Partitioning characteristics of indoor VOCs on impermeable surfaces covered by film-phase DnBP and DEHP

Zhuo Chen\textsuperscript{a,b}, Qiwei Chen\textsuperscript{a,b}, Ying Xu\textsuperscript{a,b,c}, Jinhan Mo\textsuperscript{a,b,c,}\textsuperscript{*}

\textsuperscript{a} Department of Building Science, School of Architecture, Tsinghua University, Beijing 100084, China
\textsuperscript{b} Beijing Key Laboratory of Indoor Air Quality Evaluation and Control, Beijing 100084, China
\textsuperscript{c} Key Laboratory of Eco Planning & Green Building, Ministry of Education (Tsinghua University), Beijing 100084, China

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PAEs usually adsorb on indoor surfaces to form organic films, which could be more hazardous after enriching VOCs. Two typical PAEs, DnBP and DEHP, in the film phase, were chosen to explore the enrichment capacity of gaseous toluene, hexanol, and benzyl alcohol in this study. Exposed to gaseous VOCs less than 250 ppb, film-phase DnBP and DEHP could capture benzyl alcohol significantly and hexanol slightly from the air, respectively, while toluene was hardly absorbed in the films. Henry’s law constants and partition coefficients (K) of VOCs in DnBP or DEHP films were derived, supposing films as dilute solution systems. The K value of VOC in DnBP or DEHP films was 1–2 orders larger than the octanol-air partition coefficient (K\textsubscript{oa}), indicating that the surface film composition greatly influences VOC adsorption. Benzyl alcohol was the largest VOC component in surface films, agreeing well with the molecular dynamics simulation results. The hydroxyl and phenyl groups of benzyl alcohol molecules may be key factors in VOC enrichment. They form hydrogen bonds with the ester group and π-σ stacking interaction with the phenyl group of DnBP or DEHP molecules, respectively. After enriching VOCs, film-phase PAEs could evoke combined exposure risks to human beings.

\textbf{1. Introduction}

Phthalic acid esters (PAEs) have drawn wide concerns as a kind of endocrine-disrupting chemicals (EDCs) (Braun, 2017). Many diseases like asthma (Hsu et al., 2012; Li et al., 2017), obesity (Buser et al., 2014; Li et al., 2020), infertility (Trnka et al., 2021; Wang et al., 2015), and cancers (Chuang et al., 2020) were found correlated to the exposure of PAEs by researchers. Especially, PAEs including dibutyl phthalate (DnBP), benzyl butyl phthalate (BBP), di (2-ethyl-hexyl) phthalate (DEHP), and their metabolites were found in the patient’s urine in large amounts and high detecting frequencies (Buser et al., 2014; Chuang et al., 2020; Li et al., 2017; Li et al., 2020; Trnka et al., 2021). Many studies have proved that abundant PAE sources exist in indoor environments. As plasticizers used in plastic products, PAEs are detected in toys (Babich et al., 2020), cosmetics (Kim et al., 2020; Koniecki et al., 2011), and food packages (Fasano et al., 2012; Santana et al., 2014). Since there are no covalent bonds between PAE molecules and plastic products (Holadova et al., 2007), PAEs can be released into indoor air. Due to the high boiling points and low vapor pressures (Zhou et al., 2021), gas-phase PAEs are easily adsorbed on indoor surfaces (Chen et al., 2022b; Wu et al., 2017b), clothes (Cao et al., 2017; Yang et al., 2020), airborne particles (Liu et al., 2017; Zhou et al., 2020), settled dust (Liu et al., 2020; Wei et al., 2019), and human skin (Simon, 2019; Wang et al., 2019) from the indoor air. Liu et al. (2022) summarized the dust-phase PAE concentrations in China from the literature and concluded that diisobutyl phthalate (DiBP), DnBP and DEHP were the most abundant phthalates in residences, offices and schools, which median concentrations ranging from 39.6 µg/g to 162.5 µg/g for DiBP, 74.5 µg/g to 96.3 µg/g for DnBP, and 634.2 µg/g to 1394.7 µg/g for DEHP. Meanwhile, DnBP and DEHP also had 100% detecting frequencies and the largest concentration distributions in window films in China, according to Wang et al.’s research (2021). The median concentrations were 174 µg/m\textsuperscript{2} for DnBP and 304 µg/m\textsuperscript{2} for DEHP, respectively. Human beings could touch and ingest contaminated indoor surfaces and particles as secondary pollution sources (Eichler et al., 2021; Salthammer and Schripp, 2015; Wu et al., 2021). Thus, PAEs and their substitute products were regarded as ‘emerging indoor pollutants’ (Salthammer, 2020).

Many studies focused on the adsorption behaviors of PAEs on indoor surfaces. Liang and Xu (2014b) conducted adsorption experiments of PAEs on stainless steel and determined the partition coefficients of DnBP and DEHP as 63 m and 930–2200 m, respectively. They further experimentally characterized the partition coefficient of DEHP on wood, which was 2.86 × 10\textsuperscript{7} (dimensionless) (Liang and Xu, 2015).
Wu et al. (2017a) obtained the DEHP partition coefficients on impermeable materials by diffusion experiments, and their values were 500 m, 600 m, 1200–1300 m and 600 m for acrylic, polished glass, stain- less steel and aluminum, respectively. The partition coefficients were found to be positively correlated with the roughness factors of impermeable surfaces. The partition coefficients of DnBP and DEHP on cotton T-shirts were experimentally obtained as 1.1 × 10^{-7} and 6.6–6.9 × 10^{-7} under 25°C according to Cao et al. (2016), which were found to be negatively correlated with temperature. Morrison et al. (2016) developed a mass transfer model to describe the capture of PAE by skin, in which the PAE partition coefficients between skin surface liquids and air were approximated as octanol/air partition coefficients at 32°C. However, the researchers tend to focus on the partition behaviors of PAE itself in indoor environments, and the possibility of the surface-adsorbed PAE enriching other pollutants was not reported. Due to the large partition coefficients, PAE has a strong film-formation capacity of PAEs on indoor impermeable surfaces. The film-phase PAEs can be more hazardous after enriching multiple pollutants. Weschler and Nazaroff developed a model for the organic film formation on impermeable indoor surfaces, which is meticulous in describing the partitioning behaviors of multiple PAEs between the gas phase and the surface film (Weschler and Nazaroff, 2017). The growth rates of PAE films were experimentally measured in the laboratory, quantified as 0.054–0.148 nm/day on polished glass substrates under nearly saturated gas-phase concentrations (Chen et al., 2022b). Interestingly, the film growth rate is nearly an order of magnitude smaller than those obtained from field tests (0.11–2.6 nm/day) (Wu et al., 2008). We then suppose synergistic adsorption enhancement exists on indoor surfaces exposed to multiple organic pollutants. However, details on the synergistic adsorption between different pollutants were short of study in previous research. As a kind of widespread pollutant, PAE in the film phase was well worth studying their enrichment capacities on other indoor gaseous pollutants, like VOCs, on indoor surfaces.

Adsorption among indoor air pollutants is mainly dominated by physical interaction. According to structural chemistry research, physical interactions follow the energy reduction principle, and the typical interactions contain van der Waals’ force, hydrogen bond, and π-π stacking interaction (Li et al., 2015; Liu et al., 2014; Zhou, 1993; Zuluaga et al., 2014). Besides, the hydrogen bond as a strong physical interaction was widely studied between organic compounds in the gas phase (Carvalho et al., 2016) and liquid phase (Bako et al., 2010; Ozkanlar, 2018). It is supposed that recombining different physical interactions contributes to the formation of organic films. However, short of research focused on the roles taken by different physical interactions on the organic film formation in indoor environments.

In order to explore the enrichment capacity of film-phase PAEs on VOCs, this study conducted adsorption experiments controlling PAEs as the only components in organic films formed on the surfaces of impermeable substrates. DnBP and DEHP were chosen as the target PAEs to form organic films on glass substrates. It should be noted that DnBP and DEHP were the most concerned PAEs considering their high toxicity and wide distributions. There were many rigorous studies focusing on their emission (Afshari et al., 2004; Liang and Xu, 2014a; Wu et al., 2016) and partition behaviors (Cao et al., 2016; Liang and Xu, 2014b; Morrison et al., 2016; Wu et al., 2017b). Especially, DnBP and DEHP were the PAEs with the largest surface concentrations in organic films on indoor impermeable surfaces, according to previous studies (Huo et al., 2016; Li et al., 2019; Wang et al., 2021). The polluted glass substrates were further used to detect the mass holding capacity of different VOCs, including toluene, n-hexanol (simplified as hexanol below), and benzyl alcohol. To the best of our knowledge, it is the first research that explored the enrichment capacity of film-phase PAEs on indoor VOCs. The aims of this research include 1) experimentally studying the adsorption performance of VOCs with different functional groups on PAE films; 2) applying Henry’s law to quantify the VOC adsorption capacity on PAE films supposing the organic films as dilute solution systems; 3) analyzing and summarizing the key factors contributing to adsorption enhancement for each VOC.

2. Materials and methods

2.1. Chemicals

Chemicals (anhydrous, >99%) that contained solvent, pure PAE, and VOC liquid were prepared. Methanol (Shanghai Titan Scientific Co., Ltd, anhydrous) was used as a solvent to design standards, and dichloromethane (ANPEL Laboratory Technologies Inc.) was used to clean chambers and surface substrates. Di-butyl phthalate (DnBP) and Di-2-ethyl hexyl phthalate (DEHP) were bought from Aladîn Industrial Corporation. Toluene, benzyl alcohol, and n-hexanol (written as hexanol below) were obtained from Beijing Tong Guang Fine Chemical Company, Shanghai Titan Scientific Co., Ltd, ANPEL Laboratory Technologies Inc, Meryer Chemical Technology Co., Ltd, and Shanghai Macklin Biochemical Co., Ltd, respectively. The PAE and VOC standard solutions (100 μg/mL) purchased from Accustandard Inc were used to calibrate their concentrations.

2.2. Preparation for adsorption substrates and chambers

The polished glass was chosen as the target substrate to conduct adsorption experiments. We ordered the glass substrates from GULUO glass Inc (Luoyang, China) in 60 mm × 4 mm × 1 mm. The glass substrates were ultrasonically treated and cleaned in dichloromethane for 10 min before the experiments.

A glass chamber was used to form PAE films on substrates. As shown in Fig. 1a, the chamber comprises a circle cap of 95 mm in diameter and a cylindrical body of 110 mm in diameter and 60 mm in height. A sealing ring was set between the cap and body to seal the chamber. There was a circular groove in the bottom of the chamber body. Pure PAE liquid of 10 mL was injected inside the groove. A clean glass culture dish (75 mm, Shanghai Titan Scientific Co., Ltd., China) was placed on the chamber bottom to accommodate glass substrates. After each PAE adsorption experiment, the glass dish was replaced by a new one.

Another stainless steel chamber shown in Fig. 1b was prepared for VOC adsorption experiments. A cylindrical block with a head cap covered on the top composes the body of the chamber. The block was 127.5 mm in inner diameter and 118.0 mm in height. We placed a sealing ring between the block and head cap of the chamber and then sealed the chamber with a lathedge. Two tubes with gas channels inside were manufactured on the cap. A sample platform was set inside the chamber to place glass substrates. Before the adsorption experiments, the chambers and sample platforms were cleaned with deionized water and dichloromethane. The structural details of the stainless steel chambers could be found in the previous study (Chen et al., 2022b). Photos of experimental devices and instruments are shown in Section S1 and Fig. S1 in Supplementary Material A.

2.3. Experimental methods

2.3.1. Formation of PAE films

A method was developed to quickly form PAE films on glass substrates by controlling the chamber’s temperatures. Clean glass substrates were placed in the glass dishes inside the chambers. The initial temperature and relative humidity in the chambers were approximately 20°C and 15%, respectively. The chambers were then moved into an oven set at a relatively high temperature. The PAE liquid in the bottom of the chamber was expected to deliver gaseous PAE at high temperatures constantly. After the temperature inside the chamber reached stable, the chamber was taken out and set in a fume hood for cooling. Gas-phase PAEs in chambers would adsorb on the surfaces of glass substrates to form organic films. The times spent for heating and cooling on chambers were controlled at 60 min in sequence. The oven temperature was
controlled as the variable to form PAE films with different thicknesses.

The exposed temperatures were set at 40°C, 60°C, 90°C, and 90°C, 120°C, 150°C for DnBP and DEHP film formation, respectively. Details about the temperature control of the film formation method are shown in Section S2 and Fig. S2 in Supplementary Material A.

### 2.3.2. VOC adsorption experiments

The chambers used to conduct the VOC adsorption experiments were named VOC adsorption chambers. After the PAE films were formed, the glass substrates were moved into a VOC adsorption chamber set in an incubator to control the temperature at 25°C. The tubes on the head cap of the chamber were connected with gas circuits to introduce gaseous VOCs, as shown in Fig. 1b. In previous research, we prepared an injection system to deliver gaseous VOCs, which were widely used for gaseous VOC delivery in previous research (Chen et al., 2022a; Chen et al., 2021; Xiao et al., 2018). The system contained a syringe pump with a heating unit and a 1000 μL syringe. We controlled the syringe pump by injecting the mixed VOC liquids at 0.15 μL/min injecting speed by syringe and set the heating unit at 175°C. Compressed air supplied by an air compressor was chosen as carrier gas. The compressed air first passed a pre-purifying tube to remove particles, organic pollutants and water vapor. There were HEPA filters and activated carbon filled in the pre-purifying tube. The airflow went through the syringe pump and carried the injected VOC liquids with a constant airflow rate of 1 L/min, controlled by a mass flowmeter. The mixed VOC liquids were expected to evaporate to the gas phase under a high temperature and large flow rate. After passing a cooling bottle, the gaseous VOCs were injected into the VOC adsorption chamber. The PAE films on glass substrates were expected to adsorb airborne VOCs in the chamber. After a 20-minute-adsorption, the first substrate sample was taken out from the chamber and analyzed. The rest samples were analyzed at an interval of 60 min. Tenax TA cartridges were used for a 2-minute-sampling downstream of the gas circuit at a sampling flow rate of 1 L/min to determine the gaseous VOC concentrations. The VOC capture ratio of Tenax TA cartridges was experimentally determined to be larger than 97.6% under 1 L/min sampling flow, indicating a good VOC capture capacity. (seen in Table S2). Details about the parameters of mixed VOC liquids and gaseous VOC sampling were shown in Section S3, Tables S1-S2, and Fig. S3 in Supplementary Material A.

### 2.3.3. Sample analysis

The surface PAE and VOC concentrations were quantified by a sample pretreatment platform (MPS Robotic, Gerstel, Germany) and a GC-MS (QP-2010SE, SHIMADZU, Japan). Considering the instability of VOC in PAE films, the glass substrates were expected to be analyzed as soon as possible. The devices were set to the proper conditions beforehand and ready for sample analysis. After finishing VOC adsorption, the glass substrate was taken out from the chamber by a tweezer and inserted into an empty thermal desorption (TD) cartridge. We sealed the TD cartridge rapidly with brass caps. The TD cartridge and brass caps were continuously cooled by an ice bag during the sampling process. Each TD cartridge was then detected immediately by GC-MS. The sample testing process was recorded as a video shown in Supplementary Material B. As for the organic compound estimation, the TD method used in this study had significant advantages compared to the solvent extraction method, which was widely applied in previous research (Hu et al., 2016; Liu et al., 2003; Wu et al., 2017b). There were more complex procedures in the solvent extraction method, including Soxhlet extraction (over 24 hours), filtration, separation and N2 blowing concentration. Due to the concise sample pretreatment, the TD method led to faster sample detection and less VOC loss.

In the concentration analysis, the thermal desorption unit (TDU) temperature was controlled at 320°C, and the thermal desorption process lasted 10 min. The He airflow with a 50 mL/min flow rate was introduced into the cartridge and flowed over the substrate. The PAE and VOC adsorbed on the substrate were then taken by the He carrier gas to be collected in the pretreatment platform’s cooled injection system (CIS). The temperature of CIS was set as -80°C, adjusted by liquid nitrogen, and the liners inside CIS were padded with glass wool. After thermal desorption, the CIS was immediately heated up to 270°C, and the collected PAE and VOC were injected into GC-MS to conduct concentration analysis. No split was conducted for each sample analysis. Tenax TA cartridges of gaseous VOC sampling were analyzed by the same analytical procedures introduced in our previous research (Chen et al., 2020a; Chen et al., 2020b). The split ratio for Tenax TA cartridges was set as 10:1. The quality assurance/quality control (QA/QC) analysis of GC-MS and concentration analytical method were shown in Section S4, Table S3 and Fig. S4-5 in Supplementary Material A.

### 2.3.4. Calculation of gaseous and surface concentrations

The gaseous VOC concentrations, \(C_{g,VOC}\) (ppb), could be calculated through Eq. (1).

\[
C_{g,VOC} = \frac{m_{g,VOC}/M_{VOC}}{V_s/V_g}
\]

(1)

where \(m_{g,VOC}\) stands for the mass of the sampled gaseous VOC, ng, which was obtained through the GC-MS analysis on the Tenax TA cartridge samples; \(M_{VOC}\) is the molar mass of the target VOC, g/mol; \(V_s\) means the sampled gas volume through the Tenax TA cartridge, L; \(V_g\) is the gas molar volume, equal to 24.5 L/mol at 25°C.

The formula to calculate surface concentrations of PAEs and VOCs is shown in Eq. (2).

\[
C_{s,PAE} = \frac{m_{s,PAE}}{A_g}
\]

(2)

where \(C_{s,PAE}\) is the surface concentrations of the organic compound (PAE or VOC), μg/m²; \(m_{s,PAE}\) and \(A_g\) stand for the surface mass of organic compound (μg) and surface area of the glass substrate (m²), respectively. Based on the surface concentrations, we could further calculate the mole fractions in organic films as Eqs. (3-6).

\[
\eta_{s,PAE} = m_{s,PAE}/M_{PAE} \times 10^{-6}
\]

(3)
\[ X_{TOL,PAE} = \frac{n_{x,TOl}}{n_{x,PAE} + \sum n_{x,VOC}} \]  
\[ X_{HEX,PAE} = \frac{n_{x,HEX}}{n_{x,PAE} + \sum n_{x,VOC}} \]  
\[ X_{BEN,PAE} = \frac{n_{x,BEN}}{n_{x,PAE} + \sum n_{x,VOC}} \]  

where \( n_{x,OC} \) stands for the mole quantity of surface PAEs or VOCs, \( \text{mol} \); \( M_{OC} \) is the molar mass of each organic compound, \( g/\text{mol} \); \( X_{TOL,PAE}, X_{HEX,PAE} \) and \( X_{BEN,PAE} \) are mole fractions of toluene, hexanol and benzyl alcohol in DnBP or DEHP films; \( \sum n_{x,VOC} \) is the sum of \( n_{x,TOl}, n_{x,HEX} \) and \( n_{x,BEN} \).

2.4. \( ^1 \)H-Nuclear magnetic resonance (NMR) experiments

The intermolecular forces, hydrogen bonds especially, may be the key factors that affect the VOC adsorption performances on PAE films. In order to figure out hydrogen bonds between PAE and VOC molecules, we carried out the solution \( ^1 \)H-NMR experiments to determine the existence of hydrogen bonds inside PAE and VOC hybrid solutions. The \( ^1 \)H-NMR method has been proven to be an efficient way for hydrogen bond detection in a solution system (Kumari et al., 2012). CDCl$_3$ was chosen as the deuterated solvent. Solution samples with constant VOC volume fraction (1.0%) and verified PAE volume fractions (0~1.6%) were prepared. The operations are as follows: 5 μL pure VOC liquid was injected into four 2-ml bottles. Pure PAE liquid with volumes of 0 μL, 3 μL, 5 μL, and 8 μL was then injected into the four bottles, respectively. CDCl$_3$ solvent was added to the bottles to adjust hybrid solutions at 500 μL. We then obtained four types of solution samples that contained constant 1.0% VOC and 0%, 0.6%, 1.0% and 1.6% PAE in volume fractions, respectively. The sample preparations were conducted for all VOCs and PAEs. Thus, we obtained 24 hybrid solutions in total. The \( ^1 \)H-NMR measurements of mixed solutions were performed on a JEOL JNM-ECA600 spectrometer (600 MHz for \( ^1 \)H). Meanwhile, the solution containing every single VOC or PAE was also conducted \( ^1 \)H-NMR tests.

2.5. Molecular dynamics simulation

Molecular dynamics simulations on the adsorption processes of VOC molecules caught by the glass surfaces containing PAE molecules were performed by Materials Studio software (2019 version, BIOVIA, France). A system containing glass substrates, PAE, and VOC molecules was built in a simulation box. The size of the simulation box was set as 95 Å × 80 Å × 95 Å in x, y, and z axes, respectively, imposing the periodic boundary condition on all dimensions. Na$_2$SiO$_3$ was chosen as the material of glass substrates, which were controlled as 45Å in thickness. The PAEs and VOCs with surface concentrations of 400 μg/m² and 10 μg/m², respectively, were modeled in the simulation box, and the molecule numbers were 66, 47, 5, 5, and 5 for DnBP, DEHP, toluene, hexanol, and benzyl alcohol, respectively. The designed PAE and VOC surface concentrations were in the same order of magnitude as the experimental results. The transformation from surface concentrations to molecule numbers and the model structures can be seen in Section S6 and Fig. S7 in Supplementary Material A. The Forcite molecular mechanics module was used to conduct the geometry optimization and molecular dynamics (quench process in the Forcite module) of models. The simulations were conditioned in constant molecular numbers and simulation box volume under 298 K (NVT ensemble). The force field was chosen as the Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS). As an ab-initio force field, COMPASS could be well applied to organic molecules and metallic oxides. Intermolecular interactions containing coulomb potential energy and van der Waals energy were described in the force field function to simulate the adsorption process (Sun et al., 1998). Especially, the coulomb potential energy in the force field function could describe hydrogen bond and \( \pi-\pi \) stacking interaction, both of which belong to the coulomb forces between molecules (Ahmed and Jung, 2017). The system energies were recorded every 1 ps. The system potential energy reached stable after 100 ps for every case. The adsorption energy of each VOC adsorbed on the surface, \( E_{ads} \), could then be calculated from the potential energies (Eq. (7)) when the systems reached stability after long-term iterations.

\[ E_{ads} = \frac{E_{total} - (E_{surf} + E_{VOC})}{n_{VOC}} \]  

where \( E_{total} \) means the total potential energy of the system, kcal/mol; \( E_{surf} \) stands for the potential energy of the surface contained PAE molecules, and \( E_{VOC} \) is that of VOC molecules in the system, kcal/mol; \( n_{VOC} \) is the number of VOC molecules in the simulation box, which is equal to five in these cases.

3. Results

3.1. PAE films formed on glass substrates

Different amounts of PAE films could be formed on glass substrates by controlling the chambers’ heating temperatures. Fig. 2 shows the surface concentrations of the formed PAE films. More than six organic-film samples were experimentally produced and tested for each PAE under each heating temperature. The medians of DnBP surface concentrations are 58.1 μg/m², 476.7 μg/m² and 712.9 μg/m² under 40°C, 60°C, and 90°C heating temperatures, respectively. Substrates with extremely large surface DnBP concentrations (>1000 μg/m²) were obtained after a heating process under 90°C. While, the surface DEHP films formed under 90°C, 120°C, and 150°C heating temperatures are in the median surface concentrations of 89.4 μg/m², 420.9 μg/m², and 751.2 μg/m², respectively. The standard deviations were also calculated and the values were 47.1 μg/m², 96.5 μg/m², 284.8 μg/m² for DnBP under 40°C, 60°C, 90°C heating temperatures, and 84.8 μg/m², 110.4 μg/m², 93.1 μg/m² for DEHP under 90°C, 120°C, 150°C heating temperatures, respectively. According to the previous study, the DnBP or DEHP films were liquid phases on glass substrates. The films obtained in this study were less than 5 nm in thickness following the calculation method described by Chen et al. (2022b). Table 1 summarizes the DnBP and DEHP surface concentrations sampled in the indoor environments from previous researches. The field tests on surface PAE concentrations in organic films are limited to the best of our knowledge. Thus, the reported indoor gaseous DnBP and DEHP concentrations were used to predict their sur-
face concentrations on glass. The surface PAE concentrations could be roughly obtained by multiplying gaseous concentrations and the partition coefficients on glass (DnBP: 6.5 m; DEHP: 700 m) (Chen et al., 2022b). According to the results of field tests, the ranges of surface PAE concentrations were 0.95–812 μg/m² for DnBP and 2.0–1510 μg/m² for DEHP (Bi et al., 2015b; Huo et al., 2016; Li et al., 2019; Wang et al., 2021). As for the results derived from indoor gaseous PAE concentrations, the surface concentrations on glass surfaces were predicted as 0–419 μg/m² for DnBP, which is the same magnitude as field-test results. However, those of DEHP (0–91725 μg/m²) were much larger, revealing a larger film-formation potential of DEHP (Blanchard et al., 2014; Bu et al., 2016; Huang et al., 2020a; Huang et al., 2020b; Pei et al., 2013; Rudel et al., 2010; Takeuchi et al., 2014; Tran and Kannan, 2015; Tran et al., 2017; Wang et al., 2014b). The surface PAE films formed in this study were right in the range of field tests except for a few extremums.

3.2. Gaseous VOCs delivering

Gaseous VOCs delivered by the injection system were sampled by Tenax TA cartridges to obtain the stability of the VOC delivering system. The samplings were conducted every 30 min for 6 hours, obtaining ten samples. The variation of gaseous VOC concentrations over time can be seen in Fig. S6 in Supplementary Material A. The gaseous concentrations were 223.7±15.1 ppb, 123.5±7.5 ppb, and 86.2±12.8 ppb for benzyl alcohol, hexanol, and toluene. Relative standard deviations (RSD) of benzyl alcohol (6.08%) and hexanol (6.76%) were both less than 7%, indicating good stability of gaseous VOCs delivery. Gaseous toluene concentrations show a relatively larger RSD (14.9%) over time due to the system residual in detecting devices. The t-test results in Table S4 in Supplementary Material A indicate that VOCs were delivered stably.

3.3. VOC adsorption on PAE films

After finishing PAE film formation, six glass substrates were moved into a VOC adsorption chamber. As shown in Section 3.2, stable gaseous VOCs were generated and introduced into the chamber for each adsorption experiment. The glass substrates were first sampled after 20 min adsorption. The rest samples were then sampled at the interval of one hour. The VOC mole fractions in PAE films were calculated for the samples with relatively large surface PAE concentrations (>150 μg/m²). The variations of mole fractions over time are shown in Fig. 3a-b, and their mean values and standard deviations are shown in Supplementary Table S5. There are no increasing tendencies of all VOC mole fractions of DnBP and DEHP over time, which means the VOC adsorption equilibriums were achieved before 20 min. The mole fractions are 1.70%, 0.184%, 0.013% and 1.92%, 0.195%, 0.017% for benzyl alcohol, hexanol, toluene in DnBP and DEHP films, respectively. Fig. 3c-d reveals the relationship between surface PAE and VOC concentrations on glass substrates. The detection frequencies of benzyl alcohol and hexanol are both 100%. Good linear fittings could be conducted for the adsorbed benzyl alcohol in DEHP films with an R² of 0.92. While the values of R² for hexanol (DnBP: 0.75; DEHP: 0.75) and benzyl alcohol in DEHP films (0.73) are relatively small. The reason is that errors may be introduced during sampling because the adsorbed VOCs on substrate surfaces are not stable. It should be noted that toluene shows low detection frequencies (DnBP: 31.8%, DEHP: 19.1%). The surface toluene concentrations of samples under low of detection (LOD) are set as zero in Fig. 3c and d.

4. Discussion

4.1. Theories of VOC adsorption in organic films

The gaseous VOCs could dissolve in PAE films and form dilute solution systems. According to the previous research (Schwarzenbach et al., 2002), the relationship between the VOC partial pressure and its mole fraction in PAE solutions could be shown in Eq. (8).

$$p\text{VOC} = k_{\text{VOC,PAE}} \times X_{\text{VOC,PAE}}$$  \hspace{1cm} (8)


where $p\text{VOC}$ means the vapor pressure of the target VOC, $k_{\text{VOC,PAE}}$ and $X_{\text{VOC,PAE}}$ was the saturated vapor pressure (Pa) and the mole fractions of VOC in PAE solutions; $p_{\text{VOC}}$ stands for the activity coefficient, which is determined by the physical property of PAE films. As for the dilute solution systems with small $p\text{VOC}$ and $X_{\text{VOC,PAE}}$, Henry’s law could hold that the linear relationship could be obtained between $p\text{VOC}$ and $X_{\text{VOC,PAE}}$. The linear fitting slope, $H_{\text{VOC,PAE}}$, is Henry’s law constant (Poddar and Sirkar, 1996). The formula of Henry’s law is listed as Eq. (9).

$$p\text{VOC} = H_{\text{VOC,PAE}} \times X_{\text{VOC,PAE}}$$  \hspace{1cm} (9)
According to Fig. 3a and b, the VOC mole fractions were less than 2.0% in PAE films. Dilute solutions could be assumed for the organic films covered on glass substrates. Thus, Henry’s law constant, $H_{\text{VOC,PAE}}$, could be used to quantitatively compare the adsorption capacities of VOCs in PAE films (Atkins et al., 2014; Poddar and Sirkar, 1996; Suzuki et al., 1992; Zhang et al., 2013).

Meanwhile, the Raoults’ law describes the partitioning of ideal solutions, in which the intermolecular forces between the solvent and solute molecules are the same as the ones between solute and solute molecules (Schwarzenbach et al., 2002; Wang et al., 2003). Thus, $f_{\text{PAE}}$ in Eq. (8) is equal to 1, and Raoult’s law could then be established as Eq. (10).

$$p_{\text{VOC}} = p_{\text{PAE}} f_{\text{VOC,PAE}}$$  \hspace{1cm} (10)

According to Raoult’s and Henry’s law, the relationships between vapor pressures and mole fractions in PAE films for benzyl alcohol and hexanol are shown in Fig. 4a and b, respectively. The points in Fig. 4a and b are the mole fractions of VOCs that steadily exist in PAE films when exposed to certain VOC vapor pressures. The VOC vapor pressures ($p_{\text{VOC}}$) were calculated according to Eq. (11) in Supplementary Material A and VOC mole fractions were calculated from Fig. 3a and b. No further discussion was applied to toluene because of its low detection frequency. According to the definition, Henry’s law constant could focus on the effect of physicochemical properties of PAE and VOC on sorption by normalizing the influence of the concentration. The adsorption capacity could then be comparable to VOCs. The slopes of Henry’s law curves for benzyl alcohol and hexanol are 1.28 Pa, 6.11 Pa in DNBP films and 1.18 Pa, 5.79 Pa in DEHP films, respectively, which are significantly smaller than those of Raoult’s law curves (12.5 Pa and 105 Pa for benzyl alcohol and hexanol, respectively). It means that larger VOC amounts will be captured by PAE films from the air in adsorption equilibrium than in the ideal solutions, when they were set under the same VOC vapor pressure. Therefore, the PAE-VOC intermolecular forces tend to be significantly larger than those between VOC itself. The $H_{\text{VOC,PAE}}$ of DEHP films are slightly smaller than those of DNBP films, indicating that DEHP molecules would form larger intermolecular forces with VOC molecules. To sum up, the composition of surface films could affect the adsorption performances of indoor gaseous organic matter on indoor surfaces.

4.2. Partition coefficients of VOCs

The partition coefficients of VOCs in PAE films, $K_{\text{VOC,PAE}}$, could also be obtained from their Henry’s law constants according to Eq. (11).

$$K_{\text{VOC,PAE}} = \frac{p_{\text{PAE}} f_{\text{VOC,PAE}}}{M_{\text{PAE}} H_{\text{VOC,PAE}}}$$  \hspace{1cm} (11)

where $p_{\text{PAE}}$ is the density of PAE, g/m$^3$, and the values were $1.05 \times 10^6$ g/m$^3$ and $9.86 \times 10^5$ g/m$^3$ for DNBP and DEHP, respectively, referring to the Chemical online database (http://www.basechem.org/); $R$ is the ideal gas constant, J/(mol·K), the value of which is 8.314; $T$ is the thermodynamic temperature, K; $M_{\text{PAE}}$ stands for the molar mass of PAE, g/mol. The derivative procedures can be seen in Section S7 in Supplementary Material A. Fig. 4c summarizes the partition coefficients and Henry’s law constants. The partition coefficients in DEHP films are $7.3 \times 10^4$, $1.5 \times 10^5$, and $1.3 \times 10^5$ for benzyl alcohol, hexanol, and toluene. DNBP films have relatively smaller partition coefficients, which are $7.9 \times 10^4$, $1.6 \times 10^5$, and $1.7 \times 10^5$ for benzyl alcohol, hexanol, and toluene, respectively. The results further verify that the components in organic films will affect the adsorption performances of indoor gaseous organic compounds. The underlying cause may be due to molecular interactions. Many researchers used the octanol-air partition coefficient,
\( K_{\text{oa}} \), as a partition coefficient approximation of organic films in indoor environments by assuming the similar physical property between octanol and organic matter in films (Beko et al., 2013; Little et al., 2012; Liu et al., 2012; Shi and Zhao, 2015; Weschler and Nazaroff, 2008). The assumption simplifies the calculation of adsorbed organic compounds on indoor surfaces, airborne particles, and dust, yet may introduce errors in estimating indoor pollution. We obtained the \( K_{\text{oa}} \) of benzyl alcohol, hexanol, and toluene referring to the previous research, and the values were \( 9.1 \times 10^5 \), \( 2.3 \times 10^4 \), and \( 1.9 \times 10^3 \), respectively (Ahn et al., 2020; Tamaru et al., 2018; Tamaru et al., 2019). The \( K_{\text{oa}} \) values are all 1–2 orders of magnitude smaller than the partition coefficients in PAE films. Thus, the \( K_{\text{oa}} \) assumption applied to estimate indoor surface organic matter adsorption may be less accurate when estimating the amounts of surface adsorption.

### 4.3. Comparison of adsorption capacities of PAE films

According to the discussion above, DEHP films accommodate more VOCs than DnBP. The VOCs are surmised to stay at a steadier state in DEHP films. The results of adsorption energies are shown in Fig. 4d, which are similar in general to those of DnBP and DEHP molecules. As for benzyl alcohol, adsorption energies contacting DEHP molecules (-91.9 kcal/mol) are similar and slightly larger than those of DnBP (-90.0 kcal/mol), indicating that a bit more heat would be released when benzyl alcohol molecules interact with DEHP molecules, but both of the systems stay at similarly stable states. The result agrees well with experimental results that benzyl alcohol has a larger partition coefficient in DEHP films than in DnBP films. However, the results are different for hexanol and toluene. The adsorption energies of hexanol and toluene are -65.1 and -50.8 kcal/mol, respectively, when interacting with DEHP molecules, smaller than those of DnBP molecules (hexanol: -71.8 kcal/mol, toluene: -61.1 kcal/mol). The surface concentrations of hexanol and toluene are both near the LODs of GC-MS, resulting in detection deviations. It should be noted that molecular dynamics could only simulate and obtain the state and energy of molecule motion under a vacuum diffusion condition, which may be relatively different from the experimental conditions.

### 4.4. VOC adsorption performances

As discussed above, benzyl alcohol reveals the largest adsorption capacity in PAE films compared with hexanol and toluene. Molecular structures may be the key factors that result in the difference. It should be noted that benzyl alcohol and hexanol both have the hydroxyl group in molecular structures, according to Fig. S7 in Supplementary Material A. Oxygen atoms have a larger electronegativity than hydrogen and carbon atoms, leading to large molecular polarities for benzyl alcohol and hexanol molecules (Zhou, 1993). The hydroxyl groups in molecules would have strong inter-attractations with the oxygen atoms in PAE molecules, and hydrogen bonds (-OH...O-) may be formed when benzyl alcohol and hexanol are adsorbed in PAE films (Ahmed and Jhung, 2017; Liu et al., 2014).

We then conducted \(^1\)H-NMR analysis on the prepared PAE and VOCs with hydroxyl groups in mixed solutions to experimentally detect the existence of hydrogen bonds. The results of the H-NMR analysis can be seen in Fig. 5. Obvious downfield shifts of hydroxyl \(^1\)H signals shown in Fig. 5a-b could be detected for benzyl alcohol and PAE mixed samples. The \(^1\)H chemical shifts increase with the enlargement of PAE volume fractions. It indicates that hydrogen bonds between benzyl alcohol and DEHP molecules are formed (Mokeev et al., 2020). As a comparison, the downfield shifts of the hydroxyl \(^1\)H signals are less apparent for hexanol (Fig. 5c-d). Fig. 5e summarizes the variations of chemical shift offset, \(\delta x\), over PAE volume fractions. Benzyl alcohol had a much larger \(\delta x\) compared with hexanol in PAE films. The values of \(\delta x\) were 0.089–0.092 ppm for the hydroxyl group of benzyl alcohol in the solutions containing 1.0% VOC and 1.6% PAE, several times larger than those of hexanol. Considering that the hydrogen bond intensity is positively correlated with the \(^1\)H chemical shift of the hydroxyl group (Carvalho et al., 2016), benzyl alcohol molecules could form more stable hydrogen bonds with PAE molecules in organic films, agreeing well with the result that benzyl alcohol has the largest partition coefficients and adsorption energies.
shown in Fig. 4c and d, respectively. Since the only difference between benzyl alcohol and hexanol molecules relies on the radicals connecting with hydroxyl groups, hydrogen bonds were expected to be more easily formed when the hydroxyl group connects with phenyl than the long-chain alkyl group in molecules. Thus, we deduce that the VOCs with hydroxyl groups can form strong hydrogen bonds with PAE molecules and then be enriched by film-phase PAEs.

Meanwhile, the phenyl group exists in toluene and benzyl alcohol molecules. There are also inter-attractions between phenyl groups, named π-π stacking interaction (Capim et al., 2010). However, the intensity of π-π stacking interaction is much smaller than that of hydrogen bonds, which may be why toluene had such a low detection frequency of samples (Li et al., 2015). Thus, the strong hydrogen bonds lead to the large sorption capacity of benzyl alcohol in DnBP or DEHP films, and π-π stacking interaction also has a possibility to exist between benzyl alcohol and PAE molecules to enhance the adsorption.

4.5. Limitations

There are still some limitations that remain to be refined in the future. We simplified the organic film composed of a single PAE component to control the variables for better studying the PAE characteristics on VOC enriching. Indoor organic films may be complex in composition. Further research to determine the VOC-enriching performances of ordinary indoor organic films could be conducted based on the results of this study. Another limitation is the oversight of water vapor for the sorption system. Since this study was conducted during the winter in Beijing, the relative humidity was at a low level in the heated laboratory. Meanwhile, the water vapor was removed by the pre-purified tube in the gas circuits before the VOC exposed chamber. However, water still occupies an important role in surface film partitioning due to the polarity of water molecules. The influence of water vapor is well worth further studying. Considering the strong volatility, VOCs would be easily leached out from the PAE films between substrate sampling and thermal desorption and then introduce errors in their surface concentration detection, although we endeavored to minimize the effect by cooling the substrates and shortening the detecting intervals. We only conduct a qualitative analysis of the sorption mechanism by molecular dynamics simulation and 1H-NMR detection. The adsorption energies calculated from molecular dynamics simulations were derived in a vacuum diffusion state, which, thus, could only be used to compare the attractive tendencies between molecules. Because of the difficulty of surface hydrogen bond detecting, we had to conduct 1H-NMR analysis on mixed solutions to detect the hydrogen bonds as an alternative. We believe that the results of this study will be helpful in understanding the transformation and fate of film-phase PAEs, and provide film-formation parameters.
for modeling research and field tests. Sorption experiments of film-phase PAE on other pollutants in real environments are also valuable to perform further. More elaborate work could be designed and conducted in the future.

5. Conclusions

The organic films containing PAEs could enrich indoor gaseous VOCs, increasing their hazard. The enrichment capacity of film-phase DnBP and DEHP on VOCs containing toluene, hexanol and benzyl alcohol were experimentally explored in this study. We developed a film-formation method on the glass substrate to prepare the glass sample covered by PAE film, which surface concentration ranged from 10.5 μg/m² to 1494 μg/m². The samples were used for VOC adsorption experiments. The VOC adsorption equilibriums were achieved before 20 min in organic films. Exposed to gaseous VOCs less than 250 ppb, the film-phase DnBP and DEHP could capture benzyl alcohol significantly and hexanol slightly from the air, respectively, with the surface VOC concentration proportional to PAE concentrations. Toluene could hardly be absorbed in the surface films. We derived Henry’s law constants and partition coefficients of VOCs in PAE films supposing films as dilute solution systems. The partition coefficients were 1–2 orders of magnitude larger than K_{oa}, which has been commonly used for the prediction of organic compounds partitioning on indoor surfaces in previous models. Thus, the K_{oa} assumption may be less accurate in the adsorption estimation of organic compounds on indoor surfaces and particles.

According to the results of the molecular dynamics simulation and 1H-NMR analysis, the hydrogen bonds dominated the sorption of benzyl alcohol and hexanol molecules in DnBP or DEHP films. The hydrogen bond formed between the hydroxyl group of benzyl alcohol and the ester group of PAE was stronger than that of hexanol, which led to the large sorption capacity of benzyl alcohol in DnBP and DEHP films. The π-π stacking interaction can also exist between benzyl alcohol and PAE molecules to enhance the sorption.

As an implication for further study, the enrichment of other SVOCs like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs), and bisphenol A (BPA) by film-phase PAEs could also be well worth studying. Because of the larger molecular weights and more complicated molecular structures, the SVOCs could form larger intermolecular forces with PAE (Kawanaka et al., 2009). Larger mole fractions were expected to be occupied for SVOCs in organic films than VOCs, which may induce great common health risks for humans. This study would contribute to a new understanding of the transformation and fate of film-phase SVOCs and provide film-formation parameters for modeling research.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Supplementary materials

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