



# Passive flux sampler measurements of emission rates of phthalates from poly(vinyl chloride) sheets



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## ABSTRACT

Emission rates of bis(2-ethylhexyl)phthalate (DEHP) from poly(vinyl chloride) (PVC) sheets containing DEHP as a plasticizer at various contents (0.16%–32.3%) were measured using the passive gas flux sampling method. The gas sampler was made of Pyrex glass and had a glass fiber filter inside. The sampler was placed on the surface of a PVC sheet for a given sampling period (up to 24 h), then the DEHP captured by the glass fiber filter was determined by gas chromatography-mass spectrometry. The sampling temperature was 50 °C. The surface concentration  $y_0$  (the DEHP concentration in the gas immediately adjacent to the surface of the PVC sheet) was determined from the experimental results and a transient DEHP emission model. The surface concentrations that were found agreed with values that have previously been published, most of which were determined in chamber emission experiments that require a longer test period than was used here. The method presented therefore allows the surface concentration  $y_0$ , which is considered to be one of the most important parameters determining SVOC emissions from solids such as PVC sheets, to be determined quickly and simply. The experimentally determined surface concentrations and the DEHP contents of the PVC sheets that were used correlated well.

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## 1. Introduction

Semi-volatile organic compounds (SVOCs) are organic compounds with boiling points ranging from 240 – 260 °C to 380–400 °C. The health risks posed by exposure to SVOCs in indoor environments have, up to now, been overlooked or underestimated [14,30], whereas the risks posed to human health by exposure to volatile organic compounds in indoor air have been studied intensively. SVOCs have extremely low vapor pressures at room temperature. However, continuous emissions of SVOCs from sources indoors will allow the concentrations of the SVOCs in indoor air to increase. Their low vapor pressures at ambient temperatures mean that SVOCs will strongly tend to become adsorbed onto solid surfaces, such as airborne particles, dust, and walls. The SVOCs adsorbed onto solid surfaces will then become secondary sources of SVOC emissions. The inhalation of SVOCs adsorbed to airborne particles and the dermal intake of SVOCs adsorbed onto solid surfaces will contribute to the risks posed to human health by SVOCs in the indoor environment [31,32].

The most ubiquitous SVOCs in indoor environments are plasticizers and flame retardants that are added to products made of polymers. Plasticizers are added to a polymer to increase the flexibility and moldability of the polymer. Poly(vinyl chloride) (PVC) is used in a range of products, such as bags, flooring, pipes, and toys, and it is usually mixed with plasticizers, such as phthalates, for use. The plasticizer content of PVC ranges from zero to several tens of percent, depending on what product the PVC is to be used in. The plasticizer molecules do not form chemical bonds with the PVC macromolecules, so the plasticizer may be emitted from the PVC during use. Phthalates emitted from PVC products used in the indoor environment will be taken up by humans through the inhalation of indoor air, dermal uptake when the product surface is touched, and oral intake of airborne particles with phthalates adsorbed to them. The effects of phthalates on human health have been described previously [12], and these effects include (1) impairing the development of the reproductive system [25] [15,24], (2) causing asthma, nasal inflammation, and allergies [4,13], and (3) causing hormone disorders and disrupting the endocrine system [1,27]. It is essential to understand phthalate emissions in indoor environments to allow the risks posed to human health by phthalates used as plasticizers in PVC products to be estimated and

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decreased.

There is a rather limited amount of previously published data on emissions of SVOCs such as phthalates in indoor environments. This is because of the extremely low concentrations of SVOCs in the gas phase and the strong tendencies of SVOCs to sorb to solid surfaces [20,21,23]. Most of the previous studies of SVOC emissions from solid materials have involved placing a sample of the material under investigation in a chamber and passing fresh air through the chamber. Chambers designed for the measurement of VOCs, such as FLEC and CLIMPAQ chambers, have been applied to measure the emission of SVOCs such as phthalate from PVC materials [6–9,29,33]. The adsorption of SVOCs onto the chamber walls has been minimized by using specially developed small chambers with the lowest possible surface areas [16–18,35,36]; Liang and Xu, 2015. The key parameters that determine SVOC emissions have been identified from the results of experiments using such chambers and of mechanistic emission models. Xu and Little [33] developed a mechanistic model describing SVOC emissions from solid materials. They showed that SVOC emissions are under “external control”, mass transfer being much faster through the solid material than in the gas phase. It can therefore be assumed that the concentration of a SVOC in a solid material will remain constant during an emission test. The key parameters that control SVOC emissions are  $y_0$ , which is the SVOC concentration in the gas phase immediately adjacent to the surface of the solid material surface (later called the surface concentration),  $h_m$ , which is the convective mass transfer coefficient in the gas phase in the chamber, and  $K$ , which is the adsorption equilibrium coefficient for the equilibrium achieved between the gas phase and the solid phase. The surface concentration  $y_0$  is the most important of these because it is intrinsic to the SVOC and the solid material. Clausen et al. [9] suggested that there is an empirical relationship between the surface concentration and the vapor pressure. However, the surface concentration should depend on the SVOC content of the solid phase, because the chemical potential of the SVOC in the solid material should depend on the material and the SVOC content of the material. Liang and Xu [16] proposed a simple and quick method for determining the surface concentration  $y_0$  from the results of chamber studies at steady state using Eq. (1),

$$y_0 = y_{ss} + \frac{y_{ss}Q}{Ah_m}, \quad (1)$$

where  $h_m$  is the convective mass transfer coefficient inside the chamber,  $y_{ss}$  is the surface concentration of the SVOC in the vicinity of the solid surface in the chamber, and  $Q$  is the flow rate of the air in the chamber. These parameters can be determined in separate experiments, allowing the value of  $y_0$  to be determined. However, a disadvantage of the chamber studies required to determine the surface concentration is that a long time (at least several days even in small chambers) is needed for steady state to be reached.

Passive or active sampling methods have been used to measure SVOC emission rates. Fujii et al. [11] used the passive flux sampling method to measure phthalate emissions, and their calculations were based on a simple steady-state diffusion model. They found that the emission rate increased by a factor of about 100 when the temperature was increased from 20 °C to 80 °C. Very few studies of SVOC emissions (including of phthalates) have been performed using gas sampling methods. Passive and active sampling methods have both been used to measure SVOC emissions. The advantages of the passive flux sampling method are that (1) an external power source and a tube to sample the gas with are not required, (2) sampling can be performed under ambient conditions, and (3) the samplers are easy to operate without a power supply, portable, and can be installed on any part of the target material [23].

In this study, we developed a new method, using passive flux sampling, for determining the key parameter, the surface concentration  $y_0$ , controlling (bis(2-ethylhexyl) phthalate) (DEHP) emissions. DEHP is a phthalate plasticizer, and it is the most commonly used phthalate in sheets of PVC. The DEHP emission rate was measured using a sampler made of Pyrex glass and shaped like a petri dish. A glass fiber filter was placed on the inner side of the sampler to capture the DEHP that was emitted as it diffused into the gas. PVC sheets with different DEHP contents were specially prepared, and the DEHP emission rate from each sheet to the glass fiber filter in a sampler was measured. The DEHP will have been transported within the sampler by molecular diffusion because no convection would have occurred within the sampler. The emission rate was determined from the amount of DEHP collected on the glass fiber filter. A transient transport model for DEHP in the sampler was developed, and the surface concentrations were determined from the experimental results and the equation describing the transport process in the model.

## 2. Materials and methods

### 2.1. PVC sheet samples

The samples of PVC sheet that were used were supplied by a Japanese company that produces PVC products. The DEHP contents of the PVC sheet samples were between 0.16 wt.% and 32.3 wt.%.

### 2.2. Sampling method

A photograph and a schematic of the sampler that was used are shown in Fig. 1. The sampler was made of Pyrex glass, and it had an inner diameter of 41 mm and a height of between 3 and 7 mm (to allow different diffusion path lengths to be used). A Whatman glass microfiber filter (later called a glass fiber filter) with a thickness of 170  $\mu\text{m}$  and a diameter of 41 mm (GE Healthcare Bio-Sciences, Pittsburgh, PA, USA) was placed on the underside of the sampler to capture the DEHP released from the sample.

A sampler containing a glass fiber filter was placed in an oven at 300 °C for 3 h and the sampler was placed on the surface of a PVC sheet sample, as shown in Fig. 2. The whole system was then placed in a temperature-controlled bath set at 50 °C. The glass fiber filter was removed from the sampler after a predetermined sampling

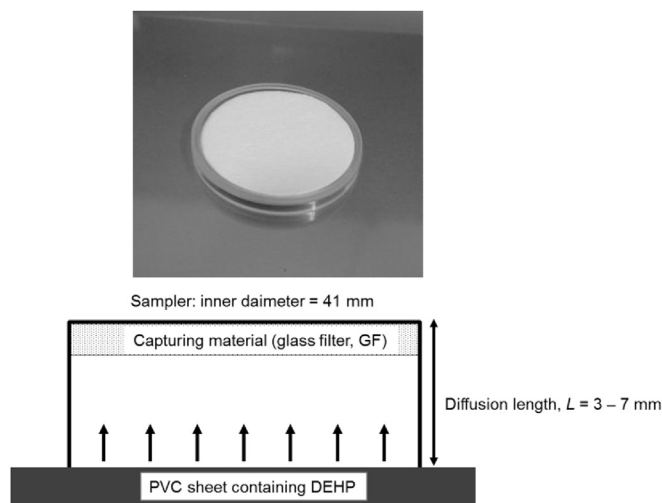


Fig. 1. Photograph and schematic of the passive flux sampler. PVC = poly(vinyl chloride) and DEHP = bis(2-ethylhexyl)phthalate.

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