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Determining personal exposure to high production volume chemicals (HPVCs) and polycyclic aromatic hydrocarbons (PAHs) with silicone wristbands: A pilot study

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ABSTRACT

High production volume chemicals (HPVCs) and polycyclic aromatic hydrocarbons (PAHs) are semi-volatile organic compounds (semi-VOCs) of great environmental concern because of their presence worldwide and health problems resulting from long-term exposure to some of them. It is essential to have robust analytical methods to monitor the concentrations of these compounds not only in environmental samples but also individual exposure. In this pilot study we develop and validate a multiresidue analytical method based on ultrasound-assisted extraction and gas-chromatography mass spectrometry for the simultaneous determination of 56 semi-VOCs using silicone wristbands (SWBs) as personal passive samplers. The developed method provided recoveries between 43% and 114% on sampled SWBs and method detection and quantification limits in the range of 0.1–35 ng/g and 0.3–119 ng/g, respectively. A preliminary study was performed with a small group of adults living in the industrial city of Tarragona (north-eastern Spain) to evaluate the applicability of SWBs for monitoring individual exposure to the studied HPVCs and PAHs. Benzothiazoles, benzenesulfonamides, UV stabilisers and phenolic antioxidants were determined for the first time in SWBs. Phthalates (PAEs), stood out above the rest, accounting for 52% of the total concentrations. Diethylhexyl phthalate was the compound found at the highest concentrations with values between 1.1 and 82 μg/g. Carcinogenic and non-carcinogenic dermal risk assessment was performed for adults and considering two scenarios (low and high). PAHs were the compounds with the highest carcinogenic and non-carcinogenic dermal risk regardless of the exposure scenario. The second family of compounds that contributed the most to the total risk were PAEs but high punctual concentrations of these compounds caused significant differences between exposure scenarios.

1. Introduction

The increasing concern about environmental pollution has prompted research on human exposure to harmful organic contaminants of different characteristics. The results obtained from the analysis of environmental samples, *e.g.* water, air, sediments and biota, provide a comprehensive overview of the accumulation of these pollutants in outdoors (Kurt-Karakus et al., 2018; Zou et al., 2018; Wania and Shunthirasingham, 2020; Huang et al., 2022; Vallecillos et al., 2024). Indoor pollution has also been a key area of focus for the scientific community. Studies have focused on the determination of volatile organic compounds (VOCs) and semi-VOCs in dust or air samples from workplaces, schools and houses (Ninyà et al., 2022; Núñez et al., 2022).

A crucial consideration in these studies is that most of them focus on collecting samples from a specific location. However, people move from place-to-place multiple times every day, and these continually changing locations make environmental samples from a single location unrepresentative. Starting in 2014, researchers began looking into the use of silicone wristbands (SWBs) for passive sample collection, which were presented as a comfortable, simple, and economical alternative

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(O'Connell et al., 2014; Anderson et al., 2017). In addition, as reported by Samon et al. (2022), SWBs not only take into account exposure to airborne pollutants but also other routes of exposure such as dermal contact. Semi-VOCs can also be transferred by particles adhering to skin or clothing or by the use of everyday products (personal care products, cleaning products, etc.). SWBs has been proved to effectively identify toxic compounds specific to tobacco, such as nicotine, and to monitor exposure to these compounds (Quintana et al., 2019). They have also been used as a monitoring method to determine semi-VOCs such as brominated flame retardants (BFRs), organophosphorus esters (OPEs), PAHs and phenols, for instance, in occupational environments and to evaluate exposure in children (Romanak et al., 2019; F. Wang et al., 2020; Hamzai et al., 2022; Levasseur et al., 2022). SWBs have also been used as sensitive passive samplers to detect population exposure to pesticides present in the diet and environment (Aerts et al., 2018; Donald et al., 2016). Increased research into the use of SWBs has led to comparisons between their use and that of other personal passive samplers, such as hand wipes and household dust, to determine the presence of various compounds (Hammel et al., 2020; Levasseur et al., 2021). Non-invasive human matrices (sweat, saliva and urine) are suitable for exposure to more polar compounds such as pesticides, illicit drugs and antibiotics, among other (Genuis et al., 2016; Brasier et al., 2020; Sotom et al., 2023). Unlike the previously mentioned passive samplers, which are cumulative over time, SWBs enable you to know the specific duration of your exposure to the pollutant.

This has led to the exploration of different alternatives for the extraction and subsequent analysis of this kind of samples in order to obtain fast and efficient analytical methods. The most extensively used extraction techniques used for SWBs include solid-liquid extraction (SLE), ultrasound-assisted extraction (UAE), solid-liquid extraction followed by solid-phase extraction (SPE), or the QuEChERS technique (Quick, Easy, Cheap, Effective, Rugged, and Safe) (De Coensel et al., 2008; Quintana et al., 2019; Xie et al., 2021). The extracts are analysed by high-pressure liquid chromatography-mass spectrometry (HPLC-MS) or gas chromatography-mass spectrometry (GC-MS) depending on the target compounds to be determined (Ratola et al., 2006; Levasseur et al., 2022). Considering the evolution of this type of personal passive sampling, we aimed to expand the catalogue of semi-VOCs effectively determined using this approach. We focused on HPVCs, as their common use in a wide range of industries and production processes favour their presence in urban and industrial environments. Many of these compounds are integral parts of everyday consumer products, such as plastics, pesticides, flame retardants, and electronic products (OECD, 2004; Herrero et al., 2014). Prolonged exposure to HPVCs through every day products may cause different health effects, such as respiratory issues (*e.g.* asthma and allergies), carcinogenesis and cardiovascular illnesses among others (Voss et al., 2005; Maceira et al., 2020; Hou et al., 2021). In addition, PAHs are also of significant interest, as they are derived from a variety of sources, such as the combustion of organic materials, the petrochemical industry, vehicle emissions and atmospheric deposition (Keith, 2015). There is a need for effective methods for precisely determining and quantifying PAHs, as they are persistent and bioaccumulative pollutants with carcinogenic and mutagenic effects. Because of this, they are of great interest for studies of human exposure and environmental toxicology (Nisbet and LaGoy, 1992; Wang et al., 2021).

Research efforts have focused on different families of compounds, including benzothiazoles (BTHs), ultraviolet stabilisers (Tinuvins), synthetic phenolic antioxidants (PAs), benzenesulfonamides (BSAs), PAEs, OPEs and PAHs. The objective of the present study was twofold. First, to develop an analytical method capable of simultaneously detecting 56 semi-VOCs, 38 HPVCs and 18 PAHs, through personal passive sampling with SWBs. Secondly, to assess human exposure and risk associated with dermal exposure to the target compounds for adults and considering high and low concentration scenarios. This would allow us to expand the body of research into personal exposure to HPVCs and PAHs, and thus, investigate how individual mobility and daily routines can affect individual exposure to these compounds.

2. Materials and methods

2.1. Chemicals and reagents

In this study we determined different HPVCs: Tinuvins: 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol (UV329), 2-(2-hydroxy-5-methylphenyl)benzotriazole (UV P), 2-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV326), 2- (2H-benzotriazol-2-yl)-4-methyl-6-(2-propeny)phenol (Ally1-BZT), 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol (UV328), 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole (UV320), and 2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol (UV327); PAs: 2,6- di-tert-butylcyclohexa-2,5-diene-1,4-dione (BHTI-Q), 3(2)-tert-butyl-4-methoxyphenol (BHA), 2-tert-butylbenzene- 1,4-diol (TBHQ), 2,6-di -tert-butyl-4-methylphenol (BHT), 3,5-di-tert-butyl-4-hydroxybenzaldehyde (BHT-CHO), 2,4-di-tert-butylphenol (2,4-DTBP), and 2-6-di-tert-butyl- 4-(hydroxymethyl)phenol (BHT-OH); BTHs: 2-chlorobenzothiazole (CIBT), 1-H-benzothiazole (BTH), 2-amino-1-H-benzothiazole (NH_2BT) 2-(methythio)-benzothiazole (MesBT), and 2-hydroxybenzothiazole (OHBT); OPEs: 2-ethylhexyl diphenyl phosphate (EHDP), tributyl phosphate (TBP), tris(2-chloroethyl)-phosphate (TCEP), triethyl phosphate (TEP), tritolyl phosphate (TTP), tris(2-chloroisopropyl) phosphate (TCPP), triphenyl phosphate (TPP), triisobutyl phosphate (TiBP), and tris(2-ethylhexyl) phosphate (TEHP); PAEs: diethylhexyl-adipate (DEHA), di-iso-butyl-phthalate (DiBP), dimethyl-phthalate (DMP), diethylhexyl-phthalate (DEHP), di-n-octyl phthalate (DnOP), and diethyl phthalate (DEP); BSAs: para-toluenesulfonamide (p-TSA), benzenesulfonamide (BSA), ortho-toluenesulfonamide (o-TSA), and N-methyl-para-toluenesulfonamide (Me-p-TSA). We also evaluated PAHs: benzo(a)pyrene (BaP), fluorene (Flu), pyrene (Pyr), benzo(e)pyrene (BeP), naphthalene (Nap), indeno (1,2,3-c,d) pyrene (InD), acenaphthene (Ace), benzo(j)fluoranthene (BjF), phenanthrene (Phe), dibenzo(a,h)anthracene (DiB), chrysene (Chr), benzo(g,h,i)perylene (BghiP), fluoranthene (Fla), benzo(k)fluoranthene (BkF), acenaphthylene (Acy), benz(a)anthracene (BaA), anthracene (Ant), and benzo(b)fluoranthene (BbF). The internal standards that we used were d10-acenaphthene (d10-Ace) for PAHs and Tinuvins, d12-chrysene (d12-Chr) for PAHs, d27-tributyl phosphate (d27-TBP) for OPEs, d8-naphthalene (d8-Nap) for PAHs, d4-1-H-benzothiazole (d4-BTH) for BTHs, d12-perylene (d12-Per) for PAHs, d10-phenanthrene (d10-Phe) for PAHs and PAs, d4-diethylhexyl-phthalate (d4-DEHP) for PAEs, and d4-para-toluenesulfonamide (d4-p-TSA) for BSAs. All compounds were purchased from Sigma Aldrich (St. Louis, MO, USA).

Individual standards of each target compound were built in ethyl acetate at a concentration of 1000 mg/L or 2000 mg/L. Working solutions of 100 mg/L in ethyl acetate were prepared for each family of compounds. The standard solutions were kept in the freezer at −20 °C until use.

The extraction solvents ethyl acetate and dichloromethane were GC grade (purity >99.9%) from Carlo Erba (Val de Reuil, France), while acetonitrile was HPLC grade, also from Carlo Erba. Isopropanol of 99.5% purity was from Fisher Scientific (Alcobendas, Madrid, Spain) and dimethylformamide (98%) was from Sigma Aldrich. Milli Q water was supplied by a Millipore purification system (Burlington, MA, USA). Helium gas with a purity of 99.999% was used for the GC-MS analysis (Carburos Metálicos, Tarragona, Spain).

2.2. Sample collection and storage

SWB samples from a group of adult volunteers living in the area of Tarragona (north-eastern Spain), one of the largest petrochemical sites in southern Europe, were used to develop the method and for

monitoring. Samples were collected using the 4.8-g SWBs with a width of 1.2 cm, an internal diameter of 6.5 cm and a length of 18 cm in Fig. 1S (Delfín Artesanias S.L., A Coruña, Spain). Each participant ($n = 24$) was provided with a conditioned SWB, and the sampling campaign took place between May and July 2023. The sampling time employed in the monitoring was 30 days. All the participants in the study work indoors and they were asked to wear the SWB 24 h a day regardless of their activity. Some of the volunteers reported that during bedtime they did not wear the SWB, but left it in the same room. The sampled SWBs were wrapped in aluminium foil, vacuum packed and stored at −20 °C until extraction and analysis.

2.3. Ultrasound-assisted extraction (UAE)

Following the procedure described by O'Connell et al. (2014), SWBs were superficially cleaned with Milli-Q water and isopropanol prior to the extraction procedure to remove any dirt or grease that might have accumulated during sampling. A total of 2 g of SWB cut lengthwise into small square pieces of approximately 1 cm in length were extracted with 10 mL of dichloromethane in a 25 mL glass vial using ultrasound for 15 min. PTFE syringe filters of 0.22 μm were used to filter the extracts. A volume of 400 μL of dimethylformamide was added to prevent loss of the most volatile target compounds and the extracts were evaporated in a vacuum laboratory rotary evaporator (Hettich Universal 32 R) to almost dryness. Next, 50 μL of a mixed solution containing 100 μg/mL of d4-p-TSA, d12-Per, and d12-Chr, and 200 μL of a mixed solution containing 10 μg/mL of d8-Nap, d4-BTH, d10-Ace, d27-TBP, d10-Phe, and d4-DEHP. Lastly, the extract was made up to 2 mL with ethyl acetate prior to GC-MS analysis.

2.4. Chromatographic analysis

An Ultra High-Performance Gas Chromatograph, GCMS-QP2010, equipped with a split/splitless injector and a mass spectrometer (Shimadzu Corporation, Izasa S.A., Madrid, Spain) was used for sample analysis. Electron impact was used as the ionisation source and a single quadrupole as the analyser. The extracts (2 μL) were automatically injected in splitless mode at a temperature of 250 °C. Chromatographic separation was achieved using a ZB-50 capillary column of 30 m × 25 mm i. d. and 0.25 μm film thickness (Phenomenex, Torrance, CA, USA). Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. The temperature program of the GC oven was initially set at 80 °C, followed by a linear temperature increase of 5 °C/min to 275 °C and at 20 °C/min to 310 °C (10 min). The GC-MS interface and ionisation source were set at 280 °C and 230 °C, respectively. The MS acquired data in SIM mode. Table 1S summarises the identification and quantification parameters for each target compound. More detailed information regarding the separation and detection of the target compounds can be found in García-Garcinuño et al. (2024).

2.5. Quality assurance & Quality control (QA/QC)

Following the conditions established in the literature for the determination of semi-VOCs (O'Connell et al., 2014; Quintana et al., 2021), all the material required for the extraction and evaporation procedures was thoroughly cleaned with isopropanol to avoid cross-contamination. Whenever possible, glassware was used to minimize the presence of some of the target compounds, specially PAEs, in the blanks. For quality assurance, instrumental blanks, procedural blanks and 1000 μg/L controls were included in the GC-MS batches.

To avoid contamination from the SWB manufacturing process, the methodologies described by Dixon et al. (2022) and Samon et al. (2022) were applied. More specifically, SWBs were conditioned in a Hereaus Thermo Scientific vacuum oven (Massachusetts, USA) at 200 °C for 24 h, wrapped in aluminium foil and stored at 4 °C until use.

The chromatographic method applied was validated by establishing the instrumental detection limits (IDLs), the instrumental quantification limits (IQLs), the linear range, the repeatability, and the reproducibility of all target compounds. The IDLs (signal-to-noise, S/N ratio equal to or higher than 3) were between 0.10 μg/L and 25 μg/L. As Table 1S shows, the IQLs (lowest calibration point) were in the range of 0.30 μg/L and 100 μg/L. Fifteen calibration levels, between 0.25 μg/L and 5000 μg/L, were evaluated. Two internal standard calibration curves by compound, for low and high concentrations, were built. The determination coefficients (r^2) of the calibration curves were always higher than 0.990. The highest calibration level was 5000 μg/L for all target compounds, except for EHDP and DiBP, which reached 2500 μg/L and DEHA which was up to 7500 μg/L. Repeatability and reproducibility at 1 mg/L ($n = 5$), in percentage of relative standard deviation (%RSD), were quite good with values between 8.5% and 17%, respectively.

2.6. Estimated dermal risk assessment

Two main pathways of human exposure to pollutants in SWBs, dermal and inhalation, have been identified in the literature (Quintana et al., 2019; Samon et al., 2022). Since Wang et al. (2019) and Dixon et al. (2018) reported that the concentrations of semi-VOCs found in SWBs strongly correlates with the ones found in handwipes and particulate matter of air (dermal exposure), rather than with the ones found in the vapour phase of air (inhalation), only daily intake via dermal absorption (EDI_{Dermal}) was evaluated. The concentrations of the target compounds found in SWB samples were used to estimate the daily intake via dermal absorption (EDI_{Dermal}). As all participants in the study were above the age of 18, EDI_{Dermal} were calculated only for adults. Two scenarios were taken into account: geometric mean concentrations and 95th percentile concentrations representing the low and high-case scenario, respectively. EDI_{Dermal} (mg/kg/day) were calculated following Eq. (1), which was based on the EPA's general equation (USEPA, 2001) and considering not only exposure during the sampling period (Yin et al., 2023), but also the average adult life expectancy needed for risk calculations (Christia et al., 2022). Following (USEPA, 2001, 2007) specifications, EDI_{Dermal} for compounds found at values lower than the method detection limits (MDLs), and the method quantification limits (MQLs) were performed by replacing the concentrations for MDL/2 and MQL/2, respectively.

$$EDI_{Dermal} = \frac{C_{SWB} \times SA_i \times ABS_d \times EF_i \times ED_i}{BW_i \times AT} \quad \text{Eq. (1)}$$

where C_{SWB} is the concentration (mg/cm^2/event) in SWB samples over a 30-day sampling; SA_i as the adult body surface of the volunteers calculated according to Du and Du Bois (1916) and taking into account a body percentage exposed of 15% (Yu et al., 2010) (2568 cm^2). The percentage of exposure was calculated considering the head, neck, hands and forearms, parts of the body that are exposed in springtime; ABS_d is the fraction of target compound absorbed through the skin and was set at 0.1 (unitless) by USEPA (2023) for semi-VOCs for which the value was not available. Published values of ABS_d were used for the following compounds: BTH 0.14 (Li et al., 2020), TBP, TPP, EHDP 0.17 (de la Torre et al., 2020); TEHP 0.219 and TCEP 0.283 (Christia et al., 2018), DMP 0.00048, DEP 0.01025, DiBP 0.0006, DEHP 0.000053 (Christia et al., 2019); EF_i as the frequency of exposure (12 event/year, event = 30-day sampling); ED_i as the exposure duration for adults (53 years); BW_i as the adult body weight of the volunteers (70 kg) and AT is the average time (days), 25,500 days for carcinogenic compounds and equal to ED_i for non-carcinogenic compounds.

The risk associated with the target compounds, differentiating between non-carcinogenic and carcinogenic compounds, was calculated through EDI_{Dermal}. For the non-carcinogenic assessment, Eq. (2), which is based on the hazard quotient (HQ_{Dermal}), was used. Eq. (3) was applied to estimate the carcinogenic risk assessment (CR_{Dermal}) (Christia et al., 2019):

Table 1
Recovery and repeatability values obtained with UAE for blank and sampled SWBs ($n = 5$, 1000 ng). Method validation parameters such as reproducibility ($n = 5$, 1000 ng), MDLs and MQL's are also shown.

Family	Compound	Blank SWB		Sampled SWB				
		Recovery (%)	Repeatability (%RSD)	Recovery (%)	Repeatability (%RSD)	Reproducibility (%RSD)	MDL (ng/g)	MQL (ng/g)
PAs	**BHT-Q**	97	5	93	8	17	0.5	1
	BHT	88	5	84	8	15	0.4	1
	2.4-DTEP	84	7	81	9	15	0.4	1
	BHA	91	10	85	16	21	0.6	1
	TBHQ	119	5	111	6	18	9	23
	BHT-CHO	85	10	79	12	16	0.4	1
	BHT-OH	80	11	75	14	21	7	10
BTHs	**BTH**	95	5	93	6	16	0.1	1
	ClBT	112	10	106	12	17	0.1	0.3
	MeSBT	109	3	102	5	15	0.3	1
	NH_2BT	112	7	103	9	15	7	10
	OHBT	93	10	84	12	27	6	60
Tinuvins	**UVP**	105	12	99	15	22	10	25
	Allyz-BZT	70	14	65	18	26	15	38
	UV320	57	6	53	6	16	1	2
	UV326	67	5	63	7	14	12	40
	UV329	71	10	66	12	20	15	38
	UV328	60	6	52	6	18	5	10
	UV327	67	5	61	7	17	8	12
OPEs	**TEP**	81	4	73	5	13	1	3
	TiBP	98	3	90	5	13	0.1	0.3
	TBP	116	1	106	3	11	0.3	0.5
	TCPP	96	8	90	10	21	0.3	11
	TCEP	55	7	51	9	18	10	15
	TEHP	61	10	54	12	20	0.2	1
	EHDP	50	9	43	11	23	1	6
	TPP	92	7	87	9	15	6	9
	TTP	95	12	90	15	26	8	28
PAEs	**DMP**	99	5	89	7	16	0.3	11
	DEP	117	5	109	7	14	0.3	1
	DiBP	82	10	77	13	25	0.1	0.4
	DEHA	42	15	38	18	28	1	7
	DEHP	128	20	114	28	49	0.1	9
	DnOP	115	15	103	17	22	0.3	1
BSAs	**BSA**	82	10	76	13	20	7	10
	o-TSA	91	14	83	16	23	0.4	1
	Me-p-TSA	107	8	98	10	19	5	3
	p-TSA	118	12	111	16	21	9	23
PAHs	**Nap**	101	5	93	7	12	0.1	0.3
	Ace	113	9	105	10	15	0.3	1
	Acy	111	6	104	8	14	0.3	0.5
	Flu	119	2	108	4	11	1	2
	Phe	120	12	114	15	19	0.3	0.4
	Ant	79	2	73	5	13	1	3
	Fla	80	10	76	13	21	1	3
	Pyr	54	10	48	12	20	1	2
	BaA	99	1	94	4	11	1	5
	Chr	115	5	111	7	16	2	23
	BbF	88	9	82	9	18	3	9
	BkF	108	1	102	3	13	7	25
	BjF	81	4	77	6	15	3	6
	BeP	119	8	112	10	17	2	4
	BaP	96	11	91	14	23	5	27
	DiB	88	10	84	12	19	30	119
	InD	91	8	86	10	25	29	58
	BghiP	78	4	71	6	12	35	70

$$HQ_{Dermal} = \frac{EDI_{Dermal}}{RfD \times ABS_{GI}} \quad \text{Eq. (2)}$$

$$CR_{Dermal} = \frac{EDI_{Dermal} \times SFO}{ABS_{GI}} \quad \text{Eq. (3)}$$

where a gastrointestinal absorption factor (ABS_{GI}) of 1 (unitless) was applied (Li et al., 2018; USEPA, 2023); RfD as the oral reference dose per compound (mg/kg/day); SFO as slope factor for oral in 1/(mg/kg/day). All RfD and SFO values were obtained from the USEPA Risk Assessment Information System database (RAIS, 2023) and are shown in Table 2S. Due to the limited number of RfD and SFO available, the non-carcinogenic risk was calculated for BTHs, OPEs, PAEs and PAHs, while the carcinogenic risk was calculated for the same families of target compounds except BTHs. As described Nisbet and LaGoy (1992), toxicity indices for PAHs were calculated from the toxic equivalency factors in relation to the potentially carcinogenic compound BaP.

3. Results and discussion

3.1. Optimisation of the extraction method

In this study, two different extraction methods were compared to maximize recoveries of target compounds from SWBs. According to previous research in the field, several extraction techniques have been

Table 2
Concentration range, average concentration, and detection rate (DR) of the target compounds organised by families.

Family	Compound	Concentration range (μg/g)	Average (μg/g)	DR (%)
PAs	**BHT-Q**	0.34–0.95	0.42	100
	BHT	n.d. - 3.7	0.30	57
	2.4-DTEP	n.d. - 0.22	0.07	74
	BHA	0.16–0.39	0.19	100
	TBHQ	4.3–9.1	5.4	100
	BHT-CHO	0.28–0.56	0.31	100
	BHT-OH	n.d. - 43	9.6	65
	∑PAs	5.1–55	16	–
BTHs	**BTH**	n.d. - 0.38	0.10	91
	CiBT	0.22–0.47	0.21	91
	MeSBT	n.d. - 0.29	0.01	78
	NH2BT	n.d. - 1.3	0.27	52
	OHBT	n.d. - 8.1	0.37	91
	∑BTHs	0.02–4.5	0.97	–
Tinuvins	**UV P**	n.d. - 0.73	0.29	61
	Allyz-BZT	n.d. - 9.5	1.6	65
	UV320	n.d. - 0.25	0.12	83
	UV326	n.d. - 1.1	0.41	91
	UV329	n.d. - 0.76	0.35	96
	UV328	n.d. - 0.50	0.26	96
	UV327	n.d. - 2.7	0.83	96
	∑Tinuvins	0.24–16	3.8	–
OPEs	**TEP**	<MQL-0.31	0.05	58
	TiBP	n.d. - 0.16	0.01	61
	TBP	<MQL - 0.24	0.08	100
	TCPP	0.41–7.6	3.3	100
	TCEP	0.11–1.1	0.30	100
	TEHP	n.d. - 1.2	0.37	91
	EHDP	n.d. - 3.5	0.21	30
	TPP	n.d. - 1.3	0.34	91
	TTP	n.d. - 0.55	0.23	96
	∑OPEs	0.53–16	4.9	–
PAEs	**DMP**	n.d. - 0.19	0.07	87
	DEP	0.08–4.4	1.3	100
	DiBP	<MQL - 1.5	0.08	100
	DEHA	0.62–12	3.6	100
	DEHP	1.1–82	34	100
	DnOP	0.72–7.8	2.1	100
	∑PAEs	2.5–11	41	–
BSAs	**BSA**	0.19–12.8	2.6	100
	o-TSA	<MQL - 2.8	0.41	100
	Me-p-TSA	n.d. - 6.1	0.84	96
	p-TSA	n.d. - 15	1.7	96
	∑BSAs	0.19–37	5.6	–
PAHs	**Nap**	n.d. - 0.28	0.10	65
	Ace	n.d. - 2.6	0.38	91
	Acy	0.24–0.50	0.27	100
	Flu	n.d. - 1.4	0.30	78
	Phe	0.22–0.52	0.24	100
	Ant	0.29–0.66	0.32	100
	Fla	0.30–0.61	0.32	100
	Pyr	0.30–0.37	0.33	100
	BaA	0.36–0.99	0.47	100
	Chr	0.35–0.70	0.38	100
	BbF	0.44–0.90	0.47	100
	BkF	n.d. - 1.1	0.39	74
	BjF	0.26–0.54	0.28	100
	BeP	0.37–0.75	0.39	100
	BaP	0.49–0.98	0.52	100
	DiB	n.d. - 0.54	0.34	61
	InD	n.d. - 0.42	0.30	57
	BghiP	n.d. - 0.47	0.23	48
	∑PAHs	3.7–15	6.0	–
	∑Total	12.3–251	78.8	–

n.d. = non detected, values below the method detection limits.
<MQL = values below the method quantification limits.

applied for the extraction of semi-VOCs from personal passive samples, including pressurised liquid extraction (PLE), UAE, and Soxhlet (De Coensel et al., 2008; Levasseur et al., 2021; Romanak et al., 2019). Recently, QuEChERS has also been used for the determination of tobacco-derived compounds in SWBs (Quintana et al., 2019). In order to develop a fast and cheap extraction method that would allow us to analyse as many SWB samples as possible per day, the two extraction techniques compared were QuEChERS and UAE.

For the optimisation process, the conditioned SWBs were cut into 1 cm segments and mixed to ensure sample homogeneity. Half of the SWB segments (2g) were spiked with 200 μL of a standard solution of 10 mg/L of the target compounds, and the other half was used to subtract those compounds still present after the conditioning step (SWB blanks). Extraction tests were performed in quintuplicate and regardless of the extraction process applied, only DEHP and DEHA were detected in the SWBs blanks and at concentrations below the IQLs.

The specific conditions for implementing the QuEChERS method were established based on previous experience in our research group and are specified in the supplementary material (Text 1S). However, the results obtained with this extraction technique were not satisfactory since most of the target compounds showed recoveries lower than 50%. The high polarity of the extraction solvent, acetonitrile, did not favour the affinity with the compounds under study, decreasing the extraction efficiency. Furthermore, the low recoveries of compounds such as BHT (8%), BHA (7%), Pyr (15%) and Chr (23%) resulted in high %RSD ($n = 5$) values between 27% and 45%. These results prompted the exploration of alternatives that would allow the use of a solvent with higher affinity for the compounds during extraction, which led us to investigate UAE.

Regarding UAE, based on the reviewed literature and the characteristics of our compounds, we selected low-polarity solvents such as ethyl acetate and dichloromethane as extraction solvents (Ratola et al., 2006; Cristale and Lacorte, 2013). In contrast to the results obtained with QuEChERS, initial trials with UAE using dichloromethane as the solvent showed good recoveries in all cases and %RSD ($n = 5$) between 1% and 20%. On the other hand, recoveries obtained with ethyl acetate as the extraction solvent (Table 3S) were significantly lower than those found with dichloromethane, ranging between 30% and 40%, especially for the more volatile compounds and poor %RSD (>30%, $n = 5$).

Once we opted for dichloromethane as extraction solvent, we optimised the UAE in terms of speed and efficiency by experimenting with different extraction times: 15 min, 30 min and 60 min. As Table 1 shows, the recoveries obtained with 15 min of extraction ranged between 70% and 128% for most of the target compounds. Slightly lower recoveries were found for the following compounds: UV320 (57%), UV326 (67%), UV328 (60%), UV327 (67%), TCEP (55%), TEHP (61%), EHDP (50%), DEHA (42%), and Pyr (54%). The %RSD ($n = 5$) values were below 16% for all target compounds, except for DEHP with 20% (Table 1). Although a slight increase in the recoveries of some compounds was observed with 30 min and 60 min extractions (Table 4S), 15 min was selected as the optimal extraction time to prioritise the development of an efficient and rapid method.

3.2. Optimisation of sampling time

The sampling time was optimised to maximize the amount of target compounds adsorbed to the SWBs but avoiding saturation and possible desorption problems. Based on the sampling periods used in previous studies for the personal passive sampling of semi-VOCs with SWBs (Bergmann et al., 2017; Manzano et al., 2019), sampling times of 15, 30 and 45 days were tested. Three conditioned silicone WBs were provided to five of the study participants and were collected at 15-day intervals. As an example, the graphs in Fig. 1 show the concentration (ng/g) of the compound in the SWB versus the sampling time of one target compound per family. The results obtained with different sampling times indicated a common trend of an optimal sampling time of 30 days for most of the target compounds. At 45 days the concentrations tended to stabilise or decrease, except for compounds such as DiBP and Me-p-TSA, which increased. Fig. 2S provides more detailed information on the concentration trend followed by the target compounds at the different sampling

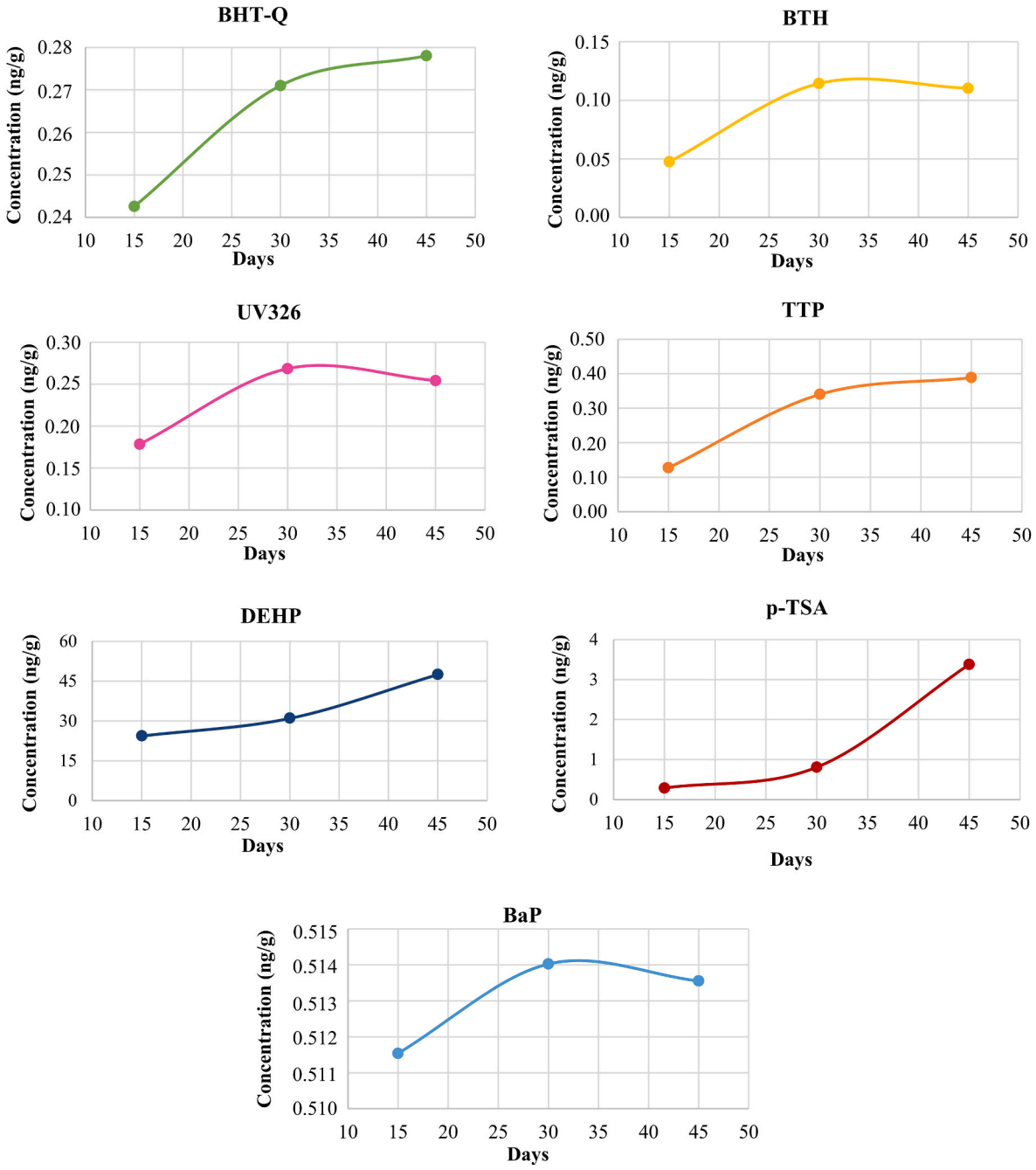

Fig. 1. Graphs showing the optimisation of the sampling time (15, 30 or 45 days) for one compound from each family. Concentration (ng/g) of the compound in the SWB vs sampling time.

times evaluated. Comparing the optimal sampling time in our study with the sampling times chosen by other authors using similar preconditioned SWBs revealed that, the number of compound families and the environments evaluated are the factors influencing the optimisation of the sampling time. Paulik et al. (2018) applied a sampling time of 21 days to assess personal exposure to PAHs of participants living or working near a rural natural gas extraction (Carroll County, Ohio, U.S.). Meanwhile, a sampling time of 14 days was used to evaluate personal exposure to OPEs in people living in Guangzhou (South China) (Xie et al., 2021). On the other hand, in studies investigating the simultaneous determination of different families of compounds such as insecticides, flame retardants, PAHs and plasticisers, the sampling time was similar to the one we chose, consisting of 30–34 days to be able to determine the target compounds at quantifiable levels in rural Peru (Bergmann et al., 2017). Shorter sampling times of 1 or 2 days were applied in studies carried out in work environments, fire stations or beauty salons, with high concentration levels of PAHs, OPEs and PAEs (Craig et al., 2019; Caban-Martinez et al., 2020; Levasseur et al., 2022).

3.3. Method validation

Once the UAE and the sampling time have been optimised, the whole method was validated. The optimal UAE/GC-MS method was applied to sampled SWBs to evaluate the recoveries in real WB samples. MDLs, MQLs, repeatability and reproducibility were also calculated.

The procedure described in section 3.1 was applied to perform recovery, repeatability and reproducibility tests with SWBs (n = 5) sampled for 30 days and spiked with 200 μL of a standard solution of 10

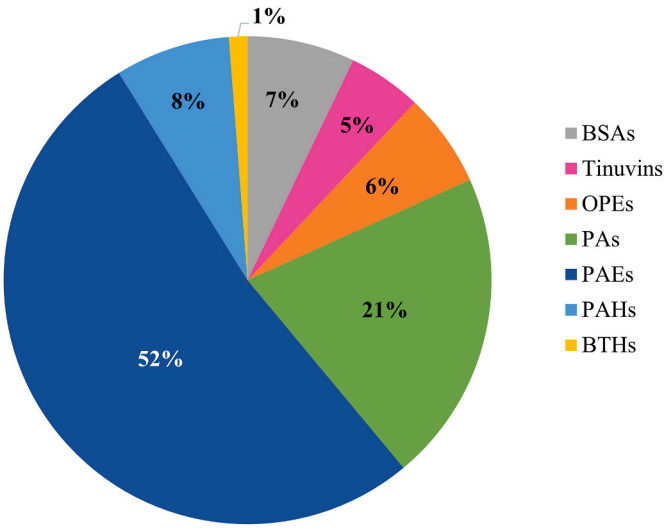

Fig. 2. Pie chart showing the percentage contributions of each family of compounds found in the WB samples analysed.

mg/L. Blanks of the SWBs were also analysed to subtract the concentration levels of the target compounds present in the sample. As Table 1 shows, the recovery values obtained for sampled SWBs ranged from 38% for DEHA to 114% for DEHP and Phe, comparable to those obtained with blank SWBs. Therefore, the target analytes were quantified by internal standard calibration and the recoveries were taken into account to obtain the final concentration in the SWB. The MDLs and MQLs were estimated from the IDLs and IQLs of each target compound (see section 2.5) taking into account the recoveries and the amount of SWB (2 g). As can be seen in Table 1, the MDLs ranged from 0.1 ng/g to 35 ng/g, while the MQLs were between 0.3 ng/g and 119 ng/g. ClBT, TiBP, DiBP and Nap were the compounds with the lowest MDLs and MQLs, while DiB, InD and BghiP had the highest ones. Method repeatability (intra-day precision), expressed in terms of %RSD ($n = 5$), was in the range of 3% and 20%. Method reproducibility (inter-day precision) was between 11% and 27% ($n = 5$), except for DEHP (49%).

3.4. Occurrence in silicone WB samples

The method developed for this study was used to monitor the presence of the target HPVCs and PAHs in 30-day samples from SWBs from 24 participants living in Tarragona (Spain). Table 2 summarises the average concentrations (μg/g), the concentration ranges (μg/g), and the detection rates (DR, %) for all the target compounds listed by families. The pie chart in Fig. 2 shows the average concentrations per compound family, expressed as percentage contribution to the total.

As Table 2 shows, all the target compounds were detected at quantifiable levels in the samples analysed. The DRs of a large number of the target compounds were between 74% and 100%. Lower DRs, ranging from 30% to 65%, were found for BHT, BHT-OH, NH_2BT, UV P, Allyz-BZT, TEP, TiBP, EHDP, Nap, DiB, InD and BghiP. Most of the quantified compounds showed average concentrations in the range of 0.01 μg/g and 0.84 μg/g (<1 μg/g). However, compounds like allyz-BZT, DEP, DnOP, BSA and p-TSA exhibited higher average concentrations, ranging from 1.3 ng/g to 2.6 μg/g, indicating an increase in personal exposure. Even higher were the average concentrations found for TBHQ, BHT-OH, TCPP, DEHA and DEHP with values between 3.3 μg/g and 34 μg/g.

Fig. 2 shows that the family of compounds with the highest contribution to the total was PAEs, which accounted for 52%, followed by PAs with a percentage 21%. The remaining compounds, OPEs, Tinuvins, BSAs, PAHs and BTHs had percentages between 1% and 8%. The fact that 73% of the concentrations found belong to two families can be attributed to the daily use of products in which these compounds are present, such as common plasticisers (PAEs) and food preservatives (PAs). DEHP was found to be the most prevalent of the PAEs evaluated, with concentrations between 11 μg/g and 82 μg/g, due to its widespread use in consumer products (Paluselli et al., 2019; Wang et al., 2022). BHT-OH (n.d. - 43 μg/g) and TBHQ (4.3 μg/g - 9.1 μg/g) were the PAs found at the highest concentrations as they are extensively used as food preservatives and we are exposed to them when handling food packaging and/or during the cooking process (Gupta et al., 2021). The most characteristic of the OPEs was a compound used as a flame retardant (Bekele et al., 2021), TCPP, with concentrations between 0.41 μg/g and 7.6 μg/g. Similar to that reported by Herrero et al. (2014), the most representative BSAs were p-TSA (n.d. - 15 μg/g) and BSA (0.19 μg/g - 13 μg/g). All BTHs studied were presented at average concentrations between 0.10 μg/g and 0.37 μg/g, except for MeSBT, with an average of 0.01 μg/g. The most prevalent Tinuvins were allyz-BZT and UV327 with average values of 1.6 μg/g and 0.83 μg/g respectively. However, the average value of allyz-BZT was conditioned by a punctual concentration of up to 9.5 μg/g in one of the SWB samples analysed. Among the PAHs, none of the compounds stands out over the rest, as all of them were found in average concentrations between 0.10 μg/g and 0.52 μg/g. The less detected PAHs were Nap, Flu, BkF, DiB, InD and BghiP with DRs of 48–78%.

This was the first time that the presence of some of the target compounds, *e.g.* BTHs, BSAs, Tinuvins and PAs, in silicone WBs has been studied and therefore the results obtained cannot be compared with previous studies. The concentrations of PAHs, OPEs and PAEs found in SWB samples have been compared with those reported by other authors in the field. Lower average values of 0.004–0.03 μg/g for TCEP, 0.005–0.06 μg/g for TEP, 0.03–0.07 μg/g for EHDP, 0.01–0.03 μg/g for Phe, 0.003–0.01 μg/g Flu and 0.003–0.02 μg/g were found in SWB samples of people living in France, Italy and USA (Indiana) (Romanak et al., 2019; Wang et al., 2019, 2020). In contrast, similar or higher average values of 0.28 μg/g for TEHP, 1.4 μg/g for DiBP and 37 μg/g for DEHP were presented in SWB samples from USA (North Carolina) (Wise et al., 2020). It should be noted that the differences between the concentration levels found in the present study and in previous studies may be due to the sampling period applied. In the present study, the sampling time has been increased from 5 or 7 days–30 days, favouring the accumulation of the target compounds in the SWBs and, consequently, increasing their concentrations in μg/g.

The results obtained in SWBs from adults living in Tarragona have

Table 3
Geometric mean (mg/g) and 95th percentile (mg/g) concentrations used to calculate the estimated daily intake (EDI_{Dermal}, mg/kg/day) for dermal absorption at low and high exposure scenarios, respectively. Non-carcinogenic (HQ_{Dermal}) and carcinogenic (CR_{Dermal}) dermal risk for target compounds families have also been added.

	Low-case				High-case			
	Geometric mean	EDI_{Dermal}	HQ_{Dermal}	CR_{Dermal}	95th Percentile	EDI_{Dermal}	HQ_{Dermal}	CR_{Dermal}
BTHs	1,91E-04	2,30E-05	9,09E-05	*	6,87E-04	8,28E-05	1,98E-04	*
OPEs	9,30E-04	1,12E-04	2,25E-03	1,76E-07	2,43E-03	2,93E-04	5,94E-03	4,25E-07
PAEs	4,17E-03	5,03E-04	2,24E-02	5,09E-06	1,37E-02	1,65E-03	7,05E-02	1,51E-05
PAHs	7,39E-04	8,92E-05	8,14E-02	1,75E-05	9,28E-04	1,12E-04	8,25E-02	2,04E-05
TOTAL	**6,03E-03**	**7,27E-04**	**1,06E-01**	**2,28E-05**	**1,77E-02**	**2,14E-03**	**1,59E-01**	**3,59E-05**

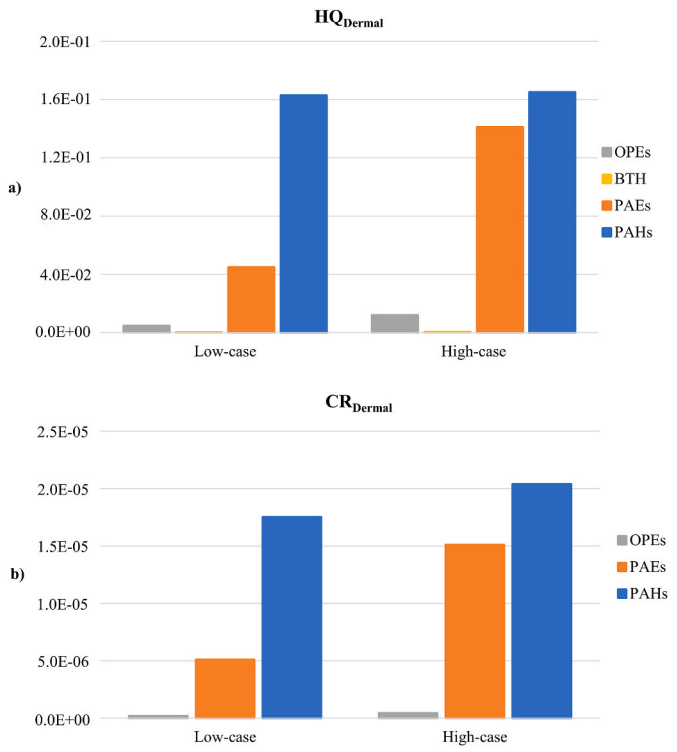

Fig. 3. Bar graphs of estimated dermal risk for adults: a) for non-carcinogenic dermal risk (HQ_{Dermal}) and b) for carcinogenic dermal risk (CR_{Dermal}). Two exposure scenarios, low (geometric mean) and high (95th percentile), were taken into account. Only the four families of target compounds with dermal toxicity factors are shown: BTHs, OPEs, PAEs and PAHs.

been compared with those reported by García-Garcinuño et al. (2024) when applying PLE followed GC-MS for the determination of the target compounds in active air samples from the same area. In both studies it was found that PAEs are the most abundant compounds representing more than 50% of the total. The remaining families of compounds showed percentages between 1% and 21% of the total. In addition, DEHP was the compound found at the highest concentrations followed by DEHA, TBHQ, BHT-Q or BHT-OH.

3.5. Estimated dermal risk assessment

The EDI_{Dermal} values were used to assess human exposure to the target compounds for adults and two exposure scenarios (low and high). The geometric means and 95th percentile concentrations listed in Table 5S were used. The obtained results showed that PAEs were the target compounds with the highest EDI_{Dermal} with individual values between 1.9E-06 mg/kg/day (DMP) and 1.1E-03 mg/kg/day (DEHP) and summations of 5.0E-04 mg/kg/day and 1.7E-03 mg/kg/day for low-case and high-case scenarios respectively. In fact, as can be seen in Table 3, PAEs account for more than 80% of the EDI_{Dermal} total (5.0E-04 mg/kg/day and 1.7E-03 mg/kg/day). The second most important family is the PAHs with individual EDI_{Dermal} in the range of 2.1E-06 mg/kg/day (Nap) and 1.2E-05 mg/kg/day (Flu) and summations of 8.9E-05 mg/kg/day (low-case) and 1.1E-04 mg/kg/day (high-case), around 10% of the EDI_{Dermal} total. OPEs and BTHs accounted for less than 3% of the EDI_{Dermal} total and had individual EDI_{Dermal} between 7.8E-07 mg/kg/day (MeSBT) and 1.9E-04 mg/kg/day (TCPP).

The total non-carcinogenic risk (HQ_{Dermal}) was calculated as the summation of the individual HQ_{Dermal} of each target compound. Table 6S summarises the individual HQ_{Dermal} for adults in the two scenarios evaluated. A $HQ_{Dermal} > 1$ indicate a definite risk of non-carcinogenic health effects, HQ_{Dermal} values between 0.1 and 1 indicate a probable risk, and $HQ_{Dermal} < 0.1$ indicate a negligible risk (Ramírez et al., 2012; Li et al., 2018). All individual HQ_{Dermal} were clearly <0.1, with values between 1.4E-05 (Ant) and 5.9E-02 (BeP). As Table 3 shows, HQ_{Dermal} per family were in the range of 9.1E-05 (BTHs) and 8.3E-02 (PAHs), below 0.1 regardless of the exposure scenario. Even in the high-case scenario, the HQ_{Dermal} total of 8.3E-02 obtained was clearly <1, indicating that no significant risk of non-carcinogenic effects is expected. Fig. 3a illustrates that the families of target compounds with higher HQ_{Dermal} were PAHs and PAEs accounting from 99% of the total HQ_{Dermal}. In the low exposure scenario PAHs with 79% of the HQ_{Dermal} total were the most characteristic compounds, while in the high case scenario similar percentages were obtained for PAEs (42%) and PAHs (56%). Although the concentrations of PAEs found were higher than those of PAHs, the HQ_{Dermal} associated with PAHs was higher due to the RfD (Table 2S) values applied.The risk of carcinogenic effects (CR_{Dermal}) was calculated only for OPEs, PAEs and PAHs due to the limited number of SFO available. Values of CR_{Dermal} between 1.0E-06 and 1.0E-05 indicate a possible risk, CR_{Dermal} between 1.0E-05 and 1.0E-04 indicate a probable risk and >1.0E-04 indicate a definite risk (Ramírez et al., 2012; Li et al., 2018). As Table 6S shows, all the individual CR_{Dermal} values obtained were in the range of 1.6E-09 (Phe) and 1.5E-05 (DEHP). The CR_{Dermal} per family in Table 3 were between 1.8E-07 and 2.0E-05 and the total CR_{Dermal} were of 2.3E-05 (low-case) and 3.6E-05 (high--case), indicating a probable risk. It important to highlight that only DEHP, BaP and DiB had CR_{Dermal} values between 1.0E-06 and 1.0E-05 (probable risk), the remaining compounds were at concentrations that did not represent a carcinogenic risk ($CR_{Dermal} < 1.0E-06$). A probable explanation for the CR_{Dermal} achieved for DEHP is the widespread use of this compound as a plasticizer in everyday products, which favors its presence in the environment and therefore in the SWBs samples analysed at high concentration levels (Fernández et al., 2012; Dueñas-Moreno et al., 2024). The presence of PAHs (BaP and DiB) in Tarragona is due to the incomplete combustion of organic matter (*e.g.* boilers or road traffic) and above all to the industrial activity linked to the two petrochemical parks of the city. Although they were not the most abundant compounds in the SWBs, BaP and DiB are the target compounds with the highest oral slope factor and, therefore, those with the highest CR_{Dermal} (Ras et al., 2009; Ramírez et al., 2012). As observed in Fig. 3b the target compounds with higher CR_{Dermal} were PAHs and PAEs accounting from >99% of the total CR_{Dermal}. In the low exposure scenario, the 68% of the CR_{Dermal} total came from PAHs and the 32% from PAEs. In the high-case scenario the percentages were similar, 54% PAHs and 45% PAEs, because the concentrations of PAHs found in SWBs were much more stable and no concentrations peaks were detected.

4. Conclusions

A new analytical method was successfully developed and validated for simultaneously assessing personal exposure to HPVCs and PAHs, including novel BTHs, BSAs, Tinuvins and PAs. SWBs were used as personal passive samplers and UAE followed by GC-MS analysis was employed for the simultaneous determination of up to 56 semi-VOCs.

The developed method was applied to evaluate the presence of the target compounds in SWBs from adults living in Tarragona. All the compounds were found at quantifiable levels with DRs mainly in the range of 74% and 100%. Among the families studied, PAEs and PAs were the compounds found at the highest concentrations accounting of 52% and 21% of the total. The most prevalent compounds were DEHP (1.1 μg/g - 82 μg/g) and BHT-OH (n.d. - 43 μg/g) due to their widespread use in consumer products and as food preservative, respectively. Tinuvins and UV filters, were determined for the first time in SWB samples.

The obtained results were used for the assessment of estimated dermal risk of both carcinogenic and non-carcinogenic compounds in adults and in two exposure scenarios (high and low concentration). The families of compounds that contributed most to the total HQ_{Dermal} and CR_{Dermal} were PAHs and PAEs with percentages ≥99% of the total.

Regardless of the exposure scenario, no estimated risk for the population is expected for non-carcinogenic compounds, as total HQ_{Dermal} values were <1. Due to the CR_{Dermal} values obtained for DEHP, BaP and DiB, the carcinogenic risk was probable (between 1.0E-06 and 1.0E-05). A long-term monitoring campaign with a larger cohort of participants should be conducted in the future to differentiate exposure profiles according to work environments and routines, as well as a more representative risk assessment study to confirm the preliminary results obtained.

CRediT authorship contribution statement

Óscar Gómez: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **Noelia Ramírez:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Conceptualization. **Laura Vallecillos:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Conceptualization. **Francesc Borrull:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2024.120107.

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