United States Environmental Protection Agency

Migration of Organophosphate Flame Retardants from Closed Cell Foam to Settled Dust

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Why is it important?

- Semi volatile organic compounds (SVOCs), e.g. flame retardants, phthalates, perfluorinated compounds (PFCs), and polychlorinated biphenyls (PCBs), are among identified chemicals that the U. S. Environmental Protection Agency (EPA) is reviewing
- The goal is to protect human health through improved risk assessments and strategies to minimize exposures.
- The EPA ORD (Office of Research and Development) research fill critical knowledge gaps – lack of standard or reliable methods to characterize SVOC sources and sinks
- Fill critical data gaps to predict the SVOC emissions and transport in indoor environment (experimental data and model parameters)

Outline

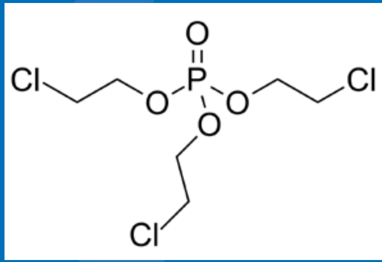
- Introductions
  - SVOCs: Flame Retardants
  - Organophosphate Flame Retardants
- Experimental Approaches
- Results
- Conclusions

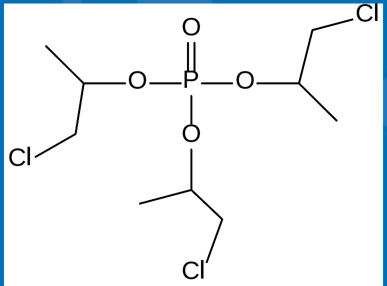
SVOCs: Flame Retardants

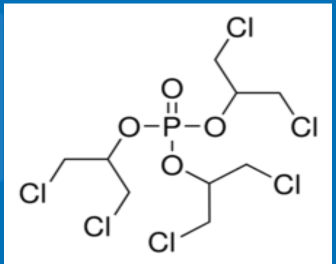
- Flame retardants (FRs) are used to meet flammability standards (hard plastics, spray foam application, polyurethane foam, electronic, mattress, textile, carpet, etc.)
- Closed cell foam products: home insulation, furniture cushion
- Organophosphate FRs (OPFRs)

Table 1. Target SVOCs- Tris Organophosphate

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







Flame Retardants (OPFRs)

- Exposure pathways
  - Inhalation
  - Ingestion
  - Dermal contact
- Fate and transport mechanisms in the indoor environment are needed for exposure assessment and risk management
  - Multiple mass transfer mechanisms
    - ✓ Material ⇔ Air
    - ✓ Material ⇔ Material
    - ✓ Dust ⇔ Air vs. Dust ⇔ Material
  - Critical parameters
    - ✓ Material/air partition coefficient (K_{ma})
    - ✓ Sorption rate constant (k_a, k_d)
    - ✓ Solid-phase diffusion coefficient (D_s)

OPFRs Migration from Source to Dust

- Inhalation exposure to gas phase SVOCs becomes less important when the solid-air partition coefficient becomes larger
- SVOC sources have large surface areas (e.g. flame retardants in furniture and home electronic equipment)
- Source-particle transfer by direct contact has been largely overlooked
- Direct source-to-dust transfer is too important to ignore

OPFRs Migration from Source to Dust

- SVOC can migrate rapidly from the source to the particles through direct contact, creating highly contaminated particles

- Complexity of indoor particulate matter

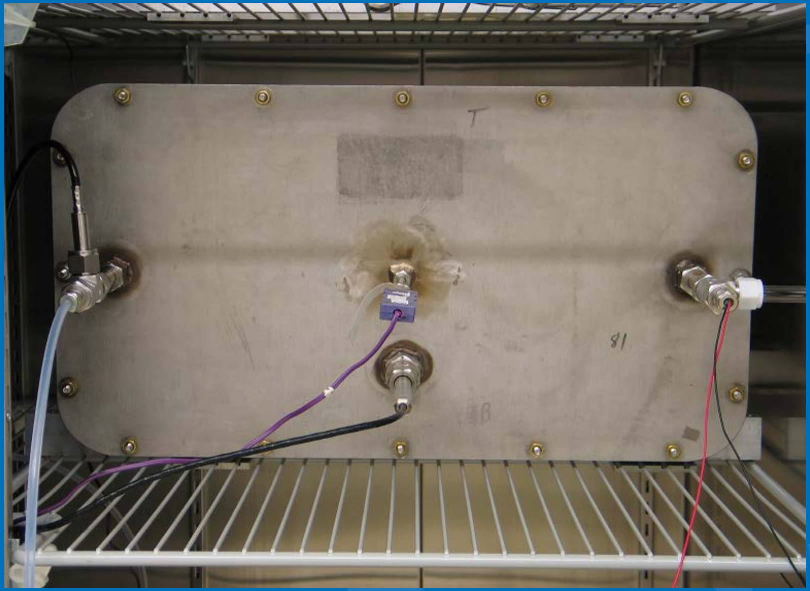
  - Size, origin, shape, density, porosity
  - solid- or liquid-phase diffusion coefficient
  - chemical composition and affinity to SVOCs (i.e. fugacity capacity)

- Important differences between airborne particles and settled dust

  - Settled particles are usually larger in size
  - May contain more earthen (crustal) and less organic carbon
  - Interactions with gas phase SVOCs are not limited by the residence time
  - May interact with the surface materials through direct contact

Experimental Approaches

- Small chamber test design



Small test chamber inside the incubator

House dust on OPFR foam, Non-OPFR foam, aluminum foil in chamber

Experimental Approaches

- Test conditions
  - 1 ACH, 50±2% RH, 23±0.1 ° C, 480 hours
  - Dust from household vacuum cleaner bags, irradiated to eliminate microbiological activity, sieved with 150 µm sieve, and then conditioned at 160°C to remove quantifiable TCEP, TCPP, and TDCPP before use
  - Polyisocyanurate rigid polyurethane foam (PIR-PUF) made by ICL Industrial Products with 0.5 % of total flame retardants (TCEP/TCPP/TDCPP) in the foam
  - Foam and aluminum foil extracted to determine OPFR concentrations before test

Experimental Approaches

- Test procedures
  - Each piece loaded with 0.1 g of house dust as evenly as possible
  - Seven OPFR-containing PIR-PUF pieces and seven non-OPFR PIR-PUF (15 cm x 3 cm x 1.1 mm each), and seven OPFR-free aluminum foil pieces (15cm x 3 cm x 0.04 mm each) placed in the small chamber
  - Pieces removed from the chamber at different times and the dust collected and extracted to determine its OPFR content. Duplicate samples collected at 408 hours
  - Air sampling with PUF/glass fiber membrane filter (~ 600 mL/min) at volume of 50 - 750 liters

Experimental Approaches

- Analytical methods
  - Organic carbon and elemental carbon (OC/EC) contents and particle properties were analyzed
  - Dust, filters, PUFs extracted with 1:1 methylene chloride/ethyl acetate
  - Analyzed on GC/MS
  - GC Internal standard (d_{27}-tributyl phosphate), extraction recovery check standard (d_{15}-triphenyl phosphate)
  - Quality assurance and quality control

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Results

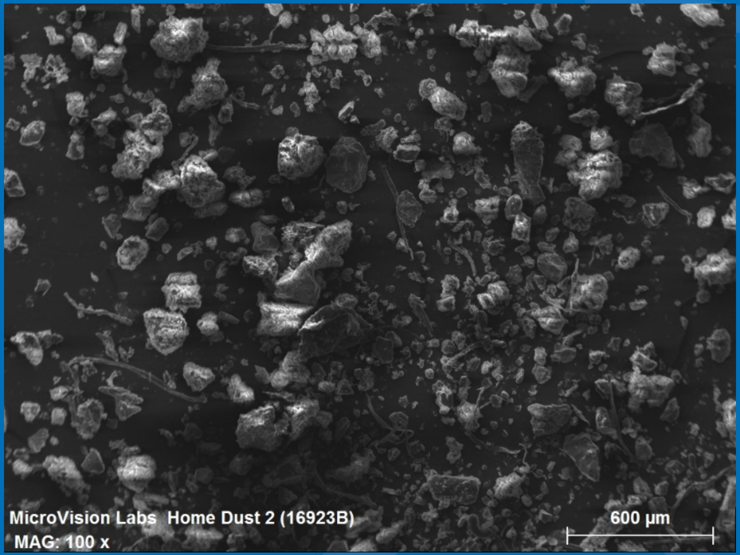
- Dust analysis

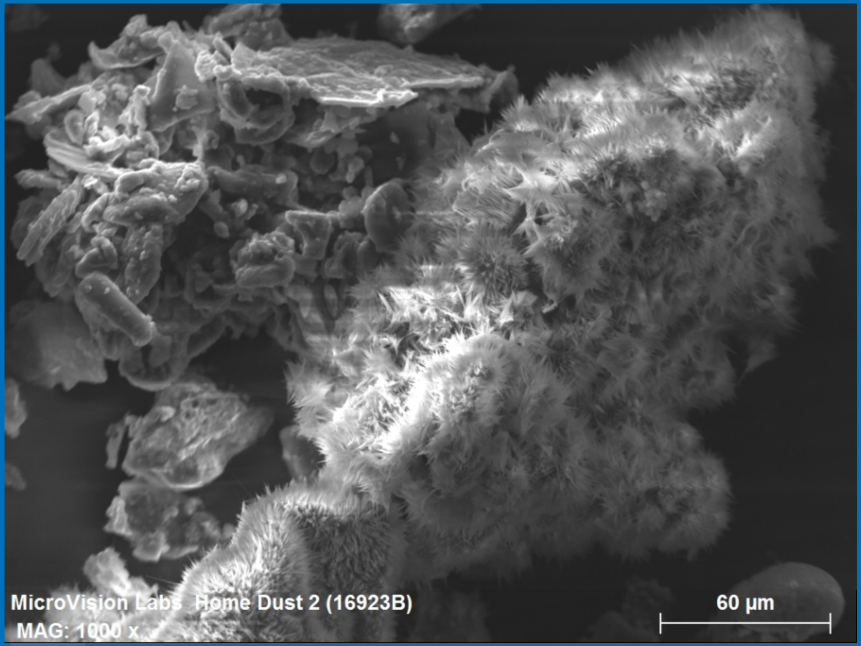
Table 1. Selected properties of the house dust

Property	House Dust	Method
Weight by volume, g/mL	0.938 ± 0.008 [a]	At room temperature by gravimetric method
Surface area, m^2/g [b]	3.60 ± 0.02 [a]	Brunauer-Emmett-Teller (BET) method with N_2
Particle size – mean, µm [b]	67.88 ± 0.21 [c]	Light scattering (ISO 13320).
Particle size – range, µm [b]	5.5 to 220 [c]	Light scattering (ISO 13320).
Particle size – 90%, µm [b]	164.54 [c]	Light scattering (ISO 13320).
Particle size –50%, µm [b]	44.22 [c]	Light scattering (ISO 13320).
Particle size – 10%, µm [b]	11.58 [c]	Light scattering (ISO 13320).
Total carbon, % (w/w)	20.83 ± 0.48 [d]	NIOSH 5040
Organic carbon, % (w/w)	20.11 ± 0.56 [d]	NIOSH 5040
[a. d] Arithmetic mean ± standard deviation (SD) [a](n=2), [d](n=4)		
[b.] Analyzed by a commercial analytical laboratory		
[c.] Weighted mean ± standard deviation (SD) (n=2)		

Results

- Dust analysis





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Results

- Source concentrations

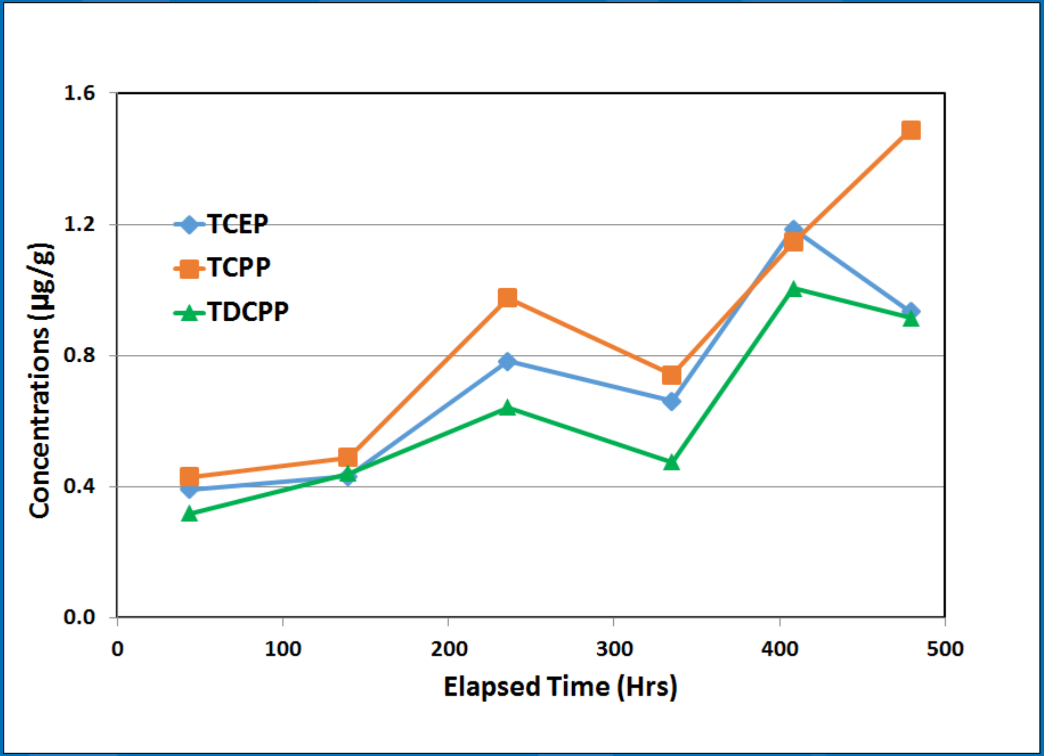
Table 2. OPFR concentrations in the source materials (Average ±SD, n=2)

FRs	FR-Foam	Non FR-Foam	Al Foil
TCEP (µg/g)	531.4±35.9	BPQL	BPQL
TCPP (µg/g)	426.8 ±2.4	60.1±0.8	BPQL
TDCPP(µg/g)	244.3±1.4	BPQL	BPQL

BPQL = below practical quantification limit (BPQL), which is the lowest calibration concentration level

Results

➢ OPFR concentrations measured in dust on OPFR foam



Results

- OPFR concentrations measured in the dust on source foam increased during test period
- OPFR concentrations measured in dust on OPFR free aluminum foil were below practical quantification limit (PQL), which was the lowest calibration concentration level
- Chamber air concentrations measured in the test
  - All membrane filter data were below PQL
  - All PUF data were below PQL

Results

- The OPFR Dust/PIR-PUF source partition coefficients were estimated

$$K_{12} = \frac{C_{m1}}{C_{m2}}$$

K_{12} = is the material/material partition coefficient between material 1 (dust) and material 2 (source foam),dimensionless
C_{m1} = concentration in material 1 in equilibrium with material 2, µg/g
C_{m2} = concentration in material 2 in equilibrium with material 1, µg/g

Results

Table 3. Roughly estimated dust/source partition coefficients for the house dust collected from FR Foam (use 408 hour data)

FRs	TCEP	TCPP	TDCPP
In dust (µg/g)	1.19	1.15	1.00
In foam (µg/g)	531.44	426.75	244.30
K_{12}	2.23×10^{-3}	2.68×10^{-3}	4.11×10^{-3}

Conclusions

- OPFR migration from OPFR sources to dust increased steadily over exposure time
- The migration due to dust/source partitioning was not significantly affected by the volatilities of the OPFRs
- The OPFR dust/PIR-PUF partition coefficients were roughly estimated
- This study will shed light on the correlation of OPFR concentrations in settled dust and the surface material
- More work is underway to better characterize the factors that affect the degree of migration of OPFRs on dust
- The results will help to fill the data gaps required for interpreting the exposure data and for risk assessment

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