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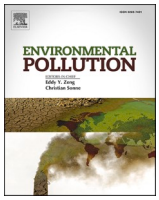

Passive sampling of high production volume chemicals and polycyclic aromatic hydrocarbons in urban atmospheres near petrochemical sites: Uptake rate determination and application☆

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ABSTRACT

This study describes the use of passive sampling followed by pressurised liquid extraction and gas chromatography-mass spectrometry for monitoring high production volume chemicals (HPVCs), such as benzothiazoles, benzesulfonamides, phthalate esters (PAEs), organophosphate esters, ultraviolet stabilizers, and phenolic antioxidants and polycyclic aromatic hydrocarbons (PAHs) in urban atmospheres close to a petrochemical area. To obtain accurate results when applying passive sampling, the uptake rates of each target compound for the sampling time applied must be known. Firstly, passive sampling was calibrated for two months and uptake rates of HPVCs and PAHs in an urban atmosphere determined using active sampling as the reference method. The obtained results showed experimental diffusive uptake rates between 1.6 m^3 day^{-1} and 27 m^3 day^{-1} for 32 of the target compounds that will allow enable cost-effective long-term monitoring campaigns of HPVCs to be performed. Secondly, the experimentally obtained uptake rates were used to monitor the concentrations of HPVCs and PAHs at six urban sampling sites close to the two petrochemicals parks in Tarragona (Spain) during a period the two months. Regardless of the sampling campaign, PAEs and PAHs were the families of compounds found at the highest concentration levels, with a sum of their mean values of 23 ng m^{-3} and 20 ng m^{-3}, respectively.

1. Introduction

Deteriorating air quality is a growing concern that impacts an ever-larger population and directly contributes to health issues such as respiratory infections, heart disease and lung cancer, (Wang et al., 2023). In recent years this problem has worsened because of the industrial development and anthropogenic activities related to population growth, such as emissions from road traffic and fuel consumption (Li et al., 2023). In addition, with climate change, weather conditions, such as temperature, humidity and wind direction and/or velocity have been altered and it is necessary to update current urban pollution profiles. Monitoring of both major (NO_X, SO_2, O_3, particulate matter, etc.) and minor (volatile organic compounds (VOCs) and semi-VOCs (SVOCs)) air pollutants in urban areas near industrial parks is therefore of great interest (Wang et al., 2008; Maceira et al., 2020). Moreover, it is important to control the presence of specific VOCs and semi-VOCs because of their potential to cause respiratory problems, endocrine disorders, dermatitis, carcinogenesis and neurotoxicity (Pei et al., 2013; Zhang et al., 2014; Hou et al., 2021; Naccarato et al., 2021). Some of these compounds, such as diethylhexyl-adipate, triethylphosphate, naphthalene, and benzo(a) pyrene, which is regulated by the European Directive 2008/50/EC, also entail a carcinogenic risk (European Parliament, 2008).

High-production volume chemicals (HPVCs) and polycyclic aromatic hydrocarbons (PAHs) are SVOCs that pose a health risk (Wang et al., 2023). More than 1,000 tonnes per year of HPVCs are manufactured in at least one member country of the Organisation for Economic Co-operation and Development (2004). HPVCs comprise benzothiazoles (BTHs), ultraviolet stabilizers (Tinuvins), organophosphate esters (OPEs), benzosulfonamides (BSAs), phenolic antioxidants (PAs), and phthalate esters (PAEs), among others. Their main applications in industry are: corrosion inhibitors (BTHs), plasticizers (Tinuvins), flame retardants (OPEs), pesticides and disinfectants (BSAs and BTHs) (Maceira et al., 2019; Garcia-Garcinuño et al., 2024). PAHs are mainly produced via traffic emission or the incomplete combustion of organic

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matter (Ramírez et al., 2011; Garcia-Garcinuño et al., 2024).

Due to their widespread use, HPVCs and PAHs have been found in urban atmospheres all over the world (Ramírez et al., 2011; Maceira et al., 2018, 2019). For instance, average concentrations of individual PAEs between 0.14 ng m^{-3} and 107 ng m^{-3} were found in air samples from urban areas close to busy streets and near industrial parks in Nanjing (China, gas phase and particulate matter) (Wang et al., 2008) and Shanghai (China, particulate matter) (Ma et al., 2014). Sánchez-Piñero et al. (2022) reported average concentrations for the sum of PAHs (∑PAHs) between 0.611 ng m^{-3} and 3.78 ng m^{-3} in particulate matter air samples from the vicinity of industrials parks in Vigo (Spain). Higher average levels of ∑PAHs, between 1.13 ng m^{-3} and 44.5 ng m^{-3}, were found in rural and urban air samples from Buenos Aires (Argentina) with passive sampling (Arias et al., 2021).

Air samples are complex and heterogeneous and for this reason SVOCs sampling must be carefully planned to ensure that the sample is representative. As SVOCs are usually in the atmosphere at trace levels, low ppb or ppt, a preconcentration step is needed to concentrate the compounds prior to chromatographic analysis. The most common methods for determining SVOCs comprise three steps: the active or passive sampling of air; the extraction of analytes from retentive material using an organic solvent and an extraction technique such as microwave-assisted extraction (MAE) (Naccarato et al., 2021), pressurised liquid extraction (PLE) (Maceira et al., 2018), ultrasound-assisted extraction (UAE) (Wong et al., 2018) or Soxhlet (Wong et al., 2018); and the separation and detection by gas chromatography-mass spectrometry (GC-MS) (Asia et al., 2003; Ma et al., 2014; Maceira et al., 2018) or gas chromatography-tandem mass spectrometry (GC-MS/MS) (Rauert et al., 2018; Tang et al., 2020; Naccarato et al., 2021).

Active sampling of SVOCs in outdoor environments in urban areas involves using high-volume air samplers for 24 h and sample volumes in the order of 1,000 m^3. The SVOCs in the particulate matter are usually deposited in quartz fibre filters or glass fibre filters (Maceira et al., 2020; Naccarato et al., 2021; Prats et al., 2022). Polyurethane foams (PUF) alone or -impregnated with XAD resins (PUF/XAD) are used to sample the gas phase (Naccarato et al., 2021; Prats et al., 2022; Wu et al., 2023). Passive sampling involves using an aluminium double bowls air sampler, which contain a uniformly porous PUF disk or PUF/XAD disk to promote the retention of SVOCs (Okeme et al., 2016; Strandberg et al., 2018; Abad et al., 2022). In this case, since SVOCs are retained in the PUF disk by molecular diffusion, sampling times of between 30 days and 80 days are required (Heo and Lee, 2014). Although commercially available passive samplers have aluminium double bowls with different shapes and different internal spaces and may or not be hung in a fixed manner, similar results have been obtained when using different designs (Melymuk et al., 2021). Active air sampling is the preferred sampling technique for the determination of SVOCs in air and has successfully been applied for the sampling of persistent organic compounds such as PAHs, dioxins and furans, as well as HPVCs *e.g.* PAEs, BTHs, BSAs, and OPEs among others (Ramírez et al., 2011; Maceira et al., 2018, 2020). However, passive sampling is increasingly used all over the world for the monitoring of dioxins (Abad et al., 2022), furans (Muñoz-Arnanz et al., 2018), and PAHs (Jariyasopit et al., 2019; Li et al., 2024) in urban and industrial areas. To a lesser extent, passive sampling has also been used to determine HPVCs, such as PAEs, in Italy (Qu et al., 2021).

In fact, passive sampling offers several advantages over active sampling, for example, it does not require the use of high-volume air samplers and does not require a power supply. This simplicity allows the passive sampling to be used simultaneously at various locations and minimises the economic investment required (Strandberg et al., 2018). Moreover, passive sampling has proven effective in capturing SVOCs, allowing the determination of the overall concentration of SVOCs in the air required for risk assessment studies (Jariyasopit et al., 2019; Alani et al., 2021). The main limitation of passive sampling is the little data available on uptake rates and for this reason the aims of the present study include: the calibration of a passive sampling-based method for monitoring of HPVCs and PAHs in air, the determination of the diffusive uptake rates of the studied compounds and the application of the developed method in urban air samples close to the petrochemical parks in Tarragona (Spain).

2. Experimental part

2.1. Reagents and standards

The families of HPVCs included in the study were benzenesulfonamides (BSAs): para-toluenesulfonamide (p-TSA), benzenesulfonamide (BSA), ortho-toluenesulfonamide (o-TSA) and N-methyl-para-toluenesulfonamide (Me-p-TSA); benzothiazoles (BTHs): 2-chlorobenzothiazole (ClBT), 2-hydroxybenzothiazole (OHBT), 1-H-benzothiazole (BTH), 2-(methythio)-benzothiazole (MeSBT), 2-amino-1-H-benzothiazole (NH_2BT) and 2-(methythio)-benzothiazole (MeSBT); ultraviolet stabilizers (Tinuvins): 2- (2H-benzotriazol-2-yl)-4-methyl-6-(2-propenyl) phenol (Allyl-BZT), 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV329), 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-(2-hydroxy-5-methylphenyl)benzotriazole (UV P), 2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol (UV327), and 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol (UV328); phthalate esters (PAEs): di-n-octylphthalate (DnOP), diethylphthalate (DEP), diethylhexyl-adipate (DEHA), diethylhexyl-phthalate (DEHP), dimethyl-phthalate (DMP) and di-iso-butyl-phthalate (DiBP); phenolic antioxidants (PAs): 3,5-di-tert-butyl-4-hydroxybenzaldehyde (BHT−CHO), 2,4-di-tert-butylphenol (2,4-DTBP), 2-6-di-tertbutyl-4-(hydroxymethyl)phenol (BHT−OH), 2,6-di-tert-butylcyclohexa-2,5-diene-1,4-dione (BHT-Q), 3(2)-tert-butyl-4-methoxyphenol (BHA), 2-tert-butylbenzene- 1,4-diol (TBHQ) and 2,6-di-tert-butyl-4-methylphenol (BHT); organophosphate esters (OPEs): tricresyl phosphate (TTP), tri-isobutylphosphate (TiBP), tris(2-ethylhexyl)-phosphate (TEHP), 2ethylhexyl-diphenyl-phosphate (EHDP), tributylphosphate (TBP), tris(2-chloroethyl)-phosphate (TCEP), triphenylphosphate (TPP), triethylphosphate (TEP) and tris(2-chloro-1-methylethyl) phosphate (TCPP). The following polycyclic aromatics hydrocarbons (PAHs) were evaluated: acenaphthene (Ace), benzo(b)fluoranthene (BbF), anthracene (Ant), benz(a)anthracene (BaA), indenol(1,2,3-c,d) pyrene (InD), benzo(a)pyrene (BaP), benzo(e) pyrene (BeP), fluorene (Flu), benzo(j)fluoranthene (BjF), acenaphthylene (Acy), benzo(k)fluoranthene (BkF), phenanthrene (Phe), chrysene (Chr), benzo(g,h,i)pyrene (BghiP), pyrene (Pyr), dibenzo(a,h) anthracene (DiB), fluoranthene (Fla) and naphthalene (Nap). The complete list of all target compounds with their CAS number can be found in Table 1S. Most of the studied compounds were supplied by Sigma-Aldrich (St. Louis, USA). BghiP, DiB and InD were from Supelco (Bellefonte, USA). BHT-CHO and UV320 were provided by LGC Standards (Barcelona, Spain). D_{10}-acenaphthene (d_{10}-Ace), d_4-1-H-benzothiazole (d_4-BTH), d_4-diethylhexylphthalate (d_4-DEHP), d_{12}-chrysene (d_{12}-Chr), d_{10}-acenaphthene (d_{10}-Ace), d_4-para-toluenesulfonamide (d_4-p-TSA), d_{12}-perylene (d_{12}-Per), d_{10}-phenanthrene (d_{10}-Phe), d_{27}-tributylphosphate (d_{27}-TBP) and d_8-naphthalene (d_8-Nap) from Sigma-Aldrich were used as internal standard.

Individual standards of 2,000 mg L^{-1} and 1,000 mg L^{-1} were made in ethyl acetate. Working solutions of 100 mg L^{-1} for each family of compounds were also in ethyl acetate. Standards were kept in the freezer (−20 °C) until use.

Acetone, dichloromethane and ethyl acetate, GC-grade and purity >99.9%, were supplied by Carlo Erba (Cornaredo, Italy). Dimethylformamide was from Sigma-Aldrich.

The nitrogen and helium gas used for PLE and GC-MS analysis were provided by Carburos Metálicos (Tarragona, Spain) with a purity of 99.999%. by Carburos Metálicos (Tarragona, Spain).

Table 1
Uptake rates (Rs), uptake rates at 25 °C (298 K, R_{298}), recoveries of blank and sampled PUF disks ($n = 3$), method detection limits (MDL), method quantification limits (MQL) and reproducibility ($n = 3$) for each compound.

		Rs (m^3 day^{-1})	R_{298} (m^3 day^{-1})	Recovery (%)[a]		MDL (pg m^{-3})	MQL (pg m^{-3})	Reproducibility (%RSD)
				Blank	Sampled			
PAs	BHT-Q	4.6	4.7	64 (10)	57 (15)	6.3	13	18
	BHT	8.3	8.5	68 (19)	74 (16)	1.4	2.7	19
	2.4-DTBP	24	24	84 (4)	77 (12)	0.40	1.3	15
	BHA	6.1	6.2	94 (14)	89 (6)	4.6	6.1	10
	TBHQ	a	a	113 (13)	105 (5)	198	794	9
	BHT-CHO	18	18	80 (8)	106 (16)	0.40	0.90	18
	BHT-OH	a	a	86 (7)	77 (5)	54	81	10
BTHs	BTH	3.2	3.3	86 (9)	88 (5)	1.2	6.0	8
	ClBT	a	a	87 (1)	104 (9)	0.80	2.0	11
	MeSBT	a	a	95 (2)	123 (13)	1.7	6.8	15
	NH_2BT	a	a	102 (5)	94 (21)	67	89	20
	OHBT	a	a	106 (12)	94 (13)	4.4	44	16
Tinuvins	UVP	21	21	96 (5)	127 (7)	13	32	10
	Allyz-BZT	16	16	109 (11)	131 (4)	16	39	16
	UV320	a	a	80 (2)	79 (7)	2.6	11	9
	UV326	a	a	98 (11)	113 (3)	55	184	8
	UV329	a	a	107 (3)	120 (7)	69	174	8
	UV328	a	a	82 (3)	88 (5)	24	47	12
	UV327	a	a	84 (5)	91 (2)	47	71	10
OPEs	TEP	a	a	78 (17)	78 (3)	11	27	19
	TiBP	10	10	83 (17)	73 (13)	0.50	1.1	18
	TBP	27	27	86 (11)	78 (6)	0.40	0.80	15
	TCPP	a	a	90 (11)	88 (12)	2.4	95	16
	TCEP	3.8	3.9	104 (7)	74 (8)	60	90	10
	TEHP	13	13	90 (2)	70 (8)	0.40	1.0	9
	EHDP	18	18	104 (2)	91 (4)	0.50	5.2	7
	TPP	a	a	93 (4)	87 (4)	48	72	9
	TTP	a	a	106 (11)	101 (3)	62	206	8
PAEs	DMP	a	a	72 (18)	103 (19)	2.0	81	20
	DEP	4.5	4.6	67 (19)	99 (14)	1.9	5.6	19
	DiBP	3.8	3.9	68 (19)	102 (13)	0.90	2.2	17
	DEHA	a	a	91 (19)	103 (6)	227	606	11
	DEHP	16	16	87 (17)	84 (9)	70	198	11
	DnOP	a	a	108 (3)	110 (12)	1.90	7.6	16
BSAs	BSA	a	a	91 (2)	107 (10)	39	58	12
	o-TSA	a	a	97 (10)	78 (9)	2.7	8.0	13
	Me-p-TSA	a	a	95 (6)	103 (6)	20	41	9
	P-TSA	a	a	106 (10)	85 (3)	98	245	10
PAHs	Nap	3.0	3.1	86 (14)	91 (5)	1.2	3.0	8
	Ace	8.2	8.3	79 (1)	92 (7)	1.1	3.3	8
	Acy	6.5	6.6	83 (3)	91 (6)	1.4	2.8	10
	Flu	6.4	6.5	85 (2)	96 (5)	4.1	14	9
	Phe	3.5	3.6	80 (7)	127 (16)	1.9	3.8	18
	Ant	16	16	84 (6)	78 (14)	1.3	6.6	17
	Fla	12	12	74 (5)	77 (12)	2.6	8.8	13
	Pyr	4.2	4.3	79 (7)	90 (4)	4.4	6.6	19
	BaA	1.6	1.6	107 (20)	108 (8)	19	97	13
	Chr	4.9	5.0	96 (20)	99 (13)	17	172	14
	BbF	11	11	115 (2)	132 (5)	5.6	17	7
	BkF	5.3	5.4	72 (5)	82 (16)	57	190	17
	BjF	a	a	91 (7)	84 (3)	25	50	8
	BeP	13	13	97 (19)	102 (11)	6.3	13	12
	BaP	9.5	9.7	89 (20)	73 (11)	24	120	13
	DiB	a	a	83 (17)	99 (3)	210	842	15
	InD	5.2	5.3	77 (19)	90 (3)	178	356	16
	BghiP	8.0	8.1	85 (19)	79 (13)	131	263	19

[a] The diffusive uptake rate could not be determined experimentally; a value of 4 m^3 day^{-1} is applied.

2.2. Sampling

Active and passive air samples collected to calibrate passive sampling for the target compounds were collected simultaneously in Constantí (Tarragona, Spain). The sampling campaign lasted three months and was carried out between January and March 2022. Active air sampling of 700 m^3 and 24 h was conducted with the high-volume sampler MCV-PM10 with a CBE-CAV from MCV S.A. (Collbató, Spain). The target compounds present in the particular matter (particle size PM_{10}, <10 μm) were deposited in quartz fibre filters with a diameter of 150 mm (QFFs, Whatman, Sigma Aldrich) and the target compounds present in the gas phase were retained in 10 × 10 cm cylindrical polyurethane foams (PUFs) from MCV S.A. (Collbató, Spain). Passive sampling was performed with an aluminium double bowl collector equipped with a 13.5 cm × 140 mm uniformly porous PUF disks (Techno Spec S. L., Barcelona, Spain) to allow the target compounds to be retained. Weather conditions affecting uptake rates (Wania and Shunthirasingham, 2020), *e.g.* temperature and wind velocity, were also recorded

during the sampling.

Once the sampling time and uptake rates were determined, passive air sampling was applied for the monitoring of selected HPVCs and PAHs at six sites in the Tarragona area. Two sampling campaigns, July–August 2022 and January–February 2023, were performed. As Fig. 1 shows, two sampling sites were located close to the center of Tarragona and Port of Tarragona, two sampling sites were located in municipalities close to the North industrial park of Tarragona (<3 km, Constantí and El Morell), and two sampling sites were set in neighbourhoods of Tarragona near the South industrial park of the city (<2 km, Bonavista), and educational centre. All the sampling sites were set at the Catalan Government's Network for Monitoring and Forecasting Air Quality stations in the Tarragona area. All passive devices were installed at a height of 2 m to avoid the shielding effect due to the presence of buildings, trees or other urban elements that could affect the results.

2.3. Analytical method

2.3.1. Sample preparation

A Dionex ASE 350 system for accelerated solvent extraction (Sunnyvale, USA) was used for the PLE of QFFs and PUFs. The following stainless steel cells were used to perform the extractions: 60 mL for active PUFs, 34 mL for passive PUFs, and 10 mL for active QFFs. Each extraction cell contained a Thermo Scientific cellulose filter (Barcelona, Spain) at the bottom and half of the QFF or PUF. The QFFs were cut in small pieces with scissors previously washed with acetone. When extracting the QFF, 1 g of diatomaceous earth from Thermo Scientific (Barcelona, Spain) was also added to compact the sample and fill the extraction cell. Dichloromethane was used as the extraction solvent and different oven temperatures, 100 °C for QFF and 80 °C for PUFs of active sampling and 80 °C for PUF disk of passive sampling, were applied. The extraction cycle performed included 5 min of preheating and 5 min of static extraction under a constant pressure of 1,500 psi. The flush volume was 50% of the extraction cell volume and a 120 s nitrogen purge was applied. Polytetrafluoroethylene (PTFE) syringe filters of 0.22 μm from Scharlab (Barcelona, Spain) were used to filter the PLE extracts. To avoid losses of the target analytes during evaporation at a Büchi rotary evaporator (Flawil, Swiss) to near dryness, dimethylformamide (400 μL) was added. Finally, the internal standards were added to the extracts and filled up to 2 mL with dichloromethane before being injected into the GC-MS. The internal standards were at concentrations of 2.5 mg L^{-1} for d_{12}-Per, d_{12}-Chr and d_4-p-TSA d_{12}-per and 1 mg L^{-1} for d_{10}-Phe, d_8-Nap, d_{27}-TBP, d_4-DEHP, d_{10}-Ace and d_4-BTH in the final extracts.

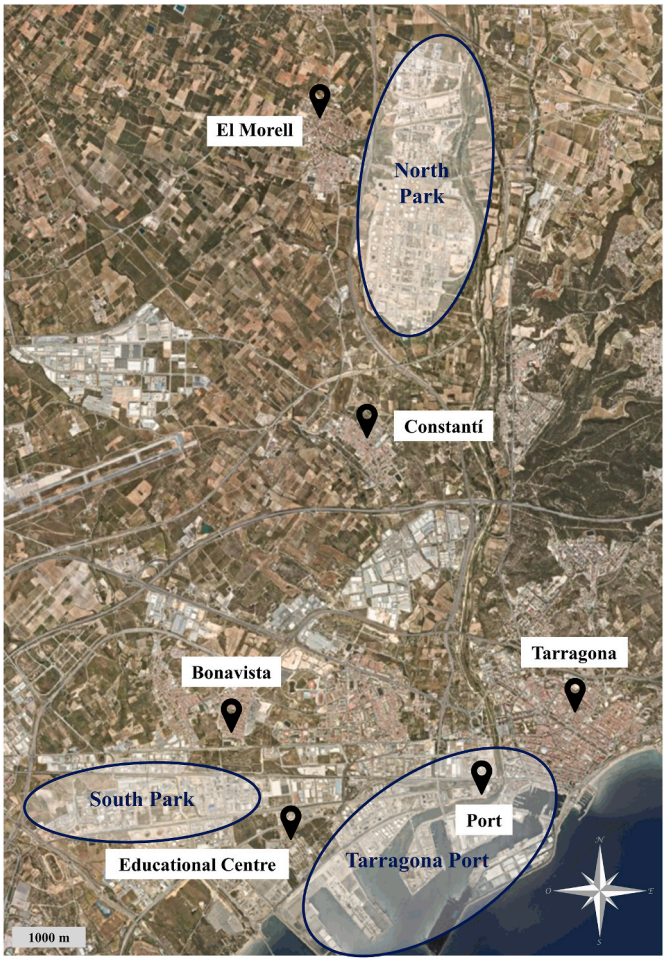

Fig. 1. Map of the area studied showing the location of the six urban sites sampled (Tarragona; Port of Tarragona; Educational centre; Bonavista; Constantí; El Morell), the two industrial parks of Tarragona and port facilities.

2.3.2. Gas chromatography-mass spectrometry analysis

Chromatographic analysis of the target compounds was performed on a Shimadzu Corporation model QP2010 GC-MS (Izasa S.A., Madrid, Spain) with a single quadrupole analyser and electron impact ionization (EI). The GC-MS was also equipped with an autosampler from Shimadzu and a split/splitless injection port. Chromatographic separation was carried out with a 30 m × 0.25 mm ID analytical column with a 0.25 μm-thick film of 50% phenyl - 50% dimethylpolysiloxane as Zebron ZB-50 (Phenomenex, Torrance, CA, USA). The injection port was set at 300 °C and 2 μL of samples were injected in splitless mode. The carrier gas was helium at a constant flow of 1.2 mL min^{-1}. The oven temperature programme began at 80 °C and was increased by 5 °C min^{-1} to 275 °C and then by 20 °C min^{-1} to 310 °C and held for 10 min, with the total analysis being 51 min (Garcia-Garcinuño et al., 2024). The transfer line and ion source temperatures were set at 280 °C and 230 °C. To improve the selectivity and sensitivity of the analytical method, quantitative analysis was performed in selective ion monitoring (SIM) mode. Table 2S summarizes the identification and quantification parameters (retention time, quantifier ad qualifier ions and relative abundance percentages) applied per compound and family.

2.4. Calculation of uptake rates

To calculate the feasibility of passive sampling as a control tool for HPVCs and PAHs in urban atmospheres, the uptake rate or sampling rate is required as the calibration data. Passive sampling consists of the accumulation of target compounds in a uniformly porous PUF disk by diffusion. During the linear accumulation stage, the uptake rate of the target compounds can be calculated by Eq. (1) which is based on the theory of passive air sampling (Bohlin-Nizzetto et al., 2020; Shoeib and Harner, 2002);

$$Rs = \frac{m_p}{C_a \times t} \quad (1)$$

where Rs in the experimental uptake rate (m^3 day^{-1}) m_p is the amount (pg) of target compound adsorbed in the PUF disk, t is the sampling time (days), and C_a (pg m^{-3}) is the average concentration of the target compound in the air determined by active sampling. In this study, linear uptake rate was assumed thought the exposure time (two months) (Mari et al., 2008; Heo and Lee).

To calculate the Rs of the HPVCs and PAHs under study, active sampling was applied as reference method to determine the C_a (pg m^{-3}) of the studied compounds in urban air over two months. Specifically, over two months twenty 24 h active samples, including QFFs and PUF (Harner et al., 2013; Wania and Shunthirasingham, 2020; Garcia-Garcinuño et al., 2024), were taken to obtain an average concentration of the target compounds in air. In parallel, three passive

Table 2
Arithmetic mean, concentration range, and detection rate of the target compounds, by family.

		Samples ($n = 12$)		
		Arithmetic mean (ng m^{-3})	Concentration range (ng m^{-3})	Detection rate (%)
PAs	BHT-Q	1.2	0.60–4.6	100
	BHT	3.7	<MQL - 7.0	100
	2.4-DTBP	1.1	0.40–1.9	100
	BHA	0.80	n.d. - 1.6	92
	TBHQ	<MQL	<MQL	17
	BHT-CHO	4.1	1.4–7.2	100
	BHT-OH	3.2	2.3–4.9	100
	∑PAs	15	9.6–21	
BTHs	BTH	1.4	0.14–3.7	100
	CiBT	0.50	n.d. - 1.2	92
	MeSBT	0.10	n.d. - 0.70	25
	NH_2BT	2.2	n.d. - 9.2	33
	OHBT	3.1	n.d. - 6.0	92
	∑BTHs	7.3	2.5–12	
Tinuvins	UVP	1.2	n.d. - 1.7	83
	Allyz-BZT	0.80	n.d. - 1.7	58
	UV320	0.80	n.d. - 1.7	75
	UV326	0.80	n.d. - 2.7	33
	UV329	0.90	n.d. - 3.5	25
	UV328	0.60	n.d. - 2.5	33
	UV327	2.2	n.d. - 3.5	83
	∑Tinuvins	7.4	4.2–13	
OPEs	TEP	0.20	<MQL - 2.2	100
	TiBP	0.15	n.d. - 0.40	83
	TBP	0.08	n.d. - 0.40	83
	TCPP	0.09	n.d. - 1.1	8
	TCEP	1.4	n.d. - 3.2	58
	TEHP	2.7	n.d. - 3.7	92
	EHDP	0.70	n.d. - 2.8	92
	TPP	0.90	n.d. - 1.6	67
	TTP	n.d.	n.d.	0
	∑OPEs	5.7	3.8–10	
PAEs	DMP	0.04	<MQL - 0.05	100
	DEP	3.7	<MQL - 12	100
	DiBP	2.1	<MQL - 7.1	100
	DEHA	7.5	1.2–18	100
	DEHP	5.5	<MQL - 21	100
	DnOP	4.2	n.d. - 8.4	83
	∑PAEs	23	4.0–52	
BSAs	BSA	2.4	n.d. - 4.1	83
	o-TSA	0.60	n.d. - 1.6	58
	Me-p-TSA	1.2	<MQL - 2.8	100
	P-TSA	2.0	n.d. - 3.7	75
	∑BSAs	5.9	2.4–8.4	
PAHs	Nap	0.60	0.2–2.7	100
	Ace	0.40	0.07–1.4	100
	Acy	0.40	n.d. - 0.6	92
	Flu	0.70	0.5–1.6	100
	Phe	1.7	0.5–5.1	100
	Ant	0.80	<MQL - 1.5	100
	Fla	0.50	<MQL - 0.90	100
	Pyr	0.50	<MQL - 0.90	100
	BaA	1.0	n.d. - 3.4	83
	Chr	0.70	n.d. - 1.6	92
	BbF	0.08	n.d. - 0.03	75
	BkF	0.90	n.d. - 1.8	75
	BjF	1.9	n.d - 2.8	75
	BeP	0.20	<MQL - 0.30	100
	BaP	0.80	n.d. - 1.6	75
	DiB	4.5	3.0–5.5	100
	InD	3.2	n.d. - 5.8	67
	BghiP	1.5	n.d. - 4.6	67
	∑PAHs	20	12–34	

n.d. = non detected, <MDL.

samplers were left for 2 months at the same site to obtain m_p (pg) values. Both passive and active sampling, were carried out in Constantí, a town close to North industrial park of Tarragona (Fig. 1), in order to maximise the presence of the target compounds at concentrations higher than the ILOQs and to obtain Rs values for a higher number of compounds and more reproducible Rs values.

Although the sampling area is characterized by a typical Mediterranean climate (METEO, 2024) and due to climate change the differences between winter and summer temperatures have been reduced, Eq. (2) was applied to correct the Rs (SUPELCO, 2024). Rs_{298} is the experimental diffusive uptake rate (m^3 $days^{-1}$) at 25 °C (298 K) and T (K) is the average temperature during sampling.

$$Rs = Rs_{298}\left(\frac{T}{298}\right)^{0.35} \quad (2)$$

Other meteorological parameters such as ambient pressure and wind velocity, were not taken into account to correct Rs. Wania and Shunthirasingham (2020), reported that with the kind of passive sampling device applied in this study (PUF disk inside an aluminium double bowl collector the ambient pressure does not affect the sampling. Even though exposure to different wind velocities can create a wind tunnel inside the dual-bowl, the prevailing soft winds (<16 km h^{-1}) in the study area do not favour this phenomenon.

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

To minimise cross-contamination, all glassware was washed with isopropanol in the ultrasound bath. The QFFs and the diatomaceous earth were conditioned in a heating muffle for 24 h at 400 °C, wrapped in aluminium, and stored at −20 °C until be used. Soxhlet extraction with dichloromethane was performed for 24 h to condition the PUFs used for active and passive sampler. After drying in a vacuum desiccator, the PUFs were kept in the fridge until analysed. To ensure quality assurance, procedural and instrumental blanks were conducted regularly. Additionally, a control standard of 1,000 μg L^{-1} was incorporated into GC-MS batches to verify the correct functioning of the instrument.

The GC-MS method applied was validated by establishing the linearity range, instrumental limits of detection (ILODs), instrumental limits of quantification (ILOQs), repeatability (intra-day precision) and reproducibility (inter-day precision) for all target compounds. Internal standard calibration curves showed good linearity up to 5,000 μg L^{-1} for all target compounds, except DEHA to 7,500 μg L^{-1} and EHDP and DiBP to 2,500 μg L^{-1}. Two calibration curves per compound were applied, for low and high concentrations levels, all determination coefficients (R^2) were greater than 0.990. The ILODs (Table 3S), set as the concentrations with a signal-to-noise ratio of three, were in the 0.10 μg L^{-1} - 25 μg L^{-1} range. The ILOQs, which were defined as the lowest concentration in the calibration curves, were between 0.30 μg L^{-1} and 100 μg L^{-1}. Instrumental intra-day and inter-day precision ($n = 5$, 500 μg L^{-1}), expressed as percentage of relative standards deviation (% RSD), were below 7% except for UVP (12%), UV329 (11%) and NH_2BT (11%) and below 12% except for OHBT (15%) and UVP (16%). Table 3S shows the detailed results for each target compound.

3. Results

3.1. Pressurised liquid extraction optimisation

For the optimisation of the extraction of the PUF disk used for the passive sampling, the initial conditions of the PLE were set taking into account our previous experience with the target compounds and active sampling (Garcia-Garcinuño et al., 2024). The extraction conditions described in section 2.3.1 were applied and two extraction temperatures, 80 °C and 100 °C, were tested. Conditioned PUF disks ($n = 3$) were cut into two halves, one half was spiked with 200 μL of a 5,000 μg L^{-1}

standard solution, and the other half was used as a blank to subtract the target compounds that during the conditioning step could not be removed. Regardless of the extraction temperature applied, average concentrations of DEHA of 79 μg L^{-1} and DEHP of 60 μg L^{-1} were found in the 2 mL extracts of the blanks.

As Table 1 shows, the recoveries obtained for PUF disks blanks at an extraction temperature of 80 °C ranged from 64% (BHT-Q) to 115% (BbF) with %RSD between 3% and 19%. At 100 °C the recoveries were similar or slightly higher but an increase in %RSD to values above 30% was obtained for some target compounds, such as DnOP, DEHA and DEHP. Therefore, an extraction temperate of 80 °C was chosen as optimal because provided recoveries comparable to those obtained when analysing PUFs and QFFs blanks used by active sampling, between 67% (BHT-Q) and 135% (MeSBT) and %RSD below 20% (Garcia-Garcinuño et al., 2024).

3.2. Passive sampling

3.2.1. Sampling time

Taking into account the sampling periods applied in previous studies (Bohlin et al., 2010, 2014; Harner et al., 2013) for the passive sampling of SVOCs such as PAHs, periods of time between one month and three months were evaluated to obtain the optimal sampling time for the target compounds. Nine passive samplers were therefore placed in Constantí for three months, three of which were taken every month for analysis.

Fig. 2 plots the curves of the amount of the target compound in the PUF disk (ng) versus the sampling time for a compound of each family. In most cases, two months was the optimal sampling time and there were no significant differences in amount of ng between the second and third months. The amount tended to stabilise or slightly decrease at three months, except for ClBT, DEP, o-TSA, TBP and TCPP, which exhibited an increase in the amount. As a compromise, a sampling time of two months was selected as the optimal, since it yielded the maximum amount for the vast majority of the target compounds in the PUF disk. Harner et al. (2013) and Healy et al., 2021) also reported that two months of sampling is needed for the adsorption of high molecular weight compounds, such as BaA or InD, on a PUF disk and that the response was linear with a longer sampling time (≥ three months).

3.2.2. Uptake rates

The experimental uptake rates (Rs) of the fifty-six target SVOCs, thirty-eight HPVCs and eighteen PAHs, were determined. However, the Rs were only calculated for target SVOCs present in all passive and active samples at concentrations higher than the ILOQs (Table 2S). There were other two reasons why the Rs could not be calculated: (i) because the target compound was found in less than half the active samples and the concentration would not have been representative (*e.g.* BSA); or (ii) because some episodic peaks of the target compound were present in the active samples, thus distorting the results (*e.g.* DEHA).

As Table 1 shows, this provided a dataset of Rs for thirty-two of the target SVOCs. It is important to highlight that the uptake rates of sixteen of the eighteen PAHs, as well as some of the most representative HPVCs in urban air, such as DEHP, DEP, DiBP, and TEHP (Kurt-Karakus et al., 2018; Maceira et al., 2020), have been obtained. Overall, the Rs values ranged from 1.6 m^3 day^{-1} (BaA) to up to 27 m^3 day^{-1} (TBP). Differences in the Rs of the target compounds are probably due to the combined effect of environment conditions and the physicochemical properties of the target compounds. Nevertheless, the results agree with the Rs values, between 1 m^3 day^{-1} and 30 m^3 day^{-1}, reported by Wania and Shunthirasingham (2020). Moreover, for many of the target compounds the Rs obtained close to the value of 4 m^3 day^{-1} suggested by Alani et al. (2021) and Harner et al. (2013). This value has been widely used in the literature (Harner et al., 2013; Herkert et al., 2018; Zhang et al., 2022) to estimate concentration values of SVOCs and we have also used it in the present study to obtain the concentrations in pg m^{-3} for target compounds for which we have not be able to calculate the Rs. Moreover, so that Rs can be applied at areas with similar climatology but different temperature and the Rs at 25 °C (Rs_{298}, see Table 1) was calculated from Eq. (2).

3.3. Method validation

The PLE/GC-MS method developed was subjected to validation with PUF disks sampled for two months. The parameters determined were as follows: recoveries, intra-day and inter-day precision, method detection limits (MDL) and method quantification limits (MQL). Recovery and precision assays were performed in triplicate ($n = 3$) and it consisted on spiking one half of the sampled PUF disks with 400 μL of a standards solutions of 5,000 μg L^{-1}. The other half of the sampled PUF disk was used to subtract the target compounds that could be contained in the sample. As Table 1 shows, the recoveries ranged from 70% (TEHP) to 132% (BbF) for most of the target compounds, except for BHT-Q (57%). Intra-day precision values for sampled PUF disks were mostly below 16%, except for DMP (19%) and NH_2BT (21%). All target compounds showed good inter-day precision since the %RSD were below 20%. The recovery values obtained for the sampled PUF disk and the blank PUF disks were quite similar, therefore, the target compounds were quantified by internal standard calibration and the recoveries were used to obtain the final sample concentration. MQLs and MDLs were calculated based on the ILOQs and ILODs, and by applying Eq. (1) and considering the recoveries. For the target compounds in the PUF disk blanks, such as

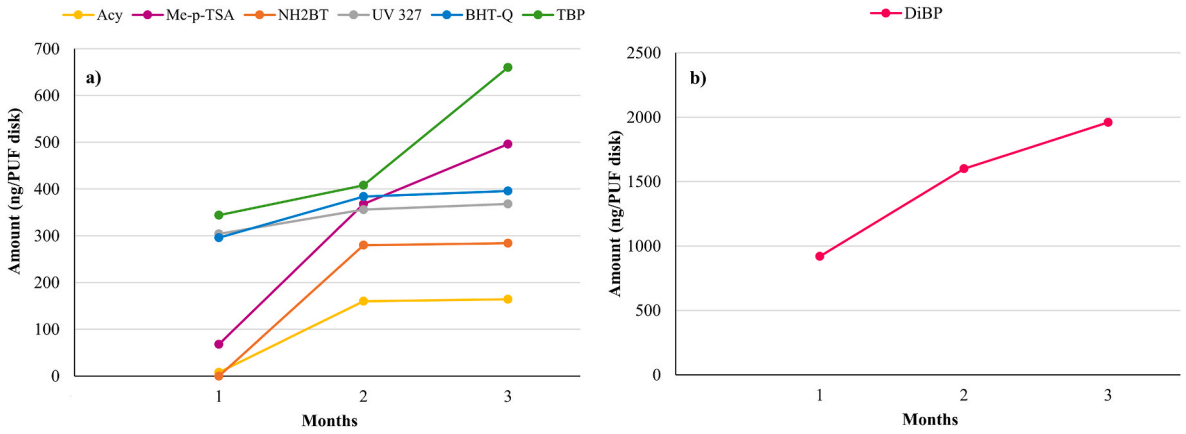

Fig. 2. Graph showing the optimisation of the sampling time for the most representative compounds. Amount of the target compound (ng/PUF disk) vs. the sampling time. Right graph for TBP and left graphs for the remaining compounds.

DEHA and DEHP, the MQLs and the MDLs were estimated as the concentrations corresponding to the average blank signal plus ten times the standard deviation and three times the standard deviation. Table 1 shows that the MDLs ranged from 0.40 pg m^{-3} (BHT-CHO) to 227 pg m^{-3} (DEHA) and that the MQLs ranged from 0.80 pg m^{-3} (BHT-CHO) to 840 pg m^{-3} (DiB). The MDLs and MQLs of DEHA and DEHP have been influenced by their presence in the PUF disks even after the conditioning procedure. These values were similar to those obtained in a previous study (Garcia-Garcinuño et al., 2024) in the active sampling of these compounds, where the MDLs ranged from 0.20 pg m^{-3} to 94 pg m^{-3} and the MQLs ranged from 0.56 pg m^{-3} to 334 pg m^{-3}.

3.4. Monitoring study

The Rs_{298} determined in the present study, corrected for the average sampling temperature, were used to monitor HPVCs and PAHs at the six sites specified in Fig. 1. Two-months passive sampling monitoring was carried out in summer and winter months.

Table 2 summarizes the arithmetic mean concentrations (ng m^{-3}), the concentration ranges (ng m^{-3}), and the detection rates (%) for all the target compounds. The boxplots in Fig. 3 shows the mean, the maximum, the minimum, and the 25th, 50th (median) and 75th percentile of the families of target compounds.

As Table 2 shows, all the target compounds except TTP were detected in the samples analysed. TCPP and TBHQ were quantified in only 8% and 17% of the samples, respectively. The family with the highest concentrations was PAEs, with a sum of total mean values of 23 ng m^{-3}, arithmetic means of individual PAEs between 0.04 ng m^{-3} (DMP) and 7.5 ng m^{-3} (DEHA) and detection rates of 100% for all compounds except DnOP (83%). As can be seen in Fig. 3, PAEs had the widest range of concentrations and a symmetric distribution of the values (median = mean). The most prevalent PAEs were DEHA and DEHP with values between < MQL and 21 ng m^{-3} and mean concentrations of 7.5 ng m^{-3} and 5.5 ng m^{-3}, respectively. These data may be explained by the fact that, according to the European Chemical Agency (ECHA, 2023), the production of these compounds ranges from 10,000 to 100,000 tonnes/year in Europe. The values found were below those obtained by Xiang et al. (2023), who obtained PAEs values with a mean concentration of 128.7 ng m^{-3} in air samples from residential areas around a petrochemical complex in southern China. In contrast, the results obtained in the present study are similar to those found by (Qu et al. (2021) in Naples (Italy), who applied passive sampling and found concentrations of 5.9 ng m^{-3} for DEHP and 2.2 ng m^{-3} for DEP.

PAHs were the second most important family in terms of concentration, with mean values of total PAHs of 20 ng m^{-3}, arithmetic means between 0.08 ng m^{-3} (BbF) and 4.5 ng m^{-3} (DiB) and detection rate values ranging from 67% to 100%. The PAHs found at all the samples analysed at relatively stable concentrations were Nap, Ace, Flu, Phe, Ant, Fla, Pyr, BeP and DiB with concentrations between < MQL and 5.5 ng m^{-3} (DiB). The concentrations of the remaining PAHs were more disperse, in some samples they were n. d. (as Acy or BaA) and in others there were concentrations peaks up to 5.8 ng m^{-3} (InD). The average concentration of BaP, including both the gas and the particulate matter of air, was of 0.8 ng m^{-3} lower than the value of 1 ng m^{-3} set by European Directive 2008/50/EC for PM_{10} (European Parliament, 2008). Fig. 3 shows that PAHs followed a positively skewed asymmetric distribution of the results (median < mean), and one outlier was detected. Passive sampling has also been applied for the monitoring of PAHs in highly industrialised cities such as Ulsan (South Korea), with an arithmetic mean of $\sum_{13}$PAHs, excluding Nap, Ace and Acy, of 43 ng m^{-3} (Choi et al., 2012) and in Bangladesh with a concentration range of $\sum_{16}$PAHs of 3.6 ng m^{-3} and 22.4 ng m^{-3} (Nargis et al., 2022). At both locations, these concentrations are higher than ours.

Another family to highlight for their high concentrations were the PAs, which ranged from n. d. (BHA) to 7.2 ng m^{-3} (BHT-CHO). All compounds had a detection rate between 83% and 100%, except TBHQ with 17% and mean concentrations between < MQL (TBHQ) and 4.1 ng m^{-3} (BHT-CHO). In general, PAs showed a wide range of concentrations and a positively skewed distribution of the results. BHT, BHT-CHO and BHT-OH were the most representative compounds with concentrations ranging from <MQL to 7.0 ng m^{-3}, from 1.4 ng m^{-3} to 7.2 ng m^{-3}, and from 2.3 ng m^{-3} to 4.9 ng m^{-3}, respectively. Overall, the concentrations found in this study were higher than those found by Maceira et al. (2019) and Garcia-Garcinuño et al. (2024), whose arithmetic mean were from n. d. to 621 pg m^{-3} (BHT-Q) and from n. d. to 4,200 pg m^{-3} (2, 4-TDP) respectively, for the same number of target compounds in Tarragona (Spain) at sites close to industrial areas.

The compounds found at lower concentration and lower detection rate were OPEs, BSAs, Tinuvins and BTHs. These families had a sum of total mean concentrations lower than 7.5 ng m^{-3}. Individual

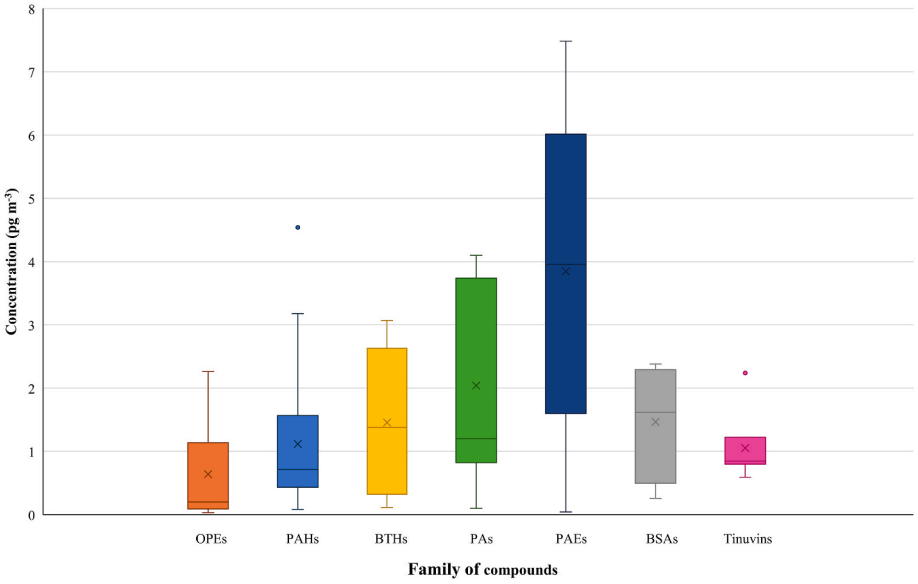

Fig. 3. Box and wishes plots showing percentile distribution for the concentrations of the families of the target compounds under study. For each family of compounds, the box plot represents 25th and 75th percentiles of concentration. Inside the box, the horizontal line represents the median concentration, while the lower and upper lines represent the minimum and maximum concentrations. The cross is the mean concentration, (n = 12).

concentrations of OPEs ranged from n. d. (as TCPP or TCEP) to 3.7 ng m^{-3} (TEHP) (detection rate = 8%–100%, except for TTP which has not been detected in any samples). As Fig. 3 shows, the OPEs had an intermediate concentration range, a positively skewed distribution of the results and the lowest median of the families of compounds studied. The most prevalent compound was TEP, with a detection rate of 100%, but the compound with the highest concentration was TEHP, with an arithmetic mean of 2.7 ng m^{-3}. These results were higher than those found by Castro-Jiménez and Sempéré (2018) and Gonçalves et al. (2023), who conducted active sampling in particulate matter and found concentrations ranging from 100 pg m^{-3} to 1,060 pg m^{-3} for $\sum_9$OPEs and from 11 μg m^{-3} to 33 μg m^{-3} for $\sum_6$OPEs, respectively.

BSAs mean concentrations ranged from 0.60 ng m^{-3} (o-TSA) to 2.4 ng m^{-3} (BSA), with detection rate between 58% and 100%. As observed with other families of compounds, the concentration range of BSAs was intermediate but in this specific case the concentrations followed a negatively skewed asymmetric distribution (median > mean). BSAs values were similar to those obtained by Nuñez et al. (2020), who reported concentrations of up to 2.67 ng m^{-3} in particulate matter (2.5 μm–10 μm) samples from sites close to industrial areas. The mean concentrations of Tinuvins and BTHs ranged from 0.6 ng m^{-3} (UV328) to 2.2 ng m^{-3} (UV327) and from 0.1 ng m^{-3} (MeSBT) to 3.1 ng m^{-3} (OHBT), respectively. The least detected BTHs and Tinuvins were MeSBT and UV329, both with detection rates of 25% and mean concentrations of 0.10 ng m^{-3} and 0.86 ng m^{-3}, respectively. The most detected compounds were BTH, UVP and UV327 with detection rates of 100%, 83% and 83%, and mean concentrations of 1.4 ng m^{-3}, 1.2 ng m^{-3} and 2.2 ng m^{-3}, respectively. Tinuvins had the narrowest concentration range, whereas that of the BTHs was intermediate. The concentrations found by Maceira et al. (2020, 2019) in PM_{10} ranged from n. d. to 0.38 ng m^{-3} for Tinuvins and from 0.17 ng m^{-3} to 8.9 ng m^{-3} for BTHs and were lower than those found in the present study. Similar values, up to 4.45 ng m^{-3} for Tinuvins and up 2.97 ng m^{-3} for BTHs, were reported by Garcia-Garcinuño et al. (2024) in the gas phase of air samples from an urban area close to a petrochemical park (Tarragona, Spain).

4. Conclusions

Data regarding the Rs for two months passive sampling for thirty-two of the target compounds, including sixteen PAHs and some of the most representative HPVCs were obtained. The Rs ranged between 1.6 m^3 day^{-1} and 27 m^3 day^{-1}. Due to the diversity of Rs obtained, the application of compound-specific Rs instead of a general one provides more accurate concentrations.

Determined Rs enabled to quantify HPVCs and PAHs at six urban sites near the petrochemical parks of Tarragona. Although the occurrence of these compounds in urban atmospheres by active sampling had already been investigated, as far as we know, this is the first time that passive sampling for the monitoring of all these families of compounds is investigated. The target compounds found at the highest concentrations were PAEs, with individual mean concentrations ranging from 0.04 ng m^{-3} to 7.5 ng m^{-3}, detection rate of 83% or 100% and DEHA and DEHP as the most representative compounds. The second most important family of compounds was PAHs, with individual concentrations ranging from <MQL to 5.8 ng m^{-3}. Some of the PAHs showed stable concentrations and detection rate of 100%, while others presented disperse concentrations and detection rates between 67% and 92%.

Overall, there was good agreement between the concentration levels obtained with passive sampling applying the uptake rates determined in this study and the values reported by active sampling. Although the obtained results showed that passive sampling can be a suitable alternative for HPVCs and PAHs monitoring when active sampling is not a practical solution (large sampling areas or long-term monitoring), further research in uptake rate determination is needed to obtain more accurate results.

CRediT authorship contribution statement

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

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.124697.

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