

DEVELOPMENT OF A SMALL CHAMBER METHOD FOR SVOC SINK EFFECT STUDY

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Keywords: Small chamber, SVOC, Source characterization, Sink effect, Langmuir sorption model, Flame retardant

SUMMARY

The transport mechanisms of semivolatile organic compounds (SVOCs) between sources, air, house dust, and interior surfaces in the residential environment needs to be better understood in order to more accurately estimate indoor SVOC exposure and develop risk management strategies that protect human health. This study describes a new design to improve an existing small chamber testing method used to characterize the sink effect of SVOCs on materials. The sink effect of organophosphorus flame retardants on the stainless steel chamber is also reported. The data are used to evaluate the applicability of the Langmuir sorption model for SVOCs. This chamber method could be used to estimate the material/air partition coefficients and solid-phase diffusion coefficients of SVOCs for sink materials in the future.

INTRODUCTION

Semivolatile organic compounds (SVOCs) have low emissions over a long period of time because their vapor pressure is lower than 10^{-4} atm (Weschler and Nazaroff, 2008). Sorption of SVOCs by interior surface materials in buildings and their subsequent re-emissions from these materials, which is often referred to as the “sink effect”, significantly affects SVOCs gas-phase concentrations in the indoor environment. Knowledge of the transport mechanisms of SVOCs between sources, air, house dust, and interior surfaces in the residential environment will help to characterize human exposure, develop and refine source-to-exposure-to-dose models, and develop risk management strategies to minimize exposures and protect human health. To characterize the sink effect of SVOCs in the indoor environment, chamber tests are often conducted. The experimental challenges for measuring SVOC emissions and transport include low SVOC concentrations in the air, difficulty measuring the mass change in the sink material, and strong sorption of SVOCs on the chamber walls and sampling lines.

The U.S. Environmental Protection Agency (EPA) recently developed a small chamber test method to measure adsorption and desorption of polychlorinated biphenyl (PCB) congeners, on materials (Guo et al., 2012, Liu et al., 2014). The small chamber system uses two 53-liter environmental chambers connected in series with the relatively stable SVOC sources in the source chamber and the test materials, made as small “buttons”, in the material chamber.

The material buttons are removed from the chamber at different exposure times and extracted to determine the amount of SVOC absorbed by the materials during the tests. SVOC

concentrations at the inlet and outlet of the material chamber are monitored. The data are used to estimate the partition and diffusion coefficients by fitting a sink model to the experimental data. This small chamber test method can be extended to other SVOCs.

During the PCB study, PCB sources were generated by clean air flushing a caulk collected from the field in the source chamber to the material chamber, a procedure that may not be applicable to other SVOCs. The material buttons were removed from the material chamber by opening the chamber under a fume hood at each sampling time, a procedure that may cause some interferences and a short pause in the testing. To overcome these disadvantages in the experiments, a new design of the source and the sink chamber were fabricated and tested. This paper describes the details of the improved chamber system and reports the sink effect study for organophosphorus flame retardants (OP-FRs), including tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) on the empty stainless steel chamber wall.

METHODOLOGIES

Source and Material Chambers

Both source and material chambers are 53-liter electro-polished stainless steel chambers that conform to the ASTM Standard Guide D5116-10 (ASTM, 2010). The interior specifications of each chamber are 50.8 cm width by 25.5 cm height by 41.0 cm depth. The chambers are connected in series through 1.3 m Teflon tubing (0.95 cm I.D.) with a stainless steel T-connector in a temperature-controlled incubator (Model SCN4-52, Environmental Equipment Co., Inc., Cincinnati, OH, USA) (Figure 1a). A 5-cm diameter computer cooling fan (Model EC4020, EVERCOOL THERMAL CORP., Ltd., Taiwan) was placed in the center of each chamber, blowing upward toward the top of the chamber to provide thorough mixing inside the chamber. The fan was set to 12 V, which generates air velocity of approximately 10 cm/sec, 1 cm above the surface. The incubator was set at 23 °C. The source chamber temperature was 24.6 °C, raised by the 67 °C heating block used for generating TDCPP emissions. Dry clean air at 362 mL/min was supplied to the source chamber and mixed with 555 mL/min humidified air from a water vapor generator at the T-connector to establish 50 % relative humidity (RH) and 1 air exchange per hour (ACH) of inlet air flow to the material chamber and at the source chamber outlet sampling port. All air flows were controlled by mass flow controllers (Teledyne, HFC-E-202, Hampton, VA, USA). The T-connector after the Teflon transfer line was set to be able to monitor SVOC concentrations from the source chamber, which was used as the SVOC inlet concentration of the material chamber. The material chamber exhaust sampling line consists of 27 cm Teflon tubing (0.95 cm I.D.) with an 18-cm glass manifold (1.6 cm I.D.). Air samples can also be collected at the faceplate of the material chamber when needed. An OPTO 22 data acquisition system (DAS, OPTO 22, Temecula, CA, USA) is used for continuous recording of the outputs of the mass flow controllers, temperature and RH in the chamber and inlet air.

To generate constant source emissions of TCEP, TCPP, and TDCPP, liquid chemicals obtained from ICL Industrial Products America, Inc. (St. Louis, MO, USA) were placed in different diameter cups in the source chamber (Table 1). The TDCPP cup was placed in an insulated heated aluminium block wrapped in aluminum foil at 67 °C due to its low emission (Figure 1b). The temperature of the heating block was controlled by a thermocouple placed directly in the TDCPP pool. A second thermocouple monitored the temperature of the heated block. The source chamber has been flushed with dry clean air.

The traditional lid assembly for the 53-L environmental chamber as described in detail in ASTM D5116-10 has been redesigned for the material chamber to accommodate the method that characterizes the sorption properties of multiple materials from a known and constant source of air contaminants (Figure 1c). Ten material entry points – 3.8 cm laser cut openings on the front of the lid with stainless steel Swagelok 3.8-cm cap assemblies (SS-2400-C) were bored through and welded to each opening. At the base of each 3.8-cm opening, a 35.6 cm long 2.5 cm wide “U” shaped stainless steel support rail was welded to the back side of the lid. The rail will be utilized as the runner for the removable test material rack. Each rail could hold up to 15 material buttons. To assist with removal of the rack a stainless steel handle was welded to the opening end of the rack. Figure 1c shows the interior wall of the sink material lid. The entire lid assembly including the removable button racks was electro-polished (KEPCO, Inc., Vicksburg, MI, USA). The design of the lid uses minimal entry points and rods to remove the exposed materials. For sink tests, the test materials could be prepared by cutting “button” coupons from the original material. Each material button will be approximately 14 mm diameter with an approximate thickness of 2 mm or less depending on the material. Each button will be mounted on aluminum pin mounts (Ted Pella, Inc., Redding, CA, USA) with double-sided tape. The mounted materials will then be secured on the button rack by inserting the pin mounts in the holes on the button rack.

Table 1. OP-FR Source Settings in the SVOC Source Chamber.

Chemicals	Cup Material	Cup Size (ID, cm × Depth, cm)	Temperature (°C)	R ± %RSD, mg/h ^a (n=8)
TCEP	Teflon	5.08 × 0.83	24.6	1.05 × 10 ⁻⁴ ± 4.68
TCCP	Teflon	3.84 × 0.81	24.6	5.74 × 10 ⁻⁴ ± 5.42
TDCPP	Aluminum	5.07 × 0.79	67.0	5.00 × 10 ⁻⁵ ± 6.14

^a. Average emission rate measured by GC/MS at the T-connector to the material chamber

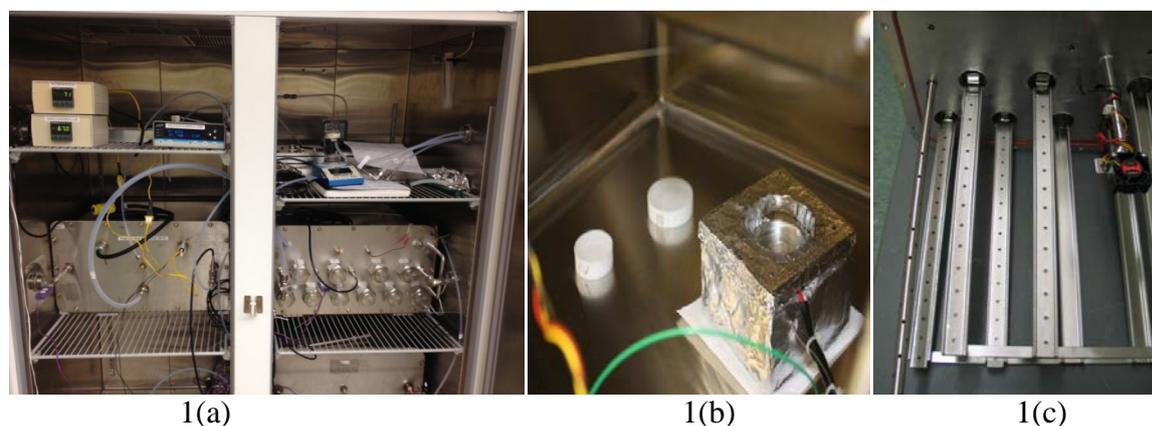


Figure 1. Source and material chambers for SVOC sink study (a. Two chambers connected inside the incubator, left - source chamber, right - material chamber. b. Inside source chamber. c. Lid of the material chamber.)

Chamber Testing

To utilize the chamber system for SVOC studies in the future, an empty chamber test was conducted to investigate the stability of the OP-FR sources and the sink effect of the stainless steel chamber wall and the sampling lines with OP-FR.

The polyurethane foam (PUF) (small pre-cleaned certified, Supelco, St. Louis, MO, USA) samples were collected at the outlet of the source chamber (600 mL/min) at volume of 70 liters. The source chamber was confirmed to generate constant emissions of TCEP, TCPP, and TDCPP before those compounds were dosed in the empty test chamber. Prior to the test, a test chamber background PUF sample was collected overnight at a sampling flow rate of approximately 600 mL/min for 16 hours. The effluent from the source chamber was then directed to the inlet of the test chamber for 810 hours. The OP-FR source was then disconnected from the test chamber and replaced by clean air flow. The test chamber was flushed with clean air for more than 800 hours. Air samples at the inlet, the faceplate and the exhaust sampling line of the test chamber were collected on PUFs at a volume of 70 to 650 liters. After collection, the glass holder with the exposed PUF inside was capped and then wrapped in aluminum foil, placed in a sealable plastic bag, and stored in the refrigerator at 4 °C until extraction.

Sample Extraction and Analysis

PUF samples were placed in individual 40-mL borosilicate glass amber I-Chem™ vials (Thermo Scientific, Pittsburgh, PA, USA) with approximately 35 mL 1:1 methylene chloride/ethyl acetate and 50 µL of 10-µg/mL d₁₅-triphenyl phosphate (Sigma-Aldrich, St. Louis, MO, USA) as recovery check standard and extracted horizontally on the Multi-purpose Lab Rotator (Barnstead International Model 2346, Thermo Scientific) for 1 hour. The extract was filtered through anhydrous sodium sulfate (Sigma-Aldrich) and further concentrated to approximately 1 mL using the RapidVap N₂ Evaporation System (Model 791000, LabConco, Kansas City, MO, USA). The concentrated extract was then transferred to a 5-mL volumetric flask and brought up to volume with rinse solution from the concentration tube. After extraction, 990 µL of the extract in a 1-mL volumetric flask containing 10 µL of 10-µg/mL internal standard, d₂₇-tributyl phosphate (Cambridge Isotope Laboratories, Inc. Tewksbury, MA, USA), was transferred to gas chromatography (GC) vials for analysis. The vials were stored at 4 °C in the laboratory refrigerator and analyzed within 30 days. Sample quantification was conducted using the Agilent 6980/5973N GC/mass spectrometer (MS) (Agilent Technologies, Santa Clara, CA, USA) with an Agilent 7683B auto sampler. The instrument was calibrated over the range of 5 to 200 ng/mL. Certified TCEP, TCPP, TDCPP calibration standards were purchased from AccuStandard Inc. (New Haven, CT, USA). The internal audit program (IAP) standard of TCEP was purchased from Sigma-Aldrich and the TDCPP was from Fluka (St. Louis, MO, USA).

Quality Assurance and Control

A quality assurance project plan was prepared and approved before the project began. The GC/MS calibration was verified by the IAP. Each batch of samples was analyzed along with its corresponding quality control samples. Extraction method blank and field blank samples were prepared and analyzed as well. All samples were extracted and analyzed with the criteria that the percentage recovery of the recovery check standards had to be within 100 ± 25%, and the precision of duplicate samples had to be within ± 25%. When the measured concentrations of OP-FRs in the sample were above the highest calibration level, the extract was diluted and reanalyzed.

RESULTS AND DISCUSSION

Constant SVOC Emission Source Generation

To maintain constant emissions of SVOCs, the source chamber was kept closed once the chemicals were placed inside the chamber. No weight loss data were collected. The emission

rates and stability of the SVOCs were monitored by measuring the SVOC concentration at the outlet of the source chamber, also at the inlet of the test chamber, by the PUF–GC/MS method described above. The results in Table 1 and Figure 2a show that constant sources of TCEP, TCPP and TDCPP were generated. This method will be applied to the study of other SVOCs in the future.

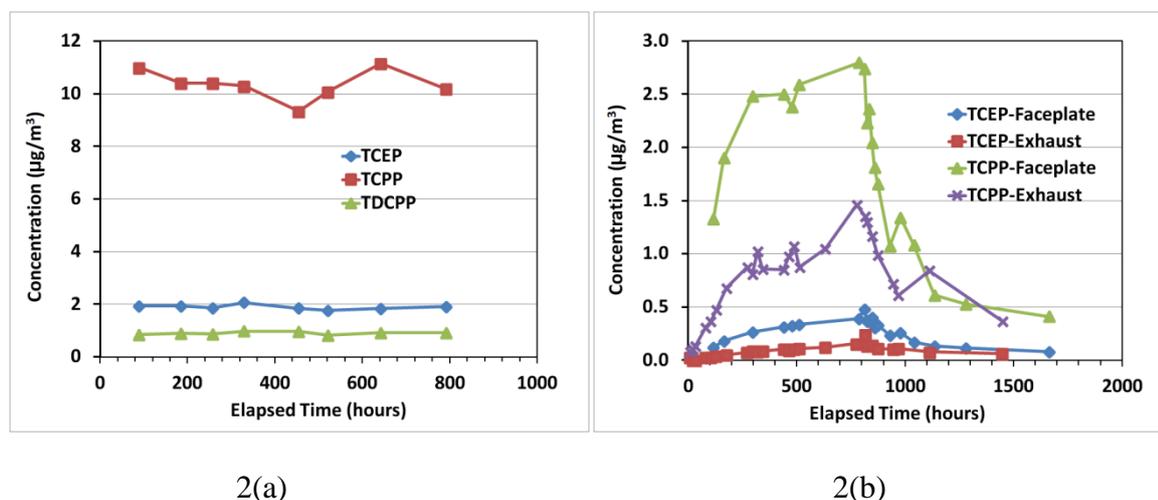


Figure 2. Concentration of the OP-FRs in the chamber air during sink test (a. source chamber. b. empty stainless steel test chamber)

Chamber Wall Sink Effect

The sorption of OP-FRs by the interior walls of the 53-L chamber was evaluated by conducting a sink test once the constant source emissions of the SVOCs were established. The material test chamber was controlled and monitored at 1 ACH, 50 % RH and 24.5 ± 0.5 °C. The chamber air concentrations of TCEP, TCPP, and TDCPP were monitored at the exhaust and the faceplate of the material chamber. The difference between these two sampling locations is that the exhaust line has the 27-cm Teflon tubing and the 18-cm glass manifold. The time profiles of TCEP and TCPP collected at both locations are presented in Figure 2b. All concentrations of TDCPP were below the lowest calibration concentration and thus not reported. More than 800 hours was required for TCEP and TCPP to closely reach the steady state. The concentrations of TCEP and TCPP measured at the material chamber exhaust were lower than the concentrations measured directly at the faceplate of the chamber, especially during the adsorption time period. Most likely this difference in measured concentrations is caused by the adsorption of OP-FRs on the Teflon tubing and glass manifold.

The amount of TCEP and TCPP adsorbed on the chamber wall at the end of the test is calculated by

$$M_{surface} = M_{in} - M_{out} - M_{air} \quad (1)$$

where

M_{in} = total mass dosed into the chamber calculated by the emission rate and dosing time, μg

M_{out} = mass leaving the chamber calculated by the trapezoid rule using concentration data, μg

M_{air} = mass remaining in the chamber air, μg

$M_{surface}$ = mass remaining on the surface of the chamber, μg

The mass balance results in Table 2 show that the sorption of TCEP and TCPP by the walls of the 53-L chamber was significant. To reduce the sink effect impact caused by the test chamber in future tests for the purpose of estimating solid-phase diffusion coefficients and material/air partition coefficients of SVOCs such as OP-FRs, using the method described in the literature (Guo, 2013; Liu et al., 2014), the stainless steel walls will be coated with SVOCs and the chamber SVOC concentrations will be monitored at the faceplate to limit the sorption of SVOCs by the sinks.

Table 2. Mass Balance of TCEP and TCPP in the Empty Stainless Steel Chamber.

	TCEP		TCPP	
	Faceplate	Exhaust	Faceplate	Exhaust
Total mass dosed,	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, μg	67.5	77.9	337	400
% Mass adsorbed ^a	77%	91%	70%	86%

^a % 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

Stainless steel is an impenetrable material. The literature reports that the Langmuir sorption model may work better for nonporous and impenetrable materials than the diffusion models (Guo, 2013). The Langmuir model was examined using the current experimental data. Equations (2) and (3) describe the rate of SVOC concentration and sink mass change in the Langmuir-isotherm sorption model (Tichenor et al., 1991).

$$\frac{dc}{dt} = \frac{R}{V} - NC - k_a CL + k_d ML \quad (2)$$

$$\frac{dM}{dt} = k_a C - k_d M \quad (3)$$

$$K_e = \frac{k_a}{k_d} \quad (4)$$

where

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

Using the above equations, the values of the sorption rate constants k_a and k_d can be determined by the least square fit method using the SCIENTIST program (MicroMath

Scientific Software, Salt Lake City, UT, USA) with the sorption data from experiments in the small environmental chamber. The estimated adsorption and desorption rate constants are presented in Table 3. Figure 3 shows that the fit is reasonably good for the adsorption period of TCEP and TCPP but not as good as for their desorption period. One of the possible reasons might be that the Langmuir model assumes a monolayer of molecules on a homogeneous surface (Tichenor et al., 1991). In the Langmuir model, the adsorption and desorption rates are proportional to the concentration on the surface. The model would be more suitable for chemicals with linear adsorption rates. The SVOCs, however, have stronger interactions with material surfaces, and multilayer molecules with heterogeneity likely exist at the molecular scale even though polished stainless steel is superficially a homogeneous material (Van Loy et al., 1997). Under these conditions, a nonlinear sorption model such as the Freundlich isothermal model, may better describe sorption equilibrium in systems with heterogeneous surfaces.

Table 3. OP-FR Sink Parameters Estimated from the Stainless Steel Empty Chamber Test.

Chemicals	k_a , m/h	k_d (/h)	K_c (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	1.86	4.16×10^{-3}	448
TDCCP-faceplate ^a	20.6	8.74×10^{-3}	2350
TDCCP – exhaust ^a	20.5	2.89×10^{-3}	7100

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

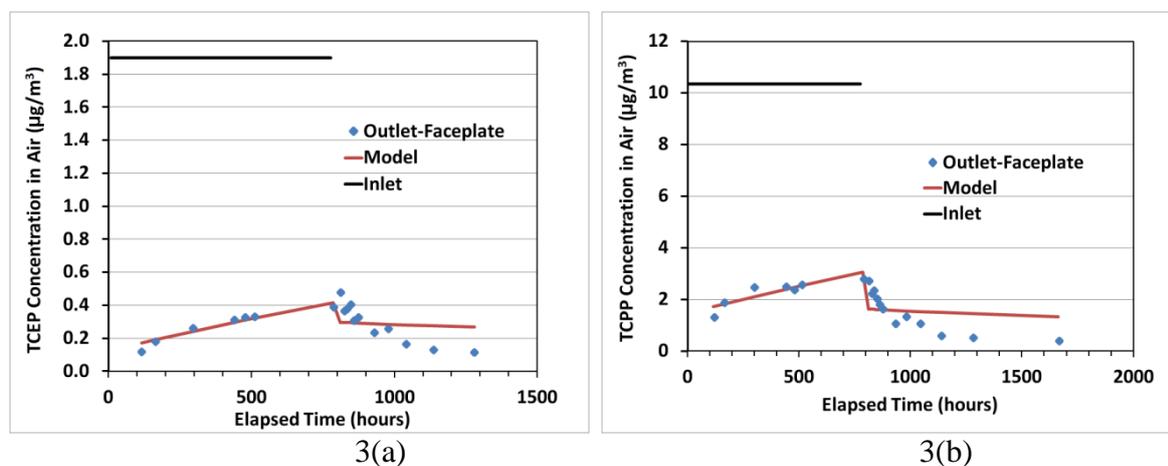


Figure 3. Experimental data vs. Langmuir sorption model (a. TCEP, b, TCPP)

CONCLUSIONS

An improved chamber test system has been fabricated and investigated for SVOC sink effect studies. The system minimizes the disruption of exposure time and SVOC concentration of the study materials during longer sink effect tests. The OP-FR empty stainless steel chamber sink effect test data were used to evaluate the reliability of the Langmuir sorption model for nonporous and impenetrable materials. The new chamber system will be used in an

experimental method that was developed to measure the sorption concentrations of the SVOCs and to estimate the partition and diffusion coefficients by fitting a sink model with experimental data in the future.

ACKNOWLEDGEMENT

The authors would like to thank Edgar Folk IV from ARCADIS U.S. Inc. for helping sample collections and analysis, Bobby Sharpe from ARCADIS U.S. Inc. for fabricating the test chamber lid, and Joel D. Tenny and Michael J. Nagridge from ICL Industrial Products America Inc. for providing the flame retardant chemicals.

DISCLAIMER

The material in this document has been subject to Agency technical and policy review, and approved for publication. The views expressed by individual authors, however, are their own, and do not necessarily reflect those of the U.S. Environmental Protection Agency.

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