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Occurrence of high production volume chemicals and polycyclic aromatic hydrocarbons in urban sites close to industrial areas. Human exposure and risk assessment

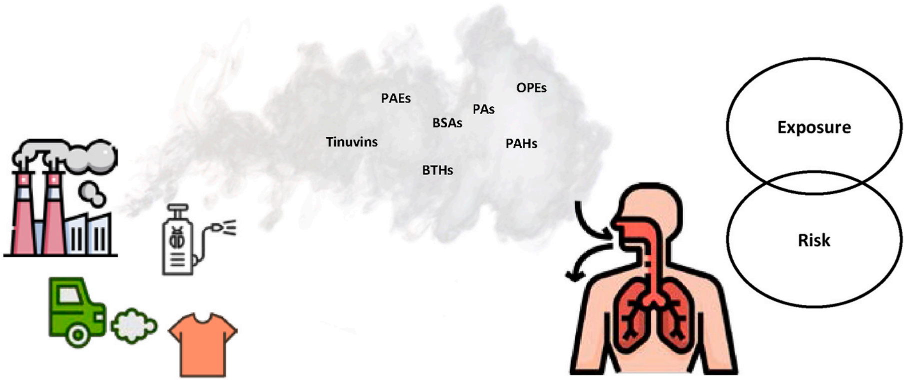
Reyes García-Garcinuño, Laura Vallecillos, Rosa Maria Marcé [*], Francesc Borrull

Universitat Rovira I Virgili, Department of Analytical Chemistry and Organic Chemistry, Campus Sescelades, Marcel·lí Domingo, 1, Tarragona, 43007, Spain

HIGHLIGHTS

- New multiresidue method based on PLE/GC-MS to determine 38 HPVCs and 18 PAHs in outdoor air samples.
- Particulate matter and gas phases were analyzed.
- There were differences between PM_{10} and gas phase depending on the summer and winter months.
- HPVCs have a lower risk contribution than PAHs for the population.

GRAPHICAL ABSTRACT



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ABSTRACT

Evaluating the occurrence of high production volume chemicals (HPVCs) and polycyclic aromatic hydrocarbons (PAHs) in the air is important because they carry a carcinogenic risk and can lead to respiratory or endocrine problems. Examples of HPVCs are organophosphate esters, benzosulfonamides, benzothiazoles, phthalate esters (PAEs), phenolic antioxidants and ultraviolet stabilizers. In this paper we develop a multi-residue method for determining HPVCs and PAHs in air samples via pressurized liquid extraction followed by gas chromatography-mass spectrometry. Air samples were collected by active sampling with high volume samplers using quartz fiber filter for the particulate matter (PM_{10}) and polyurethane foams for gas phase. The compounds found at the highest concentrations were PAEs, with a concentration of up to 24 ng m^{-3} of DEHP in gas phase and up to 109 ng m^{-3} of DEHA in PM_{10}. Non-carcinogenic risk assessment results ranged from 9.7E-05 to 9.5E-03 for most of the compounds studied. On the other hand, the results for carcinogenic risk showed that PAHs made the highest contribution.

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[*] Corresponding author.
E-mail address: rosamaria.marce@urv.cat (R.M. Marcé).

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1. Introduction

Air quality is affecting more and more people and is directly associated with health problems such as lung cancer, heart disease and respiratory infections (Wang et al., 2023). Air quality, which is influenced by meteorologic factors such as wind speed, humidity and temperature, has worsened in recent years due to industrial development and other anthropogenic activities such as road traffic emissions and fuel consumption, etc., linked to population growth (Li et al., 2023). According to the World Health Organization, it has therefore become necessary to monitor air quality, especially in urban areas near industrial parks, as by 2028 it is expected that nine out of ten people will breathe air with high levels of contamination (World Health Organization).

As well as major air pollutants such as particulate matter under 10 µm (PM_{10}) or 2.5 µm ($PM_{2.5}$), nitrogen oxides (NO_x) and ozone (O_3), high production volume chemicals (HPVCs) have aroused special interest because 1000 tons of them are produced every year (Organisation for Economic Co-operation and Development, 2004). In this group are compounds such as benzothiazoles (BTHs), phthalates esters (PAEs), benzosulfonamides (BSAs), organophosphate esters (OPEs), ultraviolet stabilizers (Tinuvins) and phenolics antioxidants (PAs). These compounds are used in industry as corrosion inhibitors (BTHs), as flame retardants and plasticizers (OPEs, Tinuvins), and in the manufacture of plastics (BTHs, PAEs), electronic products (PAEs), and fungicides (BTHs, BSAs) (Li et al., 2020; Zhang et al., 2014, 2018; Maceira et al., 2018). Exposure to these compounds can cause health problems such as dermatitis (BSAs, OPEs, Tinuvins), respiratory ailments (PAEs, BSAs) (Zhang et al., 2014; Maceira et al., 2019; Liao et al., 2018; Pei et al., 2013; Hou et al., 2021), cancer, and damage to the nervous system due to inhalation (Huo et al., 2022; Núñez et al., 2022). BTHs can be found in air samples at concentrations of up to 1.2 ng m^{-3} in PM_{10} of urban air samples from areas close to industrial zones in Tarragona (Spain) (Maceira et al., 2020). Total PAE concentrations ranged from 26,000 ng m^{-3} to 107,000 ng m^{-3} in $PM_{2.5}$ of urban air from industrial areas in Vigo (Spain) (Sánchez-Piñero et al., 2022). Ouyang et al. (2019) reported PAEs at concentrations ranging from 1042 ng m^{-3} to 3589 ng m^{-3} in gas phase and from 972.3 ng m^{-3} to 2533 ng m^{-3} in PM_{10} air samples from urban and industrial areas in Hangzhou (China). OPEs ranged from 0.8 ng m^{-3} to 9.1 ng m^{-3} in both PM_{10} and gas phase in samples from urban areas in Stockholm (Sweden) (Wong et al., 2018).

Other compounds that are extensively studied due to their toxicity are polycyclic aromatic hydrocarbons (PAHs), especially the 16 PAHs defined as priority by the U.S. Environmental Protection Agency (USEPA) (United States Environmental Protection Agency, 2001; Ravindra et al., 2008). Long-term exposure to PAHs can cause mutagenic effects or cancer. PAHs with up to four rings, which are mainly found in the gas phase, are most likely to cause cancer. PAHs with more than 4 rings, which are mainly found in the PM_{10}, are related to respiratory problems (Berthiaume et al., 2021; Fujita et al., 2007; Qiao et al., 2022; Moradi et al., 2022). Moreover, when exposure to these compounds is higher, the risk increases, as such PAHs which produce cell damage (Mahasakpan et al., 2023). These compounds are present in the environment because of combustion processes associated with road traffic and the incomplete combustion of organic matter or fossil fuels. The risk associated with these compounds has been found to be 10 times higher in urban areas than in semi-urban areas near industrial complexes (Moradi et al., 2022). Total concentrations of PAHs in areas close to the industrial complex in Tarragona (Spain) ranged from 2.13 ng m^{-3} to 361 ng m^{-3} in the gas phase and from non-detected (n.d.) to 33.3 ng m^{-3} in PM_{10} (Ramírez et al., 2011). In industrial areas of Athens, total PAHs concentrations in PM_{10} ranged from 6 ng m^{-3} to 217 ng m^{-3} (Mantis et al., 2005). Concentrations ranging from 23 ng m^{-3} to 88.9 ng m^{-3} were found in PM_{10} samples from Islamabad (Pakistan) with dense traffic and with industries located 4–22 km away (Mehmood et al., 2020).

Since HPVCs and PAHs are present at trace levels in urban atmospheres, sampling involves using high-volume samplers to preconcentrate high volumes of air. Gas phase samples are mainly collected on polyurethane foams (PUFs) (Prats et al., 2022) while PM_{10} samples are collected on quartz fiber filters (QFFs) (Mantis et al., 2005; Naccarato et al., 2021). Sometimes, these quartz fiber filters (QFFs) are impregnated with resins such as XAD-4 or XAD-2 to enable better retention of the PAHs (Wu et al., 2023). HPVCs and PAHs from PUFs and QFFs are most often extracted with an organic solvent using an extraction technique such as ultrasound-assisted extraction (UAE) (Ouyang et al., 2019; Wong et al., 2018), microwave-assisted extraction (MAE) (Naccarato et al., 2021), pressurized liquid extraction (PLE) (dos Santos et al., 2020), as well as Soxhlet extraction (Wong et al., 2018) before their determination by gas chromatography and mass spectrometry-based detection (GC-MS) (Núñez et al., 2022; Maceira et al., 2020; Liu et al., 2010). In recent years, environmentally friendly techniques such as, solid phase microextraction (SPME) (Menezes and De Lourdes Cardeal, 2011) and cold fiber solid phase microextraction (CF-SPME) (dos Santos et al., 2020) followed by GC-MS have successfully been applied for the determination of PAHs in PM_{10} and PUF samples. Due to their semi-volatile character, some of the compounds studied (e.g. PAHs) can also be determined by liquid chromatography-mass spectrometry (LC-MS) (Mahasakpan et al., 2023) (Terzi and Samara, 2004).

The main aims of this study are (1) to develop and validate a multi-residue method based on PLE followed by GC-MS to determine up to 37 HPVCs and 18 PAHs in urban air samples, (2) to monitor the presence of these compounds in particulate matter and gas phase outdoor air samples from a location influenced by industry, and (3) to evaluate human exposure and risk to these compounds through outdoor air inhalation by different age groups (infants, children and adults) in two exposure scenarios at the location studied.

2. Experimental part

2.1. Reagents and standards

The HPVCs studied were five benzothiazoles (BTHs): 1-H-benzothiazole (BTH), 2-chlorobenzothiazole (ClBT), 2-(methythio)-benzothiazole (MeSBT), 2-amino-1-H-benzothiazole (NH_2BT) and 2-hydroxibenzohiazole (OHBT); four benzenesulfonamides (BSAs): benzenesulfonamide (BSA), *ortho*-toluenesulfonamide (*o*-TSA), *N*-methyl-*para*-toluenesulfonamide (Me-*p*-TSA) and *para*-toluenesulfonamide (*p*-TSA); six phthalate esters (PAEs): dimethyl-phthalate (DMP), diethylphthalate (DEP), di-iso-butyl-phthalate (DiBP), diethylhexyl-adipate (DEHA), diethylhexyl-phthalate (DEHP) and di-*n*-octylphthalate (DnOP); nine organophosphate esters (OPEs): triethylphosphate (TEP), tri-isobutylphosphate (TiBP), tributylphosphate (TBP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(2-chloroethyl)-phosphate (TCEP), tris (2-ethylhexyl)-phosphate (TEHP), 2ethylhexyl-diphenyl-phosphate (EHDP), triphenylphosphate (TPP) and tricresyl phosphate (TTP); seven ultraviolet stabilizers (Tinuvins): 2-(2-hydroxy-5-methylphenyl)benzotriazole (UVP), 2- (2H-benzotriazol-2-yl)-4-methyl-6-(2-propenyl)phenol (Allyl-BZT), 2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-2H-benzotriazole (UV320), 2-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV326), 2,4-di-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol (UV327), 2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (UV328) and 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV329); and eight phenolic antioxidants (PAs): 2,6-di-*tert*-butyl-4-methylphenol (BHT), 3(2)-*tert*-butyl-4-methoxyphenol (BHA), 2,4-di-*tert*-butylphenol (2,4-DTBP), 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (BHT−CHO), 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (BHT−COOH), 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione (BHT-Q), 2-6-di-tertbutyl- 4-(hydroxymethyl)phenol (BHT−OH) and 2-*tert*-butylbenzene-1,4-diol (TBHQ). Eighteen polycyclic aromatic hydrocarbons (PAHs) were studied: naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene

(Fla), pyrene (Pyr), benz(*a*)anthracene (BaA), chrysene (Chr), benzo(*b*) fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(*j*)fluoranthene (BjF), benzo(*a*)pyrene (BaP), benzo(e)pyrene (BeP), indeno(1,2,3-c,d) pyrene (InD), dibenzo(a,h)anthracene (DiB) and benzo(g,h,i)perylene (BghiP). All compounds were obtained from Sigma Aldrich (St. Louis, USA) except UV320 and BHT-CHO, which were obtained from LGC Standards (Barcelona, Spain), and InD, DiB and BhhiP, which were obtained from Supelco (Bellefonte, USA). The internal standards were: d_{12}-perylene (d_{12}-Per), d_{12}-chrysen (d_{12}-Chr), d_4-*para*-toluenesulfonamide (d_4-*p*-TSA), d_8-naphthalene (d_8-Nap), d_{10}-phenanthrene (d_{10}-Phe), d_4-diethylhexyl-phthalate (d_4-DEHP), d_{27}-tributylphosphate (d_{27}-TBP), d_4-1-H-benzothiazole (d_4-BTH) and d_{10}-acenaphthene (d_{10}-Ace), all of which were obtained from Sigma Aldrich.

Individual standard solutions of 1000 mg L^{-1} or 2000 mg L^{-1} were prepared in ethyl acetate or hexane depending on the compound. Working solutions of each family of compounds of 100 mg L^{-1} in ethyl acetate were also used. All standard solutions were stored at −20 °C until use.

GC-grade ethyl acetate, hexane, acetone and dichloromethane with purity >99.9% were obtained from Carlo Erba (Cornaredo, Milan, Italy) and dimethylformamide was obtained from Sigma Aldrich.

Helium gas for chromatographic analysis and nitrogen gas for pressurized liquid extraction (PLE), both with a purity of 99.999%, were obtained from Carburos Metálicos (Tarragona, Spain).

2.2. Sampling

Sampling was conducted at the monitoring station of the Atmospheric Pollution Monitoring and Forecasting Network of the Catalan Government located in Constantí (Tarragona, Spain), a town with 6724 inhabitants located less than 3 km from Tarragona's northern petrochemical complex. Two sampling campaigns were carried out between May–July 2021 and January–March 2022. Both PM_{10} and the gas phase of air were sampled, and a total of eleven 24-h samples were collected in summer and fourteen were collected in winter.

An MCV-PM10 High Volume Air Sampler (MCV S.A., Collbató, Barcelona) equipped with a CBE-CAV was used to collect the samples. The PM_{10} (particle size < 10 μm, PM_{10}) were deposited in 150-mm-diameter quartz fiber filters (QFF) obtained from Whatman (Sigma Aldrich). Polyurethane foams (PUF), 10 cm × 10 cm (MCV S.A.), were used to sample the gas phase. 24-hour samples of 720 m^3 under a constant flow rate of 30 m^3 h^{-1} were obtained. Once the PUFs and QFFs were sampled, they were wrapped in aluminum foil, labelled, and placed in the freezer at −20 °C until analysis.

2.3. Extraction procedure

The pressurized liquid extraction (PLE) of PUFs and QFFs was performed using an ASE 350 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA, USA). The extractions were carried out with 60 mL stainless steel cells (Dionex) for PUFs and 10 mL stainless steel cells for QFFs. A cellulose filter (Thermo Scientific, Barcelona, Spain) was placed on the bottom of each cell followed by half of the PUF or QFF cut with scissors that had previously been cleaned with acetone. For the QFFs, 1 g of diatomaceous earth (Thermo Scientific), previously conditioned overnight at 400 °C, was introduced between the cellulose filter and the QFF. Diatomaceous earth was also used to refill the cell before the cell was closed tightly.

The extraction was performed with dichloromethane (DCM) as the solvent. The oven temperature was 100 °C for the QFFs and 80 °C for the PUFs. The times for preheating and static extraction were both 5 min. There was one static cycle at a pressure of 1500 psi. The nitrogen purge was 120 s and the flushing volume was 50% of the volume of the extraction cell.

PLE extracts were filtered using a 0.22 μm polytetrafluoroethylene (PTFE) filter (Scharlab, Barcelona, Spain). Then, 400 μL of dimethylformamide (DMF) was added to the extracts to prevent loss of target analytes, and the PLE extracts were evaporated in the rotary evaporator (Büchi, Flawil, Swiss) to near dryness. The internal standards were added and the extract was filtered and reconstituted to a final volume 2 mL with DCM before injection into the GC-MS system. The final extract contained a concentration of 1 mg L^{-1} of internal standards d_8-Nap, d_{10}-Phe, d_4-DEHP, d_{27}-TBP, d_4-BTH and d_{10}-Ace, and a concentration of 2.5 mg L^{-1} of internal standards d_4-*p*-TSA, d_{12}-Chr and d_{12}-Per.

2.4. Chromatographic analysis

The samples were analyzed in a GCMS-QP2010 Ultra High-Performance Gas Chromatograph equipped with an autosampler, split/splitless injection, a Mass Spectrometer with electron impact (EI) ionization, and a simple quadrupole as analyzer (Shimadzu Corporation, Izasa S.A., Madrid, Spain). The chromatographic column was a Zebron ZB-50, 50% phenyl-50% dimethylpolysiloxane (30 m × 0.25 mm, 0.25 μm film thickness) from Phenomenex (Torrance, CA, USA). For the analysis, 2 μL was injected in splitless mode at 300 °C under a constant helium flow rate of 1.2 mL min^{-1}. The GC oven temperature was initially 80 °C and this increased to 275 °C at 5 °C min^{-1} and finally to 310 °C at 20 °C min^{-1}, where it was held for 10 min. The mass spectrometer acquired data in selective ion monitoring (SIM) at an electron impact energy of 70 eV. The ion source and GC-MS interface temperatures were set at 230 °C and 280 °C, respectively. One internal standard per family was used for quantification as internal standard was not available for all target compounds. Table 1S shows the retention times, quantifier and qualifier ions selected for each target by family and their corresponding internal standard.

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

To prevent cross-contamination, the processes were performed with glassware material that had been previously washed with isopropanol. The QFFs were conditioned at 400 °C for 24 h, covered with aluminum foils, and kept in the freezer at −20 °C until use. The PUFs were conditioned using Soxhlet with DCM for 24 h and then dried in a vacuum desiccator before they were stored in the freezer until analysis.

For quality assurance purposes, instrumental and procedural blanks were performed periodically. Standard controls of 1 mg L^{-1} were also included in the GC-MS batches every ten samples to ensure correct behavior of the instrument.

2.6. Risk assessment

To estimate human exposure to the target compounds, estimated daily intake (EDI, pg kg_{bw}^{-1} day^{-1}) for ambient inhalation was calculated from equation (1) (Asante-Duah, 2002).

$$EDI = \frac{C \times IR \times RR \times ET \times EF \times ED}{BW \times AT} \tag{1}$$

In this equation, C is the concentration of the compound quantified in PM10 and gas phase in pg m-3, IR is the inhalation rate in m^3 h^{-1}, RR is the retention rate of inhaled air in %, ET is the exposure time in h day^{-1}, EF is the exposure frequency in days $years^{-1}$, ED is the exposure duration in years, BW is the average body weight over the exposure period in kg, and AT is the period in days of average exposure. The AT parameter is different for carcinogenic and non-carcinogenic risk. The values of the parameters in equation (1) (Asante-Duah, 2002) for calculating the EDIs are given in Table 2S. The EDIs were calculated for two scenarios (high and low) and three population subgroups (infants, children and adults).

To evaluate non-carcinogenic risk (HQ), the levels defined as Reference Dose (RfD) by the USEPA Integrated Risk Information System (IRIS) (IRIS, 2020; RAIS) were used to estimate non-cancer risk.

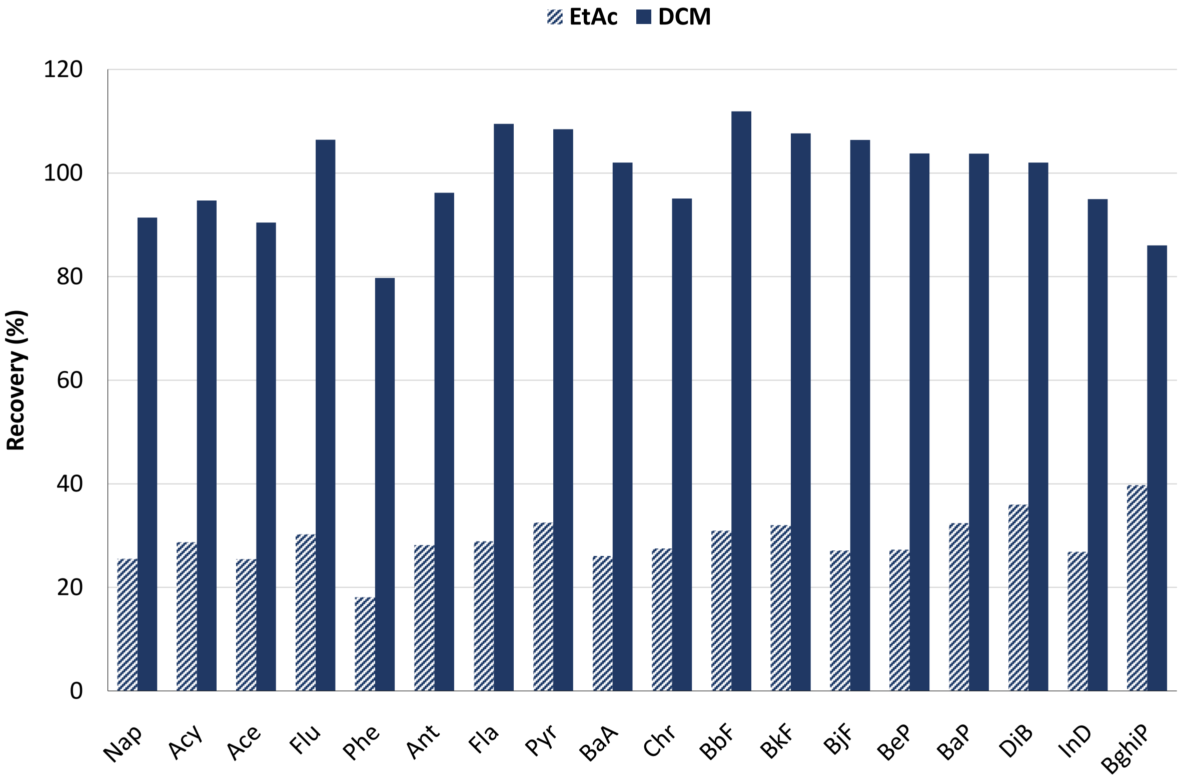

Fig. 1. Bar graph showing the recoveries of PAHs obtained with the PLE for the different solvents tested (DCM and EtAc).

Equation (2) was used to obtain HQ values. The RfD values listed in Table 3S were used to calculate HQ.

$$HQ = \frac{EDI}{RfD} \quad (2)$$

Two methods can be used to assess carcinogenic risk (CR). The first method was applied to the PAHs because those compounds have an inhalation unit risk (IUR). Using equation (3) (Sánchez-Piñero et al., 2022), where C is the concentration of the compound quantified in PM_{10} and gas phase in pg m^{-3}, IUR is the inhalation unit risk (pg $m^{-3})^{-1}$, and ET, EF, ED and AT are as explained earlier, it was possible to calculate the carcinogenic risk. To determine the IUR for each PAHs, the IUR_{BaP} (8.7E-05) (World Health Organisation (WHO), 1987) and equivalent toxicological factors (TEF) (Table 3S) (Larsen and Larsen, 1998) were used in accordance with the USEPA.

$$CR = \frac{IUR \times C \times ET \times EF \times ED}{AT} \quad (3)$$

The second method was applied to the HPVCs because those compounds do not have an inhalation unit risk and the carcinogenic risk could therefore be estimated through the EDI and the oral slope factor (SFo) as shown in equation (4). The SFo values are given in Table 3S (RAIS).

$$CR = EDI \times SFo \quad (4)$$

3. Results

3.1. GC-MS optimization

To optimize the chromatographic separation, a mixed solution of 5 mg L^{-1} of the target compounds and 2.5 mg L^{-1} of the internal standards was prepared in ethyl acetate, and 2 µL of this solution was injected directly into the GC-MS in full scan mode. Various oven temperature programs were tested based on the previous experience of our research group in the determination of HPVCs (Maceira et al., 2019, 2020) and PAHs (Ramírez et al., 2011). All compounds were separated in 51 min using the chromatographic conditions described in Section 2.4. To achieve maximum sensitivity of the compounds, selective ion monitoring (SIM) mode was applied. The target compounds were identified according to retention time, the quantifier and qualifier ions shown in Table 1S, and the relative percentage of each qualifier ion. Quantification was carried out using the internal standard calibration method with at least one internal standard per family of compounds.

GC-MS was validated by establishing the linear range, the instrumental limit of detection (ILOD), the instrumental limit of quantification (ILOQ), and the repeatability and reproducibility of all target compounds. To establish the linear range, fifteen calibration levels were evaluated (0.25 µg L^{-1}, 0.5 µg L^{-1}, 0.75 µg L^{-1}, 1 µg L^{-1}, 2.5 µg L^{-1}, 5 µg L^{-1}, 7.5 µg L^{-1}, 10 µg L^{-1}, 25 µg L^{-1}, 50 µg L^{-1}, 100 µg L^{-1}, 500 µg L^{-1}, 1000 µg L^{-1}, 2500 µg L^{-1} and 5000 µg L^{-1}). Two calibration curves per compound, one for low concentrations and other for high concentrations, were drawn and the determination coefficients (R^2) were always above 0.990. The linear range reached 5 mg L^{-1} for all the target compounds, except for DEHA, with 7.5 mg L^{-1} and EHDP and DiBP, with 2.5 mg L^{-1}. The ILOQ was set as the lowest point of the calibration curve and, as Table 1S shows, this was between 0.3 µg L^{-1} (ClBT, MeSBT, DiBP, TiBP, EHDP and Nap) and 100 µg L^{-1} (TBHQ, DiB). The ILOD, which is the concentration that provides a signal three times higher than the signal of noise, was between 0.1 µg L^{-1} (BTH, ClBT, DiBP, DEHP, TiBP and TEHP) and 25 µg L^{-1} (TBHQ, DiB, InD and BghiP). Instrumental repeatability and reproducibility were determined at 1 mg L^{-1} and the results were expressed as the relative standard deviation (% RSD). The % RSD values for repeatability ($n = 5$) were below 7% except for UVP (12%), UV329 (11%) and NH_2BT (11%). Reproducibility between days ($n = 5$) was less than 12% for all compounds except OHBT (15%) and UVP (16%).

Table 1
Recoveries of blank and sampled QFFs and PUFs (%) (RSD % $n = 3$), method detection limits (MDLs) and method quantification limits (MQLs) for each target.

Compounds	QFFs				PUFs			
	Recovery (%)		MDL (pg m^{-3})	MQL (pg m^{-3})	Recovery (%)		MDL (pg m^{-3})	MQL (pg m^{-3})
	Blank	Sampled			Blank	Sampled		
BHT-Q	89 (17)	77 (6)	1.8	3.6	67 (19)	91 (4)	1.5	3.1
BHT	86 (7)	84 (6)	0.8	1.7	89 (18)	82 (9)	0.9	1.7
2,4-DTBP	94 (8)	82 (15)	0.9	2.5	110 (20)	83 (5)	0.8	2.5
BHA	85 (6)	88 (16)	2.4	3.2	76 (18)	87 (4)	2.4	3.2
TBHQ	85 (8)	119 (8)	58	233	127 (4)	100 (3)	69	278
BHT-CHO	92 (9)	86 (1)	0.8	1.6	88 (13)	99 (3)	0.7	1.4
BHT-OH	80 (18)	80 (2)	17	26	76 (11)	87 (4)	16	24
BTH	90 (5)	85 (7)	0.3	1.6	81 (5)	93 (9)	0.3	1.5
CiBT	92 (6)	80 (17)	0.4	0.9	92 (6)	112 (6)	0.3	0.6
MeSBT	101 (8)	118 (9)	0.2	0.6	135 (14)	120 (5)	0.2	0.6
NH_2BT	83 (15)	118 (14)	0.2	0.6	103 (19)	120 (15)	0.2	0.6
OHBT	101 (14)	94 (20)	15	147	92 (20)	85 (3)	16	163
UVP	107 (9)	113 (13)	25	62	126 (11)	118 (5)	24	59
Allyz-BZT	113 (12)	112 (11)	25	62	126 (14)	131 (1)	21	53
UV320	88 (8)	87 (17)	2.4	3.2	75(1)	74 (5)	2.8	3.8
UV326	98 (9)	102 (10)	20	68	108 (7)	95 (4)	22	73
UV329	98 (14)	101 (7)	28	137	99 (11)	91 (8)	31	153
UV328	86 (8)	92 (11)	7.6	15	97 (19)	81 (9)	8.6	17
UV327	85 (10)	93 (15)	15	22	81 (4)	70 (10)	20	30
TEP	83 (15)	79 (5)	4	9.9	74 (12)	111 (12)	2.5	6.3
TiBP	83 (6)	78 (6)	0.4	0.9	78 (14)	86 (15)	0.3	0.8
TBP	89 (5)	82 (4)	0.9	1.7	80 (19)	90 (5)	0.8	1.5
TCPP	91 (1)	82 (9)	0.9	34	73 (3)	86 (3)	0.8	32
TCEP	100 (12)	95 (12)	15	22	85 (20)	105 (1)	13	20
TEHP	96 (15)	90 (1)	0.3	0.8	77 (18)	70 (4)	0.4	1
EHDP	94 (3)	103 (11)	0.7	2	77 (18)	90 (4)	0.8	2.3
TPP	100 (12)	110 (18)	13	19	110 (7)	100 (3)	14	21
TTP	114 (13)	115 (16)	18	60	103 (6)	96 (9)	22	72
DMP	80 (10)	59 (11)	1.2	47	98 (7)	122 (12)	0.6	23
DEP	106 (14)	77 (14)	58	166	105 (8)	135 (2)	0.5	1.5
DiBP	85 (9)	75 (3)	0.4	0.9	101 (9)	124 (10)	0.2	0.6
DEHA	108 (19)	100 (18)	51	77	112 (10)	96 (13)	40	64
DEHP	87 (5)	102 (9)	0.7	68	106 (6)	94 (20)	8	17
DnOP	124 (7)	41 (20)	1.7	6.8	–	–	–	–
BSA	93 (14)	82 (9)	17	25	88 (14)	100 (15)	14	21
o-TSA	85 (15)	108 (1)	0.6	1.9	82 (3)	130 (18)	0.5	1.6
Me-*p*-TSA	109 (10)	124 (11)	5.6	11	100 (13)	123 (9)	5.7	11
P-TSA	114 (4)	91 (2)	3.1	76	91 (1)	92 (2)	3	76
Nap	85 (5)	78 (16)	0.4	0.9	82 (20)	92 (6)	0.3	0.8
Acy	88 (6)	81 (12)	0.9	1.7	88 (1)	101 (7)	0.7	1.4
Ace	87 (7)	82 (13)	0.9	2.5	83 (17)	98 (6)	0.7	2.1
Flu	99 (6)	86 (12)	2.4	8.1	92 (7)	123 (5)	1.7	5.7
Phe	83 (4)	86 (9)	0.8	1.6	118 (15)	136 (1)	0.5	1
Ant	93 (5)	84 (5)	1.7	8.3	83 (19)	74 (6)	1.9	9.4
Fla	118 (18)	106 (1)	2	6.6	70 (14)	123 (5)	1.7	5.7
Pyr	121 (11)	102 (11)	1.4	2	79 (12)	104 (6)	1.3	2
BaA	117 (13)	86 (10)	3.2	16	101 (11)	99 (6)	2.8	14
Chr	112 (12)	91 (7)	7.6	76	96 (7)	103 (5)	6.7	67
BbF	119 (13)	105 (8)	6.6	20	120 (2)	114 (9)	6.1	18
BkF	116 (11)	87 (4)	24	80	112 (9)	79 (11)	26	88
BjF	117 (7)	90 (4)	7.7	15	92 (19)	77 (7)	9	18
BeP	100 (12)	88 (2)	7.9	16	92 (5)	100 (4)	6.9	14
BaP	101 (18)	90 (11)	77	154	95 (10)	109 (17)	64	127
DiB	122 (14)	83 (10)	84	334	115 (16)	100 (18)	40	160
InD	121 (18)	85 (7)	82	163	133 (12)	118 (16)	59	118
BghiP	116 (5)	74 (3)	94	188	108 (12)	134 (13)	52	104

3.2. PLE optimization

For PLE optimization, the initial conditions were set according to our previous experience (Maceira et al., 2019, 2020; Ramírez et al., 2011; Ras et al., 2009). First, dichloromethane (DCM) and ethyl acetate (EtAc) were tested as extraction solvents. The other PLE conditions were initially set as 80 °C extraction temperature, 5 min static time, 1 cycle, a flush volume of 50%, and 120 s of purge time. To conduct the optimization, previously conditioned QFFs and PUFs were divided into two halves, one of which was spiked with 400 μL of a standard solution of 5 mg L^{-1} of all target compounds, and the other was used to subtract those compounds still present after the conditioning step.

For the HPVCs the recoveries were similar when we used DCM and EtAc as extraction in QFF, as were the results obtained by Maceira et al. (2018). In the case of PAHs, as Fig. 1 shows, recovery values increased significantly up to 60% when DCM instead of EtAc was used, DCM was selected as the optimal extraction solvent.

Various extraction temperatures, times and numbers of cycles were

Table 2

Arithmetic mean (AM), concentration range (CR), and detection rate (DR) of the target compounds found in PM_{10} samples taken in winter and summer.

	Compound	Winter (n = 14)			Summer (n = 11)		
		AM (pg m^{-3})	CR (pg m^{-3})	DR (%)	AM (pg m^{-3})	CR (pg m^{-3})	DR (%)
BTHs	BTH	624	45–2611	100	776	56–3294	100
	ClBT	1	<MQL – 11	64	<MQL	<MQL	100
	MeSBT	30	n.d. – 141	36	15	n.d. – 44	55
	NH_2BT	n.d.	n.d.	0	<MQL	<MQL	100
	OHBT	<MQL	<MQL	100	151	n.d. – 380	73
BSAs	BSA	50	35–370	100	122	n.d. – 194	82
	o-TSA	30	n.d. – 312	21	29	n.d. – 54	64
	Me-*p*-TSA	23	<MQL – 149	64	56	n.d. – 148	73
	p-TSA	78	<MQL – 624	50	166	n.d. – 458	73
PAEs	DMP	20	<MQL – 24	86	230	59–478	100
	DEP	<MQL	<MQL – 823	100	4176	1178–17,600	100
	DiBP	821	418–1458	100	2496	168–4546	100
	DEHA	6007	493–15,662	100	109,331	34,604–157,190	100
	DEHP	5249	406–16,183	100	7237	1820–11,610	100
	DnOP	567	n.d. – 1530	93	497	n.d. – 2254	73
OPEs	TEP	8	15–48	93	n.d.	n.d.	0
	TiBP	72	<MQL – 354	100	220	n.d. – 456	91
	TBP	224	n.d. – 486	86	344	90–1128	100
	TCPP	115	<MQL – 499	36	672	98–1028	100
	TCEP	303	n.d. – 932	71	83	n.d. – 124	73
	TEHP	616	n.d. – 1287	57	786	n.d. – 3430	82
	EHDP	365	263–661	100	183	n.d. – 1396	82
	TPP	163	n.d. – 387	43	38	n.d. – 62	82
	TTP	42	n.d. – 309	14	46	n.d. – 76	82
Tinuvins	UVP	288	n.d. – 692	57	99	n.d. – 138	82
	Allyl-BZT	147	n.d. – 961	14	49	n.d. – 68	82
	UV320	146	n.d. – 255	64	35	n.d. – 62	82
	UV326	n.d.	n.d.	0	<MQL	<MQL	100
	UV329	127	n.d. – 842	14	59	n.d. – 88	73
	UV328	27	n.d. – 324	7	<MQL	<MQL	100
	UV327	150	n.d. – 369	43	40	n.d. – 66	64
PAs	BHT-Q	356	n.d. – 600	71	429	90–1098	100
	BHT	154	n.d. – 279	64	137	68–366	100
	2,4-DTBP	81	n.d. – 197	64	242	90–396	100
	BHA	103	n.d. – 225	64	141	n.d. – 1344	82
	TBHQ	n.d.	n.d.	0	96	n.d. – 702	18
	BHT-CHO	124	<MQL – 441	93	184	48–888	100
	BHT-OH	30	n.d. – 307	7	31	n.d. – 46	73
PAHs	Nap	131	n.d. – 169	93	110	101–127	100
	Ace	118	n.d. – 448	50	122	n.d. – 327	55
	Acy	191	n.d. – 293	71	80	n.d. – 202	55
	Flu	98	n.d. – 329	36	55	n.d. – 266	18
	Phe	165	n.d. – 279	71	429	323–559	100
	Ant	133	n.d. – 226	71	270	204–383	100
	Fla	178	n.d. – 402	64	315	n.d. – 804	82
	Pyr	141	n.d. – 423	50	51	n.d. – 95	55
	BaA	403	n.d. – 736	79	n.d.	n.d.	0
	Chr	463	n.d. – 864	79	97	82–140	100
	BbF	234	n.d. – 436	71	43	n.d. - 122	82
	BkF	536	n.d. – 835	71	186	n.d. – 447	45
	BjF	<MQL	<MQL	100	<MQL	<MQL	100
	BeP	28	<MQL – 135	100	<MQL	<MQL	100
	BaP	645	n.d. – 1024	79	379	n.d. – 669	64
	DiB	<MQL	<MQL	0	n.d.	n.d.	0
	InD	844	n.d. – 1734	50	n.d.	n.d.	0
	BghiP	387	n.d. – 731	57	n.d.	n.d.	0

tested to find the optimal extraction conditions. The results obtained when the temperature was raised to 100 °C were not significantly different for HPVCs but did improve for PAHs. The recoveries obtained at 100 °C for PAHs were comparable with those reported by Ras et al. (2009), with values ranging from 80% to 121%. Therefore, 100 °C was selected as the extraction temperature. When the extraction time was increased to 10 min and the number of cycles was increased to two, the results showed no significant differences. For this reason, one 5-min cycle was chosen as optimal. Finally, under these conditions the recoveries on QFFs ranged from 80% for BHT-OH to 122% for DiB.

The optimal PLE conditions for extracting the target HPVCs and PAHs in QFFs were also used to extract PUF. However, when PUF extracts were injected, an interference appeared right in the middle of the chromatogram that saturated the MS detector, and the target compounds that appear in the last part of the chromatogram could not be determined. According to the MS library, with a percentage match above 86%, the interfering compound could be DEHT (terephthalic acid, di(2-ethylhexyl)ester), a non-phthalate plasticizer used to substitute DEHP (Nagorka et al., 2022). However, the identity of the interference was not confirmed because the commercial standard was not available in the laboratory. To prevent or minimize extraction of the interference, PUFs were extracted at 80 °C and the results showed recoveries between 67% and 135% for all target compounds. At 80 °C the small signal of the interferent was still present in the analysis. For this reason, DnOP, the only target compound that shares ions with the interferent, was removed from the list of compounds. The extraction of PUF at lower

Table 3

Arithmetic mean (AM), concentration range (CR), and detection rate (DR) of the target compounds found in PUF samples taken in winter and summer.

	Compound	Winter ($n = 14$)			Summer ($n = 11$)		
		AM (pg m^{-3})	CR (pg m^{-3})	DR (%)	AM (pg m^{-3})	CR (pg m^{-3})	DR (%)
BTHs	BTH	853	n.d. – 1509	86	1217	418–2958	100
	ClBT	19	n.d. – 164	21	<MQL	<MQL	100
	MeSBT	9	n.d. – 121	7	982	n.d. – 2968	82
	NH_2BT	n.d.	n.d.	0	n.d.	n.d.	0
	OHBT	301	n.d. – 2621	14	n.d.	n.d.	0
BSAs	BSA	680	n.d. – 4050	29	2170	n.d. – 12,164	64
	o-TSA	23	n.d. – 323	7	45	n.d. – 254	18
	Me-*p*-TSA	432	n.d. – 5167	14	1844	n.d. – 6790	45
	p-TSA	484	n.d. – 5421	14	21	n.d. – 216	9
PAEs	DMP	<MQL	<MQL	100	253	58–434	100
	DEP	488	<MQL – 1460	73	3983	1134–5880	100
	DiBP	805	n.d. – 7116	64	16,589	1476–34,076	100
	DEHA	10,825	2094–31,823	100	7035	500–20,674	100
	DEHP	16,767	<MQL – 95,620	100	24,420	4752–73,146	100
	DnOP	–	–	–	–	–	–
OPEs	TEP	3	<MQL – 28	14	294	n.d. – 1012	45
	TiBP	79	<MQL – 444	36	196	n.d. – 1346	45
	TBP	26	n.d. – 365	7	130	n.d. – 352	45
	TCPP	912	n.d. – 6506	14	13,170	n.d. – 42,506	64
	TCEP	309	n.d. – 1551	29	1047	n.d. – 3426	64
	TEHP	353	n.d. – 1452	29	91	n.d. – 804	18
	EHDP	1785	n.d. – 3186	50	17	n.d. – 122	27
	TPP	n.d.	n.d.	0	29	n.d. – 172	27
	TTP	n.d.	n.d.	0	33	<MQL – 202	36
Tinuvins	UVP	391	n.d. – 1000	43	208	n.d. – 1588	36
	Allyl-BZT	386	n.d. – 2179	36	124	n.d. – 616	36
	UV320	n.d.	n.d.	0	n.d.	n.d.	0
	UV326	138	n.d. – 912	14	615	<MQL – 4442	73
	UV329	241	n.d. – 1771	14	1666	n.d. – 10,446	45
	UV328	n.d.	n.d.	0	219	n.d. – 538	45
	UV327	128	n.d. – 1108	14	99	n.d. – 670	27
PAs	BHT-Q	1788	n.d. – 19,187	57	1701	98–3952	100
	BHT	1019	n.d. – 3692	79	291	n.d. – 880	73
	2,4-DTBP	2657	<MQL – 7588	79	4200	1604–7754	100
	BHA	7	n.d. – 42	14	649	n.d. – 1996	73
	TBHQ	1962	n.d. – 10,251	29	1013	n.d. – 2906	45
	BHT-CHO	1121	<MQL – 3126	64	3215	n.d. – 8574	55
	BHT-OH	68	n.d. – 847	7	n.d.	n.d.	0
PAHs	Nap	420	n.d. – 2008	79	199	116–448	100
	Ace	263	n.d. – 970	50	1568	464–2732	100
	Acy	106	n.d. – 1034	21	419	175–1322	100
	Flu	701	n.d. – 2282	64	922	382–1812	100
	Phe	1706	251–5514	100	5627	895–9689	100
	Ant	126	n.d. – 489	43	840	259–2443	100
	Fla	501	n.d. – 1235	71	213	n.d. – 552	100
	Pyr	466	n.d. – 1298	57	261	n.d. – 830	82
	BaA	n.d.	n.d.	0	30	n.d. – 134	45
	Chr	110	n.d. – 437	21	1298	n.d. – 8260	82
	BbF	n.d.	n.d.	0	1556	n.d. – 4369	82
	BkF	n.d.	n.d.	0	7714	n.d. – 21,623	64
	BjF	n.d.	n.d.	0	3707	<MQL – 13,334	45
	BeP	66	n.d. – 365	21	1411	n.d. – 4200	82
	BaP	513	n.d. – 3630	14	3786	n.d. – 9667	82
	DiB	n.d.	n.d.	0	164	n.d. – 422	27
	InD	n.d.	n.d.	0	269	n.d. – 1020	18
	BghiP	n.d.	n.d.	0	168	n.d. – 519	27

temperatures, such as 70 °C or 60 °C, was discarded due to low recovery values.

The optimal conditions for PLE extraction were therefore as follows: DCM as extraction solvent, extraction temperatures of 100 °C for QFFs and 80 °C for PUF and one 5-min cycle. Under these conditions, the compounds present in the QFF and PUF blanks were below their ILOQ, except for DEP and DEHA, which were found at concentrations of 12 μg L^{-1} and 78 μg L^{-1}, respectively, in conditioned QFFs, and for DEHP and DEHA, which were found at concentrations of 160 μg L^{-1} and 48 μg L^{-1}, respectively, in conditioned PUF. Table 1 shows the recovery values for blanks of QFFs and PUFs spiked with 400 μL of a standard solution of 5 mg L^{-1} of all the target compounds obtained under PLE optimal conditions. This table also shows their repeatability, expressed as a percentage of relative standard deviation (% RSD, n = 3). All recoveries were above 80% except for BHT-Q, BHA, BHT-OH and UV320 in PUF blanks, which were between 67% and 76%.

3.3. *Method validation*

The developed PLE/GC-MS method was validated with sampled QFFs and PUFs by establishing the recoveries, method detection limits (MDLs), method quantification limits (MQLs), repeatability and reproducibility between days. To calculate the recoveries, the procedure described in section 3.2 was used for samples of PUFs and QFFs. Table 1 shows that recoveries ranged from 41% for DnOP to 124% for Me-*p*-TSA for sampled QFFs and from 70% for TEHP and UV327 and 135% for DEP

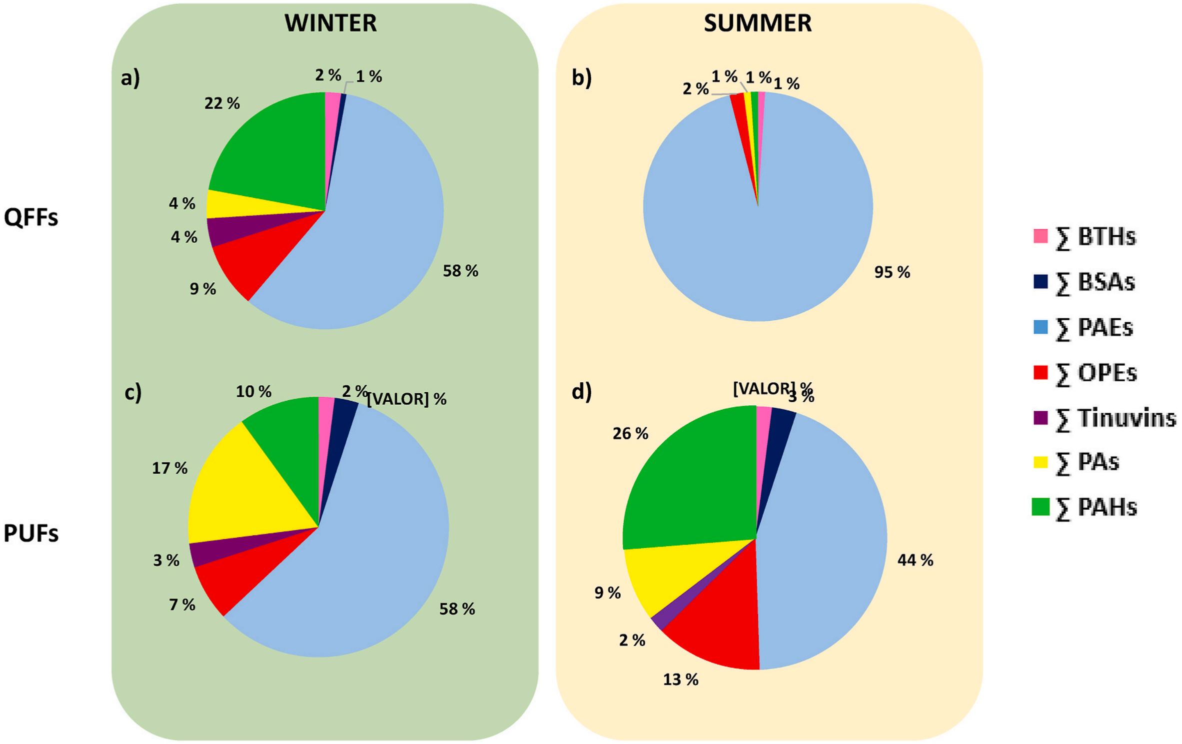

Fig. 2. Percentage of concentrations of compounds grouped according to family of compound: a) winter sampling in particulate matter; b) summer sampling in particulate matter; c) winter sampling in gas phase; d) summer sampling in gas phase.

for sampled PUF. The recoveries obtained for blank QFFs and PUFs and the sampled QFFs and PUFs were similar except to DnOP. The target compounds were quantified using internal standard and taking into account the recoveries of the method. The MDLs and MQLs were estimated from the ILODs and ILOQs of each target compound, while taking into account the recoveries and sample volume (720 m^3). For those target compounds in the PUF blank (DEHP and DEHA) or in the QFF blank (DEHA and DEP), the MDLs and the MQLs were the concentrations corresponding to the average blank signal plus three and ten times the standard deviation, respectively. As Table 1 shows, the MDLs were between 0.2 pg m^{-3} (MeSBT and NH_2BT) and 94 pg m^{-3} (BghiP) for QFFs and between 0.2 pg m^{-3} (DiBP) and 69 pg m^{-3} (TBHQ) for PUFs. MQLs ranged from 0.59 pg m^{-3} (MeSBT and NH_2BT) to 334 pg m^{-3} (DiB) for QFFs and from 0.56 pg m^{-3} (DiBP) to 278 pg m^{-3} (TBHQ) for PUFs. Method repeatability (intra-day precision), expressed as % RSD ($n = 3$), was below 18% (except for OHBT and DnOP, where it was 20%). Method reproducibility (inter-day precision) was below 20% ($n = 3$).

3.4. Occurrence in air samples

The described method was used to determine the target HPVCs and PAHs in twenty-five ($n = 11$ summer, $n = 14$ winter) samples of PM_{10} and gas phase in air from Constantí. Tables 2 and 3 show the arithmetic mean (pg m^{-3}), concentration range (pg m^{-3}) and detection rate (DR %) of each compound for the samples analyzed in gas phase and PM_{10} and gas phase for each time period, respectively.

In general, the results for these PM_{10} and gas phase samples showed that PAEs were the target compounds present at the highest concentrations, with DRs between 64% and 100%. Regardless of the season or the type of sample analyzed, DEHP had the compound found at highest concentrations with values between 5249 pg m^{-3} and 24,420 pg m^{-3}. Fig. 2 shows the percentages of each family of compounds evaluated in PM_{10} and gas phase in summer and winter, where PAEs had the highest percentages (between 44% and 95%). This is not surprising since, according to last year's record, the annual production of these two compounds, DEHA and DEHP, ranged from 10,000 to 100,000 tons (ECHA). In the summer months, the arithmetic means obtained for DEP and DiBP also stood out from among the PAEs, with values ranging from 2496 pg m^{-3} to 16,589 pg m^{-3}. Overall, these PAE concentrations agreed with those reported by Wang et al. (2008) whose concentrations for gas phase and particulate matter ranged from 3.5 ng m^{-3} to 15.5 ng m^{-3} for DEHP and from 1 ng m^{-3} to 3.9 ng m^{-3} for DEP in samples from urban zones close to industries from Nanjing (China).

After PAEs, the compounds with the highest concentrations were OPEs, PAs and PAHs, with percentage concentrations ranging from 1% to 48% depending on the season and the type of samples analyzed (Fig. 2). The OPEs with the highest concentrations were TCPP and EHDP, with arithmetic means of 3717 pg m^{-3} and 588 pg m^{-3}, respectively. The most detected OPE was TiBP, with DRs of 100% in gas phase and 91% in PM_{10}. The most prevalent PAs were BHT-Q, 2,4-TDP and BHT-CHO, with arithmetic means ranging from 356 pg m^{-3} to 1788 pg m^{-3}, 81 pg m^{-3} to 4200 pg m^{-3} and 124 pg m^{-3} to 3215 pg m^{-3}, respectively. The DRs of these compounds ranged from 55% to 100% regardless of the type of sample analyzed, with slightly higher DRs found in summer. For OPEs, the predominant concentration in the PM_{10} corresponded to TEHP (616 pg m^{-3} in winter and 786 pg m^{-3} in summer), though lower concentrations of TEHP (64 pg m^{-3} and 192 pg m^{-3} and a mean of 102 pg m^{-3}) were reported by Kurt-Karakus et al. (2018) from an industrial city in Turkey. For PAs, the most abundant compounds were BHT-Q and 2,4-TDP, with similar results to those obtained by Maceira et al. (2019), who reported PAs concentrations ranging from 307 pg m^{-3} to 898 pg m^{-3} when sampling PM_{10} at urban sites close to industrial complexes.

With regard to PAHs, concentrations of BaP were between n.d. and 1024 pg m^{-3}, with mean concentrations of 645 pg m^{-3} in winter and 379 pg m^{-3} in summer for PM_{10} samples. These values are far below the 1000 pg m^{-3} set by European Directive (2008)/50/EC (C. of the E.U, 2008) as the maximum annual average concentration in PM_{10} samples from emission zones. The most volatile PAHs, such as Nap, Ace, Acy, Flu, Phe, Ant and Fla were found at concentrations between 106 pg m^{-3} and

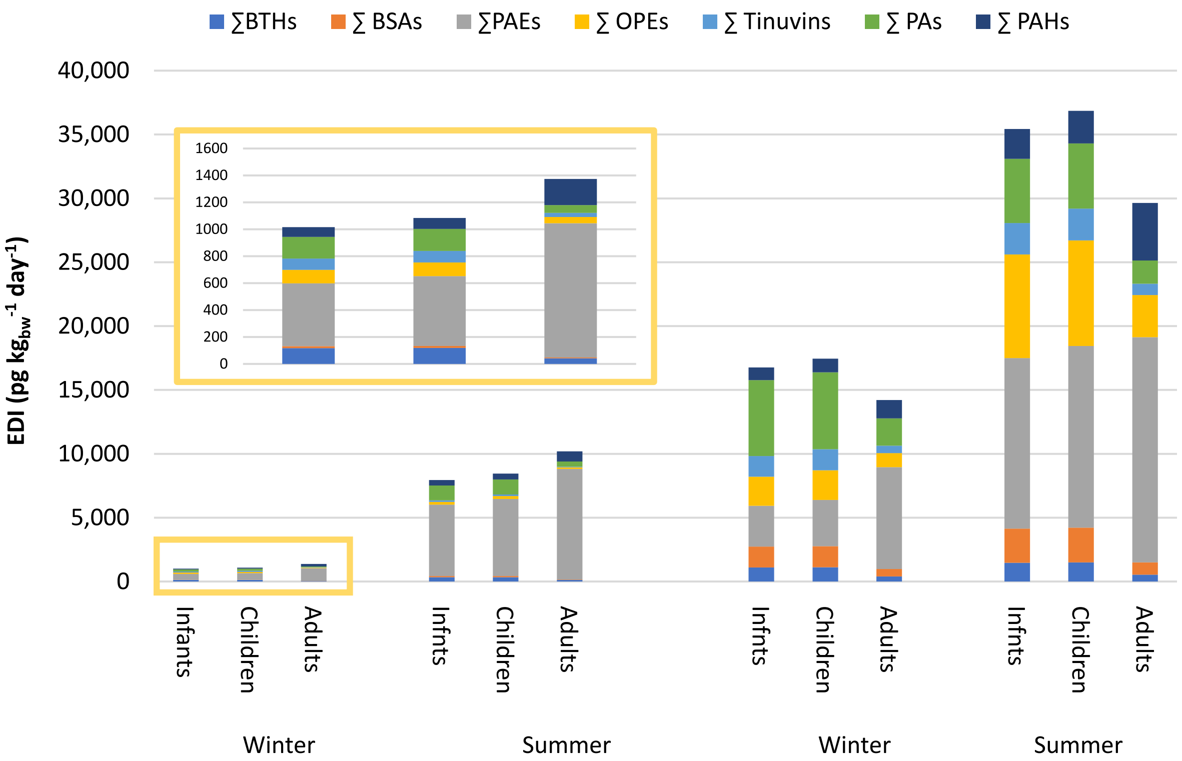

Fig. 3. EDI (pg kg_{bw}^{-1} day^{-1}) calculated for each group of compounds in two different exposure scenarios for three populations groups.

1706 pg m^{-3} in winter PUF samples (DRs = 21%–100%) and in all summer PUF samples, with values ranging from 199 pg m^{-3} to 5627 pg m^{-3}. The less volatile PAHs, except BeP and BaP, were not detected in any winter PUF sample. In summer, the DRs of these compounds increased to 18%–82% with concentration levels of 164 pg m^{-3} and 7714 pg m^{-3}. The concentrations of BeP and Phe ranged from 28 pg m^{-3} (BeP) to 5627 pg m^{-3} (Phe), which are similar to those reported by Wu et al. (2023) in the Tibetan Plateau (439 pg m^{-3} and 4666 pg m^{-3}, respectively). The higher PM_{10} concentrations in winter than in summer agree with results obtained by Guang et al. (2022) in the northern campus of Sun Yat-sen University in southern China.

BTH, BSA and Tinuvins were the least abundant and least detected compounds. Regardless of the season and type of sample, the most prevalent BTH was BTHs, with DRs above 85% and arithmetic means ranging from 624 pg m^{-3} to 1217 pg m^{-3}. BSA and Me-*p*-TSA were the BSAs found at the highest concentrations in both the PM_{10} (DRs = 64%–100%) and PUF (DRs = 14%–64%) samples, with arithmetic means ranging from 23 pg m^{-3} to 2170 pg m^{-3}. UVP and UV320 were the most prevalent Tinuvins found in PM_{10} samples, with values ranging from n.d to 288 pg m^{-3}. In the summer PUF samples, on the other hand, the most frequently found Tinuvins was UV326 (<MQL-4442 pg m^{-3}). The results for BSAs and Tinuvins are comparable to those reported by Maceira et al. (2018, 2020). However, we found that the Tinuvins with the highest concentration was UVP (with average concentrations from 99 pg m^{-3} to 391 pg m^{-3}), whereas Maceira et al. found that it was UV329 (with an average concentration of 294 pg m^{-3}) (Maceira et al., 2018).

Differences were generally observed between the concentrations found in summer and winter. The presence of PAEs such as DEHA, DiBP and DEP, especially DEHA, increased notably in summer PM_{10} samples. Indeed, the main difference in the percentages shown in Fig. 2 were due to the concentrations of DEHA found in summer PM_{10} samples because the concentrations for the other compounds were not much different. On the other hand, concentrations in PUF samples increased significantly in summer, with similar percentages found for each family of compounds. The differences in PUF concentrations were probably due to the thermal inversion phenomena observed in the area of study. However, these differences were not as clear as those reported in previous studies (Ramírez et al., 2011) because climate change caused temperature peaks of up to 20 °C during the winter sampling campaign.

3.5. *Human exposure*

The EDIs were calculated for PM_{10} and gas phase in summer and winter periods but both phases are combined because when air is inhaled both phases are included. The EDIs were calculated for two scenarios: a low-case scenario with the geometric mean of the concentrations found, and a high-case scenario with the 95th percentile concentrations. Three population groups for different ages (infants, children and adults) were analyzed. Following USEPA criteria (IRIS, 2020; Office of Pesticides Program U.S. Washington: Environmental Protection Agency et al., 2000), EDIs for the target compounds found at concentrations below the MDL and MQL were calculated by replacing the concentration values for MDL/2 and MQL/2.

Fig. 3 shows the EDIs organized by family of target compounds and subpopulation group. Regardless of the season, EDIs were greater for infants and children than for adults because their body weight is lower than that of adults. Overall, the EDIs found in summer were much higher than those found in winter due to the greater concentrations detected in the gas phase. As Table 4S shows, EDIs of PAEs were the highest, with values ranging from 467 pg Kg_{bw}^{-1} day^{-1} to 17,639 pg Kg_{bw}^{-1} day^{-1}. Comparable EDIs were found for OPEs, PAs and PAHs, while the lowest EDIs were for BTHs, BSAs and Tinuvins. In general, the EDIs obtained in this study were of the same order of magnitude as those reported by Maceira et al. (2020) for outdoor air PM_{10} samples from Tarragona, which ranged from 549.4 pg Kg_{bw}^{-1} day^{-1} to 6737.2 pg Kg_{bw}^{-1} day^{-1} for PAEs. For OPEs collected in PUF by passive sampling, Hou et al. (2021) obtained EDI values between 366 pg Kg_{bw}^{-1} day^{-1} and 22,900 pg Kg_{bw}^{-1} day^{-1} in urban zones. These are higher values than those estimated in the present study, which range from 46 pg Kg_{bw}^{-1} day^{-1} to 8264 pg Kg_{bw}^{-1} day^{-1}.

Table 4
HQ and CR values for the families of compounds in two scenarios and for three population groups in winter and summer.

		Winter						Summer					
		Low scenario (GM)			High scenario (95th percentile)			Low scenario (GM)			High scenario (95th percentile)		
		Infants	Children	Adults	Infants	Children	Adults	Infants	Children	Adults	Infants	Children	Adults
HQ	∑PAHs	6.4E-05	7.0E-05	1.1E-04	1.2E-03	1.3E-03	1.2E-03	6.2E-04	6.5E-04	5.5E-04	8.7E-03	9.2E-03	4.9E-03
	∑BTHs	2.2E-05	2.2E-05	7.8E-06	1.3E-04	1.3E-04	4,8E-05	5.6E-05	5.7E-05	2.0E-05	1.8E-04	1.8E-04	6.4E-05
	∑OPEs	1.5E-06	1.6E-06	1.8E-06	1.6E-05	1.7E-05	2.6E-05	2.0E-06	2.2E-06	3.8E-06	1.5E-05	1.7E-0.5	3.8E-0.5
	∑PAEs	9.4E-06	1.0E-05	1.7E-05	8.8E-05	1.0E-04	2.7E-04	2.2E-05	2.6E-05	7.9E-05	8.6E-05	9.8E-05	2.4E-04
	∑Total	9.7E-05	1.0E-04	1.3E-04	1.4E-03	1.5E-03	1.5E-03	7.0E-04	7.3E-04	6.5E-04	9.0E-03	9.5E-03	5.2E-03
CR	∑PAHs	4.7E-05	5.7E-05	5.5E-04	3.6E-04	1.3E-04	4.2E-03	1.6E-04	2.0E-04	1.9E-03	9.2E-04	1.1E-03	1.1E-02
	∑OPEs	1.1E-11	1.3E-11	4.6E-11	5.1E-10	6.2E-10	2.1E-09	9.9E-11	1.2E-10	4.1E-10	1.2E-09	1.5E-09	5.0E-09
	∑PAEs	3.5E-10	4.3E-10	1.5E-09	1.5E-08	1.9E-08	6.5E-08	6.2E-09	7.6E-09	2.6E-08	1.7E-08	2.1E-08	7.1E-08
	∑Total	4.7E-05	5.7E-05	5.5E-04	3.6E-04	1.3E-04	4.2E-03	1.6E-04	2.0E-04	1.9E-03	9.2E-04	1.1E-03	1.1E-02

3.6. *Risk assessment*

Table 4 shows HQ values organized by family of compounds and calculated for the two scenarios (low-case and high-case) and three age groups (infants, children and adults) in winter and summer. HQ values per family of compounds (Table 4) ranged from 1.5E-06 (OPEs, low-case scenario, infants, winter) to 9.2E-03 (PAHs, high-case scenario, children, summer).

The compounds with the highest HQ were PAHs, with values ranging from 6.4E-05 (low-case scenario, infants, winter) to 9.2E-03 (high-case scenario, children, summer). PAHs represented between 80% and 98% of total HQ (see Table 5S). BaP (38%–80%) was the PAH with the greatest contribution to HQ. BTHs, PAEs and OPEs, with values ranging from 1.50E-06 (low-case scenario, infants, winter) to 2.7E-04 (high-case scenario, adults, winter) contributed between 1% and 16% of total HQ, with BTH, DEHP, DnOP and TPP being the most prevalent compounds (see Table 5S). Individual HQs for each compound are shown in Table 5S. Overall, the sum of HQ values (∑total in Table 4) ranged from 9.7E-05 to 9.5E-0.3, which is below 0.1 so, according to the EPA (NATA, 2014), the risk is negligible.

Table 4 shows that all CR values ranged from 1.1E-11 (OPEs, low-case scenario, infants, winter) to 1.1E-02 (PAHs, high-case scenario, adults, summer) and that all except the PAHs are between four and seven orders of magnitude lower than 10^{-4}, which is the criterion set by USEPA to consider the cancer risk as severe (Ma et al., 2014). To quantitatively establish the estimated CR: $CR \leq 10^{-6}$ indicates a very low risk, $10^{-6} < CR < 10^{-4}$ indicates a low risk, $10^{-4} \leq CR < 10^{-3}$ indicates a moderate risk, $10^{-3} \leq CR < 10^{-1}$ indicates a high risk, and $CR \geq 10^{-1}$ indicates a very high risk (Alani et al., 2021). The PAH values in the high-case scenario are generally at the moderate-risk level, except in summer when the risk for adults is high. This is because the high-case scenario is the 95th percentile, which uses 5% of the highest monitoring concentrations, which were on specific days. Overall, PAHs made the highest contribution to total CR because these compounds are five orders of magnitude higher than the others. The results obtained for PAHs were comparable to those of authors such as Ramírez et al. (2011), who obtained values of 1.8E-04 in summer and 1.7E-04 in winter at sites close to industrial areas in gas and particle phases from Tarragona, Spain.

On the other hand, although PAEs had the highest concentrations, their CRs were lower (3.5E-10-7.1E-08), with a difference of two orders of magnitude, than those reported by Ma et al. (2014) (1.0E-06-8.2E-09) in a suburban area of Shanghai (China). Although this may be because the equations used to estimate the CRs for PAEs were different, the results are similar to those of previous studies by Maceira et al. (2020), who used the same estimation equation as ours.

The same occurred with the OPEs, whose risk ranged from 1.1E-11 to 5.0E-09, since only TCEP, TEHP and TBP contribute to CR values, with TCEP making the highest contribution (between 57% and 79%). These values are comparable to those of studies by Maceira et al. (2020), who obtained CR values of less than 10^{-7}. Individual CRs for each compound are given in Table 6S.

4. Conclusions

This multi-residue method based on PLE/GC-MS enabled 37 HPVCs and 18 PAHs present in PM_{10} and gas phase to be determined at pg m^{-3} concentrations.

When monitoring was conducted in urban environments close to industrial complexes, the contribution of concentrations was highest (45%–95%) for PAE compounds. The next-highest concentrations were found for PAHs, PAs and OPEs, while those for BTHs, Tinuvins and BSAs were the lowest. Slight differences were observed between summer and winter concentrations, though these were not as great as expected because 20 °C temperatures were registered in the winter months.

The compounds with the highest EDIs values were PAEs as these compounds were found at higher concentrations than the others. On the other hand, the highest CR estimations were for PAHs since these compounds have carcinogenic properties being the highest contribution, therefore the total value CR in the same that the value CR of PAHs.

CRediT authorship contribution statement

Reyes García-Garcinuño: Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Laura Vallecillos:** Investigation, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing. **Rosa Maria Marcé:** Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing – original draft, Writing – review & editing. **Francesc Borrull:** Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

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