



Measuring and modeling surface sorption dynamics of organophosphate flame retardants on impervious surfaces



Y. Liang^a, X. Liu^{b,*}, M.R. Allen^c

^a Oak Ridge Institute for Science and Education Participant at U.S. Environmental Protection Agency, USA

^b U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC, 27711, USA

^c Jacobs Technology Inc., 600 William Northern Boulevard, Tullahoma, TN, 37388, USA

HIGHLIGHTS

- Chamber tests conducted to determine sorption parameters for OPFRs.
- Langmuir and Freundlich dynamic sink models used to characterize surface sorption.
- Freundlich sink model may better represent the surface sorption in chambers.
- Sorption parameters validated in the emission test.
- Improved understanding of the transport behaviors of indoor OPFRs.

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ABSTRACT

Understanding the sorption mechanisms for organophosphate flame retardants (OPFRs) on impervious surfaces is important to improve our knowledge of the fate and transport of OPFRs in indoor environments. The sorption processes of semivolatile organic compounds (SVOCs) on indoor surfaces are heterogeneous (multilayer sorption) or homogeneous (monolayer sorption). In this study, we adopted simplified Langmuir isotherm and Freundlich isotherm in a dynamic sink model to characterize the sorption dynamics of OPFRs on impervious surfaces such as stainless steel and made comparisons between the two models through a series of empty chamber studies. The tests involve two types of stainless steel chambers (53-L small chambers and 44-mL micro chambers) using tris(2-chloroethyl) phosphate (TCEP) and tris(1-chloro-2-propyl)phosphate (TCPP) as target compounds. Our test results show that the dynamic sink model using Freundlich isotherm can better represent the sorption process in the empty small chamber. Micro chamber test results from this study show that the sink model using both simplified Langmuir isotherm and Freundlich isotherm can well fit the measured gas-phase concentrations of OPFRs. We further applied both models and the parameters obtained to predict the gas phase concentrations of OPFRs in a small chamber with an emission source. Comparisons between model predictions and measurements demonstrate the reliability and applicability of the sorption parameters.

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1. Introduction

Organophosphorus flame retardants (OPFRs) are produced and used widely as alternative additives in building materials and consumer products such as polyvinyl chloride (PVC) flooring, electrical and electronic products, furniture, textile coatings, and plastics (Van der Veen and De Boer, 2012; Wei et al., 2015; Wensing

et al., 2005; Stapleton et al., 2009). Due to their low volatility, these chemicals are classified as semivolatile organic compounds (SVOCs) (Wensing et al., 2005). Because OPFRs are usually present as additives, and are not chemically bonded to product materials, they can leach or escape from the original materials and be released to the environment (Wei et al., 2015; Stapleton et al., 2009; Hartmann et al., 2004). Acute adverse health effects associated with humans and animals have been found for OPFRs such as tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) (Bradman et al.,

* Corresponding author.

E-mail address: liu.xiaoyu@epa.gov (X. Liu).

2014; Van den Eede et al., 2011; ATSDR, 2012). The occurrence of OPFRs is extensive, and they have been detected in various environmental media including indoor air (Hartmann et al., 2004; Bradman et al., 2014; Staaf and Östman, 2005), house dust (Bradman et al., 2014; Van den Eede et al., 2011; Bergh et al., 2011; Brommer et al., 2012; Dodson et al., 2012; Yang et al., 2012; Brandsma et al., 2014), water (Andersen et al., 2007; Barnes et al., 2008; Cristale et al., 2013; Wang et al., 2015), plants (Hyland et al., 2015), and biota (Sundkvist et al., 2010).

Human exposure to OPFRs is likely to occur through inhalation of indoor air and airborne particles, dermal absorption, and dietary and non-dietary ingestion (Wei et al., 2015; ATSDR, 2012; Weschler and Nazaroff, 2008, 2012; Little et al., 2012; Stapleton et al., 2011). Emissions of OPFRs from source materials usually occur slowly, and the gas phase OPFRs are readily adsorbed to and/or absorbed by interior surfaces, airborne particles, and settled dust. Understanding the sorption mechanisms of OPFRs on indoor surfaces is a prerequisite to characterize their fate and transport in indoor environments and further develop strategies to limit exposures and protect human health.

Over the years, researchers have developed various models to describe the physical sorption of gas molecules on solid surfaces. Among all these models, the Langmuir isotherm (Langmuir, 1916) is one of the earliest and most commonly used models. The derivation of the Langmuir isotherm is based on the assumption that there is a monolayer of molecules on a homogeneous surface and all sorption sites are independent and identical. It can be presented as (Nazaroff and Alvarez-Cohen, 2001)

$$q_e = q_{\max} \frac{bC_e}{1 + bC_e} \quad (1)$$

where q_e ($\mu\text{g}/\text{m}^2$) is the amount of chemical on the material surface at equilibrium, q_{\max} ($\mu\text{g}/\text{m}^2$) is the maximum sorption capacity on the surface, C_e ($\mu\text{g}/\text{m}^3$) is the gas-phase concentration at equilibrium, and b ($\text{m}^3/\mu\text{g}$) is the equilibrium Langmuir isotherm constant. By assuming that the chemical has very low partial pressure in air, which is often the case for air pollutants, the concentration of the chemical in the air is low enough so that the fraction of surface sites covered by the chemical is much less than 1. Then Equation (1) becomes

$$q_e = K_L C_e \quad (2)$$

where K_L (m) refers to the equilibrium partition coefficient in the simplified Langmuir-isotherm.

Unlike the Langmuir isotherm, the Freundlich isotherm (Freundlich, 1906) is an empirical model for sorption that is non-linear and reversible. The Freundlich isotherm has gained popularity for describing multilayer or heterogeneous sorption, especially for organic compounds (Foo and Hameed, 2010). The Freundlich equation is usually expressed as

$$q_e = K_F C_e^n \quad (3)$$

where K_F ($\text{m}^{3n-2} \times \mu\text{g}^{1-n}$) and n are the Freundlich isotherm constant and exponential. Based on the Langmuir and the Freundlich isotherms, researchers have proposed other empirical models for the purpose of achieving better data fitting and prediction. Examples of such models are the Sips model (Sips, 1948), the Koble-Corrigan model (Koble and Corrigan, 1952), and the Redlich-Peterson model (Redlich and Peterson, 1959), all of which integrate the Langmuir and the Freundlich isotherms in different forms. Overall, these models provide valuable information and methods for scientists to study the sorption behaviors of SVOCs.

In contrast to the development of isotherm models, very little has been improved in modeling the sorption dynamics of SVOCs on indoor surfaces. Xu and Little (2006) proposed a fundamental mass transfer model to predict SVOC emissions from PVC products. In this model, they adopted the Freundlich isotherm. In their later simplified SVOC emission model, Xu et al. (2012) used the simplified Langmuir isotherm to study the equilibrium relationship between the chamber surface and the gaseous SVOCs. The linear partition relationship between chamber surface/gas phase SVOCs has been continuously adopted in more recent SVOC studies (Liang and Xu, 2014; Liu et al., 2015; Bi et al., 2015) as a basis to explain partitioning of phthalates on impervious surfaces. Despite its simplicity and convenience in use, the linear partitioning relationship should be applied cautiously to the sorption of SVOCs on indoor surfaces. A test house study conducted by Bi et al. (2015) showed that the surface concentration of phthalates on window glass is higher than the surface concentration of phthalates on plates and mirrors, though the physical properties of these surfaces are very similar. The surface concentration difference is explained by considering the organic film development on indoor surfaces that has been found in previous studies (Liu et al., 2003; Butt et al., 2004; Diamond et al., 2000). A very recent study (Wallace et al., 2017) explicitly measured organic mass accumulation on Petri dishes and foils, further demonstrating the need to use multilayer sorption models. In such cases, the Langmuir isotherm with monolayer assumption may no longer be tenable. The Freundlich isotherm, thus may explain the growth of organic films on impervious surfaces (Wu et al., 2008). Therefore, there is an urgent need to compare the two isotherms and their applications in explaining partition effect of SVOCs under different indoor scenarios.

The aim of this study is to measure and characterize OPFR sorption dynamics on indoor impervious surfaces (e.g. stainless steel, glass, and acrylic). The specific goals are as follows: 1) characterize the sorption behavior of OPFRs on electro polished stainless steel chamber surfaces using a small chamber method and on Silicosteel[®] coated stainless steel using a micro chamber method; 2) compare simplified Langmuir isotherm and Freundlich isotherm in characterizing the mechanisms governing the sorption effect; 3) obtain sorption parameters for OPFRs from chamber tests; and 4) demonstrate the applicability of the obtained parameters in an OPFR emission small chamber test.

2. Materials and methods

2.1. Chemicals

The chemicals, including liquid TCEP and TCPP, for chamber tests were obtained from ICL-IP America Inc. (Gallipolis Ferry, WV, USA). Certified TCEP and TCPP calibration standards were purchased from AccuStandard Inc. (New Haven, CT, USA). An isotopically-labeled compound, tributyl phosphate- d_{27} (99.5% purity, Cambridge Isotope Laboratories, Inc., Andover, MA) was used as the internal standard on the GC/MS system. Triphenyl phosphate- d_{15} (98% purity, Sigma Aldrich, St. Louis, MO, USA) was used as extraction recovery check standard (RCS). Chromatography-grade methylene chloride (Burdick and Jackson, Muskegon, MI, USA) and ethyl acetate (OmniSoly, Billerica, MA, USA) were used as solvents in extraction and cleaning without further purification. The solvents were regularly analyzed to monitor potential contamination with OPFRs.

2.2. Empty small chamber sink test

The test was conducted using two 53-L electro polished stainless steel chambers, one as the source chamber and the other as the

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