Seasonal variations of airborne phthalates and novel non-phthalate plasticizers in a test residence in cold regions: effects of temperature, humidity, total suspended particulate matter, and sources

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Graphical Abstract:

Highlights

- PAEs are still the dominant currently-used plasticizers in the studied residence
- Increasing molecular weights reduced the temperature dependences of PAEs and NPPs
- Concentrations of higher mass PAEs and NPPs had a positive correlation with total suspended particles
- The highest concentrations of PAEs and NPPs were identified when the haze occurred in autumn

ABSTRACT: As a class of plasticizers widely used in consumer products, some phthalate esters (PAEs) have been restricted due to their adverse health effects and ubiquitous presence, leading to the introduction of alternative non-phthalates plasticizers (NPPs) to the market. However, few studies focus on the influence of environmental parameters on the presence of these plasticizers and the potential human health risks for people living in poorly ventilated indoor spaces in cold regions. We investigated the trends of PAEs and NPPs in air in a typical indoor residence in northern China for over one year. The air concentrations of PAEs were significantly higher than those of NPPs ($p < 0.05$), indicating that PAEs are still the dominant plasticizers currently being used in the studied residence. PAEs showed seasonal fluctuation patterns of the highest levels found in summer and autumn. The temperature and relative humidity dependence for most PAEs and NPPs decreased with decreasing vapor pressure. Concentrations of the high molecular weight NPPs and PAEs positively correlated with total suspended particles (TSP). It is worth noting that the peak concentrations of PAEs and NPPs were found when the haze occurred in autumn. Principal component analysis (PCA) suggested the diverse applications of PAEs and NPPs in the indoor environment. The hazard index (*HI*) values observed in this study were all below international guidelines (<1); however, the average carcinogenic risk (*CR*) values for some compounds exceeded acceptable levels (One in a million), which raised concerns about the possibility of carcinogenicity for people living indoors for long periods of time in cold regions.

Keywords: Alternative phthalates; Seasonal variation; Haze season; Health risks.

1. Introduction

Phthalate esters (PAEs) are widely used in plastic products such as toys, construction materials, food packaging, medical parts, and cosmetics (Hauser and Calafat 2005, Guo et al. 2014). They were widely used in producing polyvinyl chloride (PVC) products and had colossal production and consumption volume. In recent years, the global production of plastic products has reached 335 million tons per year (Drzyzga and Prieto 2019). PAEs are the main plasticizers, with annual consumption of between 6 and 8 million tons between 2014 and 2015 (Net et al. 2015). China is one of the countries with the largest PVC production (Guo and Kannan 2011). In the past ten years, the production of plasticizers in China has increased, with the production volume reaching 22,000 tons in 2011 (Xu et al. 2008, CPPIU 2011). It has been reported that between 2010 and 2015, the demand for PAEs in China was expected to increase at an annual growth rate of 7.7% (Emanuel 2011). PAEs can cause acute and chronic toxicity that leads to the death of freshwater invertebrates (Call et al. 2001). The National Toxicology Program (NTP) of the United States adopted animal experiments to allow animals to ingest high doses of di-2-ethyl-hexyl phthalate (DEHP) for a long time through food and confirmed that DEHP could cause liver cancer in rats and mice (Kluwe et al. 1982). Exposure to DEHP can lead to congenital malformations, sexual dysfunction, heart disease, and even cancer in humans (Sun and Zhuang 2014).

Limited information is available focusing on the occurrence of alternative chemicals for PAEs, i.e., non-phthalate plasticizers (NPPs), in the indoor air in China. Due to the toxicological effects and environmental risks of PAEs, NPPs have been increasingly used in recent years as substitutes for PAEs (Lee et al. 2019). The production volumes of NPPs, such as di-octyl adipate (DEHA), acetyltri-n-butyl citrate (ATBC), di(2-ethylhexyl) terephthalate (DEHT), di-iso-nonyl-1,2-cyclohexanedicarboxylate (DINCH) and trioctyltrimellitate (TOTM) could have reached between 10,000 and 200,000 tons per year in Europe (Fromme et al. 2016). In the repeated dose study, the liver is the main target organ of DEHT, and reduced maternal growth is observed (Wirnitzer et al. 2011). For DEHA, repeated dose toxicity studies in animals found a decrease in body weight gain, and the incidence of liver cancer in female mice is significantly higher (Lioy et al. 2015). ATBC showed a mild effect on body weight and some biochemical parameters without adverse liver effects (Lioy et al. 2015). In a single-generation study, TOTM affected the number of spermatocytes and sperm cells (Fromme et al. 2016).

PAEs and NPPs are semi-volatile compounds (SVOCs) and could be quickly released from various consumer products, resulting in indoor environmental pollution. Due to the airtightness of buildings, indoor air pollution by PAEs is often more severe than that of outdoor, especially in winter when windows are usually kept closed. The urban population spends more than 80% of their time indoors (Hwang et al. 2008), especially for sensitive groups such as infants, pregnant women, and the elderly, with extended indoor activity periods. Therefore, indoor air quality has become an important factor affecting human health.

Indoor air pollution, which could seriously affect public health, is a major environmental problem in China. Chemical pollutants, such as PAEs and NPPs, are released from decoration materials, electronics, and furniture and become some of the primary contaminants in indoor air. Northern and southern cities face different indoor air problems due to different climates. In the winter especially, indoor air quality in northern cities could be much worse than that of southern cities due to the central heating and the poor air circulation in northern China. The influence of the environmental parameters, such as temperature and humidity, and products used in the indoor environment on the concentrations of PAEs and NPPs is still not well understood. Therefore, it is crucial to study such influencing factors in order to assess the risks of PAEs and NPPs in the indoor environment in cold regions.

In filling these gaps, we set up experiments in a test residence in northeastern China for one year. This study was carried out with the objectives (1) to investigate the occurrence and compositions of PAEs and NPPs in the indoor environment, (2) to study the seasonal variations of target compounds in the indoor environment over one year period, (3) to understand the roles of environmental factors such as temperature, relative humidity (RH), haze season, and concentrations of total suspended particles (TSP) that could affect concentrations and profiles of target compounds, (4) to explore the possible sources of target compounds under semi-control environment, and (5) to evaluate the effects of indoor air inhalation and dermal exposure to PAEs and NPPs on human health risk in the cold region of China.

2. Materials and methods

2.1. Chemicals and standard solutions

All seven PAEs and eight NPPs, including dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), di-n-butyl phthalate (DBP), benzyl butyl phthalate (BBP), DEHP, di-n-octyl phthalate (DOP), di-n-butyl adipate (DNBA), di-iso-butyl adipate (DIBA), di-iso-nonyl adipate (DINA), DEHA, ATBC, DINCH, DEHT, and TOTM were supplied by AccuStandard, New Haven, CT. The internal standards, including tetra deuterium ring designated DMP-d4, DEP-d4, DBP-d4, DiBP-d4, BBP-d4, and DEHP-d4, were provided by the Cambridge Isotope Laboratories Tewksbury, MA. The solvents used in this study were of the high-performance liquid chromatography (HPLC) grade obtained from J.T. Baker (Phillipsburg, NJ). A detailed description of PAEs and NPPs, such as abbreviations, molecular weights, chemical formulas, etc., is listed in Table S1.

2.2. Experimental setup

Detailed information on the sample collection can be found in our previous studies (Guo et al. 2020, Sun et al. 2020). Briefly, the experiment was carried out in Harbin, northeast China, where the outdoor annual temperature variation could be greater than 70 °C, from -38 to 38 °C. A representative residence that was unoccupied was chosen specifically for this experiment for the collection of air samples. The apartment on the fifth floor of a seven-floor building was built in 1994 (Fig. S1). The living room (LR) and two bedrooms were selected for sample collection. The interior materials of the three test rooms include varnished wooden floors and unpainted ceilings and walls. PVC floor covering and a baby crawling mat (expanded polystyrene panel) were placed on the floors of bedroom #1 (BR#1) and bedroom #2 (BR#2), respectively. The doors connecting the living room and two bedrooms and the windows in each were generally closed during the study. There are also some basic furniture and electrical appliances in the LR. As was customary, the room temperature was controlled by central heating from mid-October to late April, but the room temperature was not maintained during the other months. Environmental data such as temperature and RH were recorded during the sampling period.

2.3. Sample collection and preparation

A low-volume active sampler with a flow rate of 2 L/min was used to collect approximately 5.8 m^3 of air in 48 hours. A total of 104 pairs of the gas-phase and particulate-phase samples were collected with polyurethane foam (PUF) and quartz fiber filter (QFF), respectively. The PUF and GFF were purchased from Tisch Environmental, Cleves, OH. To reduce the background contaminations, the GFF was baked at 450 °C in a Muffle furnace before sampling. The PUF was first washed with soap, tap, and purified water, followed by the Soxhlet extraction with acetone for 24 h and dichloromethane/hexane (3:1, v/v) for another 24 h. After being cleaned by Soxhlet extraction, the PUF was vacuumed dry immediately and sealed in the glass jar before sampling. The sampling frequency was once every eight days from March 2017 through March 2018. Furthermore, daytime and nighttime samples were collected in the living room during the haze season to test the impacts of central heating in northern China.

Field blank samples were collected along with parallel air samples once a month. Before and after sampling, QFF was stabilized in a constant temperature and humidity chamber for 48 h, then weighed to calculate the mass of TSP in the samples. The samples were stored in the -20 °C freezer and processed within one week after sampling.

The particle sample (QFF) was placed into a clean sealed glass tube, and added a mixture of d4-labeled internal standards to equilibrate at room temperature for three hours. Particle samples were extracted in 10 mL dichloromethane/hexane (3:1, v/v) by shaking for 30 min, followed by 5 min centrifugation with a speed of 4000 r/min. The extracted solution without QFF and impurities were transferred into a new tube. The extraction was repeated three times, and the extracts were combined. The same extraction procedure was applied for gas-phase samples, except the mixed solution was 30 mL of dichloromethane/hexane (3:1, v/v). The mixed solution was concentrated by an Automated Evaporation System (TurboVap II, Biotage, Charlotte, NC, USA) with a gentle nitrogen stream until the volume of the solution was near 0.5 mL. Then, 2 mL isooctane was added as keeper, and nitrogen blowing continued until the volume reached 1.0 mL.

2.4. Instrumental analysis

The analyses of PAEs and NPPs were carried out using an Agilent 7890 GC/5977A MS equipped with an HP-5MS (30 m×0.25 mm id × 0.25 μm film thickness) capillary column in electron impact (EI) mode. The initial oven temperature was 90°C, held for 1.25 minutes, then increased to 240 °C at a speed of 10 °C/min for 15 minutes, then increased to 310 °C at a rate of 20 °C/min for 3.5 minutes. Finally, the temperature was held at 310 °C for another 5 minutes with a total run time of 24.75 min. The retention time and quantitative ion are listed in Table S2.

2.5. QA/QC

For each batch of 20 air samples, two procedural blanks, two field blanks, and two matrix spikes were processed using the same procedure. The average recoveries of DMP-d4, DEP-d4, DBP-d4, DiBP-d4, BBP-d4, and DEHP-d4 in all samples were 93 ± 9.5%, 96 ± 8.9%, 98 ± 7.5%, 114 ± 8.4 %, 91 ± 9.5% and 94 ± 12%, respectively. PAEs and NPPs found in procedural and field blanks were much lower than those found in the air samples (Table S3). The recoveries of PAEs and NPPs in the matrix spike sample ranged from 78% to 125%. The sample concentrations were blank-corrected by subtracting the mean blank values and corrected by their recoveries.

The instrument detection limit (IDL) was determined as a signal-to-noise (SN) ratio of 3, with values in the range of 0.012 – 0.76 ng/mL and 0.0074 – 0.14 ng/mL for PAEs and NPPs, respectively. The method detection limit (MDL) was calculated by the mean blank concentration plus three times the standard deviation. For PAEs or NPPs that were undetected in the blank, the MDL was defined as an SN ratio of 10. The MDLs of PAEs and NPPs were 0.020 – 13 ng/m^3 and 0.014 – 4.6 ng/m^3, respectively. The MDLs were divided by the average air volume (5.8 m^3) to compare with the actual air concentrations. If the concentration was lower than the MDL, the value was substituted with 2/3 MDL. Detailed information on procedural blanks, field blank concentrations, spike recoveries, IDLs, and MDLs is listed in Table S3. The SPSS software was used for all statistical analyses (Version 24). Specific information related to the human exposure hazard index (*HI*), and carcinogenic risk (*CR*), is described in the supporting information (S1.1).

3. Results

3.1. Occurrence and profiles of PAEs and NPPs in the indoor air

Statistics summary on the concentrations of PAEs and NPPs collected from each indoor air sample (gas-phase plus particle-phase) from the three rooms are listed in Table 1 and Fig. S2. Each measurement was treated as a separate data point in this study, regardless of where the sample was taken unless specified. Seven PAEs and eight NPPs were detected in all indoor air samples at varied detection rates. DOP (26%) and DINA (23%) had low detection frequencies of less than 30%, whereas the detection frequencies of the remaining PAEs and NPPs were high in the range of 87-100% and 83-100%, respectively. As shown in Fig. S2 and Table 1, the maximum concentrations of DEP, BBP, DIBA, DNBA, DEHA, DINCH, and TOTM in all samples were below 1000 ng/m^3.

The median concentrations of total PAEs (ΣPAEs, 2200 ng/m^3) were 21 times higher than total NPPs (ΣNPPs, 97 ng/m^3) with $p < 0.01$ by the Mann-Whitney test, which has been widely applied to investigate the differences between two sets of independent samples that are not normally distributed. DMP, with a median value of 710 ng/m^3, was the most abundant PAE, followed by DiBP (650 ng/m^3) and DBP (390 ng/m^3). As shown in Fig. S3, DMP, DiBP and DBP accounted for 34 ± 13%, 31 ± 14%, and 20 ± 6% of the total PAEs, respectively. Among NPPs, DIBA, DEHT, and DEHA were detected at the highest concentrations, with median concentrations of 28, 17, and 10 ng/m^3, respectively. The percentage of DIBA, DEHT, and DEHA was 32 ± 18%, 22 ± 18%, and 12 ± 8% of the total NPPs, respectively.

3.2. PAEs and NPPs in different rooms

Concentrations of PAEs and NPPs in the three rooms are listed in Table S4 and Fig. S4. The mean concentrations of ∑PAEs were 3100 ng/m^3 in BR#1, 1900 ng/m^3 in BR#2, and 2900 ng/m^3 in LR, respectively. In BR#1, BR#2, and LR, the average concentrations of ∑NPPs were 150 ng/m^3, 180 ng/m^3, and 120 ng/m^3, respectively. In BR#1, the most abundant PAEs were DMP, followed by DBP and DiBP; however, DiBP had the highest concentrations in both BR#2 and LR. DIBA was the dominant NPPs in BR#1, followed by DEHA and DEHT, whereas the most abundant NPPs were DEHT, DIBA, and DINCH in both BR#2 and LR.

The discrepancy between PAE and NPP concentrations among the three rooms was analyzed using the Mann-Whitney U test, and it was found that concentrations of PAEs and NPPs in BR#1 differed from the other two rooms. For BR#1 and BR#2, concentrations of DMP, DEHP, ∑PAEs, DIBA, and DEHA were significantly higher, while concentrations of BBP and ∑NPPs were significantly lower in the former than in the latter ($p < 0.01$). Between BR#1 and LR, concentrations of DMP, DBP, DIBA, and DEHA were significantly higher, while concentrations of DiBP, BBP, DEHP, DINCH, DEHT, and TOTM were significantly lower in BR#1 than those in LR ($p < 0.01$).

Significance analysis revealed significant differences in TSP and RH between BR#1 and LR ($p<0.01$).

Differences in concentrations of PAEs and NPPs were also observed between BR#2 and LR. Concentrations of DiBP, BBP DEHP, ∑PAEs, and DEHA were significantly lower, and concentrations of DEHT and ∑NPPs were significantly higher in BR#2 than those in the LR ($p < 0.01$). There was no discernible difference in concentrations of other PAEs or NPPs among the three rooms.

3.3. *Seasonal variations of PAEs and NPPs concentrations*

Figs. 1, 2, and S6 showed the time series of PAE and NPP concentrations and interior temperature in four seasons in the three rooms. Significant seasonal patterns can be found in the three rooms. Generally, the distribution patterns for measured concentrations of PAEs and NPPs were similar to the fluctuation of indoor ambient temperature, except for the samples collected in the haze season with very high levels of target compounds. For BR#1 (Table S5), the highest mean concentrations of ∑PAEs were found in summer (4300 ± 1800 ng/m^3), followed by those in autumn (3400 ± 2600 ng/m^3), spring 2017 (3000 ± 1000 ng/m^3), spring 2018 (1900 ± 540 ng/m^3), and winter 2017 (1800 ± 970 ng/m^3). For NPPs, the highest concentrations were found in summer (180 ± 90 ng/m^3), followed by those in spring 2017 (160 ± 95 ng/m^3), autumn (150 ± 100 ng/m^3), spring 2018 (100 ± 25 ng/m^3), and winter (73 ± 43 ng/m^3). The lowest concentrations are found in winter because the sources of PAEs and NPPs are indoors; thus, their concentration should be influenced by lower temperatures in winter (19.5 ±

4.7 °C) than in summer (28.0 ± 3.1 °C). These results suggest significant seasonal variations of PAEs and NPPs as they are semi-volatile compounds whose emissions to the indoor air could be controlled by ambient temperatures.

Comparisons were further conducted for environmental parameters among the four seasons by using the Mann-Whitney test, as shown in Table S6. The results indicated that the indoor RH and temperature differed among seasons ($p < 0.01$) except for temperatures between spring and autumn ($p > 0.05$). The concentrations of TSP were also significantly different between spring and winter ($p < 0.05$), summer and autumn ($p < 0.01$), and summer and winter seasons ($p < 0.01$).

Changes in concentrations and chemical compositions in the three rooms and four seasons could be due to temperature, RH, interior decoration (sources), and TSP, which were further explored in the discussion section. The differences between individual compounds can be determined by combining the three factors (temperature, RH, TSP), as demonstrated in Table S6. For example, in the case of spring vs. summer (significant differences in temperature and RH, $p < 0.01$) and spring vs. autumn (RH, $p < 0.01$), we found significant differences in DBP and ΣNPPs concentrations between the spring and summer, and significant differences in DEHP, DINCH, and TOTM concentrations between spring and autumn. The only compound whose concentration did not fluctuate significantly throughout the sampling period was DEHA.

4. Discussion

4.1. Concentrations of PAEs and NPPs in the test residence were comparable with those worldwide

The median concentrations of indoor PAEs (gas plus particle phase) are compared to other studies, as shown in Table S7 and Fig. S5**.** The total PAE concentrations in this study were similar to those found in Berlin kindergartens and apartments (Fromme et al. 2004) and households in Hangzhou, China (Huang et al. 2021) (see Fig. S5), but substantially lower than those found in Beijing, China (Huang et al. 2020) and newly renovated apartments in Hangzhou, China (Pei et al. 2013). DMP and DiBP were the dominant compounds with the highest percentages in this study, which were comparable with previous studies which found DiBP as the dominated PAEs in the indoor air in Norway (Giovanoulis et al. 2018), Xi'an (Wang et al. 2014), Stockholm (Bergh et al. 2011), Vietnam (Tri Manh et al. 2017) and Paris (Moreau-Guigon et al. 2016). However, the dominant compounds could be different due to the different use patterns of indoor products. For example, DEP showed the highest percentage in the air of households in the USA (Rudel et al. 2003, Rudel et al. 2010, Tran and Kannan 2015, Lunderberg et al. 2019). DBP was found as the dominant compound in the indoor air in Beijing (Huang et al. 2020), Berlin (Fromme et al. 2004), Tokyo (Otake et al. 2004), Guangzhou (Huang et al. 2021), and Sapporo (Kanazawa et al. 2010). These differences in profiles of PAEs in the indoor environment suggest that the use patterns of PAEs are different even in the same country.

Compared to PAEs, few studies focused on NPPs in the indoor air. As shown in Table

S8, the median concentration of ΣNPPs in this study was lower than in the air of the daycare center in German (Fromme et al. 2016) and the houses in Japan (Takeuchi et al. 2014) but slightly higher than that in Guangzhou, China (Tang et al. 2020). DEHA concentration was somewhat lower than the values reported in the United States (Rudel et al. 2001, Rudel et al. 2010) but higher than in three preschools in Sweden (Langer et al. 2021). ATBC, DEHT, and DINCH were almost always higher than those in the three preschools in Sweden (Langer et al. 2021). In general, these concentrations of NPPs in this study were in the same order of magnitude compared with previously measured concentrations in the indoor air.

4.2. Indoor temperature, humidity, TSP, and haze season significantly influenced the levels of PAEs and NPPs in cold regions

The Spearman correlations were conducted to investigate the relationships between the concentrations of target compounds with environmental factors. As shown in Table S9, ∑PAEs and ∑NPPs in all samples exhibited strong correlations with indoor temperature, RH, and TSP. Temperature and RH showed considerable influence on the PAEs and NPPs with lower molecular weight and higher vapor pressure, for example, DMP and DEP, while TSP showed substantial relationships with higher molecular weight and lower vapor pressure PAEs and NPPs, such as DEHP. However, the correlations between concentrations and the three factors (Temperature, RH, TSP) differed in the three rooms, which showed more similarities in BR#1 and BR#2 but significant differences between LR and the other two rooms. For example, significant differences in temperature, RH, and TSP were found between BR#2 and LR ($p<0.01$). In LR, the values of TSP and RH were occasionally correlated with the concentrations of higher molecular weight PAEs and NPPs.

Temperature. Significant differences in temperature between BR#1 and BR#2 ($p<0.01$), with the values of 24.8 ± 2.9 ℃ and 21.6 ± 5.6 ℃, respectively. As the emission sources are different in the three rooms, the influence of temperature should be considered separately. For example, the relationship between the concentrations of PAEs and NPPs and the indoor air temperature in BR#1 is shown in Fig. 1. With increasing molecular weights and decreasing vapor pressures, the temperature dependences of the PAE and NPP concentrations were diminishing. The vapor pressures of PAEs and NPPs are temperature dependent and increase with increasing temperature. For higher mass PAEs, BBP and DEHP were less affected by temperature than other lower mass PAEs, see Fig. 1 and Table S9. Some studies found that DEP, DIBP, and DBP concentrations (higher vapor pressure phthalates) correlated strongly with indoor temperature in a typical household, whereas DEHP was unrelated to indoor temperatures (Gaspar et al. 2014, Lunderberg et al. 2019). Higher temperatures lead to stronger source emissions, resulting in higher amounts of PAEs released into the indoor environment, according to a set of chamber experiments (Clausen et al. 2012, Wu et al. 2016, Zhou et al. 2021). A temperature increase from 25°C to 35°C in a household can increase the gas-phase concentration of PAEs by a factor of ten or more. However, the total concentration in the air may not increase as much for less volatile chemicals (Liang and Xu 2014).

For NPPs, Fig. 1 shows that only DNBA and DEHA are slightly associated with indoor temperature. In contrast, high molecular weight (HMW) NPPs such as DEHT and TOTM had no correlations with temperatures, as shown in Table S9 ($p > 0.05$). This conclusion was comparable to that of PAEs, in which concentrations of lower molecular weight NPPs were significantly affected by indoor temperature. As shown in Fig. 1, the concentrations of DINCH, TOTM, and DEHT were close to the baseline and accompanied by occasional peaks that were not associated with high temperatures. The gas-phase concentrations of DEHA and DINCH emitted from crib mattress covers in a chamber at different temperatures were calculated, showing that the two NPPs increased significantly with increasing temperatures in the chamber (Liang and Xu 2014). A recent study indicated that the concentrations of dipentyl phthalate (DPP), BBP, DIBA, DNBA, and DEHA increased as the temperature rose in a model room (Uhde et al. 2019).

Based on mechanistic understandings of the temperature dependence of SVOC concentrations, there is an exponential relationship between the concentrations of target compounds ($\ln C$) and ambient temperature (Liang and Xu 2014, Li et al. 2022a):

$$\ln C = \mathrm{A} + \mathrm{B}/T \quad (1)$$

where $\mathrm{B} = -\Delta H_{sa}/\mathrm{R}$. Here ΔH_{sa} refers to the phase change enthalpy between the source materials and indoor air. Therefore, the ΔH_{sa} can be calculated. The results for BR#1 (with PVC flooring) are shown in Fig. 3. The ΔH_{sa} values for DBP and DiBP are similar to the values of 105 and 95 kJ/mol, respectively, which are lower than the values from the values estimated by a previous study (Li et al. 2022a) with the values of 120 and 120 kJ/mol, respectively. Our values are close to the vaporization enthalpies of pure chemical (ΔH_{vap}) with the values of 97 and 95 kJ/mol, respectively (Ishak et al. 2016). The reported ΔH_{sa} of DEHP was 123 kJ/mol for vinyl flooring #1 in a previous study (Liang and Xu 2014), which is close to the values of 137 kJ/mol estimated in this study. The value of DEHA was 102 kJ/mol, lower than that measured by a previous study (Liang and Xu 2014) with the value of 179 kJ/mol for mattress cover #6. These results suggested that PVC flooring in BR#1 could be a strong source for PAEs and NPPs, especially DBP, DiBP, DEHP, DIBA, and DEHA, which showed strong correlations between indoor temperature and chemical concentrations.

RH. The RH values were 35 ±13％, 39 ±12, and 25 ±7.3％ in BR#1, BR#2, and LR, respectively. The emission rate of DEHP from vinyl flooring was studied in chamber tests independent of humidity (Clausen et al. 2007). In the residential indoor environment, few study results suggested no significant relationship between relative humidity and airborne PAE concentrations (Gaspar et al. 2014, Bu et al. 2016). However, Feng et al. confirmed that a higher concentration of humidity shows a negative correlation with PAE concentrations in laboratories (Feng et al. 2020). Huang et al. found that the concentrations of gas-phase DnBP, DiBP, and DEHP in the air were negatively correlated with relative humidity in summer (Huang et al. 2020). In contrast, no correlations were identified in winter, except for DMP, which was favorably associated with RH (Huang et al. 2020). Unfortunately, limited data on the links between RH and indoor NPP concentrations could be found. According to laboratory findings, relative humidity has only a minor impact on the direct transfer of DBP, BBP, DEHP, DEHA, and DINCH from indoor source materials to dust (Bi et al. 2021).

As a result, these studies found that RH is neither positively nor negatively linked with PAE concentrations. In contrast to previously published results, the influence of RH on PAE and NPP concentrations was positive in this study. The effect of humidity on individual indoor PAE and NPP concentrations is challenging to investigate because of the complexities of the indoor environment. While the impact of RH on PAEs emissions is not fully understood, it is well understood that the influences from temperature are strong. It is noticed that RH showed significant and positive correlations with temperature. Therefore, the positive effect of RH, in fact, revealed a substantial influence by temperature. Although it is generally agreed that humidity has less impact on the emissions of PAEs from sources, moisture may affect the distribution of PAEs, specifically from surface to airborne PAEs.

TSP. The concentrations of TSP were 18 ± 15 μg/m^3, 21± 30 μg/m^3, and 67 ± 73 μg/m^3 in BR#1, BR#2, and LR, respectively. As shown in Table S9, TSP tends to affect the levels of target compounds with higher molecular weights and low vapor pressures in all types of samples. The levels of PAEs and NPPs affected by TSP were different after splitting the samples into three rooms. DiBP, BBP, and DEHP concentrations in all samples were substantially linked with TSP in the current study. This linkage was similar to the findings of previous studies (Lunderberg et al. 2019, Yang et al. 2020), which suggested that the levels of BBP and DiBP were connected with particulate matter (Yang et al. 2020) and the higher DEHP concentrations correspond to greater concentrations of particulate matter (Lunderberg et al. 2019). Huang et al. found that indoor $PM_{2.5}$ concentrations were positively correlated with gas-phase DiBP and DBP concentrations in summer (Huang et al. 2020).

Similar to PAEs, the concentrations of HMW NPPs, such as DEHA, DINCH, DEHT, and TOTM, were substantially linked with TSP concentrations in all samples. However, no previous studies on the relationship between TSP and NPP concentrations have been reported. Particulate matter has been shown to increase the SVOC emission rate of building materials and play a crucial role in SVOC transport in indoor environments (Benning et al. 2013). The model predicted that increased particulate matter concentrations would significantly elevate the SVOC emission flow from the surface to the interior air (Liu et al. 2012).

Haze season. As illustrated in Figs. 1, 2, and S6, the concentrations of PAEs and NPPs in each of the three rooms were divided into four seasons, with temperature data displayed alongside. It is worth noting that the peak concentrations of PAEs and NPPs in autumn were found when the haze occurred, although the indoor temperature was not very high. The concentrations of PAEs and NPPs in three rooms correlated well with the indoor temperatures when excluding the haze episodes, as indicated in those figures. The increase in the concentrations of target compounds during the haze season is most likely due to the input from outdoors with a large amount of PM in the air and the release of large amounts of chemicals into the atmosphere from biomass burning in northeast China.

In Northern China, the haze results from the local burning of biomass and coal (Li et al. 2017), which produce a large quantity of particulate matter (PM). Wang et al. investigated the concentrations of phthalates in PM2.5 indoors and outdoors in Beijing, finding that phthalate concentrations were significantly higher indoors and outdoors during haze than during non-haze periods (Wang et al. 2019). Phthalate levels in the Shanghai atmosphere were found to be low in non-haze weather events (236 ng/m^3) and high in highly polluted weather events (up to 700 ng/m^3), according to a previous study (Li et al. 2018). It was reported that the indoor concentration dynamics of some less volatile SVOCs were driven by the temperature at higher temperatures and by PM at lower temperatures (Li et al. 2022b). In this study, high concentrations of DEHP in colder haze season were found, which may be because of the high amount of targeted chemical partition to the PM, elevating the total concentrations of DEHP in the air.

The mean (± Standard deviation) concentrations of PAEs and NPPs in haze events and normal weather conditions are shown in Fig. S7A (data taken from living room samples from September 17 to March 18, N = 28). Except for TOTM, the concentrations of target pollutants during haze events were higher than those in normal weather. Significant differences were found for individual PAEs, DIBA, DEHA, DINCH, ∑PAEs, and ∑NPPs ($p < 0.01$ or $p < 0.05$). As shown in Fig. S7B, the average concentrations of PAEs and NPPs in nighttime samples in haze weather were slightly higher than in the daytime, with no significant differences ($p > 0.05$).

4.3. Source apportionments indicate diverse applications of PAEs and NPPs in the

indoor environment

The mean-to-median ratios (MMR) were first utilized to identify the release of indoor species from static sources (< 1.06) or episodic events (> 1.5) (Liu et al. 2019). Table 1 showed that all compounds have MMR above 1.06 for PAEs and NPPs, indicating that these chemicals were subject to influence from both static sources and episodic outdoor sources. Conversely, much higher MMR values were found for less volatile compounds such as DEHP (2.6), ATBC (2.5), DINCH (3.1), DEHT (3.4), and TOTM (2.6), suggesting the importance of outdoor episodic occurrences influencing the levels of these compounds. However, it should be noted that the specific thresholds of MMR suggested by Liu et al. (2019) might not work here. In that study, measurement data were obtained with a 0.5-hour time resolution for 1-2 months. Herein, PAE and NPP data were collected with 48-hour time resolution for a year in this study. The key drivers for the concentration variations in the two data sets are very different, given the differences in the time resolution of the measurement, the time span investigated, and the properties of VOC and SVOCs. Herein, seasonal variation of temperature itself might drive the mean-to-mean ratio of SVOC concentrations greater than 1.06, even if only static emission is considered.

Spearman rank correlation analysis showed significant correlations between similar molecular-weight phthalates and NPPs, indicating similar sources and behavior of these compounds in the indoor environment. The correlations among the individual PAEs were significant, except for low molecular weight (LMW) and HMW compounds (such as

DMP vs. DEHP and DEHP vs. DBP), as demonstrated in Table S10. There was a particularly strong association between PAEs and their substitutes, such as DBP with DNBA (p <0.01) and DEHP with DEHT (p <0.01), suggesting similar usage in commercial products. For example, DNBA is used in a variety of consumer products (e.g., personal care products), partially replacing the endocrine-disrupting DBP (Yang et al. 2020). DEHT has been used as an alternative to DEHP (Schossler et al. 2011).

As discussed above, significant differences in PAE and NPP concentrations were noticed in the three rooms. These differences could be due to the different source and usage patterns in the three rooms. For example, DMP and DEHP are mainly added as plasticizers to PVC products and used in building materials and decoration materials (Bornehag et al. 2005, Schettler 2006) in BR#1. As previously stated, the floor of BR#1 was covered with PVC floor covering, whereas the floor of BR#2 was covered with a baby crawling mat which contained less DMP and DEHP.

The possible sources of PAEs and NPPs in the different rooms were determined using principal component analysis (PCA), as shown in Table S11 and Fig. 4. Four principal components (PC1-PC4) were identified, which account for 80 % of the overall variations. PC1 explained 35% of the total variations, dominated by relatively HMW substances, such as DEHP, DEHA, DEHT, and TOTM. These chemicals have been widely used in various polymers, such as PVC toys, child care products, vinyl floors, wires, heat-resistant PVC medical devices, and PVC plastic (Bornehag et al. 2005, Schettler 2006, Fromme et al. 2016). The score plot (Fig. 4A and 4C) shows that the most outstanding contribution of PC1 occurred for the fall sample, where haze was frequent, and these substances correlated well with TSP. Therefore, PC1 suggests the combinations of indoor sources and the impacts of outdoor sources.

PC2 explained 25% of the total variation, dominated by high loadings of DMP, DBP, and DIBA. In addition to being used as plasticizers, DMP, DiBP, and DBP can also be used in solvents, adhesives, waxes, inks, cosmetics, insecticides, and pharmaceuticals to increase the flexibility of plastic products (Bornehag et al. 2005). The most outstanding contribution of PC2 mainly occurred in BR#1 from the spring, summer, and autumn (Fig. 4A and 4C), suggesting that the source presumably was the adhesive of the floor covering in BR#1.

PC3 explained 10% of total variations, with the loadings dominated by DEP and DNBA. Most of the main contributions came from the spring and summer samples in BR 2 (Fig. 4B and 4D). DEP and DBP are commonly used in personal care products (Schossler et al. 2011), and waxes and adhesives increase the flexibility of plastic products (Bornehag et al. 2005), while DNBA is a DBP replacement. The test home, however, was unoccupied. Thus, it was assumed that the source was waxed in the baby crawling mat and toys in BR#2.

PC4 explained 10% of the total variation, dominated by ATBC (0.82) and DINCH (0.84), the main contribution samples from three rooms except for the winter (Fig. 4B and 4D). Based on the applications of ATBC and DINCH mentioned above, it is assumed that the source represented by PC4 was baby toys. ATBC is often added to cosmetics and medical products. ATBC can also be added as a plasticizer to replace PAEs in children's products; DINCH is an alternative plasticizer for DEHP that is widely used in medical devices, toys, and food packaging materials (Silva et al., 2013).

4.4. Implications for Human Exposure

The methods for estimating human exposure are given in S1.1. For five distinct age groups, the daily intake of PAEs and NPPs in the test home was estimated, and the results are listed in Table S12. Inhalation exposure of PAEs was 1200 ng/kg_BW/day in infants, 950 ng/kg_BW/day in toddlers, 7502 ng/kg_BW/day in children, 540 ng/kg_BW/day in teenagers, and 470 ng/kg_BW/day in adults. The five different groups for NPPs were 541, 43, 34, 24, and 21 ng/kg_BW/day, in that order. DMP and DIBA were mostly responsible for PAEs and NPPs inhalation exposure, respectively. This investigation found that inhalation exposure to PAEs and NPPs was higher than that reported in Guangzhou, South China (Tang et al. 2020). However, children's exposure to NPPs through inhalation was lower than in a previous study (Fromme et al. 2016).

PAEs dermal uptake exposure was 11300, 1100, 920, 780, and 610 ng/kg_BW/day for infants, toddlers, children, teenagers, and adults, respectively. For NPPs, the values were 19 ng/kg_BW/day in infants, 17 ng/kg_BW/day in toddlers, 14 ng/kg_BW/day in children, 12 ng/kg_BW/day in teenagers, and 9.4 ng/kg_BW/day in adults. DMP and DNBA were mostly responsible for PAEs and NPPs dermal exposure, respectively. The amount of dermal exposure to PAEs in this study was comparable to that reported by (Giovanoulis et al. 2018). Other than DINCH, no data on indoor air exposure via dermal exposure exists for the other NPPs.

Dermal uptake to inhalation intake is the two major pathway for PAEs exposure through indoor air. The ratio of dermal uptake to inhalation intake (D/I) ranged from 0.32 to 2.4 for PAEs and from 0.02 to 2.2 for NPPs (Table S13). The dermal uptake for LMW compounds, e.g., DMP, DEP, and DNBA, directly from indoor air was more significant than the inhalation intake, with the D/I values of 1.7-2.3, 1.5-2.3, and 1.6-2.2, respectively. Weschler and Nazaroff (2014) reported the dermal uptake of eighty organic compounds, including lower mass PAEs, was similar to or even greater than that of inhalation intake from indoor air (Weschler and Nazaroff 2014).

Fig. S8 depicts the total hazard index (*HI*) and carcinogenic risk (*CR*) values for five age groups. The value of total *HI* was 0.012 in infants, 0.016 in toddlers, 0.013 in children, 0.010 in teenagers, and 0.0084 in adults. These values are less than 1, indicating low health risks (Fig. S8A). The *HQ* through inhalation of the air was 1.2×10^{-7} to 0.0059 and 9.7×10^{-8} to 0.0026 for PAEs and NPPs, respectively. Concerning the five age groups, the infant group faced the highest risk through inhalation (HI = 0.012), and the toddler group faced the highest risk through dermal uptake (HI = 0.0070). One case of cancer incidence per million persons is considered an acceptable level of risk; hence CR $>10^{-6}$ indicates a potential high cancer risk (Maertens et al. 2008). As illustrated in Fig. S8B, more than 50% of the CR values for the infant and toddler age groups were greater than 10^{-6}. For the remaining three age groups, more than 25% of the CR values were greater than 10^{-6}. The median values of CR were 1.8×10^{-6} for infants, 1.1×10^{-6} for toddlers,

8.6×10^{-7} for children, 6.9×10^{-7} for teenage, and 5.6×10^{-7} for adults. This finding raises concerns about potential carcinogenicity for the five age groups.

5. Conclusion

This work presented comprehensive investigations on the over one-year trends of PAEs and alternative NPPs in a typical indoor residence in Harbin, China. High detection rates of NPPs suggest that new plasticizers are gradually introduced to the market, although their concentrations in this study were still lower than that of PAEs, indicating that PAEs are still the dominating currently-used plasticizers in the studied residence. Significant seasonal variations were found for most PAEs and NPPs, suggesting that the emissions of these plasticizers were influenced by seasonal fluctuations in environmental parameters. The temperature dependences of the PAE and NPP concentrations were diminishing with increasing molecular weights and decreasing vapor pressures. Individual PAE and NPP concentrations were positively affected by humidity in the indoor environment. TSP significantly affects the levels of target compounds with low vapor pressures in all types of samples. It is worth mentioning that the highest PAE and NPP concentrations were noted in autumn, when the haze started to occur in Northeast China, indicating that biomass/coal burning had significant impacts on indoor air quality. PCA was used to investigate the potential sources of PAEs and NPPs, suggesting the possible sources from the decoration materials and children's toys. Inhalation exposure is higher than dermal exposure for PAEs and NPPs, except for the LMW and high vapor pressure compounds. The *CR* values exceeded acceptable levels

(10^{-6}), raising concerns about the possibility of carcinogenicity.

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. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016.

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TABLES AND FIGURES

Table 1. Statistics summary on the PAEs and NPPs concentrations in air samples (gas phase plus particle phase, ng/m^3) from the three rooms.

	Mean	SD	Min	Max	Median	5th	95th	%Det	MMR
DMP	860	710	BDL	3100	710	130	2200	99	1.2
DEP	84	95	3.2	650	50	6.7	230	100	1.7
DBP	510	390	78	2600	390	150	1100	100	1.3
DiBP	830	650	120	4300	650	250	1700	100	1.3
BBP	0.31	0.70	BDL	6.8	0.19	BDL	0.84	87	1.6
DEHP	340	580	BDL	3200	130	22	1200	97	2.6
DOP	0.13	0.57	BDL	3.9	BDL	BDL	0.12	26	NA
ΣPAEs	2600	1800	400	11000	2200	800	6200	100	1.2
DIBA	40	38	BDL	200	28	6.6	120	99	1.4
DNBA	11	11	0.05	72	8.5	2.6	28	100	1.3
ATBC	10	16	BDL	96	3.8	BDL	34	85	2.5
DEHA	18	28	0.47	220	10	1.6	65	100	1.9
DINA	0.98	5.0	BDL	48	BDL	BDL	4.6	23	NA
DINCH	19	29	BDL	150	6.0	BDL	93	83	3.1
DEHT	58	220	BDL	1700	17	BDL	140	92	3.4
TOTM	0.19	0.31	BDL	2.2	0.07	BDL	0.74	87	2.6
ΣNPPs	180	320	18	2200	97	32	380	100	1.6

MMR: mean-to-median ratio

BDL: below detection limit

NA: not available

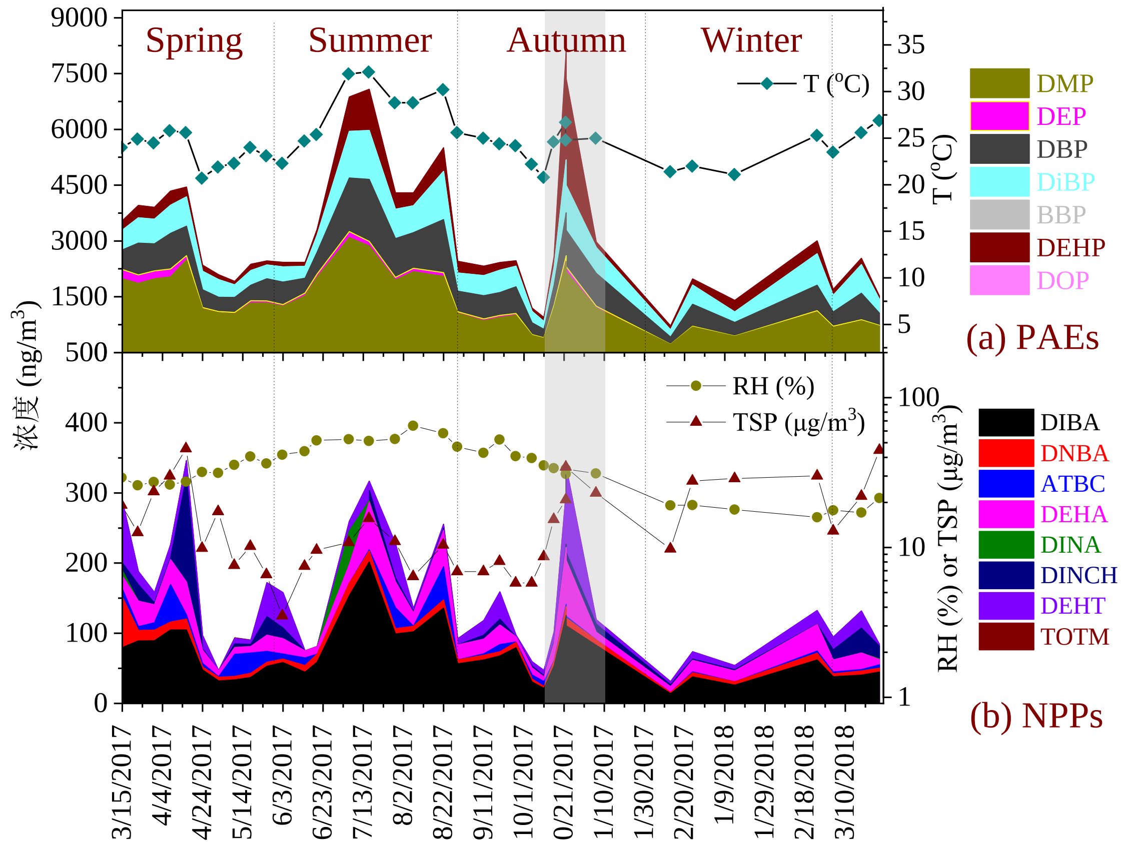

Fig. 1. Time series of PAE and NPP concentrations and interior temperature in four seasons in BR#1 (Haze season on gray background).

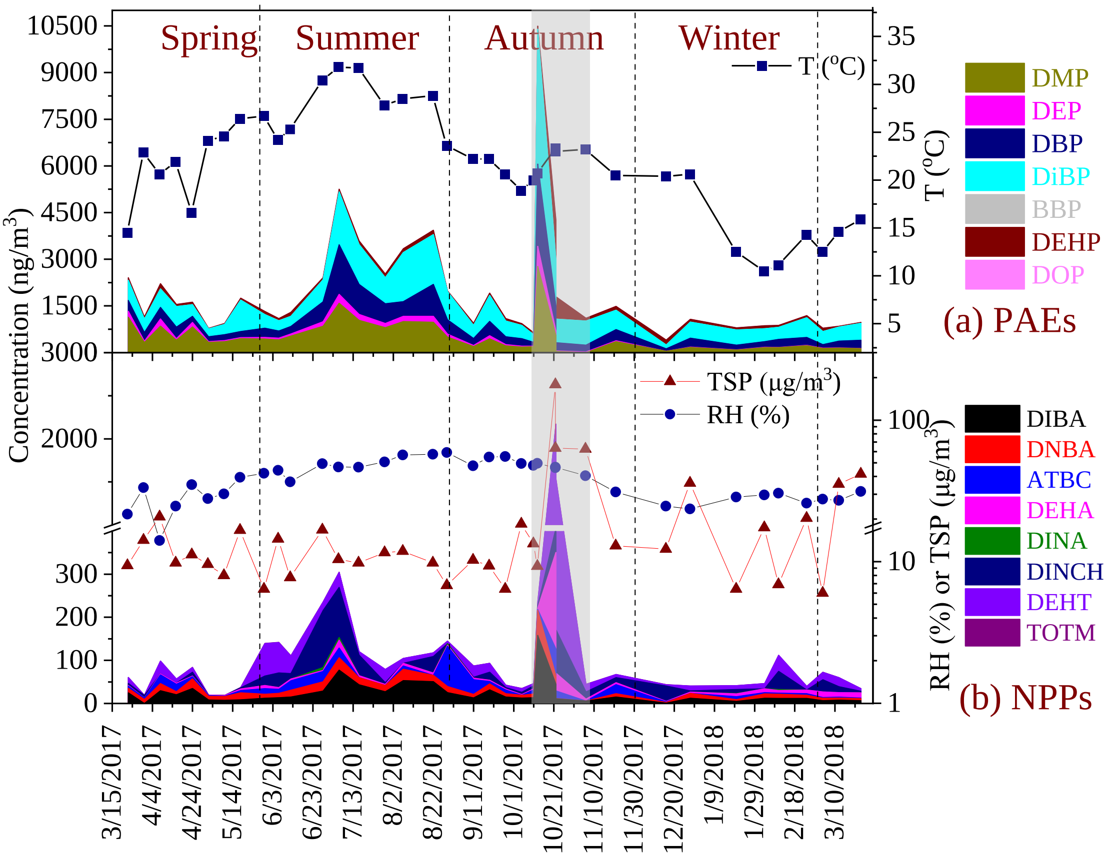

Fig. 2. Time series of PAE and NPP concentrations and interior temperature in four seasons in BR#2 (Haze season on gray background).

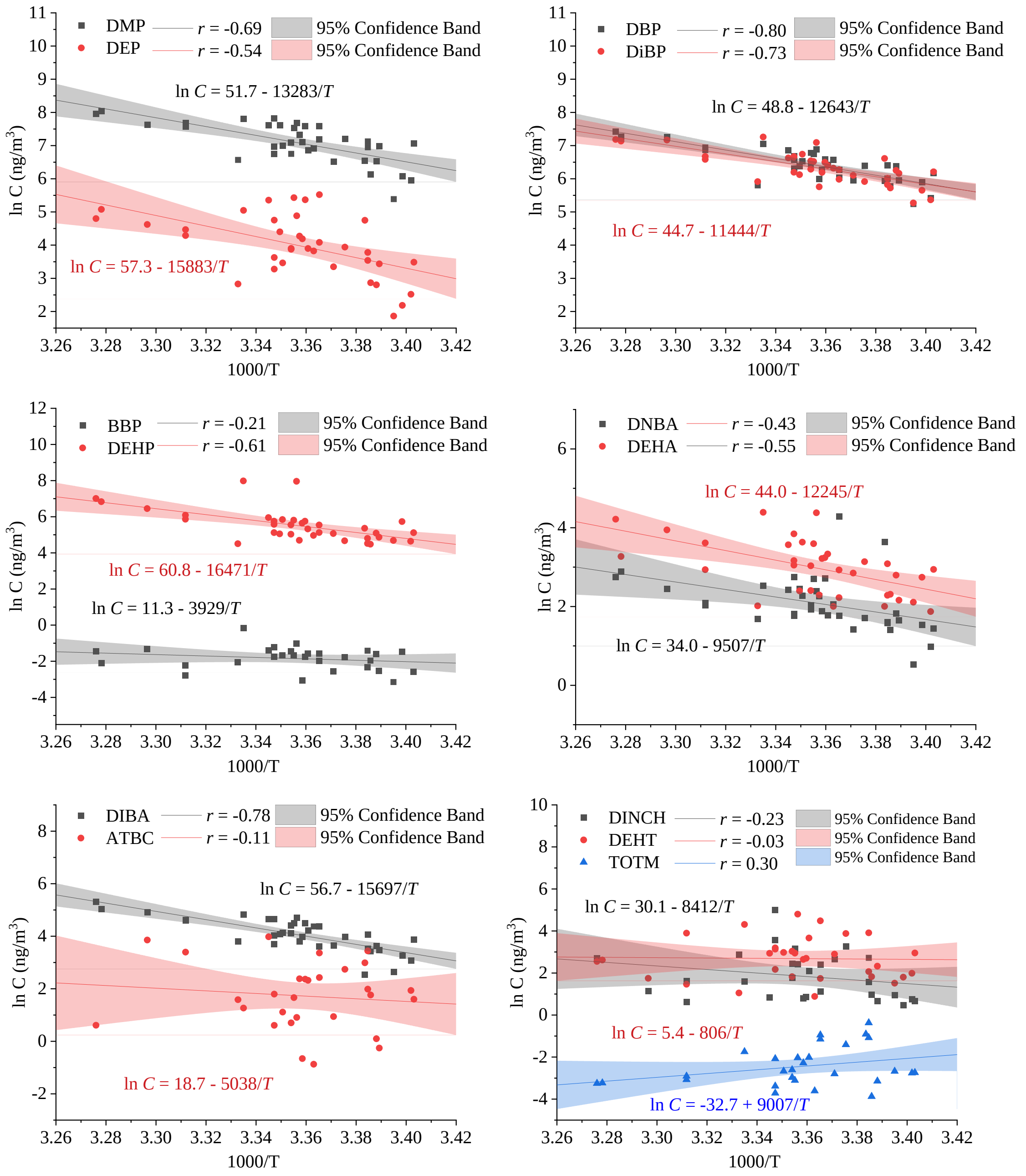

Fig. 3. Plotting the natural logarithm concentrations (ln C, in ng/m^3) of PAEs and NPPs versus indoor temperatures (T, in K) in BR#1.

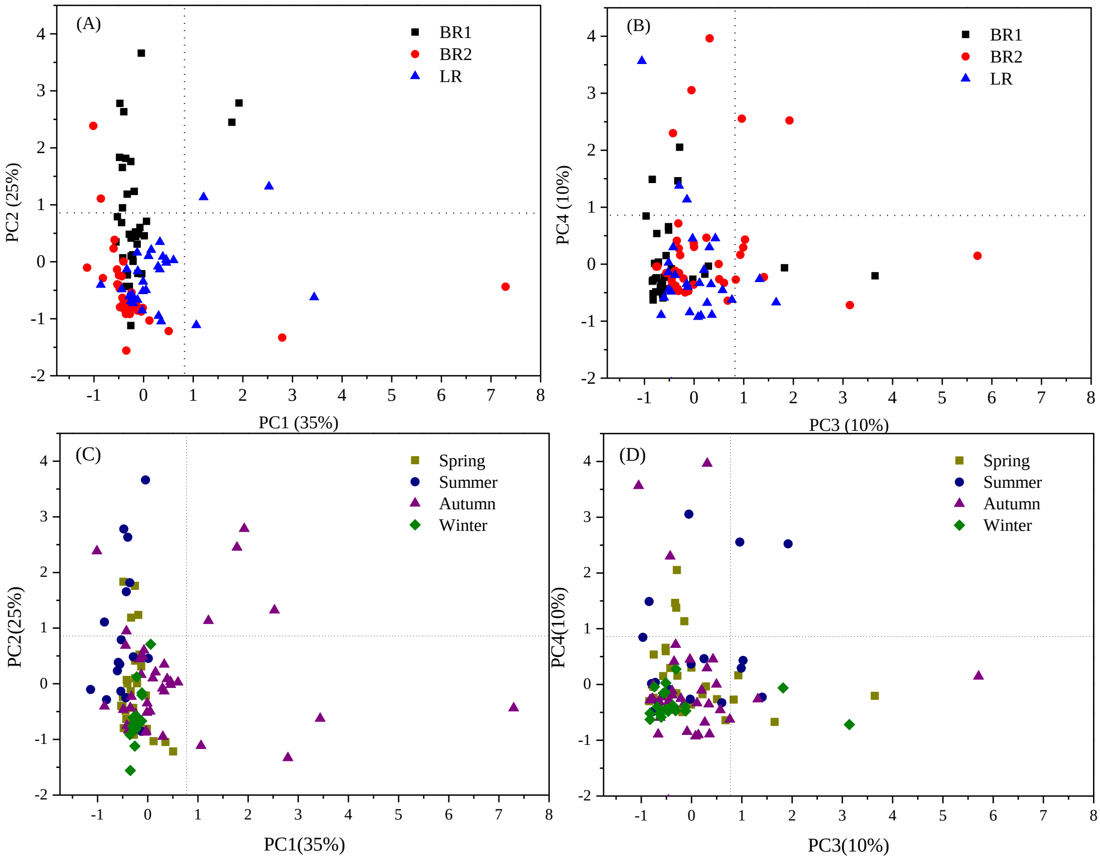

Fig. 4. The score plots of PCA for PAEs and NPPs in different rooms (A, B) and four seasons (C, D).