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Assessment of the presence and risk associated with volatile and semi-volatile organic compounds in urban areas close to petrochemical parks

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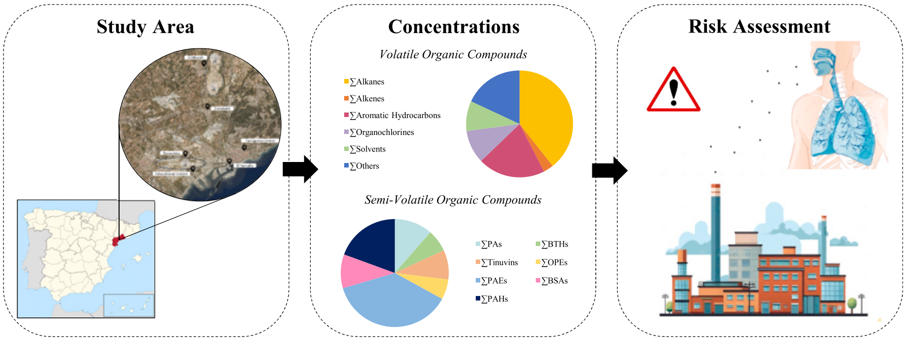
HIGHLIGHTS

- One-year monitoring of VOCs and SVOCs in urban air near Southern Europe's largest chemical pole.
- The most prevalent families of compounds were alkanes and phthalate esters.
- Non-cancer risk results were between 0.10 and 1.00, indicating a "probable risk".
- Constantí was the only urban area with a moderate carcinogenic risk.
- 1,3-Butadiene, benzene, 12-dichloroethane and ethylbenzene made up ≤ 40 % of the carcinogenic risk.

GRAPHICAL ABSTRACT



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ABSTRACT

This study monitored volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in urban areas near petrochemical industries using passive sampling. Sampling at six urban sites was conducted throughout 2023, with VOCs sampled every 14 days and SVOCs every 2 months, resulting in a total of 180 samples. VOCs and SVOCs were determined by gas chromatography-mass spectrometry, coupled to thermal desorption in the case of VOCs and after pressurised liquid extraction in the case of SVOCs. Alkanes were the VOCs found at the highest concentrations, with average concentrations between 11.6 μg m^{-3} to 30.5 μg m^{-3}. Particular attention was focused on benzene and 1,3-butadiene due to their carcinogenic nature and their involvement in the local industrial activities. Despite some concentration peaks, the average values of these compounds were always below the limits set by current air quality regulations, with maximum values of 1.70 μg m^{-3} for both benzene and 1,3-butadiene. The phthalate ester family stood out among the SVOCs, with average concentrations ranging from 28.1 ng m^{-3} to 41.8 ng m^{-3}. The average values of benzo(a)pyrene were always below the 1 ng m^{-3} limit established in air quality regulations for PM_{10}.

The risk assessment results showed that the total non-carcinogenic risk ranged from 0.02 to 1.30, with two VOCs, benzene and 1,3-butadiene, contributing the most to the risk. The total carcinogenic risk was between 1.5E-06 and 1.3E-04, with 1,3-butadiene (VOC) being the most significant contributor, accounting for between

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18 % and 50 % of the overall risk. Phthalate esters (SVOCs) also made a substantial contribution, representing between 10 % and 39 % of the total risk.

1. Introduction

In recent years, the scientific community has shown growing concern about global air quality, driven not only by its effects on human health but also by its impact on the environment (*e.g.* the formation of photochemical smog, ozone layer depletion, etc.) (Rovira et al., 2024; Sánchez-Piñero et al., 2022). Initially, studies mainly focused on the monitoring of the presence of major air pollutants, such as ozone (O_3), nitrogen oxides (NO_x) and particulate matter (PM_{10} and $PM_{2.5}$) (Selvam et al., 2020; Sorte et al., 2019), whose concentrations in urban air are regulated by the European Directive 2008/50/EC (ED, 2008). Currently, the monitoring of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in urban environments, particularly in proximity to chemical facilities, has attracted significant attention due to their potential risk to human health, as well as their adverse effects on animal and plants ecosystems (Mukerjee et al., 2020; Garcia-Garcinuño et al., 2024a; Vallecillos et al., 2024). Short-term exposure to VOCs can cause eye, skin and throat irritations, as well as respiratory issues, while long-term exposure may damage the nervous system or vital organs such as the liver, kidneys, or brain (Gallego et al., 2016; Sánchez-Piñero et al., 2022). Special attention should be paid to the family of SVOCs known as high production volume chemicals (HPVCs), which are produced or imported at 1000 tons annually in an Organisation for Economic Co-operation and Development country (OECD, 2004) and are used in industrial processes like corrosion inhibition, flame retardation, plasticisation, and fungicide production (Maceira et al., 2020; Zhang et al., 2024). Other families of SVOCs, such as polycyclic aromatic hydrocarbons (PAHs), need to be monitored as they may cause dermatitis, respiratory issues, cancer, and damage to the nervous system (Maceira et al., 2018, 2019; Hou et al., 2021).

VOC and SVOC concentrations vary according to location and environment conditions (Malik et al., 2023; Garcia-Garcinuño et al., 2024a). For example, in Puertollano (Spain), the concentrations of 27 VOCs were between 28 μg m^{-3} and 149 μg m^{-3} in urban areas and between 13 μg m^{-3} and 131 μg m^{-3} in industrial areas (Villanueva et al., 2018). In industrialized cities in Turkey, such as Gebze, concentrations of HPVCs, including 12 phthalate esters (PAEs), ranged from 9.24 ng m^{-3} to 115 ng m^{-3} (Celik-Saglam et al., 2023), while in Bursa, 6 organophosphate esters (OPEs) were between 529 pg m^{-3} and 19.1 pg m^{-3} (Kurt-Karakus et al., 2018). The concentrations of 15 PAHs in areas near industrial activity in Vigo (Spain) were found to be in the range of 0.19 ng m^{-3} and 16.0 ng m^{-3} (Sánchez-Piñero et al., 2022). Furthermore, due to their presence in the atmosphere at trace levels, a preconcentration step is essential to concentrate the compounds of interest prior to analysis by gas chromatography-mass spectrometry (GC-MS).

Active and passive sampling has been used to determine these compounds and monitor air samples. Passive air samplers are characterised by their simple construction, cost efficiency, independence from external energy sources, silent operation and extensive sampling sites for improved spatial resolution and detailed pollutant distribution information (Herkert et al., 2018; Garcia-Garcinuño et al., 2024a). Passive sampling of VOCs using axial or radial diffusion configuration involves retaining the compounds in solid adsorbent tubes, usually graphitised carbon blacks, followed by a thermal or liquid desorption step before chromatographic analysis (Vallecillos et al., 2019, 2024). Materials like polyurethane foam (PUF), low-density polyethylene, and silicone elastomers are effective for passive sampling of SVOCs, as they can collect both gaseous and particle phases (Nargis et al., 2022; Garcia-Garcinuño et al., 2024a). Although passive samplers may have limitations in extreme environments where local meteorological conditions play a crucial role (Herkert et al., 2018), they provide means for monitoring time-integrated air concentrations of various chemicals. Moreover, they provide average values based on diffusive uptake rates, which facilitates risk calculations (Johannessen et al., 2022; Vallecillos et al., 2024). It is also important to highlight the ease of placing a passive sampler in any location, which simplifies the sampling.

In this study, passive sampling was employed for a year-long monitoring of 74 of the more characteristic VOCs and 56 SVOCs in urban areas near one of the largest petrochemical complexes in Europe, located in Tarragona. Air samples were analysed by thermal desorption gas chromatography-mass spectrometry (TD-GC-MS) for VOCs, and by pressurised liquid extraction (PLE) and gas chromatography-mass spectrometry (GC-MS) for SVOCs. This region has the particularity that the industrial parks are very close to the residential areas, between 0.2 km and 2 km. With a population of 535,000 inhabitants (IDESCAT, 2024), the air quality of this region is expected to be affected by various minority organic compounds released through industrial processes, storage, loading and unloading of goods, as well as transport by road, rail or sea (Yao et al., 2021; Johannessen et al., 2022; Vallecillos et al., 2024). For this reason, the objective of this study is not only to monitor the concentrations of VOCs and SVOCs in this region, but also to assess their impact on air quality and their inhalation risk (non-carcinogenic and carcinogenic) for local communities.

2. Material and methods

2.1. Reagents and standards

The standards for the 74 target VOCs, including alkanes, alkenes, aromatic hydrocarbons, and organochlorines, among others, involved individual standard solutions of 2000 mg L^{-1} in methanol for the compounds listed in Table 1S. All these compounds have a purity greater than 97 % and were provided by Sigma-Aldrich (Steinheim, Germany) or Fluka (Buchs, Switzerland), depending on the target compound. The commercial mixtures EPA 524.2 Revision 4 Mix and EPA 502/524 Volatile Organic Calibration Mix SS, both at a concentration of 2000 mg L^{-1} in methanol (Supelco, Bellefonte, USA), were also used. Working solutions of 100 mg L^{-1} were also prepared in methanol and stored in the freezer at −20 °C. Successive dilutions of 1,3-butadiene, supplied by Sigma-Aldrich as a 20 wt% solution in toluene, were applied to obtain the corresponding working solutions.

The 56 SVOCs comprised HPVCs such as benzothiazoles (BTHs), benzenesulfonamides (BSAs), Tinuvins, OPEs, phenolic antioxidants (PAs), PAEs, and PAHs, which are listed in Table 2S. All of these were supplied by Sigma-Aldrich or LGC Standards (Barcelona, Spain), with purities equal to or greater than 96 %. The internal standards used were as follows: d27-tributylphosphate (d27-TBP), d4-1-H-benzothiazole (d4-BTH), d10-phenanthrene (d10-phe), d12-chrysen (d12-chr), d4-diethylhexyl-phthalate (d4-DEHP), d12-perylene (d12-per), d4-*para*-toluenesulfonamide (d4-*p*-TSA), d8-naphthalene (d8-nap) and d10-acenaphthene (d10-ace), all from Sigma-Aldrich, Individual standard solutions of 1000 or 2000 mg L^{-1}, depending on the target compound, were made with ethyl acetate. Working solutions of 100 mg L^{-1} in ethyl acetate were prepared for each compound family and kept at −20 °C until use.

All the solvents used, ethyl acetate, dichloromethane, methanol, toluene and acetone, were GC-grade (purity of >99.9 %) and were obtained from Carlo Erba (Cornaredo, Milan, Italy). Dimethylformamide was provided by Sigma Aldrich.

Nitrogen for thermal desorption and PLE and helium for the chromatographic analysis were of 99.999 % purity from Carburos Metálicos (Barcelona, Spain) and Linde (Tarragona, Spain), respectively.

Table 1
The VOCs found in air samples from the sampling sites evaluated six different points (Tarragona Centre, El Serrallo, Constantí, El Morell, Bonavista and Educational Centre) with their minimum (Min), maximum (Max) and average (Avg) concentrations, N = 14, 14-day passive sampling.

Compounds		Concentration (μg m^{-3})																	
		Tarragona Centre			El Serrallo			Constantí			El Morell			Bonavista			Educational Centre		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
1	i-pentane	1.80	18.0	6.50	1.80	31.6	8.50	2.40	24.8	10.4	2.30	18.0	8.20	3.20	18.6	7.40	4.60	35.2	13.8
2	n-pentane	0.77	7.90	2.70	0.53	11.8	3.50	1.60	13.2	6.20	1.00	6.90	3.40	1.60	11.0	4.10	2.00	22.7	7.40
3	n-hexane	0.06	2.20	0.83	0.33	4.40	1.40	0.40	3.0	1.50	0.21	5.80	1.10	0.12	3.40	1.20	0.16	8.00	2.30
4	2,3-dimethylbutane	n.d.	0.54	0.12	n.d.	2.20	0.24	n.d.	1.30	0.24	n.d.	0.21	0.06	n.d.	4.10	0.38	<MQL	4.10	0.50
5	2-methylpentane	n.d.	0.43	0.15	n.d.	1.90	0.28	n.d.	1.50	0.24	n.d.	0.35	0.08	n.d.	0.45	0.16	n.d.	3.60	0.57
6	3-methylhexane	0.02	2.40	0.66	0.09	3.0	0.84	0.19	2.30	0.77	0.07	1.60	0.71	0.21	4.90	1.40	0.62	15.8	3.50
7	i-octane	<MQL	0.15	0.05	<MQL	0.45	0.09	<MQL	0.08	0.04	<MQL	0.15	0.06	0.02	0.09	0.04	0.02	0.16	0.07
8	n-heptane	<MQL	1.10	0.33	0.10	1.20	0.42	0.19	1.40	0.47	0.12	0.74	0.37	0.23	2.40	0.66	0.46	5.90	1.70
9	n-octane	0.05	0.51	0.24	0.14	1.90	0.47	0.15	1.80	0.51	0.11	0.91	0.36	0.13	0.88	0.37	0.28	2.40	0.81
	∑Alkanes	3.80	31.6	11.6	4.10	54.9	15.8	7.40	43.6	20.3	4.10	28.3	14.3	6.80	41.7	15.5	9.60	82.7	30.5
10	2-trans-pentene	<MQL	0.26	0.12	0.07	0.52	0.22	<MQL	0.26	0.11	0.04	0.58	0.23	0.06	0.22	0.12	0.05	0.37	0.17
11	isoprene	0.04	1.80	0.33	0.03	0.61	0.20	0.07	0.75	0.40	0.08	0.74	0.33	0.10	0.79	0.29	0.13	1.00	0.44
12	2-cis-pentene	<MQL	0.32	0.11	0.04	0.64	0.20	<MQL	0.28	0.12	<MQL	1.40	0.26	<MQL	0.25	0.13	<MQL	0.40	0.19
13	1-hexene	<MQL	0.97	0.34	0.11	2.20	0.48	0.10	0.99	0.30	0.16	1.10	0.33	0.05	0.97	0.42	0.12	3.10	0.90
	∑Alkenes	0.16	2.40	0.91	0.60	3.50	1.10	0.32	2.30	0.92	0.32	3.00	1.20	0.33	1.90	0.96	0.59	4.70	1.70
14	benzene	<MQL	2.00	0.79	0.20	2.00	0.82	0.79	4.10	1.60	0.30	1.90	0.93	0.31	1.50	0.88	0.37	3.60	1.70
15	toluene	0.27	3.50	1.40	0.53	3.40	1.60	0.53	18.6	2.40	0.52	5.60	2.50	0.56	3.80	1.90	1.30	16.0	3.80
16	ethylbenzene	0.12	1.50	0.46	0.16	1.30	0.49	0.10	3.80	0.80	0.35	3.00	1.10	0.17	1.90	0.64	0.28	4.90	1.50
17	m,p-xylene	0.11	1.70	0.66	0.30	1.60	0.83	0.23	1.10	0.52	0.29	2.70	1.20	0.25	1.30	0.68	0.26	9.20	1.60
18	styrene	0.07	1.10	0.33	0.11	9.30	0.81	0.14	2.00	0.55	0.02	0.96	0.37	0.05	3.70	0.46	0.08	1.70	0.68
19	o-xylene	0.09	1.30	0.51	0.25	1.20	0.64	0.11	0.75	0.36	0.21	1.90	0.83	0.12	1.00	0.50	0.16	6.20	1.10
20	isopropylbenzene	<MQL	0.06	0.03	0.02	0.09	0.04	0.01	0.08	0.04	0.01	0.17	0.05	n.d.	0.06	0.03	0.01	0.12	0.05
21	n-propylbenzene	0.02	0.25	0.12	0.07	0.36	0.19	0.05	0.92	0.20	0.06	0.70	0.23	0.04	0.37	0.15	0.02	0.98	0.33
22	3-ethyltoluene	0.02	0.23	0.10	0.05	0.35	0.15	0.04	0.61	0.14	0.05	1.20	0.22	0.02	0.22	0.10	0.02	0.47	0.20
23	4-ethyltoluene	0.03	0.31	0.15	0.09	0.70	0.27	0.03	0.27	0.15	0.06	1.60	0.37	0.04	0.42	0.18	0.03	0.68	0.32
24	1,3,5-trimethylbenzene	0.01	0.60	0.22	0.04	1.00	0.27	<MQL	0.43	0.17	0.15	1.30	0.35	<MQL	0.61	0.18	0.01	1.10	0.37
25	2-ethyltoluene	0.02	0.36	0.14	0.07	0.43	0.18	0.02	0.41	0.11	0.03	0.96	0.22	<MQL	0.34	0.13	0.01	0.53	0.22
26	tert-butylbenzene	<MQL	0.26	0.06	n.d.	<MQL	<MQL	0.01	0.15	0.05	n.d.	0.85	0.16	<MQL	0.35	0.08	n.d.	0.28	0.11
27	1,2,4-trimethylbenzene	0.07	1.10	0.49	0.18	1.90	0.79	0.08	1.20	0.51	0.12	3.00	0.98	0.08	1.10	0.51	0.08	2.60	1.00
28	*p*-isopropyltoluene	0.02	0.47	0.16	n.d.	0.90	0.25	0.01	0.88	0.23	0.03	0.80	0.25	<MQL	0.45	0.14	0.04	1.30	0.47
29	1,2,3-trimethylbenzene	0.03	0.34	0.15	0.06	0.59	0.28	<MQL	0.45	0.17	0.05	1.70	0.37	0.02	0.50	0.19	0.02	1.10	0.38
30	1,3-diethylbenzene	<MQL	0.04	0.01	n.d.	0.07	0.02	<MQL	0.14	0.03	n.d.	0.15	0.03	<MQL	0.03	0.01	n.d.	0.15	0.03
31	1,4-diethylbenzene	<MQL	0.22	0.06	n.d.	0.38	0.14	0.02	0.87	0.16	n.d.	0.98	0.19	<MQL	0.16	0.08	n.d.	0.73	0.22
32	n-butylbenzene	n.d.	0.96	0.08	n.d.	0.35	0.12	n.d.	5.60	0.61	n.d.	0.50	0.13	<MQL	0.16	0.06	n.d.	2.40	0.45
33	1,2-diethylbenzene	n.d.	0.13	0.02	n.d.	1.80	0.27	n.d.	0.83	0.07	n.d.	1.00	0.22	<MQL	0.22	0.04	n.d.	2.70	0.40
34	2-methylnaphtalene	n.d.	0.02	<MQL	<MQL	0.05	0.01	n.d.	0.06	0.01	n.d.	0.11	0.02	n.d.	0.03	0.01	<MQL	0.22	0.03
35	1-methylnaphtalene	n.d.	0.03	0.01	<MQL	0.04	0.02	n.d.	0.05	0.02	n.d.	0.07	0.02	n.d.	0.06	0.01	<MQL	0.29	0.06
	∑Aromatic Hydrocarbons	1.50	14.7	6.00	3.20	22.5	8.30	3.40	21.1	9.10	2.80	22.8	10.8	1.70	13.3	10.8	3.70	35.2	15.3
36	dichloromethane	<MQL	11.0	1.60	<MQL	1.90	0.34	n.d.	16.2	1.10	0.08	13.7	1.40	0.05	5.40	0.94	n.d.	4.50	0.51
37	chloroform	n.d.	0.36	0.12	n.d.	0.31	0.06	n.d.	0.31	0.06	n.d.	0.65	0.12	n.d.	0.36	0.12	<MQL	0.91	0.26
38	1,1,1,-trichloroethane	<MQL	0.06	<MQL	<MQL	0.03	<MQL	<MQL	0.04	0.02	n.d.	0.08	0.02	n.d.	0.06	<MQL	0.01	0.11	0.04
39	1-chlorobutane	n.d.	0.10	0.02	<MQL	0.05	0.02	<MQL	0.08	0.02	n.d.	0.12	0.03	n.d.	0.17	0.04	n.d.	0.39	0.08
40	1,2-dichloroethane	n.d.	0.59	0.20	0.03	1.60	0.26	0.03	0.47	0.15	0.03	0.28	0.09	0.05	1.20	0.27	0.14	1.90	0.48
41	carbon tetrachloride	0.23	2.70	0.93	0.29	1.60	0.98	0.07	2.40	1.00	0.31	2.10	0.91	0.38	2.70	1.13	0.66	4.50	1.60
42	tetrachloroethene	n.d.	0.13	<MQL	n.d.	0.03	<MQL	n.d.	0.02	<MQL	n.d.	0.05	<MQL	n.d.	<MQL	<MQL	n.d.	0.05	<MQL
43	chlorobenzene	n.d.	0.23	0.05	<MQL	0.13	0.05	n.d.	0.19	0.03	n.d.	0.09	0.02	n.d.	0.16	0.04	<MQL	1.30	0.17
	∑Organochlorines	0.29	11.9	3.00	0.83	4.10	1.70	0.20	17.6	2.40	0.59	15.6	2.60	0.55	9.20	2.60	0.95	7.80	3.10
44	ethanol	n.d.	5.8	0.55	<MQL	0.57	0.03	n.d.	0.74	0.05	n.d.	1.50	0.11	n.d.	2.30	0.27	n.d.	11.6	0.90
45	isopropyl alcohol	n.d.	17.0	1.20	<MQL	<MQL	<MQL	n.d.	1.30	0.07	n.d.	4.10	0.23	<MQL	8.70	0.73	n.d.	6.90	1.20
46	1-propanol	<MQL	1.40	0.48	n.d.	0.74	0.51	<MQL	0.85	0.48	n.d.	0.75	0.34	n.d.	1.30	0.38	<MQL	1.10	0.50

(*continued on next page*)

Table 1 (*continued*)

	Compounds	Concentration (µg m^{-3})																	
		Tarragona Centre			El Serrallo			Constantí			El Morell			Bonavista			Educational Centre		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
47	2-butanone	n.d.	0.55	0.20	n.d.	0.91	0.22	n.d.	2.40	0.44	n.d.	0.86	0.15	n.d.	0.72	0.22	n.d.	1.80	0.49
48	ethyl acetate	n.d.	1.90	0.21	n.d.	<MQL	<MQL	n.d.	0.17	0.01	n.d.	0.30	<MQL	n.d.	3.10	0.38	n.d.	1.10	0.15
	∑Solvents	0.30	18.9	2.7	0.15	1.30	0.76	0.32	2.80	1.10	0.02	4.50	0.85	0.10	10.3	2.00	0.25	18.4	3.20
49	1,3-butadiene	0.06	2.2	0.45	0.07	2.00	0.39	0.25	7.90	1.70	0.37	5.50	1.70	0.11	2.90	1.20	0.34	4.20	1.60
50	diethyl ether	n.d.	0.41	0.05	<MQL	<MQL	<MQL	<MQL	0.60	0.09	n.d.	0.20	0.03	<MQL	0.07	<MQL	<MQL	0.27	<MQL
51	acrylonitrile	n.d.	0.29	0.07	<MQL	0.48	0.09	n.d.	0.97	0.18	n.d.	0.17	0.03	n.d.	0.55	0.07	n.d.	0.26	0.11
52	methyl acetate	n.d.	13.1	1.9	n.d.	9.10	1.50	n.d.	1.80	0.28	0.04	2.60	0.26	n.d.	26.8	6.40	n.d.	98.3	18.4
53	carbon disulfide	<MQL	3.9	0.81	<MQL	2.10	0.72	<MQL	5.60	1.00	<MQL	1.70	0.46	0.05	2.00	0.60	0.08	8.40	1.40
54	*tert*-butyl methyl ether	<MQL	3.2	0.64	0.05	13.9	1.50	n.d.	2.00	0.48	0.03	1.70	0.41	0.09	2.60	0.48	0.11	5.50	0.90
55	vinyl acetate	<MQL	4.4	0.55	0.21	1.70	0.58	0.21	1.90	0.49	n.d.	1.20	0.26	n.d.	2.40	0.74	0.15	25.8	5.70
56	tetrahydrofuran	n.d.	0.52	0.15	n.d.	0.59	0.18	0.04	0.57	0.27	n.d.	0.42	0.13	n.d.	0.76	0.29	0.06	1.60	0.55
57	*tert*-butyl ethyl ether	n.d.	1.40	0.59	<MQL	2.20	0.80	<MQL	1.10	0.40	n.d.	3.20	0.81	<MQL	2.30	0.57	0.01	5.00	1.00
58	1,4-dioxane	n.d.	<MQL	<MQL	n.d.	0.06	<MQL	<MQL	0.02	<MQL	n.d.	0.02	<MQL	n.d.	0.16	0.01	n.d.	0.11	0.04
59	methyl methacrylate	<MQL	0.55	0.11	n.d.	2.30	0.26	n.d.	0.17	0.04	n.d.	0.08	<MQL	n.d.	0.53	0.10	n.d.	1.00	0.23
	∑Others	0.74	22.2	5.30	0.54	31.4	6.10	0.80	13.1	5.00	0.88	10.6	4.10	3.30	32.2	10.5	2.40	120.7	29.9
∑VOC		9.10	69.4	29.7	10.1	104	33.8	16.8	74.7	38.6	12.1	74.1	34.2	15.2	80.5	38.6	21.2	205	83.9

2.2. *Sampling*

The area of Tarragona, located on the southern coast of Catalonia (Spain), is famous for its beaches and historical sites. However, the area also has one of the largest chemical complexes in Europe, consisting of two main industrial parks: north and south. The northern park hosts an oil refinery and various chemical industries, while the southern park is focused on the manufacturing of plastics. These industrial parks extend over 1200 ha and house more than 30 chemical companies, collectively producing approximately 21 million tons of fuels, plastics and other products annually (AEQT, 2024). The port of Tarragona, equipped with chemical handling and storage facilities and a small refinery, exports more than 50 % of the production of the petrochemical parks of the city (Maceira et al., 2019).

A one-year monitoring study was carried out from January 2023 to January 2024 to evaluate the presence of VOCs and SVOCs in residential areas close to the industrial parks of Tarragona. The monitoring covered six sites within the Tarragona area. Fig. 1S shows that two sampling sites were situated in close proximity to Tarragona city (Tarragona Centre and El Serrallo), two were located in municipalities near the north industrial park in the Tarragona area (Constantí and El Morell), and two were set in neighbourhoods near the south industrial park in Tarragona city (Bonavista and Educational Centre). All sampling sites were placed at the Catalan Government's Network for Monitoring and Forecasting Air Quality stations in the Tarragona area. To minimise the potential impact of buildings, trees, or other urban elements on the results, all passive devices were installed at a height of 2 m (EPA, 2019a).

A total of 180 samples were collected, of which 144 were for VOCs determination, sampled every 14 days, and the rest of the samples were for SVOCs determination, sampled every two months. Passive sampling of VOCs was performed following US EPA methods 325A (EPA, 2019a) and 325B (EPA, 2019b) guidelines for the monitoring of these compounds in fugitive and area sources. Each passive sampler consisted of a pre-conditioned Carbopack X (CX) adsorbent tube and a diffusion cap from Supelco (Bellefonte, USA). For SVOCs, aluminium double bowl air samplers with a 13.5 cm × 140 mm porous PUF disk from Techno Spec S. L. (Barcelona, Spain) were used to retain the target compounds (Garcia-Garcinuño et al., 2024a).

2.3. *Analytical methods*

2.3.1. *Determination of VOCs*

The analytical method for determining VOCs was carried out based on a previous study (Vallecillos et al., 2019). CX adsorbent tubes containing target VOCs were desorbed using a Unity Xr thermal desorption system coupled with an UltrA Xr TD autosampler (Markes Internation Limited, Llanistrant, UK). Subsequently, the VOCs were refocused onto a general-purpose graphitised carbon cold trap and subsequently separated using a 7890A gas chromatograph (GC) (Agilent Technologies, Palo Alto, CA, USA), with a 5975C MS inert quadrupole mass spectrometry (MS) (Agilent Technologies). For tube desorption, the system was pre-purged for 1 min at room temperature with a helium flow rate of 20 mL min^{-1} in split mode (5 mL min^{-1}). The tube was then heated to 330 °C for 10 min while maintaining a helium flow rate of 20 mL min^{-1} to desorb the analytes and focus them into a graphitised carbon cold trap, which was kept at −30 °C. No split flow was applied during this step. Next, the cold trap was heated to 330 °C for 10 min with a split flow of 5 mL min^{-1}. The target compounds were rapidly desorbed from the trap in a narrow band and injected into the chromatographic column via a flow path heated to 180 °C. The analysis was performed using a ZB-5 capillary column (5 % phenyl-95 % dimethylpolysiloxane) with dimensions of 60 m × 0.32 mm ID, and a film thickness of 1.0 µm (Phenomenex, Torrance, CA, USA). The chromatographic separation was carried out with a constant helium flow rate of 1.2 mL min^{-1}. The oven temperature programme began at 40 °C for 5 min and was increased by 6 °C min^{-1} to 140 °C and then by 15 °C min^{-1} to 220 °C (8 min). The

Table 2
The SVOCs found in air samples from the six sampling sites evaluated (Tarragona Centre, El Serrallo, Constantí, El Morell, Bonavista and Educational Centre) with their minimum (Min), maximum (Max) and average (Avg) concentrations, N = 6, 2-month passive sampling.

Compounds		Concentration (ng m^{-3})																	
		Tarragona Centre			El Serrallo			Constantí			El Morell			Bonavista			Educational Centre		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
1	BTH	0.60	2.10	1.60	2.00	3.70	2.60	0.45	2.50	2.00	1.20	2.40	1.90	0.23	2.60	1.50	0.99	2.30	1.70
2	CiBT	0.21	1.40	1.10	0.22	1.40	1.10	0.25	1.40	1.10	0.19	1.60	1.10	0.21	2.30	1.30	n.d.	1.40	0.91
3	MeSBT	<MQL	<MQL	<MQL	n.d.	1.10	0.23	n.d.	1.10	0.19	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	1.00	0.17
4	NH_2BT	n.d.	2.40	1.10	n.d.	n.d.	n.d.	n.d.	4.70	0.88	n.d.	1.80	0.59	n.d.	1.60	0.46	n.d.	2.30	0.92
5	OHBT	0.02	4.00	1.60	0.47	4.80	3.10	1.60	5.30	3.30	1.30	3.80	2.70	n.d.	4.00	2.20	0.55	4.60	2.40
	∑BTHs	1.50	8.20	5.30	4.40	8.80	7.00	3.40	12.0	7.40	4.80	8.70	6.30	2.20	8.80	5.40	3.00	10.5	6.10
6	BSA	0.74	3.60	2.80	n.d.	4.30	2.50	n.d.	4.00	2.80	n.d.	6.20	2.60	n.d.	3.20	2.00	0.51	3.50	2.40
7	*o*-TSA	n.d.	2.60	1.70	n.d.	2.70	0.61	n.d.	2.90	1.40	<MQL	3.70	1.80	0.19	3.40	1.80	0.02	2.60	1.60
8	Me-*p*-TSA	0.70	1.80	1.40	0.16	4.40	2.00	1.20	4.20	2.30	<MQL	2.70	1.40	0.56	3.00	2.00	0.31	2.40	1.40
9	P-TSA	n.d.	4.10	2.70	n.d.	6.40	2.40	3.30	6.50	4.80	1.90	3.90	3.10	2.04	5.47	3.81	2.10	6.50	3.30
	∑BSAs	4.50	11.8	8.50	1.80	11.4	7.50	6.30	16.8	11.3	3.50	13.1	8.90	3.40	13.5	9.50	3.60	11.6	8.70
10	DMP	<MQL	2.10	0.38	<MQL	0.93	0.38	<MQL	0.10	0.05	<MQL	0.04	0.04	<MQL	0.14	0.06	<MQL	1.10	0.23
11	DEP	n.d.	8.10	4.00	5.68	11.9	8.80	4.50	17.1	9.80	1.40	14.9	6.80	3.10	13.7	7.60	2.61	12.1	8.20
12	DiBP	<MQL	3.30	2.30	0.28	9.80	3.80	<MQL	4.40	2.30	<MQL	4.60	1.70	0.13	6.80	3.60	<MQL	3.80	2.30
13	DEHA	1.70	6.90	4.60	2.20	13.1	6.80	3.50	9.90	6.40	3.20	17.8	6.10	3.50	8.80	5.60	3.50	7.50	5.30
14	DEHP	0.78	22.2	7.00	1.90	18.9	7.40	4.00	19.9	12.8	1.10	23.1	7.00	4.60	10.7	6.90	3.20	11.7	6.00
15	DnOP	n.d.	34.8	9.90	4.10	11.0	7.40	n.d.	31.5	10.5	4.00	18.9	8.80	2.60	12.5	7.50	n.d.	25.0	10.6
	∑PAEs	6.60	75.3	28.1	19.0	57.9	34.7	24.1	65.7	41.8	15.0	67.2	30.5	17.0	41.6	31.2	23.2	49.9	32.7
16	TEP	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	0.01	<MQL	0.01	0.01	<MQL	0.01	0.01
17	TiBP	n.d.	2.20	0.55	<MQL	1.70	0.65	n.d.	2.30	0.53	n.d.	1.80	0.50	n.d.	1.60	0.47	n.d.	1.90	0.51
18	TBP	n.d.	n.d.	n.d.	n.d.	0.04	0.01	<MQL	0.06	0.01	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	0.08	0.01
19	TCPP	n.d.	3.10	1.10	n.d.	1.70	0.74	n.d.	1.80	0.36	n.d.	2.50	1.10	n.d.	2.40	0.44	n.d.	3.00	0.83
20	TCEP	n.d.	3.50	2.30	0.03	3.40	2.30	n.d.	3.30	1.10	n.d.	3.70	2.00	n.d.	3.80	2.20	n.d.	3.00	1.30
21	TEHP	0.16	4.30	2.30	0.51	5.00	2.70	0.80	4.30	2.30	1.10	4.50	2.40	1.10	5.60	2.60	0.12	4.20	2.10
22	EHDP	0.76	1.80	1.10	0.67	0.80	0.75	n.d.	0.78	0.62	0.68	0.78	0.75	0.68	0.79	0.75	0.67	0.82	0.75
23	TPP	n.d.	1.70	1.40	n.d.	1.70	0.97	n.d.	1.70	1.40	1.50	1.70	1.60	n.d.	1.70	1.10	1.50	1.70	1.60
24	TTP	n.d.	n.d.	n.d.	n.d.	0.28	0.08	n.d.	2.10	0.44	n.d.	0.53	0.11	n.d.	2.80	0.64	n.d.	0.10	0.04
	∑OPEs	2.60	11.6	8.70	4.90	12.7	8.20	1.90	11.2	6.70	3.90	11.9	8.50	3.00	13.1	8.20	2.50	10.3	7.20
25	UVP	n.d.	1.50	0.91	0.53	1.20	1.00	n.d.	1.30	0.99	0.54	1.40	1.10	0.55	1.40	1.10	n.d.	1.20	0.84
26	Allyz-BZT	n.d.	1.70	0.44	n.d.	1.30	0.27	n.d.	1.40	0.95	n.d.	1.30	0.58	n.d.	1.70	0.61	n.d.	1.40	0.72
27	UV320	n.d.	1.70	0.82	n.d.	1.70	0.56	n.d.	1.70	1.00	n.d.	1.70	1.30	n.d.	1.70	0.82	n.d.	1.70	0.48
28	UV326	n.d.	2.70	0.91	n.d.	2.80	1.70	n.d.	2.70	1.40	n.d.	2.70	2.10	n.d.	2.80	1.70	n.d.	2.80	0.92
29	UV329	n.d.	4.80	2.40	n.d.	4.70	1.60	n.d.	3.30	1.60	n.d.	4.70	2.40	3.30	4.60	3.50	n.d.	3.30	1.60
30	UV328	n.d.	2.60	1.30	n.d.	2.80	1.80	n.d.	2.60	1.00	n.d.	2.50	1.30	n.d.	2.50	0.84	n.d.	2.50	0.43
31	UV327	n.d.	3.40	2.20	n.d.	3.50	2.60	n.d.	3.60	2.80	n.d.	3.60	2.80	n.d.	3.50	2.20	n.d.	3.50	2.80
	∑Tinuvins	5.20	11.9	9.00	7.45	13.0	9.50	3.51	16.0	9.90	4.90	15.6	11.5	7.70	15.2	10.8	2.8	12.1	7.80
32	BHT-Q	n.d.	1.50	0.63	0.60	1.50	0.94	0.34	0.79	0.62	n.d.	1.80	0.92	n.d.	1.10	0.45	0.22	1.20	0.62
33	BHT	0.33	1.20	0.81	n.d.	1.80	0.92	0.48	2.30	1.00	0.24	1.00	0.75	0.35	0.95	0.72	n.d.	1.40	0.82
34	2.4-TDP	0.54	2.00	1.50	0.42	4.70	2.00	0.41	2.00	1.50	0.34	1.90	1.30	0.39	1.90	1.40	0.45	2.70	1.60
35	BHA	0.84	1.60	1.50	n.d.	1.60	1.30	n.d.	1.60	1.20	0.72	1.60	1.40	0.79	1.60	1.50	0.61	1.60	1.40
36	TBHQ	n.d.	4.80	0.96	n.d.	0.40	0.20	n.d.	4.60	0.92	n.d.	0.40	0.16	n.d.	0.53	0.15	n.d.	0.45	0.19
37	BHT-CHO	1.80	5.40	3.70	3.00	5.60	3.80	2.60	5.40	4.20	2.60	5.60	4.20	2.30	5.10	3.30	1.40	5.90	4.10
38	BHT-OH	0.24	5.40	3.20	0.41	6.00	3.50	0.69	5.30	3.30	0.72	6.10	3.00	0.32	5.30	3.10	1.20	5.50	3.30
	∑PAs	8.20	15.5	12.2	7.60	18.1	12.6	6.90	15.5	12.7	8.40	17.6	11.7	7.00	13.3	10.5	9.10	14.5	12.1
39	Nap	0.06	0.75	0.35	0.98	1.60	1.30	0.03	0.94	0.48	0.04	1.20	0.56	0.12	1.50	0.59	0.11	0.99	0.50
40	Acy	0.14	1.10	0.50	0.17	0.92	0.48	0.18	1.60	0.66	0.04	1.10	0.35	0.14	1.20	0.64	0.32	2.10	0.95
41	Ace	0.07	0.50	0.23	0.19	1.40	0.77	0.09	0.62	0.34	0.10	0.57	0.32	0.07	0.50	0.24	0.05	1.50	0.40
42	Flu	0.07	1.20	0.43	0.31	2.20	1.40	0.19	1.60	0.62	0.19	1.90	0.72	0.07	1.40	0.46	0.10	1.30	0.47
43	Phe	0.42	3.70	1.70	4.90	13.7	7.50	n.d.	5.90	2.50	1.20	4.70	2.80	0.11	3.70	1.90	0.27	3.90	2.00
44	Ant	n.d.	1.50	0.56	0.15	1.50	0.66	0.15	1.50	0.66	0.19	1.50	0.60	0.10	1.70	0.78	0.06	1.50	0.63

(*continued on next page*)

Table 2 (*continued*)

Compounds		Concentration (ng m^{-3})																	
		Tarragona Centre			El Serrallo			Constantí			El Morell			Bonavista			Educational Centre		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
45	Fla	0.33	1.80	0.86	0.89	2.30	1.30	0.38	2.10	1.00	0.45	1.80	1.02	0.29	1.80	0.93	0.30	1.80	0.95
46	Pyr	n.d.	1.30	0.50	0.70	2.30	1.10	0.51	2.50	1.10	0.38	2.10	0.95	0.34	2.00	0.90	n.d.	4.40	1.50
47	BaA	0.06	12.2	2.20	0.17	0.75	0.35	0.06	12.2	2.30	n.d.	12.2	2.20	0.09	12.2	2.30	0.08	12.2	2.30
48	Chr	0.04	4.300	0.90	0.26	0.45	0.35	0.29	4.30	0.98	n.d.	4.30	0.92	0.27	4.30	0.96	0.23	4.30	1.60
49	BbF	n.d.	0.52	0.14	<MQL	0.21	0.06	0.02	0.52	0.13	<MQL	0.52	0.13	n.d.	0.52	0.10	0.02	0.52	0.13
50	BkF	n.d.	1.40	0.82	0.47	0.94	0.84	n.d.	1.40	0.78	n.d.	1.40	0.78	n.d.	1.40	0.71	0.45	1.40	0.93
51	BjF	n.d.	1.80	0.78	<MQL	1.80	0.82	<MQL	1.80	0.89	n.d.	1.80	0.76	0.01	1.80	0.90	<MQL	1.80	0.88
52	BeP	0.06	1.40	0.66	0.06	1.30	0.63	0.03	1.30	0.65	0.02	1.30	0.64	0.04	1.30	0.65	n.d.	1.30	0.64
53	BaP	0.83	1.20	0.90	0.16	0.86	0.71	0.06	0.85	0.71	0.08	0.87	0.71	0.60	0.95	0.82	0.20	0.90	0.73
54	DiB	0.92	6.90	3.30	n.d.	2.20	1.00	n.d.	6.90	2.90	n.d.	5.10	2.00	n.d.	7.10	2.80	n.d.	6.90	2.40
55	InD	n.d.	5.70	2.30	n.d.	5.70	2.40	n.d.	5.80	3.10	n.d.	5.80	3.00	0.71	5.80	3.10	n.d.	5.70	1.50
56	BghiP	n.d.	4.50	1.20	n.d.	4.60	1.40	n.d.	4.60	1.90	n.d.	4.50	1.60	n.d.	4.60	0.90	n.d.	4.50	1.20
	∑PAHs	11.4	43.1	18.4	16.6	30.5	23.1	13.1	43.5	21.6	14.6	34.0	20.0	12.2	44.9	19.6	11.6	43.7	19.6
∑SVOC		40.0	178	90.3	61.7	152	103	59.2	181	111	55.0	168	97.3	52.5	150	95.2	55.8	153	94.3

temperature of the ion source was at 230 °C, and the temperature of the transfer line was 280 °C. The MS detector worked in full scan mode, scanning from 35 to 280 *m/z*, with an electron impact energy set at 70 eV.

The occurrence of VOCs was confirmed with the retention time, quantifier and qualifier ions and their ratio, included in Table 3S. Target VOCs were quantified with external standard calibration curves that were built by adding 1 μL of the target compounds at different concentrations into the CX adsorbent tubes. According to UNE-EN 14662-1 (UNE-EN, 2006), the sorbent tubes were connected to a Calibration Solution Loading Rig (Markes Internation Limited) and purged for 5 min with a helium flow rate of 50 mL min^{-1} to ensure solvent evaporation and repeatability of the spiking procedure.

Most target compounds showed satisfactory linearity up to 10 ng, and methyl acetate and vinyl acetate, up to 50 ng and 100 ng, respectively. A calibration curve was created for each compound, with determination coefficients (R^2) exceeding 0.990. The instrumental limits of detection (ILODs) ranged from 0.01 ng to 0.25 ng, except for methyl acetate and vinyl acetate which were 1.0 ng and 2.5 ng, respectively. The instrumental limits of quantification (ILOQs), representing the lowest concentration in the calibration curves, ranged from 0.05 ng to 0.5 ng, with the exception of methyl acetate and vinyl acetate, which were 2.5 ng and 5.0 ng. Instrumental precision, both intra-day and inter-day ($n = 5$, 1 ng), expressed as the percentage of relative standard deviation (% RSD), remained below 20 %. The method detections of limits (MDLs) and the method quantification of limits (MQLs) were estimated based on the ILODs and ILOQs of each compound present in air samples and the diffusion rates from a previous study (Vallecillos et al., 2019). The validation parameters for each target compound are included in Table 3S.

2.3.2. Determination of SVOCs

For the SVOCs, the PUF disks were extracted with pressurised liquid extraction (PLE) using an ASE 350 (Dionex, Sunnyvale, CA, USA) equipment and the experimental conditions optimized by Garcia-Garcinuño et al. (2024a). The extraction was carried out with a stainless-steel cell of 34 mL. To extract the analytes, the PUFs were cut with scissors, previously cleaned with acetone, into two halves, one of which was introduced into the extraction cell that contained a cellulose filter on the bottom (Thermo Scientific, Barcelona, Spain). Dichloromethane was used as the extraction solvent. The extractions conditions were 100 °C, one extraction cycle with a preheating period of 5 min and a static extraction time of 5 min. The flush volume was 50 % of the volume of the extraction cell, the pressure was 1500 psi and the nitrogen purge was 120 s. The PLE extracts were filtered through polytetrafluoroethylene (PTFE) 0.22 μm filters supplied by Scharlab (Barcelona, Spain). 400 μL of dimethylformamide was added to avoid losing target analytes when the extract was evaporated to near dryness in the rotary evaporator (Büchi, Flawil, Swiss) (Garcia-Garcinuño et al., 2024b). Finally, the extract was filled up to 2 mL with dichloromethane including the internal standard and injected into the GC-MS. The final extract contained a concentration of 2.5 mg L^{-1} of d_{12}-per, d_4-*p*-TSA and d_{12}-chr and 1 mg L^{-1} of d_4-DEHP, d_{10}-phe, d_{10}-ace, d_{27}-TBP, d_4-BTH and d_8-nap as internal standards.

The target compounds were analysed using a GCMS-QP2010 ultra high performance gas chromatograph (Shimadzu Corporation, Izasa S. A., Madrid, Spain), with electron impact ionisation (EI) and a quadrupole analyser. The instrument included an autosampler from Shimadzu and a split/splitless injection port. A Zebron ZB-50 (Phenomenex) analytical column (30 m × 0.25 mm, 0.25 μm-thick film) of 50 % phenyl - 50 % dimethylpolysiloxane was used for chromatographic separation. 2 μL of samples were injected in the splitless mode with a temperature of 300 °C in the injection port. A constant flow rate of 1.2 mL min^{-1} of helium was used as the carrier gas. The GC 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 (10 min). The temperature of the ion

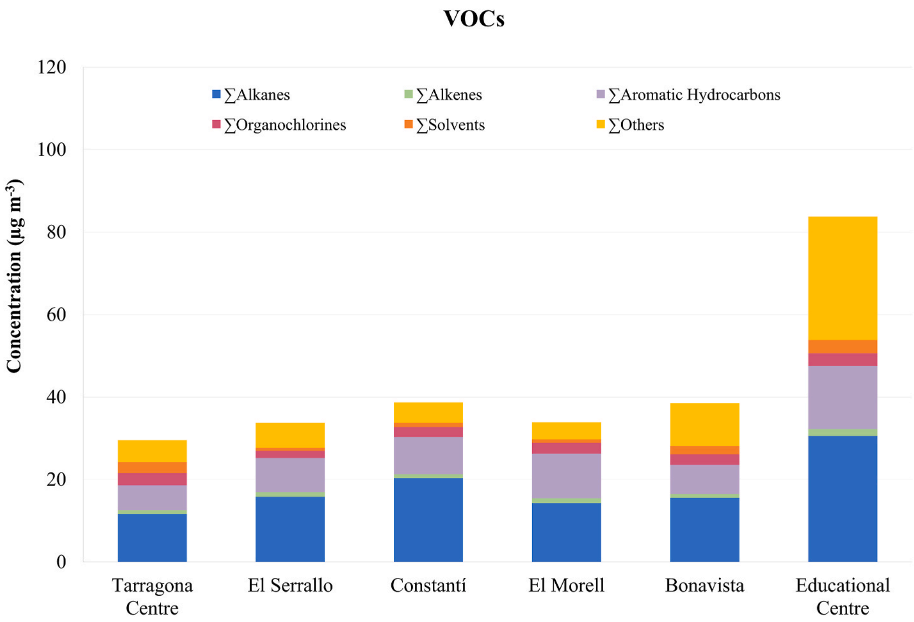

Fig. 1. Average concentration of each family of VOCs (µg m^{-3}) at the sampling points.

source and the temperature of transfer line were 230 °C and 280 °C, respectively. Analyses were performed in selection ion monitoring (SIM) mode to improve the sensitivity. The retention time, the quantifier and qualifier ions and their relative abundances selected for each compound are included in Table 4S.

Quantification was carried out with the internal standard calibration approach. Most target compounds exhibited satisfactory linearity up to 5 mg L^{-1}, DEHA up to 7.5 mg L^{-1}, and DEHP and DiBP up to 2.5 mg L^{-1}. For each compound, two calibration curves were established, one for low concentrations and another for high concentrations, with R^2 greater than 0.990. The ILODs were in the 0.1 µg L^{-1} - 25 µg L^{-1} range and the ILOQs ranged from 0.3 µg L^{-1} to 100 µg L^{-1}. In terms of instrumental precision, both intra-day and inter-day ($n = 5$, 0.5 mg L^{-1}) remained between 4 % and 15 %. The MDLs and MQLs were estimated from the ILODs and ILOQs and taking into account the recoveries and diffusion rates (Garcia-Garcinuño et al., 2024a) of each compound. Detailed results for each target compound are presented in Table 4S.

2.4. Quality control/quality assurance

The passive sampling of VOCs in air followed the quality control and quality assurance (QA/QC) measures specified in USEPA methods 325A (EPA, 2019a) and 325B (EPA, 2019b). To avoid background contamination, both the TD trap and the analytical column were conditioned before and after sample analysis. The CX adsorbent tubes were thermally conditioned, and blank tests were conducted prior to use. For detailed information on the conditioning process of CX adsorbent tubes and quality assurance procedures, see Vallecillos et al. (2019).

In order to minimise the risk of cross-contamination with SVOCs, all glassware underwent a cleaning process using isopropanol in an ultrasound bath. The PUF disks were conditioned in a Soxhlet for 24 h with dichloromethane. Dried in a vacuum desiccator, wrapped in aluminium and stored in the freezer (−20 °C) until use. Conditioned PUF disks blanks were performed and average amount of 0.12 µg in the half filter for DEHP and 0.16 µg in the half filter for DEHA were detected in the blanks.

To ensure quality control, instrumental and procedural blanks were regularly performed. In additionally, standard controls of 1 mg L^{-1} were incorporated into batches to verify that the instrument were performing properly.

2.5. Risk assessment

To assess the human exposure to the target compounds, the estimated daily intake (EDI, µg kg_{bw}^{-1} day^{-1} to VOCs and ng kg_{bw}^{-1} day^{-1} to SVOCs) for ambient inhalation was determined using Eq. (1) (Asante-Duah, 2002).

$$\mathrm{EDI} = \frac{\mathrm{C} \times \mathrm{IR} \times \mathrm{RR} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \qquad \text{Eq.(1)}$$

where C represents the concentration of the quantified compound in the passive sampling (µg m^{-3} to VOCs and ng m^{-3} to SVOCs), IR is the inhalation rate (m^3 h^{-1}), RR is the retention rate of inhaled air (expressed as a percentage), ET is the exposure time (hours per day), EF is the exposure frequency (days per years), ED is the exposure duration (years), BW is the average body weight over the exposure period (kg), and AT is the period of average exposure (days). AT represents the average time (days), over which exposure is averaged for the target compounds. The specific values of the parameters required for calculating EDIs according to equation (1) (Asante-Duah, 2002) are provided in Table 5S. EDIs were calculated for two scenarios, a high scenario with the 95th percentile concentrations, and a low scenario with the geometric mean of the concentration, and across two different population subgroups (children and adults).

The Reference Concentration (RfC) and the Reference Dose (RfD) levels from the USEPA's Integrated Risk Information System (IRIS) (IRIS, 2020; RAIS, 2024) were used to assess non-carcinogenic risk values expressed as hazard quotients (HQ). For VOCs, Eq. (2) (Rovira et al., 2024) was employed since an inhalation RfC (µg m^{-3}) was available, whereas for SVOCs, Eq. (3) (Garcia-Garcinuño et al., 2024b) was used because an oral RfD (mg kg_{bw}^{-1} day^{-1}) was available. The RfD values are presented in Table 6S.

$$\mathrm{HQ}_{\mathrm{VOCs}} = \frac{\mathrm{C} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{RfC} \times \mathrm{AT} \times \frac{24\ \mathrm{h}}{1\ \mathrm{day}}} \qquad \text{Eq.(2)}$$

$$\mathrm{HQ}_{\mathrm{SVOCs}} = \frac{\mathrm{EDI}}{\mathrm{RfD} \times 10^6} \qquad \text{Eq.(3)}$$

Two methods were used to evaluate the carcinogenic risk (CR). The first method was used for target compounds with an inhalation unit risk (IUR). The CR value can be calculated with Eq. (4) (Garcia-Garcinuño et al., 2024b), where IUR in the inhalation unit risk ($(\mu g\ m^{-3})^{-1}$), C, EF, ED, ET and AT (hours) have been previously defined for EDI values. For PAHs, BaP is the only compound with a specific IUR value, however, IUR values for other PAHs can be obtained from IUR_{BaP} (RAIS, 2024) using their respective equivalent toxicological factors (TEF). Table 6S shows TEF values according to Larsen and Larsen (1998).

$$CR_{VOCs} = \frac{IUR \times C \times ET \times EF \times ED}{AT} \qquad \text{Eq.(4)}$$

Fort the compounds without an IUR value, the CR was estimated using the oral slope factor (SFo, $(\text{mg kg}_{bw}^{-1}\text{ day}^{-1})^{-1}$) and the EDI was calculated with Eq. (5) (Maceira et al., 2019). Table 6S shows the SFo values (RAIS, 2024).

$$CR_{SVOCs} = EDI \times 10^{-6} \times SFo \qquad \text{Eq.(5)}$$

3. Results and discussion

3.1. Occurrence of VOCs and SVOCs

This section provides the concentrations of VOCs and SVOCs determined at the six sampling sites in the study. The results of VOCs and SVOCs determined at the six points were organised into two tables that show the minimum (Min), maximum (Max), and average (Avg) concentrations of the VOCs and SVOCs that were identified in at least one of the analysed samples. These results are shown in Tables 1 and 2.

3.1.1. Monitoring VOCs

Overall, 59 of the 74 VOCs included in the analytical method were determined at concentrations equal to or above the MQL. These results are shown in Table 1, where they are described by families, as well as Others which incorporate some compounds that cannot be included in the rest of the families, for instance 1,3-butadiene. As Fig. 1 shows, the highest average sum of concentrations ($\sum$VOC) was 83.9 μg m^{-3} at the educational Centre. At this site, the $\sum$VOC values in November and December 2023 increased fourfold, probably due to planned maintenance activities at the South industrial park of Tarragona, which increased the annual average value of $\sum$VOC. The other sampling sites has average $\sum$VOC between 29.7 μg m^{-3} at Tarragona Centre and 38.6 μg m^{-3} at Constantí. As shown in Fig. 1, the most prevalent family of compounds was alkanes with average values ranging from 11.6 μg m^{-3} (Tarragona Centre) to 30.5 μg m^{-3} (Educational Centre). Two compounds stood out from the rest: i-pentane (6.50–13.8 μg m^{-3}) and n-pentane (2.70–7.40 μg m^{-3}).

At a lower concentration level, aromatic hydrocarbons were found with average values ranging from 6.00 μg m^{-3} (Tarragona Centre) to 15.3 μg m^{-3} (Educational Centre), and others, with average concentrations ranging from 4.10 μg m^{-3} (El Morell) to 29.3 μg m^{-3} (Educational Centre). Methyl and vinyl acetates were the most representative others with maximum values of up 98.3 μg m^{-3} and 25.8 μg m^{-3} at the Educational Centre (November 2023). BTEX (benzene, toluene, ethylbenzene and o,m,p-xylene) and styrene were the aromatic hydrocarbons found at the highest concentrations, with average concentrations ranging from 0.33 μg m^{-3} (Tarragona Centre) to 3.80 μg m^{-3} (Educational Centre). The average concentrations of these compounds were in line with those obtained by Vallecillos et al. (2024) during a three-year monitoring in the same study area (0.16–2.6 μg m^{-3}). Although these compounds do not have a specific emission source, in urban atmospheres they are likely to originate from traffic emissions, heating boilers or the combustion of organic matter (Nagpure et al., 2016; Bari and Kindzierski, 2017). Similar to the study by Vallecillos et al. (2024), the present study showed an increase in average concentrations at sampling sites close to the industrial areas. This confirmed, in the case of Tarragona, VOCs are mainly originated from industry, with urban emission sources playing a secondary role. Villanueva et al. (2018) reported similar concentrations of toluene (1.84 μg m^{-3}) and m,p-xylene (1.55 μg m^{-3}) in urban areas close to the petrochemical park of Puertollano (Ciudad Real, Spain).

Organochlorines, solvents and alkenes were the families of compounds found at the lowest concentrations with average concentrations ranging from 0.76 μg m^{-3} (El Serrallo) to 3.20 μg m^{-3} (Educational Centre). Carbon tetrachloride and dichloromethane were the prevailing organochlorines, with average values between 0.34 μg m^{-3} (El Serrallo) and 1.60 μg m^{-3} (Educational Centre). Although carbon tetrachloride is banned by the "Montreal Protocol on Substances that Deplete the Ozone Layer", its concentration in outdoor air could be explained by uncertainly about its atmospheric lifetime, incomplete historical production data and unreported emission sources (HMPSDOL, 2020). Similar average values of dichloromethane (0.70–4.60 μg m^{-3}) and carbon tetrachloride (0.39–1.30 μg m^{-3}) were reported in urban areas in the vicinity of industrial parks in Spain (Villanueva et al., 2018; Vallecillos et al., 2024), China (Yao et al., 2021) and Turkey (Dumanoglu et al., 2014).

In the study of VOCs, particular attention needs to be given to some pollutants due to their industrial production in nearby areas. These compounds include benzene, 1,2-dicloroethane and 1,3-butadiene. Benzene, in particular, requires stringent monitoring as per the European Directive 2008/50/EC (ED, 2008), which sets an annual average concentration limit of 5 μg m^{-3} in urban areas. Measured average benzene levels range from 0.79 μg m^{-3} in Tarragona Centre to 1.70 μg m^{-3} at the Educational Centre site. A maximum episodic concentration of 4.10 μg m^{-3} was found in Constantí in February 2023, as this town in located <3 km south of the production plants of benzene and the prevailing wind direction in winter was north. Slightly lower benzene concentrations, between 0.13 μg m^{-3} and 1.30 μg m^{-3}, were found in urban air samples close to petrochemical parks in Italy (de Gennaro et al., 2013), USA (Mukerjee et al., 2020) and Spain (Villanueva et al., 2018).

1,3-Butadiene average concentrations were between 0.39 μg m^{-3} (El Serrallo) and 1.70 μg m^{-3} (Constanti and El Morell) below the annual benchmark of 2.0 μg m^{-3} set in the air directive from Ontario (OR, 2025). Slightly lower 1,3-butadiene concentrations, between 0.061 μg m^{-3} and 1.50 μg m^{-3}, were found in air samples from urban and industrialized towns of Canada (Curren et al., 2006). Maximum concentrations of 5.50 μg m^{-3} in El Morell and 7.90 μg m^{-3} in Constantí were found in the first and second half of November 2023, respectively. This concentrations peaks can be attributed to their proximity to the northern industrial park, El Morell (<1 km, west) and Constantí (<3 km, south), where 1,3-butadiene is produced, handled and stored and prevailing winds of east/north-east and north in the first and second half of November 2023, respectively. At that time of the year there is thermal inversion in the region of Tarragona, which favours the presence of concentrations peaks of VOCs, especially 1,3-butadiene.

For 1,2-dicloroetane, the average concentrations were from 0.09 μg m^{-3} (El Morell) to 0.48 μg m^{-3} (Educational Centre). The highest concentrations in the Educational Centre were consistent with its proximity to the southern industrial park and the port of Tarragona, where this compound is synthesised, stored handled and transported by ship. Higher average concentrations of 1,2-dichloroethane were found in urban areas of Aliaga (Turkey, 2.7 μg m^{-3}) and Handan (China, 7.4 μg m^{-3}) close to vinyl chloride factories (Dumanoglu et al., 2014; Yao et al., 2021).

3.1.2. Monitoring SVOCs

All the SVOCs included in the study, as shown in Table 2, were determined in the 36 samples collected. The average sum of concentration ($\sum$SVOC) was between 90.3 ng m^{-3} (Tarragona Centre) and 111 ng m^{-3} (Constantí) with no significant differences between sampling sites.

Fig. 2 shows that the family of SVOCs with the highest average concentrations was PAEs, with average concentration values between 28.1 ng m^{-3} (Tarragona centre) and 41.8 ng m^{-3} (Constantí). It is no wonder that these compounds exhibited the highest concentrations,

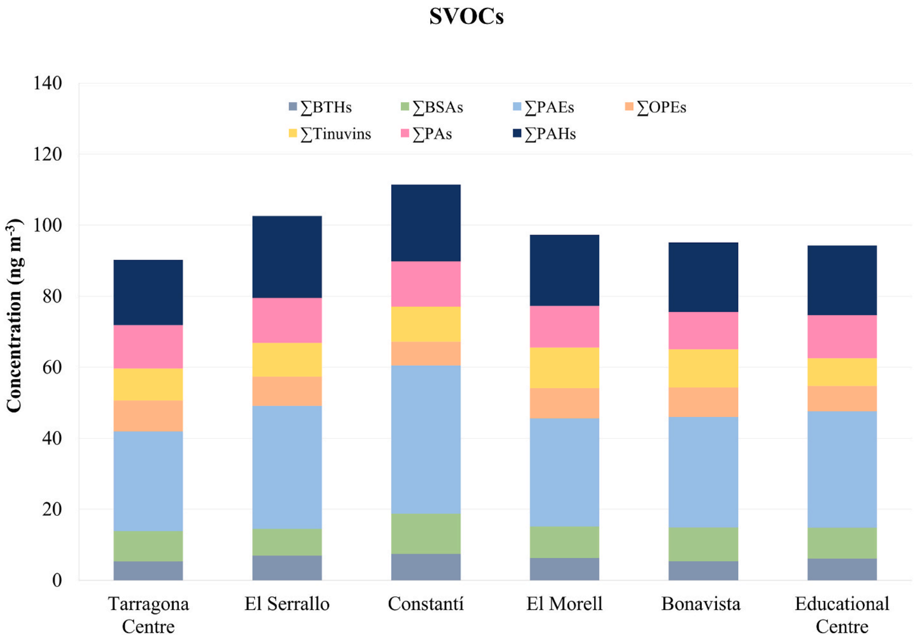

Fig. 2. Average concentration of each family of SVOCs (ng m^{-3}) at the sampling points.

considering that substances like DEHP and DEHA are produced and/or imported into the European Economic Area in quantities of 10,000 to just under 100,000 tonnes annually, according to European Chemicals Agency (ECHA, 2024). Following PAEs, PAHs were prevalent with average concentrations from 18.4 ng m^{-3} (Tarragona Centre) up to 23.1 ng m^{-3} (El Serrallo). The similarity in PAH levels at all locations is due to the fact that the main emission source in the Tarragona area is road traffic. El Serrallo, in particular, shows slightly higher levels because of the heavy flow of cars and trucks associated with cargo ship activity. In addition, the companies in the petrochemical parks of Tarragona work with natural gas to reduce PAHs emissions (MTED, 2024), and for this reason the values found in the study were lower than those found in urban areas with industrial activity. For instance, Pozo et al. (2012) and Křůmal and Mikuška (2020) reported average concentrations for the sum of 15 of our PAHs ($\sum_{15}$PAHs) ranging from 26 pg m^{-3} to 230 pg m^{-3} and of 60.8 pg m^{-3} passive air samples from urban areas near industries in Conception (Chile) and Ostrava (Czech Republic), respectively. In contrast, the results from our samples show higher levels than concentrations from cities that do not have an industrial influence. For instance, Ukpebor et al. (2023) obtained concentrations of $\sum_{16}$PAHs in urban areas of 0.817 μg m^{-3} using the same sampling methodology. Among the PAHs, for BaP, the European Directive 2008/50/EC (ED, 2008) sets the maximum concentration at 1 ng m^{-3} for PM$_{10}$. In this monitoring study, the highest concentration of BaP was found in Tarragona Centre with an average concentration of 0.9 ng m^{-3}. However, since passive sampling was used, this concentration includes both particulate matter and the gas phase, not just PM$_{10}$, and therefore it would not exceed the limit established. The results found in this study are higher than those found in other studies, such as in Maragheh (Iran) where average concentrations for BaP of 0.47 ng m^{-3} were obtained in particulate matter (<50 μm) (Soleimani et al., 2024), and in Spain, where an average annual concentration of 0.17 ng m^{-3} in Vigo (Sánchez-Piñero et al., 2022) and a median value of 0.05 ng m^{-3} in Guipuzkoa (Oleagoitia et al., 2019) were obtained in PM$_{2.5}$ samples.

Subsequently, PAs exhibited similar concentrations across all sites, with total average concentrations ranging from 10.5 ng m^{-3} (Bonavista) to 12.7 ng m^{-3} (Constantí). Other SVOC families appeared at lower concentrations; for instance, BTHs, Tinuvins, OPEs and BSAs with average concentrations between 5.3 ng m^{-3} (Tarragona Centre) and 11.5 ng m^{-3} (El Morell). Zhang et al. (2024) reported average concentrations of OPEs ranging from 0.08 ng m^{-3} to 1.07 ng m^{-3} in urban and suburban/rural passive air samples from Thailand, Vietnam, Cambodia and Laos in Southeast Asia. The sampling sites evaluated by Zhang et al. (2024) were characterized by low industrial activity and probably for this reason the OPEs values obtained were lower than those of the present study. Hou et al. (2021) also reported a lower average concentration of 2.78 ng m^{-3} for sixteen OPEs in passive air samples from Jinan, a large city in northern China. On the other hand, similar concentrations of OPEs between 0.53 ng m^{-3} and 19.1 ng m^{-3} were found in passive air samples from Busa, a highly industrialized city in Turkey (Kurt-Karakus et al., 2018). The concentrations of the remaining SVOCs were similar to those reported by Maceira et al. (2018, 2019) and Garcia-Garcinuño et al. (2024b) when analysing 24-h active air samples (PM$_{10}$) from the same area of study, between 0.17 ng m^{-3} and 8.9 ng m^{-3} for BTHs, between 0.02 ng m^{-3} and 2.17 ng m^{-3} for BSAs, between 0.31 ng m^{-3} and 1.81 ng m^{-3} for Pas and up 0.384 ng m^{-3} for Tinuvins.

3.2. Risk assessment

The EDIs for all the target compounds were calculated for two exposure scenarios: low (geometric mean of the concentrations) and high (95th percentile concentrations) and two demographic groups, children (6–12 years) and adults. According to USEPA guidelines, for compounds with concentrations below the MDLs and MQLs, their concentration values were replaced with half of MDLs and half of the MQLs, respectively (EPA, 2007). The EDIs obtained are shown in Table 7S for VOCs (μg kg$_{bw}^{-1}$ day^{-1}) and Table 8S for SVOCs (ng kg$_{bw}^{-1}$ day^{-1}).

Among the VOCs, alkanes exhibited the highest EDI values, ranging from 18.3 μg kg$_{bw}^{-1}$ day^{-1} (Tarragona Centre, children, low scenario) to 240 μg kg$_{bw}^{-1}$ day^{-1} (Educational Centre, adults, high scenario). On the other hand, among SVOCs, can be shown the PAEs with the highest values, ranging from 9.1 ng kg$_{bw}^{-1}$ day^{-1} (Tarragona Centre, children, low scenario) to 197 ng kg$_{bw}^{-1}$ day^{-1} (Constantí, adults, high scenario).

Non-carcinogenic risk data, expressed as HQ, were obtained for those of the target VOCs and SVOCs that have an established RfC or RfD value and are shown in.Table 9S The HQ values were organised by family of compounds and calculated for the two scenarios and two age groups. Overall, ∑Total (∑HQVOCs+∑HQSVOCs) values were between 0.02 (Tarragona Centre, low scenario, children) and 1.30 (Constantí, high scenario adults). As Fig. 3 shows, the ∑Total values for adults were

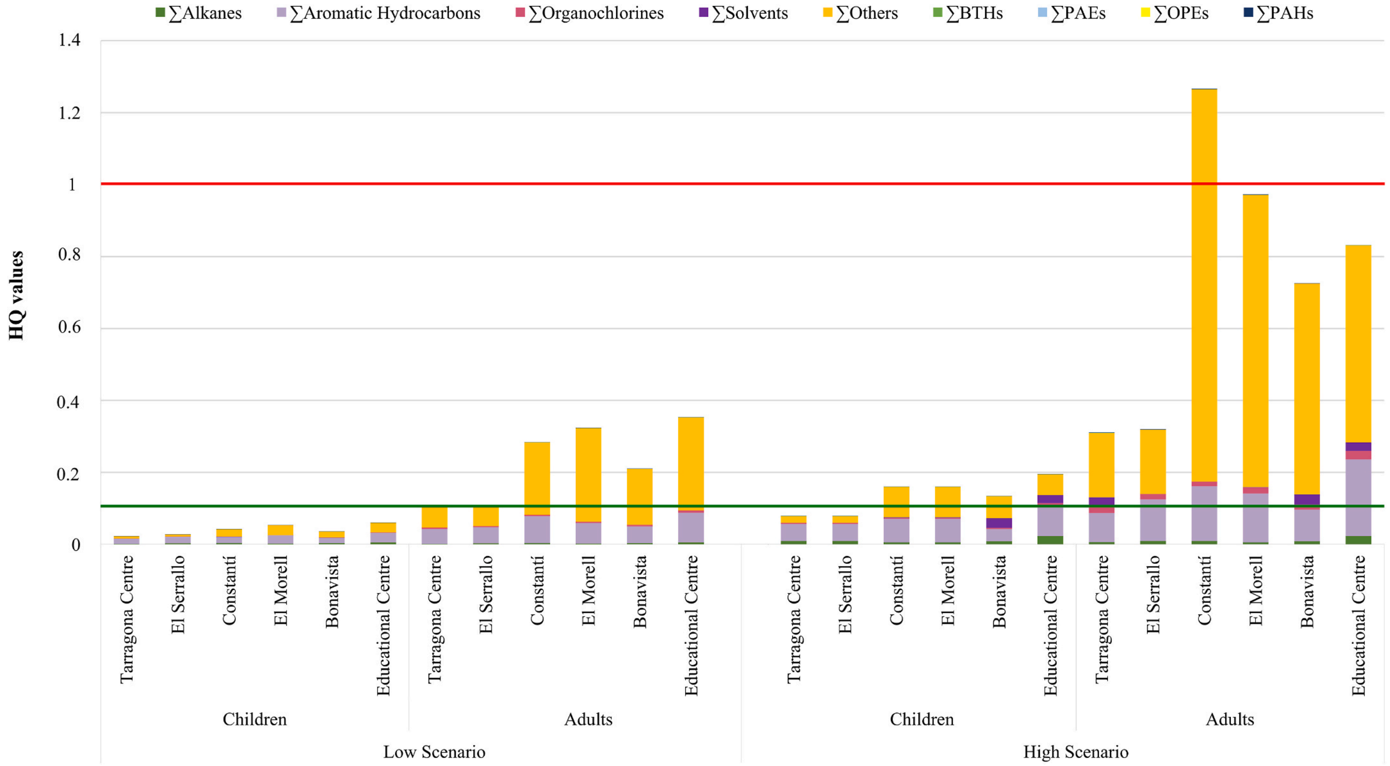

Fig. 3. Non carcinogenic risk (HQ) of each family of VOCs in two scenarios (low and high) and in two population groups (children and adults). The red line marks the limit of HQ of 1 and the green line marks the limit of HQ of 0.1.

between 0.10 and 1.00 and can be considered as "probable risk" (NATA, 2014). Close attention should be paid to the high scenario for adults in Constantí, as there was a ∑Total value greater than 1, suggesting a risk of non-cancer adverse effects (NATA, 2014). On the other hand, the ∑Total values for children were in general below 0.10 a negligible risk (NATA, 2014), except for the high scenario in the sampling sites in Constantí (0.16), El Morell (0.16), Bonavista (0.13) and the Educational Centre (0.19).

Most of these compound families falls below a non-carcinogenic risk level considered negligible (∑HQ < 0.10) (NATA, 2014). The "∑Others" and the ∑Aromatic Hydrocarbons families showed ∑HQ values between 0.08 and 1.10 for adults from all the sampling sites evaluated and in the high exposure scenario. For adults in Constantí, El Morell, Bonavista and the Educational Centre, the values of ∑Others even in a low scenario were higher than 0.10, between 0.16 and 0.26. The two compound families that contributed the most to the ∑Total were ∑Others and ∑Aromatic Hydrocarbons, which together accounted for between 73 % and 99 %. 1,3-Butadiene and benzene -both produced, stored, and handled at the petrochemical parks and the port of Tarragona-were the most prevalent compounds. Within the SVOCs, ∑PAHs showed the greatest contribution to the ∑Total, ranging from 0.1 % to 0.9 %. Probably for this reason, the HQs obtained in the present study for benzene were higher than those reported by Yao et al. (2021), between 0.004 and 0.035, in different urban and suburban areas in China. The same tendency was observed for ethylbenzene, in the present study the HQs were between 1.1E-05 and 3.0E-04, while Yao et al. (2021) found 9.81E-05 and 6.44E-04.

Regarding carcinogenic risk, CR values organised by family of compounds and the exposure scenarios and age groups considered in the present study were listed in Table 10S. It should be noted that CRs could only be calculated for the 32 target compounds, 10 VOCs and 22 SVOCs, that have an established IUR or a SFo. The estimated CR can be considered in the following way: a CR of 10^{-6} or less signifies a very low risk, a CR between 10^{-6} and 10^{-4} indicates a low risk, a CR from 10^{-4} to 10^{-3} represents a moderate risk, a CR between 10^{-3} and 10^{-1} indicates a high risk, while a CR of 10^{-1} or greater signifies a very high risk (Mitra et al., 2019; Alani et al., 2021). As shown in Fig. 4, in general the ∑Total ($\sum CR_{VOCs}+\sum CR_{SVOCs}$) values were found to be between 1.5E-06 (El Serrallo, children, low scenario) and 9.6E-05 (Educational Centre, adults, high scenario) indicating a low carcinogenic risk. Only in one case (Constantí, adults, high scenario) the risk was moderate with a ∑Total of 1.3E-04.

In general, the ∑CRs of the VOC compound families (aromatic hydrocarbons, organochlorines and others) were slightly higher than those of the SVOCs (OPEs, PAEs and PAHs) with values between 2.2E-07 and 8.9E-05 and between 6.8E-09 and 1.9E-05, respectively. The minimum ∑CR value of 6.8E-09 was found for OPEs in the Educational Centre (adults and high scenario), while the maximum was 9.8E-05 for Others in Constantí (adults and high scenario). All compound families exhibited a low or very low risk, as they were below 10^{-4}. Others is the family with the highest ∑CR, with values in the range of 4.3E-07 and 8.9E-05. The most representative compound of this family was 1,3-butadiene with CRs between 3.5E-07 (Tarragona Centre, children, low scenario) and 6.5E-05 (Constantí, adult, high scenario). As observed in Fig. 5, 1,3-butadiene contributed between 18 % and 58 % of ∑Total regardless of the sampling site and the scenario evaluated. Some compounds produced in the study area can also be highlighted such as benzene, 1,2-dicloroethene and ethylbenzene with CRs between 3.4E-08 (Ethylbenzene, Tarragona, infants, low scenario) and 9.0E-06 (1,2-dicloroethene, El Serrallo, adults, high scenario). These four compounds contributed between 35 % and 76 % of the ∑Total at all the sampling sites. PAEs were the SVOCs family with the highest ∑CR values, ranging from 4.3E-07 to 1.9E-05. Two compounds, DEHA and DEHP, contributed between 10 % and 39 % of the ∑Total. PAHs accounted for up to 6 % of the ∑Total, with Bap -the only SVOC regulated in PM_{10} samples (ED, 2008)- contributing between 0.2 % and 1.4 % of the ∑Total.

Our results were slightly higher than those obtained in other studies. For example, in the study carried out by Liu et al. (2021) in Beijing

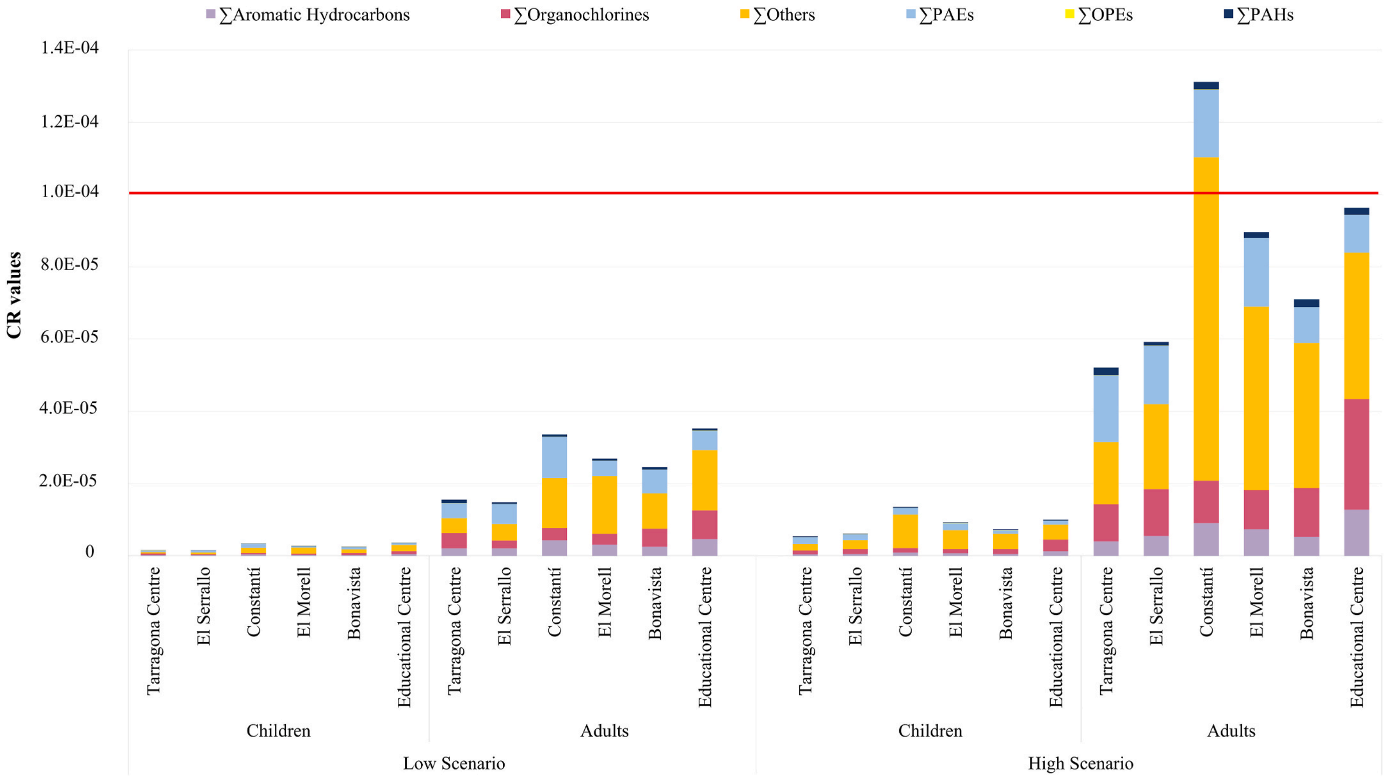

Fig. 4. Carcinogenic risk (CR) of each compound family in two scenarios (low and high) and in two population groups (children and adults). The red line marks the limit between moderate risk and low risk.

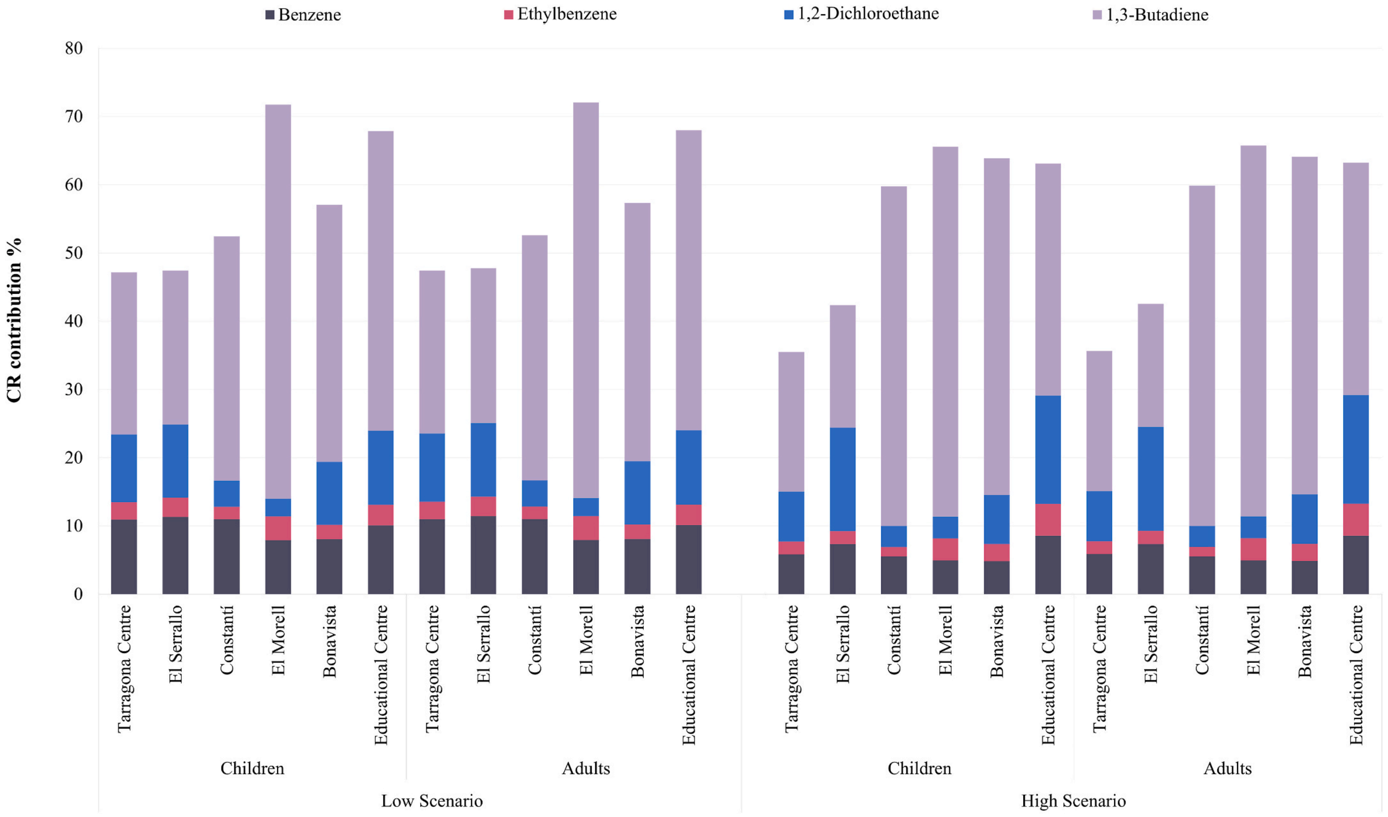

Fig. 5. Contribution (%) of the most relevant compounds to the total CR at the different sampling points in the low and high scenarios and in two population groups.

(China), the carcinogenic risk for 22 VOCs were between 10^{-5} and 10^{-1} (negligible). In the same study, the carcinogenic risk for 11 of the VOCs, ranged from 8.1E-10 to 5.6E-05. Contrary to what was found in Tarragona, the carcinogenic risk values for benzene, 1,3-butadiene, ethylbenzene and 1,2-dichloroethanefound by Liu et al. (2021) were lower than 10^{-6} (very low risk). Similarly, Yao et al. (2021) obtained non-carcinogenic risk values between 9.1E-06 and 1.1E-01 for 26 VOCs in air samples from the southeast of Handan. Only the carcinogenic risk values associated with tetrachloride, 1,2-dibromoethane, benzene, 1, 2-dichlroethane, hexachlorobutadiene and chloroform were higher than 10^{-6} (low risk). Maceira et al. (2020) when analysing 24-h PM_{10} air samples from Tarragona, reported non-carcinogenic risk values lower or equal to 5.80E-04 (negligible) for the same BTHs, OPEs and PAEs of the present study. These authors also found carcinogenic risk values between 1.6E-07 and 4.5E-12 for OPEs and PAEs (very low risk). On the other hand, higher risk values were found after analysing passive air samples from Dhanbad (India, VOCs) (Malik et al., 2023) and Lagos (Nigeria, SVOCs) (Alani et al., 2021). More specifically, the individual non-carcinogenic risk values for 22 VOCs in India were between 0.1 and 1 but the total risk was always higher than 1.38. The individual cancer risk values for these VOCs and 15 PAHs (SVOCs) in Lagos were in the range of 9.8E-08 and 9.7E-05 with total cancer risk values greater than 10^{-4}, which is a moderate risk (Mitra et al., 2019; Alani et al., 2021).

4. Conclusions

Comprehensive annual air quality monitoring of both VOCs and SVOCs has consistently shown that air quality is highly influenced by the local environmental conditions. In the Tarragona area, the results clearly indicate that the compounds present in the air are predominantly associated with the activities in the petrochemical parks of the city and the port. These nearby industries are likely to be direct emission sources of the compounds that are produced, processed or used in their operations. Therefore, the main carcinogenic risks identified in the area are directly related to these industrially derived substances.

This study found that VOC concentrations for one year ranged from 29.7 μg m^{-3} to 83.9 μg m^{-3}, while SVOCs were detected at levels between 90.3 ng m^{-3} and 111 ng m^{-3}. Risk assessment results generally indicated a probable non-carcinogenic risk at the evaluated sampling sites, with values between 0.1 and 1.00 and benzene and 1,3-butadiene contributing the most. A low carcinogenic risk was observed with values in the range of 1.5E-06 and 9.6E-05. Only in one specific case (Constantí, adults, high scenario), the risk could be considered moderated (1.3E-04). It was also identified that four specific VOCs, 1,3-butadiene, benzene, 1,2-dicloroethane and ethylbenzene, which are produced in the area under study account for between 35 % and 76 % of the total risk. The SVOCs with the highest contribution to the overall risk were two PAEs, DEHA and DEHP, which together accounted for between 10 % and 39 %. One compound in particular, 1,3-butadiene, was responsible for between 18 % and 58 % of the total carcinogenic risk.

In view of the results, it is crucial to establish a system of continuous monitoring for the compounds that pose the highest health risks, allowing for a better understanding of their behavior in the atmosphere. Furthermore, specific industrial measures can be implemented to reduce the presence of these compounds in the air, improving air quality and minimizing risks to the local community.

CRediT authorship contribution statement

Reyes García-Garcinuño: Writing – original draft, Validation, Methodology, Investigation. **Laura Solé-Domènech:** Writing – original draft, Validation, Methodology, Investigation. **Rosa M. 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

There is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2025.144432.

Data availability

Data will be made available on request.

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