Journal of Hazardous Materials 416 (2021) 125758

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Research Paper

Chlorinated paraffins and tris (1-chloro-2-propyl) phosphate in spray polyurethane foams – A source for indoor exposure?

Sicco. H. Brandsma [a,*], Martin Brits [b], Jacob de Boer [a], Pim E.G. Leonards [a]

[a] Department of Environment and Health, Vrije Universiteit, Amsterdam, De Boelelaan 1085, 1081HV Amsterdam, The Netherlands
[b] National Metrology Institute of South Africa, CSIR Campus, Meiring Naude Road, Pretoria 0040, South Africa

ARTICLE INFO

Editor: Dr. R Teresa

Keywords:
Chlorinated paraffins
Tris (1-chloro-2-propyl) phosphate
One-component foam (OCF)
Spray polyurethane foam (SPF)
Dermal exposure

ABSTRACT

In this study, we investigated chemical additives present in new and used spray polyurethane foams (SPFs) and assessed the dermal transfer through direct contact. This first study shows that cured do-it-yourself spray one-component SPFs (OCFs) often contain chlorinated paraffins (C_{14}-C_{37}), and tris (1-chloro-2-propyl) phosphate (TCIPP), ranging 0.2–50%, and 0.9–30% *w/w*, respectively. Six OCFs contained CP levels ranging 22–50% *w/w*, whereas nine OCFs used for similar applications only contained CP levels ranging 2–17% *w/w*. It is unclear if the combination CPs/TCIPP is meant to improve the flame retardancy of products, and could suggest an unnecessary use of high CPs/TCIPP concentrations in OCFs. The two-component SPFs (TCFs) contained only TCIPP with levels ranging from 7.0% to 9.0%. The CPs and TCIPP were easily transferred from cured OCFs to the hands. Levels up to 590 μg per hand for CPs and up to 2.7 μg per hand for TCIPP were found. After end-of-life, it is challenging to recycle used SPFs. They may, therefore, end up at landfills where the TCIPP/CPs may leach into the environment. Therefore, further investigation is needed to assess potential exposure risks associated with general and occupational use, and the impact of landfill leaching on the environment.

1. Introduction

Due to the rising concern about climate change, property owners are more conscious of their carbon footprint. Improved thermal insulation in houses and buildings reduces heat energy losses and contributes to decreased use of fossil fuels (Pavel and Blagoeva, 2018). Subsequently, the Dutch government decided for example to subsidize homeowners who improve the energy performance of their houses (Netherlands Enterprise Agency RVO, 2020). Energy saving does not only impact the environment by reducing the carbon footprint but is also financially attractive because heating costs are reduced. Various insulation materials can be used to improve the heat energy performance of houses. The most common isolation materials used in Europe are stone, glass wool, and polymer foams, e.g. expanded/extruded polystyrene (EPS/XPS), polyisocyanurate (PIR), and polyurethane (PU) (Pavel and Blagoeva, 2018). Chemical additives, such as cross-linking agents, catalysts, plasticizers, and flame retardants, are added to these polymer foams to improve the physical properties for insulation applications (Dzhordzhio Naldzhiev et al., 2020). The focus during the development of the insulation foam is mainly on improving the thermal resistance (increasing the R-values), rather than the associated exposure to the potential toxic additives present in the plastic foams. Therefore, in this study, we focus on the additives present in spray PU foams (SPFs).

SPFs consist of two parts, the first part comprises an isocyanate component, and the second one is a mixture of various ingredients such as polyols, flame retardants, catalysts, and blowing agents (Dzhordzhio Naldzhiev et al., 2020; Bello et al., 2018). Two types of SPFs were studied, the one-component SPFs (OCFs), and the two-component SPFs (TCFs). OCFs are PU foams stored in relatively small quantities (0.5–0.75 L) in aerosol cans; the components (isocyanate and polyols) are partly mixed and react in the canister, and undergo further reaction with ambient moisture during application (Netherlands Enterprise Agency RVO, 2020). OCFs are used professionally in the building industry but are also available in do-it-yourself (DIY) construction markets to fill gaps around door and window frames, as thermal insulation, sound insulation, bonding, passive fire protection, and to create an energy-efficient building envelope (US Environmental Protection Agency EPA, 2020). TCFs are used professionally in the building industry for insulation larger areas (roof and wall) to provide thermal and acoustic insulation whereby the two components (isocyanate and

* Corresponding author.
E-mail address: sicco.brandsma@vu.nl (Sicco.H. Brandsma).

https://doi.org/10.1016/j.jhazmat.2021.125758
Received 14 January 2021; Received in revised form 22 March 2021; Accepted 23 March 2021
Available online 31 March 2021

polyols) are stored separately and mixed when applying the foam. The global OCF production was more than 750 million cans in 2018 and for TCF more than 600,000 tonnes in 2018, both increasing every year (IAL consultants, 2020). The relatively high production volumes and use of OCFs and TCFs in houses highlight the importance to characterize the additives present in these foams. In this study, we will determine the levels of chlorinated paraffins (CPs) and tris (1-chloro-2-propyl) phosphate (TCIPP) in SPFs (OCFs and TCFs). The selection of the additives, with the focus on flame retardants, included in this pilot study was based on a pre-screening that was performed on a high-resolution quadrupole time-of-flight mass spectrometer (TOF-HRMS) equipped with a direct insertion probe (DIP) and operated in atmospheric pressure chemical ionization (APCI) negative mode (Ballesteros-Gómez et al., 2014).

CPs are complex mixtures of chlorinated alkanes with varying carbon chain lengths and degrees of chlorination and are divided into three subgroups, based on their carbon length: short-chain CPs (SCCPs, $\leq C_{13}$), medium-chain CPs (MCCPs, $C_{13}-C_{17}$), and long-chain CPs (LCCPs, $\geq C_{18}$). The LCCPs with a chain length longer than C_{20} (average carbon chain length of approximately C_{25}) are referred to as wax-grade or very long CPs (WLCCPs or vLCCPs). Due to their environmental persistency, long-range transport, bioaccumulation potential, and toxicity of SCCPs (Glüge et al., 2016), they are restricted by European Union (EU) and designated as persistent organic pollutants (POPs) and listed in Annex A of the United Nations Stockholm Convention (POPRC Persistent Organic Pollutants Review Committee, 2017). For some applications, these restrictions have led to a shift in the use and production of longer chain chlorinated paraffins (MCCPs and LCCPs) (Yuan et al., 2017; Stockholm Convention, 2020). Due to the high global production of CPs (estimation of >2 million tonnes/year) and the use in a wide range of applications such as lubricants, metal cutting fluids, sealants, and as a flame retardant, SCCPs and MCCPs are ubiquitously present in different environmental compartments (SETAC, 2020; van Mourik et al., 2016), whereas for LCCPs data is scarce. There is limited chronic toxicity data available on CP mixtures especially information on the toxicokinetics in humans and animals regarding the impact of the chlorination degree, position of chlorine, and carbon chain length (Schrenk et al., 2020). However, the LCCPs appear to be less toxic to organisms than MCCPs and SCCPs (De Boer, 2010). In general, it seems that the toxicity is increasing with decreasing chain-length and greater degrees of chlorination (El-Sayed Ali and Legler, 2010). A recent study with human liver microsomes showed that shorter chain CPs can be formed from longer chain CPs during the biotransformation (He et al., 2021). This indicated that besides SCCPs, the exposure to MCCPs and LCCPs is also highly relevant because both MCCPs and LCCPs have been detected in human blood (Li et al., 2017) and various wildlife samples (van Mourik et al., 2016; Yuan et al., 2019) and may eventually transform into the regulated SCCPs.

No peer-review data is available on the characterization of CPs in SPFs and only limited data on TCIPP (Dzhordzhio Naldzhiev et al., 2020; Estill et al., 2019). TCIPP is a high production volume chemical that is mainly used as a flame retardant in polyurethane (rigid) foams in construction (insulation) and furniture (matrasses, sofas, and seats) (Wang et al., 2019; Stapleton et al., 2009). TCIPP is found in freshwater biota, marine environment, and human breast milk and blood (Sundkvist et al., 2010; Kim et al., 2014; Brandsma et al., 2015; Zhao et al., 2016). Studies regarding the adverse effects of TCIPP on humans are limited, however, TCIPP is classified as a suspected carcinogen (World Health Organization, 1998) and animal toxicity studies have shown that TCIPP can interfere with the endocrine system causing adverse health effect (Liu et al., 2012; Farhat et al., 2013). Despite environmental and human health concerns, halogenated FRs are still in use (De Boer and Stapleton, 2019).

Few studies have shown that non-chemically bound additives such as e.g. CPs and TCIPP can migrate from consumer products to air and dust, and are therefore a significant source for indoor exposure (Marklund et al., 2005; Olofsson et al., 2009; Brandsma et al., 2014; He et al., 2018; Lucattini et al., 2018). Peer-reviewed studies on the emission of TCIPP from SPFs are limited (Bello et al., 2018; Estill et al., 2019; NIST Technical Note, 1921, 2017), and no data exists for CPs. The EU risk assessment report from 2008 stated that during curing of the OCFs, TCIPP is embedded in the polycondensate structure and have, no tendency to migrate (EU risk assessment, 2008). However, previous micro-chamber experiments conducted to determine the impact of foam type, chemical type, flow rate, temperature, and humidity on TCIPP emissions, showed that TCIPP emits from cured spray SPFs. This study also shows that there was no statistical difference between TCIPP emission rates from freshly sprayed open-cell SPF and SPF tested two years after application (NIST Technical Note, 1921, 2017). Bello et al. (2018) found that the urinary TCIPP biomarker levels of workers applying SPFs significantly increased (25–35 times higher than the general population) during the work shift. They suggested that dermal exposure is an important exposure pathway, although, the contribution of inhalation and incidental ingestion could not be ruled out. Evidence of occupational exposure to TCIPP during application by SPF workers was also observed by Estill et al. (2019). These findings confirm that TCIPP migrate from SPFs to air, dust, and skin (through air diffusion and direct skin contact) and appear to be a source for TCIPP exposure.

Until now, no information is available on the characterization and emission of CPs in spray SPFs. CPs and TCIPP are one of the dominant chemicals in house dust (Lucattini et al., 2018; Brits et al., 2020) Multiple sources can be responsible. For example, a significant positive correlation between CP levels on hand-wipes and factors related to the indoor environment and product use was reported by Yuan et al. (2020) and Hilger et al. (2013). They suggest that the SCCPs in the sealing contributed to the high SCCP levels in the dust. Therefore, insulation foams containing high CP levels could be an important exposure source for CPs. The vapor pressures of CPs tend to decrease with increasing carbon chain length and degree of chlorination (Drouillard et al., 2009). Due to the lower vapor pressure of CPs compared to TCIPP, it is most likely that the emission to air will be lower, except for SCCPs with a low chlorination degree. MCCPs and LCCPs are more likely bound to dust. This indicates that exposure through direct contact (dermal exposure) or abrasion of the SPFs to dust will probably be the predominant exposure pathway for MCCPs and LCCPs, whereas migration from the foams to air, dust, and skin appears to be a source for TCIPP exposure.

These findings highlight the need to investigate the presence of CPs in SPFs, to estimate potential health risks. Therefore, in this study, we focused on the characterization of CPs (C_9-C_{40}) and TCIPP in cured SPFs, and assessed the dermal transfer of CPs and TCIPP from cured OCFs through direct hand contact studies.

2. Materials and methods

Information about the standards, chemicals, and suppliers is provided in the Supporting Information (SI) of this manuscript, as well as the homologue patterns of the ten reference mixtures used for the deconvolution of the SCCPs, MCCPs and (W)LCCPs patterns in the OCF and TCF samples.

2.1. Sampling, screening, cleanup, and fractionation

The SPF samples (n = 24) collected and prepared for this study are listed in Table 1. Briefly, ten spray OCFs were prepared from ten new OCF-cans (representing seven different brands) purchased in 2019 at do-it-yourself (DIY) stores in the Netherlands. Each OCF-can had different property descriptions, e.g., high speed, high volume, high efficiency, ultra-insulation, or a fire classification (see Table S1). Seven of the ten OCF-cans listed MCCPs as an ingredient in the material but no concentrations were provided. TCIPP was listed on the data safety sheets of three of the OCFs-cans with levels ranging from 1% to 30% (Table S1). Ten cured OCF samples, applied as insulation and filling material, were collected from nine houses and one office. In addition, four TCFs applied as floor insulation were collected from four different houses (Table 1).

Table 1
Percentage (% w/w) MCCPs, LCCPs, and TCIPP detected in the cured one component spray PU foams (OCFs) and two-component spray PU foams (TCFs) samples. The goodness of fit (R^2) and the contribution of each CP standard in each sample are also given in this Table. **Bold** values highlight the most dominant standards that contribute to the CP pattern and values reported in Italic indicate levels < LOQ. The reconstructed CP pattern was compared to the initial CP pattern of the analysed sample to determine the goodness of fit (R^2). An $R^2 > 0.5$ shows an acceptable agreement between the reconstructed and initial CP pattern (Bogdal et al., 2015; Brandsma et al., 2017).

	OCFs new products	Contribution MCCP standards			Conc. (% w/w)		Contribution LCCP standards				Conc. (% w/w)		Conc. (% w/w)
No.	Sample description	42% Cl	52% Cl	57% Cl	∑MCCPs	R^2	36% Cl	49% Cl	Wax 42% Cl	Wax 48% Cl	∑LCCPs	R^2	TCIPP
OCF1	New product 2019	**74%**	26%	0.0%	13%	0.5	7%	13%	**62%**	18%	0.6%	0.6	3.4%
OCF2	New product 2019	**77%**	23%	0.0%	11%	0.6	19%	22%	44%	14%	0.5%	0.9	3.6%
OCF3	New product 2019	**77%**	23%	0.0%	4.0%	0.6	0.0%	0.0%	**81%**	19%	25%	0.9	*< 0.1%*
OCF4	New product 2019	**69%**	31%	0.0%	1.3%	0.6	1.0%	0.0%	**67%**	32%	29%	0.9	4.1%
OCF5	New product 2019	1.0%	**80%**	20%	49%	0.7	0.0%	**100%**	0.0%	0.0%	0.9%	0.7	0.9%
OCF6	New product 2019	8.0%	**92%**	0.0%	50%	0.6	–	–	–	–	*< 0.1%*	–	*< 0.1%*
OCF7	New product 2019	**61%**	39%	0.0%	10%	0.9	35%	**65%**	0.0%	0.0%	1.3%	0.9	12%
OCF8	New product 2019	15%	26%	58%	49%	0.7	–	–	–	–	*< 0.1%*	–	*< 0.1%*
OCF9	New product 2019	46%	**54%**	0.0%	0.2%	0.7	0.0%	0.0%	**79%**	21%	5.6%	0.9	23%
OCF10	New product 2019	**55%**	45%	0.0%	1.0%	0.5	1.0%	0.0%	**77%**	23%	1.0%	0.9	30%
	OCFs used products												
OCF11	House (ventilation) 2007	–	–	–	*< 0.1%*	–	–	–	–	–	*< 0.1%*	–	13%
OCF12	House (fuse box) 2009	–	–	–	*< 0.1%*	–	–	–	–	–	< 0.1%	–	13%
OCF13	House (roof) 2011	**69%**	31%	0.0%	17%	0.5	–	–	–	–	*< 0.1%*	–	*< 0.1%*
OCF14	House (fuse box) 2011	**64%**	36%	0.0%	22%	0.5	29%	**71%**	0.0%	0.0%	0.2%	0.8	*< 0.1%*
OCF15	House (attic) 2012	**65%**	35%	0.0%	8.0%	0.6	27%	73%	0.0%	0.0%	0.2%	0.9	11%
OCF16	Office (ceiling) 2015	**69%**	31%	0.0%	12%	0.5	–	–	–	–	*< 0.1%*	–	*< 0.1%*
OCF17	House (kitchen) 2019	0.0%	**76%**	24%	10%	0.7	19%	**81%**	0.0%	0.0%	0.2%	0.9	5.6%
OCF18	House (living room) 2020	–	–	–	*< 0.1%*	–	–	–	–	–	*< 0.1%*	–	16%
OCF19	House (bathroom) 2020	–	–	–	*< 0.1%*	–	–	–	–	–	*< 0.1%*	–	15%
OCF20	House (bathroom) 2020	–	–	–	*< 0.1%*	–	–	–	–	–	*< 0.1%*	–	17%
	TCFs used products												
TCF21	House (floor insulation) 2011	–	–	–	*< 0.1%*	–	–	–	–	–	*< 0.1%*	–	7.0%
TCF22	House (floor insulation) 2015	–	–	–	*< 0.1%*	–	–	–	–	–	*< 0.1%*	–	9.0%
TCF23	House (floor insulation) 2015	–	–	–	*< 0.1%*	–	–	–	–	–	*< 0.1%*	–	7.4%
TCF24	House (floor insulation) 2017	–	–	–	*< 0.1%*	–	–	–	–	–	*< 0.1%*	–	8.6%

The foam samples from the houses and offices were between 1 and 13 years old.

The new SPF samples were prepared by shaking the spray cans for 30 s, according to the instructions, and applying approximately 10 g on aluminium foil. The samples were left to cure for 24 h at room temperature and wrapped in aluminium foil. The samples consisted of uncovered foam applied in ventilation shafts, round cables in fuse boxes, and roof/attic and floor insulation. The floor insulation samples were collected from crawl spaces. OCFs 18–20 were collected from a bathroom and living room before they were covered with plaster. An adequate amount of sample was removed with a knife using gloves, wrapped in aluminium foil, and transported to the laboratory. To eliminate external contamination (from dust), the outer layer of the foam was removed and a subsample of the internal part was collected by cutting a 5 × 10 cm piece from the applied foam using a pre-cleaned knife. The samples were wrapped in aluminium foil and stored at room temperature.

Prior to quantitative analysis, screening experiments were performed on the OCF and TCF samples to investigate which additives (with a focus on flame retardants) were present and predominant, and to estimate dilution volumes for analysis. The screening analysis was performed on a TOF-HRMS (microTOF II, Bruker, Bremen, Germany) equipped with a direct insertion probe and operated in APCI negative ionization mode (Ballesteros-Gómez et al., 2014). This screening technique allows for fast detection of CPs and TCIPP with levels above 0.05% *w/w*. The results of the screening analysis are listed in Table S2. Based on the results, an indication could be made on how far the samples had to be diluted before analysis on the LC- qTOF-MS (CPs) and GC-MS (TCIPP).

Approximately 50–100 mg of OCF and TCF were weighed in a pre-cleaned 15 mL glass tube. The extraction was performed by adding 5 mL dichloromethane (DCM) and shaking for 30 min. The supernatant was removed and transferred to a pre-cleaned glass tube and the extraction was repeated twice. The combined DCM extract was further diluted (100 times) in hexane. Based on the screening results 0.03 – 1 mL of the hexane dilution was taken for cleanup and fractionation. Detailed information on fractionation and cleanup is described in Brits et al. (2020). Briefly, the required volume of the diluted hexane extract was spiked with labeled TCIPP-d18 (50 μL; 1000 ng/mL) and quantitatively transferred to the pre-conditioned (20 mL hexane) multicolumn (0.5 g Silica gel, 0.5 g Florisil and 0.5 g Na_2SO_4). The multicolumn was eluted with 15 mL hexane (washed) followed by 15 mL DCM/hexane (1:1, v/v) (CPs fraction) and 15 mL ethyl acetate (TCIPP fraction). All fractions were evaporated to near dryness at 30 °C under a gentle stream of nitrogen. The CP fraction was reconstituted in 0.6 mL acetonitrile and ^{13}C Dechlorane plus (50 μL; 2000 ng/mL) was added as injection standard and analysed by APCI-qTOF-MS (Compact, Bruker, Bremen, Germany). The TCIPP fraction was reconstituted in 0.6 mL iso-octane and analysed by GC-MS (Agilent Technologies, Amstelveen, The Netherlands).

2.2. Direct hand contact with cured OCF (hand-wipes)

The experimental setup of the OCF hand contact studies (Fig. 1) consisted of a combination of hand washing, hand wipe sampling, and contact with the OCFs (10 s). The hand-wipe experiment was performed by one male adult participant. Prior to participation, consent was obtained from the participant. According to the medical-ethical review

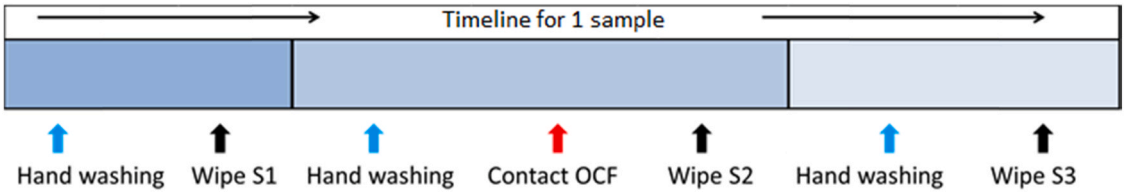

Fig. 1. The experimental setup for the direct hand contact with the OCFs (hand wipes).

committee of the VUmc in Amsterdam ethical permission was not required for this study. Four different new OCF samples were selected for the hand contact study. The hand was initially washed with soap and water for 10 s, and dried using a paper towel. The effect of skin oil removal during washing of the hands was not considered in this study. A wipe sample (Wipe S1) was taken from only one hand. Then, the hand was placed on the cured PU foam sample for direct contact of 10 s and a second wipe sample (Wipe S2) was taken. The PU foam was completely cured (>24 h) and no foam material itself was transferred to the hand. The wipe was taken from the entire surface of the hand that had been in contact with the foam sample. The hand was washed again in the same way and wipe S3 was taken. A sterile gauze compress (Bevaplast, 5 ×5 cm), wetted with 3 mL of isopropanol was used to wipe the hand. Gloves were replaced between sample collection to prevent sample cross-contamination. Triplicate experiments were performed for each OCF sample. The hand-wipes were stored in a pre-cleaned 15 mL glass tubes. After adding labeled TCIPP-d18 (50 μL; 1000 ng/mL), the hand-wipes were 3 times extracted with 5 mL DCM for 10 min in an ultrasonic bath at room temperature. The extracts were evaporated to near dryness at 30 °C under a gentle stream of nitrogen and reconstructed in 1 mL of hexane. Cleanup and fractionation of the hand-wipes were done as previously described for the SPF samples.

2.3. Instrumental analysis

CP analysis of the OCFs, TCFs, and hand-wipes was performed with a slightly adopted analytical method developed by Bogdal et al. (2015) as previously described in detail in Brandsma et al. (2019). Further detailed information on the CP and TCIPP analysis of the foams is given in the Supporting Information.

2.4. Quality assurance and quality control

The method limit of quantification (LOQ) for the CPs and TCIPP in the OCFs and TCFs was set at 0.1% *w/w,* which was calculated based on the lowest calibration standards which were at least 10 times the S/N. Three method blanks were included in the analysis of the samples, the blank levels were an order of magnitude lower than the LOQ of 0.1%. For the hand-wipe analyses, three method blanks were also included which consists of a clean hand-wipe wetted with 3 mL isopropanol. The LOQs for CPs and TCIPP in hand-wipes were calculated as 10 times the S/N or as 10 times the standard deviation of the blank. The average blank value of TCIPP was 5.5 ng/hand-wipe with a LOQ of 24 ng/hand-wipe. The average blank for the ΣSCCPs was 5 ng/hand-wipe, 15 ng/hand-wipe for the ΣMCCPs, and no blank was observed for the ΣLCCPs. The LOQ for ΣSCCPs, ΣMCCPs, and ΣLCCPs were 50, 95, and 20 ng/hand-wipe, respectively. The recovery of the labeled internal standard TCIPP-d18 ranged from 76% to 103% for both the SPFs and the hand-wipes. TCIPP values were corrected for the recovery of the TCIPP-d18. For CPs, relative recoveries were calculated for SCCPs, MCCPs, LCCPs, and WLCCPs. The recovery standards underwent the same extraction, cleanup, and analysis procedures as SPFs and hand-wipes. Acceptable recoveries were observed and ranged from 92% to 119% (Table S3). Matrix-effect was investigated by performing standard addition experiments on two OCF samples (OCF4 and 5). The extracts were diluted to a concentration of approximately 100 ng and spiked with 0 ng, 75 ng, 150 ng, and 250 ng of the CP standard. OCF4 contained 29.2% wax-grade LCCPs and was spiked with wax-grad LCCPs 42% (similarity of 67% with wax-grade LCCPs 42%, see Table 1). OCF5 contained 49.0% MCCPs and was spiked with MCCPs 52% (similarity of 80% with MCCPs 52%, see Table 1). The linearity was > 0.99 (Figs. S1 and S2) for both OCFs and the concentration calculated by the standard addition method was 28.6% wax-grade LCCPs for OCF4 and 47.8% MCCPs for OCF5 which resulted in acceptable recoveries of 102% and 103%, respectively (Table S4). The homogeneity of the prepared foams was tested by analyzing OCF5 in quintet, by preparing four 10 g foams as previously described. The MCCP concentrations observed in the quintet analysis of OCF5 was 46 ± 3% *w/w*. The low relative standard deviation of 7% indicates acceptable homogeneity. The goodness of fit (R^2) for the ΣMCCPs, ΣLCCPs, and ΣWLCCPs were all higher than 0.5 which indicates acceptable deconvolution (Table 1). The ΣSCCPs were lower than the LOQ (<0.1% *w/w*).

3. Results and discussion

3.1. Cured OCFs - new products

CPs were detected in all cured foams from new OCF cans with levels ranging from 0.2% to 50% *w/w* (Table 1 and Fig. 2). The MCCPs were dominant followed by the WLCCPs. The ΣSCCPs levels were all < 0.1% *w/w*. Although the use of CPs in insulation materials has been described (van Mourik et al., 2016; Hilger et al., 2013), this is the first report on MCCPs and (W)LCCPs in OCFs. In addition to CPs, the suspect carcinogen organophosphate flame retardant (OPFR) (World Health Organization, 1998), TCIPP was also detected in the OCFs. In cured OCF of seven of the ten new OCF-cans TCIPP was found with levels ranging from 0.9% to 30% *w/w* (Fig. 2 and Table 1).

As shown in Fig. 2 and Table 1 high variations in CP and TCIPP concentrations and CP groups were observed between the different OCF-cans. OCF1 and 2 contain between 11% and 14% *w/w* CPs (mainly MCCPs), whereas OCF5, 6, and 8 contain up to 50% *w/w* MCCPs, and OCF3 and 4 contain mainly WLCCPs (25% and 29% *w/w*). Subsequently, we observed that OCFs which contains high LCCPs levels (5.6–29% *w/w*) are in general WLCCPs, whereas the OCFs with high MCCPs and low LCCPs levels have LCCPs with a carbon chain length of C_{18}-C_{20}, which are likely present in the OCFs as an impurity in the MCCPs technical mixture (Table 1). Two OCF cans had a fire classification, OCF7 has a B2 rating and OCF9 a B1 rating. According to DIN 4102–1 the B1 rating stands for high fire resistance and B2 for normal flammable (DIN, 4102–1, 1998). High levels of TCIPP were detected in OCFs 7 and 9 (12% and 23% *w/w*, respectively, which suggests that more TCIPP is needed to increase the rating from B2 (containing 12% w/w TCIPP) to B1 (containing 23% w/w TCIPP). In addition to TCIPP, both OCF cans also contained CPs, OCF7 contained 10% w/w MCCPs and OCF9 contained 5.6% w/w WLCCPs, which may also increase the flame retardancy of the OCFs. OCF10 contained the highest TCIPP level (30% *w/w*). However, no fire classification was given to this OCF can. High variation in CP and TCIPP concentrations were observed for OCF cans from the same brand which might relate to different properties of the foam applications. In general, all the new OCF cans collected are easily available and sold as insulation and mounting foams for filling cracks, holes, gaps, and crevices. Although each OCF-can has specific property descriptions

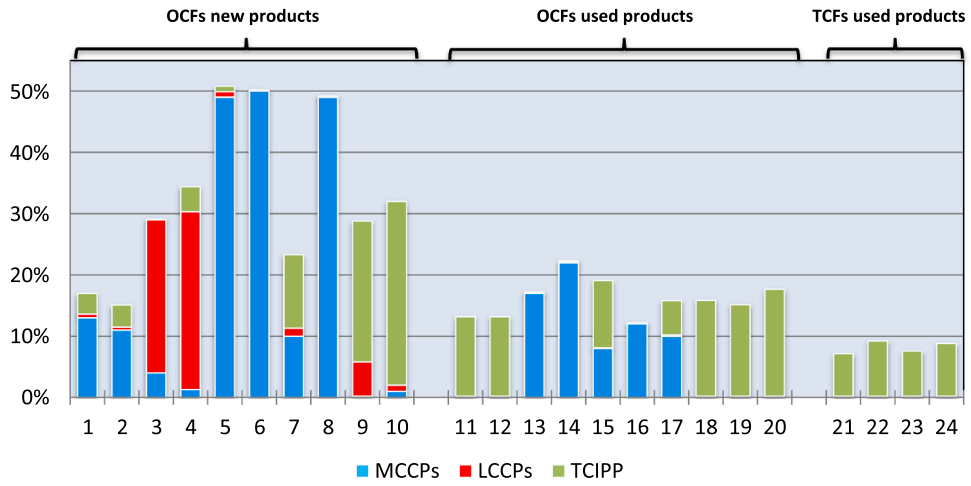

Fig. 2. MCCP and (W)LCCP and TCIPP levels (% w/w) in cured new (1−10) and used (11−20) one component spray PU foams (OCFs) and used (21−24) two-component spray PU foams (TCFs).

or a fire classification, no relation between the specific description on the OCF-cans and the CP and TCIPP levels was observed. Results further show that some of the inexpensive OCF cans contained the highest CP levels. It is further unclear why some of the OCFs contain CP levels up to 50% *w/w* whereas OCF foams with comparable property descriptions only contain 12–15% *w/w* of CPs. It is also uncertain if the combination of CPs and TCIPP are taken into account in determining the flame retardancy rating. This may imply that unnecessary high concentrations of CPs and/or TCIPP are used in the OCFs.

It is known that CPs are used in OCF foams and seven out of the ten OCF cans listed it as an ingredient in the formulations (Table S1). However, no information was present regarding the concentrations. On two of the OCF cans were stated that the formulations contain chloro-alkanes (C_{14}-C_{17}) MCCPs, although the formulations were dominated by WLCCPs (C_{20} >). For three of the OCF cans no ingredient information was provided. However, these did contain CPs. Ingredient information for TCIPP was only provided on the data safety sheets of three of the OCF cans with levels ranging 1–30%. The levels of TCIPP observed in these three OCFs were within the indicated ranges. However, for four other OCFs containing TCIPP no ingredient information was provided (Table S1). This means that the description on the OCF cans might provide misinformation for CPs and for the suspected carcinogen TCIPP information is sometimes lacking.

3.2. OCFs and TCF in used products

The concentrations for TCIPP and ΣMCCPs were dominant in the PUR foams collected from the nine houses and one office building with levels ranging from < 0.1–17% *w/w* and < 0.1–22% *w/w*, respectively. The ΣLCCPs (most likely present as an impurity in the MCCP technical mixture) were only present in low levels 0.2% *w/w* in the OCFs that contain relatively high levels of MCCPs (OCFs 14, 15, 17). The WLCCPs and SCCPs were all < 0.1% *w/w*. The four TCFs used as floor-insulation, did not contain any CPs (levels were <0.1% *w/w*; only relatively high levels of TCIPP were observed ranging from 7% to 9% *w/w*). The TCIPP levels in TCFs 21–24 are comparable with the TCIPP levels Estill et al. (2020) found in seven TCFs with a mean level of 10.3 ± 1.7% *w/w*. The low detection frequency of CPs in TCFs could be related to the small number of TCFs included in this study. However, TCFs consists of two components that are stored separately and mixed when applying the foam whereas OCFs are pre-mixed and reacted in the canister, and undergo further reaction with ambient moisture during application. Applying TCFs is more critical and is generally performed by professionals. It may be that the addition of CPs to the TCFs negatively influences the spraying and curing reaction of the foam.

Despite the small data set, we observed that the total sum of CPs and TCIPP levels in the used OCFs, which ranged from 13% to 22% w/w, were lower than the levels found in the new OCFs which ranged from 15% to 51% w/w. The lower levels observed in the used OCFs is most likely related to high variation in CP and TCIPP concentrations used in the original OCF applications than to the migration of the CPs and TCIPP to the air or dust. However, various studies have shown that semi-volatile organic compounds (SVOCs) such as CPs and TCIPP can easily migrate from consumer products into the indoor air and dust (Marklund et al., 2005; Olofsson et al., 2009; Brandsma et al., 2014; He et al., 2018; Lucattini et al., 2018). Although many of the reported physico-chemical properties are derived via modelling rather than empirically, all CPs are in general poorly water -soluble, semi-volatile and have high octanol-water (Kow) and high octanol air partition coefficients (Koa) (van Mourik et al., 2016). Hilger et al. (2013) investigated the source of the relatively high SCCPs levels (up to 2050 μg/g) found in house dust samples by analyzing the sealing masses sampled between concrete piers and walls and floor plate and walls. The sealing masses contain SCCPs levels up to 50,345 μg/g. Because of the high SCCPs levels in the sealing masses and the similarities of the alkane compositions with the house dust samples, Hilger et al. (2013) argued that this strongly indicates that the sealing contributed to the high levels observed in the dust. Therefore, migration of the CPs and TCIPP from the OCFs to the air and dust could not be ruled out and further research on migration properties is recommended. This is particularly important because of the high CP (up to 50% *w/w*) and TCIPP levels (up to 30% *w/w*) present in the OCFs and generally high quantities of OCFs used in the indoor environment. Another difference observed between the used and new OCFs was that WLCCPs were not detected in the used OCFs, but were dominant in three of the new OCF cans. WLCCPs have only been recently detected in the environment (Yuan et al., 2017; Brandsma et al., 2017) and data on WLCCPs is still scarce. The finding of WLCCPs in a sediment core from the early 1930s nearby a steel factory in Sweden indicated that WLCCPs have already been produced for at least 80–90 years (Yuan et al., 2017). Restrictions regarding the use of SCCPs have led for some applications to increased use of MCCPs and LCCPs (Yuan et al., 2017; Stockholm Convention, 2020). Concern regarding the potential toxicity of the MCCPs may even lead to a shift by the industry to the even longer WLCCPs, based on the assumption that the toxicity is decreasing with increasing chain-length and lower degrees of chlorination (El-Sayed Ali and Legler, 2010), which may explain the finding of WLCCPs only in the new OCF cans.

3.3. CP carbon and chlorine homologue patterns observed in the OCFs

The MCCP and (W)LCCP carbon and chlorine homologue patterns observed in the new and used OCFs are shown in Fig. 3. Comparing the CP homologue patterns with other studies is challenging because carbon and chlorine homologue patterns are depending on the analytical system and instrument used (Krätschmer and Schächtele, 2019). Therefore, comparison can only be done within the same study or with previous studies that used the same analytical system. Comparable MCCP carbon homologue patterns were observed in the OCFs, with average contributions of 32% for C_{14}, 30% for C_{15}, 25% for C_{16}, and 12% for C_{17}. The carbon homologue pattern for one of the new foam products (OCF7), was dominated by C_{14} (56%) (Fig. 3A and C). The carbon homologue pattern in the three commercial technical mixtures (MCCP 42% Cl, 52% Cl, and 57% Cl) used for quantification, were similarly dominated by C_{14} followed by C_{15}. However, the average contributions were much higher (67–69% for C_{14} and 26–27% for C_{15}).

The MCCP chlorine homologue pattern in most of the OCFs were dominated by Cl_6 (34%), although three of the new foam products (OCF5, 6, and 8) showed higher contributions from Cl_6 (25%), Cl_7 (31%), and Cl_8 (21%) (Fig. 3B). The three commercial technical mixtures showed that Cl_5 (44%) and Cl_6 (30%) were the predominant chlorine homologue group in MCCP 42% Cl, Cl_6 (34%) and Cl_7 (33%) in MCCP 52% Cl and Cl_7 (33%) and Cl_8 (32%) in MCCP 57% Cl.

The calculated chlorination degree for the MCCPs in the OCFs ranged 49–54%. Contrary to the MCCPs, more variation in carbon and chlorine homologue patterns was observed for the (W)LCCPs in the OCFs (Fig. 3 C and D). In general, three different carbon patterns were visible, the first group was dominated by C_{18}, C_{19}, and C_{20}, which are LCCPs. The second group was dominated by C_{24} to C_{27}, which are WLCCPs, and the third group was dominated by C_{18} and C_{24} to C_{27}, a combination of LCCPs and WLCCPs.

The MCCP homologue patterns observed in the OCFs were comparable with the MCCP patterns observed in car tires/rubber granulates (Brandsma et al., 2019) and house dust samples from South Africa (Brits et al., 2020), dominating with an average contribution of 44% for C_{14} and 27% for C_{15} with Cl_6 (34%) and Cl_7 (25%) and 45% for C_{14} and 26% for C_{15} with Cl_6 (20%) and Cl_7 (28%), respectively. In both studies, the same analytical system was used. WLCCPs, dominated by C_{24} to C_{27}, were also observed in the car tires/rubber granulates from Europe and in the South African house dust samples. This indicates that both the MCCP and WLCCP homologue patterns observed in the OCFs are not unique for OCFs. It makes it therefore not possible to relate, only based on the CPs homologue patterns, the MCCPs and WLCCPs observed in the South-African house dust samples to the use of SPFs. Therefore, further research (such as migration tests) are needed to investigate if the SPFs may be a possible source. Overall, it can be concluded that not only different CP concentrations and CP groups were observed in OCFs but also differences in carbon and chlorine homologue patterns.

3.4. Direct hand contact with OCFs (hand-wipes)

The high CP and TCIPP levels detected in the OCFs and the high amounts of OCFs used in houses to reduce energy loss may indicate that there is an exposure risk associated with the general and occupational use of OCFs. Therefore, we investigated the exposure of direct hand contact (hand-wipes) with OCFs. In this pilot study four OCFs were selected, OCFs 2, 4, 5 and, 9 which were dominated by MCCPs (11% *w/w*), WLCCPs (29% *w/w*), MCCPs (50% *w/w*) and TCIPP (29%), respectively (Fig. 2, Table 1). A significant increase in CPs ($P \leq 0.05$) and TCIPP ($P < 0.05$) levels was observed on the hands after contact with the OCFs with levels higher than 0.9% (Table 2 and S5). The highest levels up to 590 μg MCCPs per hand were detected after contact with OCF5, which contained the highest levels of MCCPs (49% *w/w*) (Table 2 and S5). The MCCP levels significantly increased ($P = 0.05$) 3 orders of magnitude after comparing the levels before (hand-wipe 1) and after

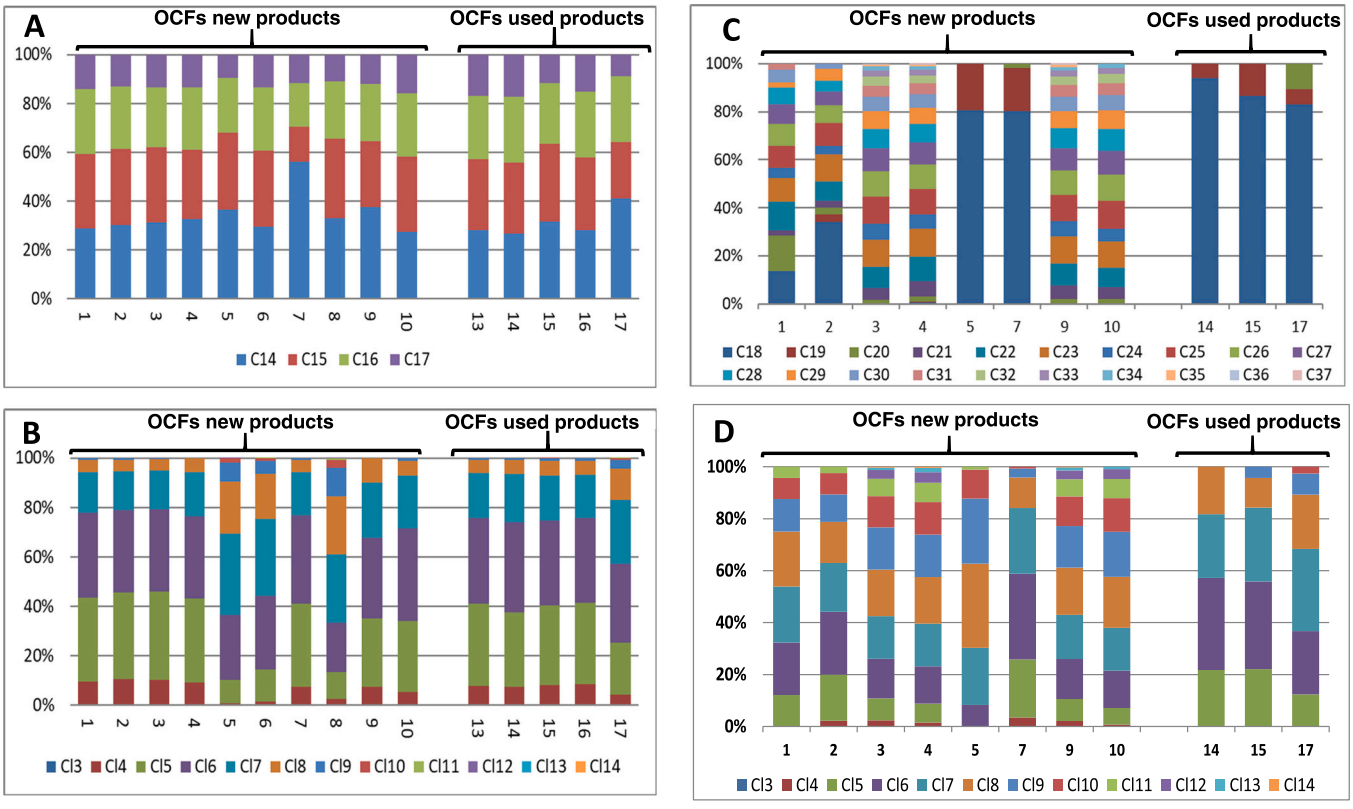

Fig. 3. MCCP and LCCP carbon and chlorine homologue patterns observed in the new and used OCFs. 3A and B represent the MCCP carbon and chlorine homologue patterns, respectively, and 3C and D represent the (W)LCCP carbon and chlorine homologue patterns, respectively.

Table 2
The results of the direct hand contact study performed in triplicate with four different OCFs. CPs and TCIPP levels found on the hand-wipes are given in ng/wipe. A) OCF2; B) OCF4; C) OCF5; D) OCF9.

	A (OCF2)			B (OCF4)			C (OCF5)			D (OCF9)		
	∑MCCPs	∑(W) LCCPs	TCIPP	∑MCCPs	∑WLCCPs	TCIPP	∑MCCPs	∑LCCPs	TCIPP	∑MCCPs	∑WLCCPs	**TCIPP**
	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	**% (w/w)**
CPs in the OCF (% w/w)	11%	0.5%	3.6%	1.3%	29%	4%	49%	0.9%	0.9%	0.2%	5.6%	23%
Exp1	ng/wipe	ng/wipe	ng/wipe	ng/wipe	ng/wipe	ng/wipe	ng/wipe	ng/wipe	ng/wipe	ng/wipe	ng/wipe	ng/wipe
Hand wipe S1	260	530	60	< 95	90	< 24	< 95	92	25	*	*	< 24
Hand wipe S2	1930	220	600	360	17,500	760	590,000	11300	1230	460	1040	2780
Hand wipe S3	130	40	< 24	< 95	650	50	18,300	360	30	260	80	< 24
Exp2												
Hand wipe S1	< 95	130	< 24	< 95	430	< 24	< 95	< 20	< 24	170	< 20	< 24
Hand wipe S2	1900	210	560	230	4700	620	340,000	6500	1190	160	690	2400
Hand wipe S3	140	50	< 24	< 95	680	< 24	38,000	880	< 24	160	80	17
Exp3												
Hand wipe S1	< 95	80	< 24	95	< 20	< 24	< 95	105	< 24	110	< 20	< 24
Hand wipe S2	3850	530	1130	390	8000	881	152,000	4060	840	130	670	2400
Hand wipe S3	120	40	< 24	95	320	< 24	14,700	460	< 24	120	60	< 24

*** lost during cleanup.**

(hand-wipe 2) contact with OCF5. This indicated that the CPs easily transfer from the cured OCF to the hand after only one single hand contact of 10 s. After handwashing for 10 s, MCCPs were still present on the hand (hand-wipe 3) with levels ranging from 14.7 to 38.0 μg per hand, corresponding to 3–11% of the total MCCPs observed after contact with OCF5 (hand-wipe 2). In addition to MCCPs, OCF5 also contained 0.9% w/w LCCPs and 0.9% w/w TCIPP (Table 2). Comparable to the MCCPs, a significant increase in LCCPs ($P < 0.05$) and TCIPP ($P < 0.01$) levels was observed on the hand (hand-wipe 2) after contact with OCF5, with levels ranging from 4.3–11 μg and 0.8–1.2 μg per hand, respectively. The variation between the triplicate analyses for the LCCPs was 51%, which is comparable to the 61% observed for the MCCPs with the same downward trend, indicating that the initial transfer is more noticeable, although it is not so severe at lower concentrations. The variation between the triplicate analysis for TCIPP was lower, only 20%. This might indicate that TCIPP is more homogeneously distributed on the surface in the foam. After handwashing, the LCCPs were still present on the hands with levels ranging from 0.4 to 0.9 μg per hand, TCIPP was easily washed off from the hands, probably because TCIPP is more water-soluble than the CPs. Liu et al. (2017) also demonstrated that 76% of the TCIPP was removed from the hands after washing with soap and water.

For the other three samples (OCF2, 4, and 9) which were dominated by MCCPs (11% *w/w*), WLCCPs (29% *w/w*), and TCIPP (23%), respectively, similar findings were observed compared to OCF5 (Table 2). A significant increase ($P < 0.05$) in MCCP levels (up to two orders of magnitude) was observed after contact with OCF2 (hand wipe 2), with levels ranging from 1.9 to 3.9 μg per hand. For OCF4, an increase in WLCCP levels (up to two others of magnitude) were found with levels ranging from 4.7 to 17.5 μg per hand. After contact with OCF9 the TCIPP levels significantly increased ($P < 0.01$) two orders of magnitude with levels ranging from 2.4 to 2.7 μg per hand. Overall, these findings indicate that CPs and TCIPP easily migrate from the cured OCFs to our hands after direct contact for only 10 s

OCF4 also contained 1.3% w/w MCCPs and 4% w/w TCIPP and for both compounds increased levels were observed after contact which OCF4. However, after handwashing, only the WLCCPs were still present with levels ranging from 0.3 to 0.8 μg per hand (hand-wipe 3) corresponding to 4–14% of the total WLCCPs observed after contact with OCF4 (hand-wipe 2). The MCCPs and TCIPP levels after handwashing (hand-wipe 3) were comparable with the levels found before contact with the OCF (hand-wipe 1). Similar findings were observed for OCF2 and 9 whereby the less dominant CPs with levels < 4 μg per hand were washed from the hands. The TCIPP levels were easily washed from the hand after hand contact with all four OCFs.

In general, the higher CPs and TCIPP concentrations in the OCFs resulted in a greater transfer after 10 s hand contact, whereby an exponential trend was observed. For example, the relative amount of MCCPs migrating from the OCF to the hand (hand-wipe 2), related to the total amount in the OCF, was for OCF5 (containing 49% w/w MCCPs) approximately 20 times higher than for OCF2 (containing 11% w/w MCCPs) and OCF4 (containing 1.3% MCCPs). The relatively high MCCP level (49% *w/w*) in OCF5 seems to enhance the migration of the LCCPs and TCIPP from the OCF. The relative amounts of LCCPs and TCIPP that migrate from OCF5 (containing 0.9% w/w LCCPs) are approximately 23 times higher compared to OCF4, which contains a much higher LCCPs level (29% *w/w*). The same finding was observed for TCIPP. The relative amount of TCIPP migrating from OCF5 to the hand was approximately 11 times higher compared to OCF9 although the TCIPP level in OCF5 (containing 0.9% w/w TCIPP) was much lower than that in OCF9 (containing 23% w/w TCIPP). This suggests that the overall percentage of CPs and/or TCIPP in the OCFs may influence the characteristics and/or structure of the OCFs, and therefore, the overall migration rates to the hands. Most likely, it is especially the composition change of the foam that causes this, rather than the CP mixtures in a chemical sense. A relatively high variation (RSD = 61%) was observed between the triplicate analyses (OCF5), showing that compounds transferred from the foam to the hand decreased after the first experiment and to a lesser extent after the second and third experiments. This might indicate that after the first contact most of the CPs on the outer surface of the foam are transferred to the hand and, therefore, the second and third contact results in lower CP levels on the hands. Nevertheless, this decreasing trend was not as clear for the other OCFs.

This pilot study shows that even after 10 s of handwashing the CPs were still present on the hand, which may explain why CPs were also detected on hand-wipe 1. However, the CPs detected on hand-wipe 1 were, in some cases, not related to the OCFs but probably to different sources. For example, in experiments 1, 2, and 3 with OCF5 the MCCP homologue patterns in hand-wipe 1 were dominated by MCCP 42%Cl, whereas the homologue pattern, after contact with OCF5, on hand-wipes 2 and 3 were dominated by MCCP 52%Cl, comparable to the pattern in OCF5. Therefore, interference is negligible (Table S5). A visual example of the different homologue patterns observed in hand-wipes 1, 2, and 3 after hand contact with OCF5 is given in Fig. 4. This figure shows that the MCCPs pattern in hand-wipe 1 is different from that in hand-wipes 2 and 3 which are comparable with the MCCP pattern in OCF5. This

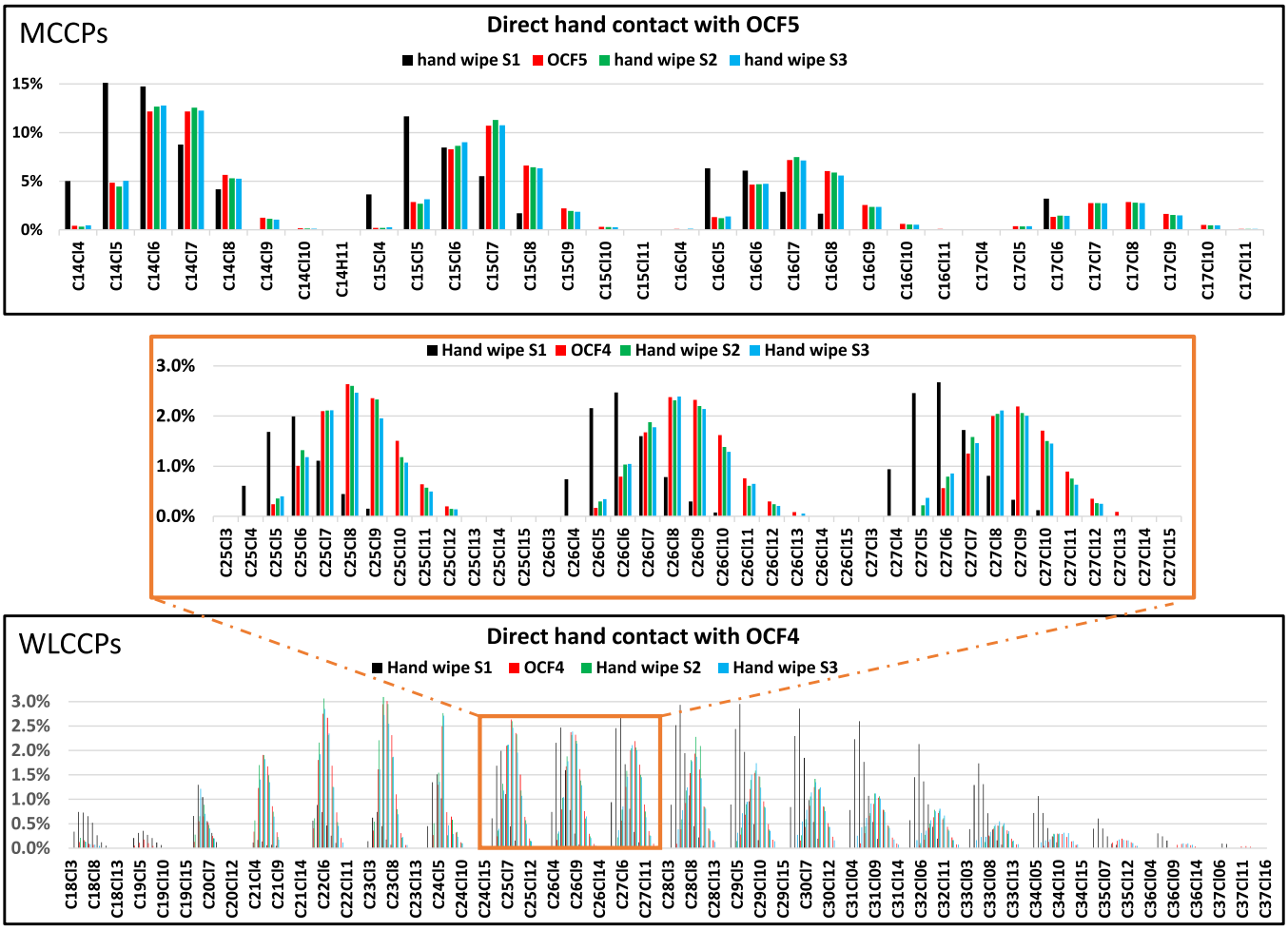

Fig. 4. Visual examples of the MCCPs and WLCCPs homologue pattern observed in the OCF4 and 5 compared with the levels observed in the hand-wipes before and after contact with OCF4 (Exp. 2) and 5 (Exp. 1).

highlights that the CPs found on hand-wipe 1 are not related to OCF5 but to a different source. Comparable findings were observed for the WLCCP pattern observed in OCF4 (Fig. 4). Differences in CP homologue patterns were also observed for experiment 1 with OCF2 whereby relatively high MCCP levels of 260 ng per hand (hand-wipe 1) were found. The MCCPs homologue pattern in hand-wipe 1 was dominated by MCCP 52%Cl, whereas hand-wipes 2 and 3 were dominated by MCCP 42%Cl, comparable to the pattern in OCF2. This indicated that despite the relatively high MCCPs level (260 ng per hand) in hand-wipe 1, it indirectly does not interfere with the experiment. This highlights the importance of not only reporting the CP concentrations but also the CP homologue patterns, which may help to distinguish between the CP levels in the blank and the samples. No explanation could be given for the relatively high WLCCPs concentration observed in exp. 1 with OCF2 of 530 ng per hand (hand-wipe 1).

3.5. Human and environmental exposure

Various studies (Estill et al., 2019; Stapleton et al., 2014; Sugeng et al., 2017; Tan et al., 2018) have shown that TCIPP can be present on our hands. Recently, evidence was also found for the presence of CPs (Yuan et al., 2020). TCIPP concentrations were found on hand-wipes of toddlers (n = 21) from the Netherland (Sugeng et al., 2017), children (n = 43) from the US (Stapleton et al., 2014), and adults (n = 51) and children (n = 31) from South-China (Tan et al., 2018) with levels ranging from 23 to 817 ng/wipe, < 13–532 ng/wipe, and < 2–115 ng/wipe, respectively. The highest TCIPP levels were found on hand-wipes from spray polyurethane foam workers after a one-day shift (median = 88,700 ng/wipe; n = 29) (Estill et al., 2019). The highest average TCIPP level (2520 ng per hand) on hand-wipe 2 after contact with OCF9 was 6–44 times higher compared to the highest levels observed on the hand-wipes of children and adults from the Nederlands, US, and South-China. Comparing our results to the hand-wipes of the spray polyurethane workers (Estill et al., 2019) the TCIPP levels were 18 times lower, which is probably influenced by the shorter contact time (10 s in our study compared to one day).

Yuan et al. (2020) detected CPs (C_7 –C_{48}) in the range of 0.04–18 μg (median of 0.95 μg) on hand-wipes taken from sixty individual participants in a Norwegian cohort study. The highest average CP levels (360 μg per hand) on hand-wipe 2 after contact with OCF5 was 40 times higher than the highest CP level observed by Yuan et al. (2020). Although TCIPP and CPs may already present be on our hands in relatively high concentrations (Estill et al., 2019; Yuan et al., 2020; Stapleton et al., 2014; Sugeng et al., 2017; Tan et al., 2018), contact with cured OCFs containing TCIPP and CPs significantly increases these TCIPP and CPs levels. Therefore, insulation foams such as OCFs could be a source of indoor exposure to TCIPP and CPs, especially because OCFs are commonly used in houses and office buildings for filling cracks, holes, gaps, and crevices, insulating pipes, tubes, electrical lines to increase the heat, draft, and sound insolation. When used appropriately, OCFs are in general applied to the inner shell of buildings. Therefore, 60–80% of the OCFs are covered with plaster (EU risk assessment, 2008). This may indicate that most of the exposure risk to CPs or TCIPP is during applying the foam or shaving, removing, or cutting away

excess of cured foam. However, various studies have shown that TCIPP migrates from the SPFs to air, which is depending on ventilation (flow rate), temperature, humidity, and type of SPF and chemical (Estill et al., 2019; NIST Technical Note, 1921, 2017).

The product description of the OCF1 can state that the foam could also be used for creating model landscapes and three-dimensional models (maquettes). However, the significantly increased CPs and TCIPP levels on the hand after contact with the cured OCFs highlights the importance of protection (such as gloves) also after the OCFs have cured. The US Environmental Protection Agency (EPA) recommends strongly that "*this product is inappropriate for "creative" uses such as science or art projects and should not be used around children*" (US Environmental Protection Agency EPA, 2020).

Only four used TCFs were analysed, although each TCF was applied by different companies it is not representative for all TCFs used as floor insulation in the Netherlands. None of the TCFs contained CPs. Only TCIPP with levels ranging from 7% to 9% w/w were detected. TCFs are mainly applied by professionals which use personal protective equipment (PPE) when applying the foam. Previous work of Bello et al. (2018) investigating the exposure to OPFRs in SPF applicators, showed that dermal exposure may be the primary exposure pathway for TCIPP, although inhalation or incidental ingestion could not be excluded. Even when the workers used PPE, an increase (25–35 times) of the urinary TCIPP biomarkers was observed during work shifts (Bello et al., 2018). The physicochemical properties of TCIPP are different than those of CPs which also vary depending on their carbon chain length and degree of chlorination (Hilger et al., 2011; Glüge et al., 2013). However, the importance of dermal exposure as a pathway for TCIPP from SPFs (Bello et al., 2018), highlights the importance of further investigating dermal exposure from OCFs as an exposure pathway for CPs.

A recent advisory report by the Dutch Council's Committee on SPF estimated that SPFs have been used to insulate around 250,000 homes in the Netherlands and participating residents have reported health problems (Health Council of the Netherlands, 2020). The Committee believes that SPF-related complaints are not always investigated or registered and therefore recommends that there should be a central registry for residents. The committee also notices that even if the SPF is professionally correctly applied, the low levels of hazardous chemicals that still migrate from the cured foam over time may not be directly harmful, however long-term exposure effects are unknown and should be studied. Information on the exposure of residents to flame retardant (e.g. TCIPP) present in the SPFs is also lacking. Until today, only one peer-reviewed paper reported on the in-vitro absorption of CPs through human skin (Scott, 1989). Two technical mixtures were tested in this study: Cereclor 56L (SCCP mixture) and Cereclor S52 (MCCP mixture). Scott (1989) found that Cereclor 56 L was absorbed by the skin after 7 h of contact with a mean rate of 40 ng/h/cm^3. However, no absorption by the skin was observed for Cereclor S52 after 56 h of contact. Unfortunately, there were some limitations to this study. First of all, no CPs were analysed in the receptor fluid, only ^{14}C-n-pentadecane was selected to represent Cereclor S52, and the ^{14}C-n-undecane represented Celeclor 56 L. Furthermore, the accumulation of CPs in the skin layer was not taken into account. However, this may also contribute to the overall exposure to CPs. This was suggested by Abdallah et al. (2015) for polybrominated diphenyl ethers (PBDEs) after studying the effect of bromine substitution on human dermal absorption of PBDEs. They observed that lower brominated PBDEs were found in higher amounts in the receptor fluid (indication for dermal absorption) compared to the higher brominated PBDEs. The opposite pattern was observed for the accumulation in the skin itself, whereby the more lipophilic higher brominated PBDEs (up to hexabromodiphenyl ethers) were more dominant and may more slowly migrate to the bloodstream over time. Similar findings were observed for polychlorinated biphenyls (PCBs) by Garner and Matthews (1998) where the accumulation of the PCBs in the skin of male rats increased with increasing halogenation. Abdallah et al. (2015) argue that for the risk assessment, also the chemicals that are accumulated in the skin and become systemically available over time should be considered. Based on our results, CP could not be completely removed from the hands indicating that exposure studies should also consider chemicals remaining in the skin.

The global OCFs production was $>$ 750 million cans in 2018 and increases every year (IAL consultants, 2020). Based on the average CPs levels of 25% *w/w* found in this study in the 500 mL OCF cans, approximately 94 million litres of CPs are distributed globally per year through OCFs cans, representing 5% of the total CPs production per year base on a global production for CPs of 2 million tonnes /year (SETAC, 2020). Although only a few TCFs were analysed in this study, similar calculations were performed for TCIPP in TCFs. The global SPF production was $>$ 600,000 tonnes in 2018. With an average TCIPP concentration of 8% *w/w* the global distribution for TCIPP through TCFs would be 48,000 tonnes per year. These findings suggest that OCFs and TCFs can be an important emission pathway of CPs and TCIPP to the environment. TCFs are used as floor insulation especially in older houses to reduce heat energy losses. In the older houses, the floor of the crawl area under the house is typically unpaved ground. Through condensation, TCIPP may leach from the isolated floor into the soil and groundwater.

After end-of-life, it is challenging to recycle used OCFs and TCFs because they adhere to almost all surfaces. It is therefore hard to separate the SPF from the construction waste such as bricks, concrete, cement board, plastic pipes, and wood. Therefore, in most countries, the OCF and TCF waste is incinerated or ends up at landfills. There are techniques available to separate the SPFs from brick, concrete, and wood by using cyclones or wind-sifting although it is not economically attractive to recycle the foam due to inconsistent supply and the low cost for producing new SPFs. Even after sorting SPFs from concrete or bricks, the foams are incinerated (EU risk assessment, 2008; Kennisplatform Gespoten PURschuim, 2020). In Europe, only Germany recycles the OCF cans because, unlike the cured PU foams, they have been classified as hazardous waste (EU risk assessment, 2008).

Based on laboratory leaching experiments with furniture polyurethane foams containing 1.7% *w/w* TCIPP, Stubbings & Harrad (Stubbing and Harrad, 2018) concluded that landfill leaching is a potentially significant pathway for TCIPP emissions to the environment. Christale et al. (2019) quantified TCIPP in well water downstream of a bulk waste storage area (mattresses, upholstered furniture, etc.), and concluded that improper disposal can pollute groundwater with TCIPP. Therefore, further research is needed to investigate the leachability of the TCIPP and CPs from the SPFs and OCFs, also because after end-of-life, the SPFs and OCFs may end up at landfills from which TCIPP and CPs may leach into the environment.

CRediT authorship contribution statement

Sicco Brandsma: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Funding acquisition. **Martin Brits**: Conceptualization, Methodology, Writing - review & editing, Formal analysis, Validation, Investigation. **Jacob de Boer**: Conceptualization, Methodology, Writing - review & editing. **Pim Leonards**: Conceptualization, Methodology, Writing - review & editing.

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.

Acknowledgments

This study was funded by the Dutch Research Council (NWO) (VENI2017-grant 722.017.009).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.125758.

References

Abdallah, M.A.E., Pawar, G., Harrad, S., 2015. Effect of bromine substitution on human dermal absorption of polybrominated diphenyl ethers. Environ. Sci. Technol. 49, 10976–10983.

Ballesteros-Gómez, A., Brandsma, S.H., de Boer, J., Leonards, P.E.G., 2014. Direct probe atmospheric pressure photoionization/atmospheric pressure chemical ionization high-resolution mass spectrometry for fast screening of flame retardants and plasticizers in products and waste. Anal. Bioanal. Chem. 406, 2503–2512.

Bello, A., Carignan, C.C., Xue, Y., Stapleton, H.M., Bello, D., 2018. Exposure to organophosphate flame retardants in spray polyurethane foam applicators: role of dermal exposure. Environ. Int. 113, 55–65.

Bogdal, C., Alsberg, T., Diefenbacher, P.S., MacLeod, M., Berger, U., 2015. Fast quantification of chlorinated paraffins in environmental samples by direct injection high-resolution mass spectrometry with pattern deconvolution. Anal. Chem. 87, 2852–2860.

Brandsma, S.H., De Boer, J., Van Velzen, M., Leonards, P.E.G., 2014. Organophosphorus flame retardants (PFRs) and plasticizers in house and car dust and the influence of electronic equipment. Chemosphere 116, 3–9.

Brandsma, S.H., Leonards, P.E.G., Leslie, H.A., de Boer, J., 2015. Tracing organophosphorus and brominated flame retardants and plasticizers in an estuarine food web. Sci. Total Environ. 505, 22–31.

Brandsma, S.H., Mourik, L., O'Brien, J.W., Eaglesham, G., Leonards, P.E.G., De Boer, J., Gallen, C., Mueller, J., Gaus, C., Bogdal, C., 2017. Medium-chain chlorinated paraffins (CPs) dominate in Australian sewage sludge. Environ. Sci. Technol. 51, 3364–3372.

Brandsma, S.H., Brits, M., Groenewoud, Q., van Velzen, M., Leonards, P.E.G., de Boer, J., 2019. Chlorinated paraffins in car tires recycled to rubber granulates and playground tiles. Environ. Sci. Technol. 53, 7595–7603.

Brits, M., de Boer, J., Rohwer, E.R., De Vos, J., Weiss, J.M., Brandsma, S.H., 2020. Short-, medium-, and long-chain chlorinated paraffins in South African indoor dust and cat hair. Chemosphere 238, 124643.

Christale, J., Bele, T.G.A., Lacorte, S., de Marchi, M.R.R., 2019. Occurrence of flame retardants in landfills: a case study in Brazil. Environ. Res. 168, 420–427.

de Boer, J., Stapleton, H.M., 2019. Toward fire safety without chemical risk. Science 364, 231–232.

Handbook of environmental chemistry. In: De Boer, J. (Ed.), 2010, Chlorinated Paraffins, Vol. 10. Springer, Heidelberg, Germany.

DIN 4102–11998. Fire Behavior of Buildings Materials and Buildings Components—Part 1: Buildings Materials, Concepts, Requirements and Tests.

Drouillard, K.G., Hiebert, T., Tran, P., Tomy, G.T., Muir, D.C.G., Friesen, K.J., 2009. Estimating the aqueous solubilities of individual chlorinated n-alkanes (C10-C12) from measurements of chlorinated alkane mixtures. Environ. Toxicol. Chem. 17, 1261–1267.

Dzhordzhio Naldzhiev, D., Mumovic, D., Strlic, M., 2020. Polyurethane insulation and household products – a systematic review of their impact on indoor environmental quality. Build. Environ. 169, 106559.

El-Sayed Ali, T., Legler, J., 2010. Overview of the Mammalian and Environmental Toxicity of Chlorinated Paraffins. In: de Boer, J. (Ed.), The Handbook of Environmental Chemistry. Springer, pp. 135–154.

Estill, C.F., Slone, J., Mayer, A.C., Phillips, K., Lu, J., Chen, I., Christianson, A., Streicher, R., La Guardia, M.J., Jayatilaka, N., Ospina, M., Calafat, A.M., 2019. Assessment of spray polyurethane foam worker exposure to organophosphate flame retardants through measures in air, hand wipes, and urine. J. Occup. Environ. Hyg. 16, 477–488.

Estill, C.F., Slone, J., Mayer, A., Chen, I.C., Guardi, M.J., 2020. Worker exposure to flame retardants in manufacturing, construction and service industries. Environ. Int. 135, 105349.

EU risk assessment, 2008. European Union Risk Assessment Report Tris(2-chloro-1-methylethyl) phosphate (TCPP). CAS No: 13674–84-5, May.

Farhat, A., Crump, D., Chiu, S., Williams, K.L., Letcher, R.J., Gauthier, L.T., Kennedy, S. W., 2013. In ovo effects of two organophosphate flame retardants—tcpp and tdcpp—on pipping success, development, mrna expression, and thyroid hormone levels in chicken embryos. Toxicol. Sci. 134, 92–102.

Garner, C.E., Matthews, H.B., 1998. The effect of chlorine substitution on the dermal absorption of polychlorinated biphenyls. Toxicol. Appl. Pharmacol. 149, 150–158, 150−15.

Glüge, J., Bogdal, C., Scheringer, M., Buser, A.M., Hungerbühler, K., 2013. Calculation of physicochemical properties for short- and medium-chain chlorinated paraffins. J. Phys. Chem. Ref. Data 42, 023103.

Glüge, J., Wang, Z., Bogdal, C., Scheringer, M., Hungerbühler, K., 2016. Global production, use, and emission volumes of short-chain chlorinated paraffins – a minimum scenario. Sci. Total Environ. 573, 1132–1146.

He, C., Wang, X., Thai, P., Baduel, C., Gallen, C., Banks, A., Bainton, P., English, K., Mueller, J.F., 2018. Organophosphate and brominated flame retardants in Australian indoor environments: levels, sources, and preliminary assessment of human exposure. Environ. Pollut. 235, 670–679.

He, C., van Mourik, L., Tang, S., Thai, P., Wang, X., Brandsma, S.H., Leonards, P.E.G., Thomas, K.V., Mueller, J.F., 2021. In vitro biotransformation and evaluation of potential transformation products of chlorinated paraffins by high resolution accurate mass spectrometry. J. Hazard. Mater. 405, 124245.

Health Council of the Netherlands2020. Spray Polyurethane Foam Insulation and Health. The Hague: Health Council of the Netherlands, publication no. 2020/24.

Hilger, B., Fromme, H., Volkel, W., Coelhan, M., 2011. Effects of chain length, chlorination degree, and structure on the octanol-water partition coefficients of polychlorinated n-alkanes. Environ. Sci. Technol. 45, 2842–2849.

Hilger, B., Fromme, H., Völkel, W., Coelhan, M., 2013. Occurrence of chlorinated paraffins in house dust samples from Bavaria, Germany. Environ. Pollut. 175, 16–21.

IAL consultants ⟨http://www.ialconsultants.com/uploads/CUBE_press_release/2018–12-18/SPF%20Press%20Release%202018.pdf⟩ Accessed October 2020.

Kennisplatform Gespoten PURschuim. ⟨https://www.gespotenpurschuim.nl/gespoten-purschuim/⟩. Accessed October 2020.

Kim, J.W., Isobe, T., Muto, M., Tue, N.M., Katsura, K., Malarvannan, G., Sudaryanto, A., Chang, K.H., Prudente, M., Viet, P.H., Takahashi, S., Tanabe, S., 2014. Organophosphorus flame retardants (PFRs) in human breast milk from several Asian countries. Chemosphere 116, 91–97.

Krätschmer, K., Schächtele, A., 2019. Interlaboratory studies on chlorinated paraffins: evaluation of different methods for food matrices. Chemosphere 234, 252–259.

Li, T., Wan, Y., Gao, S., Wang, B., Hu, B., 2017. High-throughput determination and characterization of short-, medium-, and long-chain chlorinated paraffins in human blood. Environ. Sci. Technol. 51, 3346–3354.

Liu, X., Ji, K., Choi, K., 2012. Endocrine disruption potentials of organophosphate flame retardants and related mechanisms in h295r and mvln cell lines and in zebrafish. Aquat. Toxicol. 114–115, 173–181.

Liu, X., Yu, G., Cao, Z., Wang, B., Huang, J., Deng, S., Wang, Y., 2017. Occurrence of organophosphorus flame retardants on skin wipes: Insight into human exposure from dermal absorption. Environ. Int. 98, 113–119.

Lucattini, L., Poma, G., Covaci, A., de Boer, J., Lamoree, M.H., Leonards, P.E.G., 2018. A review of semi-volatile organic compounds (SVOCs) in the indoor environment: occurrence in consumer products, indoor air and dust. Chemosphere 201, 466–482.

Marklund, A., Andersson, B., Haglund, P., 2005. Organophosphorus flame retardants and plasticizers in air from various indoor environments plasticizers in air from various indoor environments. J. Environ. Monit. 7, 814–819.

Netherlands Enterprise Agency (RVO) Accessed website on 2810 2020 ⟨https://www.rvo.nl/subsidie-en-financieringswijzer/seeh/eigenaar-en-bewoner⟩.

NIST Technical Note 1921. Characterization of emissions from spray polyurethane foam final report to U.S. consumer product safety commission. September 2017. https://doi.org/10.6028/NIST.TN.1921.

Olofsson, U., Brorström-Lundén, E., Kylin, H., Haglund, P., 2009. Comprehensive mass flow analysis of Swedisch sludge contaminations. Chemosphere 90, 28–35.

Pavel, C.C., and Blagoeva, D.T. 2018. Competitive Landscape of the EU's Insulation Materials Industry for Energy-efficient Buildings. ISBN 978–92-79–96383-4, ISSN 1831–9424. Accessed website on 28102020: ⟨https://publications.jrc.ec.europa.eu/repository/bitstream/JRC108692/kj1a28816enn.pdf⟩.

POPRC (Persistent Organic Pollutants Review Committee), 2017. Recommendation by the Persistent Organic Pollutants Review Committee to List Short-chain Chlorinated Paraffins in Annex A to the Convention. (UNEP/POPS/COP.8/14).

Schrenk, D., Bignami, M., Bodin, L., Chipman, J.K., del Mazo, J., Grasl-Kraupp, B., Hogstrand, C., Hoogenboom, R., Leblanc, J., Nebbia, S.C., Ntzani, E., Petersen, A., Sand, S., Schwerdtle, T., Vleminckx, C., Wallace, H., Brüschweiler, B., Leonards, P., Rose, M., Binaglia, M., Horváth, Z., Bordajandi, L.R., Nielsen, E., 2020. Risk assessment of chlorinated paraffins in feed and food. EFSA J. 18 (3) https://doi.org/10.2903/j.efsa.2020.5991.

Scott, R.C., 1989. In vitro absorption of some chlorinated paraffins through human skin. Arch. Toxicol. 63, 425–426.

SETAC ⟨https://globe.setac.org/setac-scicon-session-summaries/⟩ Accessed 2810 2020.

Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. Environ. Sci. Technol. 43 (19), 7490–7495.

Stapleton, H.M., Misenheimer, J., Hoffman, K., Webster, T.F., 2014. Flame retardant associations between children's handwipes and house dust. Chemosphere 0, 54–60.

Stockholm Convention. Short-chain chlorinated paraffins (SCCPs) ⟨http://chm.pops.int/Implementation/Alternatives/AlternativestoPOPs/ChemicalslistedinAnnexA/Shortchainchlorinatedparaffins(SCCPs)/tabid/5986/Default.aspx⟩ (Accessed 2810 2020).

Stubbing, W.A., Harrad, S., 2018. Leaching of TCIPP from furniture foam is rapid and substantial. Chemosphere 193, 720–725.

Sugeng, E.J., Leonards, P.E.G., van de Bor, M., 2017. Brominated and organophosphorus flame retardants in body wipes and house dust, and an estimation of house dust hand-loadings in Dutch toddlers. Environ. Res. 158, 789–797.

Sundkvist, A.M., Olofsson, U., Haglund, P., 2010. Organophosphorus flame retardants and plasticizers in marine and fresh water biota and in human milk. J. Environ. Monit. 12, 943–951.

Tan, H., Chen, D., Peng, C., Liu, X., Wu, Y., Li, X., Du, R., Wang, B., Guo, Y., Zeng, E.Y., 2018. Novel and traditional organophosphate esters in house dust from South China: association with hand wipes and exposure estimation. Environ. Sci. Technol. 52, 11017–11026.

US Environmental Protection Agency (EPA). Spray Polyurethane Foam Product Types. Website: ⟨https://www.epa.gov/saferchoice/spray-polyurethane-foam-product-types⟩ Accessed October 2020.

van Mourik, L.M., Gaus, C., Leonards, P.E.G., de Boer, J., 2016. Chlorinated paraffins in the environment: a review on their production, fate, levels and trends between 2010 and 2015. Chemosphere 155, 415–428.

Wang, Y., Yang, Y., Zhang, Y., Tan, F., Li, Q., Zhao, H., Xie, Q., Chen, J., 2019. Polyurethane heat preservation materials: the significant sources of organophosphorus flame retardants. Chemosphere 227, 409–415.
World Health Organization, 1998. Environmental Health Criteria 209, Flame Retardants: Tris(chloropropyl) phosphate and tris(2-chloroethyl) phosphate. Geneva, Switzerland.
Yuan, B., Brüchert, V., Sobek, A., de Wit, C., 2017. A.Temporal trends of C8−C36 chlorinated paraffins in Swedish coastal sediment cores over the past 80 years. Environ. Sci. Technol. 51, 14199–14208.
Yuan, B., Vorkamp, K., Roos, A.M., Faxneld, S., Sonne, C., Garbus, S.E., Lind, Y., Eulaers, I., Hellström, P., Dietz, R., Persson, S., Bossi, R., de Wit, C.A., 2019. Accumulation of short-, medium-, andlong-chain chlorinated paraffins in marine and terrestrial animalsfrom scandinavia. Environ. Sci. Technol. 53, 3526–3537.
Yuan, B., Tay, J.H., Papadopoulou, E., Haug, L.S., Padilla-Sánchez, J.A., de Wit, C.A., 2020. Complex mixtures of chlorinated paraffins found in hand wipes of a Norwegian cohort. Environ. Sci. Technol. Lett. 7, 198–205.
Zhao, F., Wan, Y., Zhao, H., Hu, W., Mu, D., Webster, T.F., Hu, J., 2016. Levels of blood organophosphorus flame retardants and association with changes in human sphingolipid homeostasis. Environ. Sci. Technol. 50, 8896–8903.