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Experimental Procedures to Measure SVOC Sorption Parameters

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Introduction

- SVOCs are released from a vast number of building materials and consumer products
- SVOCs can affect indoor environmental quality and human health
- It is important to develop reliable, accurate and efficient test methods to quantify SVOC emissions and transport in the indoor environment
- There are substantial difficulties associated with experimental measurements involving SVOCs

Experimental Challenges

- SVOCs vapor pressure between 10^{-4} – 10^{-14} atm
  - Slow emissions but long-term effects
  - Formation of concentration gradients inside the sources and sinks
- Low concentration in the air
  - Long sampling times (at least several hours)
  - Large sampling volume
- Very small mass gain in the sink material
  - Difficult to measure the mass change
- Strong sorption by the wall and sampling lines

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Experimental Challenges

- Existing chamber methods for measuring D_s & K_{ma}
  - Conventional chamber
  - Microbalance chamber (Little)
  - Dual diffusion chamber (Corsi, Zhang)
  - Specially-designed SVOC emission chamber (Little & Xu)
  - Field and laboratory emission cell (FLEC, Clausen)
  - Cup method (ASHRAE)
  - Others

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Data Needed

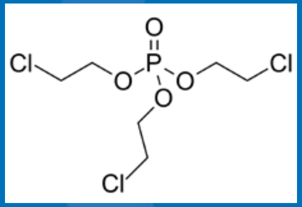
- Multiple mass transfer mechanisms in indoor environment
  - Material ⇔ Air
  - Material ⇔ Material
  - Dust ⇔ Air vs. Dust ⇔ Material

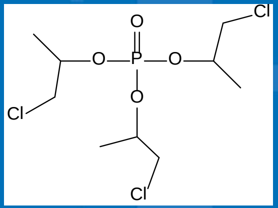
- Critical parameters for fate and transport study
  - Material/air partition coefficients (K_{ma})
  - Solid-phase diffusion coefficients (D_s)
  - Sorption rate constants (e.g. k_a, k_d)

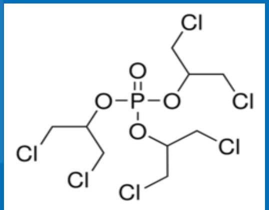
SVOC: OP-FRs

- Flame retardants (FRs) are used to meet flammability standards (hard plastics, spray foam application, polyurethane foam, electronic, mattress, textile, carpet)
- Organophosphate FRs (OP-FRs)

Synonyms	Synonyms	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







Experimental Approaches

- Small chamber design
  - Two chambers connected in series – source and sink chambers
  - Source chamber generated constant emissions of target SVOCs
  - Test materials as small “buttons” in the sink chamber, removed at different adsorption time
  - The rail, hold up to 15 material buttons (1.4 cm I. D.), utilized as the runner for the removable test material rack
  - Air concentrations monitored at the inlet and outlet of the sink chamber
  - Concentrations in the materials measured by extraction

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Experimental Approaches

Pictures of the source chamber and test chamber

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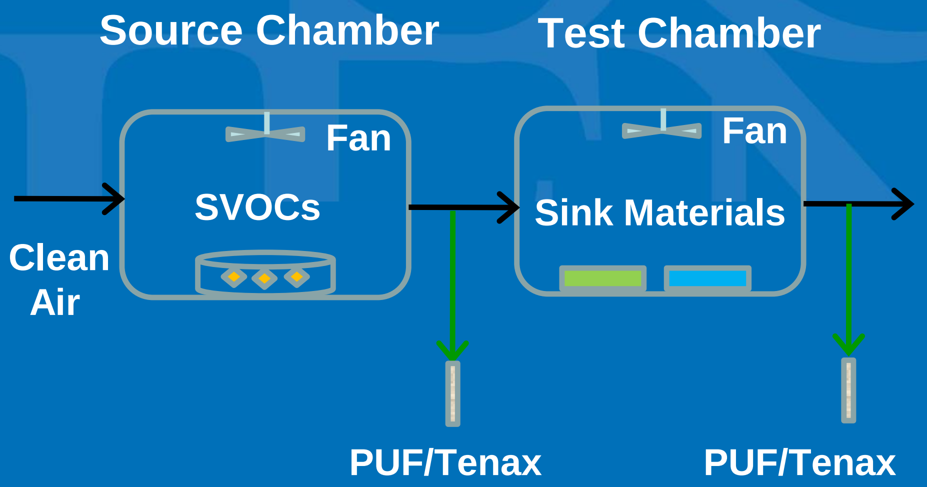
Experimental Approaches

Pictures of test materials

Experimental Approaches



Schematic of the air flow between two chambers

Experimental Approaches

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- Test conditions
  - Source chamber
    - ✓ TDCPP in an insulated heated aluminium block wrapped in aluminum foil at 67 ° C controlled by a thermocouple
    - ✓ Flushed with dry clean air

Table 2. OP-FR source settings in the SVOC source chamber

FRs	Cup Materials	Cup Size (ID, cm x Depth, cm)	Temperature (° C)	Emission Rate ± %RSD, mg/h
TCEP	Teflon	5.08 x 0.83	24.6	$1.05 \times 10^{-4} \pm 4.68$
TCPP	Teflon	5.07 x 0.81	24.6	$5.74 \times 10^{-4} \pm 5.42$
TDCPP	Aluminum	5.07 x 0.79	67.0	$5.00 \times 10^{-5} \pm 6.14$

Experimental Approaches

- Test conditions
  - Test chamber
    - ✓ 1ACH, 50% RH, 24.5±0.5 °C
    - ✓ OP-FR sources dosed into the empty chamber
    - ✓ FR sources replaced by clean air at 810 hours
    - ✓ PUF sampling (600 mL/min) at volume of 70 - 650 liters
    - ✓ Exhaust sampling line consisted of 27 cm Teflon tubing (0.95 cm I.D.) with an 18-cm glass manifold (1.6 cm I.D.)
    - ✓ "Pre-Coated" the chamber with OP-FR before placing the test materials

Experimental Approaches

- Test conditions
  - Analytical
    - ✓ PUFs extracted with 1:1 methylene chloride/ethyl acetate by Lab Rotator
    - ✓ Materials were extracted by sonication
    - ✓ Analyzed on GC/MS
    - ✓ GC Internal standard (d_{27}-tributyl phosphate), extraction recovery check standard (d_{15}-triphenyl phosphate)
    - ✓ Quality assurance and control

Results

➢Constant OP-FR sources

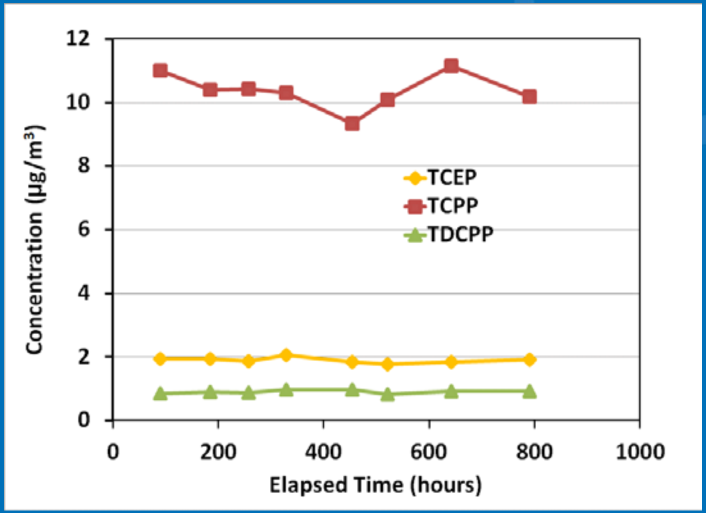
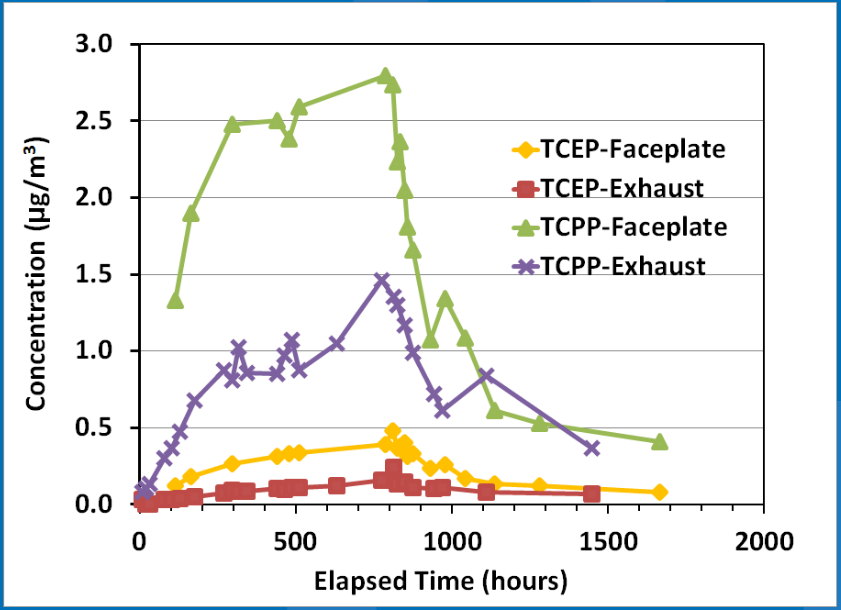


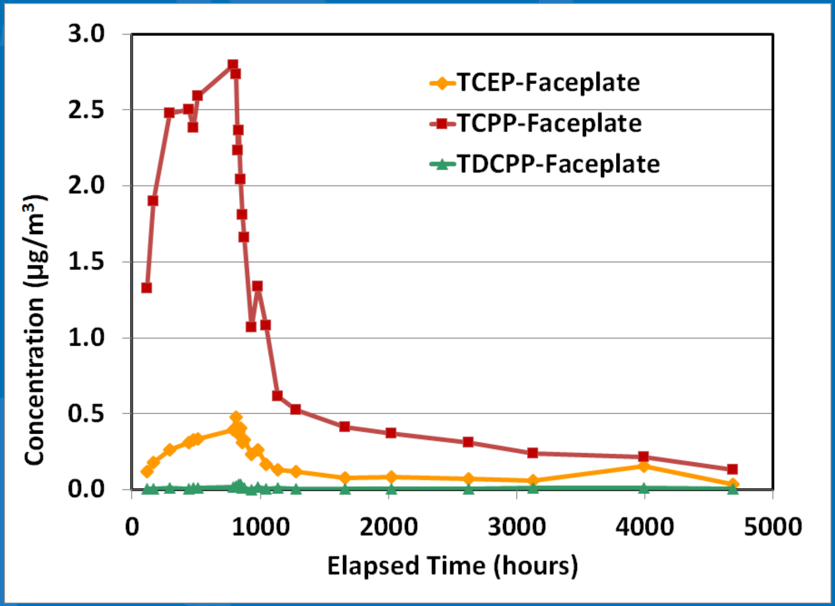
Table 3. Measured concentration of OP-FRs from source chamber (October 2013 to May 2014, N=33)

FRs	Avg ($\mu g/m^3$)	STD	%RSD
TCEP	2.1	0.4	19
TCPP	10	1.2	12
TDCPP	0.8	0.2	23

Results

➢Chamber air concentrations measured in the empty chamber sink test





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Results

- Collected data for estimating parameters (D_s & K_{ma})
  - Experimental data of sorption concentrations
  - Use Degree of Sorption Saturation(DSS) model (Deng et al. 2010) to estimate D_s & K_{ma} (Liu et al. 2014)

$$\mathrm{DSS} = \frac{M(t)}{M_{max}} = \frac{M(t)}{C_a K_{ma} A \delta} = \mathrm{f}(N_l, \Theta, Fo_m)$$

  - Develop correlation equations to predict model parameters based on compound properties

Conclusions

- Improved small chamber testing method for characterizing the sink effect of SVOCs on materials
  - The design of the lid uses minimal entry points and rods to remove the exposed materials.
  - Multiple sink materials can be tested at the same time
  - SVOC concentrations in the materials determined individually
  - The new method can detect the SVOCs in the sink materials in the microgram range

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