Research paper

Partitioning of airborne PAEs on indoor impermeable surfaces: A microscopic view of the sorption process

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ABSTRACT

Organic films were widely found on indoor impermeable surfaces exposed to gaseous organic compounds, but few studies have addressed the film growth details on different indoor substrates. In this study, we observed the topography evolution of phthalic acid ester (PAE) organic films on three impermeable substrates: polished glass (G-P), mirror-polished stainless steel (SS-M) and drawn stainless steel (SS-D). PAE organic films were preferentially formed upon the flat surface with sparse inherent nano-peaks of substrate G-P and in valleys of substrate SS-M and SS-D. Surface uniformity of substrates and viscosity of PAE molecules were inferred as critical parameters determining the surface average adhesion forces. We obtained the partition coefficients of DEP, DnBP, BBP and DEHP on substrate G-P, SS-M and SS-D by fitting the initial monolayer adsorption process. Organic films continuously grew instead of reaching adsorption equilibrium after long-term PAE exposure, indicating that multilayer adsorption may occur. The organic film growth rates in saturated gas-phase PAE concentrations were quantified as about one-tenth of the results in previous studies where substrates were simultaneously exposed to multiple pollutants. To sum up, the results outline PAE adsorption details on impermeable materials and provide a reference for better estimation on PAE exposure assessment.

1. Introduction

As a kind of indoor pollutants, phthalic acid esters (PAEs) are widely found in building materials (Liang and Xu, 2014b; Yang et al., 2020), food (Gonzalez-Salamo et al., 2018) and personal products (Kim et al., 2020). Severe diseases like asthma (Bamai et al., 2014), obesity (Kim et al., 2016), infertility (Liu et al., 2017), breast cancer (Lopez-Carrillo et al., 2010) and thyroid cancer (Liu et al., 2020) would be induced when humans over uptake this hazardous material (Benjamin et al., 2017). PAEs with relatively small molecular weights, such as diethyl phthalate (DEP) and dibutyl phthalate (DnBP), tend to be used as solvents in liquid-phase products. DEP was found in body lotion (Fisher et al., 2019) and hair-styling products (Lim and Lee, 2020). Kim et al. (2020) had detected DnBP in foam cleansing agents and perfumes. In contrast, PAEs with large molecular weights are mainly added in solid-phase materials to enhance their flexibility and elasticity (Gao and Wen, 2016). Di (2-ethyl-hexyl) phthalate (DEHP) is widely used in vinyl floorings (Xu et al., 2010) and polyvinyl chloride (PVC) floorings (Afshari et al., 2004). Al-Natsheh et al. (2015) found DEHP, Di-n-octyl phthalate (DnOP) and Diisononyl phthalate (DINP) in PVC toys. Liang and Xu (2014a) detected butyl benzyl phthalate (BBP), DEHP and DINP from some vinyl floorings and crib mattresses in the United States. According to the urinary phthalate metabolite detection, food packaging materials used for school lunches were identified as PAE sources. Children who always consumed school lunches had high urinary concentrations of DEHP metabolites, mono-(carboxy-octyl) phthalate (MCOP) and mono-n-butyl phthalate (MBP) (Munoz et al., 2018).

In indoor environments, children uptake PAEs through three pathways: dermal absorption, inhalation, and dust ingestion (Beko et al., 2013; Liang and Xu, 2014b; Raffy et al., 2018). Dermal exposure and inhalation are the main pathways to uptake dialkyl PAEs with small molecular weights, such as DEP and DnBP. For the dialkyl PAEs with large molecular weights like DEHP or alkyl aryl PAEs like BBP (Xu et al., 2006), dust ingestion makes up large proportions of exposure (Beko et al., 2013). Therefore, accurately evaluating PAE concentrations on different indoor surfaces is highly important in PAE exposure assessment (Bu et al., 2016; Yang et al., 2020). Partition coefficient (K), the ratio between the equilibrium solid-phase concentration of PAEs and the
gas-phase concentration, represents surface adsorption capacity (Weschler et al., 2008). It is well worth studying how to obtain the K values for different PAEs on indoor permeable and impermeable materials to estimate PAE amount on indoor surfaces accurately.

Some researchers studied the K values of PAEs on different indoor materials (Weschler and Nazaroff, 2008; Weschler et al., 2008). Guo (2002) had summarized some empirical formulas to obtain K values of different compounds. The octanol-air partition coefficient (K_{oa}) obtained from the estimation program interface (EPI) suite and SPARC online calculator (Schosier et al., 2011) was commonly used to calculate K values of particles, dust and indoor surfaces (Weschler and Nazaroff, 2008). For porous materials, K is dimensionless (Guo, 2002). The K values can be measured from the emission process of source materials (Kumar and Little, 2003; Liu et al., 2013; Xu and Little, 2006) and the sorption process of sink materials (Cao et al., 2016; Liang and Xu, 2015). The K value of DEHP in vinyl flooring (source material) was experimentally obtained as 7 × 10^{-6} through emission processes (Liang and Xu, 2014b). The K values of DEHP and DINP in wood (sink materials) were experimentally obtained as 2.86 × 10^{-2} and 2.52 × 10^{-2}, respectively (Liang and Xu, 2015). For impermeable materials, the unit of K is ‘m’. The pollutants adsorbed on impermeable surfaces were usually assumed following the Langmuir equation (Liu et al., 2014). The K value can be calculated by C_{surface}/C_{air} (g/m²) and C_{air} (g/m³) are the concentrations on the surface and in the air, respectively (Liang and Xu, 2014b, 2015; Liu et al., 2014; Wu et al., 2017; Xu et al., 2012). The K value of DEHP on stainless steel surface was reported as 1800 m (Xu et al., 2012). Liang and Xu (2014b) detected K values of DnBP, BBP, DEHP and DINP on stainless steel surfaces were 63 m, 620 m, 1500 m and 2100 m, respectively. They also revealed a linear relationship between log(K) and log(V_{p}) for different PAEs on stainless steel, where V_{p} is the vapor pressure. Wu et al. (2017) developed an experimental approach based on a diffusion model to obtain the K values of DEHP on a series of impermeable surfaces, including steel, glass and acrylic. The K values range from 500 m to 4200 m.

Organic films (PAEs, PBDEs and PAHs) would form on different substrates, including windows, stainless steels and mirrors (Das et al., 2003; Huo et al., 2016; Pan et al., 2012; Weschler and Nazaroff, 2017). Das et al. (2003) studied the effect of substrates on organic film growth by X-ray diffraction (XRD), X-ray reflectivity (XRR), Raman spectroscopy and atomic force microscopy (AFM). Huo et al. (2016) conducted field tests on six PAE films on indoor windows and reported a linear relationship between the film mass and the growth duration. The masses of PAH films on exterior windows were more significant than those on interior windows by Pan et al. (2012). The film growth rate in winter was more prominent than in summer (Huo et al., 2016). A model for the growth of organic films on impervious substrates was presented by Weschler and Nazaroff (2017). They found that the film growth was primarily dominated by semi-volatile organic compounds (SVOCs) with the log(K_{oa}) ranged from 10 to 13. The model’s predictions agreed very well with the results of other field tests (Bi et al., 2015; Huo et al., 2016). The existence of organic films will enlarge the dermal and even the ingestion exposure risk for children when they touch the contaminated surfaces. Meanwhile, SVOC organic film will perform as solvents to absorb other volatile organic pollutants (such as formaldehyde, toluene), which may lead to higher health risks than PAE itself. However, few studies focused on the detailed forming process of organic films on impermeable surfaces. The organic film coverage on substrates is also hard to characterize due to the heterogeneity of different indoor surfaces. Lim and Abbatt (2020) conducted a field test of SVOC film growth from natural sources and consumer products. They found that the rate of film growth was at least 0.05 nm/day. However, the environmental parameters were not controlled, and the heterogeneity of the organic film growth was not considered.

In this study, PAE adsorption experiments were conducted on typical indoor impermeable surfaces. DEP, DnBP, BBP and DEHP were chosen as target PAEs. The impermeable materials include glass and stainless steel. This research aims: 1) experimentally testing the K values of different impermeable surfaces; 2) observing the changes of surface topographies during PAE exposure and studying the variation of surface characteristics; 3) analyzing the film growth mechanisms for different PAEs and substrates.

2. Materials and methods

2.1. Experimental chamber

Fig. 1 shows the schematic and picture of adsorption chambers and substrates in this experimental study. The chamber is a stainless steel cylinder jar, 127.5 mm in inner diameter and 118.0 mm in height. A lid is used to cover the chamber. A seal ring is placed between the chamber and lid. Then the chamber is fastened by a lathedog. Two stainless steel tubes with a diameter of 6 mm are welded symmetrically on the lid for nitrogen purging. The lengths of the tubes are 30 mm and 85 mm, respectively, with 20 mm exposed outside of the chamber. A hole with a diameter of 4 mm was drilled on the lid for gas-phase concentration sampling by solid-phase microextraction (SPME) needles (7 μm PDMS, SUPELCO, USA). A stainless steel platform used to place the target impermeable substrates was set inside the chamber, as shown in Fig. 1 (a).

2.2. Materials for PAEs adsorption

We chose polished glass and two kinds of stainless steel with different surface roughness as target impermeable substrates. We named the polished glass as G-P, mirror-polished stainless steel as SS-M, and drawn stainless steel as SS-D. All substrates were prepared in the size of 60 mm × 4 mm × 1 mm. The polished glass was ordered from GULUO glass Inc, Luoyang, China. The stainless steel was purchased from a local steel manufactory. The scanning electron microscopic (SEM) images (×500) of target substrates are shown in Fig. S1 in Supporting Information.

2.3. Experimental methods

2.3.1. Pretreatment of chambers and substrates

The chambers and substrates were cleaned before each experiment. The chambers were washed by cleaning soap-suds and then ultrasonically treated in deionized water for 10 min. Each substrate was sonicated for 10 min successively in acetone (>99.5%, Titan Tech, China) and dichloromethane (>99.9%, Beijing MREDA Technology Co., Ltd, China). Then, the substrates were inserted into blank thermal desorption (TD) cartridges to conduct one-hour thermal desorption at 350 °C with a nitrogen flow rate of 100 mL/min.

2.3.2. Preparation of experimental platforms

Before each adsorption experiment, PAE liquid was coated uniformly on the inner surfaces of chambers and the legs of the sample platform by brushes as the source of gas-phase PAEs. The brushes were weighed before and after each coating to obtain the PAE amounts inside the chambers, which values ranged from 0.8644 g to 1.5482 g. Detailed information about PAE amounts coated inside the chambers could be seen in Section 1 in Supporting Information, including Table S1. The target PAEs chosen in this study are DEP, DnBP, BBP and DEHP. DEP (99.0%) and BBP (98.0%) were from Shanghai Macklin Biochemical Co., Ltd. and Meryer (Shanghai) Chemical Technology Co., Ltd, respectively. DnBP (> 97.0%) and DEHP (98.0%) were obtained from Aladdin Industrial Corporation.

We parallely prepared three chambers for each PAE to conduct adsorption experiments (twelve chambers in total). The first two chambers were used to obtain PAE amounts adsorbed on the surfaces of substrates. Three duplicate samples for each substrate were located on the platform in these two chambers to obtain the surface adsorption
amounts. The substrates exposed in the third chamber were used for surface topography observation. Nitrogen gas was introduced into each chamber from the short tube on the lid to remove the particles inside. The gas flow rate and time were controlled as 1.5 L/min and 5 min, respectively. After the tubes and holes were sealed, all chambers were moved into an incubator (DHP-250B, SAIDELISI, China) to control their temperatures at 25.0 ± 0.5 °C during the exposure experiments.

2.3.3. PAE sampling and sample pretreatment

In the first two chambers for each PAE, gas-phase PAE concentrations were sampled by SPME probes, proven to be an efficient way for PAE sampling (Cao et al., 2017). The SPME probes were inserted into the hole on the chamber lid and the SPME sampling times were set as 0.5, 3, 30 and 60 min for DEP, DnBP, BBP and DEHP, respectively. The validation of the SPME sampling method was shown in Section 3 in Supporting Information. The background of gas-phase PAE concentration in empty chambers was also detected by SPME and the values were lower than LOQ (low of quantification) of sampling methods. After the SPME sampling, the substrates were taken out at the designated time and then immediately inserted into blank TD cartridges to conduct thermal desorption for surface adsorbent quantification.

The substrates in the third chamber were taken out and stored in a refrigerator at 4 °C. The storage time was no more than 24 h before the surface topography characterization with AFM (Dimension FastScan, Bruker, Germany).

2.4. Sample analysis

PAE adsorption mass on the substrates was quantified. The adsorbed PAE was first thermally desorbed in the TD cartridges using a sample pretreatment platform (MPS Robotic, Gerstel, Germany). The sample pretreatment temperature for the thermal desorption unit (TDU) was set at 50 °C for 0.5 min. Then the temperature was elevated to 320 °C by 150 °C/min and held constant at 320 °C for 3, 3, 10 and 10 min for DEP, DnBP, BBP and DEHP, respectively. The desorption pressure and flow were 81.0 kPa and 50 mL/min, respectively. The compounds desorbed from the cartridges were collected in the cooled injection system (CIS) at −50 °C, adjusted by liquid nitrogen. The liners of CIS were padded with glass wool. After the thermal desorption, the desorbed compounds were analyzed by GC-MS (QP-2010SE, SHIMADZU, Japan) as introduced in a previous study (Chen et al., 2020). Gas-phase concentrations in the experimental chambers were obtained by analyzing the sampled SPME probes in GC-MS with the same program mentioned above. The quality assurance/quality control (QA/QC) analysis on GC-MS, gas-phase PAE sampling by SPME and PAE amounts on the substrates is shown in Sections 2–4 in Supporting Information, including Tables S2–S7 and Fig. S2–S4.

We used AFM to scan the substrate surface on areas of 10 × 10 µm². The quantitative nanoscale mechanical characterization (QNM) mode of AFM was used to detect the surface topographies and obtain their roughness and adhesion forces after different exposure durations. The cantilever of AFM detecting was SCANASYST-AIR (Bruker, USA) with 650 nm in thickness, 115 µm in length and 25 µm in width. The values of spring constant and resonance frequency were 0.4 N/m and 70 kHz for the cantilever, and they were calibrated before each measurement.

2.5. Data processing

The gas-phase concentrations inside the chambers were hypothesized as stable. Thus, the mass transfer model for PAE adsorption on substrates can be expressed as Eqs. (1) and (2).
\[ \frac{dM}{dt} = k_A \cdot (C_{\text{air}} - C_{\text{surf,substrate}}) \]  
\[ C_{\text{surf,substrate}} = \frac{M}{A} \]  

where \( M \) is the PAE amount adsorbed on the target surface, ng; \( t \) is the exposure time, h; \( k_A \) is the mass transfer coefficient of the gas-phase PAE adsorbing onto the surface, m/h; \( A \) is the surface area of the substrate, \( m^2 \); \( C_{\text{air}} \) and \( C_{\text{surf,substrate}} \) are the gas-phase concentrations in the chamber and near the exposed substrate, ng/m\(^3\); \( K \) is the partition coefficient of the impermeable substrate, m.

If \( K \) is constant, the solution of Eq. (1) is as follows:

\[ M = K A C_{\text{air}} \left[ 1 - \exp \left( -\frac{k_A}{k} t \right) \right] \]  

The gas-phase PAE concentration in the chamber was calculated according to Eq. (4).

\[ M_c = k_A \cdot (C_{\text{air}} - C_{\text{surf,SPME}}) \cdot t \]  

where \( M_c \) is the PAE mass adsorbed by SPME, ng; \( k \) is the mass transfer coefficient of each PAE adsorbed on the SPME surface, cm/min, and \( A \) is the surface area of SPME adsorbent, cm\(^2\). The values of \( k \cdot A \) for different PAEs were obtained and shown in Section 3.2 in Supporting Information, including Table S4; \( C_{\text{surf,SPME}} \) is the PAE concentration in the SPME adsorbent, ng/mL; \( t \) stands for the sampling time, min. Since the SPME sampling times were within the linear regime of PAE adsorption (shown in Section 3.1 in Supporting Information), the values of \( C_{\text{surf,SPME}} \) can be narrowly regarded as zero (Duyang and Pawliszyn, 2007). Therefore, \( C_{\text{surf}} \) can be obtained as follow.

\[ C_{\text{surf}} = \frac{M_c}{k_A \cdot t} \]  

We used NanoScope Analysis (Version 1.80) software to analyze the AFM results and obtain surface topography, roughness and adhesion force. The surface roughness is given as Eq. (6).

\[ r_{\text{RMS}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (h_i - \overline{h})^2} \]  

where \( r_{\text{RMS}} \) is the surface roughness, nm; \( h_i \) and \( \overline{h} \) are the local and the average height of films on the surface, respectively, nm; \( n \) is the number of the tested points.

3. Results

3.1. Surface characteristics of clean substrates

Characteristics and surface topographies of the tested substrates before adsorption tests are summarized in Table 1 and Fig. S1, respectively. There are few small peaks on the surface of substrate G-P, but there are large peaks and valleys of 100–300 nm on the surfaces of substrate SS-D. The roughness of substrate SS-M is between those of substrates G-P and SS-D. The adhesion forces of the three clean substrates are all no more than 1.53 nN.

3.2. Quantification of gas-phase and surface PAE concentrations

The substrates G-P, SS-D, SS-M were exposed in the chambers with different PAEs for 33–45 days. The gas-phase PAE concentrations inside the chambers and PAE amounts on the substrate surfaces were measured along the exposed time.

Fig. S5 in Supporting Information shows the gas-phase PAE concentrations inside the chambers. The dash lines stand for the saturated concentrations of PAEs. We obtained the saturated PAE concentrations from literature, and the results were summarized in Table S4 in Supporting Information (Liang and Xu, 2014b; Weschler et al., 2008; Wu et al., 2018). Weschler et al. (2008) have made a sufficient summary of PAE vapor pressure. The median of DEP vapor pressure was used to calculate the saturated DEP concentration (7668 \( \mu \)g/m\(^3\)) in this study (Weschler et al., 2008). Liang and Xu (2014b) and Wu et al. (2018) further experimentally verified the saturated concentrations of DnBP, BBP and DEHP as 464 \( \mu \)g/m\(^3\), 12.3 \( \mu \)g/m\(^3\) and 2.7 \( \mu \)g/m\(^3\), respectively.

The gas-phase PAE concentrations were measured at six different times for all PAEs. Relative standard deviations (RSD) of sampling data for DEP, DnBP, BBP and DEHP were 11.4%, 2.9%, 22.6% and 23.2%, respectively. The gas-phase PAE concentrations in chambers can narrowly keep stable and therefore the concentration-stable hypothesis made in Section 2.5 can be established. The fluctuation of temperature and sampling errors caused by the sampling process may be the main reason for the relatively large RSDs of gas-phase PAE concentrations.

The PAE adsorption masses on substrates are shown in Fig. 2(a)–(d). During initial adsorption processes (approximately less than 5 days for DEP and 30 days for the others), the adsorbed PAE amounts were used to conduct non-linear fitting based on Eq. (3). The detailed information about whether the data used for non-linear fitting or not and the chosen basis could be seen in Section 5 in Supporting Information. The \( R^2 \) values of DEP fitting curves ranged from 0.609 to 0.708, while \( R^2 \) values of other PAEs ranged from 0.874 to 0.985. Detailed information is shown in Table 2. The adsorbed PAE amounts on substrates increased rapidly for all PAEs and substrates. The mass accumulating rates in the initial adsorption process decreased with large PAE molecular weights. With a long exposure time (approximately more than 30 days), the adsorbed PAE amounts tend to be relatively larger than those of the fitting curves. The outliers are shown in Fig. 2 as shadowed points. The adsorbed PAE amounts on substrate SS-M are slightly smaller than those on substrate SS-D. In contrast, the amounts on substrate G-P are significantly smaller than those on substrates SS-M and SS-D.

3.3. Characterization of substrates in the sorption process

We measured the variation of surface roughnesses and adhesion forces of substrates G-P, SS-M and SS-D after being exposed to DEP for 0, 4, 12, 17 and 45 days. The columns in Fig. 3 stand for the measured surface roughness of different substrates. The surface roughness of G-P enlarged from 0.81 nm to 4.65 nm after 45 days of exposure. In contrast, the surface roughness of substrate SS-D declined from 94.8 nm to 60–70 nm. Large error bars of surface roughness on substrate SS-D resulted from the surface heterogeneity. The SS-M surface roughness slightly declined from 6.9 nm to 4.0 nm after 4-day exposure and then narrowly changed. The scatter in Fig. 3 represent the adhesion forces between surfaces and AFM probes. The adhesion forces all increased after being exposed to DEP. The adhesion force of substrate G-P increased from 1.6 nN to 4.7 nN, which is the largest among all substrates. While the adhesion force increases of substrate SS-M (from 1.1 nN to 2.9 nN) and SS-D (from 1.3 nN to 2.6 nN) are relatively small.

Fig. 4 summarized the surface characteristics between substrates before and after 45-day exposure to DEP, DnBP, BBP and DEHP. The surface roughnesses of substrate G-P increased while those of substrate SS-D decreased. Substrate SS-M became slightly smoother after 45 days except for those exposed to DEP. The adhesion forces increased in all cases with different PAEs and substrates. The increases of adhesion...
forces for substrate G-P were 3.14, 2.68, 0.89, 1.43 nN for DEP, DnBP, BBP, DEHP, respectively. For substrates SS-M and SS-D, the increases of adhesion forces for all PAEs range from 0.51 to 1.81 nN. Compared with other PAEs, BBP has the smallest increase of adhesion forces among all substrates. Except for DEHP, the increase of adhesion force decline with the increase of PAE molecular weight.

4. Discussion

4.1. Partition coefficient

During the initial adsorption process, gas-phase PAEs were firstly adsorbed on the active sites of substrate surfaces according to the Langmuir adsorption isotherm (Liu et al., 2010). We fitted the initial adsorption process in Fig. 2 by Eq. (3) to obtain the partition coefficients ($K$) of different PAEs on substrates, as shown in Table 2. The $R^2$ values of fitting curves for DEP are relatively small. It may be because of the sampling and detection deviation for DEP.

The $K$ values of different PAEs on the polished glass and stainless steel measured in this study (Table 2) are in the same order of magnitude as those reported by the literature (Bi et al., 2015; Liang and Xu, 2014b; Wu et al., 2016, 2017). Thus, the results are consistent with the hypothesis of Langmuir adsorption isotherm in the initial PAE adsorption process. The measured $K$ values enlarge with the increase of PAE molecular weights. DEP has the smallest $K$ values and DEHP has the largest $K$ values for all substrates. Liang and Xu reported a linear relationship between log($K$) and log($V_p$), where $V_p$ was PAE’s vapor pressure (Liang and Xu, 2014b). However, the same PAE’s vapor pressure reported by different studies has significant differences, varying by one order of magnitude (Weschler et al., 2008). In this study, we obtained a similar linear relationship between log($K$) and molecular weights, as shown in Fig. 5, and the empirical formulas were presented in Table S9 in Supporting Information. The linear fitting of substrate G-P ($R^2 = 0.987$) is relatively better than that of substrates SS-M ($R^2 = 0.892$) and SS-D ($R^2 = 0.868$) respectively.

Table 2
Partition coefficients for different PAEs and substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Partition coefficient (K), m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DEP</td>
</tr>
<tr>
<td>G-P</td>
<td>0.4 (0.609)</td>
</tr>
<tr>
<td>SS-M</td>
<td>3.0 (0.671)</td>
</tr>
<tr>
<td>SS-D</td>
<td>3.5 (0.708)</td>
</tr>
<tr>
<td>Polished glass</td>
<td>123 at 21 °C, 600°, 758 at 21 °C; 83.6 at 30 °C, 413 at 30 °C</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>63, 1200°, 1300°, 930°, 1500°, 2200°, 1700°, 1900°</td>
</tr>
</tbody>
</table>

$^a$ The values in brackets are the $R^2$ of fitting curves.
$^b$ Bi et al. (2015).
$^c$ Wu et al. (2017).
$^d$ Liang and Xu (2014b).
$^e$ Wu et al. (2016).
It may be because the measurement uncertainty of PAE concentrations on substrate G-P is smaller than those of substrates SS-M and SS-D, as shown in Fig. 2. Substrates SS-M and SS-D have larger K values than the G-P substrates for all PAEs. This may be due to stainless steel’s larger surface roughnesses (Fig. S1), resulting in more contact sites for PAE adsorption. Fig. 5 revealed that the K values of substrate SS-D for all PAEs are narrowly equal to those of substrate SS-M. The K values of substrates G-P, SS-M and SS-D agree with the results of Wu’s study (Wu et al., 2017).

As the adsorption process went on, PAE molecules tend to pile on the surface layer by layer instead of adsorbing on the active sites under high gas-phase PAE concentrations, following the Brunauer-Emmett-Teller (BET) multilayer adsorption theory (Mooney et al., 1952). This BET adsorption mechanism enlarges surface PAE intake capacity, leading to larger apparent partition coefficients ($K_{app}$) than monolayer adsorption. Therefore, the PAE adsorption amounts after long-term exposure remarkably exceeded the prediction of the monolayer fitting trendlines in Fig. 2. It should be noted that the error bars of PAE adsorption amount may be introduced because of the large PAE detecting amounts.

### 4.2. PAE organic films growing on different substrates

As reported in previous studies, the substrate surfaces constantly accumulate PAE molecules, and nanometer-thick organic films would gradually grow (Eichler et al., 2019; Lim and Lee, 2020; Lim and Abbatt, 2020; Weschler and Nazaroff, 2017). In this study, the growth rates of PAE organic film were approximately constant during the initial adsorption process. After long-term exposure, PAE molecules continued to accumulate in organic films instead of reaching adsorption equilibrium, as demonstrated in Fig. 2. It indicated that PAE adsorption followed BET multilayer adsorption theory instead of Langmuir monolayer on the tested substrates.

Fig. 6 shows the surface topographies measured by AFM. There are several nano-peaks sparsely distributed on the G-P surfaces. The
sections between peaks are much larger than the height of peaks. Thus, it looks like there are sparse peaks on a flat surface. Organic films were formed on the flat surface and also around the sparse peaks to broaden and heighten them. Thus, the tiny peaks became higher and detectable, and the surface roughnesses of substrate G-P increased after 45-day DEP exposure.

There were intrinsically large valleys on the SS-D surface. Organic films tended to grow in the valleys of surfaces according to the Kelvin equation (Yin et al., 2018), as shown in Eq. (7).

\[
\ln \frac{p}{p_0} = \frac{2\gamma V}{RTr}
\]

(7)

where, \(p\) is the actual vapor pressure on the curved surface with a certain curvature radius, \(r\); \(r\) is the local curvature radius of the surface, \(m\); \(p_0\) (Pa) is the saturated vapor pressure of a flat surface; \(\gamma\) is the surface tension of PAE, N/m; \(V\) is the molar volume of gas-phase PAE, L/mol; \(R\) is the ideal gas constant, J/(mol·K); \(T\) is the temperature, K. The sign of \(r\) is defined as positive for the raised surface and negative for the concave surface. Thus, valleys as concave surfaces could significantly minish the actual PAE vapor pressure and lead to the formation of organic films.

The substrate SS-M contained both peaks and valleys on the surfaces. The valleys were narrower but deeper than those of substrate SS-D (Fig. 6 and Fig. S1). After 45-day exposure, peaks grown on the surface were fewer and shorter than substrate G-P, according to Fig. 6. Substrates SS-M and SS-D had similar adhesion forces after 45-day exposure, both smaller than substrate G-P. It reveals that PAE molecules accumulated firstly in the valleys rather than around peaks when substrates exposed to BBP were smaller than the others. However, the variations of surface roughness did not have the same tendencies as adhesion force changes. It may be because the uneven substrates would influence the detecting deviation of surface roughness.

The variations of surface roughness and adhesion force are determined by the PAE viscosity and mass of PAE organic film on surfaces. We define \(A_s\), the adhesion force per surface concentration ((nN·m²)/μg), to quantify the featured viscosity of different PAE molecules.

\[
A_s = \frac{A_{d_{\text{clean}}} - A_{d_{\text{adhesive}}}}{Sc_{\text{w}}}
\]

(8)

where \(A_{d_{\text{clean}}}\) and \(A_{d_{\text{adhesive}}}\) stand for the adhesion forces of clean substrates and substrates after exposed to PAEs, respectively, nN; \(Sc_{\text{w}}\) means the surface PAE concentration, μg/m². The exposure times are chosen as 33 days for DEP and 45 days for DnBP, BBP and DEHP.

Fig. 5 revealed that the values of \(A_s\) enlarged with the increase of PAE molecular weights. A linear relationship was better fitted for substrate G-P but not for substrate SS-M and substrate SS-D. As we discussed above, gas-phase PAEs tend to adsorb on substrate G-P more uniformly and generate organic films to cover a large part of surfaces. Therefore, \(A_s\) of substrate G-P could represent the featured adhesion forces of PAE organic films better than the others.

PAEs with small molecular weights like DEP and DBP had high vapor pressure (Weschler and Nazaroff, 2008) and high gas-phase concentration in chambers, as shown in Fig. S5. In contrast to BBP and DEHP, more DEP and DnBP existed in the gas phase and then accumulated on the substrates. Thus, as shown in Fig. 4, the large adhesion forces of DEP and DnBP resulted from the significant increase of adsorption amounts after 45-day exposure, the featured viscosity, \(A_s\), of which are minor. The adhesion forces of BBP were smaller than those of DEP and DnBP. Still, substrates exposed to DEHP had larger adhesion forces than others.
which may be because the DEHP molecule’s featured viscosity (quantified by As) is far more significant than the others.

The densities of target PAEs were obtained from SPARC (http://ibmlc2.chem.uga.edu/sparc/) (Arp et al., 2010). The values are 1.13 g/cm³, 1.05 g/cm³, 1.14 g/cm³ and 1.01 g/cm³ for DEP, DnBP, BBP and DEHP, respectively. We then calculated the thickness of organic film growth after 45 days of PAE exposure, and the calculating methods and results are shown in Section 5 in Supporting Information, including Table S10. The film growth rates contributed by DEP on substrates are the largest with the values of 0.148 nm/day, 0.875 nm/day and 0.819 nm/day, respectively, for substrate G-P, substrate SS-M and substrate SS-D. The film growth rates were decreased with the increase of PAE molecular weights except for DEHP, whose film growth rates are larger than BBP but smaller than DEP and DnBP. It is supposed that the film growth rate is determined by PAE gas-phase concentration and partition coefficient. Substrate SS-M and SS-D showed larger average organic film growth rates than substrate G-P. Considering the rough surfaces of substrate SS-M and SS-D, the organic film growth on the surfaces tends to be heterogeneous, which leads to the films locally formed in valleys and crevices of substrates.

Previous researches detected the organic film growth rate in the environments (Lim and Abbott, 2020; Liu et al., 2003; Wu et al., 2008). The film growth rate on glass contributed by multiple pollutants is 0.05–3.1 nm/day. The film growth rates on glass reported by Wu et al. (2008) (1.6–2.6 nm/day, multiple pollutants) are more than ten times larger than the maximum value in this research (0.148 nm/day, DEP only). The reason why the film growth rate could maintain at a relative level shown in the field test results may be that multiple organic matters or particles could enhance the organic film formation. There are four classes of polar compounds contained n-alkanes, PAH, PCBs and OC pesticides detected in organic films, according to Liu et al. (2003). Wu et al. found up to 15 PCB congeners in the sampling surface films (Wu et al., 2008). Lim et al. used a non-targeted manner with direct analysis in real-time mass spectrometry to determine the chemical composition of indoor surface films. Many organic matters like DEHP, acetyl tributyl citrate (ATBC), γ-decalactone were discovered inside organic films (Lim and Abbott, 2020). Therefore, synergistic enhancement may exist in organic film formation when exposed to multiple organic pollutants. And the organic films would be more hazardous with the possibility of adsorbing other pollutants like VOCs, PCBs and PAHs.

5. Conclusions

The PAE organic films on indoor surfaces could significantly enlarge the PAE uptake of human beings through conceiving the contaminated surfaces. In this work, we first observed the microscopic growth process of PAE organic films on impermeable substrates, including polished glass (G-P), mirror-polished stainless steel (SS-M), and drawn stainless steel (SS-D). Organic films were formed on the flat surface and also around the inherent nano-peaks on G-P surfaces to broaden and heighten the peaks. Valleys on substrate SS-D also provided active sites for PAE molecules, which led to the organic films formed in the valleys. Both peaks and valleys existed on the surface of SS-M substrates, and organic films were precedently grown in the valleys. We also obtained the partition coefficients of DEP, DnBP, BBP, and DEHP on substrate G-P, SS-M, and SS-D by fitting the initial monolayer adsorption process. However, multilayer adsorption occurs when the surface is exposed to PAE concentrations for a long time, which enlarges the apparent partition coefficients. Indoor PAE pollution is a widely concerned problem, affecting the health of human beings, children especially. Better understandings of PAE organic films can support better estimates of PAE exposures resulting from children’s contact with surface films.

CRediT authorship contribution statement

Jinhan Mo: Conceptualization, Methodology, Project administration, Funding acquisition, Writing – review & editing, Supervision. Zhuo Chen: Conceptualization, Methodology, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. Qianying Wu: Methodology, Data curation. Ying Xu: Methodology, Writing – review & editing, Supervision.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.127326.

References
