WORKSHOP ON SVOC EMISSIONS TO INDOOR ENVIRONMENTS

Sponsored by ASTM Committee D22.05 on Indoor Air Quality

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New Orleans, LA

Workshop Co-Chairs: Dustin Poppendieck, Ph.D.
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OBJECTIVE

Actively transfer the academic knowledge on techniques described in literature to measure various SVOC emissions and emission parameters (K, yo, Co, D, hm, etc.) into useable formats that the industry can use to better understand their product performance and impacts on the indoor environment. In addition, we need citable, consensus standards that regulatory agencies can guide industry to use when requesting chemical information for risk evaluation.

THURSDAY OCTOBER 12, 2017

8:00 AM
Opening Remarks
Xiaoyu Liu, U.S. Environmental Protection Agency, USA

8:05 AM
What is an SVOC?
Dustin Poppendieck, Environmental Engineer. National Institute of Standards and Technology, USA

8:15AM
How Should We Characterize Emissions, Transport, and the Resulting Exposure to SVOCs In The Indoor Environment?
John C. Little. Professor. Department of Civil and Environmental Engineering, Virginia Tech, USA
SESSION 1: STATIC SVOC TESTING METHODS

8:35 AM
Passive Sampling Techniques to Measure Emission Parameters for SVOCs in the Indoor Environment?
John C. Little. Professor. Department of Civil and Environmental Engineering, Virginia Tech, USA

9:10 AM
Measuring Key SVOC Source/Sink Parameters Using Static Chambers with SPME.
Yinping Zhang, Professor, Dept. of Building Science, Tsinghua University, Beijing, China

9:45 AM BREAK

10:00 AM
Application of Methods for Measuring SVOC Emission Parameters for Vinyl Flooring and Spray Polyurethane Foam.
Mengyan Gong. Guest Researcher, National Institute of Standards and Technology, USA

SESSION 2: DYNAMIC SVOC TESTING METHODS

10:30 AM
An Improved Method for Measuring and Characterizing Phthalate Emissions from Building Materials
Ying Xu, Associate Professor, Civil, Architectural and Environmental Engineering, University of Texas at Austin, USA

11:05 AM
Measuring and Modeling Surface Sorption Dynamics of Organophosphate Flame Retardants in Empty Chambers.
Yirui Liang, ORISE Research Fellow, U.S. Environmental Protection Agency, USA

11:40 AM
Discussion: All Speakers
Xiaoyu Liu, U.S. Environmental Protection Agency, USA and Dustin Poppendieck, National Institute of Standards and Technology, USA

12:15 PM WORKSHOP ADJOURNS
ABSTRACTS
How Should We Characterize Emissions, Transport, and the Resulting Exposure to SVOCs in the Indoor Environment?
John C. Little, Ph.D.  Professor. Department of Civil and Environmental Engineering, Virginia Tech, USA

A systematic and efficient strategy is needed to assess and manage the potential risks to human health that arise from the manufacture and use of thousands of chemicals. For both volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), exposure is strongly influenced by the types of materials and products in which the VOC or SVOC occur, the concentration of the VOC or SVOC in the material or product, and the way in which the material or product is used or applied indoors. For VOCs, the rate of emissions from various materials and products are generally characterized in small chambers. The results are scaled up to represent what happens in a larger room, and then used to estimate the expected gas-phase concentration and associated health effects. For SVOCs, however, the characteristics of the room play a much larger role in controlling the process of emissions, transport, and exposure. For example, partitioning of SVOCs to interior surfaces including walls, windows, furniture, clothing, dust and airborne particles, all substantially affect the emissions and transport processes, as well as the resulting exposure. Given the inherent complexity of the situation, what is needed is a screening-level approach which is based on rapid estimates of exposure to a specific SVOC that is present within a specific material or product. These rapid estimates of exposure are then combined with estimates of toxicity to create a screening-level estimate of the risk associated with the specific SVOC/product combination. The SVOC/product combinations with relatively high risks can then be evaluated, focusing on more accurate measurements of the key parameters that govern emissions, transport, and the resulting exposure to SVOCs in the indoor environment. These parameters include the gas-phase concentration in equilibrium with the product surface, the partition coefficient between air and indoor surfaces, the vapor pressure of liquid SVOCs, and the partition coefficient between air and airborne particles.
Passive Sampling Techniques to Measure Emission Parameters for SVOCs in the Indoor Environment
John C. Little, Ph.D.  Professor. Department of Civil and Environmental Engineering, Virginia Tech, USA

A systematic strategy is needed to manage the potential risks to human health that arise from the manufacture and use of thousands of chemicals. Among available tools for rapid assessment of large numbers of chemicals, significant gaps are associated with the capability to evaluate exposures to semi-volatile organic compounds (SVOCs) that occur indoors. We have developed simple methods to measure some of the key parameters that govern emissions, transport, and the resulting exposure to SVOCs in the indoor environment. These parameters include the gas-phase concentration in equilibrium with the product surface, the partition coefficient between air and indoor surfaces, the vapor pressure of liquid SVOCs, and the partition coefficient between air and airborne particles. In this presentation, we focus on passive sampling techniques to measure the gas-phase SVOC concentration (y0) immediately adjacent to the material surface of a consumer product as well as the air/surface partition coefficients (Ks). The method employs cylindrical diffusion tubes, with disks made of the target material as the receiving phase, and values of y0 and Ks obtained by fitting a diffusion model to the sampling data. Phthalates in polyvinyl chloride flooring were selected to test the method. The results agree well with those measured in previous tests and the method is being expanded to other combinations of SVOCs, sources and sorption materials. As increasing numbers of such measurements are completed, the method should substantially improve our ability to estimate the potential exposure to SVOCs in indoor environments and can help with the exposure based prioritization of chemicals and products.
Measuring Key SVOC Source/Sink Parameters Using Static Chambers with SPME
Yinping Zhang, Ph.D  Professor, Dept. of Building Science, Tsinghua University, Beijing, China

Semi-volatile organic compounds (SVOCs) are originally present or distributed via sorption in many indoor materials. Indoor SVOC source emissions can be characterized in part by a critical parameter, $y_0$, the gas-phase SVOC concentration in equilibrium with the source material. While indoor SVOC sink characteristic can be characterized with diffusion coefficient, $D_m$, and the partition coefficient, $K$. All of them are essential for estimating exposure to SVOCs. Solid-phase micro-extraction (SPME) is regarded as a non-exhaustive sampling technique with a smaller extraction volume and a shorter extraction time than traditional sampling techniques, and is hence suitable for sampling in static chambers.

Based on the SPME and static chamber methods, we developed a method to measure $y_0$ of source materials. The experimental time can be less than 24 hours, with the relative errors of less than 5%. The measured $y_0$’s agreed well with results obtained by independent methods. The saturated vapor pressure ($V_p$) of one typical indoor SVOC, DEHP, was also measured. Based on the Clausius-Clapeyron equation, a correlation that reveals the effects of temperature, the mass fraction of the target SVOC in the source material, and $V_p$ on $y_0$ was established.

We also developed a method to measure $D_m$ of clothing materials. A thin sealed chamber is formed by a circular ring and two pieces of flat SVOC source materials that are tightly covered by the targeted clothing materials. We found that $D_m$’s of three SVOCs, di-iso-butyl phthalate (DiBP), di-n-butyl phthalate (DnBP), and tris(1-chloro-2-propyl) phosphate (TCPP), in a cotton T-shirt can be obtained within 16 days, with relative standard deviations less than 3%.

The proposed methods should prove useful for measuring indoor SVOCs source/sink characteristics. More studies are expected to improve them and facilitate their applications.
An Improved Method for Measuring and Characterizing Phthalate Emissions from Building Materials
Ying Xu, Ph.D. Associate Professor, Civil, Architectural and Environmental Engineering, University of Texas at Austin, USA

This work developed a rapid, novel method to measure phthalate emissions; emission measurement results can be connected to exposure assessment and help health professionals estimate screening-level exposures associated with SVOCs and conduct risk-based prioritization for SVOC chemicals of concern.

It is time-consuming and costly using existing chambers to test SVOC emissions due to the low ratio of emission surface to sorption surface, large amount of mass loss of phthalates onto sampling pathways, and limited air mixing inside the chamber. To overcome these limitations, a specially-designed stainless steel chamber system was developed to measure phthalate emissions from vinyl floorings. The time for phthalate concentrations to reach steady state was 2 to 5 days for all experiments in this work, which was significantly reduced compared to previous studies using existing chambers (1 to 5 months).

The gas-phase concentration of phthalates in equilibrium with the material phase (y0) is the key parameter controlling phthalate emissions from vinyl flooring, which is also important to quantify phthalate concentrations in different environmental media and the subsequent human exposures. An innovative approach was developed to determine y0 based on the chamber measurements. Independently measured or calculated parameters were used to validate a semi-volatile organic compounds (SVOCs) emission model, with agreement between model predictions and the observed chamber concentrations. With the knowledge of y0 and emission mechanisms, human exposure to phthalates from tested floorings was assessed; the levels were comparable to previous studies.
Semi-volatile organic compounds (SVOC) are ubiquitous indoors, commonly used in consumer products as additives to enhance product performance, and may be up to tens-of-percent of product content by mass. Humans may be exposed to SVOCs after their emission or transport into the indoor environment. Exposure to some SVOCs has been associated with adverse health effects, including endocrine disruption, asthma and allergies. Therefore, there is interest in quickly and accurately predicting human exposure to SVOCs. Measuring emission of SVOCs from indoor materials are important for assessment and control of SVOC exposure. Several methods have been developed for measuring SVOC emission parameter using either ventilated chamber with active air sampling or the sealed chamber with passive sampling. Each method has its advantages and disadvantages or limitations. Overall, the sealed chamber with passive sampling methods require shorter experimental time and may have higher accuracy by eliminating the measuring of convective mass transfer coefficient. However, in the published papers, those methods using sealed chamber are only applied to one kind of material, e.g. vinyl flooring, and one group of chemical, e.g. phthalates. And, there is no direct comparison of those methods for measuring the same material within same lab. Hence, to develop consensus standard methods (i.e., ASTM) for SVOC emission measurement, a better understanding of current methods is needed. The present study focuses on: 1). compare two different sealed chamber methods using the same material as used in the published papers, e.g. vinyl flooring, to see if the methods are reproducible, identify the potential problems of the methods and how the results by different methods are compared; 2) apply the two methods to measure emission of other chemical from other material that hasn’t been measured, e.g., Tris(2-chloro-1-methylethyl) Phosphate (TCPP) from spray polyurethane foam (SPF).
Measuring and Modeling Surface Sorption Dynamics of Organophosphate Flame Retardants in Empty Chambers
Yirui Liang, Ph.D. ORISE Research Fellow. U.S. Environmental Protection Agency, USA

Organophosphorus flame retardants (OPFRs) are produced and used widely as alternative additives in building materials and consumer products such as spray polyurethane foam (SPF), polyvinyl chloride flooring, electrical and electronic products, furniture, textile coatings, and plastics. Due to their low volatility, these chemicals are classified as semivolatile organic compounds (SVOCs). Emissions of SVOCs from source materials usually occur slowly, and the gas phase SVOCs are readily adsorbed or absorbed by interior surfaces, airborne particles, and settled dust. Sorption to chamber walls can serve as significant sinks for SVOC emissions in chamber studies. The sorption process of SVOCs on surfaces involves heterogeneous (multilayer adsorption) and homogeneous (monolayer adsorption). Understanding the sorption mechanisms for SVOCs on the stainless steel chamber wall will improve the methods for measuring SVOCs emission rates and parameters that could be used for modeling the fate and transport of indoor SVOCs. We adopted Langmuir (monolayer adsorption) and Freundlich isotherms (multilayer adsorption) models, which are widely used to describe indoor sorption behaviors, to characterize the adsorption/desorption dynamics of OPFRs on stainless steel surfaces and made comparisons between the two models through a series of empty chamber studies. The tests involve two types of chambers, 53-L small chambers and 44-mL micro chambers, dosed by constant gas phase OPFRs. Stainless steel surface/air partition coefficients of OPFRs were obtained from the tests. Test results show that the Freundlich model can better represent the adsorption/desorption process in the empty small chamber. Micro chamber test results show that both Langmuir and Freundlich models can well fit the measured gas-phase concentrations of OPFRs. We further apply the Freundlich model and the obtained parameters to predict the gas phase concentrations of OPFRs in a small chamber with a piece of SPF as an emission source. The study also illustrates that any test protocol for SVOC emissions testing must include characterization of the sink effect.