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Characteristics of Tris(chloropropyl)phosphate (TCPP) emission from upholstered furniture in offices and consequence on indoor air quality

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ABSTRACT

Tris (chloropropyl)phosphate (TCPP) is a flame retardant currently used in upholstered furniture. This study provides the results of a follow up of TCPP concentrations in indoor air and at the surface of indoor materials in two offices after introduction of fireproof upholstered furniture (cushions made of PU foam containing TCPP). An emission cell coupled to solid-phase microextraction sampling was used as measurement means for direct measurement of gaseous TCPP concentration at the surface of the source material. Indoor TCPP concentrations reached high levels from 400 to 880 ng m⁻³ in correlation with gaseous concentrations measured at the surface of source materials (cushions) ranging from 5.5 to 17.7 µg m⁻³. The changes in these concentrations showed no decline over more than 220 days and were mainly explained by temperature influence on emission. By applying the Clausius-Clapeyron equation, it was shown that the emission is close to vaporization of pure liquid TCPP. A model taking into account only the processes of emission/diffusion of compound in air and its removal by ventilation provided an acceptable prediction. Exposure by inhalation of occupants to TCPP in two offices were assessed to be 2933 ng.day⁻¹ (with median level) and 4692 ng.day⁻¹ (with maximum level).

Keywords:

Fireproofed material emission

Organophosphate flame retardants

Polyurethane foams

Emission cell

SPME

1. Introduction

Tris (chloropropyl)phosphate (TCPP) (CAS n°13674-84-5) is a chlorinated organophosphate ester mainly used as flame retardant in flexible Polyurethane (PUR) foams in articles such as mattresses, car seats, and residential upholstered furniture [1]. It is part of organophosphate flame retardants (OPFRs). Since the 1990s, OPFRs have gradually replaced in many products the bromine-based flame retardants which have been banned worldwide because of their environmental persistence, biotoxicity, bioaccumulation and migration characteristics [2]. The total consumption of organophosphate flame retardants (OPFRs) worldwide account for 16% of the global market share in 2019 [3,4]. It has increased from 100,000 tons to 500,000 tons from 1992 to 2011 and reached 680,000 tons in 2015 [2].

Over 40,000 tons of TCPP were consumed in the EU in the year 2000. Most TCPP (over 98%) is used as a flame retardant in the production of PUR for use in construction and furniture [1].

Many studies revealed that due to their widespread use, OPFRs were

found in a variety of environmental matrices, including dust [5], sediments [6], soil [7], indoor environments [8,9], ocean surface water [10], surface water [2], and various biological samples [11–13]. Almost all of the OPFRs produced in the past decade were also detected in human samples. OPFRs were detected in human placenta in Eastern China with Tri (2-chloroethyl) phosphate (TCEP) as the most abundant [14]. This shows that OPFRs have capabilities of migration, persistence and biological enrichment. Among OPFRs, TCPP is considered as an emerging pollutant in indoor air due to potential sources such as insulation foams, upholstered furniture, mattresses and baby accessories [1]. Based on the recent toxicity studies, TCPP may impact nervous system development as well as thyroid hormone levels [1]. Carcinogenicity testing has not been completed on TCPP, but its molecular similarity to the cancer-causing chlorinated organophosphate esters like TCEP raises concerns of similar toxicity and there is evidence of reproductive and developmental toxicity [15].

Since TCPP is mainly used as an additive chemical, it is not chemically bound to PUR foams, and can therefore migrate into the

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environment by means of volatilization, leaching, and abrasion and direct transfer to dust [16–18]. People can be exposed to TCPP via multiple pathways (ingestion, inhalation and dermal contact). Due to the low volatility of OPFRs, the screening assessment has primarily focused on the exposure from mouthing and dermal contact [1]. A high risk for carcinogenicity and reproductive effects was identified for baby mattresses with OPFRs including TCPP, which was explained by a large contact surface area and a long contact duration [1]. However, a recent study based on exposure assessed using active personal air samplers [16] concluded that in the case of TCPP, inhalation may be more important than previously hypothesized. Exposure via inhalation for TCPP was estimated at $4540 \text{ ng}\cdot\text{day}^{-1}$ i.e. up to 30 times higher than that from dust ingestion, which was previously considered as the most important exposure route. In comparison, Allen et al. [19] estimated inhalation for Decabromodiphenyl ether (BDE-209) at $5.6 \text{ ng}\cdot\text{day}^{-1}$, a rate from 1.6 to 39 times lower than dust ingestion. For the risk assessment of human exposure to TCPP, a better knowledge about indoor emission characteristics and indoor levels is still required.

Previous studies identified TCPP as one of the most abundant OPFRs indoors with airborne concentrations from 1 to 500 ng m^{-3} in Germany [20], from 0.4 to 730 ng m^{-3} in Sweden [21] and from 140 to 1400 ng m^{-3} in the United States [22]. Public buildings (offices, schools, etc.) tended to have higher levels of TCPP than domestic buildings [15,21] and TCPP was mainly found in the gas phase and in suspended particles and very few in settled dust [21].

A description of the emission characteristics of OPFR sources is needed for predicting indoor concentrations, assessing occupant exposure to OPFRs and exploring effective control means for OPFR indoor pollution. As shown by Xu and Little [23], the gas-phase concentration in equilibrium with the source material (y_0 , $\mu\text{g}\cdot\text{m}^{-3}$) is the relevant emission parameter in the case of Semi-Volatile Organic Compounds (SVOCs) like TCPP. The traditional way to determine y_0 is to deduct it from the steady-state gaseous concentration reached in a ventilated emission chamber containing the source material [24]. This approach requires very long times (several days or even several months) due to the slow-release of SVOCs from materials [25] and the estimation of convective mass transfer coefficient which is a source of uncertainty [24]. Recent methods based on solid-phase microextraction (SPME) coupled to closed devices like an emission cell [26], a sandwich-like chamber [24] or a sealed chamber [6] give a direct measurement of y_0 (assimilated to the steady SVOC concentration in the device air) and reduce the test time to less than one day. Although some of these SPME-based closed device methods enable on-site measurement of y_0 in real conditions, the studies were limited to a few SVOC/material couples tested in laboratory [6,24]. To the best of our knowledge, a compared description of temporal dynamics of y_0 and indoor concentration for SVOCs has not yet been presented.

An SPME based method using a glass cell called MOSEC was developed in our laboratory [26,27]. This work is the first application of this SPME based-MOSEC cell method for on-site measurement of y_0 of source material in indoor environments.

The objectives of this study are therefore: (1) to analyze the temporal dynamics and relationships between y_0 and indoor concentration for TCPP after introduction of source material in two rooms, (2) to identify the environmental conditions favoring the release of TCPP from material and the increase in concentration, (3) to develop a better understanding of how the SPME based-MOSEC cell method can be used to predict indoor concentration, and (4) to assess the inhalation exposure of occupants to TCPP.

2. Materials and methods

2.1. Source material

The chair cushions used as source materials are made of a CMHR (combustion modified high resilient) PUR foam covered with a polyester

fabric. Only the PUR foam contains TCPP as flame retardant with 2% mass fraction. The manufacturing method of PUR foam followed a current procedure by polymerization of a polyol mixture with isocyanate and addition of flame retardant in the reactant mixture during polymerization phase. This PUR foam has a density of 35 kg m^{-3} . Pieces of $45 \times 30 \text{ cm}$ (for seat) and $45 \times 45 \text{ cm}$ (for back) with a thickness of 8 cm were cut and placed in the polyester cushion covers. The cushions placed in one of the field experiment rooms (described below in section 2.4) were subject to an accelerated mechanical ageing process according to NF EN 1728 standard [28].

The ageing process consisted of applying a weight corresponding to 1000 N on the cushion of chair seat and to 300 N on the cushion of chair back repeated 50,000 times with an applying time of 2s. This fatigue test simulates to get in and out of the chair for an adult.

The cushions were then wrapped in aluminum foil and stored at room temperature prior to the field experiments.

2.2. Passive sampling method for measuring TCPP gas-phase concentrations at the material surface

The passive sampling device used for the determination of gaseous SVOC concentration at the material surface was already described in previous articles [26,27]. It consists of a home-made emission glass cell (named MOSEC) of 60 mL covering a sampling area of 17 cm^2 . The top of the cell has a cap with a septum for SPME fiber introduction. First of all, the emission cell is placed directly on material surface (Fig. 1a), the SVOCs released from the material diffuse inside the air volume of cell and are partially sorbed onto the cell walls. When the gaseous concentration is stable in the cell, the mass transfers from the source material to air and from air to the cell walls become zero. Previous studies [26,29] showed that this steady state for TCPP emitted from PUR foams can reach up to 16 h after placing the MOSEC cell on the material surface. The gaseous concentration is then measured from the sampling of a $100 \mu\text{m}$ PDMS SPME fiber in the linear sorption conditions (Fig. 1b). Previous works [26] showed that this gaseous TCPP concentration can be assimilated to y_0 . Analysis of SPME fibres is carried out with a gas chromatograph equipped with dual MS/FID detection. Analytical conditions, method performance characteristics and the external calibration mode used were given in detail by Plaisance et al. [27]. The limits of detection and quantification were assessed to 0.6 and $1.9 \mu\text{g m}^{-3}$ for 15 min extraction. Reproducibility was evaluated to 9.3% (RSD) from a series of ten

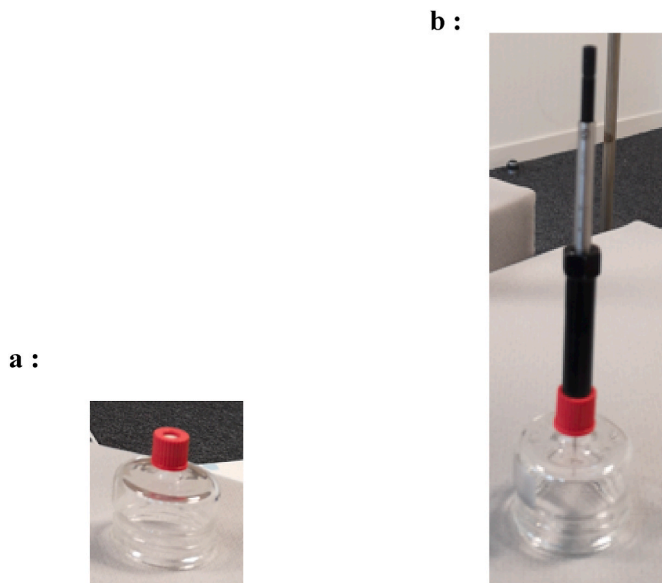


Fig. 1. Pictures showing the emission cell placed on the material source of TCPP before sampling (a) and during sampling by SPME in the cell (b).

replicate measurements made on a PUR foam containing TCPP for a mean y_0 value of $29.6 \mu\text{g m}^{-3}$ [27]. Reproducibility was also tested for the cushioning material used as source of TCPP in this study (described in 2.1 section). A RSD of 10.8% for a mean y_0 value of $3.4 \mu\text{g m}^{-3}$ was obtained from six replicate samplings at the surface of the cushioning material under laboratory conditions.

2.3. Active sampling method for measuring gaseous concentration of TCPP

Airborne TCPP was collected by continuously pumping air through a URG personal pesticide sampler (University Research Glassware, Chapel Hill, NC) made of two parts: a 76-mm polyurethane foam (PUF) (SKC, Eighty Four, PA, USA) to sample gas phase and a 25-mm quartz fiber filter (QFF) (Whatman, Maidstone, Kent) fitted in front of the PUF to sample particulate phase. URG samplers used a size-selective impactor inlet with an average particle size cut point of $10 \mu\text{m}$. The air was pumped through the device using a GilAir-5 pump (Sensidyne, St. Petersburg, FL, USA) for 4.5 days at $2 \text{ L}\cdot\text{min}^{-1}$ corresponding to a sampled air volume of about 13 m^3 . One field blank was included for each set of sampling. More details about the preparation and storage of sampling media were given by Raffy et al. [30].

TCPP was extracted from PUF and QFF together by adding dichloromethane and using a pressurized liquid extractor (PLE) ASE (Accelerated Solvent Extractor) 350 (Thermo Fisher Scientific, Waltham, MA USA, USA). Organic extracts were then concentrated to 0.5 mL at $30 \text{ }^\circ\text{C}$ under a nitrogen stream and stored at $-18 \text{ }^\circ\text{C}$ prior to analysis. GC/MS/MS analyses were performed on a 7890B GC System gas chromatograph coupled to a 7010B Triple Quad mass spectrometer (Agilent technologies) operating in electron impact ionization (EI) mode (70 eV). Sample extraction and analytical method were adapted from the author's previous work [30,31]. For a sampled air volume of 13 m^3 , the limit of quantification is 0.8 ng m^{-3} and the precision of the method 5.4% (RSD calculated from the analysis of five sampling media spiked with a standard solution).

2.4. Description of sampled rooms and sampling design

Field measurements were carried out from October 2019 to August 2020 in two unoccupied offices located on the ground floor of the same building. The two rooms are of similar configuration and size with a volume of 30.3 m^3 , a large bay window, and a door made of particle-board leading out into a same corridor. The office floors are covered with carpet, the walls are plasterboard covered with painted fibre cloth and the ceiling is made of suspended plasterboard tiles. The building is equipped with a central heating and ventilation system. Air intake and

- In the two PUR rooms, temperature, relative humidity and CO_2 concentration were continuously monitored and recorded using a multi-function probe (Testo 480 n°0632 1543, Testo, Forbach, France) for the whole experimental period.
- The air exchange rate (AER) was determined by injecting CO_2 in the room and following its decay according to the method previously described by Plaisance et al. [32]. As AER can change in time, the test was regularly repeated (6 times) in the two rooms for the field campaign.
- The active sampling using URG cartridge for 4.5 days were monthly performed in the two offices to measure airborne concentration of TCPP. The sampling point was chosen at the middle of the room at the height of 1.2 m. It corresponds to the height of the respiratory tract of a person sitting on one of the chairs. The shorter distance between the sampling point and the cushions (the source materials) was 0.6 m. In each room, one air sample was carried out before introduction of cushions.
- Eight measurements of TCPP concentrations at the indoor surfaces were carried out using SPME based-MOSEC cell method in the two rooms: four at the surface of cushions (TCPP source), one at the ceiling, one at the floor, one at the walls and one at the bay window. These samples were carried out monthly, the day before the beginning of air sampling in the room B9 (containing aged materials) and the day after the end of air sampling in the room B10 (containing new materials).

The instruments set up for the experiments in the rooms and their location are shown in Fig. 2.

The sampling period was spread over 274 days (from April 10, 2019 to 08/31/2020) in the room B10 and 226 days (from 11/22/2019 to 08/31/2020) in the room B9. The cushions (TCPP source) were introduced in the room B10 on 11/18/2019 and in the room B9 on September 12, 2019.

2.5. One-compartment mass balance model

The simple one-box model (or single zone model) describes the change in TCPP indoor concentration in a well-mixed room as a differential equation, in which production processes add to the concentration with time and loss processes subtract from the concentration with time. Variants of the model differ in terms of production and loss processes that are considered. Many studies have focused on the chemical reactivity of indoor pollutants, based on data from tropospheric chemistry [33–35] or on the sorption of VOCs on building materials [36,37]. Here, the objective is to assess the potential of on-site measurements obtained with SPME based-MOSEC cell method to predict the TCPP indoor con-

$$\frac{dy}{dt} = \underbrace{\frac{h_{m0}A_0}{V} (y_0 - y)}_{\text{Source term}} - \underbrace{ay}_{\text{Removal term}} \quad [1]$$

centration. So, the modeling used is deliberately simplified. Only processes of emission/diffusion of compound in air (transfer from the source material to air) and its removal by ventilation are taken into account. The model assumes that the concentration of compound in air (y) is homogeneous in the room volume (V) and subjected to an air exchange rate (a). We consider that there is a boundary layer between the surface of the source material (A_0) and air with an associated convective transfer coefficient (h_{m0}). The variation in the concentration in the room is described by the following equation:

exhaust located to the ceiling of each room provide a continuous air circulation in the rooms. On the control unit, the heating and ventilation system was kept in normal operation during the whole experimental period.

Two metal chairs with cushions made of the TCPP treated PUR foam and fabric were introduced in the center of the two rooms. The cushions of the first room (called B9) have previously undergone mechanical aging, whereas those of the second room (called B10) are new.

The sampling design applied for the field campaign in the two rooms was as follows:

centration. So, the modeling used is deliberately simplified. Only processes of emission/diffusion of compound in air (transfer from the source material to air) and its removal by ventilation are taken into account. The model assumes that the concentration of compound in air (y) is homogeneous in the room volume (V) and subjected to an air exchange rate (a). We consider that there is a boundary layer between the surface of the source material (A_0) and air with an associated convective transfer coefficient (h_{m0}). The variation in the concentration in the room is described by the following equation:

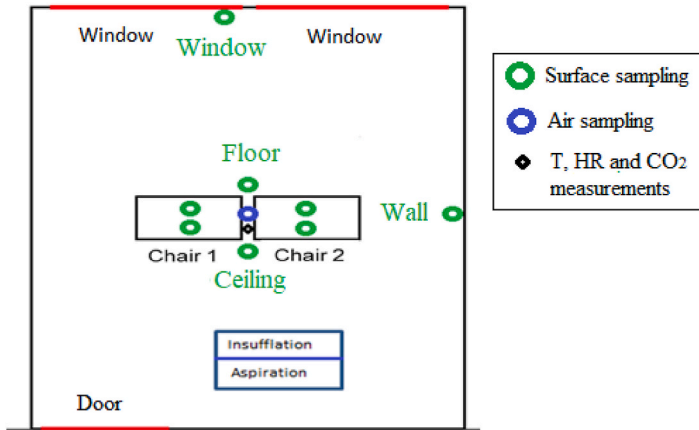
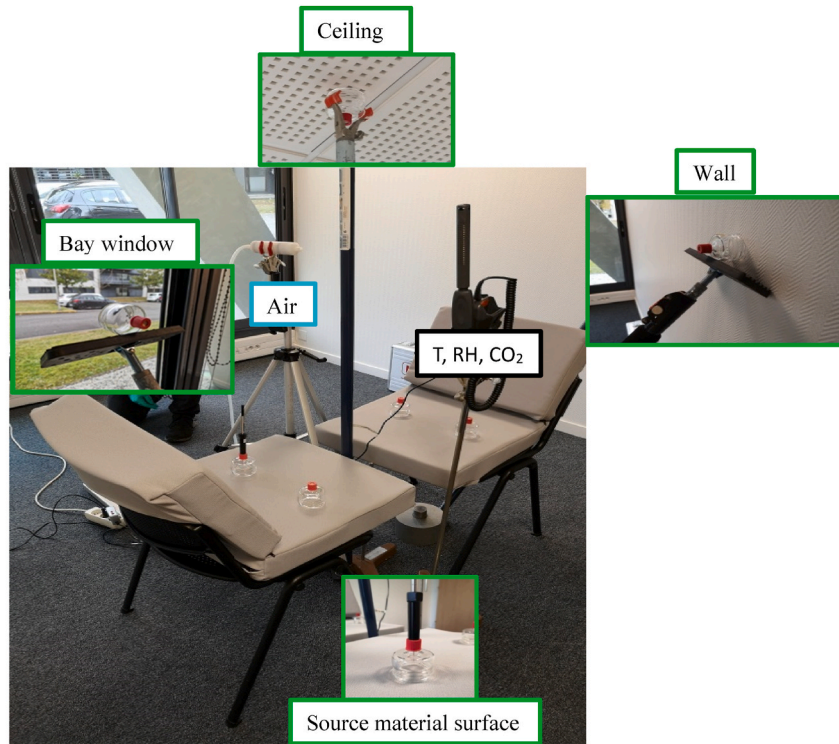


Fig. 2. Sampling design and instrumentation used in the two rooms.

Under steady state conditions ($\frac{dy}{dt} = 0$), equation (1) becomes as

$$y = y_0 / \left(1 + \frac{aV}{h_{m0}A_0} \right) \quad (2)$$

The terms of equation (2) were directly measured or estimated.

V : the volume of two rooms is 30.3 m^3 ,

A_0 : the apparent surface of the source material was assessed to 1.86 m^2 ,

a : The mean of the air exchange rates measured during the sampling period was 1.13 h^{-1} for the room B10 and 1.01 h^{-1} for the room B9,
 y_0 : The mean of the gaseous TCPP concentrations at the source material surface for each sampling series (ranging from 5.5 to $11.4 \mu\text{g m}^{-3}$ in the room B10 and from 5.8 to $17.7 \mu\text{g.m}^{-3}$ in the room B9 as reported in section 3.2).

h_{m0} : the convective transfer coefficient was determined based on the repeated measurements of air velocity made at 2 cm above the surface of the source material using an anemometric probe (Testo 480

n°0635 1050, Testo, Forbach, France) giving 0.07 m s^{-1} in average, the diffusion coefficient of TCPP ($4.37 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$) given by Isetun et al. [38] and applying Fick's first law and the calculation of Reynolds, Schmidt and Sherwood numbers as described in the PARAMS program of the US EPA [39]. h_{m0} varies from 0.95 to 0.98 m h^{-1} depending on the conditions for sampling.

3. Results and discussion

3.1. Ambient conditions in the two rooms

The air exchange rates with windows and door closed were regularly determined in Room B9 and Room B10 during the experimental period. In all cases, the CO_2 time vs. concentration curves followed a single exponential law. As shown in Fig. 3, AER varied with no apparent trend from 0.94 to 1.08 h^{-1} for Room B9 and from 0.93 to 1.34 h^{-1} for Room B10. The two rooms have similar conditions of ventilation with an average AER of 1.01 h^{-1} for Room B9 and of 1.13 h^{-1} for Room B10 during the experimental phase. The profiles for temperature and relative

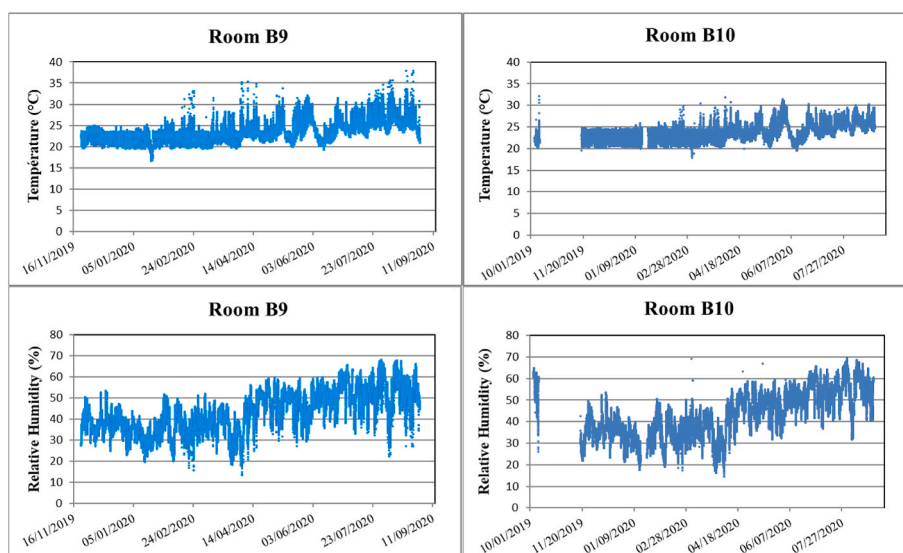
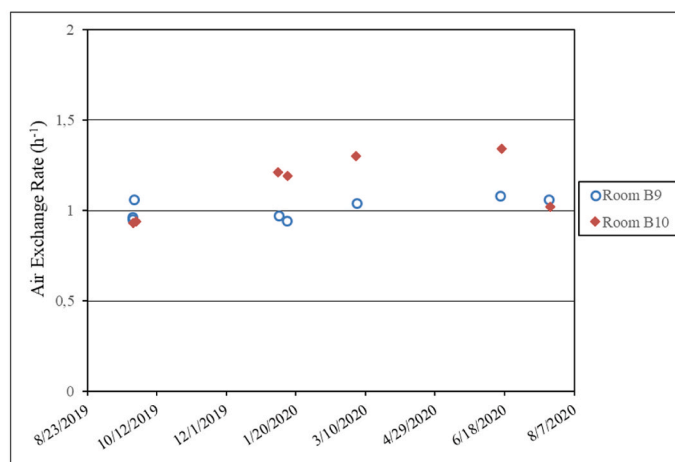


Fig. 3. Air exchange rate, temperature and humidity profiles in the two rooms during the whole of experimental periods. Temperature, relative humidity are 10-min average values and air exchange rates are individual values obtained from tests based on of the injection of CO₂ in the room and follow-up of its decay (Plaisance et al., 2013).

humidity are shown as average 10-min values in Fig. 3. Although both rooms have a heating and ventilation control system, a regular temperature rise was observed from winter period (start of experiment) to summer period (end of experiment). Over the experimental period, temperature in the Room B9 varied between 16.6 and 37.8 °C, with an average value of 22.7 °C, and in the Room B10 between 17.9 and 32.1 °C, with an average value of 23.4 °C. Both rooms face west and are subject to significant solar radiation in the late afternoon (from 17 to 20

h GMT) which led to an increase in temperature. This effect is more pronounced in room B9 where the temperature frequently exceeded 30 °C and more occasionally 35 °C. The average relative humidity was 41.7% (Room B9) and 40.2% (Room B10).

As for temperature, there is an upward trend in relative humidity during the summer period (Fig. 3).

3.2. Changes in TCPP concentrations at the source material surface and in the air of rooms and influence of ambient conditions

The concentrations measured in the two rooms are summarized in Table 1 and their changes over time are shown in Fig. 4. The introduction of cushioning materials in the rooms caused a rapid increase in indoor TCPP concentrations in three days. They rose from 3 to 4 ng m⁻³ in the absence of source materials to more than 400 ng m⁻³ three days after the date of introduction. Then, they ranged from 400 to 880 ng m⁻³ with maxima between May–August during the warmest period of the year. For such a small amount of source material (volume of 0.052 m³) introduced in a room of 30 m³, the 100 to 300-fold increase in airborne TCPP concentrations shows that the transfer rate of this compound from the material to the air is high.

The indoor concentrations measured in the two rooms are close suggesting that the aged materials introduced in the room B9 have an impact on indoor air quality equivalent to that of the new materials in

Table 1

Summary of airborne concentration and y₀ at the surface of cushions found in the two rooms.

	Airborne concentration (ng. m ⁻³) without source material	Airborne concentration (ng. m ⁻³) with source material Average [min_max]	Mean y ₀ values of each series (μg.m ⁻³) Total average [min_max]
Room B9 (containing aged materials)	3.5	604 [450_740] n = 5	10.8 [5.8_17.7] n = 31 for 8 series
Room B10 (containing new materials)	3.8	579 [400_880] n = 7	8.7 [5.5_11.4] n = 32 for 8 series

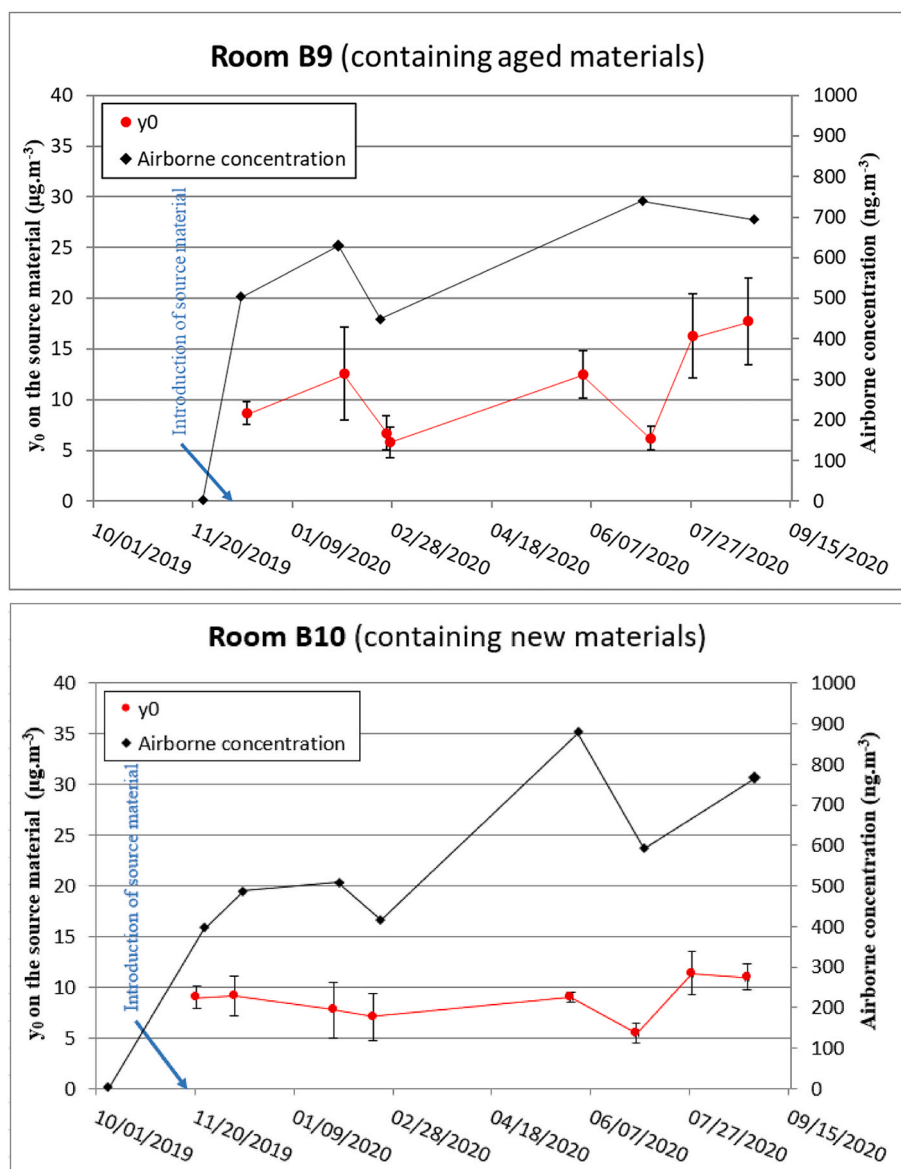


Fig. 4. Changes over time in TCPP concentrations at the source material surface and in the air of two rooms. Error bars indicate ± 1 standard deviation.

the room B10. This concentration range is consistent with the highest levels of TCPP found in offices in many European countries [20]. Airborne concentrations of TCPP in offices were reported in Germany ($n = 11$, range = 4.497 ng m^{-3} , median = 34 ng m^{-3}) by Zhou et al. [20], in Sweden ($n = 10$, range = 91.850 ng m^{-3}) by Björklund et al. [40], in Switzerland ($n = 4$, range = n.d. 130 ng m^{-3}) by Hartmann et al. [41] and in Finland ($n = 4$, median = 20 ng m^{-3}) by Mäkinen et al. [42].

The TCPP concentrations at the surface of cushions (y_0) follows the overall trend observed in indoor concentrations with fairly stable values around $5\text{--}12 \text{ } \mu\text{g m}^{-3}$ in the first seven months of experimental period and rising levels in the hottest months (July–August) (Fig. 4). A higher magnitude of concentrations at the surface of cushions in room B9 was recorded. This may be due to the impact of daytime peak temperatures occurring more frequently in room B9 (see Fig. 3). In contrast to the emissions of volatile organic compounds from indoor materials, no decay in the TCPP emission over time was observed. The y_0 concentrations measured at the surface of cushions are comparable to values reported in recent studies for PUR foams containing TCPP from 8 to $16 \text{ } \mu\text{g m}^{-3}$ using a sandwich cell for a PUR foam containing TCPP in 0.697% mass fraction [24] and $29.6 \text{ } \mu\text{g m}^{-3}$ with MOSEC cell for a PUR foam containing TCPP in 7.6% mass fraction [27].

For the other surfaces (floor, ceiling, walls and bay window) sampled with MOSEC cell, no measurement exceeded the limit of quantification ($1.9 \text{ } \mu\text{g m}^{-3}$ for 15 min extraction), revealing no quantifiable amount of TCPP deposited on the indoor surfaces. This result depends on the limitation of method in terms of quantification and the duration of experiments, which may be too short to highlight these loss processes.

Liang et al. [43] examined the relationship between the ratio of y_0 and saturated vapor pressure concentration (V_p , $\mu\text{g.m}^{-3}$) and the mass fraction in the source materials using the available data from the literature on phthalates and OPFRs. They found that the ratio of y_0/V_p is linearly related to the mass fraction at low levels ($<15\%$) in the source material at room temperature ($23\text{--}25 \text{ }^\circ\text{C}$):

$$\frac{y_0}{V_p} = 3.40 \times \text{mass fraction} \quad (3)$$

The vapor pressure of $1.4 \times 10^{-3} \text{ Pa}$ at $25 \text{ }^\circ\text{C}$ for TCPP is the most commonly value reported in the literature [1,44]. In addition, the enthalpy of vaporization of pure liquid TCPP was estimated to 81 kJ mol^{-1} by Tian et al. [44]. Using these two physical values and the Clausius-Clapeyron equation, the vapor pressure of TCPP can be calculated to $1.12 \times 10^{-3} \text{ Pa}$ at $23 \text{ }^\circ\text{C}$.

Using Eq. (3) with $V_p = 149 \mu\text{g m}^{-3}$ corresponding to the vapor pressure of TCP P at 23 °C converted from Pa to $\mu\text{g.m}^{-3}$ using the ideal gas law [44] and mass fraction of TCP P in the source material (2%), the estimated y_0 value is $10.2 \mu\text{g m}^{-3}$.

This value is in the range of y_0 measured in the two rooms and close to averages (Table 1) confirming that the empirical relationship proposed by Liang et al. [43] provides a good approximation of y_0 basing on V_p and the mass fraction only.

However, many studies give opposite results on the time dependence of y_0 for TCP P emitted from PUR foam. Pei et al. [24] found that y_0 of TCP P decreased by 36–49.4% after 60 days in an emission chamber and in laboratory conditions. In contrast, no decay in y_0 of TCP P was recorded after 228 days in laboratory conditions [27]. This is also found in our field campaign where the y_0 values did not decrease over time in the two rooms. These contrasted trends over time could result from difference in the mass fraction of TCP P in the material, in ageing of material and in the environmental conditions.

3.3. Influence of ambient conditions

The influences of three environmental factors (temperature, absolute humidity and air exchange rate) on the airborne concentrations and y_0 at the surface of cushions were examined. Bivariate analysis of the data showed the highest correlations between y_0 and temperature ($r = 0.74$ with $p < 0.01$) and airborne concentration and temperature ($r = 0.82$ with $p < 0.01$). Weak correlations were also identified between y_0 and absolute humidity ($r = 0.41$ with $p < 0.05$) and airborne concentration and absolute humidity ($r = 0.67$ with $p < 0.05$). No significant correlation was found with air exchange rate. The temperature dependence of y_0 is often described by a relation derived from Clapeyron equation [6] which means that the logarithm of y_0 is linearly related to the reciprocal of the temperature (T):

$$\ln(y_0) = \frac{-\Delta H_p}{RT} + B \quad (4)$$

where $-\Delta H_p$ is the enthalpy of TCP P phase change from the PUR foam to the air, R the universal gas constant and B a constant. This equation has the same form as the Clausius-Clapeyron equation addressing the phase change from pure chemical liquid to the air. Considering the results from both rooms, the logarithms of the y_0 and also of airborne concentration against $1/T$ are shown in Fig. 5. The data of y_0 can be adjusted through a linear function ($r = 0.64$ with $p < 0.05$). The enthalpy of TCP P phase change from the PUR foam to the air was calculated to 91 kJ mol^{-1} from Equation (3). This value is close to the enthalpy of vaporization of pure liquid TCP P estimated to 81 kJ mol^{-1} by Tian et al. [44] using the Clausius-Clapeyron equation with saturation vapor pressures at 23, 40, and 65 °C. This result suggests that the TCP P emission from a fireproofed

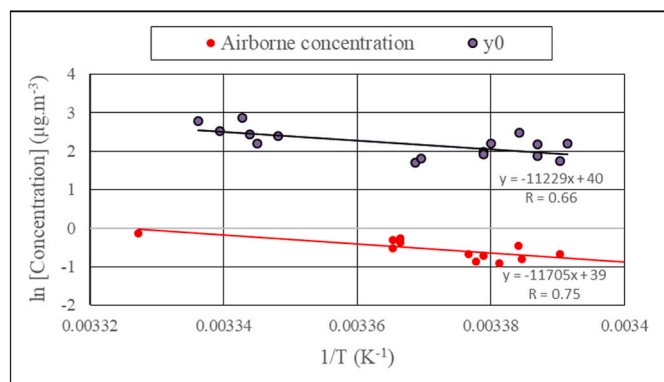


Fig. 5. Logarithms of air concentration and surface concentration (y_0) versus the reciprocal temperature $1/T$ (in Kelvin) obtained from data of the two rooms. The data were fitted to a straight line.

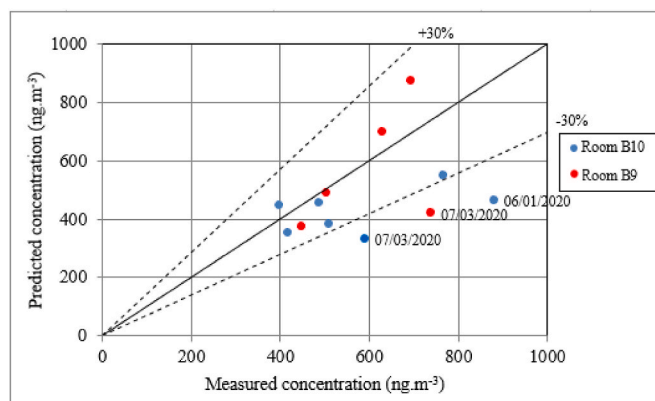


Fig. 6. Airborne concentrations predicted by the model versus measured concentrations.

Table 2

Comparison of measured and modeled TCP P concentrations in air of two rooms.

	n	Average of measured concentrations (ng. m^{-3})	Average of modeled concentrations (ng. m^{-3})	Mean relative deviation (%) [min_max]
Room B10	7	579	427	-21.9 [-47_ +12]
Room B9	5	604	571	-5.4 [-43_ +26]

PUR foam can be assimilable to the vaporization of pure liquid TCP P. The regression line of airborne concentration data has a slope close to that of y_0 data showing that the vaporization remains the main process controlling the TCP P concentration changes at the room scale. The linear gradients show that with a temperature increase of 10 K, both concentrations increase by a factor of 2–4.

3.4. Modeling of TCP P airborne concentrations

Equation (2) describing the mass balance TCP P in the room is used to calculate the indoor concentrations. Fig. 6 and Table 2 show the comparison between the concentrations predicted by the model and the measured concentrations.

An acceptable agreement is found considering the mean values of all series with mean deviations of -5.4 and -21.9% (Table 2). For 9 of 12 measurements series, deviations are low, comprised within $\pm 30\%$, showing an acceptable modeling prediction. The results of 3 series exceed $\pm 30\%$ corresponding to the warm periods of the year. Due to technical limitations, it was not possible to carry out air and material surfaces samplings at the same time. The measurements with SPME based-MOSEC cell method were done the day before the beginning of air sampling in the room B9 and the day after the end of air sampling in the room B10. This time-lag may lead to errors of model prediction when there is a difference of temperature conditions between the two sampling periods. The mean temperatures during the sampling period of MOSEC cell are systematically lower than that of air sampling for these three series with differences of -0.4, -0.5 and -1.6 °C and mean values higher than 24 °C. The underestimation of model for these three series could be explained by differences of temperature conditions.

3.5. Inhalation exposure

Inhalation is considered as the main exposure route in the case of TCP P. Schreder et al. [15] estimated that exposure via inhalation was up to 30 times higher than that from dust ingestion which was commonly considered as the major exposure route for most SVOCs as

Polybrominated Diphenyl Ethers. Exposure via inhalation was assessed in our study based on the median and maximum air concentration levels (550 and 880 ng m⁻³, respectively), an inhalation rate of an adult without physical activity, i.e. 16 m³.day⁻¹ [45] and a time spent in the office of 8 h per day (corresponding to an usual working day). Inhalation intakes of TCPP were thus estimated to 2933 ng.day⁻¹ (with median level) and 4692 ng.day⁻¹ (with maximum level). These values are in agreement with the estimate of 4540 ng.day⁻¹ found by Schreder et al. [15] for an adult living in Washington State using active personal air samplers and including exposures during all the daily activities.

Exposure via inhalation could be increased when more than two pieces of upholstered furniture treated with TCPP is introduced in the offices or when the source material contains a mass fraction of TCPP higher than 2%. Note that the loading rates for TCPP in PUR foams reported by producers are between 2 and 14% with an average loading rate of around 7–8% [1]. It is therefore likely that inhalation exposures higher than that estimated in our study are commonly found in offices.

There is currently no toxicology reference value (TRV) for inhalation exposure to TCPP. A Draft European Union Risk Assessment Report [1] used a reasonable worst case air concentration of 3.8 µg m⁻³ for exposure to TCPP indoors in risk assessment. The airborne TCPP concentrations measured over our study in the two rooms are only 4 to 10 times lower than this reasonable worst case value. The definition of toxicology reference values is needed to improve the risk assessment and prevent adverse health outcomes related to exposure to TCPP. Known human health risks associated with exposure to TCPP are reproductive and developmental effects. Although the current chronic toxicity or carcinogenicity studies are insufficient to reach a conclusion, there is evidence to suggest that TCPP may have carcinogenic potential [46]. These results confirm that inhalation is an important exposure route that should be taken into consideration in risk assessment of this compound.

3.6. Limitations of the present study

The model used is a simplified approach which provided a relationship between the gas-phase concentration at the surface of source material (y_0) and the airborne concentration (gas phase plus particle phase). Due to its low volatility, TCPP can be found in gaseous phase but also sorbed onto suspended and settled particles and on indoor surfaces. This partition is not considered in the model and the separate analysis of these different fractions has not been performed in this study. Very few data are available in the literature where TCPP was simultaneously quantified in several phases. Recent results of Cao et al. [47] pointed out that TCPP is more likely to be found in the particle phase, especially coarse particles rather than in the gas phase. These results are contradictory with those of our study which tend to show that the airborne concentration is mainly driven by the gas-phase TCPP emission from the source and removal of compound by ventilation (the two components of model). Cao et al. [47] also mentioned that this gas-particle partition can greatly vary depending on the nature of indoor sources and kinetics of emission processes as well as non-steady state in this partition. Sampling artefacts leading to an over-estimated particulate fraction for OPFRs were also reported by these same authors. The $K_{\text{octanol air}}$ -based model (assuming that adsorption dominates the gas/particle partitioning process and the system is in equilibrium) and J-P model which is based on partial pressure (assuming that adsorption to particle surface dominates gas/particle partitioning process and the system was in equilibrium) both predict for TCPP a gas-phase fraction higher than particle-bound fraction [47]. More field and experimental data are needed to clarify the partitioning of TCPP indoors. In our study case, the samplings were performed after introduction of source material in an unoccupied room with any other TCPP indoor source. It is possible that, the steady state in the partition of TCPP between the different phases has not been reached and that these conditions favored the presence of TCPP in the gas-phase. Consequently, the model proposed may not be relevant to all the situations.

Another limitation is the non-quantification of gaseous concentration on the indoor surfaces (floor, ceiling, walls and bay window) with SPME based-MOSEC cell method probably due to a limit of quantification too high. The re-emission of TCPP from these indoor surfaces could not be demonstrated.

4. Conclusion

This field study highlights a significant emission potential of TCPP from fireproofed upholstered furniture. The variations in the concentrations at the surface of the source material and in indoor air show no decreasing trend over more than 220 days leading to a potential risk of long-term exposure to TCPP via inhalation. TCPP intake from prolonged dermal contact with treated upholstered furniture could be significant [46] and should be considered in exposure assessment. Additional data is needed to better describe and quantify TCPP intake via dermal route.

Although knowledge on exposure levels and quantitative data on the effects of TCPP is still insufficient to assess a risk/benefit ratio, the widespread use of TCPP as a flame retardant in upholstered furniture is not recommended.

The release rate of TCPP from the source material to the air is mainly governed by the influence of temperature. According to the application of the Clausius-Clapeyron equation, the emission is close to vaporization of pure liquid TCPP indicating that PUR foam has a minor influence on the release process.

Modeling gave an acceptable prediction for the mean concentrations estimated in the two rooms. The model only takes into account the processes of emission/diffusion of compound in air and its removal by ventilation. It allowed to find a relationship between the gas-phase concentration at the surface of source material (y_0) and the airborne concentration from in-situ conditions.

Because of its ease of use on site, the SPME based-MOSEC cell method is relevant for the identification of source materials and also find the emission-concentration relationships in indoor environments.

CRedit authorship contribution statement

Herve Plaisance: Writing – original draft, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Gaëlle Raffy:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Barbara Le Bot:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Emilie Bossanne:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Clemence Rawas:** Resources, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Pierre Cardin:** Resources, Funding acquisition, Formal analysis, Conceptualization. **Valerie Desauziers:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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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