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Outdoor air 1,3-butadiene monitoring near a petrochemical industry (Tarragona region) and in several Catalan urban areas using active multi-sorbent bed tubes and analysis through TD-GC/MS

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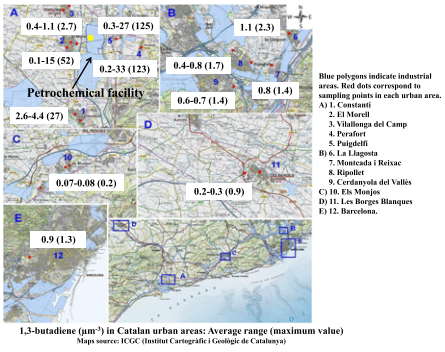
HIGHLIGHTS

- 1,3-Butadiene was sampled in 12 Catalan urban areas from 2013 to 2017.
- 1,3-Butadiene was sampled with multi-sorbent tubes and analysed by TD-GC/MS.
- Urban areas near petrochemical facilities were the most impacted locations.
- The other urban areas showed 1,3-butadiene concentrations around 1 μg m^{-3}.
- 1,3-Butadiene regulation should be implemented as soon as possible in Spain.

GRAPHICAL ABSTRACT



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ABSTRACT

1,3-Butadiene is a carcinogenic compound that can be emitted to the atmosphere from several sources, such as the combustion of organic matter or traffic. However, petrochemical industry is one of the main origins of this compound. Several campaigns (2013–2017) were conducted in twelve Catalan urban areas to determine 1,3-butadiene concentrations in outdoor air, five of which were close to Tarragona petrochemical region. 1,3-Butadiene was dynamically sampled in multi-sorbent bed tubes (Carbotrap, Carbopack X and Carboxen 569) using portable pump equipment. The analysis was performed by automatic thermal desorption coupled with capillary gas chromatography/mass spectrometry detector. El Morell, Perafort and Puigdelfí, located near petrochemical facilities, were the most impacted locations, with average concentrations up to 15 ± 33, 33 ± 41 and 27 ± 39 μg m^{-3}, respectively. Maximum 24 h concentrations of 125 μg m^{-3} were observed in Puigdelfí. However, 1,3-butadiene average and maximum concentrations in the Tarragona petrochemical region diminished significantly ($p \leq 0.05$) in a drastic way (40–80%) since the first monitoring program in 2013. On the other hand, average concentrations in the rest of studied Catalan urban areas generally presented average values below 1 μg m^{-3}, ranging from 0.07–1.1 μg m^{-3}. Spain does have neither a monitoring strategy nor standard regulations related to 1,3-butadiene. Taking into account that relevant values can be found in locations near petrochemical facilities, a regulation should be implemented as soon as possible, at least in this specific areas.

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1. Introduction

1,3-Butadiene can be emitted to the atmosphere from several sources, such as the combustion of organic matter, residential heating, traffic or fuel distribution (Arayasiri et al., 2010; Curren et al., 2006; Delgado-Saborit et al., 2011; Gustafson et al., 2007; Nagpure et al., 2016; Özkaynak et al., 2008; Sapkota and Buckley, 2003). Petrochemical industry is another important source of 1,3-butadiene, especially the manufacturing plants using or producing this compound (Axelsson et al., 2010; Bari and Kindzierski, 2017; Mo et al., 2015; Myers et al., 2015), where fugitive emissions can be very important (Czader and Rappenglück, 2015), up to a 44% of the total air emissions (Grant et al., 2007). Accidental emissions of 1,3-butadiene is another aspect that has to be taken into account for this kind of facilities, as punctual/episodic concentrations can be very high, in the order of hundreds to thousands of μg m^{-3} (Czader and Rappenglück, 2015).

1,3-Butadiene is carcinogenic to humans (Group 1) according to IARC (2012), can cause DNA damage (Arayasiri et al., 2010; Bari and Kindzierski, 2017; Logue et al., 2010; Ruchirawat et al., 2010) and has been found to have a relevant contribution to inhalation estimated cancer risk worldwide (Chen et al., 2016; Curtis et al., 2006; de Blas et al., 2012; Loh et al., 2007; Zhou et al., 2011). Furthermore, 1,3-butadiene is a highly reactive volatile organic compound (HRVOC) that can contribute to elevated ozone concentration pollution events (Wang et al., 2016). Hence, its evaluation when determining air quality will be essential in the long term, especially taking into account that a 90% of the source contribution to inhalation exposure comes from outdoors (Loh et al., 2007).

On the other hand, 1,3-butadiene is rapidly oxidized and has a low residence time in the atmosphere (Martin et al., 2005; Sakurai et al., 2013). Therefore, its concentrations in air are quite local, as this compound has little low-range transport potentiality (Curren et al., 2006). Additionally, some of its photochemical degradation products, such as 1,2-epoxy-3-butene or 1,2,3,4-diepoxybutane, can cause potentially major negative health effects than 1,3-butadiene itself (Czader and Rappenglück, 2015; Doyle et al., 2004; Kramp and Paulson, 2000). Accordingly, Delgado-Saborit et al. (2011) suggested that further research is needed to clarify the association between ambient 1,3-butadiene concentrations and personal exposure, as it is a complex aspect, possibly due to the high reactivity of this compound.

The simplicity, high sampling versatility, high concentration power, easy portability, low cost and easy storage of sorbent tubes (Gallego et al., 2009a; Ribes et al., 2007) led us to adopt a sorbent-based method for sampling 1,3-butadiene in ambient air. Thermal Desorption (TD), coupled with Gas Chromatography/Mass Spectrometry (GC/MS), was the chosen instrumental technique. TD-GC/MS methodology has been widely used in VOC analysis (Gallego et al., 2009a, 2012). It is a selective methodology which allows good chromatographic separation, identification and quantification of target analytes through their characteristic mass spectrum and quantification ion, respectively (Ribes et al., 2007). Methods based on solvent extraction are much less sensitive, due to the dilution factor of 1000 that occurs during extraction (Sakurai et al., 2013).

In this manuscript we present the evaluation of 1,3-butadiene concentrations in outdoor air in several Catalan locations, some of them close to a petrochemical industrial area, the Tarragona petrochemical sector. Several countries, regions and city councils have been measuring 1,3-butadiene in ambient air for several decades, such as Canada (Curren et al., 2006), the United Kingdom (Bush et al., 2014; Brunt et al., 2016; Royal Borough of Kensington and Chelsea, 2014), Texas (USA) (Grant et al., 2007; Hendler et al., 2010; Myers et al., 2015), and Auckland (New Zealand) (Reid, 2014). On the other hand, Spain does have neither a monitoring strategy nor standard regulations related to this compound, both for emission and immission categories. The problematic of this compound could be compared to the one from benzene (Arayasiri et al., 2010; Laowagul and Yoshizumi, 2009; Ruchirawat et al., 2010). Both compounds are carcinogenic, widely distributed in the atmosphere and are ozone precursors, which can generate a variety of respiratory adverse effects (Reiss, 2006). 1,3-Butadiene sources can be related to combustion (Ruchirawat et al., 2010), as well as, in the Tarragona region, to direct and indirect emissions from production factories in the petrochemical area (Mo et al., 2015). However, unlike benzene, 1,3-butadiene is not evaluated in outdoor air monitoring stations in Spain. In addition to that, 1,3-butadiene emissions are not quantified in Spain, being their immission concentrations unknown and unable to be predicted if not directly measured in the field outdoors. Hence, the only way to evaluate population exposure is through the determination of immission concentrations. To our knowledge, the results regarding 1,3-butadiene concentrations would be the first to be published accurately in Spain. Consequently, monitoring programs devoted to determine 1,3-butadiene concentrations in immission outdoor air are still necessary until thorough emission quantification and inventories would be mandatory for industries in the country.

A reliable methodology for determining 1,3-butadiene, together with a wide range of VOCs, is shown in the present paper, and a control of this compound is requested.

2. Materials and methods

2.1. Chemicals and materials

1,3-Butadiene solution (20% wt in toluene) was obtained from Sigma-Aldrich Chemie (Steinheim, Germany). Toluene for gas chromatography (SupraSolv®) with a purity ≥99.8% was obtained from Merck (Darmstadt, Germany). Perkin Elmer glass tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanized wool, and Carbotrap (20/40 mesh), Carbopack X (40/60 mesh) and Carboxen 569 (20/45 mesh) adsorbents were purchased from Supelco (Bellefonte, PA, USA).

2.2. 1,3-Butadiene sampling tubes

The multi-sorbent bed tubes used for 1,3-butadiene sampling were custom packed and composed of Carbotrap (activated graphitized black carbon, weak sorption strength, 70 mg), Carbopack X (activated graphitized black carbon, medium sorption strength, 100 mg) and Carboxen 569 (spherical carbon molecular sieve, high sorption strength, 90 mg). They were developed in an earlier study and found to be highly versatile regarding polarity and volatility of the target VOCs (Ribes et al., 2007). They have been successfully used for the determination of a wide range of VOC families (alkanes, aromatic hydrocarbons, alcohols, ketones, aldehydes, ethers, esters, halocarbons, terpenoids, carboxylic acids, organonitrogentaed and organosulfur compounds and glycols) in different applications (Gallego et al., 2009b, 2012, 2017). Sampling tubes were conditioned before use at 400 °C, sealed with Swagelock end caps fitted with PTFE ferrules and stored at 4 °C for 1 week at most before use.

1,3-Butadiene in air was actively sampled during 24 h connecting the self-packed glass multi-sorbent cartridge tubes to air collector pump samplers specially designed in the LCMA-UPC laboratory (Roca et al., 2003). The flow sampling rate was set at 70 ml min^{-1}. The sorbents are hydrophobic enough to avoid interferences derived from the humidity in the air sampled (Ribes et al., 2007). Furthermore, as an additional measure, tubes are purged at ambient temperature during 2 min with a Helium flow of 50 ml min^{-1} prior to TD-GC/MS.

1,3-Butadiene can be evaluated by both active and passive sampling methods (e.g. U.S. EPA Method 325A/B). Passive methodologies are not advisable when dealing with episodic pollution periods, as we observed in a study conducted in El Morell (results in progress to be published). In this case, 24 h active samples (multi-sorbent bed tubes) were taken during 9 consecutive days (21–30/6/2017) and at the same time 4 Radiello® passive samplers (Carbopack X) were exposed. During that period of time, an important episodic period occurred, with three

days presenting 24 h average 1,3-butadiene concentrations of 8.7, 39 and 7.5 μg m^{-3}. The average active concentration of the 9 days was 6.6 ± 12.5 μg m^{-3}, concentrations ranging from 0.1 to 39 μg m^{-3}. On the other hand, the Radiello® passive samplers presented an average value for the 9 days of 0.9 ± 0.2 μg m^{-3}. This aspect confirms that 24 h active sampling is the best 1,3-butadiene collecting methodology when relevant episodes are expected, as it is the case in the Tarragona petrochemical area.

2.3. 1,3-Butadiene analytical instrumentation

1,3-Butadiene analysis was performed by TD-GC/MS using a Markes Unity Series 2 (Markes International Ltd., Lantrisant, UK) via Thermo Scientific Focus GC fitted with a Thermo Scientific DSQII MSD (Thermo Fisher Scientific, Austin, Texas, USA).

The methodology is described in the literature (Ribes et al., 2007; Gallego et al., 2009b). Primary thermal desorption of the sampling tubes was carried out at 300 °C with a helium flow rate of 55 ml min^{-1} for 10 min. A double split was applied to the TD system (cold trap inlet and outlet splits of 11 ml min^{-1}). The cold trap (U-T15ATA: TO-15/TO-17 Air Toxics trap, Markes) was maintained at −30 °C. After primary desorption, the cold trap was rapidly heated from −30 °C to 300 °C (secondary desorption) and maintained at this temperature for 10 min. Analytes were then injected onto the capillary column (DB-624, 60 m × 0.32 mm × 1.8 μm, inert for active compounds) via a transfer line heated at 200 °C. The column oven temperature started at 40 °C for 1 min, increased to 230 °C at a rate of 6 °C min^{-1} and was then maintained at 230 °C for 5 min. Helium (99.999%) carrier gas flow in the analytical column was approximately 1.8 ml min^{-1} (1.4 bar). The chromatographic parameters allow the determination, in an only sample and an only analysis, of 1,3-butadiene together with a wide range of VOC families present in outdoor air (alkanes, aromatic hydrocarbons, alcohols, ketones, aldehydes, ethers, esters, halocarbons, terpenoids, carboxylic acids, organonitrogenated and organosulfur compounds and glycols). Even though in the present paper only 1,3-butadiene results are shown.

The electron impact source was obtained with an electron energy of 70 eV. Mass spectral data were acquired over a mass range of 20–300 amu. $m/z = 54$ was used as 1,3-butadiene quantification ion. Quantification of samples was conducted by the external standard method according to Ribes et al., 2007. Calibration curves of 1,3-butadiene were freshly prepared, clean tubes were spiked and they were injected onto the TD-GC/MS daily.

2.4. Quality control

Extreme precautions are required to ensure reproducible quality results. Every day the mass spectrometer was manually tuned at $m/z =$ 69, 131, 264 and 502 and air leaks ($m/z = 4$, 18 and 28) were controlled.

To avoid artifacts generation, both TD trap and sampling tubes were properly conditioned. Analytical blank samples, i.e. two clean tubes, were analysed daily before the injection of the samples and standards. Precision, repeatability of 7 standards, was found to be 1% for 1,3-butadiene, reaching the EPA performance criteria (US EPA, 1999). Method detection limit (MDL) was calculated through the analysis of 7 replicates of the lowest concentrated standard, which presented a signal to noise factor between 2.5 and 10. The obtained standard deviation (SD) for the replicates concentration was multiplied for 3.14 (Student's *t* value at the 99% confidence interval), according to the U.S. EPA (Part 136-Guidelines establishing test procedures for the analysis of pollutants, Appendix B). MDL was 0.2 ng of 1,3-butadiene per sample. The linearity range of the multi-point calibration was ≥0.99. Breakthrough, calculated as the percentage of the analyte in the back tube in respect to the total amount of analyte in two tubes in series, presented an average value of 4%, accomplishing the US EPA criteria (US EPA, 1999).

2.5. Data analysis

Data treatment and statistical analysis was undertaken using Microsoft Excel™ 2010 and IBM SPSS Statistics Version 22 (2013). Kolmogorov-Smirnov (K-S) test was used to check normal distribution of the experimental data. Two-tailed *t*-test was used to evaluate significant differences between normal data. *U* of Mann-Whitney was used to evaluate significant differences between not normal data.

3. Sampling locations

1,3-Butadiene was evaluated in outdoor air in twelve Catalan urban areas, five of which corresponded to the surroundings of a petrochemical industry, located in the Tarragona region (Fig. 1, A). The rest of the evaluated Catalan urban areas (Fig. 1, B–E) were not impacted by this kind of industry, even though some of them had the influence of other types of industrial facilities. Table S1 presents the number of samples taken in each urban area during each sampling date and the meteorological conditions during the sampling period. Table S2 presents the number of inhabitants, close motorways, estimated Average Daily Traffic (ADT), annual average temperature, air velocity, humidity and solar radiation for each studied area. Annual average meteorological conditions are similar in all evaluated locations in a high degree, with annual average temperature of 15.7 ± 0.5 °C (14.4–16.8 °C), air velocity of 2.1 ± 0.4 m s^{-1} (1.1–2.6 m s^{-1}), relative humidity of 68 ± 4% (62–74%) and daily solar radiation of 16.5 ± 0.3 MJ m^{-2} (16.0–16.8 MJ m^{-2}). Regarding ADT, the sampling locations with higher figures are the ones located in the Barcelona metropolitan area, i.e. Barcelona, La Llagosta, Montcada i Reixac, Ripollet and Cerdanyola del Vallès, with ADT values between 100,000 and 200,000 vehicles day^{-1}. Tables S3 and S4 present the vehicle type and age for Catalan and Spanish vehicle fleets, respectively, in 2016.

The differences in the number of samples obtained for each campaign in each urban area depended basically on the number of sampling points in each location and the number of consecutive sampled days. This last aspect depended on the developed project, as other VOC (between 60 and 80 compounds) were quantified together with 1,3-butadiene in the samples, but their values are out of the scope of the present paper.

3.1. Petrochemical industry surroundings

Nine sampling points were selected in the Tarragona industrial area (urban areas 1 to 5), covering the territorial area most affected by the petrochemical industry (Fig. 1, A).

A 1,3-butadiene manufacturing plant with an annual production of 202,000 tn is located at 41°11′26.8″ N and 1°13′13.9″ E in the petrochemical complex (Fig. 1, A). As has been said previously, 1,3-butadiene emissions to the atmosphere, both channelled and diffusive, are not quantified in Spain. An important number of studies have been conducted in the Tarragona petrochemical influential area in order to determine the health risks of exposure to different pollutants, due to the fact that it is the largest chemical site in southern Europe and the Mediterranean region (Ramírez et al., 2012). The studies have been mainly focused in persistent organic pollutants (polyclorinated dibenzo-*p*-dixoins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), polycyclic aromatic hydrocarbons (PAHs)), heavy metals (e.g. As, Cd, Cr, Hg, Mn, Pb and V) and VOC (Nadal et al., 2006, 2010, 2011; Ramírez et al., 2012; Ras et al., 2009; Ras-Mallorquí et al., 2007). However, up to this date, 1,3-butadiene concentrations have not been reported.

Several sampling campaigns (6–15 days each) were conducted in each sampling point during 2013 and 2016. The total number of samples in the Tarragona petrochemical area was 240.

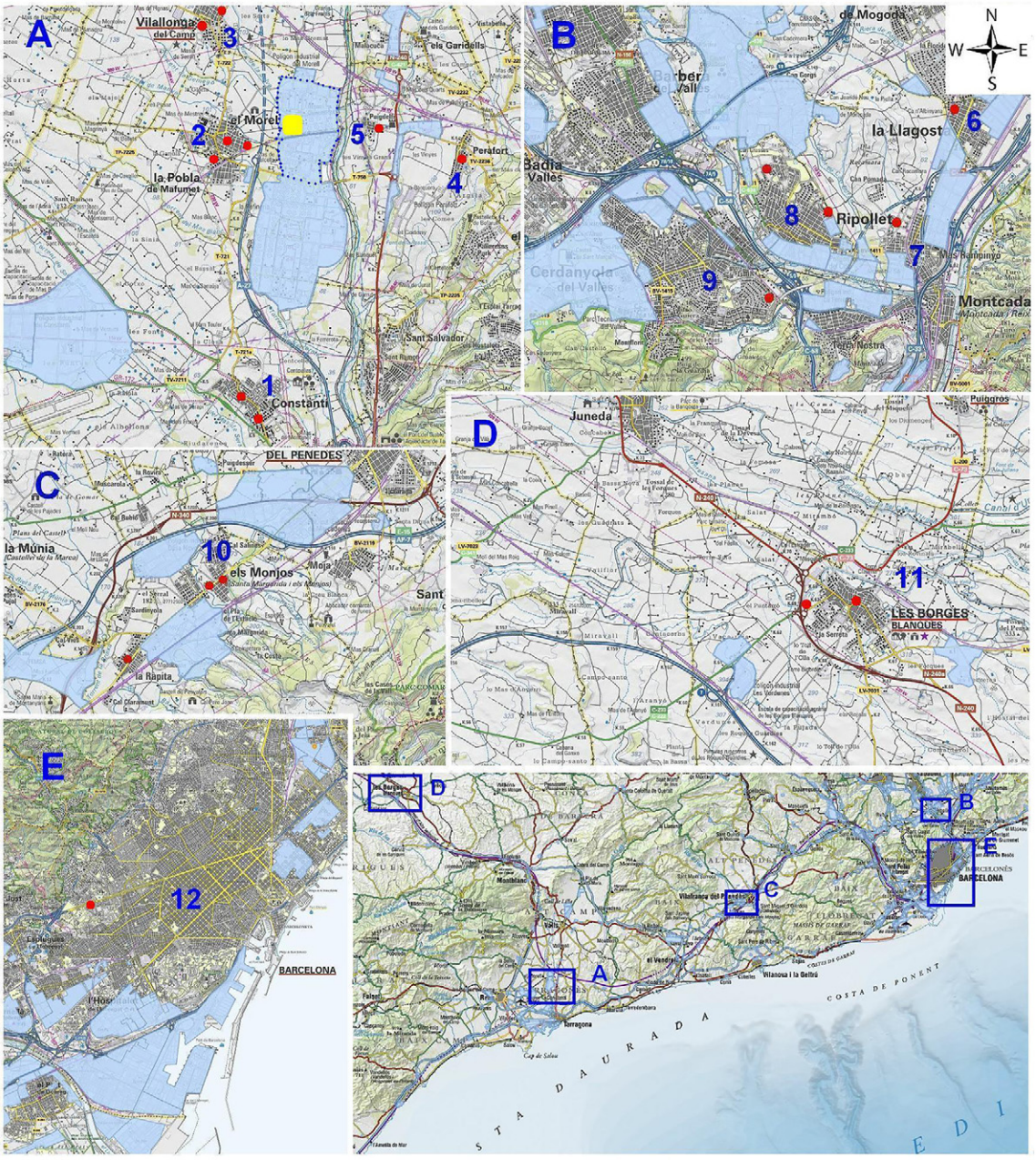

Fig. 1. 1,3-Butadiene sampling locations. Blue polygons indicate industrial areas. The petrochemical area in the Tarragona region is indicated with blue dots. 1,3-Butadiene plant is indicated with a yellow polygon. Red dots correspond to sampling points in each urban area. A) 1. Constantí; 2. El Morell; 3. Vilallonga del Camp; 4. Perafort; 5. Puigdelfí; B) 6. La Llagosta; 7. Montcada i Reixac; 8. Ripollet, 9. Cerdanyola del Vallès; C) 10. Els Monjos; D) 11. Les Borges Blanques; E) 12. Barcelona.
Maps source: ICGC (Institut Cartogràfic i Geològic de Catalunya).

3.2. Catalan urban areas

1,3-Butadiene was evaluated in other seven urban areas from Catalonia, urban areas 6 to 12 (Fig. 1, B–E). Campaigns of 7 to 12 days were conducted in several sampling points of each studied urban area. The total number of samples in the rest of Catalan urban areas was 175.

4. Results and discussion

4.1. 1,3-Butadiene concentrations near the petrochemical industry

1,3-Butadiene concentrations in several urban areas near the petrochemical complex of the Tarragona region are presented in Table 1. El Morell, Perafort and Puigdelfí are the most impacted locations, with average concentrations up to 15 ± 33, 33 ± 41 and 27 ± 39 μg m^{-3}, respectively. As can be derived from these data, variability in 1,3-butadiene concentrations was really high, as far as three orders of magnitude, especially during the first year of monitoring program. This indicates that important episodic periods with really high concentrations of 1,3-butadiene (up to >120 μg m^{-3}) took place in this neighbourhoods, as can be seen in Fig. 2. These peak concentrations had the duration of one to two consecutive days. Fugitive episodic releases of 1,3-butadiene in petrochemical facilities and/or tyre production activities have been reported in Houston, Texas (USA) (Knighton et al., 2012; Wang, 2011), with maximum values of 40 μg m^{-3} in 2008. Additionally, Czader and Rappenglück (2015) observed a very important 1,3-butadiene accidental episodic emission in Milby Park, Houston, in 2006. The

Table 1
1,3-Butadiene concentrations (μg Nm^{-3}) in Tarragona petrochemical industrial area. n = number of samples. SP = sampling point.

Location	Sample type	Concentration (μg Nm^{-3})	Range (μg Nm^{-3})	n
El Morell (SP1)				
June 2013	All samples	1.32 ± 1.54*	0.15–5.76	15
	Weekdays	1.15 ± 1.03	0.15–2.98	11
	Weekend	1.79 ± 2.67	0.24–5.76	4
March 2014	Weekdays	0.36 ± 0.32*	0.06–1.08	10
June 2015	Weekdays	0.13 ± 0.10	0.05–0.31	10
El Morell (SP2)				
June 2013	All samples	14.75 ± 32.70†	0.29–121	15
	Weekdays	15.18 ± 36.05	0.36–121	11
	Weekend	13.55 ± 25.63	0.29–51.99	4
March 2014	Weekdays	2.26 ± 4.14†	0.003–12.30	10
April 2015	Weekdays	4.13 ± 7.31	0.08–22.28	9
June 2015	Weekdays	0.89 ± 1.97	0.05–6.45	10
June 2016	Weekdays	2.67 ± 2.59	0.31–7.55	10
El Morell (SP3)				
April 2015	Weekdays	0.36 ± 0.47	0.05–1.55	9
Constantí (SP1)				
April 2013	All samples	2.56 ± 2.39	0.12–7.35	12
	Weekdays	2.73 ± 2.60	0.12–7.35	10
	Weekend	1.69 ± 0.32	1.47–1.92	2
January 2014	Weekdays	2.51 ± 4.80	0.10–17.33	12
Constantí (SP2)				
April 2013	All samples	3.30 ± 2.22	0.26–8.34	12
	Weekdays	3.20 ± 2.30	0.26–8.34	10
	Weekend	3.78 ± 2.40	2.08–5.48	2
January 2014	Weekdays	4.43 ± 7.29	0.22–26.60	12
Perafort				
September 2013	All samples	32.83 ± 40.97*	0.75–123	10
	Weekdays	38.94 ± 43.97	0.75–123	8
	Weekend	8.40 ± 9.20	1.89–14.91	2
February 2014	Weekdays	1.06 ± 1.25*	0.13–1.61	11
March 2015	Weekdays	0.23 ± 0.31	0.04–0.85	6
Puigdelfí				
September 2013	All samples	26.82 ± 39.18†	1.33–125	10
	Weekdays	24.47 ± 41.78	1.33–125	8
	Weekend	36.23 ± 37.08	10.01–62.45	2
February 2014	Weekdays	1.56 ± 2.27†	0.11–8.17	11
March 2015	Weekdays	0.25 ± 0.39	0.02–1.03	6
Vilallonga (SP1)				
July 2013	All samples	1.28 ± 1.52	0.24–1.85	10
	Weekdays	1.50 ± 1.63	0.24–1.85	8
	Weekend	0.39 ± 0.19	0.26–0.52	2
April 2014	Weekdays	0.22 ± 0.21	0.05–0.62	10
Vilallonga (SP2)				
July 2013	All samples	1.11 ± 0.96*	0.13–2.67	10
	Weekdays	1.19 ± 1.06	0.13–2.67	8
	Weekend	0.79 ± 0.22	0.64–0.94	2
April 2014	Weekdays	0.37 ± 0.36*	0.15–1.38	10

* Significant differences (t-test, $p < 0.05$) observed between 2013 and 2014 samples.
† Significant differences (U Mann-Whitney, $p < 0.05$) observed between 2013 and 2014 samples.

maximum 1,3-butadiene concentration arrived at 3625 μg m^{-3}. Fugitive emissions, more than stack or flare emissions, were assumed to be the responsible for this episodes in Houston, the concentrations of this compound in the nearby neighbourhoods depending in great part on the source strength, the distance of the urban areas from the source and the meteorological conditions during its release (Knighton et al., 2012). All in all, average 1,3-butadiene concentrations in Tarragona petrochemical area are of the same order of magnitude than the observed in worldwide petrochemical areas (Table 2). However, it has to be noted that the first year of sampling, 2013, presented higher average 1,3-butadiene concentrations, mainly due the fact that important episodic concentrations were observed during that sampling period (Fig. 2). From 2014 onwards, average and maximum concentrations decreased in an important way (Table 1, Table 2).

Significant differences ($p \leq 0.05$) were not observed between weekday and weekend samples. Even though weekday samples generally presented higher concentrations, 1,3-butadiene values found in weekend samples were also relevant, with a maximum value of 63 μg m^{-3} in a Sunday (8/09/2013) in Puigdelfí (Table 1). This clearly indicates that the petrochemical facility operated continuously during the sampling period.

As has been said before, and can be seen in Fig. 3, 1,3-butadiene average concentrations in the Tarragona petrochemical area diminished drastically (40–80%) since the first monitoring program in 2013. Significant differences ($p \leq 0.05$) were observed between 2013 and 2014 average 1,3-butadiene concentrations in El Morell SP1 and SP2, Perafort and Puigdelfí (Table 1). Additionally, maximum 1,3-butadiene concentrations also decreased, up to two orders of magnitude, in El Morell SP2, Perafort and Puigdelfí, shifting from 121 to 7.6 μg m^{-3} (2013–2016), 123 to 0.9 μg m^{-3} (2013–2015) and 125 to 1.0 μg m^{-3} (2013–2015), respectively (Table 1).

In Texas (USA), regulatory and voluntary actions have diminished 1,3-butadiene emissions to a half since 1990, and the effectiveness of the applied control strategies has been evaluated adopting long-term measurement programs (Hendler et al., 2010). In the present case, it seemed clear that the control applied had an influence in the reduction of the episodic periods. During the course of the years, as can be seen in Table 2, 1,3-butadiene concentrations near petrochemical facilities have diminished worldwide, for example in Stenungsund (Sweden), the concentrations observed were 0.2 μg m^{-3} in 2001–2002 and 0.07 μg m^{-3} in 2006–2007, or downwind petrochemical sites in Texas (USA), going from 5.0 μg m^{-3} in 2003 to 1.0 μg m^{-3} in 2012. Therefore, 1,3-butadiene control in these areas, coupled with technological improvements in the industries emitting this compound, lead to a decrease in 1,3-butadiene concentrations in ambient air (Curren et al., 2006; Grant et al., 2007; Hendler et al., 2010; Knighton et al., 2012; Myers et al., 2015), even though it is quite difficult to manage accidental emissions such as vapour leaks (Shie and Chan, 2013).

4.2. 1,3-Butadiene concentrations in several Catalan urban areas

1,3-Butadiene concentrations in several Catalan urban areas are presented in Table 3. Average concentrations are generally below 1 μg m^{-3}, ranging from 0.07–1.1 μg m^{-3}, with a maximum daily value of 2.3 μg m^{-3} in La Llagosta. As could be expected, urban areas with no specific impact of 1,3-butadiene industrial emissions presented much lower concentrations than the found in the Tarragona petrochemical area (Fig. 3). In urban areas, vehicle exhaust is one of the main potential sources of exposure to 1,3-butadiene (Arayasiri et al., 2010; Bari and Kindzierski, 2017; Curren et al., 2006; de Blas et al., 2012; Lee et al., 2002; Nagpure et al., 2016; Reid, 2014; Ruchirawat et al., 2010; Sapkota and Buckley, 2003; Serrano-Trespalacios et al., 2004; Yu and Stuart, 2017), but is much lower than the emissions to air from 1,3-butadiene plants (European Communities, 2002). Additionally, the use of catalytic converters since the 90s decade and the introduction of low emission fleets since 2000 has reduced in an important way 1,3-butadiene emissions from vehicles (Bush et al., 2014; Curren et al., 2006). Due to this aspect, 1,3-butadiene levels have decreased in great part in several worldwide cities, such as London (UK) (Royal Borough of Kensington and Chelsea, 2014), Auckland (New Zealand) (Reid, 2014) and several Canadian cities (Curren et al., 2006). For example, 1,3-butadiene concentrations in Marleybone road and Cromwell road sampling points in London decreased from 2.3 to 0.5 μg m^{-3} (2000 to 2013) and 1.4 to 0.4 μg m^{-3} (2000 to 2012), respectively (Royal Borough of Kensington and Chelsea, 2014). On the other hand, 1,3-butadiene concentrations in Khyber Pass sampling point in Auckland decreased from 1.7 to 0.6 μg m^{-3} (2007 to 2013) (Reid, 2014).

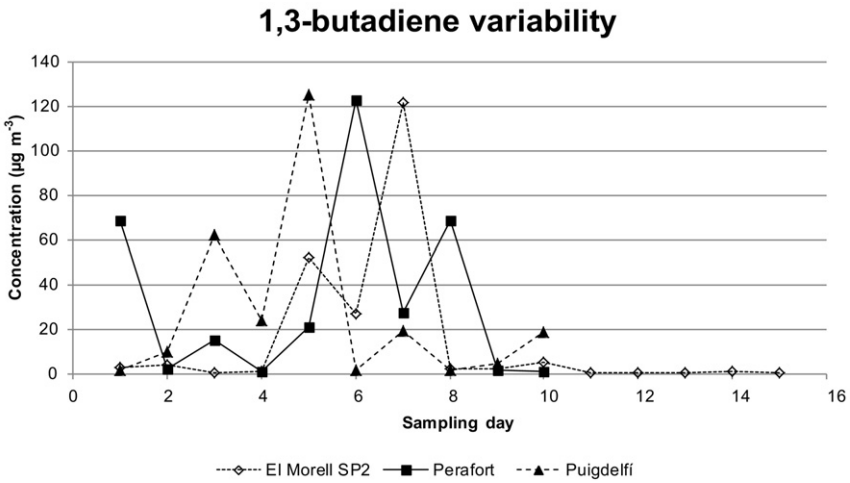

Fig. 2. 1,3-Butadiene variability during 2013 sampling programs in El Morell SP2 (12-26/06/2013), Perafort (6-17/09/2013) and Puigdelfí (6-17/09/2013).

In the present case, even though the highest Average Daily Traffic values were observed in Barcelona metropolitan area (100,000–200,000 vehicles day^{-1}) in respect to the figures from the Tarragona area (15,000–20,000 vehicles day^{-1}) (Table S2), 1,3-butadiene concentrations were much lower in the first locations, as the higher 1,3-butadiene concentrations observed in the Tarragona petrochemical area are related to episodic emissions coming from the 1,3-butadiene plant. Moreover, Spain presents a 68% of its vehicle fleet with ages between 0 and 15 years (Table S4), all of them from 2002 onwards, when low emission vehicles were introduced (Curren et al., 2006). On the other hand, the highest 1,3-butadiene concentrations observed in La Llagosta in respect to the rest of evaluated Catalan urban areas, excluding the Tarragona petrochemical area, are in accordance with the highest ADT observed in this location, an aggregated value of 207,272 vehicles day^{-1}.

Table 2
1,3-Butadiene concentrations in outdoor air (µg m^{-3}) in several worldwide locations: industrial, urban and rural/background areas.

Location	Average (µg m^{-3})	Range (µg m^{-3})	Year	Reference
Industrial areas				
Petrochemical sites, Tarragona, Spain	9.9 ± 24.6	0.1-125	2013	Present study
Petrochemical sites, Tarragona, Spain	1.7 ± 3.8	0.003-27	2014	Present study
Petrochemical sites, Tarragona, Spain	1.1 ± 3.7	0.02-22	2015	Present study
Petrochemical sites, Tarragona, Spain	1.8 ± 2.4	0.1-7.5	2016	Present study
Petrochemical sites, Stenungsund, Sweden	0.2	0.1-0.2	2001-2002	Axelsson et al., 2010
Petrochemical sites, Stenungsund, Sweden	0.07		2006-2007	Axelsson et al., 2010
Downwind petrochemical, Texas, USA	5.0	<0.6-41	2003	Grant et al., 2007
Downwind petrochemical, Texas, USA	1.0	<0.02-9.4	2012	Myers et al., 2015
Petrochemical sites, Texas, USA	0.9	<0.6-17	2003	Grant et al., 2007
Petrochemical sites, Texas, USA	0.5	<0.02-12	2012	Myers et al., 2015
Heavily industrialized area, Pittsburgh, USA	0.1-0.2		2006-2008	Logue et al., 2010
Industrial area, Hong Kong	1.3 ± 1.2		1997-1999	Lee et al., 2002
Urban areas				
Urban areas, Catalonia, Spain	0.5 ± 0.4	n.d.-1.7	2015-2017	Present study
Bilbao, Basque Country, Spain	0.6	0.2-1.5	2008	De Blas et al., 2012
Bilbao, Basque Country, Spain	0.5	0.4-0.6	1998-2004	Durana et al., 2006
Urban areas, Canada	0.3	0.1-0.9	1995-2003	Curren et al., 2006
Mexico city, Mexico	0.9		1998-1999	Serrano-Trespalacios et al., 2004
Pittsburgh, USA	0.2		2006-2008	Logue et al., 2010
New York, USA	0.3		2006	Czader and Rappenglück, 2015
Los Angeles, USA	0.3		2006	Czader and Rappenglück, 2015
Seattle, USA	0.1		2006	Czader and Rappenglück, 2015
Urban areas, Texas, USA	0.6	4.3*	2006	Czader and Rappenglück, 2015
Cardiff, UK	0.03 ± 0.03	n.d.-0.1	2005-2007	Delgado-Saborit et al., 2011
London, UK		0.2-0.6	2003-2013	Royal Borough of Kensington and Chelsea, 2014
Auckland, New Zealand		0.2-1.7	2005-2013	Reid, 2014
Urban areas, Hong Kong		0.5-2.4	1997-1999	Lee et al., 2002
Tianjin, China	0.4 ± 0.6		2008	Zhou et al., 2011
Bangkok, Thailand	4.1 ± 0.7		2006	Arayasiri et al., 2010
Bangkok, Thailand	10.1 ± 2.2	0.4-28		Ruchirawat et al., 2010
Rural areas/Background sites				
Rural sites, Canada	0.02	0.002-0.05	1995-2003	Curren et al., 2006
Stenungsund, Sweden	<0.06		2006-2007	Axelsson et al., 2010
South Fayette, Pittsburgh, USA	0.05		2006-2008	Logue et al., 2010
Hagfors, Sweden	0.1		2003	Gustafson et al., 2007
Harwell, UK	0.01 ± 0.06	n.d.-0.6	2005-2007	Delgado-Saborit et al., 2011
London Eltham, UK	0.06 ± 0.02		2005-2007	Delgado-Saborit et al., 2011
London Eltham, UK		0.06-0.2	2003-2013	Royal Borough of Kensington and Chelsea, 2014
Background site, Hong Kong	0.2 ± 0.2		1997-1999	Lee et al., 2002
Chonburi, Thailand	0.9 ± 0.1	0.7-1.1		Ruchirawat et al., 2010

* Maximum value. n.d. = Not detected.

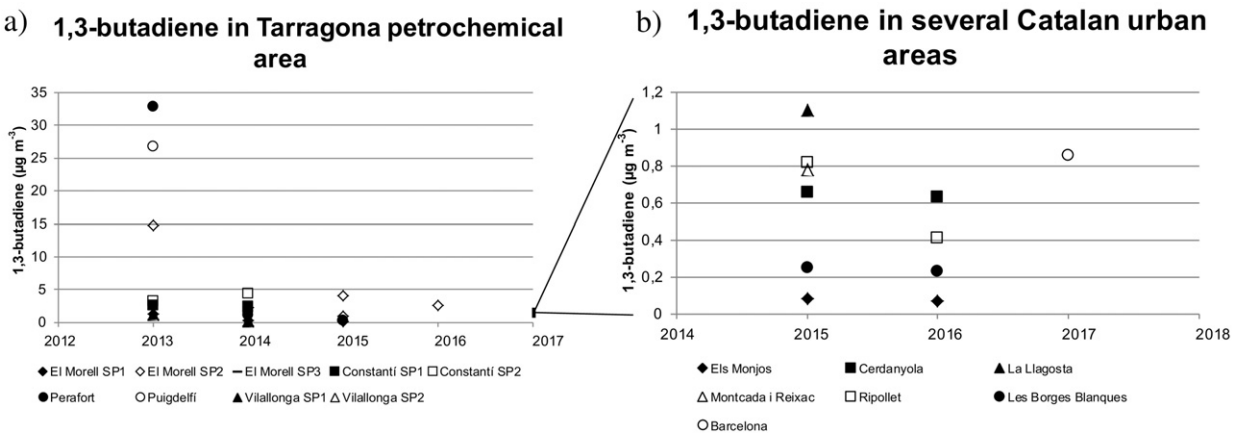

Fig. 3. Average 1,3-butadiene concentrations (μg Nm^{-3}) in a) Tarragona petrochemical area, and b) Catalan urban areas.

Hence, the observed concentrations in Catalan urban areas were among the expected in developed countries urban areas, as can be seen in Table 2. Although differences between weekdays and weekend samples have been observed in several urban areas (Curren et al., 2006; Durana et al., 2006; Czader and Rappenglück, 2015), with weekday values higher than weekend values, significant differences were observed neither between weekday and weekend samples in Catalan urban areas nor between the different sampled years (2015 and 2016) in Els Monjos, Cerdanyola del Vallès and Les Borges Blanques, indicating a background level of 1,3-butadiene concentrations. On the other hand, they were much lower than the concentrations observed in developing countries urban areas, such as Bangkok (Thailand) (Table 2).

Table 3
1,3-Butadiene concentrations (μg Nm^{-3}) in several Catalan urban areas. n = number of samples.

Location	Sample type	Concentration (μg Nm^{-3})	Range (μg Nm^{-3})	n
Els Monjos				
June 2015	All samples	0.08 ± 0.03	0.02–0.14	26
	Weekdays	0.07 ± 0.03	0.02–0.13	20
	Weekend	0.10 ± 0.04	0.05–0.14	6
April 2016	All samples	0.07 ± 0.06	n.d.-0.21	14
	Weekdays	0.08 ± 0.07	n.d.-0.21	10
	Weekend	0.07 ± 0.02	n.d.-0.09	4
Cerdanyola del Vallès				
January–February 2015	Weekdays	0.66 ± 0.29	0.31–1.00	8
January 2016[a]	All samples	0.63 ± 0.38	0.02–1.35	32
	Weekdays	0.57 ± 0.34	0.20–1.35	23
	Weekend	0.79 ± 0.46	0.02–1.26	9
La Llagosta				
January–February 2015	Weekdays	1.10 ± 0.72	0.47–2.29	7
Montcada i Reixac				
January–February 2015	Weekdays	0.78 ± 0.39	0.13–1.35	9
Ripollet				
January–February 2015	Weekdays	0.82 ± 0.44	0.37–1.68	18
May 2016	Weekdays	0.41 ± 0.19	0.02–0.68	12
Les Borges Blanques				
October 2015	Weekdays	0.25 ± 0.21	n.d.-0.94	20
January–February 2016	All Samples	0.23 ± 0.13	n.d.-0.34	18
	Weekdays	0.22 ± 0.08	n.d.-0.34	14
	Weekend	0.28 ± 0.24	0.04–0.23	4
Barcelona				
February–March 2017	Weekdays	0.86 ± 0.34	0.48–1.33	11

[a] Semi-industrial area. n.d. = Not detected.

4.3. 1,3-Butadiene air quality standards

Even though there is no safe level for 1,3-butadiene concentrations in ambient air due to its carcinogenic characteristics, 1,3-butadiene annual mean limits have been established in several countries and/or regions. The United Kingdom, Auckland (New Zealand) and Ontario (Canada), have a maximum running annual mean of 2.25, 2.4 and 2.0 μg m^{-3}, respectively (Bush et al., 2014; Ontario Ministry of the Environment, 2012; Reid, 2014). Additionally, Ontario has an ambient air quality criterion of 10 μg m^{-3} for 24 h samples.

Spain neither has a field program for measuring 1,3-butadiene nor legislation in respect to this compound's concentrations in outdoor air, as it is not covered by any European Union Directives, and is one of the compounds less documented in the country (Durana et al., 2006). Taking into account that relevant values can be found in locations near petrochemical facilities, 24 h sample concentrations up to 12.5 times higher than the established as air quality criterion by Ontario (Canada), a regulation should be implemented as soon as possible, at least in regions under the influence of petrochemical industrial complexes (Mo et al., 2015). Additionally, 1,3-butadiene monitoring coupled to a reliable program of modeling could be very helpful to develop population exposure studies (Czader and Rappenglück, 2015).

1,3-Butadiene concentrations in Catalan urban areas meet the annual average quality criteria found in several countries of 2.0–2.4 μg m^{-3}, presenting a maximum average concentration of 1.10 ± 0.72 μg m^{-3} in La Llagosta. The maximum 1,3-butadiene value found in these urban locations also meets with the Ontario 10 μg m^{-3} criterion for 24 h samplings, as the highest observed concentration was 2.29 μg m^{-3} (Table 3). However, concentrations in the Tarragona petrochemical area are generally found above Auckland 2.4 μg m^{-3} annual air quality criterion, especially samples from El Morell SP2, Constantí, Perafort and Puigdelfí. On the other hand, El Morell SP2 (2013–2015), Constantí (2014), Perafort (2013) and Puigdelfí (2013) presented maximum 1,3-butadiene concentrations above the Ontario 10 μg m^{-3} criterion, with values up to twelve times much higher in El Morell SP2, Perafort and Puigdelfí (Table 1).

5. Conclusions

Active multi-sorbent bed tube sampling and analysis through TD-GC/MS has proven to be an effective methodology to evaluate 1,3-butadiene in outdoor air. Additionally, the sampling tubes and the chromatographic parameters allow the determination of a wide range of VOC together with this compound. 1,3-Butadiene in several Catalan urban areas which are not impacted directly from 1,3-butadiene industrial sources are generally below 1 μg m^{-3}, as has been observed

in developed countries worldwide. On the other hand, 1,3-butadiene concentrations in the urban areas in the vicinity of a petrochemical industry are very variable, with maximum concentrations up to 125 μg m^{-3} in 24 h samples. However, the establishment of a control strategy has proved to be an effective method to diminish 1,3-butadiene concentrations near the petrochemical industry, with a decrease in average concentrations of a 40–80% since the first sampling campaign in 2013. Hence, monitoring programs coupled to emission regulatory measures should be applied as soon as possible in Spain, especially near 1,3-butadiene emission sources, as this substance is a Group 1 carcinogenic compound according to IARC. Additionally, as some of 1,3-butadiene photochemical degradation products such as 1,2-epoy-3-butene or 1,2,3,4-diepoxybutane can cause potentially major negative health effects than 1,3-butadiene itself, the inclusion of these compounds in exhaustive VOC evaluations, especially near petrochemical industries, would be advisable in future studies.

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