



Development of a Small Chamber Method to Study SVOCs Sink Effect

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Why this is important?

- SVOCs, e.g. Flame retardants, phthalates, PFCs, are among high-profile toxic chemicals that EPA plans to review
- Aligns development of strategies that enlighten risk assessments and policy decisions to minimize exposures and protect human health with EPA Chemical Safety and Sustainability (CSS) program
- SVOC sinks affect indoor environmental quality and human health
- Fill critical knowledge gaps – lack of standard or reliable methods for characterizing SVOC sources and sinks
- Fill critical data gaps to predict the SVOC emissions and transport in indoor environment (experimental data and model parameters)

What are SVOCs?

- SVOCs vapor pressure between 10^{-4} – 10^{-14} atm
 - Slow emissions but long-term effects
 - Strong sorption by interior surfaces and dust
- Where SVOCs are found
 - Sludge and wastewater
 - Surface/ground water/sediments
 - Indoor air/dust
 - Furniture and building materials
 - Consumer products
 - Human blood, milk, and urine
 - Environmental biota

Why Study SVOCs?

➤ Health Effects

- Endocrine disruption
- Asthma
- Neurotoxic effects
- Probable or known carcinogens

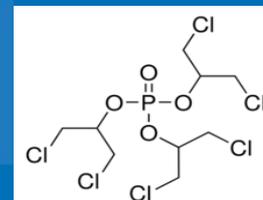
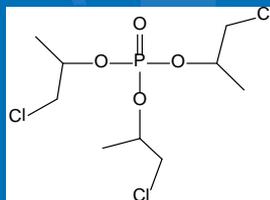
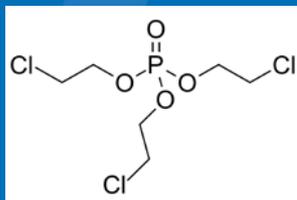
➤ Fate and transport mechanisms in indoor are needed for exposure assessment and risk management

- Multiple mass transfer mechanisms
 - ✓ Material ⇔ Air
 - ✓ Material ⇔ Material
 - ✓ Dust ⇔ Air vs. Dust ⇔ Material
- Need input data for exposure models in the absence of field measurement data

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



Flame Retardants

➤ Exposure pathways

- Inhalation and dermal exposure during spray application of paints or coatings and handling products (occupational)
- Inhalation of indoor air, dust and incidental ingestion of dust in the home environment (adults, children, infants)
- Ingestion via direct mouthing of children's products (children)

➤ 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)

Experimental Challenges

- 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

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

Experimental Approaches

➤ Small chamber design

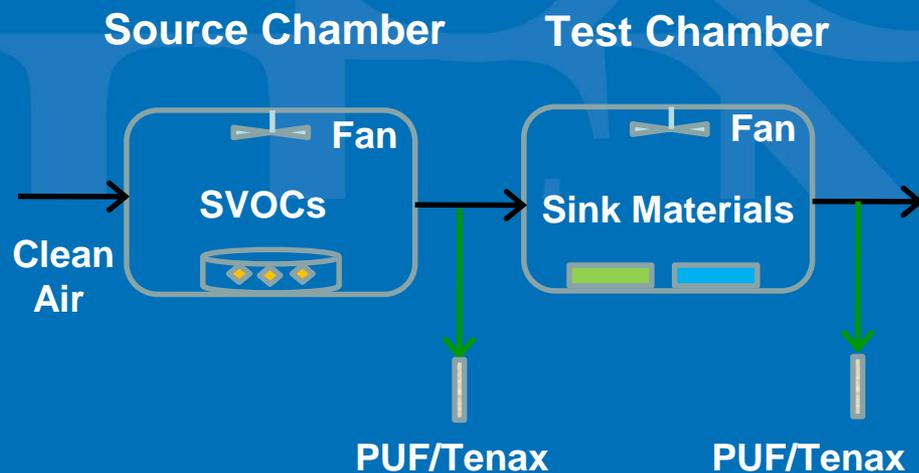
- Two chambers connected in series – source and sink chambers
- Source chamber generated constant emissions of target SVOCs
- Test materials as small “buttons” in the sink chamber, removed at different adsorption time
- The rail, hold up to 15 material buttons (1.4 cm I. D.), utilized as the runner for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

Experimental Approaches



Pictures of the source chamber and test chamber

Experimental Approaches



Schematic of the air flow between two chambers

➤ Test conditions

- Empty stainless steel chamber investigated
- 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	$1.05 \times 10^{-4} \pm 4.68$
T CPP	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	$5.00 \times 10^{-5} \pm 6.14$

➤ 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

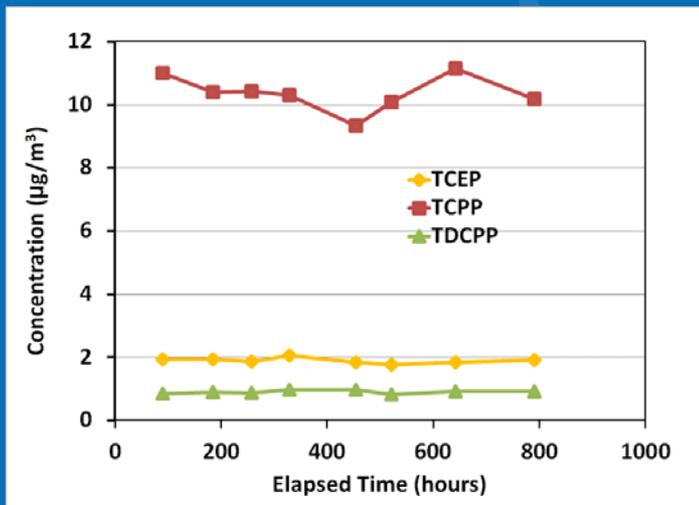
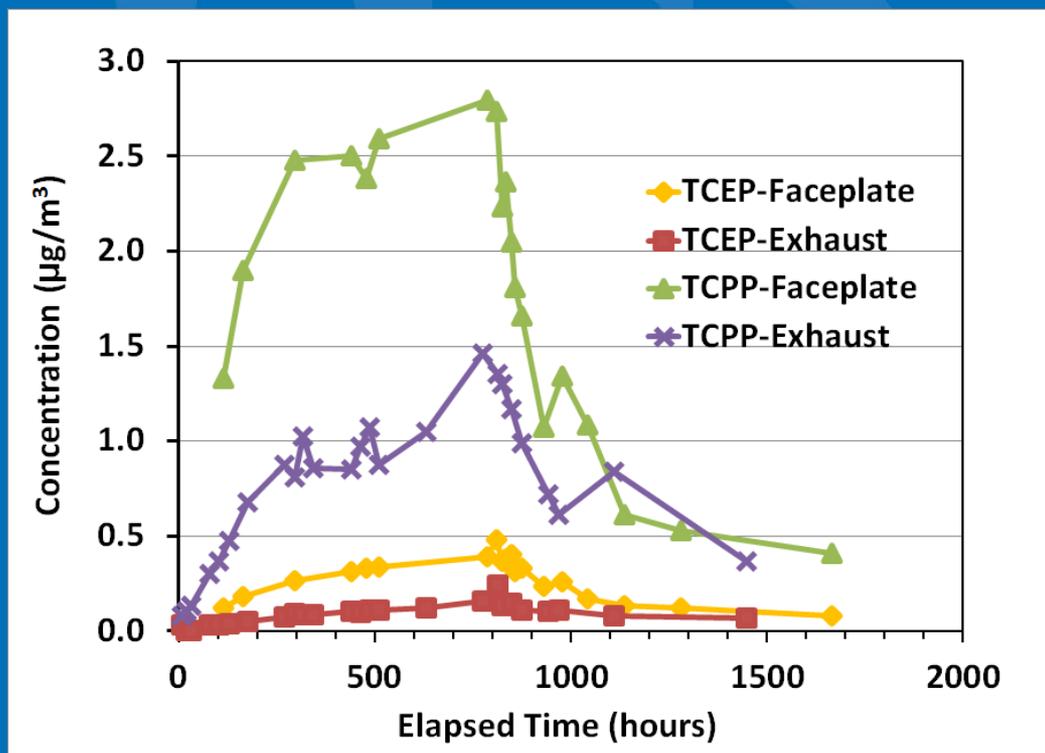


Table 3. Measured concentration of OP-FRs from source chamber (October 2013 to May 2014, N=33)

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

Results

➤ Chamber concentrations measured in the empty chamber sink test



Results

➤ Adsorption on the chamber wall and sampling line

Table 4. Mass balance of TCEP and TCPP in the empty stainless steel chamber (data up to 1700 hours)

	TCEP		TCPP	
	Faceplate	Exhaust	Faceplate	Exhaust
Total mass dosed, μg	85.1	85.1	464	464
Mass adsorbed during adsorption, μg	73.5	81.4	369	428
Mass desorbed during desorption, μg	5.96	3.53	31.6	28.1
Mass on chamber surface ^a , μg	67.5	77.9	337	400
% Mass adsorbed ^b	77%	91%	70%	86%

^a $M_{\text{surface}} = M_{\text{in}} - M_{\text{out}} - M_{\text{air}}$ ^b % Mass adsorbed was calculated by mass adsorbed by the chamber wall at the end of the test divided by total mass dosed.

➤ Langmuir sorption model evaluation

$$\frac{dC}{dt} = \frac{R}{V} - NC - k_a CL - k_d ML \quad (1)$$

$$\frac{dM}{dt} = k_a C - k_d M \quad (2)$$

$$K_e = \frac{k_a}{k_d} \quad (3)$$

C = SVOC concentration in the chamber air, $\mu\text{g}/\text{m}^3$

k_a = sorption rate constant, m/h

k_d = desorption rate constant, h^{-1}

K_e = equilibrium partition coefficient, m

L = loading material area/chamber volume, m

M = mass of the SVOC adsorbed on the material surface, $\mu\text{g}/\text{m}^2$

N = air change rate, h^{-1}

R = constant emission rate of SVOC to the chamber, $\mu\text{g}/\text{h}$

t = time, h

V = chamber volume, m^3

Results

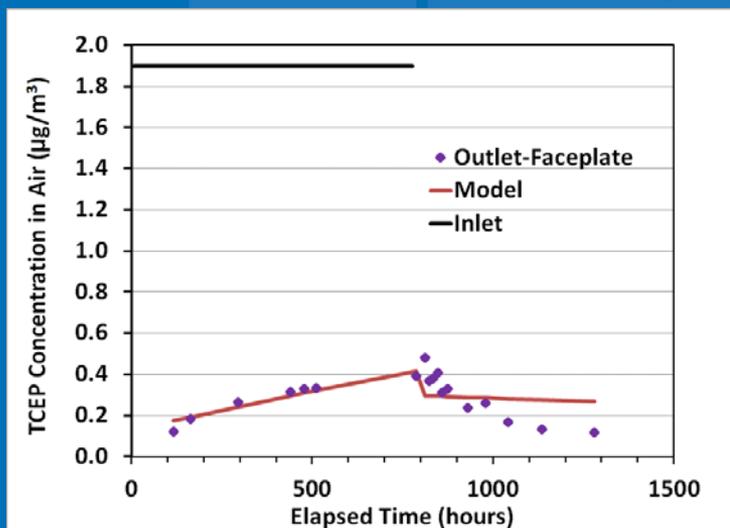
➤ Langmuir sorption model evaluation

FRs	k_a , m/h	k_d , /h	K_e , m
TCEP-Faceplate	0.838	3.37×10^{-3}	249
TCEP-Exhaust	4.86	7.28×10^{-3}	668
TCPP-Faceplate	0.367	1.76×10^{-3}	208
TCPP-Exhaust	0.1.86	4.16×10^{-3}	448
TDCPP-Faceplate ^a	20.6	8.74×10^{-3}	2350
TDCPP-Exhaust ^a	20.5	2.89×10^{-3}	7100

^a. TDCCP experimental data below the lowest calibration concentration but above instrument detection limit

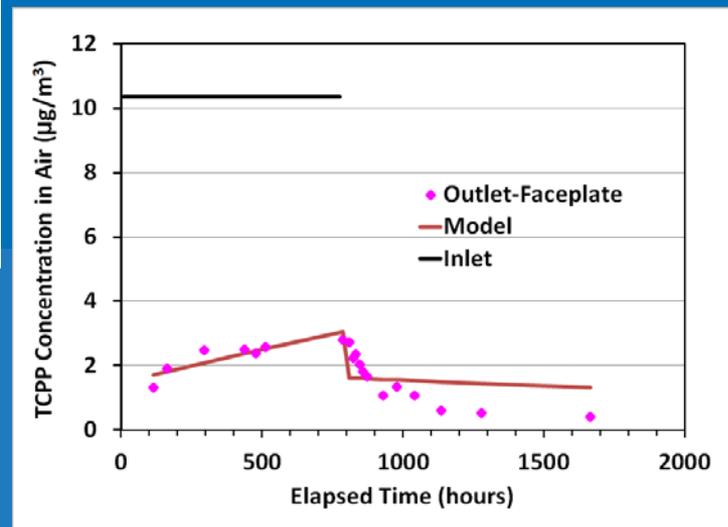
Results

➤ Langmuir sorption model evaluation



TCEP

TCPP



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

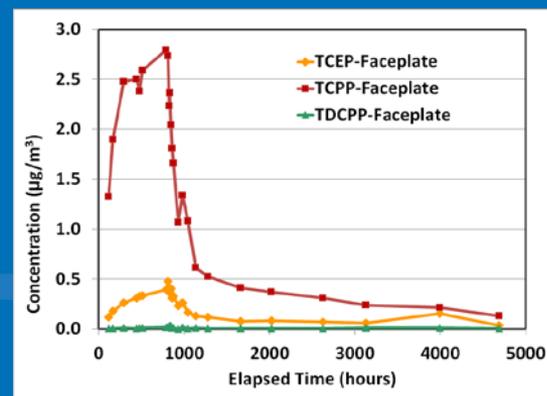
Conclusions

- OP-FRs have strong adsorption on the stainless-steel chamber wall and sampling lines
 - TDCPP > TCPP > TCEP
 - Air samples collected at faceplate more reflect the air concentrations in the chamber

- Langmuir sorption model evaluation
 - k_a , k_d and K_e were obtained
 - The model is reasonably good in simulating the adsorption period of TCEP and TCPP but not as good as for their desorption period.

Future Work

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



Future Work



Pictures of test materials



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