



# Preliminary assessment of personal exposure to emerging organic compounds in relation to occupational settings using silicone wristbands

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## ABSTRACT

Emerging organic compounds (EOCs) in everyday products such as fragrances, preservatives and solvents are of concern because of their high concentrations in humans. These concentrations are associated with high daily exposure to cleaning and personal care products, especially in indoor environments with poor ventilation or frequent use of such products (e.g. hairdressing salons). In this study, we developed a fast and robust analytical method to evaluate personal exposure to EOCs depending on the occupational environment, using silicone wristbands (SWBs) as passive samplers. A multiresidue method based on ultrasound-assisted extraction and gas chromatography-mass spectrometry was optimised and validated to detect the following 22 EOCs: six synthetic musk fragrances, nine fragrances, two preservatives and five solvents. This method provided recoveries between 27 % and 92 % on sampled SWBs and method quantification limits between 0.006 µg/g and 0.11 µg/g. Applicability was tested in four different occupational settings with a pilot group of adults in Tarragona (Spain). Most of the target compounds were found at quantifiable levels, thus confirming the effectiveness of SWBs as personal passive samplers of EOCs. Musk fragrances stood out from the rest, with average concentrations of 18 µg/g and 9.4 µg/g in individuals working in offices and hairdressing salons, respectively. Galaxolide had the highest average concentrations, with values ranging from 2.0 µg/g to 14 µg/g. Risk assessment showed that musks, followed by solvents and preservatives, contributed the most to estimated daily intake. Non-carcinogenic dermal risk values were below safety thresholds, thus confirming that risk across all occupational settings evaluated was not significant.

## 1. Introduction

Air quality has become a significant focus in environmental research due to high levels of pollution and their impact on human health. Numerous studies on the contaminants responsible for these health risks have been conducted (WHO, 2018; Manisalidis et al., 2020; de Paula Santos et al., 2021). Initially, most studies focused on outdoor environments, especially in urban and industrial regions where contaminant concentrations are higher than in rural areas. Active air sampling techniques have predominantly been used for these investigations. These techniques have enabled researchers to obtain detailed data on the presence and variability of contaminants in the air, thus facilitating risk assessments in urban (Arias et al., 2021; Cao et al., 2022;

Schachterle et al., 2024) and industrial areas (Miyake et al., 2017; Maceira et al., 2019; Vallecillos et al., 2024). In recent years, however, passive sampling has gained popularity in the scientific community thanks to its simplicity, cost-effectiveness and ability to use average concentrations for efficient exposure or risk calculations (Manzano et al., 2019; Ninyà et al., 2022; Zhang et al., 2022).

As people spend most of their time indoors, interest has also grown among researchers to study indoor air pollution, which can lead to high exposure in enclosed spaces such as homes, schools and workplaces. Volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), especially those associated with everyday items such as cleaning or personal care products, which can contribute to daily exposure, have been evaluated in these indoor environments (Lucattini

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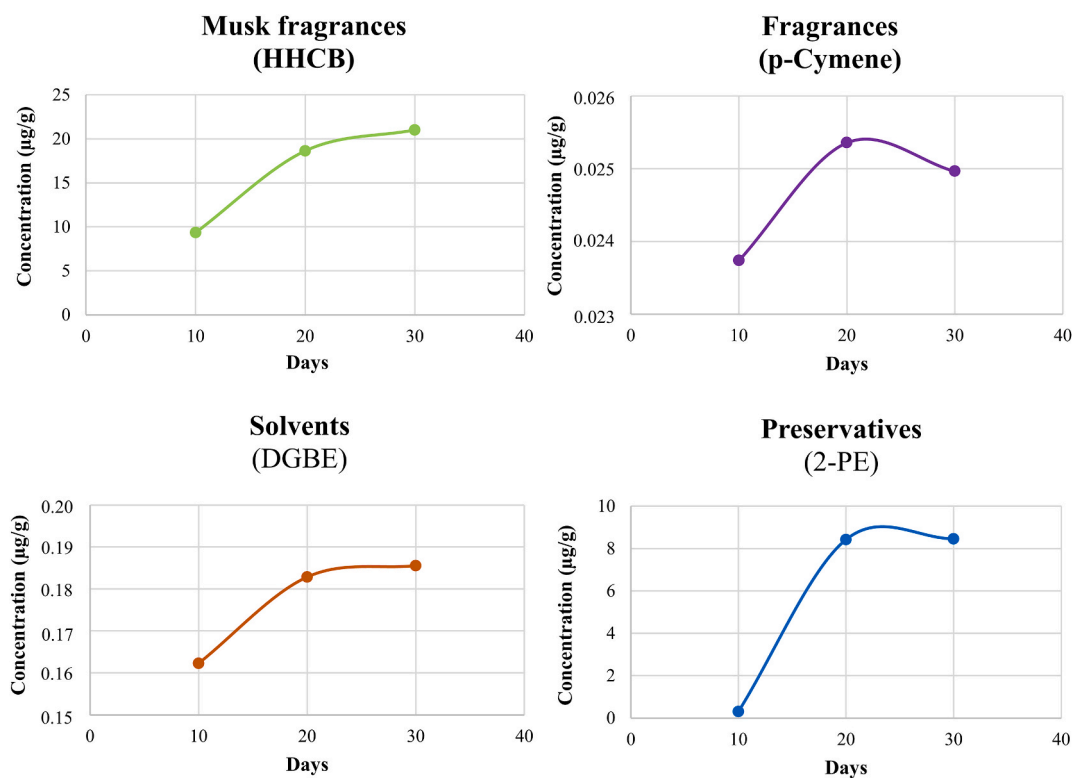


Fig. 1. Graphs showing the optimisation of the sampling time (10, 20 and 30 days) for one compound from each family when the SWBs were used as a personal passive sampler. Concentration ( $\mu\text{g/g}$ ) of compound in the SWB vs sampling time.

et al., 2018; Langer et al., 2021; Yeoman et al., 2021; Ninyà et al., 2022). Although a range of sampling techniques exists, most studies share a common feature that can be optimised: the sample collection is typically conducted at fixed locations, people move between environments during the day, frequently transitioning between indoor and outdoor spaces with varying levels of pollution. This has led to the development of personal passive sampling techniques such as silicone wristbands (SWBs) (O'Connell et al., 2014), hand wipes (Hammel et al., 2016; Levasseur et al., 2021), clips attached to clothing near breathing zones (Niu et al., 2024), and Markes POD samplers (Pérez Ballesta et al., 2023) to assess levels of pollution exposure to individuals.

SWBs are particularly notable for their low cost, efficient monitoring and ease of use throughout the day without causing discomfort in most daily activities (Fuentes et al., 2022; O'Connell et al., 2022; Samon et al., 2022a,b; Waclawik et al., 2022). Moreover, they assess exposure not only to airborne contaminants but also to routes such as dermal contact and contributions from everyday personal care or cleaning products (Dixon et al., 2018; Wang et al., 2019). SWBs have also been used to successfully assess specific tobacco-related compounds (Quintana et al., 2019, 2021), high-production volume chemicals (HPVCs) and polycyclic aromatic hydrocarbons (PAHs), thus providing useful data for exposure and risk assessment (Romanak et al., 2019; Hamzai et al., 2022; Gómez et al., 2024).

The most common analytical techniques used to analyse SVOCs are chromatographic methods such as gas chromatography (GC) and liquid chromatography (LC) coupled with mass spectrometry (MS) or tandem mass spectrometry (MS/MS) detection. However, these require sample pre-treatment methods such as ultrasound-assisted extraction (UAE), pressurised liquid extraction (PLE) and QuEChERS (Quintana et al., 2019; Wang et al., 2019; García-Garcinuño et al., 2024). Also, few of the numerous studies on contaminant exposure have evaluated personal risk directly, with most focusing on household dust or static samplers. Following studies such as those by Gómez et al. (2024) and Christia et al. (2019), other authors are now evaluating personal dermal risk for every

day-use compound, thus addressing a gap in previous risk assessments for these families of compounds.

In this context, the aims of the current study were: (1) to develop and validate an UAE-GC-MS method for the simultaneous determination of 22 emerging organic compounds (EOCs), including fragrances, preservatives and solvents, using personal passive sampling with SWBs; (2) to determine the target compounds in SWBs from adults living in Tarragona who are exposed to different occupational settings; and (3) a preliminary assessment of human exposure and the risk associated with dermal exposure to the target compounds for adults and considering different occupational settings. Although there are two main exposure routes to EOCs in SWBs - dermal and inhalation - only dermal risk has been considered. This is due to previous studies showing a stronger correlation between SVOCs in SWBs and those in airborne particles or dust, rather than in the gaseous phase of air (Dixon et al., 2018; Quintana et al., 2019; Wang et al., 2019). This approach will facilitate further research on personal exposure to these compounds while taking into account the influence of individual mobility and daily routines on personal exposure levels.

## 2. Materials and methods

### 2.1. Chemicals and reagents

The group of EOCs studied included: six synthetic musk fragrances [6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (>99.9 %) (Cashmeran, DPMI); 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran (>99.9 %) (Galaxolide, HHCB); 1,2,3,4,4,6-Hexamethyl-7-naphthyl methyl ketone (>99.9 %) (Tonalide, AHTN); 2,4,6-Trinitro-1,3-dimethyl-5-tert-butylbenzene (>99.9 %) (Musk xylene, MX); 1,1,3,3,5-Pentamethyl-4,6-dinitro-2H-indene (>99.9 %) (Musk moskene, MM); and 4-tert-Butyl-2,6-dimethyl-3,5-dinitroacetophenone (97 %) (Musk ketone, MK)]; nine fragrances [3,7,7-Trimethylbicyclo[4.1.0]hept-3-ene (90 %) (3-Carene); (1R,5R)-2,6,6-

**Table 1**

Method validation results obtained with blank and sampled SWBs organised by compound families. Recovery (%), repeatability (RSD%) and reproducibility (%RSD) values were calculated by spiking  $n = 5$  SWBs (blank or sampled) at 1 µg. Method detection limits (MDLs) and method quantification limits (MQLs) in µg/g are also shown.

Family	Compounds	Blank SWBs		Sampled SWBs				
		Recovery	Repeatability	Recovery	Repeatability	Reproducibility	MDL	MQL
Musk fragrances	DPMI	84	3	83	3	13	0.002	0.006
	AHTN	86	7	81	6	9	0.002	0.006
	HHCB	97	7	88	7	14	0.002	0.006
	MX	86	9	75	6	11	0.004	0.01
	MM	86	3	72	8	15	0.004	0.01
	MK	121	13	90	12	20	0.003	0.01
Fragrances	α-Pinene	27	6	27	5	11	0.006	0.02
	Camphene	30	7	32	6	11	0.009	0.03
	β-Pinene	38	7	38	7	8	0.004	0.01
	3-Carene	48	8	44	6	7	0.003	0.01
	D-Limonene	58	9	55	7	14	0.003	0.01
	p-Cymene	61	8	57	7	10	0.005	0.02
	Eucalyptol	59	10	66	9	13	0.005	0.02
	L-Camphor	75	8	63	11	20	0.005	0.02
	2-PEA	92	7	88	5	11	0.002	0.01
	PGMAE	57	6	58	4	8	0.02	0.07
Solvents	EGBE	84	9	73	10	15	0.02	0.07
	TMPD	75	8	64	13	22	0.02	0.08
	DGBE	104	11	92	9	13	0.03	0.11
	Toluene	62	4	55	11	16	0.003	0.01
	Phenol	86	6	79	9	16	0.002	0.01
Preservatives	2-PE	107	5	90	12	15	0.003	0.01

Trimethylbicyclo[3.1.1]hept-2-ene (>99.9 %) (α-Pinene); 2,2-Dimethyl-3-methylenenorbornane (95 %) (Camphene); (1S,5S)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptane (>99.9 %) (β-Pinene); (R)-4-Isopropenyl-1-methyl-1-cyclohexene (97 %) (D-Limonene); 1-Isopropyl-4-methylbenzene (99 %) (p-Cymene); 1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octane (99 %) (Eucalyptol); (1S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (95 %) (L-Camphor); and 2-phenyl ethyl alcohol (99 %) (2-PEA)]; five solvents [propylene glycol monomethyl ether acetate (99.5 %) (PGMEA); diethylene glycol butyl ether (99 %) (DGBE); ethylene glycol butyl ether (>99.9 %) (EGBE); 2,2,4-Trimethyl-1,3-pentanediol (97 %) (TMPD); and toluene (99 %)]; and two preservatives [2-phenoxy ethanol (99 %) (2-PE); and phenol (99 %)]. All compounds were purchased from Sigma Aldrich (St. Louis, MO, USA). Individual standard solutions of each target compound were prepared in methanol at a concentration of 4000 mg/L. Working solutions in ethyl acetate were prepared at 100 mg/L for each compound family and at 10 mg/L for all compounds. Standard solutions were kept in the freezer at -20 °C until use.

All solvents tested to optimise the UAE of the target EOCs, ethyl acetate, n-hexane, dichloromethane and methanol, were GC grade (purity >99.9 %) and were provided by Carlo Erba (Val de Reuil, France). Isopropanol with 99.5 % purity, supplied by Fisher Scientific (Alcobendas, Madrid, Spain), was also used. Milli-Q water was obtained from a Millipore water purification system (Burlington, MA, USA). Helium gas with a purity of 99.999 %, supplied by Linde (Tarragona, Spain), was used for chromatographic analysis.

## 2.2. Sampling

We used SWBs to determine personal exposure to a group of EOCs as a function of the working environment. Twenty adult volunteers, comprising hairdressers, cleaners, secretaries and sports coaches, were recruited. The occupational settings were selected based on the use of fragrances and/or cleaning products in order to obtain various exposure scenarios. The volunteers selected had similar household characteristics (e.g. dimensions, family size or use of cleaning products) and lived in the same area (share ambient air) to specifically assess the impact of occupational exposure. The sampling campaign took place between April and May 2024 in Tarragona, a coastal city in the northwest of Spain. The

SWBs used for the sampling procedure weighed 4.8 g, had an internal diameter of 6.5 cm, and measured 1.2 cm wide and 18 cm long (Delfin Artesanías S.L., A Coruña, Spain). An image of the SWBs is provided in Fig. 1S.

Each participant was provided with a conditioned SWB to wear continuously for 24 h a day over a sampling period of 20 days. Sampled SWBs were collected, wrapped in aluminium foil and vacuum-sealed at -20 °C until extraction and analysis. Maximum storage time was one month.

## 2.3. Analytical method

A UAE-based method followed by GC-MS was used to determine EOCs in SWBs samples. As described by O'Connell et al. (2014) and Gómez et al. (2024), prior to the extraction process the SWBs were superficially cleaned with Milli-Q water and isopropanol to remove any grease or dirt that had accumulated during sampling. Two grams of SWB, cut into small square pieces, were weighed into a 25 mL glass flask and 5 mL of ethyl acetate was added. The extraction was performed in an ultrasonic bath for 5 min. The extract was then filtered using a PTFE syringe filter with a pore diameter of 0.22 µm. The extract was evaporated to near dryness under a gentle stream of nitrogen and reconstituted to 2 mL with ethyl acetate.

The instrument used to analyse SWB samples was a GCMS-QP2010 Ultra High-Performance Gas Chromatograph equipped with a split/splitless injector and a single quadrupole mass spectrometer (Shimadzu Corporation Izasa, S.A.). The injector was set at 250 °C and the extracts (2 µL) were injected in splitless mode. Chromatographic separation was conducted with a ZB-50 column (30 m × 0.25 mm i.d. and 0.25 µm film thickness) from Phenomenex (Torrance, CA, USA). Helium was used as carrier gas at a constant flow rate of 1.2 mL/min. The initial GC oven temperature of 40 °C was increased linearly at a rate of 5 °C/min to 100 °C and then further increased at a rate of 10 °C/min to 290 °C, where it was held for 4 min. The ionisation source and GC-MS interface temperatures were set at 230 °C and 280 °C, respectively. The ionisation source and GC-MS interface temperatures were set at 230 °C and 280 °C, respectively. Electron-ion ionisation was applied, and the MS acquired data in selected ion monitoring (SIM) mode. Table 1S shows the retention times, quantifier ions, qualifier ions and relative abundances for

**Table 2**

Concentrations of the target compounds found in personal samples and indoor air samples in µg/g. The table shows the average concentrations, and the minimum and maximum values obtained (average (min-max)), organised by compound family and working environment evaluated.

Compounds	Cleaners		Secretaries		Hairdressers		Sport coaches	
	Personal	Indoor	Personal	Indoor	Personal	Indoor	Personal	Indoor
<b>Musk Fragrances</b>								
<b>DPMI</b>	<b>0.15</b> (0.06–0.48)	<b>0.05</b> (0.02–0.10)	<b>0.09</b> (0.06–0.16)	<b>0.05</b> (0.02–0.08)	<b>0.09</b> (0.05–0.13)	<b>0.13</b> (0.10–0.20)	<b>0.11</b> (0.09–0.12)	<b>0.06</b> (0.04–0.16)
<b>HHCB</b>	<b>4.7</b> (0.83–9.8)	<b>0.02</b> (<MQL-0.05)	<b>14</b> (7.2–30)	<b>0.08</b> (0.04–0.10)	<b>7.5</b> (4.5–10)	<b>0.63</b> (0.40–1.2)	<b>2.0</b> (0.92–4.2)	<b>0.09</b> (0.06–0.13)
<b>AHTN</b>	<b>0.97</b> (0.11–3.3)	<b>0.09</b> (0.05–0.12)	<b>1.9</b> (0.19–4.2)	<b>0.01</b> (<MQL-0.02)	<b>0.53</b> (0.40–0.61)	<b>0.10</b> (0.07–0.20)	<b>0.68</b> (0.43–1.2)	<b>0.02</b> (0.01–0.05)
<b>MX</b>	<b>0.03</b> (<MQL-0.09)	<b>0.02</b> (n.d.-0.06)	<b>0.09</b> (<MQL-0.28)	<b>0.03</b> (0.02–0.07)	<b>0.02</b> (<MQL-0.03)	<b>0.02</b> (<MQL-0.05)	<b>0.05</b> (0.02–0.13)	<b>0.03</b> (<MQL-0.05)
<b>MM</b>	<MQL	<MQL	<b>0.02</b> (n.d.-0.05)	<MQL	<MQL	n.d.	<MQL	<MQL
<b>MK</b>	<b>0.67</b> (0.05–1.3)	<b>1.8</b> (1.0–2.9)	<b>1.56</b> (0.95–2.2)	<b>1.7</b> (1.0–2.0)	<b>1.2</b> (0.95–1.4)	<b>1.9</b> (1.1–3.6)	<b>1.6</b> (1.2–2.0)	<b>1.4</b> (0.83–2.0)
<b>Fragrances</b>								
<b>α-Pinene</b>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>Camphene</b>	<MQL	<b>0.05</b> (<MQL-0.09)	<MQL	<b>0.06</b> (0.04–0.07)	<MQL	<b>0.05</b> (0.04–0.09)	<MQL	<b>0.06</b> (0.04–0.09)
<b>β-Pinene</b>	n.d.	<MQL	n.d.	<MQL	n.d.	<b>0.01</b> (<MQL-0.05)	n.d.	<MQL
<b>3-Carene</b>	n.d.	<MQL	n.d.	<MQL	n.d.	<MQL	n.d.	<MQL
<b>D-Limonene</b>	<b>0.04</b> (0.01–0.05)	<b>0.03</b> (0.02–0.06)	<b>0.16</b> (0.04–0.37)	<b>0.01</b> (<MQL-0.02)	<b>0.09</b> (0.06–0.10)	<b>0.50</b> (0.38–0.74)	<b>0.10</b> (0.05–0.15)	<b>0.08</b> (0.05–0.19)
<b>P-Cymene</b>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>Eucalyptol</b>	<b>0.15</b> (0.04–0.21)	<b>0.08</b> (0.05–0.17)	<b>0.27</b> (0.14–0.32)	<b>0.07</b> (0.05–118)	<b>0.13</b> (0.07–0.21)	<b>0.35</b> (0.21–0.55)	<b>0.18</b> (0.14–0.23)	<b>0.07</b> (0.04–0.14)
<b>L-Camphor</b>	<b>0.03</b> (n.d.-0.15)	<b>0.04</b> (<MQL-0.07)	<MQL	<b>0.02</b> (0.01–0.07)	<b>0.03</b> (n.d.-0.08)	<b>0.08</b> (0.05–0.16)	<b>0.03</b> (n.d.-0.04)	n.d.
<b>2-PEA</b>	<b>0.06</b> (0.03–0.09)	<b>0.12</b> (<MQL-0.30)	<b>0.17</b> (0.05–0.30)	<b>0.11</b> (0.09–0.15)	<b>0.15</b> (0.08–0.21)	<b>1.2</b> (0.94–1.8)	<b>0.04</b> (0.02–0.07)	<b>0.09</b> (0.06–0.10)
<b>Solvents</b>								
<b>PGMAE</b>	<MQL	n.d.	n.d.	n.d.	n.d.	<MQL (<MQL-0.16)	n.d.	n.d.
<b>EGBE</b>	<b>0.16</b> (0.14–0.18)	<b>0.76</b> (0.67–0.91)	<b>0.16</b> (0.14–0.19)	<b>0.69</b> (0.60–0.78)	<b>0.16</b> (0.13–0.21)	<b>0.69</b> (0.65–0.79)	<b>0.12</b> (0.10–0.15)	<b>0.80</b> (0.70–0.95)
<b>TMPD</b>	n.d.	n.d.	n.d.	n.d.	<MQL	<b>0.08</b> (<MQL-0.16)	<MQL	n.d.
<b>DGBE</b>	<b>1.3</b> (0.51–2.7)	<b>1.2</b> (0.45–2.0)	<b>0.83</b> (0.33–1.4)	<b>2.3</b> (1.5–2.7)	<b>0.47</b> (0.29–0.61)	<b>2.0</b> (1.6–3.1)	<b>3.0</b> (1.9–4.8)	<b>9.0</b> (7.2–11)
<b>Toluene</b>	<b>0.02</b> (0.01–0.03)	<MQL	<b>0.11</b> (0.08–0.17)	<b>0.02</b> (0.01–0.06)	<b>0.05</b> (0.01–0.12)	<b>0.02</b> (0.01–0.05)	<b>0.03</b> (0.01–0.10)	<b>0.01</b> (<MQL-0.02)
<b>Preservatives</b>								
<b>Phenol</b>	<b>0.08</b> (<MQL-0.10)	<b>0.03</b> (0.02–0.05)	<b>0.02</b> (<MQL-0.04)	<b>0.03</b> (0.01–0.08)	<b>0.01</b> (<MQ-0.10)	<b>0.04</b> (0.02–0.05)	<b>0.03</b> (0.01–0.05)	<b>0.06</b> (0.04–0.09)
<b>2-PE</b>	<b>0.77</b> (0.22–1.8)	<b>2.2</b> (1.6–2.5)	<b>0.46</b> (0.12–0.66)	<b>1.9</b> (1.5–2.6)	<b>1.3</b> (1.1–1.6)	<b>6.7</b> (5.4–12)	<b>0.16</b> (0.11–0.19)	<b>0.36</b> (0.32–0.42)
<b>ΣMusk</b>	<b>6.5</b> (2.4–11)	<b>2.0</b> (1.1–3.0)	<b>18</b> (11–35)	<b>1.8</b> (1.2–2.2)	<b>9.4</b> (6.2–13)	<b>2.8</b> (2.1–5.2)	<b>4.4</b> (2.7–7.0)	<b>1.6</b> (1.0–2.3)
<b>ΣFragrances</b>	<b>0.31</b> (0.11–0.45)	<b>0.33</b> (0.29–0.38)	<b>0.63</b> (0.34–0.97)	<b>0.30</b> (0.23–0.35)	<b>0.43</b> (0.31–0.64)	<b>2.2</b> (1.7–3.4)	<b>0.37</b> (0.29–0.47)	<b>0.33</b> (0.28–0.40)
<b>ΣSolvents</b>	<b>1.5</b> (0.73–2.9)	<b>2.0</b> (1.2–2.9)	<b>1.1</b> (0.58–1.6)	<b>3.0</b> (2.2–3.4)	<b>0.70</b> (0.51–0.83)	<b>2.9</b> (2.4–4.2)	<b>3.2</b> (2.1–5.0)	<b>9.8</b> (8.0–12)
<b>ΣPreservatives</b>	<b>0.77</b> (0.22–1.8)	<b>2.2</b> (1.6–2.5)	<b>0.48</b> (0.12–0.68)	<b>1.9</b> (1.5–2.7)	<b>1.3</b> (1.1–1.6)	<b>6.7</b> (5.4–12)	<b>0.19</b> (0.15–0.24)	<b>0.42</b> (0.36–0.47)
<b>ΣTotal</b>	<b>9.1</b> (3.5–15)	<b>6.5</b> (4.6–7.7)	<b>20</b> (13–37)	<b>7.0</b> (5.6–8.1)	<b>12</b> (8.3–15)	<b>15</b> (12–25)	<b>8.1</b> (5.5–12)	<b>12</b> (9.6–15)

<MQL = below the limit of quantification of the method n.d. = non detected

each compound.

#### 2.4. Quality assurance & quality control

The conditions described in the literature were followed to minimise the risk of cross-contamination between samples (O’Connell et al., 2014; Quintana et al., 2019; Gómez et al., 2024). All equipment (e.g. glassware, utensils and scissors) was cleaned with isopropanol before each extraction. SWBs were conditioned at a temperature of 200 °C for 24 h using a Hereaus Thermo Scientific vacuum oven (Massachusetts, USA) to eliminate potential contamination resulting from manufacturing, handling, or storage (Dixon et al., 2022; Samon et al., 2022a,b). Blanks of the conditioned SWBs showed that all the target compounds were below the instrumental detection limits (IDLs). The conditioned SWBs were stored at 4 °C and wrapped in aluminium foil until sampling. To

address background contamination, procedural blanks (analytical method without SWBs) and blanks of conditioned SWBs were performed periodically. Standard controls of 1000 µg/L of all target compounds were included in the GC-MS batches to verify signal stability and ensure correct behaviour of the instrument.

#### 2.5. Dermal risk assessment

Two main exposure pathways to EOCs are commonly identified in SWBs: dermal exposure and inhalation exposure (Quintana et al., 2019; Samon et al., 2022a,b). Studies by Dixon et al. (2018) and Wang et al. (2019) reported that SVOC concentrations obtained using SWBs, e.g. PAHs, organophosphorus esters (OPEs) and phthalate esters (PAEs) among others, showed a stronger correlation with levels found airborne particles or surface dust (dermal contact) than with those in the gaseous

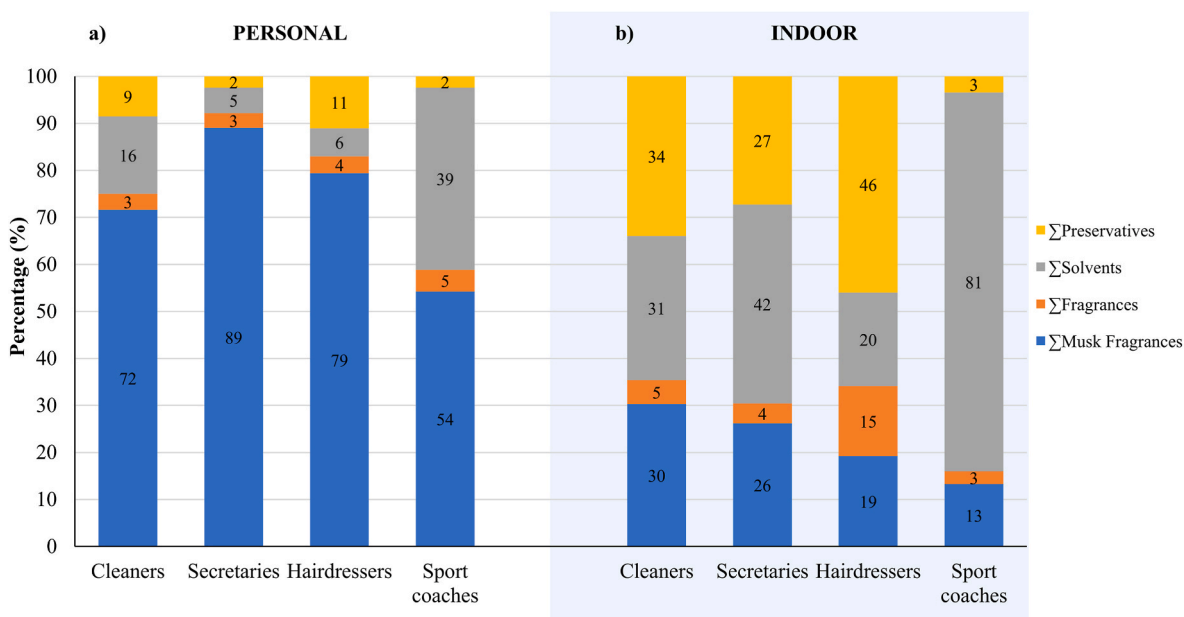


Fig. 2. Stacked bar chart showing the percentage contributions of each family of compounds found in SWBs from different occupational settings (cleaners, secretaries, hairdressers, sports coaches). SWBs were used to study a) personal exposure and b) indoor work environments.

phase of air (inhalation). Consequently, only daily intake via dermal absorption ( $EDI_{dermal}$ ) was evaluated. The concentrations of the target compound in SWB samples were used to calculate the  $EDI_{dermal}$  for adults (all participants were over 18 years old). Using geometric mean and 95th percentile concentrations, two exposure scenarios were considered to represent low and high concentration scenarios, respectively.

$EDI_{dermal}$  (mg/kg/day) was calculated from the general EPA equation (USEPA, 2001) (shown in Eq. (1)) by taking into account not only exposure during the sampling period (Yin et al., 2023) but also the average adult life expectancy required for risk calculations (Christia et al., 2022). In accordance with EPA specifications (USEPA, 2001, 2007),  $EDI_{dermal}$  for compounds with concentrations below the method detection limits (MDLs) or method quantification limits (MQLs) were calculated by replacing the concentrations with MDL/2 or MQL/2, respectively:

$$EDI_{dermal} = \frac{C_{SWB} \times SA_i \times ABS_d \times EF_i \times ED_i}{BW_i \times AT} \quad 1$$

where  $C_{SWB}$  is the concentration (mg/cm<sup>2</sup>/event) in SWB samples over a 20-day sampling period;  $SA_i$  is the adult body surface area of the volunteers calculated in accordance with Du Bois and Du Bois (1916) and considering an exposed body percentage of 15% (Yu et al., 2010) (2568 cm<sup>2</sup>) (to calculate the percentage exposure we took into account parts of the body that are exposed in spring, such as the hands, neck, head and forearms);  $ABS_d$  is the fraction of the target compound that is absorbed through the skin, which is set at 0.1 (unitless) by the USEPA (2024) for SVOCs without available values;  $EF_i$  is the exposure frequency (18 events/year, event = 20-day sampling);  $ED_i$  is the exposure duration for adults (53 years);  $BW_i$  is the adult body weight of the volunteers (70 kg); and  $AT$  is the average time (days), which for non-carcinogenic compounds is equal to  $ED_i$ .

Using the  $EDI_{dermal}$  results, the dermal risk estimation for non-carcinogenic compounds ( $HQ_{dermal}$ ) was calculated from Eq. (2) (Christia et al., 2019):

$$HQ_{dermal} = \frac{EDI_{dermal}}{RfD \times ABD_{GI}} \quad 2$$

where a gastrointestinal absorption factor  $ABS_{GI}$  of 1 (unitless) was

applied (Li et al., 2018) and  $RfD$  is the oral reference dose per compound (mg/kg/day). All  $RfD$  values were obtained from the USEPA Risk Assessment Information System database (RAIS, 2024) and are shown in Table 2S.

### 3. Results and discussion

#### 3.1. Optimisation of method

##### 3.1.1. Chromatographic method

Chromatographic separation was optimised by injecting 2 µL of a mixed solution of 1 mg/L of all target compounds into the GC-MS in full scan mode. Based on our experience in determining SVOCs, we applied several oven temperature programmes (Maceira et al., 2020; Vallecillos et al., 2020; Garcia-Garcinuño et al., 2024). The chromatographic conditions described in section 2.3. provided the best separation of the target compounds in the shortest time (less than 30 min). The parameters specified in Table 1S (retention time, quantifier and qualifier ions, and relative abundance percentages) were used to identify the target compounds. To maximise sensitivity of the target compounds, the MS operated in selective ion monitoring (SIM) mode. A chromatogram of a 1 mg/L standard solution containing the 22 target EOCs, obtained under optimised conditions, is shown in Fig. 2S.

Quantification was performed using the external standard calibration method. The validation parameters evaluated for each target compound were: linear range, IDLs, instrumental quantification limits (IQLs), repeatability and reproducibility. Table 1S shows that IDLs and IQLs ranged from 0.002 mg/L to 0.03 mg/L and from 0.005 mg/L to 0.10 mg/L, respectively. The linear ranges began at the IQL (the lowest calibration point) and increased to 2.0 mg/L with determination coefficients ( $r^2$ ) greater than 0.990. Repeatability and reproducibility data ( $n = 5$ , 1.0 mg/L) expressed as relative standard deviation (RSD%), ranged from 3% to 11% and from 7% to 16%, respectively.

##### 3.1.2. Extraction method

We set the initial conditions for UAE optimisation based on our experience in determining HPVCs and PAHs in similar matrices (García-Garcinuño et al., 2024; Gómez et al., 2024). First, dichloromethane, ethyl acetate, hexane, methanol and a mixture of hexane and acetone (1:1) were evaluated as extraction solvents. The other UAE

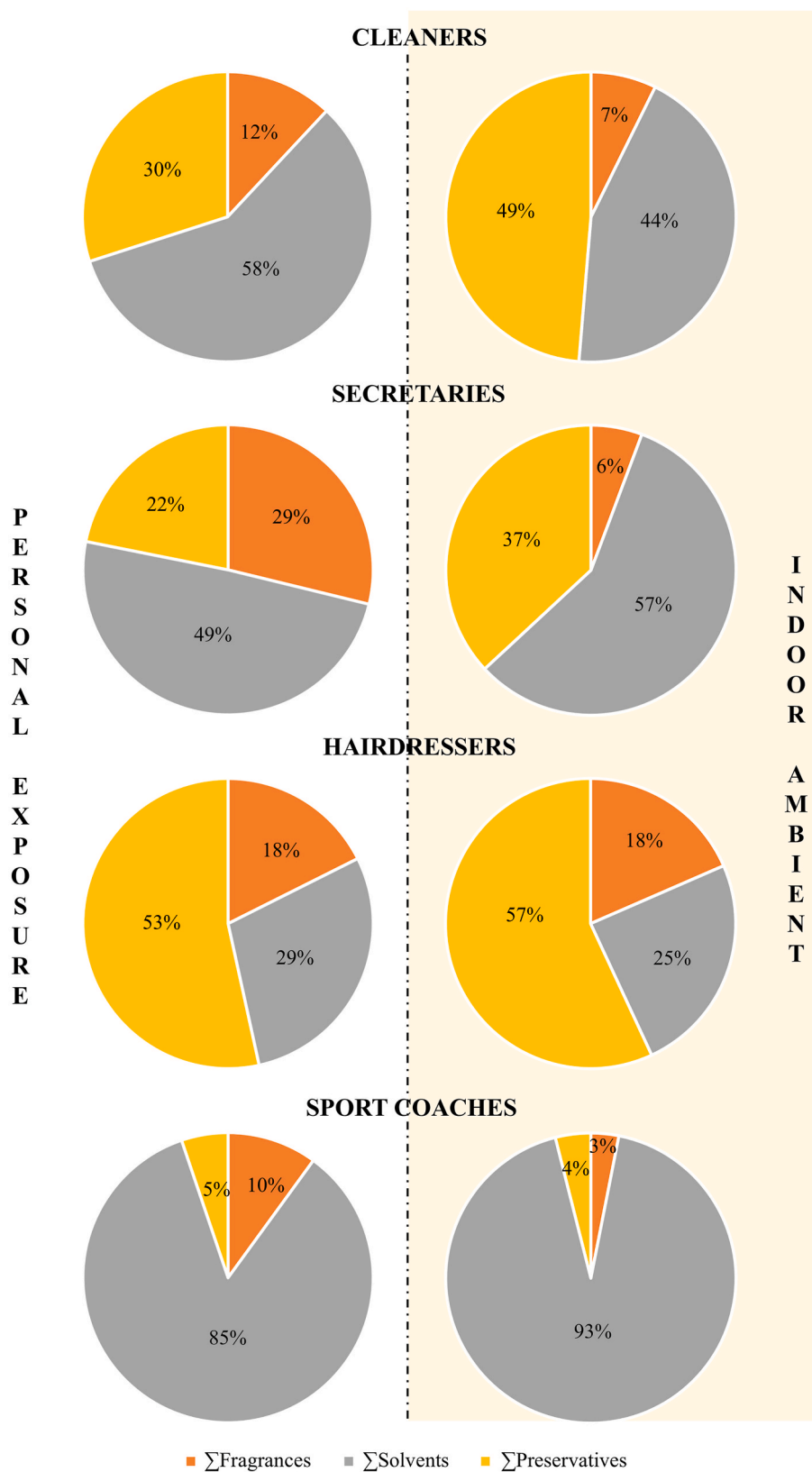


Fig. 3. Pie chart showing the percentage contributions of each family of compounds (except musk fragrances) found in SWBs from different occupational settings (cleaners, secretaries, hairdressers, sports coaches). SWBs were used to study personal exposure and indoor work environments.

conditions were initially set at 10 mL of extraction solvent and 10 min of extraction time. To perform the optimisation,  $n = 5$  conditioned SWBs were cut (1 cm pieces), mixed to homogenise, and divided into two halves. One half (2 g) was spiked with 100  $\mu\text{L}$  of a 10 mg/L standard solution of all target compounds, thus allowing the target compounds to adsorb on the SWB for roughly 30 min. The other half was used to perform SWB blanks and enable subtraction of the target compounds still present in the SWBs after the conditioning procedure. Regardless of the extraction solvent used, none of the target compounds was found in SWB blanks at concentrations above the IQLs.

We observed that ethyl acetate was the most suitable extraction solvent since it provided recovery values ranging from 58 % to 121 % for most target compounds. Slightly lower recoveries were obtained for  $\alpha$ -pinene (27 %), camphene (30 %),  $\beta$ -pinene (38 %) and 3-Carene (48 %). All RSD% obtained with ethyl acetate as the extraction solvent ranged from 3 % to 13 %.

Other extraction parameters, such as extraction volume and extraction time, were also optimised to improve recoveries while minimising solvent consumption and extraction time. We chose 5 mL as the optimal extraction volume as no significant differences were observed between the extraction volumes evaluated (5 mL–20 mL). As Table 1 shows, the highest recovery values were obtained with 5 mL ethyl acetate and an extraction time of 5 min, with values ranging from 27 % ( $\alpha$ -Pinene) to 121 % (MK) and with RSD% less than or equal to 13 % in all cases.

### 3.2. Optimisation of sampling time

The sampling time of the SWBs was optimised to adsorb the highest concentration of target compounds without reaching saturation. Prior research on personal sampling of SVOCs with SWBs (Romanak et al., 2019) and concentration data on the target compounds in indoor environments (Vallecillos et al., 2020) were taken into account to establish the sampling periods to be evaluated (10, 20 and 30 days).

Five volunteers were selected for these sampling trials, each of whom wore three SWBs. The first SWBs were removed after 10 days, the second were removed after 20 days, and the third were removed after 30 days. The graphs in Fig. 1 show the concentration ( $\mu\text{g/g}$ ) of the target compound in the SWB versus sampling time for a representative compound of each family. These results indicated that the concentrations of most compounds tended to stabilise after 20 days of sampling. There were exceptions, such as with PGMAE, phenol, MX, and MK, in which SWBs continued to adsorb compounds for up to 30 days. However, we chose an optimal sampling time of 20 days since this is the most suitable time for most compounds. This optimal sampling time is in line with those used in studies that focused on determining personal exposure to PAHs or OPEs with SWBs (e.g. 14–21 days) (Paulik et al., 2018; Xie et al., 2021). However, depending on the sampling environments and the compounds evaluated, longer monitoring periods of up to 30 or 40 days are also found (Bergmann et al., 2017).

### 3.3. Method validation

The optimised analytical method was validated by establishing the recoveries in sampled SWBs and the repeatability and reproducibility of the compounds. Method detection limits (MDLs) and method quantification limits (MQLs) were also determined.

For the recovery, repeatability and reproducibility tests, we used SWBs sampled over a 20-day period. Half of the sampled SWB (2 g) were analysed to subtract the target compounds in the sample, while the other half was spiked with a known amount of target compound. Each test was conducted in quintuplicate. In the SWBs samples used for the validation, HHCB, ATHN, MX, MK and 2-PE were the only target compounds detected at quantifiable levels, with concentrations ranging from 0.16  $\mu\text{g/g}$  (MX) to 1.9  $\mu\text{g/g}$  (HHCB). The SWBs were spiked with 100  $\mu\text{L}$  of a 10 mg/L standard solution for the compounds that were not detected in the samples and 100  $\mu\text{L}$  of a 100 mg/L standard solution for the

compounds presented at quantifiable levels. Table 1 shows that the recoveries ranged from 27 % for  $\alpha$ -pinene to 90 % for MK and that recoveries for most compounds were above 50 %. Precision of the method was also assessed, with RSD% for repeatability ranging from 3 % to 15 % and those for reproducibility ranging from 6 % to 22 %. Method detection limits (MDLs) and method quantification limits (MQLs) were estimated based on instrumental limits while taking into account method recoveries and the amount of SWB used (2 g). As Table 1 shows, MDLs ranged from 0.002  $\mu\text{g/g}$  to 0.03  $\mu\text{g/g}$  and MQLs ranged from 0.006  $\mu\text{g/g}$  to 0.11  $\mu\text{g/g}$ . The linear ranges of the method began at the MQL (the lowest calibration point) and increased to values between 1.1  $\mu\text{g/g}$  ( $\alpha$ -Pinene) and 3.7  $\mu\text{g/g}$  (DGBE) depending on the recoveries of the target compounds. All the determination coefficients ( $r^2$ ) were greater than 0.990. For those target compounds, HHCB, AHTN, DGBE and 2-PE, found in the SWBs analysed at concentration levels above the linear range, a dilution process was implemented to be able to apply the calibration lines and obtain an accurate concentration.

### 3.4. Occurrence in SWB samples

The optimised and validated analytical method was applied to real SWB samples obtained after a 20-day monitoring period. In this section we summarise the concentrations of EOCs found in SWB samples from adults living in the Tarragona area and from SWBs used as passive samplers from indoor occupational environments. Table 2 presents the minimum, maximum and average concentrations of the target EOCs detected for at least one of the SWBs analysed. The concentrations are expressed in ng/g and classified by compound family, occupational setting and sample type (personal or indoor environment).

#### 3.4.1. Personal sampling

Table 2 shows that the sum of the average concentrations of the target EOCs ( $\Sigma$ Total) found in the SWBs of people working in the four occupational settings ranged from 8.1  $\mu\text{g/g}$  (sports coaches) to 20  $\mu\text{g/g}$  (secretaries). The minimum  $\Sigma$ Total value of 3.5  $\mu\text{g/g}$  was from a cleaner and the maximum  $\Sigma$ Total value of 37  $\mu\text{g/g}$  was from a secretary. Generally, the compounds found at the highest concentrations in personal SWBs were from the family of synthetic musk fragrances ( $\Sigma$ Musk Fragrances), with average values ranging from 4.4  $\mu\text{g/g}$  (sports coaches) to 18  $\mu\text{g/g}$  (secretaries). Fig. 3S shows a chromatogram of one of the analysed SWB, highlighting the difference in abundance between musk fragrances and the other target compounds. Fragrances ( $\Sigma$ Fragrances), preservatives ( $\Sigma$ Preservatives) and solvents ( $\Sigma$ solvents) were also found in all SWBs analysed, with average concentrations ranging from 0.31  $\mu\text{g/g}$  (cleaners) to 3.2  $\mu\text{g/g}$  (sport coaches).  $\Sigma$ Fragrances were the most stable, with values ranging from 0.11  $\mu\text{g/g}$  to 0.97  $\mu\text{g/g}$ , regardless of the person's job. The concentration ranges of  $\Sigma$ Solvents and  $\Sigma$ Preservatives were wider, e.g. from 0.51  $\mu\text{g/g}$  to 5.0  $\mu\text{g/g}$  and from 0.12  $\mu\text{g/g}$  to 1.8  $\mu\text{g/g}$ , respectively, depending on the workplace.

As the stacked bar chart in Fig. 2a shows,  $\Sigma$ Musk Fragrances were ubiquitous in all personal SWBs analysed, representing between 54 % (sports coaches) and 89 % (secretaries) of all compounds. HHCB was the most prevalent compound, with average values ranging from 2.0  $\mu\text{g/g}$  to 14  $\mu\text{g/g}$ . The minimum and maximum values of HHCB were found, respectively, in the SWBs from cleaners (0.83  $\mu\text{g/g}$ ) and secretaries (30  $\mu\text{g/g}$ ). Since the concentrations obtained for the secretaries exceeded the linearity range, we had to dilute the samples that surpassed this threshold. The AHTN and MK concentrations, between 0.05  $\mu\text{g/g}$  and 4.2  $\mu\text{g/g}$ , also stood out from the other synthetic musk fragrances. The percentage of other  $\Sigma$ Fragrances was less than or equal to 5 % in all cases. The average concentrations of three fragrances stood out from the rest: 0.04  $\mu\text{g/g}$ -0.16  $\mu\text{g/g}$  for D-limonene, 0.13  $\mu\text{g/g}$ -0.27  $\mu\text{g/g}$  for eucalyptol, and 0.04  $\mu\text{g/g}$ -0.17  $\mu\text{g/g}$  for 2-PEA. The highest average values of D-limonene and eucalyptol were found in SWBs from secretaries and sports coaches. The highest average concentrations of 2-PEA were found in SWBs from secretaries and hairdressers. At a second level

**Table 3**

Estimated non-carcinogenic personal dermal risk for the different compounds of interest ( $HQ_{\text{dermal}}$ ), calculated from the dermal EDI<sub>dermal</sub> obtained. Four occupational settings and two exposure scenarios, low and high, have been taken into account.

Compounds	$HQ_{\text{dermal}}$							
	Cleaners		Secretaries		Hairdressers		Sport coaches	
	Low-case	High-case	Low-case	High-case	Low-case	High-case	Low-case	High-case
<b>Musk Fragrances</b>								
DPMI	$1.8 \times 10^{-6}$	$7.4 \times 10^{-6}$	$1.5 \times 10^{-6}$	$2.7 \times 10^{-6}$	$1.4 \times 10^{-6}$	$2.3 \times 10^{-6}$	$1.2 \times 10^{-6}$	$1.9 \times 10^{-6}$
HHCB	$4.3 \times 10^{-6}$	$1.1 \times 10^{-5}$	$1.4 \times 10^{-5}$	$3.3 \times 10^{-5}$	$8.6 \times 10^{-6}$	$1.2 \times 10^{-5}$	$4.0 \times 10^{-6}$	$1.0 \times 10^{-5}$
AHTN	$1.7 \times 10^{-7}$	$8.8 \times 10^{-7}$	$3.2 \times 10^{-7}$	$1.3 \times 10^{-6}$	$1.7 \times 10^{-7}$	$1.9 \times 10^{-7}$	$1.5 \times 10^{-7}$	$1.9 \times 10^{-7}$
MK	$5.4 \times 10^{-7}$	$1.9 \times 10^{-6}$	$2.2 \times 10^{-6}$	$3.0 \times 10^{-6}$	$1.7 \times 10^{-6}$	$2.0 \times 10^{-6}$	$1.6 \times 10^{-6}$	$1.7 \times 10^{-6}$
<b>Fragrances</b>								
Camphene	$5.6 \times 10^{-9}$	$5.6 \times 10^{-9}$	$5.6 \times 10^{-9}$	$5.6 \times 10^{-9}$	$5.6 \times 10^{-9}$	$5.6 \times 10^{-9}$	$5.6 \times 10^{-9}$	$5.6 \times 10^{-9}$
3-Carene	$1.4 \times 10^{-9}$	$2.2 \times 10^{-9}$	$1.7 \times 10^{-9}$	$4.0 \times 10^{-9}$	$2.3 \times 10^{-9}$	$4.5 \times 10^{-9}$	$2.9 \times 10^{-9}$	$4.5 \times 10^{-9}$
D-Limonene	$2.9 \times 10^{-8}$	$4.5 \times 10^{-8}$	$1.0 \times 10^{-7}$	$2.9 \times 10^{-7}$	$7.2 \times 10^{-8}$	$8.4 \times 10^{-8}$	$9.5 \times 10^{-8}$	$1.2 \times 10^{-7}$
P-Cymene	$2.9 \times 10^{-9}$	$2.9 \times 10^{-9}$	$4.0 \times 10^{-9}$	$9.4 \times 10^{-9}$	$4.0 \times 10^{-9}$	$9.4 \times 10^{-9}$	$4.5 \times 10^{-9}$	$9.8 \times 10^{-9}$
Eucalyptol	$4.7 \times 10^{-8}$	$7.5 \times 10^{-8}$	$9.2 \times 10^{-8}$	$1.2 \times 10^{-7}$	$4.4 \times 10^{-8}$	$7.0 \times 10^{-8}$	$6.5 \times 10^{-8}$	$8.4 \times 10^{-8}$
2-PEA	$2.0 \times 10^{-7}$	$3.2 \times 10^{-7}$	$4.7 \times 10^{-7}$	$1.0 \times 10^{-6}$	$5.0 \times 10^{-7}$	$7.3 \times 10^{-7}$	$2.4 \times 10^{-7}$	$7.0 \times 10^{-7}$
<b>Solvents</b>								
EGBE	$2.0 \times 10^{-7}$	$2.2 \times 10^{-7}$	$2.0 \times 10^{-7}$	$2.4 \times 10^{-7}$	$2.0 \times 10^{-7}$	$2.6 \times 10^{-7}$	$2.2 \times 10^{-7}$	$2.6 \times 10^{-7}$
DGBE	$2.4 \times 10^{-6}$	$5.4 \times 10^{-6}$	$1.6 \times 10^{-6}$	$3.0 \times 10^{-6}$	$1.0 \times 10^{-6}$	$1.3 \times 10^{-6}$	$1.4 \times 10^{-6}$	$3.9 \times 10^{-6}$
Toluene	$2.2 \times 10^{-8}$	$2.4 \times 10^{-8}$	$1.5 \times 10^{-7}$	$1.5 \times 10^{-7}$	$2.5 \times 10^{-8}$	$3.6 \times 10^{-8}$	$2.1 \times 10^{-8}$	$2.5 \times 10^{-8}$
<b>Preservatives</b>								
Phenol	$1.8 \times 10^{-8}$	$2.3 \times 10^{-8}$	$2.8 \times 10^{-8}$	$4.9 \times 10^{-8}$	$1.8 \times 10^{-8}$	$2.2 \times 10^{-8}$	$3.7 \times 10^{-8}$	$1.0 \times 10^{-7}$
2-PE	$5.4 \times 10^{-6}$	$1.4 \times 10^{-5}$	$3.5 \times 10^{-6}$	$6.0 \times 10^{-6}$	$1.2 \times 10^{-5}$	$1.4 \times 10^{-5}$	$6.5 \times 10^{-6}$	$1.4 \times 10^{-5}$
$\Sigma$ Musk Fragrances	$6.9 \times 10^{-6}$	$2.1 \times 10^{-5}$	$1.8 \times 10^{-5}$	$4.0 \times 10^{-5}$	$1.2 \times 10^{-5}$	$1.7 \times 10^{-5}$	$7.0 \times 10^{-6}$	$1.4 \times 10^{-5}$
$\Sigma$ Fragrances	$2.8 \times 10^{-7}$	$4.5 \times 10^{-7}$	$6.7 \times 10^{-7}$	$1.4 \times 10^{-6}$	$6.3 \times 10^{-7}$	$9.1 \times 10^{-7}$	$4.2 \times 10^{-7}$	$9.2 \times 10^{-7}$
$\Sigma$ Solvents	$2.6 \times 10^{-6}$	$5.7 \times 10^{-6}$	$1.9 \times 10^{-6}$	$3.4 \times 10^{-6}$	$1.2 \times 10^{-6}$	$1.6 \times 10^{-6}$	$1.7 \times 10^{-6}$	$4.2 \times 10^{-6}$
$\Sigma$ Preservatives	$5.4 \times 10^{-6}$	$1.4 \times 10^{-5}$	$3.5 \times 10^{-6}$	$6.0 \times 10^{-6}$	$1.2 \times 10^{-5}$	$1.4 \times 10^{-5}$	$6.5 \times 10^{-6}$	$1.4 \times 10^{-5}$
$\Sigma$ Total	$1.5 \times 10^{-5}$	$4.1 \times 10^{-5}$	$2.4 \times 10^{-5}$	$5.1 \times 10^{-5}$	$2.5 \times 10^{-5}$	$3.3 \times 10^{-5}$	$1.6 \times 10^{-5}$	$3.3 \times 10^{-5}$

of importance were camphene and L-camphor, with average values of between <MQL and 0.03  $\mu\text{g/g}$ . The other fragrances studied,  $\alpha$ -, $\beta$ -pinene, 3-carene and p-cymene, were not detected in any of the SWBs analysed. The daily use of personal care and cleaning products such as perfumes, creams and shower gels containing various kinds of fragrances favours the presence of these compounds in all SWBs regardless of workplace (Madureira et al., 2016; Yang et al., 2018). For instance, Correia et al. (2013) reported HHCB concentrations of 87  $\mu\text{g/g}$  in shampoos and 29  $\mu\text{g/g}$  in hair conditioners.

$\Sigma$ Solvents and  $\Sigma$ Preservatives represented between 2 % (secretaries and sport coaches) and 39 % (sports coaches) of  $\Sigma$ Total. DGBE, and to a lesser extent EGBE, were the most abundant  $\Sigma$ Solvents. The average concentrations of DGBE ranged from 0.47  $\mu\text{g/g}$  to 3.0  $\mu\text{g/g}$ , with the highest values found in the SWBs from sports coaches probably because of construction activities conducted at the gym during the sampling period. The values of EGBE dropped to between 0.12  $\mu\text{g/g}$  and 0.16  $\mu\text{g/g}$ , with no significant differences between workplaces. The most prevalent  $\Sigma$ Preservatives was 2-PE with average concentrations between 0.16  $\mu\text{g/g}$  (sport coaches) and 1.3  $\mu\text{g/g}$  (hairdressers). The minimum (0.11  $\mu\text{g/g}$ ) and maximum (1.8  $\mu\text{g/g}$ ) values of this compound were also found in SWBs from sport coaches and hairdressers, respectively. The widespread presence of 2-PE can be explained by its extensive use in personal care products due to its low cost, good stability and low risk of exposure (Dréno et al., 2019).

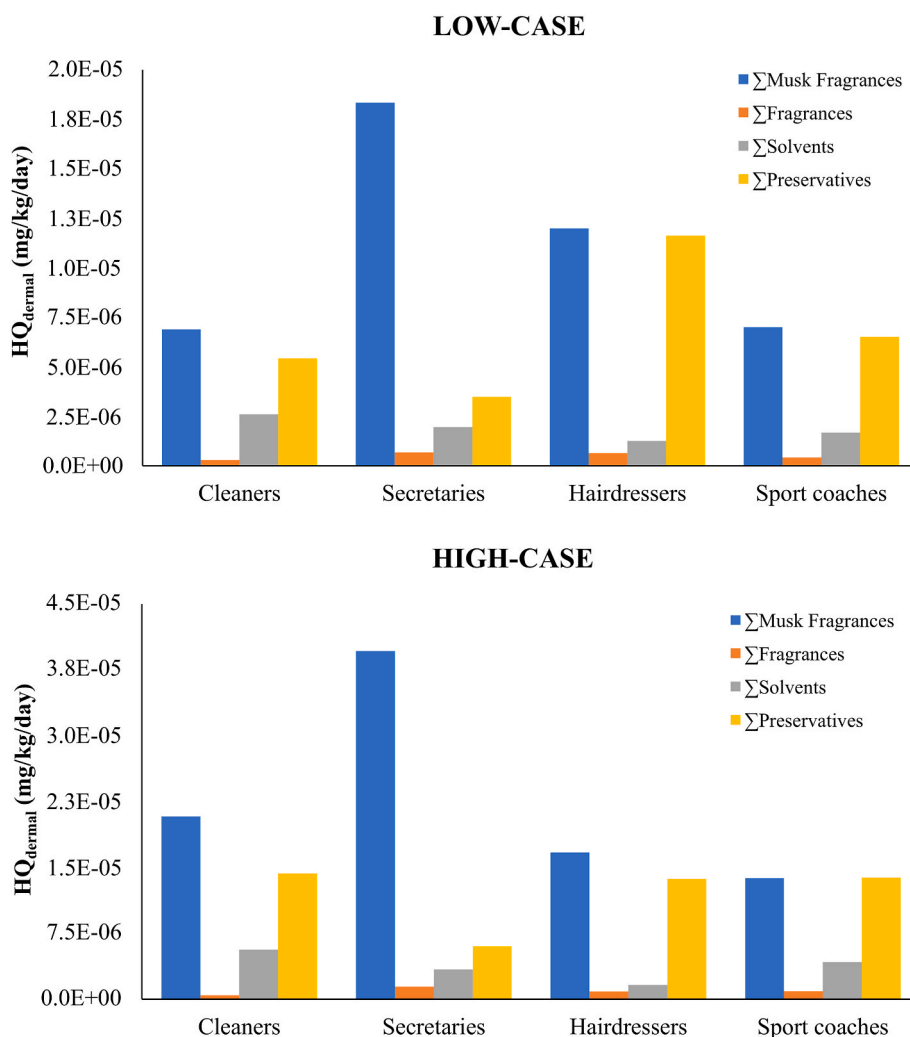
### 3.4.2. Indoor sampling vs personal sampling

The working environments of the adult volunteers participating in the personal sampling study were also sampled with SWB to assess how their environment impacts their personal exposure to the target compounds. Indoor-environment sampling lasted 10 days to avoid saturation with the SWBs. Table 2 shows that  $\Sigma$ Total in the indoor settings evaluated ranged from 6.5  $\mu\text{g/g}$  (cleaners) to 15  $\mu\text{g/g}$  (hairdressers). The compounds found at the highest concentrations were  $\Sigma$ Solvents and  $\Sigma$ Preservatives, with average values ranging from 2.0  $\mu\text{g/g}$  (cleaners) to 9.8  $\mu\text{g/g}$  (sports coaches) and from 0.42  $\mu\text{g/g}$  (sports coaches) to 6.7  $\mu\text{g/g}$  (hairdressers), respectively. As observed in relation to personal sampling, DGBE (1.2  $\mu\text{g/g}$  – 9.0  $\mu\text{g/g}$ ) and 2-PE (0.36  $\mu\text{g/g}$  – 6.7  $\mu\text{g/g}$ ) were

the most prevalent compounds. Fig. 2b shows that  $\Sigma$ Solvents reached 81 % of  $\Sigma$ Total in the gym while  $\Sigma$ Preservatives reached 46 % of  $\Sigma$ Total in the hair salon.

The average concentrations of  $\Sigma$ Musk Fragrances in the indoor environments ranged from 1.6  $\mu\text{g/g}$  (sports coaches) to 2.8  $\mu\text{g/g}$  (hairdressers). These values were much lower and much more stable than those found in the SWBs for personal sampling and were strongly related to MK average values (1.4  $\mu\text{g/g}$  – 1.9  $\mu\text{g/g}$ ).  $\Sigma$ Musk Fragrances accounted for 13 %–30 % of  $\Sigma$ Total depending on the indoor environment. These results showed that synthetic musk fragrances are strictly related to body care and/or cleaning products used on a daily basis rather than on occupational setting. Neither the prevalent compounds nor the behaviour or amount found in SWBs from personal sampling match those from indoor sampling. Except for the 2.2  $\mu\text{g/g}$  found in the hair salon, the average values of  $\Sigma$ Fragrances in indoor environments were similar in amount, prevalent compounds and observed trend to those found in SWBs from personal sampling (see Fig. 3). The average  $\Sigma$ Fragrances found in the hair salon was clearly influenced by the high average concentrations of D-Limonene (0.50  $\mu\text{g/g}$ ), Eucalyptol (0.35  $\mu\text{g/g}$ ) and, especially, 2-PEA (1.2  $\mu\text{g/g}$ ).

As Fig. 3 shows, in general two indoor environments were clearly distinguished: the gym, with a prevalence of  $\Sigma$ Solvents of 93 %, and the hair salon, with a prevalence of  $\Sigma$ Preservatives of 57 %. The indoor environments of secretaries and cleaners, with percentages ranging from 37 % to 57 %, were similar with regard to all families of compounds except  $\Sigma$ Fragrances. This is probably because the cleaners who participated in the study are responsible for cleaning the building where the secretaries are located and because cleaning products were the main source of the target EOCs. The highest concentrations were found in the hairdressing salon and gym because of the activities conducted there and the materials used during working hours. Ventilation and the dimensions of the facilities are also directly related to the EOCs values observed. The hairdressing salon, for example, was the smallest and least-ventilated indoor environment evaluated, and personal hygiene products (shampoos, hair conditioners, etc.) are used there continuously. The gym was the largest space, but the high solvent values observed can be explained by the construction work that was being



**Fig. 4.** Bar charts of estimated dermal risk for adults and of non-cancer dermal risk ( $HQ_{\text{dermal}}$ ). Two exposure scenarios were considered: low (geometric mean) and high (95th percentile). The four working environments studied are shown.

carried out there.

The pie charts in Fig. 3 also corroborate the influence of the working environment on personal exposure to the target EOCs. Specifically, a clear impact on exposure to preservatives and solvents was observed for hairdressers and sports coaches, respectively. This suggests that, although workers may be exposed to EOCs outside the workplace, daily 8-h occupational exposure to them significantly influences their personal exposure profile. This is particularly noticeable in relatively small workplaces, such as the hair salon, where personal care products are continually used.

### 3.5. Estimated dermal risk assessment

The concentrations of the target compounds found in the SWBs from personal sampling were used to calculate  $EDI_{\text{dermal}}$ . Two exposure scenarios - low (geometric mean) and high (95th percentile) - were taken into account. Table 3S shows  $EDI_{\text{dermal}}$  results by target compound and work environment. These results indicate that synthetic musk fragrances contributed between 68 % and 91 % of total  $EDI_{\text{dermal}}$ , with individual values ranging from  $7.7 \times 10^{-7}$  mg/kg/day (MM) to  $4.9 \times 10^{-3}$  mg/kg/day (HHCB). The highest  $EDI_{\text{dermal}}$  values for  $\Sigma$ Musk Fragrances were observed in the office environment (secretaries) with values of  $2.6 \times 10^{-3}$  mg/kg/day for the low scenario and  $6.1 \times 10^{-3}$  mg/kg/day for the high scenario. The next most significant families of compounds were solvents and preservatives, which represented 2 %–19 % of total  $EDI_{\text{dermal}}$ , with

values ranging from  $7.1 \times 10^{-5}$  mg/kg/day (low scenario; secretaries) and  $4.8 \times 10^{-4}$  mg/kg/day (high scenario; cleaners). Fragrances accounted for less than 5 % of total  $EDI_{\text{dermal}}$  in all work environments, with values ranging from  $4.6 \times 10^{-5}$  mg/kg/day (low scenario; cleaners) to  $1.8 \times 10^{-4}$  mg/kg/day (high scenario, secretaries).

Individual  $HQ_{\text{dermal}}$  for each target compound and total  $HQ_{\text{dermal}}$  were calculated for adults while taking into account the above two scenarios. Table 3 shows the estimated  $HQ_{\text{dermal}}$  values for the work environments under study and the two exposure scenarios considered. As stated in previous studies (Ramírez et al., 2012; Gómez et al., 2024),  $HQ_{\text{dermal}} > 1$  indicates a clear risk of non-carcinogenic effects,  $HQ_{\text{dermal}}$  between 0.1 and 1 indicates a probable risk, and  $HQ_{\text{dermal}} < 0.1$  suggests an insignificant risk. Table 3 shows that the  $HQ_{\text{dermal}}$  of the target compounds ranged from  $1.4 \times 10^{-9}$  for 3-carene (low scenario; cleaners) to  $3.3 \times 10^{-5}$  for HHCB (high scenario; secretaries). Regardless of the working environment, all individual  $HQ_{\text{dermal}}$  were clearly below  $< 0.1$  (negligible risk).  $HQ_{\text{dermal}}$  per family of compound ranged from  $2.8 \times 10^{-7}$  for fragrances (low scenario; cleaners) to  $4.0 \times 10^{-5}$  for musk fragrances (high scenario; secretaries) and were below 0.1 regardless of exposure scenario or occupational setting. HHCB, 2-PEA, DGBE and 2-PE, with  $HQ_{\text{dermal}}$  ranging from  $2.0 \times 10^{-7}$  to  $3.3 \times 10^{-5}$ , were the most prevalent compounds in each family. Even in the worst scenario, total  $HQ_{\text{dermal}}$  was clearly below 1 (between  $3.3 \times 10^{-5}$  and  $5.1 \times 10^{-5}$ ), which indicates that no significant risk of non-carcinogenic effects is expected. Fig. 4 shows that one family of target compounds (musk fragrances)

stood out from the rest, accounting for 42 %–78 % of total HQ<sub>dermal</sub>. Solvents and preservatives represented 5 %–46 % of total HQ<sub>dermal</sub> regardless of the indoor environment or exposure scenario. High percentages of solvents were characteristic of sports coaches, while preservatives were most common in hairdressers. Cleaners also had solvent and preservative percentages of between 7 % and 14 %. Fragrances had the lowest percentage contribution ( $\leq 3$  %) to total HQ<sub>dermal</sub> regardless of the working environment or exposure scenario.

#### 4. Conclusions

A new analytical method based on UAE followed by GC-MS was successfully developed and validated for assessing personal exposure to everyday chemicals, including fragrances, solvents, and preservatives, in various occupational settings. SWBs were used as passive personal samplers and 20-days sampling allowed the determination of up to 22 EOCs.

Four occupational settings with different casuistic, including cleaners, secretaries, hairdressers and sport coaches, were monitored with SWBs. All the target compounds, except some fragrances, were found at quantifiable levels in both the indoor environments evaluated and in the SWBs worn by the workers. Musk fragrances were identified as the primary source of total exposure regardless of the occupational setting, accounting for 54 %–89 % of total exposure. Solvents and preservatives were found at a lower concentration level with maximum average values of 3.2  $\mu\text{g/g}$  (sport coaches) and 1.3  $\mu\text{g/g}$  (hairdressers), respectively. HHCB, DGBE and 2-PE were the most prevalent compounds in these three families. Fragrance values were residual with percentages  $\leq 5$  % of the total EOCs. The analysis of the SWBs from the different indoor environments confirms that musk fragrances are strictly related to body care and/or cleaning products rather than the occupational setting. However, the behaviours observed for the other families of compounds corroborated the influence of the work environment on personal exposure to the target EOCs.

The results obtained were used to evaluate the dermal risk associated with personal exposure to non-carcinogenic compounds. Estimated values were below the critical threshold of 1, indicating generally low dermal risk. Nonetheless, certain environments, such as hairdressing salons, exhibited elevated concentrations of preservatives and musk fragrances, underscoring the importance of monitoring occupational exposure to safeguard workers' health.

#### 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, Laura Vallecillos Marsal, 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.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apr.2025.102747>.

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