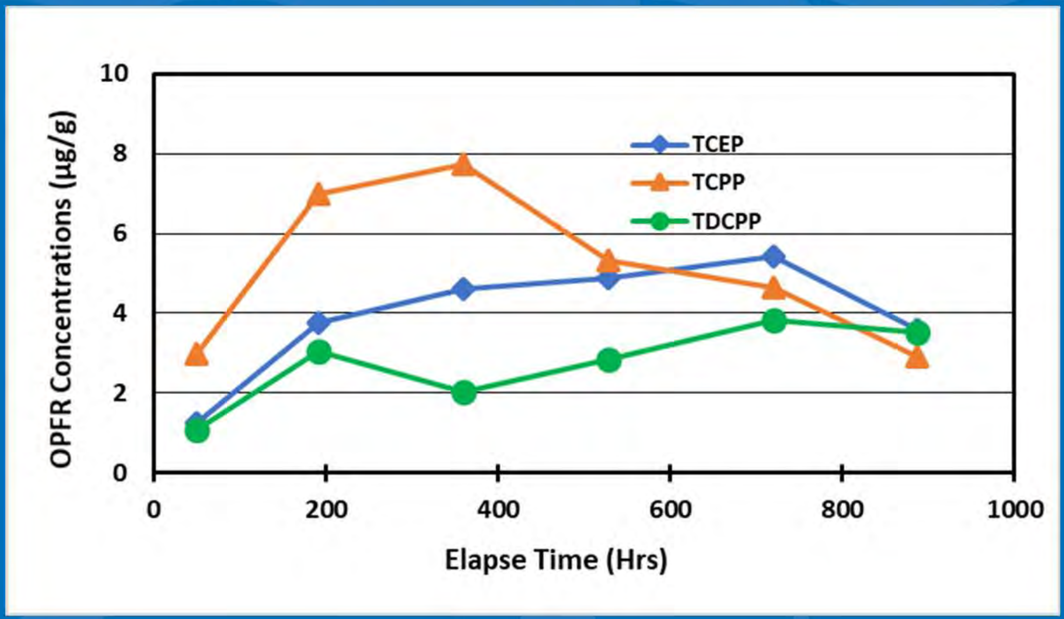
Sorption Concentrations Measured in House Dust on OPFR-free PIR Foam



T4

Results

Sorption Rates Measured in House Dust on OPFR-free PIR Foam

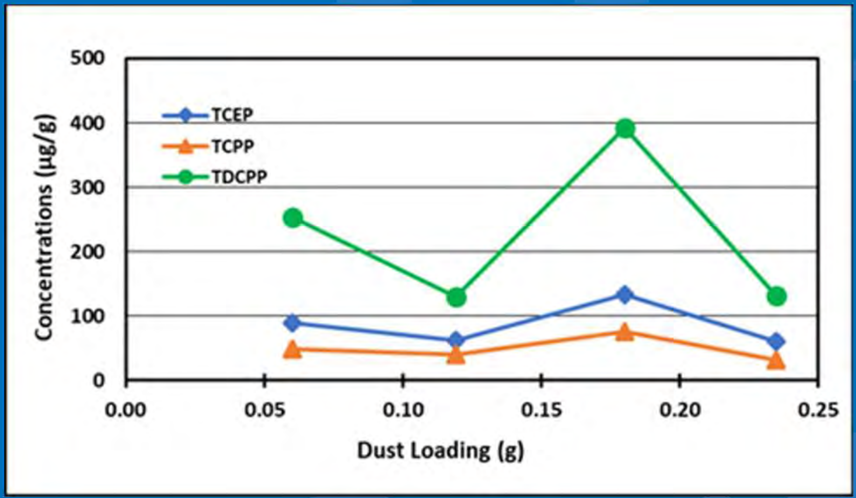


T4

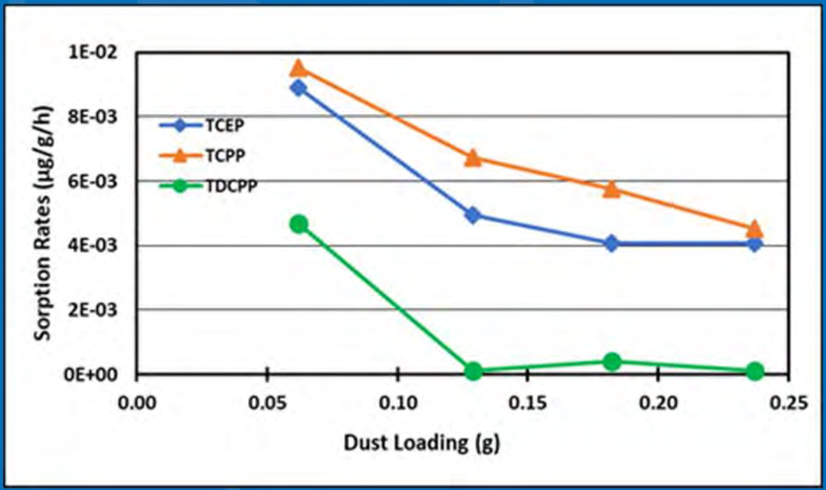
The time-averaged sorption rate (μg/g/h) was calculated by the experimentally determined sorption concentration divided by the exposure duration, t (h).

Results

Migration and Sorption Concentrations Measured under Different Dust Loadings on PIR Foam



Migration



Sorption

T3

Results

Table 3. Summary of OPFR dust/material partition coefficients

Test ID	TCEP	TCPP	TDCPP
T1	1.76×10^{-3}	3.49×10^{-3}	3.74×10^{-3}
T2	1.34×10^{-2}	1.80×10^{-2}	3.51×10^{-3}
T3	2.59×10^{-3}	2.69×10^{-3}	2.38×10^{-3}
T4	6.84×10^{-3}	7.63×10^{-3}	6.53×10^{-3}
T5	8.55×10^{-3}	9.31×10^{-3}	8.77×10^{-3}
T6	0.80	0.55	0.39

OPFR dust/material partition coefficients were estimated by the ratio of the migration concentration of OPFRs in the dust at the end of the test to its concentration in the source.

Conclusions

- The settled dust absorbed OPFRs emitted from the materials to the chamber air due to dust/air partition, whereas OPFRs migrated from the materials to the settled dust via direct contact through dust/source partitioning.
- Mass transfer through direct contact is highly effective.
- The properties of OPFR, source material and dust, dust loading, and air change rate impacted the sorption from the air and migration from the source to dust.
- This study sheds light on the correlation between OPFR concentrations in settled dust and the surface materials.
- Our results could help to fill the data gaps required for interpreting the exposure data and for risk assessment.

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- Charles Bevington, U. S. EPA former employee

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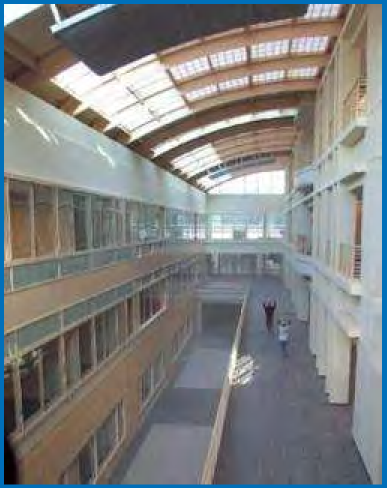
Thank You !



Images from the U.S. EPA Facility in Research Triangle Park, NC