



Air monitoring with passive samplers for volatile organic compounds in atmospheres close to petrochemical industrial areas. The case study of Tarragona (2019–2021)

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ABSTRACT

This study reports a three-year monitoring campaign of 62 volatile organic compounds (VOCs) of increasing concern in urban atmospheres near petrochemical industrial areas. A total of 770 air samples were taken during the sampling campaigns conducted monthly between January 2019 and December 2021. The analytical method applied involved a 14-day passive sampling in Carbpac X tubes followed by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). To gain insight into the correlations between VOCs, multivariate data analysis was used to assess the similarities and differences between datasets. Special attention was paid to benzene, 1,3-butadiene and 1,2-dichloroethane, because they are carcinogenic and are produced, handled and stored in the petrochemical industrial areas studied. The compounds found in the highest concentrations were alkanes, which were 21–66% of the total. Aromatic hydrocarbons and solvents were also detected at all the sampling sites, with BTEX and ethanol as the most prevalent compounds. Various concentration peaks of up to $4.8 \mu\text{g m}^{-3}$ for benzene and up to $4.0 \mu\text{g m}^{-3}$ for 1,3-butadiene were detected during the monitoring campaigns performed. Nevertheless, the average concentrations of these two compounds were always below the values set in the current air quality regulations, with maximum values of $1.3 \mu\text{g m}^{-3}$ for benzene and $1.5 \mu\text{g m}^{-3}$ for 1,3-butadiene near the North industrial park of Tarragona. Multivariate analysis results revealed four different patterns at the reference sites and discriminated between the sampling sites close to the petrochemical areas evaluated. The autumn-winter months, with thermal inversion phenomena and prevailing north and north-westerly winds, were the ones with the highest concentration levels of VOCs.

1. Introduction

The city of Tarragona (north-east Spain) is a first-class tourist attraction because of its beaches, Mediterranean climate, historical tradition and artistic heritage (the archaeological ensemble was declared a UNESCO world heritage site in 2000). It is located alongside one of the largest chemical sites in southern Europe, consisting of 34 large international companies in the sector and divided into two industrial parks, North and South. It occupies an area of 1200 ha, including port facilities. The member companies produce a total of 20 million tons per year of a wide range of chemical industry-related

products, mainly plastic and fuels. The North industrial park comprises a petroleum refinery and chemical industries specializing in the manufacture of 1,3-butadiene, styrene and benzene, among others. The South industrial park includes mainly industries focuses on the production of plastics (*i.e.* polypropylene and acrylonitrile butadiene styrene), but also, production plants of chlorine derivatives (*i.e.* vinyl chloride and 1,2-dichloroethane) and ethylene oxide. The port of Tarragona also has a small refinery and a storage facility for the import and export of chemical products (AEQT, 2023; PO, 2023; REP, 2023).

Chemical production, storage, daily loading and unloading of goods, as well as road and train transport and shipping are expected to affect

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the air quality of nearby urban environments (Dumanoglu et al., 2014; Chen et al., 2015; Xiao et al., 2018; Yao et al., 2021; Johannessen et al., 2022). Initially, studies have mainly focused on monitoring the concentrations of major air pollutants such as PM₁₀ particles, nitrogen oxides (NO_x) and ozone (O₃) (Civan et al., 2015; Ledoux et al., 2018; Sorte et al., 2019; Selvam et al., 2020). In recent years the monitoring of volatile organic compounds (VOCs) in urban areas, especially close to chemical facilities, has attracted a great deal of attention, because they are a latent threat to human health animals and plants (Han et al., 2019; Dörter et al., 2020; Mukerjee et al., 2020; Besis et al., 2021; Ghaffari et al., 2021; da Rocha et al., 2023). Short-term exposure to VOCs is linked to skin, eye, and throat irritations while long-term exposure is linked to cancer and nervous system damage (Ramírez et al., 2012; Sakizadeh, 2020; Jia et al., 2021). VOCs have been reported to be responsible for the photochemical smog that affects metropolis around the world and are ozone precursors at ground level, and also to be part of the greenhouse effect, among others (Ling and Guo, 2014; Gu et al., 2021; Xuan et al., 2021). Despite the effects of VOCs on the environment and health, the European Directive 2008/50/EC (ED, 2008) only fixes a maximum concentration level in urban areas for benzene (5 µg m⁻³, annual average value), and recommends that the VOCs classified as ozone precursors be monitored. In the specific case of the Tarragona area, the Catalan Government's Network for Monitoring and Forecasting Air Quality has nine fixed stations for the continuous monitoring of PM_{2.5} and PM₁₀ particles, NO_x and O₃ in urban areas. Minor air pollutants - *i.e.* VOCs (ozone precursors) and polycyclic aromatic hydrocarbons - are not monitored in all the stations and the samples analysed are episodic (XVPCA, 2023).

Present in the atmosphere at trace level, a preconcentration step is required to concentrate the VOCs of interest before analysis by gas chromatography-mass spectrometry (GC-MS). As reported in Kumar and Viden (2007), the following parameters must be taken into account when choosing the most suitable sample preconcentration technique: kind of contaminant, the phase associated with the organic contaminant, expected concentration levels, the duration of the sampling campaign and the information sought. The most widely used sampling technique for preconcentrating VOCs retains the compounds in solid adsorbent tubes, either by active or passive sampling, followed by a desorption step with heat or an organic solvent (Maceira et al., 2017; Raysoni et al., 2017; Vallecillos et al., 2018). Although several types of adsorbent tubes are commercially available, graphitized carbon blacks are the most extensively used for VOCs because of their high retention capacity (Król et al., 2010). Active sampling provides information about episodic concentrations of VOCs in the atmosphere and generally involves short periods of time (Civan et al., 2015; Hsu et al., 2018; Zheng et al., 2020; Yao et al., 2021). Passive sampling, in both radial and axial diffusion configuration, involves seven-day or fourteen-day monitoring and provides average concentration values, but underestimates episodic concentrations (Vallecillos et al., 2019a; Dörter et al., 2020; Healy et al., 2018, 2021). Although active sampling is considered more versatile than passive sampling, the latter is preferred by many authors in the field. The simplicity of passive sampling together with the fact that it is easy to implement and cost-effective make it possible to carry out long-term monitoring campaigns with a tight budget that provide the average concentration values required for risk assessment (Villanueva et al., 2018; Vallecillos et al., 2019a).

In this study, we used passive sampling for a three-year monitoring of VOCs (2019–2021) in urban atmospheres close to the petrochemical industry in Tarragona (Spain) and in five reference sites set up in a metropolis, the countryside and three towns of equal size but different industrial presence. The target VOCs were determined by means of thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). The results from the 770 measurements of VOCs were used to assess their annual distribution, the impact of industrial activity on the values of specific VOCs, and the impact of anti-COVID measures such as mobility restrictions on VOC concentrations.

2. Materials and methods

2.1. Reagents and standards

The standards of the 62 VOCs under study contain the commercial mixtures EPA 524.2 Revision 4 Mix and EPA 502/524 Volatile Organic Calibration Mix SS both of 2000 mg L⁻¹ in methanol (Supelco, Bellefonte, USA). Individual standard solutions of 2000 mg L⁻¹ in methanol of the following VOCs were also prepared: *n*-pentane, *i*-pentane, *n*-hexane, *n*-heptane, *n*-octane, isoprene, (*cis/trans*) 2-pentene, 1-hexene, 2-butanone, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, ethanol, 1-propanol, isopropyl alcohol, ethyl acetate, isopropyl acetate, *n*-propyl acetate (Sigma-Aldrich, Steinheim, Germany), 1-methylnaphthalene and 2-methylnaphthalene (Riedel-de Haën, Seelze, Germany), 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, 1,3-diethylbenzene and 1,4-diethylbenzene (Fluka, Buchs, Switzerland). All the above-mentioned VOCs were of purities higher than 97%. The 1,3-butadiene standard solution of 2000 mg L⁻¹ in *n*-hexane was prepared from a commercial solution of 1,3-butadiene of 15% wt (*n*-hexane) supplied by Sigma-Aldrich.

Working solutions of the 61 VOCs were prepared with methanol, while 1,3-butadiene solutions were made up with *n*-hexane (Carlo Erba, Barcelona, Spain, purity >99.91%). Thermal desorption of the samples and chromatographic analysis were carried out with nitrogen and helium gas of 99.9 % purity from Carbueros Metálicos (Tarragona, Spain), respectively.

2.2. Sampling

A three-year monitoring campaign was conducted from January 2019 to December 2021 to determine the presence of VOCs in several urban atmospheres in Catalonia (Spain). As Fig. 1 shows, 17 sampling sites were set in municipalities and neighbourhoods of between 1275 inhabitants and 106,084 inhabitants close to the two petrochemical parks of Tarragona (north-east Spain) (IDESCAT, 2023). Nine sampling sites were located in municipalities close to the North industrial park of Tarragona (N1–N9) and its 1,3-butadiene and benzene production plants. Eight sampling sites were set in municipalities near the South industrial park of Tarragona (S1–S8) and its 1,2-dichloroethane production plant. Another factor that was taken into account to determine the sampling sites was the prevailing wind direction, north (N) and north-westerly (NW) in winter and regular thermal breezes in summer (METEO, 2022). Five further sampling sites were selected to provide reference information on VOC concentrations: three in the centre of cities of about 100,000 inhabitants (Tarragona -R1, Girona -R3 and Lleida -R4), one in the centre of a metropolis of 1,636,732, inhabitants (Barcelona -R2) and one in a rural town of 602 inhabitants (Prades -R5) (IDESCAT, 2023).

14-Day passive sampling was performed monthly at each sampling site. A total of 770 samples, 35 samples/site, were collected over the three-year monitoring campaign. Following US EPA methods 325A (EPA, 2019a) and 325B (EPA, 2019b) guidelines to determine VOCs from Fugitive and Area sources, sampling sites were set at a height of 2 m. Passive sampling devices consisted of a previously conditioned Carbo-pack X (CX) adsorbent tube with a diffusion cap at the open end (Supelco, Bellefonte, USA). Passive samplers also had a stainless-steel protective hood to protect the tube from adverse weather conditions. Data from the Meteorological Service of Catalonia (METEO, 2022), in particular temperature and pressure, were used to adjust the diffusive uptake-rates of the target VOCs during the sampling period. For those municipalities without a weather station, pressure and temperature during sampling were recorded with TH0160 data loggers (Perfect Prime, London, UK).

2.3. TD-GC-MS analysis

Air samples were analysed by thermal desorption-gas

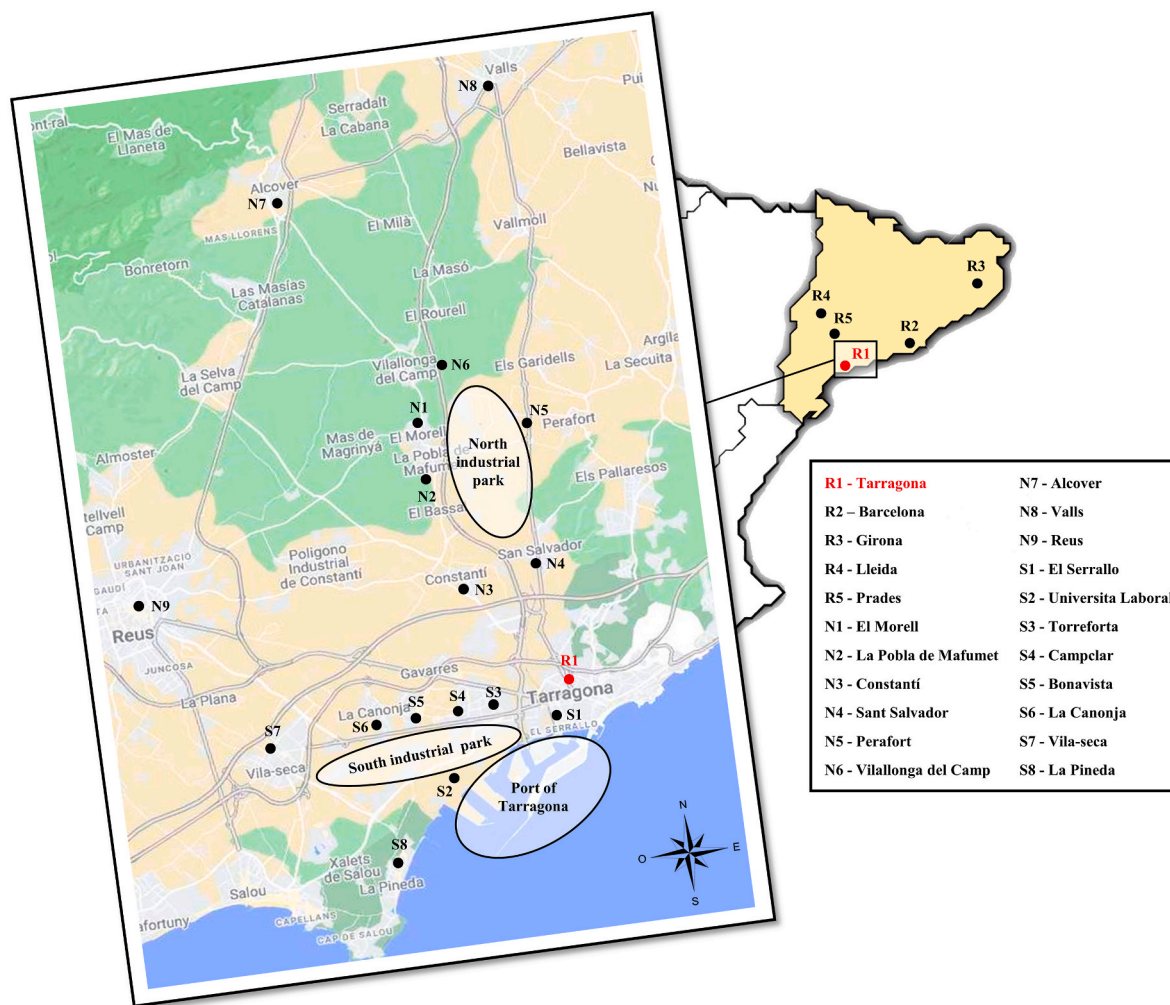


Fig. 1. Map of the area under study showing the location of the two industrial parks of Tarragona, the port facilities and the urban sites sampled.

chromatography-mass spectrometry (TD-GC-MS) in a 7890A gas chromatograph (GC) (Agilent Technologies, Palo Alto, CA, USA) equipped with a Unity 2 Thermal Desorption system and an Ultra A automatic sampler both from Markes International Limited (Llantrisant, UK). Separation of the target VOCs was carried out on a ZB-5 (5 % phenyl-95 % dimethylpolysiloxane) capillary column from Phenomenex (Torrance, CA, USA) and detection by single quadrupole MS in a 5975C inert MS (Agilent Technologies). TD-GC-MS conditions are given in Table 1S and more detailed information of the chromatographic method applied is available in Maceira et al. (2017) and Vallecillos et al. (2019a). Table 2S shows the identification parameters of the 62 VOCs studied.

2.4. Data handling and statistics

All data were maintained in Microsoft Office 365 Excel®. Statistical evaluations were made using Matlab 2022a (Mathworks Inc, Natick, MA, USA) and PLS Toolbox 9.0 (Eigenvector Inc, Manson, WA, USA) for Matlab. Prior to any model calculation, data were autoscaled to take into account any disparity in the concentration ranges of the target VOCs. Principal component analysis (PCA) was applied to assess similarities, correlations and differences between the sampling sites. The variables, individual compounds or families of VOCs, that most influence the atmosphere of the different sites were also evaluated.

For all quantitative assessments, concentrations below MDL and below MQL were set at MDL/2 and MQL/2, respectively (EPA, 2000). All concentrations were reported in $\mu\text{g m}^{-3}$ and the target VOCs were

grouped in six families - alkanes, alkenes, aromatic hydrocarbons, organochlorines, solvents and others - for an easier interpretation of the results. Equation 1S (Andrietta et al., 2010), which is based on Fick's first law, and the experimental diffusive uptake-rates previously calculated by Vallecillos et al. (2019a) were applied to report VOC values in $\mu\text{g m}^{-3}$. Theoretical diffusive uptake-rates provided by the supplier of the CX adsorbent tubes (Supelco, 2017) were used for those VOCs for which these rates had not been experimentally calculated. The diffusive uptake rates in Table 2S were corrected for the average temperature and pressure of the 14-day sampling period with Equation 2S.

2.5. Quality control and quality assurance

Quality assessment and quality control (QA/QC) measures specified in US EPA methods 325A (EPA, 2019a) and 325B (EPA, 2019b) for the passive sampling of VOCs in air were applied. To avoid background contamination, both the TD trap and the analytical column were conditioned before and after analysing the samples. The CX adsorbent tubes were thermally conditioned, and blanks were carried out before use. Control samples were taken during the fourteen-day passive samplings. More detailed information about the conditioning procedure of the CX adsorbent tubes and the quality assurance procedures applied can be found in Vallecillos et al. (2019a, 2019b). Neither of the target VOCs were detected in the blanks or control samples analysed, thus demonstrating a lack of laboratory cross-contamination.

External standard calibration curves were built by enriching CX

Table 1

Concentrations of the target compounds found at the nine sampling sites near the North industrial park of Tarragona (N1–N9) expressed as $\mu\text{g m}^{-3}$. $N = 35$, 14-day passive sampling.

	Northern Industrial Park of Tarragona																										
	N1			N2			N3			N4			N5			N6			N7			N8			N9		
	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
Alkanes																											
1 i-Pentane	2.1	26	7.9	2.8	23	7.1	2.9	34	14	1.7	13	5.0	0.62	18	8.1	1.2	22	5	0.89	12	3.3	1.2	16	5.0	3.9	17	9.1
2 n-Pentane	1.1	6.5	2.7	1.1	12	2.5	2.6	22	7.6	0.56	4.8	2.0	0.33	7.2	3.1	0.88	11	2.1	0.40	3.0	1.5	0.71	8.7	1.9	0.94	6.3	2.7
3 n-Hexane	0.23	3.8	0.90	0.13	7.2	0.98	0.13	5.1	1.9	<MQL	3.4	0.71	0.053	3.4	0.75	0.094	3.0	0.51	n.d.	1.2	0.44	0.037	2.9	0.60	0.11	2.9	0.76
4 n-Heptane	<MQL	0.92	0.40	0.089	0.98	0.31	0.070	2.0	0.66	<MQL	2.6	0.35	<MQL	0.63	0.19	0.060	0.86	0.22	0.023	0.67	0.24	n.d.	2.4	0.49	0.011	0.87	0.28
5 n-Octane	0.078	0.85	0.21	<MQL	0.71	0.23	0.071	2.0	0.32	0.040	0.67	0.15	0.020	0.46	0.13	0.019	0.79	0.16	0.042	1.16	0.24	n.d.	0.56	0.20	0.043	0.43	0.20
Alkenes																											
6 2-trans-Pentene	<MQL	0.60	0.16	<MQL	0.36	0.12	<MQL	0.26	0.092	n.d.	0.52	0.084	<MQL	0.40	0.090	<MQL	0.32	0.15	n.d.	0.37	0.070	<MQL	0.51	0.10	<MQL	0.47	0.17
7 Isoprene	0.020	1.2	0.38	n.d.	0.85	0.26	0.041	2.4	0.58	<MQL	3.5	0.33	0.040	1.6	0.36	0.080	2.2	0.69	<MQL	3.1	0.64	0.030	2.3	0.34	0.069	2.5	0.73
8 2-cis-Pentene	<MQL	1.6	0.17	<MQL	0.96	0.12	<MQL	2.4	0.16	n.d.	1.5	0.11	<MQL	1.9	0.13	<MQL	1.6	0.15	n.d.	2.2	0.13	<MQL	1.1	0.094	<MQL	4.0	0.23
9 1-Hexene	0.060	2.4	0.33	0.020	1.7	0.31	0.069	4.7	0.38	0.018	8.0	0.49	<MQL	8.2	0.53	0.030	0.51	0.16	0.020	1.2	0.22	<MQL	3.7	0.34	0.040	1.1	0.26
Aromatic Hydrocarbons																											
10Benzene	0.28	1.4	0.62	0.26	1.4	0.65	0.65	2.5	1.3	0.24	1.4	0.52	0.50	0.96	0.71	0.14	0.80	0.41	0.14	0.64	0.35	0.20	0.79	0.39	0.22	0.90	0.47
11Toluene	0.66	4.5	2.0	0.57	4.2	1.7	0.34	2.9	1.3	0.13	2.5	0.89	0.060	1.9	0.93	0.64	3.2	1.7	0.19	3.6	1.1	0.74	14	2.3	0.32	5.1	1.6
12Ethylbenzene	0.050	1.9	0.79	0.15	1.7	0.63	0.18	1.4	0.69	0.036	1.6	0.35	0.17	1.6	0.72	0.17	1.4	0.46	0.022	0.66	0.29	0.10	3.8	0.54	0.14	0.78	0.43
13m.p-Xylene	0.16	2.1	0.89	0.19	1.6	0.67	0.14	1.0	0.52	0.10	3.3	0.43	0.14	1.4	0.39	0.12	1.8	0.63	0.040	1.5	0.42	0.16	7.9	0.88	0.091	1.7	0.56
14o-xylene	0.10	1.5	0.62	0.15	1.2	0.47	0.11	0.72	0.38	0.049	2.6	0.32	0.10	1.1	0.29	0.19	1.1	0.43	0.027	1.1	0.29	0.12	3.2	0.56	0.17	1.3	0.45
15Styrene	0.060	1.1	0.23	0.030	2.0	0.25	0.010	1.2	0.33	<MQL	0.77	0.21	<MQL	1.8	0.46	n.d.	0.42	0.13	n.d.	0.42	0.10	n.d.	0.34	0.11	<MQL	1.3	0.18
16Isopropylbenzene	0.010	0.27	0.061	0.009	0.58	0.078	<MQL	0.24	0.056	n.d.	0.12	0.026	n.d.	0.16	0.039	n.d.	0.20	0.055	n.d.	0.22	0.065	n.d.	0.35	0.030	<MQL	0.19	0.051
17n-Propylbenzene	0.017	0.27	0.089	0.008	0.52	0.091	<MQL	0.33	0.072	n.d.	0.47	0.10	n.d.	0.40	0.058	<MQL	0.22	0.063	n.d.	0.51	0.091	n.d.	0.51	0.10	n.d.	0.25	0.078
183-Ethyltoluene	0.062	0.35	0.19	0.030	0.60	0.19	0.020	1.3	0.21	<MQL	0.35	0.13	<MQL	0.45	0.14	<MQL	0.34	0.15	0.020	0.48	0.12	0.010	0.58	0.19	0.020	0.35	0.13
194-Ethyltoluene	0.044	0.36	0.15	0.022	0.45	0.15	<MQL	0.65	0.12	<MQL	0.71	0.11	n.d.	0.43	0.077	<MQL	0.33	0.094	<MQL	0.45	0.070	<MQL	0.81	0.13	0.020	0.36	0.13
201.3.5-Trimethylbenzene	<MQL	0.53	0.16	0.018	0.46	0.14	<MQL	0.63	0.13	<MQL	0.47	0.11	<MQL	0.35	0.086	<MQL	0.30	0.082	n.d.	0.86	0.12	n.d.	0.55	0.12	<MQL	0.46	0.17
212-Ethyltoluene	<MQL	0.35	0.091	0.008	0.58	0.084	n.d.	0.37	0.066	n.d.	0.35	0.047	n.d.	0.35	0.037	<MQL	0.24	0.061	n.d.	0.34	0.057	n.d.	0.33	0.060	<MQL	0.40	0.10
22tert-Butylbenzene	n.d.	0.12	0.052	n.d.	0.33	0.040	n.d.	0.22	0.027	n.d.	0.63	0.050	n.d.	0.48	0.034	n.d.	0.16	0.023	n.d.	0.31	0.039	n.d.	0.59	0.047	n.d.	0.32	0.067
231.2.4-Trimethylbenzene	0.080	1.4	0.43	0.050	1.8	0.38	<MQL	1.8	0.31	<MQL	1.5	0.25	n.d.	1.2	0.17	n.d.	1.2	0.23	n.d.	1.3	0.21	n.d.	5.1	0.50	0.020	0.86	0.29
24p-Isopropyltoluene	<MQL	0.89	0.14	<MQL	0.69	0.15	<MQL	0.79	0.15	n.d.	1.8	0.22	n.d.	1.1	0.13	n.d.	0.90	0.12	n.d.	1.5	0.26	n.d.	0.87	0.23	n.d.	0.40	0.14
251.2.3-Trimethylbenzene	<MQL	0.38	0.12	0.01	0.65	0.13	n.d.	0.30	0.084	n.d.	1.3	0.11	n.d.	0.50	0.070	n.d.	0.33	0.062	n.d.	0.40	0.062	n.d.	1.3	0.14	n.d.	0.25	0.071
261.3-Diethylbenzene	n.d.	0.050	0.011	n.d.	0.080	<MQL	n.d.	0.037	<MQL	n.d.	0.43	0.028	n.d.	0.32	0.013	n.d.	0.040	<MQL	n.d.	0.022	n.d.	n.d.	0.067	<MQL	n.d.	0.071	0.012
271.4-Diethylbenzene	n.d.	0.24	0.084	n.d.	0.42	0.061	n.d.	0.20	0.037	n.d.	2.9	0.13	n.d.	0.34	<MQL	n.d.	0.19	0.014	n.d.	0.084	0.010	n.d.	0.48	0.057	n.d.	0.18	0.034
28Naphthalene	n.d.	0.10	0.021	n.d.	0.65	0.037	n.d.	0.15	<MQL	n.d.	0.29	0.019	n.d.	0.090	<MQL	n.d.	0.13	0.020	n.d.	0.066	<MQL	n.d.	0.070	<MQL	n.d.	0.067	<MQL
292-Methylnaphthalene	n.d.	0.11	0.011	n.d.	0.18	0.019	n.d.	0.088	0.013	n.d.	0.23	0.012	n.d.	0.030	<MQL	n.d.	0.16	0.011	n.d.	0.13	<MQL	n.d.	0.22	0.020	n.d.	0.050	0.015
301-Methylnaphthalene	n.d.	0.16	0.020	n.d.	0.19	0.017	n.d.	0.057	0.014	n.d.	0.11	0.015	n.d.	0.044	0.010	n.d.	0.10	0.010	n.d.	0.088	<MQL	n.d.	0.026	0.014	n.d.	0.058	0.010
Organochlorines																											
31Dichloromethane	<MQL	5.4	0.64	<MQL	2.2	0.52	<MQL	4.5	0.75	n.d.	4.8	0.55	<MQL	2.2	0.51	<MQL	2.6	0.55	0.080	2.7	0.58	<MQL	13	3.3	0.054	2.0	0.47
32Chloroform	n.d.	0.29	0.078	<MQL	0.65	0.12	n.d.	4.4	0.23	n.d.	1.9	0.13	n.d.	0.30	0.060	n.d.	0.49	0.078	n.d.	0.34	0.081	n.d.	2.3	0.24	n.d.	0.59	0.14
331.1.1-Trichloroethane	n.d.	0.056	0.029	n.d.	0.058	0.020	n.d.	0.080	0.031	n.d.	0.060	0.030	n.d.	0.060	0.031	n.d.	0.23	0.030	n.d.	0.14	0.030	n.d.	0.41	0.041	n.d.	0.10	0.03
341-Chlorobutane	n.d.	0.20	0.020	n.d.	0.053	<MQL	n.d.	0.18	0.033	n.d.	0.072	0.010	n.d.	0.20	0.024	n.d.	0.23	0.014	n.d.	0.16	0.022	n.d.	0.25	0.036	n.d.	0.49	0.060
351.2-Dichloroethane	n.d.	0.47	0.13	n.d.	0.60	0.15	0.04	1.1	0.27	n.d.	0.73	0.20	n.d.	0.31	0.12	n.d.	0.42	0.11	n.d.	0.29	0.10	n.d.	0.73	0.12	n.d.	0.84	0.22
36Carbon tetrachloride	<MQL	2.0	1.1	<MQL	2.3	1.0	0.31	3.4	1.5	n.d.	3.2	1.3	0.21	2.2	1.2	0.19	3.1	1.0	0.34	2.8	1.1	0.21	5.4	1.4	0.14	2.7	1.2

(continued on next page)

Table 1 (continued)

	Northern Industrial Park of Tarragona																										
	N1			N2			N3			N4			N5			N6			N7			N8			N9		
	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
37Tetrachloroethene	n.d.	<MQL	<MQL	n.d.	<MQL	<MQL	n.d.	0.022	<MQL	n.d.	0.023	<MQL	<MQL	0.048	0.012	n.d.	0.030	0.010	n.d.	0.042	<MQL	n.d.	0.11	0.031	<MQL	0.44	0.10
38Chlorobenzene	n.d.	0.030	0.010	n.d.	0.040	0.011	n.d.	0.029	0.010	n.d.	0.26	<MQL	n.d.	0.018	0.010	n.d.	0.040	<MQL	n.d.	0.051	<MQL	n.d.	0.064	0.012	n.d.	0.34	0.038
Solvents																											
39Ethanol	n.d.	15	1.2	n.d.	12	1.5	n.d.	4.7	0.35	n.d.	16	1.0	n.d.	6.5	0.54	n.d.	16	2.4	n.d.	12	1.5	n.d.	20	3.4	n.d.	32	3.3
40Isopropyl alcohol	n.d.	1.5	0.089	n.d.	7.0	0.40	n.d.	1.3	0.060	n.d.	33	1.3	n.d.	0.67	0.020	n.d.	6.2	0.33	n.d.	3.9	0.14	n.d.	34	5.2	n.d.	1.9	0.19
411-Propanol	n.d.	2.2	0.40	n.d.	5.4	0.59	n.d.	5.4	0.48	n.d.	5.4	0.66	n.d.	5.7	0.62	n.d.	6.0	0.68	n.d.	7.7	0.79	n.d.	1.9	0.46	n.d.	2.5	0.55
422-Butanona	n.d.	2.5	0.29	n.d.	1.5	0.23	n.d.	1.4	0.27	n.d.	1.8	0.28	n.d.	1.4	0.27	n.d.	4.0	0.47	n.d.	1.8	0.34	n.d.	2.2	0.46	n.d.	1.3	0.25
43Ethyl acetate	n.d.	15	0.84	n.d.	1.7	0.12	n.d.	0.87	0.059	n.d.	0.32	0.031	n.d.	0.53	0.037	n.d.	1.7	0.15	n.d.	1.4	0.056	n.d.	11	1.2	n.d.	11	0.35
Others																											
441.3-Butadiene	0.29	3.6	1.5	0.32	4.0	1.0	0.42	3.5	1.3	<MQL	0.76	0.31	0.11	2.3	0.68	0.11	0.77	0.39	0.078	0.69	0.23	0.13	1.2	0.36	0.080	1.0	0.43
45Diethyl ether	n.d.	0.18	0.026	n.d.	0.2	<MQL	n.d.	0.24	0.021	n.d.	0.96	0.040	n.d.	0.14	<MQL	n.d.	0.14	0.020	n.d.	0.040	<MQL	n.d.	0.41	0.041	n.d.	0.24	0.044
46Acrylonitrile	<MQL	0.20	0.058	<MQL	0.86	0.091	n.d.	1.9	0.21	<MQL	0.13	0.038	<MQL	1.4	0.19	n.d.	0.27	0.051	n.d.	0.13	0.031	<MQL	0.66	0.056	n.d.	0.16	0.023
47tert-Butyl methyl ether	<MQL	0.67	0.18	n.d.	0.48	0.11	<MQL	1.1	0.18	n.d.	0.33	0.10	n.d.	0.33	0.088	<MQL	0.42	0.089	n.d.	0.23	0.062	<MQL	2.1	0.34	n.d.	1.0	0.17
∑Alkanes	5.4	33	12	4.5	38	11	6.5	59	24	3.5	18	8.3	1.4	25	12	3.1	34	8.3	1.8	16	5.7	2.9	20	8.2	5.8	27	13
∑Alkenes	0.18	3.8	1.1	0.086	2.7	0.80	0.15	5.7	1.2	0.10	8.6	1.0	0.15	9.2	1.1	0.29	2.7	1.2	0.10	3.5	1.1	0.087	4.4	0.87	0.36	5.1	1.5
∑Aromatic Hydrocarbons	3.2	14	6.7	2.0	12	5.9	1.9	13	5.8	1.4	16	4.1	1.7	7.9	4.4	2.2	8.7	4.7	0.68	12	3.7	1.6	18	6.5	1.9	10	5.0
∑Organochlorines	0.64	6.5	2.0	0.084	3.3	1.9	0.78	7.7	2.8	0.24	10	2.3	0.25	3.8	1.9	0.43	3.8	1.8	0.48	4.3	1.9	1.0	15	5.3	0.41	4.9	2.2
∑Solvents	0.010	24	2.9	0.011	21	2.9	0.011	6.8	1.2	0.011	35	3.3	0.011	7.2	1.5	0.011	22	4.0	0.011	19	2.8	0.011	47	11	0.011	33	4.6
∑Others	0.51	4.0	1.7	0.38	4.3	1.3	0.50	3.9	1.7	0.024	1.7	0.48	0.19	2.7	1.0	0.22	1.0	0.55	0.14	0.76	0.34	0.22	2.6	0.80	0.19	1.6	0.67
∑Total	12	56	27	12	72	24	18	75	37	9.0	72	19	6.5	40	22	7.1	58	21	4.7	40	15	11	76	32	12	52	27

Avg = average.

n.d. = non detected = below MDL.

<MQL = below MQL.

Table 2
Concentrations of the target compounds found at the eight sampling sites near the Sout industrial park of Tarragona (S1–S8) expressed as $\mu\text{g m}^{-3}$. $N = 35$. 14-day passive sampling.

		Southern Industrial Park of Tarragona																							
		S1			S2			S3			S4			S5			S6			S7			S8		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
Alkanes																									
1	i-Pentane	1.11	69	19	1.9	29	10	1.2	56	18	1.8	31	11	1.3	33	8.2	4.3	38	10	0.28	29	5.0	0.64	25	7.6
2	n-Pentane	0.47	13	4.7	1.5	14	4.7	2.0	13	6.1	0.31	12	4.7	0.84	10	3.5	1.6	6.9	3.4	0.27	14	2.1	0.81	10	4.1
3	n-Hexane	0.14	4.6	1.3	0.21	5.2	1.4	0.32	9.2	1.7	0.48	3.4	1.4	0.24	3.2	1.0	0.22	6.1	0.96	0.051	2.4	0.69	0.22	5.8	1.3
4	n-Heptane	0.054	0.97	0.38	n.d.	3.0	0.72	0.040	1.3	0.53	0.040	3.1	0.56	0.18	4.4	0.80	0.10	1.5	0.57	n.d.	1.9	0.29	0.092	3.7	0.73
5	n-Octane	0.052	0.54	0.20	n.d.	0.81	0.23	0.033	1.7	0.31	0.038	0.84	0.26	0.040	1.2	0.22	0.039	0.56	0.20	0.030	1.2	0.30	0.058	1.2	0.22
Alkenes																									
6	2-trans-Pentene	n.d.	1.1	0.30	<MQL	0.72	0.10	<MQL	1.1	0.29	<MQL	1.1	0.13	<MQL	0.32	0.090	0.067	0.43	0.17	<MQL	0.93	0.12	<MQL	0.29	0.080
7	Isoprene	n.d.	0.81	0.27	<MQL	1.6	0.31	<MQL	0.87	0.31	<MQL	1.2	0.22	<MQL	0.85	0.22	<MQL	1.2	0.32	<MQL	7.0	0.62	<MQL	3.2	0.62
8	2-cis-Pentene	n.d.	0.77	0.24	n.d.	0.81	0.12	n.d.	1.4	0.25	n.d.	1.3	0.14	n.d.	0.40	0.093	n.d.	0.31	0.12	n.d.	2.8	0.22	n.d.	0.88	0.12
9	1-Hexene	n.d.	4.2	0.38	<MQL	1.9	0.60	<MQL	5.7	0.63	0.040	1.2	0.34	n.d.	2.3	0.51	0.038	5.2	0.58	n.d.	1.1	0.24	0.070	2.5	0.52
Aromatic Hydrocarbons																									
10	Benzene	0.18	1.1	0.48	0.25	1.7	0.69	0.24	1.6	0.71	0.32	1.6	0.81	0.20	4.1	0.67	0.22	0.88	0.51	0.16	1.6	0.42	0.22	4.8	0.69
11	Toluene	0.26	3.0	1.7	0.68	4.2	2.1	0.24	12	2.6	0.54	5.3	1.6	0.55	3.7	1.6	0.55	6.0	2.3	0.40	3.7	1.3	0.37	3.7	1.5
12	Ethylbenzene	0.056	1.1	0.43	0.13	1.3	0.56	0.080	1.4	0.65	0.15	1.8	0.62	0.11	1.1	0.40	0.080	1.9	0.59	0.061	0.95	0.38	0.10	1.3	0.56
13	m,p-Xylene	0.10	1.5	0.70	0.071	1.6	0.54	0.11	1.8	0.87	0.15	2.8	0.64	0.10	1.9	0.53	0.11	1.8	0.70	0.088	1.4	0.57	0.059	1.7	0.65
14	o-xylene	0.071	1.1	0.49	0.078	1.1	0.39	0.073	1.2	0.61	0.12	2.1	0.46	0.080	1.6	0.39	0.091	1.3	0.49	0.057	1.1	0.46	<MQL	0.99	0.44
15	Styrene	<MQL	1.4	0.24	0.040	0.82	0.25	0.024	0.84	0.36	0.061	1.5	0.36	n.d.	0.65	0.16	n.d.	0.92	0.21	n.d.	4.4	0.49	n.d.	5.0	0.38
16	Isopropylbenzene	n.d.	0.087	0.031	n.d.	0.17	0.034	n.d.	0.20	0.060	n.d.	0.27	0.054	<MQL	0.13	0.034	n.d.	0.36	0.053	<MQL	1.1	0.17	n.d.	0.12	0.041
17	n-Propylbenzene	n.d.	0.28	0.073	n.d.	0.30	0.073	0.010	0.65	0.13	n.d.	0.45	0.090	n.d.	0.75	0.085	n.d.	0.52	0.10	n.d.	1.2	0.23	n.d.	0.22	0.060
18	3-Ethyltoluene	n.d.	1.7	0.20	n.d.	0.68	0.15	0.030	0.91	0.29	0.023	0.63	0.19	0.019	1.2	0.17	0.014	0.73	0.19	<MQL	1.1	0.30	<MQL	0.76	0.16
19	4-Ethyltoluene	n.d.	0.59	0.14	n.d.	0.38	0.11	<MQL	1.2	0.19	<MQL	0.59	0.13	n.d.	1.6	0.14	0.020	1.2	0.17	<MQL	1.4	0.31	<MQL	0.38	0.12
20	1,3,5-Trimethylbenzene	n.d.	1.7	0.16	n.d.	0.48	0.091	<MQL	0.93	0.18	n.d.	0.59	0.13	n.d.	1.3	0.11	n.d.	0.60	0.15	n.d.	1.3	0.26	<MQL	0.67	0.11
21	2-Ethyltoluene	n.d.	0.54	0.084	n.d.	0.26	0.050	n.d.	0.65	0.11	n.d.	0.36	0.081	n.d.	0.96	0.070	n.d.	0.41	0.071	<MQL	1.2	0.22	<MQL	0.22	0.054
22	tert-Butylbenzene	n.d.	0.11	0.029	n.d.	0.28	0.031	n.d.	0.81	0.081	n.d.	0.21	0.044	n.d.	0.64	0.041	n.d.	0.58	0.067	n.d.	1.3	0.23	n.d.	0.13	0.033
23	1,2,4-Trimethylbenzene	n.d.	1.5	0.37	n.d.	1.3	0.25	0.020	3.1	0.62	n.d.	1.5	0.34	n.d.	5.4	0.44	n.d.	5.9	0.58	0.010	7.1	0.60	n.d.	1.3	0.29
24	p-Isopropyltoluene	n.d.	0.71	0.13	n.d.	1.0	0.20	n.d.	1.1	0.18	n.d.	1.1	0.15	n.d.	0.96	0.11	n.d.	1.1	0.17	n.d.	1.2	0.31	n.d.	0.70	0.13
25	1,2,3-Trimethylbenzene	n.d.	0.67	0.12	n.d.	0.43	0.077	n.d.	0.90	0.17	n.d.	0.54	0.11	n.d.	1.3	0.11	n.d.	1.5	0.16	n.d.	1.8	0.30	n.d.	0.71	0.13
26	1,3-Diethylbenzene	n.d.	0.090	<MQL	n.d.	0.24	0.018	n.d.	0.12	0.011	<MQL	0.26	0.010	n.d.	0.058	<MQL	n.d.	0.084	<MQL	n.d.	0.99	0.15	n.d.	0.11	0.011
27	1,4-Diethylbenzene	n.d.	0.37	0.080	n.d.	0.40	0.046	n.d.	0.48	0.090	n.d.	0.30	0.050	n.d.	0.48	0.060	n.d.	0.58	0.071	n.d.	1.1	0.23	n.d.	0.79	0.12
28	Naphtalene	n.d.	0.12	<MQL	n.d.	0.35	<MQL	n.d.	0.33	<MQL	n.d.	0.10	<MQL	n.d.	0.12	<MQL	n.d.	0.12	<MQL	n.d.	1.2	0.19	n.d.	0.058	<MQL
29	2-Methylnaphtalene	n.d.	0.11	0.010	n.d.	0.050	<MQL	n.d.	0.018	<MQL	n.d.	0.072	<MQL	n.d.	0.041	<MQL	n.d.	0.13	0.010	n.d.	0.031	<MQL	n.d.	0.037	<MQL
30	1-Methylnaphtalene	n.d.	0.059	0.011	n.d.	0.040	<MQL	n.d.	0.077	0.010	n.d.	0.081	0.010	n.d.	0.033	<MQL	n.d.	0.14	0.011	n.d.	0.040	<MQL	n.d.	0.040	0.010
Organochlorines																									
31	Dichloromethane	n.d.	2.0	0.42	n.d.	3.5	0.54	<MQL	6.7	0.67	<MQL	1.1	0.46	n.d.	1.5	0.49	0.14	2.0	0.47	<MQL	3.2	0.55	n.d.	1.6	0.34
32	Chloroform	n.d.	0.31	0.059	n.d.	2.3	0.13	n.d.	0.81	0.22	n.d.	1.1	0.10	<MQL	1.0	0.14	n.d.	0.50	0.13	n.d.	3.2	0.33	n.d.	0.76	0.11
33	1,1,1-Trichloroethane	n.d.	0.066	<MQL	n.d.	0.10	<MQL	n.d.	0.091	<MQL	n.d.	0.074	0.029	n.d.	0.075	<MQL	n.d.	0.040	<MQL	n.d.	0.60	0.042	n.d.	0.074	<MQL
34	1-Chlorobutane	n.d.	0.10	0.020	n.d.	0.24	0.026	n.d.	0.062	<MQL	n.d.	0.13	<MQL	n.d.	0.20	0.025	n.d.	0.34	0.050	<MQL	0.70	0.074	n.d.	0.092	<MQL
35	1,2-Dichloroethane	n.d.	0.79	0.30	0.11	2.6	0.43	n.d.	0.99	0.30	0.072	1.1	0.28	0.040	1.2	0.24	0.084	2.2	0.34	0.094	3.9	0.52	n.d.	2.2	0.42
36	Carbon tetrachloride	0.030	2.8	1.1	0.25	3.4	1.2	0.17	3.2	1.3	0.22	2.8	1.2	0.080	2.6	1.0	0.24	2.9	1.2	0.075	2.9	1.2	n.d.	2.0	1.0
37	Tetrachloroethene	n.d.	<MQL	<MQL	n.d.	0.070	<MQL	n.d.	0.068	<MQL	n.d.	0.060	<MQL	n.d.	0.074	<MQL	n.d.	<MQL	<MQL	n.d.	0.85	0.14	n.d.	<MQL	<MQL
38	Chlorobenzene	n.d.	0.10	0.010	n.d.	0.15	0.010	n.d.	0.23	0.022	n.d.	0.23	0.011	n.d.	0.092	0.011	n.d.	0.15	0.016	n.d.	0.89	0.14	n.d.	0.37	0.044
Solvents																									
39	Ethanol	n.d.	62	3.0	n.d.	49	3.8	n.d.	23	2.1	n.d.	34	1.7	n.d.	23	2.0	n.d.	7.2	0.64	n.d.	41	3.1	n.d.	12	0.91
40	Isopropyl alcohol	n.d.	2.0	0.16	n.d.	5.4	0.38	n.d.	3.0	0.30	n.d.	3.1	0.19	n.d.	5.7	0.23	n.d.	5.5	0.36	n.d.	15	0.78	n.d.	1.6	0.11
41	1-Propanol	n.d.	5.5	0.91	n.d.	1.4	0.43	n.d.	4.9	0.83	n.d.	1.4	0.38	n.d.	1.4	0.34	n.d.	6.4	0.72	n.d.	5.4	0.62	n.d.	5.5	0.46
42	2-Butanona	n.d.	5.3	0.43	n.d.	1.4	0.25	n.d.	2.1	0.49	n.d.	2.3	0.33	n.d.	3.4	0.41	n.d.	1.9	0.37	n.d.	1.4	0.26	n.d.	1.5	0.25
43	Ethyl acetate	n.d.	12	0.51	n.d.	17	0.86	n.d.	3.9	0.68	n.d.	1.9	0.17	n.d.	4.4	0.37	n.d.	6.1	0.55	n.d.	14	0.64	n.d.	12	0.69
Others																									
44	1,3-Butadiene	0.060	2.1	0.45	0.39	4.0	1.3	0.20	2.5	0.76	0.29	2.8	0.91	0.24	2.7	1.0	0.34	2.6	0.97	0.13	1.9	0.43	0.11	2.1	0.66
45	Diethyl ether	n.d.	0.63	<MQL	<MQL	0.38	<MQL	n.d.	0.26	<MQL	n.d.	0.36	<MQL	n.d.	0.18	<MQL									

Table 2 (continued)

		Southern Industrial Park of Tarragona																							
		S1			S2			S3			S4			S5			S6			S7			S8		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
46	Acrylonitrile	n.d.	0.16	0.040	<MQL	0.19	0.069	<MQL	0.45	0.12	<MQL	0.24	0.040	n.d.	0.38	0.061	<MQL	0.53	0.066	n.d.	0.37	0.055	n.d.	0.37	0.055
47	tert-Butyl methyl ether	n.d.	0.81	0.26	n.d.	1.2	0.26	<MQL	1.0	0.27	n.d.	0.40	0.15	<MQL	0.39	0.17	n.d.	0.55	0.13	n.d.	0.44	0.13	n.d.	0.44	0.13
\sum	Alkanes	3.5	84	26	4.1	45	17	6.3	72	27	4.1	47	14	6.8	47	16	1.5	46	8.4	3.3	36	14	3.3	36	14
\sum	Alkenes	0.14	5.2	1.2	0.22	3.3	1.1	0.078	5.9	1.5	0.22	2.9	0.91	0.26	5.9	1.2	0.12	7.5	1.2	0.26	4.1	1.32	0.26	4.1	1.32
\sum	Aromatic Hydrocarbons	1.2	12	5.5	1.4	16	5.7	1.0	19	7.9	1.8	23	5.1	1.2	18	6.6	1.2	22	7.2	1.1	14	5.5	1.1	14	5.5
\sum	Organochlorines	0.15	3.9	2.0	0.78	8.5	2.4	0.19	8.1	2.5	0.89	4.6	2.0	1.1	4.4	2.2	0.89	9.5	3.0	0.16	4.2	2.0	0.16	4.2	2.0
\sum	Solvents	0.014	63	5.0	0.015	50	5.8	0.31	25	4.4	0.013	35	3.4	0.02	14	2.6	0.017	57	5.4	0.017	15	2.4	0.017	15	2.4
\sum	Others	0.10	2.6	0.79	0.55	4.2	1.7	0.32	2.7	1.2	0.38	3.1	1.2	0.37	2.9	1.2	0.20	2.8	0.67	0.14	2.5	0.88	0.14	2.5	0.88
\sum	Total	9.8	109	40	12	99	34	12	92	45	11	68	26	12	69	29	6.7	87	26	8.4	58	26	8.4	58	26

Avg = average.

n.d. = non detected = below MDL.

<MQL = below MQL.

tubes with 1 μL of the corresponding standard solution. As specified in UNE-EN 14662-1 (UNE-EN, 2006), a Calibration Solution Loading Rig (Markes International Limited) was used to perform the enrichment process of the tubes. The determination coefficients (R^2) of all calibration curves were greater than 0.990 and met the quality assurance criteria for the determination of VOCs in ambient air of the US EPA Method TO-17 (EPA, 1999). The limits of quantification (LOQ) were fixed as the lowest calibration point and ranged from 0.050 ng to 0.50 ng (Table 2S). The limits of detection (LOD) were estimated as the concentration that provides a signal-to-noise ratio equal to or higher than three and were between 0.010 ng and 0.25 ng. The analytical method applied showed good precision for the 62 VOCs under study, with intra-day repeatability (expressed as %RSD) below 10% and inter-day repeatability below 18% for $n = 5$ CX tubes spiked at 1 ng (Table 2S). The results met the requirements of relative standard deviation percentage (RSD %) values under 25% fixed by the OSHA for chromatographic methods used to analyze air samples (OSHA, 2010).

Following equation 1S (Andrietta et al., 2010), method detection limits (MDLs) and method quantification limits (MQLs) for 14-day passive sampling were calculated from the LODs and LOQs. They ranged from 0.00084 to 0.023 $\mu\text{g m}^{-3}$ and from 0.0042 to 0.056 $\mu\text{g m}^{-3}$, respectively. Precision of passive sampling was evaluated by installing $n = 3$ passive samplers in N1, N3, S2 and S5. The RSDs% obtained for the target compounds in the samples were between 8% and 20%.

3. Results and discussion

In this section we report the concentrations of VOCs found in the 22 urban atmospheres under study between January 2019 and December 2021 and the results of the multivariate analyses. The data obtained were presented in tables according to the geographic location of the sampling sites - Table 1 for municipalities near the North industrial park of Tarragona, Table 2 for municipalities near the South industrial park of Tarragona and Table 3 for reference sites. Tables 1–3 show the minimum, maximum and average values of the target VOCs detected for at least one of the samples analysed.

3.1. Overview of VOC concentrations

In total, 47 of the 62 target VOCs included in the analytical method were quantified in the urban air samples analysed. As Tables 1–3 show, the highest sum of the average concentrations of the target VOCs (\sum Total) was 59 $\mu\text{g m}^{-3}$ in R2, while the lowest one was 9.0 $\mu\text{g m}^{-3}$ in R5. However, the bulk of the \sum Total average values were between 15 $\mu\text{g m}^{-3}$ (N7) and 45 $\mu\text{g m}^{-3}$ (S3). The most prevalent compounds were alkanes with average values between 1.9 $\mu\text{g m}^{-3}$ (R5) and 27 $\mu\text{g m}^{-3}$ (S3). As Fig. 2 shows, two compounds - i-pentane and n-pentane - stood out from the rest, with percentages between 16% and 59% of the \sum Total. Maximum episodic values of 69 $\mu\text{g m}^{-3}$ for i-pentane and 22 $\mu\text{g m}^{-3}$ for n-pentane were found in S1 (October 2020) and N3 (December 2021), respectively.

Aromatic hydrocarbons and solvents were ubiquitous with average concentrations between 1.2 $\mu\text{g m}^{-3}$ (N3) and 14 $\mu\text{g m}^{-3}$ (R2) or between 3% and 46% of the \sum Total. BTEX (benzene, toluene, ethylbenzene and o,m,p-xylene) and styrene were the most representative aromatic hydrocarbons, with average concentrations ranging from 0.064 $\mu\text{g m}^{-3}$ (R5) to 4.7 $\mu\text{g m}^{-3}$ (R2). Ethanol was the most common of the solvents evaluated with average concentrations in the range of 0.35 $\mu\text{g m}^{-3}$ (N3) and 11 $\mu\text{g m}^{-3}$ (R4). A maximum episodic value of 73 $\mu\text{g m}^{-3}$ (R1) was found in November 2020, probably because some of the factories in the petrochemical parks of Tarragona changed their production to supply cleaning and/or disinfectant by-products during the COVID-19 pandemic.

Alkenes, organochlorines and others have been relegated to the background with percentages between 2% and 16% of the \sum Total. Dichloromethane and carbon tetrachloride were the prevailing

Table 3

Concentrations of the target compounds found at the five reference sites (R1-R5) expressed as $\mu\text{g m}^{-3}$. $N = 35$, 14-day passive sampling.

	References														
	R1			R2			R3			R4			R5		
	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
Alkanes															
1	0.90	23	8.2	8.6	31	18	4.4	26	8.2	0.83	24	6.5	<MQL	5.9	1.1
2	0.76	4.4	2.3	2.4	12	5.3	1.4	5.8	2.6	0.59	6.0	2.5	n.d.	1.6	0.40
3	0.30	2.6	0.89	n.d.	3.7	1.1	0.19	7.1	0.96	0.21	3.2	1.3	<MQL	2.6	0.24
4	n.d.	1.7	0.34	0.22	2.7	0.72	n.d.	1.0	0.28	0.14	0.77	0.32	<MQL	0.48	0.080
5	<MQL	1.3	0.18	0.068	1.1	0.38	0.052	0.76	0.17	0.049	0.55	0.25	0.033	0.48	0.12
Alkenes															
6	<MQL	0.53	0.14	<MQL	1.2	0.43	0.10	1.5	0.25	0.075	0.38	0.15	n.d.	0.072	<MQL
7	0.031	1.1	0.26	0.074	1.9	0.63	0.070	2.6	0.51	0.10	4.6	0.81	n.d.	2.4	0.28
8	n.d.	0.97	0.15	<MQL	1.7	0.44	n.d.	0.66	0.19	n.d.	0.35	0.13	n.d.	3.5	0.13
9	n.d.	0.73	0.27	0.06	7.1	0.66	0.06	3.5	0.57	n.d.	1.2	0.37	n.d.	2.8	0.16
Aromatic Hydrocarbons															
10	0.30	0.90	0.48	0.32	1.5	0.65	0.29	0.92	0.47	0.20	0.80	0.43	<MQL	0.35	0.13
11	0.43	3.3	1.6	1.5	13	4.7	0.76	12	2.5	0.59	5.9	2.4	<MQL	2.2	0.27
12	0.12	0.95	0.41	0.28	2.0	1.1	0.23	3.9	0.61	0.14	1.9	0.50	<MQL	0.81	0.069
13	0.18	2.0	0.64	0.35	4.8	2.0	0.089	8.0	1.2	0.25	2.4	0.86	0.021	0.81	0.12
14	0.11	1.4	0.48	0.26	3.5	1.5	0.18	9.7	1.0	0.19	1.8	0.61	0.013	0.63	0.10
15	n.d.	1.9	0.22	0.065	0.48	0.20	<MQL	1.0	0.21	0.051	0.97	0.29	n.d.	0.63	0.064
16	n.d.	0.10	0.030	0.017	0.16	0.061	0.011	0.16	0.041	0.010	0.21	0.051	n.d.	0.070	0.010
17	n.d.	0.50	0.079	0.051	0.64	0.19	n.d.	0.20	0.078	0.042	0.26	0.11	n.d.	0.19	0.038
18	0.019	0.49	0.17	0.015	1.0	0.38	0.060	0.96	0.21	0.038	1.3	0.31	0.010	0.22	0.074
19	0.020	0.45	0.13	0.048	1.3	0.34	0.039	0.46	0.13	0.053	0.43	0.17	n.d.	0.20	0.028
20	n.d.	0.72	0.13	0.051	1.3	0.34	n.d.	0.77	0.17	0.045	3.6	0.34	n.d.	0.18	0.039
21	<MQL	0.32	0.071	<MQL	0.79	0.18	0.015	0.19	0.084	0.031	0.23	0.080	n.d.	0.11	0.018
22	n.d.	0.25	0.042	n.d.	0.63	0.11	n.d.	0.10	0.031	n.d.	0.78	0.077	n.d.	0.15	0.014
23	0.017	1.5	0.34	0.070	6.1	0.91	0.091	1.3	0.34	0.066	1.1	0.43	n.d.	0.50	0.079
24	<MQL	1.2	0.18	n.d.	0.75	0.22	0.013	0.66	0.14	0.019	0.56	0.21	n.d.	0.65	0.12
25	n.d.	0.50	0.12	n.d.	2.0	0.26	0.024	0.31	0.11	n.d.	0.41	0.11	n.d.	0.14	0.027
26	n.d.	0.059	<MQL	n.d.	0.15	0.020	n.d.	0.079	<MQL	n.d.	0.040	0.014	n.d.	0.017	<MQL
27	n.d.	0.39	0.059	n.d.	1.2	0.16	n.d.	0.21	0.070	n.d.	0.32	0.092	n.d.	0.13	0.012
28	n.d.	0.051	<MQL	n.d.	0.21	0.034	n.d.	0.047	<MQL	n.d.	0.051	<MQL	n.d.	0.13	<MQL
29	n.d.	0.064	<MQL	n.d.	0.13	0.025	n.d.	0.11	0.015	n.d.	0.19	0.018	n.d.	0.043	<MQL
30	n.d.	0.079	0.010	n.d.	0.059	0.021	n.d.	0.087	0.022	n.d.	0.046	0.020	n.d.	0.028	<MQL
Organochlorines															
31	n.d.	1.9	0.64	<MQL	4.0	1.0	0.066	2.6	0.67	0.019	9.6	0.99	n.d.	0.92	0.21
32	n.d.	1.0	0.17	n.d.	1.5	0.37	n.d.	0.61	0.20	0.011	1.4	0.36	n.d.	0.21	0.028
33	n.d.	0.070	<MQL	n.d.	0.11	0.039	n.d.	0.092	<MQL	0.014	0.039	<MQL	n.d.	0.058	<MQL
34	n.d.	0.14	0.020	n.d.	0.44	0.047	n.d.	0.37	0.071	n.d.	0.076	0.018	n.d.	0.047	<MQL
35	0.071	1.7	0.37	0.052	0.65	0.15	<MQL	0.49	0.077	n.d.	0.34	0.088	n.d.	0.15	0.033
36	0.29	2.2	1.2	0.40	3.9	1.3	0.061	1.4	0.91	0.090	2.5	1.1	<MQL	1.9	0.67
37	n.d.	0.073	<MQL	n.d.	0.35	0.12	n.d.	0.51	0.048	n.d.	0.76	0.071	n.d.	0.012	<MQL
38	n.d.	0.024	<MQL	n.d.	0.091	0.010	n.d.	0.34	0.041	n.d.	0.23	0.022	n.d.	0.017	n.d.
Solvents															
39	n.d.	73	6.2	n.d.	38	8.6	n.d.	28	3.2	n.d.	52	11	n.d.	21	1.7
40	n.d.	1.2	0.16	n.d.	5.6	1.4	n.d.	22	1.5	n.d.	7.0	1.5	n.d.	27	1.7
41	n.d.	5.9	0.79	n.d.	5.1	0.93	n.d.	1.8	0.44	n.d.	2.1	0.75	n.d.	5.6	0.50
42	n.d.	1.7	0.30	n.d.	12	1.2	n.d.	1.8	0.32	n.d.	6.7	0.56	n.d.	1.7	0.22
43	n.d.	11	0.85	n.d.	11	2.3	n.d.	3.8	0.47	n.d.	3.6	0.66	n.d.	1.6	0.091
Others															
44	0.12	0.95	0.37	0.16	0.79	0.44	0.13	0.49	0.28	0.13	0.72	0.34	n.d.	0.22	0.074
45	n.d.	0.42	<MQL	n.d.	0.22	<MQL	n.d.	0.18	<MQL	n.d.	0.22	<MQL	n.d.	0.082	<MQL
46	n.d.	0.90	0.24	0.10	5.4	0.68	n.d.	0.81	0.26	n.d.	1.1	0.19	n.d.	0.43	0.037
47	n.d.	0.14	0.031	n.d.	0.27	0.059	n.d.	0.18	0.028	n.d.	0.22	0.048	n.d.	0.40	0.018
∑Alkanes	3.3	28	12	14	40	25	7.0	33	12	3.6	30	11	0.32	7.3	1.9
∑Alkenes	0.32	2.1	0.83	0.38	10	2.2	0.31	4.1	1.5	0.26	3.4	1.4	0.034	3.7	0.59
∑Aromatic Hydrocarbons	1.7	12	5.2	3.2	33	13	3.6	36	7.4	3.4	14	7.1	0.24	5.2	1.3
∑Organochlorines	0.72	4.7	2.4	1.0	6.6	3.1	0.89	4.9	2.0	0.43	11	2.6	0.11	2.2	0.98
∑Solvents	0.016	74	8.4	0.011	57	14	0.015	42	6.0	0.020	59	14	0.012	28	4.1
∑Others	0.18	1.7	0.69	0.54	5.9	1.2	0.22	1.1	0.62	0.22	1.5	0.62	0.036	0.60	0.14
∑Total	10	98	29	27	99	59	16	92	30	9.7	79	37	1.3	33	9.0

Avg = average.

n.d. = non detected = below MDL.

<MQL = below MQL.

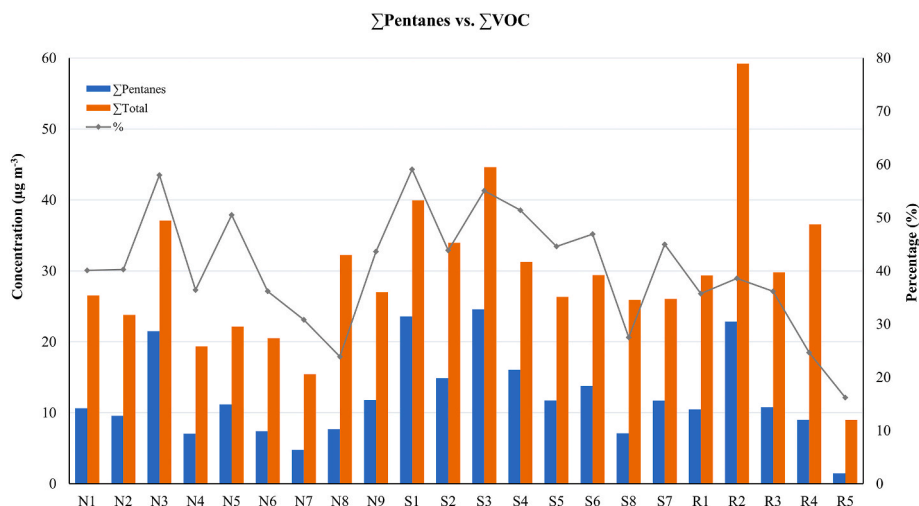


Fig. 2. Stacked bar chart showing the total average concentrations of VOCs (Σ Total) and the average sum of pentanes (Σ Pentanes) found at the 22 sites studied expressed as $\mu\text{g m}^{-3}$. The line chart illustrates the percentage of pentanes in Σ Total.

organochlorines, with average values between $0.21 \mu\text{g m}^{-3}$ (R5) and $3.3 \mu\text{g m}^{-3}$ (N8). Maximum episodic peaks of up to $13 \mu\text{g m}^{-3}$ for dichloromethane (October 2020) and to $5.4 \mu\text{g m}^{-3}$ for carbon tetrachloride (July 2021) were reported in N8. Although the production and use of carbon tetrachloride is banned by “The Montreal Protocol on Substances that Deplete the Ozone Layer”, three main points could explain its concentration in outdoor air; incomplete data on historical production, uncertainties in its atmospheric lifetime and unreported or underestimated emission sources (HMPSDOL, 2020). Similar average concentrations of carbon tetrachloride ($0.39 \mu\text{g m}^{-3}$ - $1.3 \mu\text{g m}^{-3}$) and dichloromethane ($0.70 \mu\text{g m}^{-3}$ - $4.6 \mu\text{g m}^{-3}$) were found in urban areas close to industrial parks in Spain (Ramírez et al., 2012; Gallego et al., 2016), Turkey (Dumanoglu et al., 2014) and China (Yao et al., 2021).

It should be noted that most of the target VOCs found at the highest concentrations in the sampling sites belong to the group of ozone precursors which, according to the European Directive 2008/50/EC (ED, 2008), should be monitored in urban areas. The maximum average concentrations for VOCs without a specific emission source, *i.e.* isoprene, toluene, ethylbenzene, xylenes and ethyl acetate, were reported in reference sites R2 and R4. As Tables 2 and 3 show, the average values for these VOCs at sampling sites close to the industrial parks of Tarragona were between $0.031 \mu\text{g m}^{-3}$ and $2.6 \mu\text{g m}^{-3}$. The highest concentrations of isoprene ($7 \mu\text{g m}^{-3}$), toluene ($14 \mu\text{g m}^{-3}$), ethylbenzene ($3.8 \mu\text{g m}^{-3}$), xylenes ($7.9 \mu\text{g m}^{-3}$) and ethyl acetate were all detected in February 2020 in N8. Slightly higher concentration levels of these VOCs, between $0.35 \mu\text{g m}^{-3}$ and $4.3 \mu\text{g m}^{-3}$, were reported by Ramírez et al. (2012) when analysing air samples from the same study area. Similarly, Hsu et al. (2018) reported VOCs concentrations between $0.019 \mu\text{g m}^{-3}$ and $4.4 \mu\text{g m}^{-3}$ in air samples from residential areas near the petrochemical complex of Mailiao (central Taiwan). Civan et al. (2015) and Dörter et al. (2020) found comparable average concentrations of these VOCs, in the range of $0.070 \mu\text{g m}^{-3}$ and $7.7 \mu\text{g m}^{-3}$, in air samples from the heavily industrialized region of Aliaga (Turkey) and the region of Bolu plateau (Black Sea, Turkey) with forests and small-scale factories, respectively.

The ratios toluene/benzene (T/B) and xylene/benzene (X/B) has been widely used as indicators of air age and tracer of emission source (Lyu et al., 2016; Hsu et al., 2018). In this case, we used a B/T ratio below 0.40 and a X/B ratio higher than 1.1 as indicators of fresh air (Liu et al., 2008). Fig. 1S shows that 114 out of 140 samples from reference sites R1-R4 were in the domain of fresh air. The fact that 81% of the samples at reference sites R1-R4 met the criterion suggests a certain number of VOCs from fresh air. As these sites were in the city centre, these fresh VOCs are likely to be from traffic emissions, heating boilers

or the combustion of organic matter (Nagpure et al., 2016; Bari and Kindzierski, 2017). On the other hand, only a 24% of the samples from R5 were fresh air. This suggests that aged VOCs were transported from long-distance sources and explains the low levels of VOCs found in this sampling site (rural town). In the sampling sites close to the industrial parks of Tarragona (N1–N9 and S1–S8) a 55% of the samples, 328 out of 595 samples, were in the domain of fresh air. These fresh VOCs may have different emission sources, such as industrial activities, fugitive emissions and road traffic, among others (Villanueva et al., 2018; Duan et al., 2023).

3.2. VOCs related to chemical and petrochemical industries

The highest average concentrations of VOCs from chemical and petrochemical industries were found at the sampling sites close to the two petrochemical parks of Tarragona (Raysoni et al., 2017; Villanueva et al., 2018). As Tables 1 and 2 summarizes, 1,2-dichloroethane, acrylonitrile and styrene were found at average concentrations between $0.018 \mu\text{g m}^{-3}$ and $0.52 \mu\text{g m}^{-3}$. In February 2020, maximum concentration values of $3.9 \mu\text{g m}^{-3}$ for 1,2-dichloroethane (S7), $1.9 \mu\text{g m}^{-3}$ for acrylonitrile (N5) and $5.0 \mu\text{g m}^{-3}$ for styrene (S8) were determined. The concentration peak of acrylonitrile in N5 may be explained by the proximity to the North industrial park of Tarragona (<1 km), where this compound is handled and transported (REP, 2023). The proximity to the storage tanks in the port of Tarragona (3 km) together with the prevailing wind direction of north-easterly favoured the presence of an episodic peak of styrene in S8. The average concentrations of 1,2-dichloroethane were slightly higher at the sampling sites located near the South industrial park of Tarragona, due to the proximity to the production plant of this compound (1–3 km). This sampling sites were also close to the port of Tarragona where 1,2-dichloroethane is stored, handled and distributed by ship. As Fig. 3 shows, the boxplots of this compound were slightly wider and the number of episodic peaks increased. Dumanoglu et al. (2014) observed the same situation in Aliaga (Turkey), but in this specific case the episodic peaks of 1,2-dichloroethane reached $136 \mu\text{g m}^{-3}$, the average concentration was $2.7 \mu\text{g m}^{-3}$ and the main source of this compound was as an intermediate in the synthesis of vinyl chloride from ethylene and chlorine (Leuchner and Rappenglück, 2010). 1,2-Dichloroethane was found to be one of the top ten VOCs in Handan (China), with an average concentration of $7.4 \mu\text{g m}^{-3}$ and vinyl chloride production as the main emission source (Yao et al., 2021).

Along this line, the average concentrations of benzene were between $0.13 \mu\text{g m}^{-3}$ (R5) and $1.3 \mu\text{g m}^{-3}$ (N3). Only one site had an average

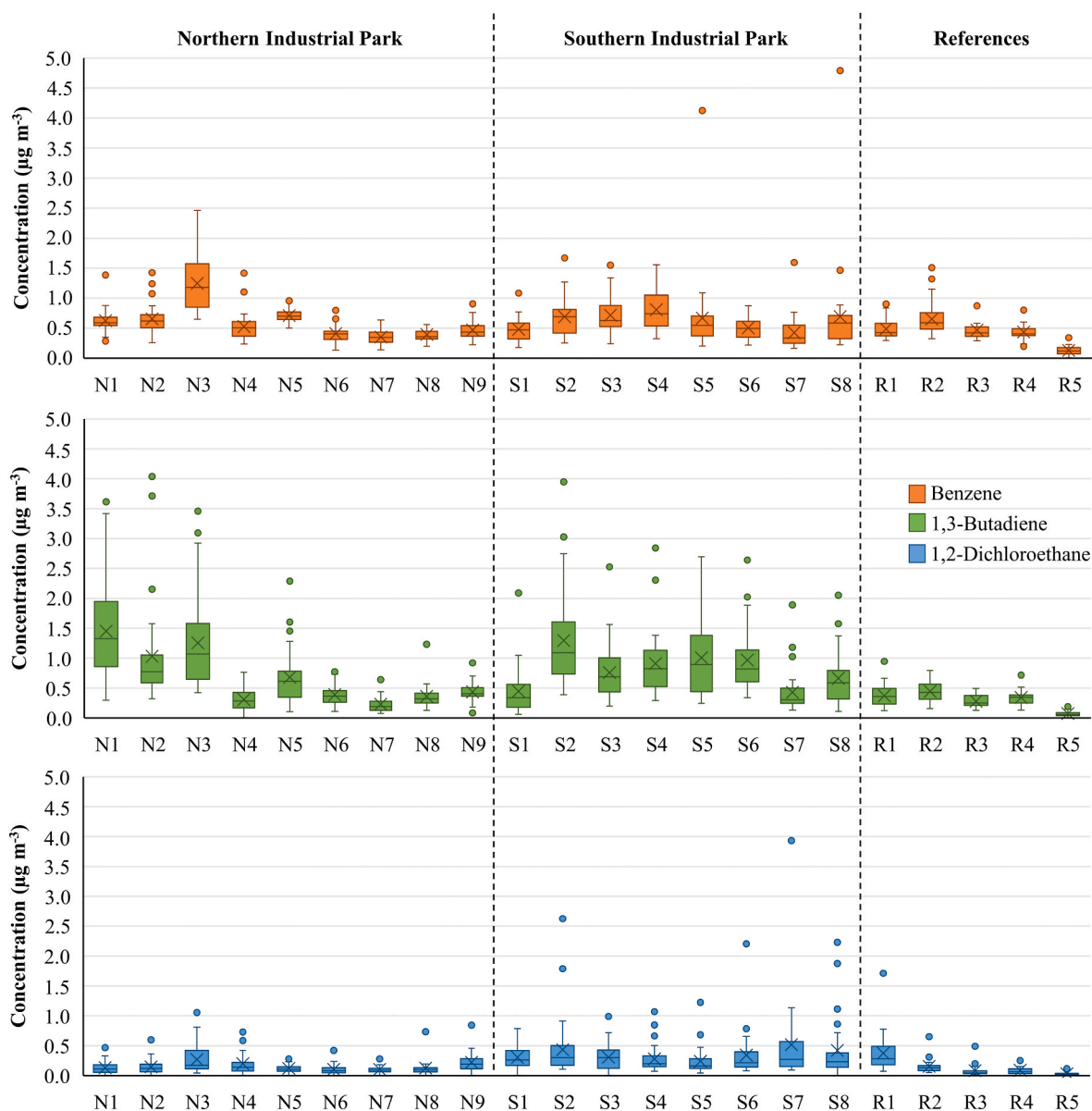


Fig. 3. Box-and-whisker plots showing percentile distributions for the concentrations of benzene, 1,3-butadiene and 1,2-dichloroethane in the sampling sites under study. For each compound, the box plot represents the 25th and 75th percentile of the concentration values found. The line inside the box is the median and the cross is the average concentration. The whiskers indicate the minimum and the maximum concentrations, while the dots outside the whiskers are outliers.

concentration over $1.0 \mu\text{g m}^{-3}$ (N3) because it was the receptor of the pollution generated in the benzene production plant situated in the North industrial Park of Tarragona when northerly winds blow (see Fig. 1). The values obtained at N3 (Benzene_{passive}) were compared to those online recorded with the gas chromatograph-photoionization detection (GC-PID) analyzer installed by the Catalan Government's Network for Monitoring and Forecasting Air Quality (Benzene_{XVPCA}) (XVPCA, 2023) at the same site. Comparable results were obtained with Benzene_{XVPCA}/Benzene_{passive} ratios in the range of 0.93 and 1.3, thus ensuring the correct performance of the analytical method applied. In February 2020 a concentration peak of benzene of $4.8 \mu\text{g m}^{-3}$ was detected in S8. Probably linked to episodic industrial activities, *i.e.* loading and unloading of benzene transport trains, carried out in the port of Tarragona. The narrow boxplots in Fig. 3, as well as the small number of episodic peaks, show that the concentrations of benzene remained stable over time at the sampling sites studied. Moreover, the average concentrations were always below the $5.0 \mu\text{g m}^{-3}$ set by the European Directive 2008/50/EC (ED, 2008) as the maximum annual

average concentration in urban atmospheres. These results agree with the average concentrations, between $0.14 \mu\text{g m}^{-3}$ and $1.0 \mu\text{g m}^{-3}$, reported by De Gennaro et al. (2013) and Villanueva et al. (2018) in industrial and suburban air samples from Italy and Spain. Similarly, average concentrations of benzene in the range of $0.61 \mu\text{g m}^{-3}$ and $0.83 \mu\text{g m}^{-3}$ were reported in Rubbertown (Louisville, Kentucky, USA), an industrialized area home to several chemical manufacturing plants, petroleum and chemical facilities, among others (Mukerjee et al., 2020). Slightly higher average concentrations of benzene, between $0.22 \mu\text{g m}^{-3}$ and $2.7 \mu\text{g m}^{-3}$, were found in urban sites close to the petrochemical parks of Aliaga and Bolu Plateau both in Turkey (Dumanoglu et al., 2014; Civan et al., 2015; Dörter et al., 2020).

Although 1,3-butadiene is still unregulated in Europe, we have focused our attention on it because of its carcinogenic properties (EPA, 2009; RAR, 2002). It is also produced, stored and handled at the two petrochemical parks of Tarragona. Regardless of the sampling site, average concentrations ranging from $0.074 \mu\text{g m}^{-3}$ (R5) to $1.5 \mu\text{g m}^{-3}$ (N1) were found. As can be seen in Fig. 3, the boxplots of this compound

were intermediate or wide. At sampling sites close to the petrochemical parks of Tarragona there were a considerable number of episodic peaks of 1,3-butadiene, with a maximum of $4.0 \mu\text{g m}^{-3}$ in N2 (April 2019) and S2 (November 2020). However, the average concentrations of 1,3-butadiene were always below the maximum annual average of $2.0 \mu\text{g m}^{-3}$ set in Ontario (AAQC, 2011). Only 4% of the 14-day average concentrations exceeded this figure. Vallecillos et al. (2018) and Gallego et al. (2018) reported slightly higher 1,3-butadiene concentrations, between $0.13 \mu\text{g m}^{-3}$ and $8.4 \mu\text{g m}^{-3}$, and sporadic peaks up to $39 \mu\text{g m}^{-3}$ when analysing air samples from the same study area. Comparable 1,3-butadiene average concentrations, between 0.061 and 0.83, were found by Curren et al. (2006) in air samples from urban and industrialized towns of Canada. All the authors identified proximity to production plants or industrialized areas, as well as prevailing wind direction, as key factors explaining 1,3-butadiene concentrations. They also agreed on the toxicity of this compound and the need for its continuous monitoring (Curren et al., 2006; Gallego et al., 2018; Vallecillos et al., 2018). Accordingly, Vallecillos et al. (2024) reported that the use of a GC-PID analyzer for continuous monitoring of 1,3-butadiene in urban and industrial atmospheres is a useful tool to relate concentrations peaks to specific industrial activities.

3.3. Multivariate analyses

3.3.1. VOCs correlations

In order to check possible correlations between target VOC concentrations, the correlation map of the variables was inspected. The target VOCs were grouped into the nine families or variables shown in Fig. 2S, where the scale of the numbers and the intensity of the colours are proportional to the correlation coefficients (r). The positive correlations are coloured red and negative correlations blue. As observed in the figure, no negative correlations were detected so if one of the families of VOCs is present, the others should be present as well. In general, most of the families of compounds show weak or non-significant correlation with r values in the range 0.10–0.50. The strongest correlations were found between alkanes and the following compounds: 1,3-butadiene, alkenes, benzene and aromatic hydrocarbons. Solvents and organochlorines on the other hand, showed the weakest correlations.

3.3.2. Spatial distribution

A principal components analysis (PCA) was performed for all the air samples analysed to check possible spatial patterns for families of target VOCs and sample location. The Kaiser criterion, also known as the average eigenvalue criterion, was chosen to select the number of

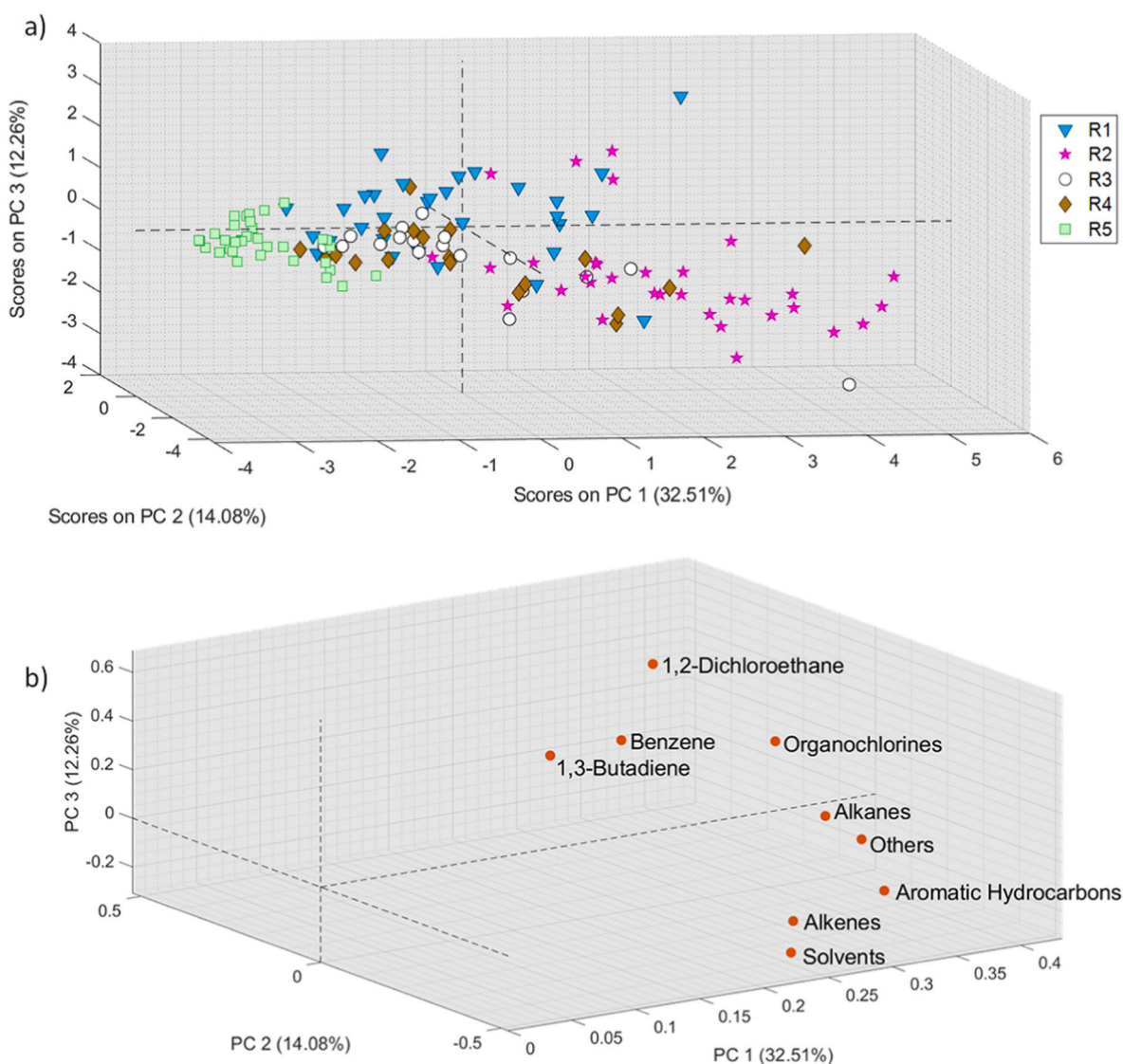


Fig. 4. PCA results for the concentrations found at reference sites R1-R5. a) Scores plot to illustrate the distribution of the sampling sites. b) Loading plot showing the spatial distribution of the target VOCs grouped by families.

components (Ballabio, 2015). Three principal components (PCs) were selected, so that they could be displayed in a single plot.

Fig. 4a shows the scores of the PCA analysis of the reference samples (R1-R5) and Fig. 5b shows the loadings of the target VOC families defined for the PCA analysis. In the PCA plot, air samples from R5 (rural town) were located on the left-hand side of the scores graph, while samples from R2 (metropolis) were on the right side. In the loadings plot in Fig. 4b, PC1 shows the overall level of pollution: the more to the right the sampling sites appeared, the more polluted the atmosphere was, with all the families of VOCs on the right side of the plot. PC2 and PC3 show the specific type of pollution. Positive values of PC2 denote an important contribution of benzene and 1,3-butadiene. Negative values of PC2 are mainly influenced by solvents and organochlorines. Positive values of PC3 indicate an important contribution of chlorinated compounds (1,2-dichloroethane and organochlorines). Negative values of PC3 correspond to samples with important contributions of mainly alkenes, aromatic hydrocarbons, solvents and alkanes.

Most of the samples from R3 and R4 were close to R5 samples in Fig. 4a indicating only a slightly contaminated atmosphere. R2 followed a different pollution pattern with most of the samples at the bottom right of the plot and noteworthy concentration values of solvents, alkanes, alkenes and aromatic hydrocarbons. Although R1 (Tarragona) is similar

in size and number of inhabitants to R3 and R4, the samples analysed followed a different pattern with a considerable number of samples at the top right of the plot. These uncommon concentrations of organochlorines and 1,2-dichloroethane were probably due to the impact of the petrochemical industrial parks on the air quality of the town.

As Fig. 3S shows, using three PCs it was difficult to discern a clear separation between samples from the two industrial parks of Tarragona. A plausible explanation for this could be that some of the chemicals manufactured in the North industrial park are used to synthesize chemical-related products in the South industrial park and vice versa (AEQT, 2023). Both industrial parks are also surrounded by roads, which are used for access to Tarragona.

The data from individual sampling sites showed differences between pollution levels and prevalent VOCs. As Fig. 5a shows, most of the samples from N1–N3 were on the right side of the plot and the highest scores were on PC1, indicating a more polluted atmosphere. These three sampling sites presented mainly positive values on PC2, denoting that they were characterized by lightly higher concentrations of benzene and/or 1,3-butadiene. Because of their proximity to the North industrial park of Tarragona, the prevailing north and north-westerly winds in winter, and the regular thermal breezes in summer (METEO, 2022). N8 and N9 were also on the right-hand side of the graph, but they had

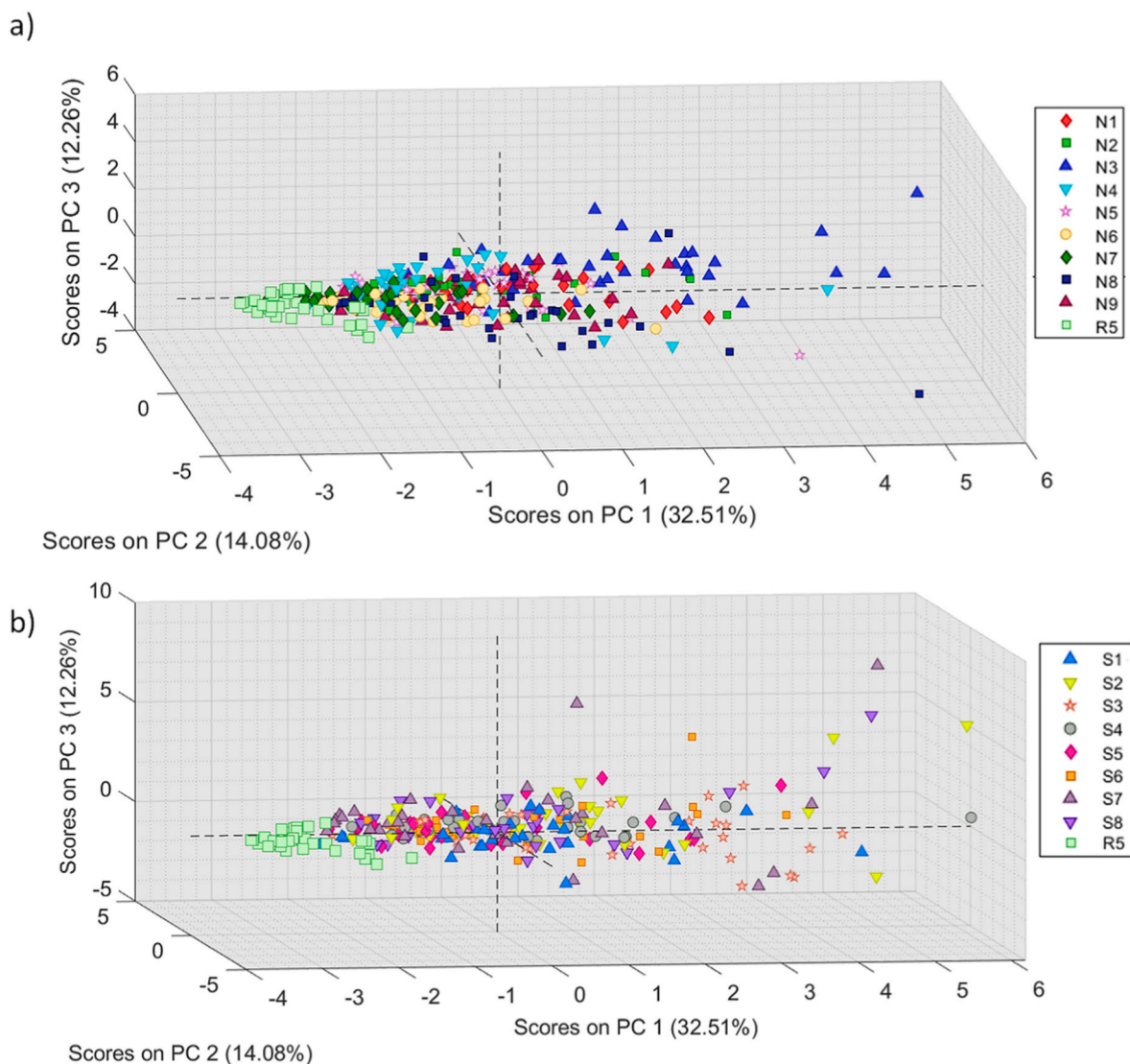


Fig. 5. PCA scores for the concentrations found in a) North industrial park of Tarragona (N1–N9) and b) South industrial park of Tarragona (S1–S8) versus R5 (rural town).

negative scores on PC2 with notable values of solvents and organochlorines, and, to a lesser extent, aromatic hydrocarbons and alkenes. The samples from the North industrial park of Tarragona that were most similar to R5 were N6 and N7 with most of the samples on the left-hand side of the graph.

As Fig. 5b shows, the South industrial park of Tarragona has fewer air samples close to R5, than the North industrial park. This was probably due to the fact that all the sampling sites were located between 0.3 km and 2 km from the South industrial park of Tarragona and the nearby roads. Due to the variety of emission sources of VOCs in the South industrial park of Tarragona, it was difficult to differentiate between pollution patterns of sites S1–S8. Only, some S7 samples followed a slightly different behaviour (positive scores on PC3) characterized by the presence of organochlorines and 1,2-dichloroethane, probably because of the presence of factories which produce chlorinated products and 1,2-dichloroethane within 1 km.

3.3.3. Seasonal variation

As Fig. 4S shows, the highest concentrations of the target VOCs in the area of Tarragona (N1–N9, S1–S8 and R1) were found during the autumn–winter months. As reported by (Gallego et al., 2018; Vallecillos et al., 2019a), thermal inversion caused by proximity to the sea and the north and north-westerly winds in winter favour the presence of VOCs at higher concentrations in the sampling sites close to the petrochemical parks under study (N1–N9 and S1–S8). Seasonal variations in VOCs concentrations observed in Tarragona were much smaller than those reported by Dörter et al. (2020) due to the extreme temperatures in Bolu plateau (Black Sea, Turkey). In addition, climate change caused temperature peaks of up to 20 °C and thermal breezes during the winter sampling campaign in Tarragona that mitigated seasonal variations (METEO, 2022). In reference sites R2–R4 there were two concentration peaks during the year, the first in summer and the second in autumn. The concentration peaks at the end of the year could be caused by thermal inversion (R2 and R3) or fog (R4). As these are tourist towns, summer peaks could be due to increased mobility by road traffic, airports and cruises for R2 (Nagpure et al., 2016; Bari and Kindziński, 2017).

The concentration levels of the target VOCs found per year were compared to evaluate the effect of anti-COVID-19 measures, such as, mobility restrictions, full/partial lockdown or cleaning and disinfection, on outdoor air quality. As illustrated in Fig. 5S, most of the samples that appeared on the right side of the scores plot were from 2019 (pre-COVID-19) and 2020 (emergence of COVID-19). In 2021 the number of samples on the left side of the plot increased, which indicate a less polluted atmosphere and lower concentrations of VOCs. The concentrations found in 2021 were also more stable than in previous years and the number of episodic peaks of VOCs decreased. Nonetheless, different situations could be observed. In R2 (metropolis), the highest concentrations of VOCs were mostly from 2019, while the lowest concentrations were found between February–June 2020, coinciding with the COVID-19 lockdown and a drastic decrease in mobility. In 2021, the levels of VOCs found in R2 did not reach those of 2019. These results agree with the decrease in major air pollutant concentrations reported by Tobías et al. (2020) in the same town and in other cities around the world (Gualtieri et al., 2020; El-Sayed et al., 2021).

On the other hand, in R1 (Tarragona) and the sampling sites close to the two industrial parks of Tarragona (N1–N9 and S1–S8), slightly higher concentrations of VOCs were found in 2019. A slight decrease in VOC concentrations was detected in 2020 due to the COVID-19 pandemic. Probably because most of the surrounding industries continued to operate at the same pace or even increased production to meet the needs of the health sector and to respond to the demand for cleaning and disinfection by products. Changes in mobility in these sampling sites were relegated to the background. The VOC concentrations found in 2020 were more dispersed and the presence of episodic peaks of solvents distorted the \sum Total values. In 2021, the concentrations of VOCs found in the sampling sites close to the petrochemical

parks of Tarragona stabilized and the number of episodic peaks of solvents decreased gradually. The obtained results were in line with those detected by Ninyà et al. (2022) in air samples from the same area of study between April–June 2021.

4. Conclusions

Passive sampling was successfully applied for a three-year monitoring campaign of 62 VOCs in outdoor air samples from urban areas close to the two petrochemical parks of Tarragona and reference sites in the centre of towns of different sizes and industrial realities in Catalonia (Spain). Multivariate data analysis was applied to assess similarities, correlations between VOCs and differences between datasets.

Overall \sum Total values ranged from 9.0 $\mu\text{g m}^{-3}$ to 59 $\mu\text{g m}^{-3}$ with i-pentane and n-pentane as the most representative compounds. Aromatic hydrocarbons and solvents were ubiquitous throughout the sampling sites, with BTEX and ethanol being the most prevalent. The values found for solvents, especially ethanol, rose at the beginning of the COVID-19 pandemic (2020) and gradually decreased in the middle of 2021. Alkenes, organochlorines and others were relegated to the background. At the sampling sites in city centres, VOCs from traffic emissions, heating boilers and the combustion of organic matter were predominant. At the sampling sites close to the two petrochemical parks of Tarragona, VOCs mainly came from production plants, industrial activities and fugitive emissions.

The PCA results allowed us to separate the sampling sites by pollution level and family of VOCs. Five different pollution patterns were observed for the reference sites; rural town (R5), metropolis (R2), town (R3 and R4) and town with petrochemical industry (R1). The samples from the two petrochemical industrial parks of Tarragona could not be discriminated, but there were differences in terms of the sampling sites. The pollution levels of N1–N3 and S7 stood out from the rest with 1,3-butadiene, benzene and 1,2-dichloroethane as the most prevalent compounds, respectively. Autumn–winter months were identified as the most favourable for high VOC concentrations because of thermal inversion and prevailing winds. The effect of COVID-19 on air quality was only clearly observed in R2 (metropolis) due to the huge impact of the decrease in mobility caused by the lockdown. However, the VOCs values found in 2020 were more dispersed, with concentration peaks of solvents disturbing the results.

Author contributions statement

Laura Vallecillos: Introduction, method development and Validation, Writing – original draft, review, and editing. Jordi Riu: Multivariate Formal analysis, Writing – original draft, review, and editing. Rosa Maria Marcé: Introduction, method development and Validation, research, writing, review, editing, Supervision, project management, and Funding acquisition. Francesc Borrull: Introduction, method development and Validation, research, writing, review, editing, Supervision, project management, and 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apr.2023.101986>.

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