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Evaluation of air quality in indoor and outdoor environments: Impact of anti-COVID-19 measures

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HIGHLIGHTS

• The effect of anti-COVID-19 measures on indoor and outdoor air quality has been evaluated.
• The indoor presence of VOCs and semi-VOCs is currently three times higher than it was in 2019.
• Solvents were the most prevalent target compounds in the indoor settings evaluated.
• Cleaning products and hydroalcoholic gel used against COVID-19 are the main solvent source.
• In outdoor air samples, solvent concentrations were twenty times lower than in indoor samples.

ABSTRACT

This study monitors the presence of 88 volatile organic compounds (VOCs) and semi-volatile organic compounds (semi-VOCs) at the gas phase of seven indoor settings in a school in the city of Tarragona, Spain, and five outdoor locations around the city. The VOCs and semi-VOCs monitored were solvents (∑Solvents), aldehydes (∑Aldehydes), emerging organic compounds (∑EOCs), and other VOCs and semi-VOCs (∑Others). Passive sampling campaigns were performed using Carbopack X tubes followed by thermal desorption coupled to gas chromatography with mass spectrometry (TD-GC-MS). Overall, 70 of the target compounds included in the method were determined in the indoor air samples analysed, and 42 VOCs and semi-VOCs in the outdoor air samples. Our results showed that solvents were ubiquitous throughout the school at concentrations ranging from 272 μg m⁻³ to 423 μg m⁻³ and representing 68%–83% of total target compounds (∑Total). The values of ∑Total in 2021 were three times as high as those observed at the same indoor settings in 2019, with solvents experiencing the greatest increase. A plausible explanation for these observations is the implementation of anti-COVID-19 measures in the indoor settings, such as the intensification of cleaning activities and the use of hydroalcoholic gels as personal hygiene.

The ∑Total values observed in the indoor settings evaluated were twenty times higher than those found outdoors. ∑Solvents were the most representative compounds found indoors (74% of the ∑Total). The concentrations of VOCs and semi-VOCs observed in the outdoors were strictly related to combustion processes from automobile traffic and industrial activities, with ∑Others contributing 58%, ∑Solvents 31%, and ∑Aldehydes 11% of the ∑Total. EOCs, on the other hand, were not detected in any outdoor sample.

ARTICLE INFO

Editor: Philip M. Hopke

Keywords:

Air quality
Impact of anti-COVID-19 measures
Indoor and outdoor environments
Semi-volatile organic compounds
Volatile organic compounds

1. Introduction

Numerous studies in recent years have focused on monitoring the presence of volatile organic compounds (VOCs) and semi-volatile organic compounds (semi-VOCs) at the gas phase of indoor and outdoor environments in various settings including schools and cities, and the effect of anti-COVID-19 measures on air quality has been evaluated. The indoor presence of VOCs and semi-VOCs is currently three times higher than it was in 2019. Solvents were the most prevalent target compounds in the indoor settings evaluated. Cleaning products and hydroalcoholic gel used against COVID-19 are the main solvent source. In outdoor air samples, solvent concentrations were twenty times lower than in indoor samples.
compounds (semi-VOCs) in outdoor environments such as industrial and urban atmospheres (Gallego et al., 2016; Maceira et al., 2017; Wania and Shunthirasingham, 2020; Xuan et al., 2021). This is because of the negative impact on human health and the environment associated with their accumulation in the atmosphere and the contribution of these compounds to the formation of photochemical smog via chemical reaction in the presence of light. Major anthropogenic sources of VOCS are combustion processes associated with road traffic (Nagpure et al., 2016; Raysoni et al., 2017) and industrial areas, especially petrochemical facilities where VOCS are produced, stored, handled and present in petroleum fuels (An et al., 2014; Vallecillos et al., 2019). Semi-VOCs comprise combustion products such as polycyclic aromatic hydrocarbons (PAHs) and a wide range of commercially available substances, including additives to consumer products, industrial chemicals or pesticides (Ma et al., 2021; Wania and Shunthirasingham, 2020).

It is known that VOCS and semi-VOCs are also found in indoor environments at even higher concentrations (Ma et al., 2021; Madureira et al., 2016; Yang et al., 2018). Indoor air quality has become an important focus area for the scientific community in order to evaluate the presence of VOCS and semi-VOCs in places where humans spend most of their time (PHE, 2019; WHO, 2000). The indoor environments evaluated include workplaces (Dugheri et al., 2018), schools (Becerra et al., 2020; Vallecillos et al., 2020a) and homes (Lizana et al., 2020; Villanueva et al., 2015b). Special attention is paid to monitoring VOCS and semi-VOCs in schools because, according to the United States Environmental Protection Agency (USEPA), children may be more sensitive to pollutants. Household products such as cosmetics, disinfectants, other cleaning products, glues, permanent markers, building materials, furniture and cooking products are the main sources of VOCS and semi-VOCs in indoor environments (CHI et al., 2016; Vallecillos et al., 2020a; Wang et al., 2020).

The VOCS and semi-VOCs found mainly in indoor environments include solvents, emerging organic compounds (EOCs) such as preservative agents, plasticizers, flame retardants and fragrances, and other VOCS classified as ozone precursors (Lucattini et al., 2018; Vallecillos et al., 2020b; Yang et al., 2018). As a result of primary alcohol degradation or the photo-oxidation of natural and anthropogenic hydrocarbons, secondary pollutants such as aldehydes may also be generated (Carey et al., 2007; Herrington and Hays, 2012). The most abundant of these is formaldehyde, which is produced industrially in large quantities, and acetaldehyde (Dugheri et al., 2018). Formaldehyde is used as a disinfectant because it kills most bacteria, viruses, and fungi (PHE, 2019). Depending on their physical-chemical properties, VOCS and semi-VOCs, can have various adverse short- or long-term health effects on humans (Gallego et al., 2012). Health effects linked to short-term exposure to VOCS and semi-VOCs are eye, throat and skin irritations, while those linked to long-term exposure are nervous system damage and cancer (Durmusoglu et al., 2010; Jia et al., 2008). Generally, aldehydes are reactive compounds with cytotoxic, mutagenic and carcinogenic properties (Ahmed Laskar and Younus, 2019).

Representativeness in the sampling technique is important because air samples are heterogeneous and complex. Due to their low concentration in the atmosphere, a preconcentration step is needed to monitor VOCS and semi-VOCs usually before analyses are conducted by gas chromatography coupled to mass spectrometry (GC-MS) (Laborie et al., 2016; Vallecillos et al., 2018; Villanueva et al., 2015a). The most efficient and most common sampling technique comprises retaining the compounds in solid adsorbent tubes, either by passive sampling or active sampling followed by a desorption step with organic solvents or heat (Wang et al., 2016). Thanks to their high retention capacity and the wide range of compounds they can retain, the most common adsorbent tubes for VOCS and semi-VOCs are graphitized carbon blacks (Król et al., 2010; Vallecillos et al., 2020a). However, to sample VOCS such as aldehydes, a derivatization procedure is needed to make the compound more stable. The most widely used derivatization agents, such as 2,4-dinitrophenylhydrazine, are hydrazine based and the derivatization products are determined by liquid chromatography (LC) coupled to a UV detector (de Lima et al., 2018; Dugheri et al., 2018; Rosenberger et al., 2016). Active sampling is commonly used for a short period of time and provides information about episodic emissions of VOCS and semi-VOCs in the atmosphere (Gallego et al., 2018; Maceira et al., 2017). Passive sampling, in both axial and radial diffusion mode, involves monitoring for seven or fourteen days and yields average concentrations data, but underestimates episodic emissions of VOCS and semi-VOCs (Poulihet et al., 2014; Vallecillos et al., 2019; Villanueva et al., 2018). Although active sampling is believed to be more versatile, passive sampling is the preferred sampling technique for many authors in the field due to its simplicity, low price and easy implementation (Hoang et al., 2017; Vallecillos et al., 2020b; Walgraeve et al., 2011; Wania and Shunthirasingham, 2020).

In this study, passive sampling was used to monitor VOCS and semi-VOCS, such as aldehydes, solvents and EOCs in the gas phase of various indoor and outdoor environments. All the target compounds except aldehydes were determined by means of TD-GC-MS. Due to their thermal instability, aldehydes were determined using liquid desorption followed by LC-DAD. To evaluate the effect of anti-COVID-19 measures on indoor air quality, we compared the concentrations of solvents at indoor settings in a school in Tarragona (Spain) with those reported before the COVID-19 pandemic (Vallecillos et al., 2020a, 2020b).

2. Materials and methods

2.1. Reagents and standards

The standards for the target VOCS and semi-VOCs involved individual standard solutions of 2000 mg L\(^{-1}\) in methanol for the following compounds: 1- pentane, n-pentane, ethanol, isopropyl alcohol, (cis/trans) 2- pentene, isoprene, 1-propanol, 1-hexene, 2-butanol, n-hexane, ethyl acetate, 1-butanol, isopropyl acetate, 1-methoxy-2-propanol, n-heptane, n-propyl acetate, 1-etoxy-2-propanol, n-octane, propylene glycol methyl ether acetate (PGMEA), ethylene glycol butyl ether (EGBE), diethylene glycol ethyl ether (DEEGE), 2,2,4-trimethyl-1,3-pentanediol (TMPD), diethylene glycol butyl ether (DGBE) (Sigma-Aldrich, Steinheim, Germany), 2- 3- and 4-ethyltoluene, 1-3- and 1,4-dihydriobenzene (Fluka, Buchs, Switzerland), 1- and 2-methylnaphthalene (Riedel-de Haën, Seelze, Germany). All of them with purities higher than 95%. The commercial mixtures 502/524 Volatile Organics Calibration Mix and EPA 524.2 Revision 4 Mix of 2000 mg L\(^{-1}\) in methanol were provided by Supelco (Bellefonte, USA). Successive dilutions of 1,3-butadiene, supplied by Sigma-Aldrich as a 15% wt. solution in n-hexane, were applied to obtain the corresponding working solutions. Table 1S shows the complete list of target VOCS included in this study along with the compounds classified as semi-VOCS according to the definitions of VOCS stated in the European Directives 1999/13/EC (EU, 1999) and 2004/42/CE (EU, 2004).

The following compounds, which are extensively used in cleaning and painting products, were defined as solvents in this study: ethanol, isopropyl alcohol, dichloromethane, 1-propanol, 2-butanol, n-hexane, ethyl acetate, 1-butanol, isopropyl acetate, 1-methoxy-2-propanol, -propyl acetate, 1-etoxy-2-propanol, toluene, PGMEA, EGBE, DEEGE, TMPD and DGBE. As Table 1S shows, the compounds defined as “Others” included ozone precursors and some VOCS and semi-VOCs typically generated throughout combustion processes or fugitive emissions (Raysoni et al., 2017; Vallecillos et al., 2019).

The EOCs evaluated included fragrances and preservatives and were 1R-α-pinene, (−)-β-pinene, camphene, p-cymene, β-limonene, eucalyptol, 2-phenyl ethyl alcohol and 2-phenoxycethanol supplied by Sigma-Aldrich, while L-camphor, δ 3-carene and phenol supplied by Supelco. All EOC standards were of purities between 95% and 99.5%.

A standard solution of 2,4-dinitrophenylhydrazine derives of formaldehyde, acetaldehyde, acrolein, propanal, butanal, isopentanal, pentanal, hexanal and benzaldehyde of 50 μg mL\(^{-1}\) in acetonitrile was commercially obtained from Supelco.

Working solutions of all the target compounds, except aldehydes, of 100 μg mL\(^{-1}\) were prepared in methanol (99.9%) (Teugezeweg, Deventer, Netherlands) and kept in the fridge at 4 °C. Chromatographic analysis and
thermal desorption were performed with helium and nitrogen gas of purities above 99.9% (Carburos Metálicos, Tarragona, Spain), respectively. Working solutions of the derivatized aldehydes were prepared in acetonitrile (ACN) and Milli-Q (50:50 v/v) the initial conditions of the mobile phase and kept in the fridge until used. Acetonitrile HPLC grade was purchased from Chem-Lab (Zedelgem, Belgium) and a Milli-Q water system (MilliPore, Billerica, MA, USA) was used to obtain ultrapure water.

2.2. Sorbent tubes

As specified in EPA methods 325A and 325B (EPA, 2019a, 2019b), stainless-steel Carbopack X (CX) tubes 9 cm in length × 6.35 mm in o.d. × 5 mm in i.d were used for the axial passive sampling of all the target compounds except aldehydes. To avoid cross contamination, CX adsorbent tubes were conditioned before each use at 330 °C for 60 min under a constant nitrogen flow rate of 100 mL min⁻¹. The CX tubes were then resealed with long-term brass endcaps and stored in hermetically sealed glass jars to prevent ambient contamination of the tubes. Blanks of the conditioned tubes were made before use to ensure that none of the target compounds were present.

Radiello® tubes (Supelco, 2021) were used to monitoring aldehydes in air as passive sampling devices with radial configuration. The adsorbent tubes consisted of a stainless-steel mesh body 60 mm in length and 4.8 mm in diameter filled with florisor as adsorbent and 2,4-DNPH as derivatization agent. These adsorbent tubes do not require preconditioning and are disposable since solvent desorption is performed. However, various blanks of the tubes were performed to ensure that none of the target compounds were present.

2.3. Sampling

Monitoring campaigns to determine the presence of the target compounds in the gas phase of indoor and outdoor environments were conducted between April and June 2021 (n = 5). Two passive sampling periods were used: seven-day sampling indoors to avoid saturation of the adsorbent tubes and fourteen-day sampling outdoors since the target compounds were present. The seven-day passive sampling campaigns were conducted at seven indoor sites with differing characteristics (i.e. volume, floor of the school building, activity or internal covering) at a school in Tarragona and three living rooms in different houses. The fourteen-day passive sampling measurements were conducted at outdoor sites in Tarragona city centre and four towns near Tarragona’s northern industrial complex (Constantí, Perafort, Sant Salvador and Els Pallaressos). Further information about sampling sites is found in Table 1. As recommended in USEPA methods 325A and 325B for determining VOCs from Fugitive and Area sources (EPA, 2019a, 2019b), all sampling points were installed at a height of 2 m.

VOCs and semi-VOCs passive sampling devices consisted of a previously conditioned CX tube with a diffusion cap (Supelco) and a stainless-steel protective hood. TH0160 data loggers (Perfect Prime, London, UK) were used to monitor temperature and pressure during the sampling period. The Radiello® samplers used to monitor aldehydes included an adsorbent tube of florisor and 2,4-DNPH, a diffusive body (Supelco) intended to prevent the entrance of particulate matter, and a Triangular Support (Supelco).

2.4. GC–MS analytical method for VOCs and semi-VOCs

A thermal-desorption gas-chromatography mass-spectrometry-based method previously developed by Maceira et al. (2017) and Vallecillos et al. (2020b) for determining VOCs and semi-VOCs was applied. The target compounds trapped in the CX adsorbent tubes were thermally desorbed using a Unity 2 Thermal Desorption system connected to an Ultra A automatic sampler, both of which were supplied by Markes International Limited (Llantrisant, UK). Thermal desorption was performed in two steps known as primary and secondary desorption. For the primary desorption, CX tubes were heated to 330 °C for 10 min while a constant flow rate of 20 mL min⁻¹ of helium was applied. This step was performed in splitless mode. The target VOCs and semi-VOCs desorbed from the tubes were then focused into a general-purpose graphitized carbon cold trap set at −30 °C. For the secondary desorption, a constant split flow rate of 5 mL min⁻¹ was applied, while the cold trap was speed-heated at 330 °C for 10 min.

Chromatographic analyses were performed by gas chromatographic separation on a 7890 gas chromatograph (GC) with a quadrupole mass spectrometric detection system using a 5975 inert MS, both of which were supplied by Agilent Technologies (Palo Alto, CA, USA). GC separation was conducted on a 60 m × 0.32 mm i.d. x 1 μm film thickness capillary column with a film of 5% phenyl-95% dimethylpolysiloxane obtained as ZB-5 (Phenomenex, Torrance, CA, USA). The oven-temperature programme was as follows: an initial temperature 40 °C (5 min), which increased at 6 °C min⁻¹ to 140 °C and at 15 °C min⁻¹ to 220 °C (8 min) with helium as carrier gas at a flow rate of 1.2 mL min⁻¹. The transfer line, ion source and quadrupole temperatures were set at 280 °C, 230 °C and 150 °C, respectively. Identification of the target compounds was based on the coincidence of the retention times and ratios of the quantifier and qualifier ions when working in full scan mode (35–280 m/s) at an electron impact energy of 70 eV. Quantification was performed via integration of the quantifier ion peak areas of each compound. Table 15 shows the retention times and the qualifier and quantifier ions of each compound.

2.5. LC-DAD analytical method for aldehydes

Radiello® tubes were desorbed with 2 mL of ACN in 20 mL glass vials. The extraction was performed in an ultrasound bath for 30 min. The extracts were then filtered using a paper filter to remove the granules from the adsorbent, and ACN was added to a volume of 2 mL. The extracts

| Indoor Houses  | H1  | Living room close to the kitchen (bleach cleaning) |
|----------------|-----|---------------------------------------------------|
| H2  | Living room (cleaning) |
| H3  | Living room (intensive cleaning) |
| S1  | Kindergarten (old floor with windows, handicrafts) |
| S2  | First year of primary school (old building, first floor with windows, main classroom) |
| S3  | Fourth year of primary school (new building, second floor with windows, main classroom) |
| S4  | Last year of primary school (old building, second floor with windows, main classroom) |
| S5  | High school (old building, second floor with windows, main classroom) |
| S6  | Workshop (new building, second floor with windows, art activities, robotics and technological activities) |
| S7  | Main entrance* |

* Painted during the first sampling.

Table 1

Indoor and outdoor sampling sites where the target compounds were monitored plus a brief description of the characteristics of each site.

| Outdoor Towns | Constantí  | Near an industrial area |
|---------------|------------|------------------------|
| Perafort      |            |                        |
| Sant Salvador |            |                        |
| Els Pallaressos |          |                        |
| Tarragona  | City centre |                        |
were evaporated to 1 mL under a gentle stream of nitrogen and reconstituted to 2 mL with Milli-Q water to obtain a 50:50 (v/v) water/ACN solution (initial conditions of the mobile phase). Before analysis by LC-DAD, the extracts were filtered with a 0.45 μm PTFE syringe filter to avoid small particles damaging the analytical column.

The instrument used to quantify DNPH-aldehydes in air samples was an Agilent Technologies series 1100 Liquid Chromatograph system (Palo Alto, CA, USA) with a diode array detector (DAD). Chromatographic separation was conducted with a reverse phase C18 Brisa column (15 mm × 4.6 mm, 5 μm) from Teknokroma (Sant Cugat del Vallès, Barcelona, Spain). The separation was performed in gradient mode with Milli-Q water and acetonitrile (ACN) as the mobile phase. The gradient began at 38% ACN and increased to 70% at minute 2, then increased to 80% at minute 8 and held for 2 min. Finally, it was increased to 100% at minute 11 before returning to the initial conditions at minute 15, where it was held for a couple of minutes. The flow rate was 0.8 mL min⁻¹ and the injection volume was 20 μL. The column oven was set at 35 °C and UV detection was performed at 365 nm (Andrietta et al., 2000; Rosenberger et al., 2016).

To identify the aldehydes, it was established that the retention time should coincide or have a variation of less than 0.1 min. The retention times are shown in Table 1S.

### 3. Results and discussion

In this section we report the validation parameters obtained by each analytical method and the concentrations of the target compounds observed in the indoor and outdoor environments evaluated. To obtain these concentrations in μg m⁻³, we applied the equation based on Fick’s first law described by Andrietta et al. (2010) and the experimental diffusive uptake rate previously calculated by Vallecillos et al. (2020a), Vallecillos et al. (2020b) corrected according to the average temperature and pressure of the sampling period (Qₚ, Table 1S). For the aldehydes we used the theoretical diffusive uptake rate provided by the supplier of Radiello® tubes corrected for temperature and pressure (Supelco, 2021).

#### 3.1. Validation

The validation parameters evaluated for each compound were linear range, instrumental limit of detection (LOD), instrumental limit of quantification (LOQ), method detection limit (MDL), method quantification limit (MQL), repeatability and reproducibility. Table 1S shows the instrumental validation parameters obtained with TD-GC-MS and LC-DAD used to determine the target compounds in indoor and outdoor air samples.

As specified in UNE-EN 14662-1 (UNE-EN, 2006), multistep external standard calibration curves for the target compounds were constructed by connecting sampling tubes to a Calibration Solution Loading Rig (Markes International Limited) and enriching the tubes with 1 μL of the corresponding standard solution. The tubes were purged for 5 min under a helium flow rate of 50 mL min⁻¹ to ensure the evaporation of the solvent as well as the repeatability of the spiking procedure. To achieve the quality assurance conditions for determining VOCs and semi-VOCs in ambient air by USEPA Method TO-17 (EPA, 1999), the determination coefficients (r²) of all calibration curves were above 0.999. LODs and LOQs ranged from 0.005 to 0.25 ppm and from 0.01 to 0.50 ppm, respectively. Repeatability and reproducibility values (n = 5, 1 ppm) expressed as relative standard deviations (RSD, %), ranged from 3% to 12% and from 4% to 18%, respectively. MDLs and MQIs were calculated from the LOQs and LOQs and the equation described by Andrietta et al. (2010). MDLs and MQIs for fourteen-day passive sampling dropped to roughly half depending on the average temperature and pressure during the sampling period. Repeatability of the method was tested in the real working conditions used in this study. Specially, repeatability of the seven-day passive sampling was conducted at one of the indoor sites while that of the fourteen-day passive sampling was carried out at one of the outdoor sites. The results show that, regardless of the sampling site, % RSD (n = 5) were between 6% and 21% for the target compounds detected in the samples.

The TD trap and analytical column were conditioned before and after the air samples were analysed to avoid background contamination. Blanks of the conditioned tubes were performed before use, and control samples were carried out during the sampling periods. More information about the method validation and quality assurance procedures are available from Vallecillos et al. (2019).

#### 3.2. Application to air samples

##### 3.2.1. Indoor air quality

In this section we report the concentrations of the target compounds observed at the seven indoor environments of a school in Tarragona evaluated between April and June 2021. Table 2 shows the maximum, minimum and average gas phase concentrations of the 70 target compounds detected in at least one of the samples analysed. Target compounds are listed by families, solvents, EOCs, aldehydes and others, and the semi-VOCs are in bold. The median concentrations and detection rates found for the detected compounds are in Table 2S.

As Table 2 shows, the sum of the average concentrations of the target compounds (ΣTotal) observed at the indoor settings of the school ranged from 343 μg m⁻³ (S7) to 563 μg m⁻³ (S2) with detection rates percentages higher than 93.6% in all cases. In general, the average and the median values of ΣTotal obtained were similar, except for S2, indicating that they followed a normal distribution.

The ΣSolvents were ubiquitous throughout the school and had the highest concentrations, which ranged from 277 μg m⁻³ (S1) to 458 μg m⁻³ (S4), or between 71% and 85% of the ΣTotal. Ethanol and isopropyl alcohol were the most prevalent solvents, with average concentrations ranging from 74.2 μg m⁻³ (S1) to 301 μg m⁻³ (S2). ΣEOCs and ΣOthers were found in all indoor air samples analysed, with average concentrations between 13.1 μg m⁻³ (S1) and 39.9 μg m⁻³ (S2) and between 25.5 μg m⁻³ (S5) and 79.7 μg m⁻³ (S6), respectively. The concentration of 2-phenoxyethanol stood out from the other target EOCs with average values ranging from 2.47 μg m⁻³ (S7) to 28.1 μg m⁻³ (S2). With regard to ΣOthers, the most prevalent compounds were pentanes, chloroform, carbon tetrachloride, ethylbenzene and xylene with concentrations ranging from 0.20 μg m⁻³ (S1) to 23.9 μg m⁻³ (S5). In general, pentanes had the highest concentrations, representing between 37% and 74% of the ΣOthers. Except for S2 and S6 where chloroform, ethylbenzene and xylene were found at concentrations higher than pentanes. Overall, S7 showed the lowest values for each family of compounds except ΣSolvents, while the highest values were observed at S6 for ΣOthers and S2 for ΣSolvents and ΣEOCs.

The concentrations observed at the seven indoor environments of this school can be compared with those found by Vallecillos et al. (2020a) at the same school in 2019. As Fig. 1 shows, the ΣTotal values observed in 2021 were three times higher than those observed in 2019. Regardless of the indoor setting, the compounds with the greatest increase in 2021 were ΣSolvents. In fact, the percentage of ΣSolvents in ΣTotal increased from 29%-71% in 2019 to 68%-83% in 2021. Ethanol and isopropyl alcohol contributed the most to this increase in ΣSolvents, as their concentrations increased 2-8 fold and 4-18 fold, respectively. Although the concentrations of ΣOthers found in 2021 were generally higher than those reported by Vallecillos et al. (2020a), they still represent only 6%-22% of the ΣTotal. Moreover, the ΣOthers values found in 2021 at the kindergarten (S1) and the elementary school (S2-S4) were lower than those reported by Villanueva et al. (2018) when monitoring the concentrations of VOCs in schools with radial passive samplers (kindergarten, ΣOthers = 48 μg m⁻³, elementary school, ΣOthers = 69 μg m⁻³). Regarding high school classroom results, the concentration range of ΣOthers at S5 was higher than that detected by de Gennaro et al. (2013) through the passive sampling of VOCs in four schools in Italy (ΣOthers = 2.46 μg m⁻³-32.1 μg m⁻³). The concentrations of EOCs did not follow the same pattern at all indoor settings studied. For example, in some cases the...
| No. | Compounds      | Indoor air | Average | Range |
|-----|----------------|------------|---------|-------|
| 1   | Ethanol        | –          | 20.4    | 15.1  |
| 2   | Isopropyl alcohol | 1.9       | 0.7     | 2.8   |
| 3   | Butanol        | 0.06      | 0.01    | 0.11  |
| 4   | i-Butanol      | 0.15      | 0.08    | 0.25  |
| 5   | n-Butanol      | 0.16      | 0.08    | 0.22  |
| 6   | tert-Butanol   | 0.18      | 0.09    | 0.26  |
| 7   | Methanol       | 0.06      | 0.03    | 0.09  |
| 8   | 1-Propanol     | 0.07      | 0.04    | 0.11  |
| 9   | 2-Propanol     | 0.07      | 0.04    | 0.11  |
| 10  | 3-Propanol     | 0.07      | 0.04    | 0.11  |
| 11  | n-Propanol     | 0.07      | 0.04    | 0.11  |
| 12  | 1-Butanol      | 0.07      | 0.04    | 0.11  |
| 13  | 2-Butanol      | 0.07      | 0.04    | 0.11  |
| 14  | 3-Butanol      | 0.07      | 0.04    | 0.11  |
| 15  | 2-Methylpropanol | 0.07   | 0.04    | 0.11  |
| 16  | 3-Methylpropanol | 0.07   | 0.04    | 0.11  |
| 17  | tert-Butyl methyl ether | 0.07 | 0.04    | 0.11  |
| 18  | n-Butyr aldehyde | 0.07 | 0.04    | 0.11  |
| 19  | 1-Phenylethanol | 0.07 | 0.04    | 0.11  |
| 20  | 2-Phenylethanol | 0.07 | 0.04    | 0.11  |
| 21  | Toluene        | 0.07      | 0.04    | 0.11  |
| 22  | Benzene        | 0.07      | 0.04    | 0.11  |
| 23  | Fluorobenzene  | 0.07      | 0.04    | 0.11  |
| 24  | Xylenes        | 0.07      | 0.04    | 0.11  |
| 25  | Styrene        | 0.07      | 0.04    | 0.11  |
| 26  | Benzaldehyde   | 0.07      | 0.04    | 0.11  |
| 27  | Acetaldehyde   | 0.07      | 0.04    | 0.11  |
| 28  | 2-Methoxyethanol | 0.07 | 0.04    | 0.11  |
| 29  | 3-Methoxyethanol | 0.07 | 0.04    | 0.11  |
| 30  | 1,2-Benzenediol | 0.07 | 0.04    | 0.11  |
| 31  | 1,3-Benzenediol | 0.07 | 0.04    | 0.11  |
| 32  | 1,4-Benzenediol | 0.07 | 0.04    | 0.11  |
| 33  | Phenol         | 0.07      | 0.04    | 0.11  |
| 34  | Phenol         | 0.07      | 0.04    | 0.11  |
| 35  | Phenol         | 0.07      | 0.04    | 0.11  |
| 36  | Phenol         | 0.07      | 0.04    | 0.11  |
| 37  | Phenol         | 0.07      | 0.04    | 0.11  |
| 38  | Phenol         | 0.07      | 0.04    | 0.11  |
| 39  | Phenol         | 0.07      | 0.04    | 0.11  |
| 40  | Phenol         | 0.07      | 0.04    | 0.11  |
| 41  | Phenol         | 0.07      | 0.04    | 0.11  |
| 42  | Phenol         | 0.07      | 0.04    | 0.11  |
| 43  | Phenol         | 0.07      | 0.04    | 0.11  |
| 44  | Phenol         | 0.07      | 0.04    | 0.11  |
| 45  | Phenol         | 0.07      | 0.04    | 0.11  |
| 46  | Phenol         | 0.07      | 0.04    | 0.11  |
| 47  | Phenol         | 0.07      | 0.04    | 0.11  |
| 48  | Phenol         | 0.07      | 0.04    | 0.11  |

(continued on next page)
Table 2 (continued)

| No. | Compounds                  | Indoor air |           |           |           |           |           |           |           |           |
|-----|----------------------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|     |                            | S1 Range   | S2 Average | S3 Range  | S4 Average | S5 Range  | S6 Average | S7 Range  | S8 Average |
| 49  | o-Xylene                   | 0.19–0.25  | 0.23      | 0.22–0.17 | 2.56       | 0.32–0.63 | 2.10       | 0.24–0.57 | 0.38       | 0.55–0.66  |
| 50  | n-Propylbenzene            | 0.02–0.10  | 0.05      | 0.02–0.12 | 0.05       | 0.02–0.05 | 0.03       | 0.02–0.18 | 0.09       | 0.03–0.05  |
| 51  | Isopropylbenzene           | 0.07–0.42  | 0.21      | 0.03–0.23 | 0.11       | 0.02–0.49 | 0.49       | 0.03–0.32 | 0.12       | 0.44–1.80  |
| 52  | 3-Ethyltoluene             | 0.04–1.04  | 0.28      | 0.05–0.4  | 0.14       | 0.04–2.00 | 0.94       | 0.20–0.71 | 0.39       | 0.45–3.14  |
| 53  | 4-Ethyltoluene             | 0.18–0.58  | 0.09      | 0.17–0.51 | 0.09       | 0.18–0.45 | 0.18       | 0.18–0.62 | 0.20       | 0.61–2.90  |
| 54  | 1,3,5-Trimethylbenzene     | 0.13–0.87  | 0.12      | 0.09–0.72 | 1.22       | 0.14–0.24 | 0.18       | 0.18–0.61 | 0.21       | 0.56–1.02  |
| 55  | 2-Ethyltoluene             | 0.08–0.56  | 0.11      | 0.02–0.13 | 0.08       | 0.08–0.12 | 0.10       | 0.02–0.18 | 0.09       | 0.03–0.08  |
| 56  | 1,2,4-Trimethylbenzene     | 0.11–1.64  | 0.07      | 0.10–0.33 | 0.23       | 0.11–3.96 | 1.42       | 0.17–0.38 | 0.25       | 1.36–8.82  |
| 57  | p-Tolualdehyde             | 0.30–0.47  | 0.09      | 0.35–0.29 | 0.69       | 0.45–4.28 | 1.57       | 0.30–0.97 | 0.75       | 0.65–0.76  |
| 58  | 1,2,3-Trimethylbenzene     | 0.07–0.40  | 0.07      | 0.12–0.05 | 0.05       | 0.18–0.89 | 0.26       | 0.14–0.77 | 0.18       | 0.26–2.62  |
| 59  | 1,4-Diethylbenzene         | 0.04–0.70  | 0.07      | 0.07–0.12 | 0.05       | 0.18–0.89 | 0.26       | 0.14–0.77 | 0.18       | 0.26–2.62  |
| 60  | Naphthalene                | 0.05–1.16  | 0.29      | 0.16–0.38 | 0.46       | 0.45–4.28 | 1.57       | 0.30–0.97 | 0.75       | 0.65–0.76  |
| 61  | 2-Methylnaphthalene        | 0.05–1.16  | 0.29      | 0.16–0.38 | 0.46       | 0.45–4.28 | 1.57       | 0.30–0.97 | 0.75       | 0.65–0.76  |
| 62  | 1-Methylnaphthalene        | 0.05–1.16  | 0.29      | 0.16–0.38 | 0.46       | 0.45–4.28 | 1.57       | 0.30–0.97 | 0.75       | 0.65–0.76  |

**VOCs**

| No. | Compounds                  | Indoor air |           |           |           |           |           |           |           |           |
|-----|----------------------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|     |                            | S1 Range   | S2 Average | S3 Range  | S4 Average | S5 Range  | S6 Average | S7 Range  | S8 Average |
| 63  | Formaldehyde               | 4.05–6.22  | 5.13      | 6.53–10.4 | 8.46       | 3.44–16.6 | 10.0       | 3.66–7.34 | 5.50       | 3.65–7.24  |
| 64  | Acetaldehyde               | 2.90       | 3.15–7.25 | 5.20       | 7.00–5.10  | 2.90       | 3.15–7.25 | 5.20       | 7.00–5.10  | 2.90       |
| 65  | Acrolein                   | 5.40–5.56  | 5.48      | 5.35–8.04 | 6.80       | 2.67–10.7 | 6.69       | 4.35–10.6 | 7.49       | 4.28–9.69  |
| 66  | Propional                  | 0.66–1.07  | 0.86      | 0.77–1.80 | 1.30       | 0.17–0.82 | 0.50       | 0.49–1.18 | 0.84       | 0.46–1.00  |
| 67  | Butanal                    | 3.15–4.29  | 3.72      | 3.74–8.01 | 5.88       | 0.52–8.60 | 4.56       | 3.93–9.73 | 5.93       | 3.08–6.86  |
| 68  | Benzaldehyde               | 0.30–0.35  | 0.32      | 0.37–0.55 | 0.46       | 0.22–0.30 | 0.30       | 0.09–0.29 | 0.21       | 0.09–0.38  |
| 69  | Pentanal                   | 1.19–1.49  | 1.34      | 1.62–2.92 | 2.27       | 1.63–3.16 | 1.66       | 0.85–2.37 | 1.61       | 0.53–1.37  |
| 70  | Hexanal                    | 6.97–7.96  | 7.46      | 10.3–17.0 | 13.6       | 2.74–6.14 | 4.44       | 4.56–7.80 | 6.18       | 1.75–3.92  |

**Solvents**

| No. | Compounds                  | Indoor air |           |           |           |           |           |           |           |           |
|-----|----------------------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|     |                            | S1 Range   | S2 Average | S3 Range  | S4 Average | S5 Range  | S6 Average | S7 Range  | S8 Average |
| 251 | 251                      | 251        | 277       | 344–604  | 432       | 253–315  | 285       | 286–671  | 458       | 308–355  |
| 456 | 456                      | 456        | 456       | 539–545  | 439       | 326–417  | 368       | 326–774  | 541       | 405–473  |

n.d. = not detected; "MQL" = below method quantification limit.

PGMEA = propylene glycol methyl ether acetate, EGBE = ethylene glycol butyl ether, DEGEE = diethylene glycol ethyl ether, TMPD = 2,2,4-trimethyl-1,3-pentanediol, DGBE = diethylene glycol butyl ether.

In bold are shown the target compounds classified as semi-VOCs according to the definitions of VOCs stated in the European Directives 1999/13/EC (EU, 1999) and 2004/42/CE (EU, 2004).

* The theoretical diffusive uptake rates provided by the suppliers of the tubes were applied for the quantification.
concentrations of solvents detected in 2021 is strictly related to the COVID-19 measures implemented in schools, while other indoor sources of the target compounds are relegated to the background. More specifically, these measures include more intensive cleaning activities conducted in the classrooms and other indoor settings, and the use of hydralcoholic gels for personal hygiene. Although the classrooms were periodically ventilated, this was not sufficient to counteract the increase in the use of cleaning products and avoid the increase in solvent concentrations.

Due to the high concentrations of Solvents found in the school in 2021, the concentrations of aldehydes were monitored since they are known to be degradation products of primary alcohols (Carey et al., 2007). As Table 2 summarizes, aldehydes were ubiquitous throughout the school and the sum of their average concentrations (ΣAldehydes) ranged from 23.6 μg m⁻³ (S7) to 46.7 μg m⁻³ (S6). The aldehydes that contributed the most to ΣAldehydes were formaldehyde, acrolein and hexanal, with concentrations ranging from 4.09 μg m⁻³ (S7) to 23.2 μg m⁻³ (S6). The remaining aldehydes were found at average concentrations ranging from 0.21 μg m⁻³ (S4 and S6) to 6.92 μg m⁻³ (S6) while isopentanal was not detected in any of the samples analysed. The range of aldehyde concentrations in the kindergarten (S1) and primary school (S2-S4) were generally comparable to those found in urban schools from Central-Southern Spain, 0.5 μg m⁻³-35.7 μg m⁻³ for kindergartens and 0.5 μg m⁻³-31.1 μg m⁻³ for primary schools, using the same method (Villanueva et al., 2018). On the other hand, they reported average concentrations for formaldehyde (14.8 μg m⁻³-35.7 μg m⁻³) that at least treble those found in this study (Villanueva et al., 2018). Formaldehyde levels found by Bradman et al. (2017) in early childhood education centers in California using active sampling were between 0.7 μg m⁻³ to 48.8 μg m⁻³ thus doubling the values found in this study. The concentrations of aldehydes found in the school settings were also compared with those found in the living rooms of three houses (H1 – H3). Table 3 summarizes the average and the median concentrations of the target aldehydes found in the houses under study, as well as the concentration ranges of each aldehyde. As Fig. 2 shows, houses H1 and H2 presented similar values for ΣAldehydes, i.e. 35.1 μg m⁻³ and 49.3 μg m⁻³, respectively. As Table 3 shows, slightly lower concentrations of aldehydes were found in H1 because the weekly cleaning was done with bleach, known by-products of which are carbon tetrachloride and chloroform (Odabasi et al., 2014). H3, on the other hand, showed an average value for ΣAldehydes of 164 μg m⁻³, with acrolein as the most prevalent aldehyde (135 μg m⁻³). A probable explanation for that is the intensive cleaning carried out with chemical products. In fact, the presence of acrolein in the composition labels of the cleaning products used was confirmed. The concentrations of aldehydes found in H1 and H2 were generally comparable to those found in the school in terms of average ΣAldehydes and the most prevalent compounds. The values of ΣAldehydes found in H1 and H2 were slightly lower than those reported by Diodiu et al. (2016) in Romanian houses in which the same sampling methodology was used.

Table 3

| No. | Compounds      | Indoor air |
|-----|----------------|------------|
|     |                | H1         | H2         | H3         |
|     |                | Range      | Median     | Average    | Range      | Median     | Average    | Range      | Median     | Average    |
| 1   | Formaldehyde   | 5.85-8.84  | 6.50       | 7.35       | 8.69-13.8  | 10.9       | 11.3       | 10.9-12.7  | 11.3       | 11.8       |
| 2   | Acetaldehyde   | 0.60-4.20  | 1.85       | 2.40       | 3.59-7.39  | 5.68       | 5.49       | 2.55-2.97  | 2.75       | 2.77       |
| 3   | Acrolein       | 3.66–16.5  | 8.54       | 10.1       | 11.0–12.2  | 11.8       | 11.6       | 119–151    | 128        | 135        |
| 4   | Propanal       | “MQL”–0.98 | 0.45       | 0.50       | 1.29–2.08  | 1.81       | 1.68       | n.d.       |            |            |
| 5   | Butanal        | “MQL”–9.37 | 1.05       | 4.72       | 4.77–7.55  | 5.87       | 6.16       | 4.29–4.55  | 4.35       | 4.51       |
| 6   | Benzaldehyde   | 0.15–0.24  | 0.18       | 0.20       | n.d.       | 1.75–1.81  | 1.85       | 1.78       |            |            |
| 7   | Pentanal       | 1.22–2.54  | 1.76       | 1.88       | 1.57–3.97  | 2.55       | 2.77       | 147–181    | 168        | 164        |
| 8   | Hexanal        | 5.42–10.5  | 6.24       | 7.98       | 7.24–13.5  | 8.54       | 10.4       | 7.85–7.90  | 7.89       | 7.88       |
| ΣAldehydes | 17.0–53.2    | 27.8       | 35.1       | 38.2–60.6  | 45.4       | 49.3       | 147–181    | 168        | 164        |

n.d. = not detected; “MQL” = below method quantification limit.

The theoretical diffusive uptake rates provided by the suppliers of the tubes were applied for the quantification.
(5 μg m⁻³⁻150 μg m⁻³). Even so, the average concentrations of formaldehyde (50 μg m⁻³) and acrolein (25 μg m⁻³) found in the Romanian houses were five and two times higher, respectively, than those observed in H1 and H2. The average levels of formaldehyde (55.0 μg m⁻³) and acetaldehyde (28.8 μg m⁻³) found in different houses of the Central-Southern Spain using radial passive sampling were also much higher than the values found in H1 and H2 (Villanueva et al., 2015b).

3.2.2. Outdoor air quality

The target compounds were monitored at five outdoor sites in Tarragona city centre and four towns close to Tarragona’s northern industrial complex between April and June 2021. Table 4 shows the maximum, minimum and average gas phase concentrations found for the 42 target compounds detected in at least one of the outdoor air samples analysed. Information on median concentrations and detection rates can be found in Table 3S.

The ΣTotal values observed at the outdoor sites ranged from 12.8 μg m⁻³ (Sant Salvador) to 30.0 μg m⁻³ (Constanti). The target compounds classified as ΣOthers were present at average values ranging from 4.47 μg m⁻³ (Els Pallaresos) to 22.5 μg m⁻³ (Constanti), which represent 16%-78% of the ΣTotal. The ΣSolvents, on the other hand, represented 9%-72% of the ΣTotal, with concentrations ranging from 1.59 μg m⁻³ (Perafort) to 20.0 μg m⁻³ (Els Pallaresos). None of the EOCS included in the present study were detected in the outdoor air samples. Even with some ups and downs in the concentrations of the target compounds conditioned the average values obtained, the global concentrations found by families followed a normal distribution.

Although the ΣOthers included in this study can be generated by different combustion processes (Pandit et al., 2011), our results are clear evidence that traffic is one of the main sources of ΣOthers when sampling is conducted in urban zones. Irrespective of the outdoor setting evaluated, i-pentane was the most prevalent target compound, with average concentrations ranging from 1.29 μg m⁻³ (Els Pallaresos) to 10.2 μg m⁻³ (Constanti). Other compounds that stood out from the rest were n-pentane and carbon tetrachloride (CCl₄) with values between 0.57 μg m⁻³ (Els Pallaresos) and 4.89 μg m⁻³ (Constanti) and from 0.99 μg m⁻³ (Els Pallaresos) to 2.21 μg m⁻³ (Constanti), respectively. Although the production and use of CCl₄ was banned by the “Montreal Protocol on Substances that Deplete the Ozone Layer”, the concentrations found in this study were comparable to those reported by some authors in the field in the region of Tarragona or in other regions of Spain (Gallego et al., 2016; Maceira et al., 2017; Ramírez et al., 2012). Three main points could explain the concentrations of CCl₄ still found in outdoor air samples; incomplete data on historical production of CCl₄, uncertainties in the atmospheric lifetime of CCl₄ and CCl₃ from unreported or underestimated emission sources, (HMPSDOL, 2020).

However, future research is needed for a better understanding of the behaviour of CCl₄ in the atmosphere.

The concentrations of ethanol in Tarragona city centre and Els Pallaresos also stood out since their average values were 3.38 μg m⁻³ and 2.10 μg m⁻³, respectively. The concentrations of 1-propanol (7.96 μg m⁻³) and ethyl acetate (7.64 μg m⁻³) in Els Pallaresos were much higher than those found in the rest of outdoor sites evaluated, probably due to proximity of the sampling point to a printing company. Overall, the Others data obtained in this study was comparable, in terms of prevalent compounds and concentrations levels, with that reported by Ramírez et al. (2012) when monitoring the presence of VOCs in the same sampling area. On the other hand, the levels of Others in Constanti were lower than those found in 6 L punctual air samples by Maceira et al. (2017).

The highest average concentrations of VOCs linked to the chemical and petrochemical industries were found in Constanti and Perafort due to the proximity of these towns to Tarragona’s northern industrial complex and the prevailing north (N) and north-westernly (NW) wind directions during the period of study. The average concentrations of benzene were 0.70 μg m⁻³ in Perafort and 0.76 μg m⁻³ in Constanti, both of which were below the 5 μg m⁻³ established as the maximum annual average value permitted in immission zones in accordance with Spanish Royal Decree 102/2011 (RD, 2011) and in line with the values measured in other industrial and suburban sites in Spain and Italy (de Gennaro et al., 2013; Villanueva et al., 2018). Higher concentrations of benzene, between 0.48 μg m⁻³ and 1.50 μg m⁻³, were reported by Ramírez et al. (2012) at the same sampling zone. Still unregulated in Spain, the average concentrations of 1,3-butadiene at Perafort were 0.75 μg m⁻³ and 0.84 μg m⁻³ at Constanti, which were far below the 2.00 μg m⁻³ maximum annual average concentration in Ontario (AAQC, 2011) and the concentrations reported by Vallecillos et al. (2018) and Gallego et al. (2018) at the north industrial park of Tarragona (0.17–5.20 μg m⁻³). The average concentration of styrene found at Perafort (0.82 μg m⁻³) also stood out from the rest.

Aldehydes were also evaluated at outdoor sites since they can be emitted directly into the atmosphere via the incomplete combustion of biomass or fossil fuels or as secondary air pollutants from the photo-oxidation of hydrocarbons (Herrington and Hays, 2012; Marchand et al., 2006). As several authors have reported (EPA, 2021; Troquet et al., 2021), the average concentrations of total aldehydes observed outdoors were much lower than those observed indoors. The ΣAldehydes found outdoors ranged from 1.12 μg m⁻³ to 3.83 μg m⁻³, with the highest average concentrations being found at Constanti and Els Pallaresos due to the proximity of those towns to industrial areas. Formaldehyde, whose values ranged from 0.33 μg m⁻³ (Sant Salvador) to 1.55 μg m⁻³ (Constanti), was the aldehyde found at the highest concentrations. Acetaldehyde, acrolein, propanal and butanal were also found at all outdoor samples, with values ranging from...
Table 4 Concentrations of the target compounds (μg m⁻³) found in the gas phase of outdoor air samples from five towns with different casuistries. N = 14 fourteen-day passive sampling.

| No. | Compounds | Outdoor air | Perafort | Sant Salvador | Tarragona | Els Pallaresos |
|-----|-----------|-------------|---------|---------------|-----------|----------------|
|     |           | Range       | Average | Range         | Average   | Range          | Average |
| Solvents |           | n.d. | 0.12 | 0.20 | n.d. | 0.06 | 0.09 | 0.12 | 0.09 | 0.06 | 0.09 |
| n.d. | Ethanol  | MQI-4.72   | 0.79 | n.d. | MQI-0.34 | 0.06 | MQI-16.2 | 3.38 | 0.72-3.84 | 2.10 |
| 2   | Isopropyl alcohol | MQI-0.41 | 0.11 | n.d. | MQI-0.41 | n.d. | n.d. | 0.58-1.39 | 0.97 |
| 2   | Dichloromethane | 0.16-2.45 | 1.01 | 0.16-0.72 | 0.30 | 0.17-0.58 | 0.46 | 0.26-1.54 | 0.87 | 0.14-0.26 | 0.18 |
| 4   | 1-Propanol | MQI-0.37 | 0.07 | MQI-0.32 | 0.10 | MQI-0.69 | 0.35 | MQI-0.80 | 0.25 | 3.12-14.0 | 7.96 |
| 5   | 2-Butanone | MQI-0.20 | 0.12 | n.d. | MQI-0.20 | n.d. | n.d. | 0.18-1.53 | 0.70 |
| 5   | n-Hexane | 0.40-2.10 | 1.17 | 0.05-1.11 | 0.51 | 0.11-0.38 | 0.26 | MQI-0.13 | 0.05 | MQI-0.19 | 0.09 |
| 7   | Ethyl acetate | MQI-0.34 | 0.06 | MQI-0.34 | n.d. | MQI-0.33 | 0.15 | 2.08-17.1 | 7.64 |
| 8   | Toluene | 0.49-1.19 | 0.88 | 0.42-0.80 | 0.63 | 0.31-0.72 | 0.51 | 0.75-1.56 | 1.02 | 0.18-0.58 | 0.42 |
| Others | 1,3-butadiene | 0.47-1.77 | 0.84 | 0.23-1.50 | 0.75 | 0.15-0.45 | 0.27 | 0.16-0.53 | 0.33 | 0.14-0.26 | 0.19 |
| 22  | Ethylbenzene | 0.18-0.80 | 0.43 | 0.21-1.62 | 0.75 | 0.11-0.40 | 0.25 | 0.12-0.35 | 0.24 | 0.22-0.15 | 0.18 |
| 23  | x-Pyrene | 0.14-0.69 | 0.30 | 0.14-0.48 | 0.26 | 0.13-0.43 | 0.26 | 0.21-0.50 | 0.36 | 0.11-0.29 | 0.19 |
| 24  | Styrene | 0.09-0.21 | 0.22 | 0.01-1.80 | 0.82 | 0.03-0.30 | 0.19 | 0.01-0.18 | 0.09 | MQI-0.08 | 0.04 |
| 25  | o-Xylen | 0.11-0.49 | 0.22 | 0.10-0.34 | 0.21 | 0.11-0.30 | 0.20 | 0.16-0.37 | 0.28 | 0.13-0.18 | 0.16 |
| 26  | Isopropylbenzene | 0.01-0.09 | MQI | 0.01-0.06 | 0.03 | 0.01-0.07 | 0.03 | 0.01-0.03 | 0.02 | MQI |
| 27  | n-Propylbenzene | 0.01-0.12 | MQI | 0.01-0.14 | 0.04 | 0.02-0.15 | 0.17 | 0.01-0.05 | 0.03 | 0.02-0.08 | 0.05 |
| 28  | 1,3,5-Trimethylbenzene | 0.01-0.19 | MQI | 0.01-0.16 | 0.10 | 0.03-0.20 | 0.13 | 0.01-0.12 | 0.06 | 0.04-0.10 | 0.06 |
| 29  | 1,2,4-Trimethylbenzene | 0.03-0.54 | MQI | 0.03-0.28 | 0.10 | 0.04-0.18 | 0.36 | 0.02-0.15 | 0.10 | 0.04-0.31 | 0.18 |
| 30  | 1,4-Dichlorobenzene | 0.01-0.12 | MQI | 0.01-0.14 | 0.04 | 0.02-0.15 | 0.17 | 0.01-0.05 | 0.03 | 0.02-0.08 | 0.05 |
| 31  | 1,2,3-Trimethylbenzene | MQI | MQI | MQI | MQI | MQI | MQI | MQI |
| 32  | Naphthalene | MQI | MQI | MQI | MQI | MQI | MQI | MQI |
| 33  | 2-Methylnapthalene | MQI | MQI | MQI | MQI | MQI | MQI | MQI |
| 34  | 1-Methylpyridine | MQI | MQI | MQI | MQI | MQI | MQI | MQI |
| Aldehydes | Formaldehyde | 0.38-2.72 | 1.55 | MQI-1.14 | 0.52 | MQI-0.67 | 0.33 | MQI-1.81 | 0.76 | MQI-0.85 | 0.47 |
| 36  | Acetaldehyde | 0.33-0.41 | 0.37 | MQI-0.77 | 0.32 | MQI-0.34 | 0.15 | MQI-0.68 | 0.28 | MQI-0.52 | 0.26 |
| 36  | Acrolein | 0.29-0.87 | 0.58 | MQI-1.83 | 0.77 | MQI-0.73 | 0.31 | MQI-1.94 | 0.44 | MQI-1.31 | 0.65 |
| 39  | Propional | MQI | MQI | MQI | MQI | MQI | MQI | MQI |
| 39  | Butanal | MQI-0.69 | MQI-1.14 | 0.51 | MQI-0.46 | MQI-0.94 | 0.42 | MQI-1.11 | 0.56 |
| 40  | Benzaldehyde | MQI-0.11 | MQI-0.17 | MQI | MQI | MQI | MQI | MQI |
| 41  | Pentanal | MQI-0.58 | MQI-0.15 | MQI | MQI-0.52 | MQI-0.81 | 0.41 |
| 42  | Hexanal | MQI-0.46 | 0.21 | n.d. | MQI-0.52 | 0.24 | MQI-0.81 | 0.41 |
| Solvents | 0.14 μg m⁻³ (Sant Salvador) to 0.76 μg m⁻³ (Perafort). Our results were higher than those reported by Villanueva et al. (2018) for urban and industrial air samples from central-southern Spain. Furthermore, Li et al. (2018) reported much higher concentrations of aldehydes, between 0.21 μg m⁻³ and 9.29 μg m⁻³, in suburban air samples from Louisville (U.S.). Regardless of the study, the most prevalent aldehydes were the same, and formaldehyde, whose average values ranged from 1.00 μg m⁻³ to 5.96 μg m⁻³, also stood out from the rest (Li et al., 2018; Villanueva et al., 2018).

3.2.3. Indoor vs. outdoor air quality

The concentrations of the target compounds observed at the indoor sites, i.e. the school and houses, were much higher than those found at the outdoor sites due to the limited dispersion of the target compounds even with periodic ventilation. The average ΣTotal obtained at the indoor sites was 442 μg m⁻³, whereas outdoors this figure dropped to 21.5 μg m⁻³. The average ΣTotal outdoor figure was twenty times lower than the indoor figure. Moreover, as the pie charts in Fig. 3 show, the part played by each family of target compounds at the indoor sites was different from the part they played outdoor. Indoors, ΣSolvents contributed the most (79%) to ΣTotal. The contributions of ΣEOCs, ΣOthers and ΣAldehydes ranged from 5% to 10%. On the other hand, the outdoor environments were characterized by an average ΣOthers contribution of 58%, while ΣSolvents represented a 31% and ΣAldehydes an 11%. EOCS were not detected in any outdoor sample analysed. Although the concentrations of ΣTotal
were much higher indoors than outdoors, the target compounds with the greatest contribution ($\Sigma$Solvents) often did not present a health risk or their reference values for risk-assessment estimations for inhalation of these compounds is much lower than for the most common VOCs and semi-VOCs in outdoor atmospheres. The USEPA Risk Assessment Information System (RAIS, 2021), does not provide risk-assessment data on the EOCs evaluated in this study, while the compounds that contribute most to risk assessment are aldehydes and VOCs and semi-VOCs linked to industrial processes.

The high solvent content in the chemical formulations of cleaning products and the intensive use of these compounds during COVID-19 pandemic is a likely explanation for the high contribution of solvents to the $\Sigma$Total observed indoors. Other important sources of VOCs and semi-VOCs at the school, such as building materials and the students and teachers themselves (Even et al., 2020; Trocquet et al., 2021; Yang et al., 2018), have been relegated to the background. Our analyses of outdoor air samples provide clear evidence of the contribution to air quality of incomplete combustion processes, especially traffic emissions, in urban zones (Pandit et al., 2011). The towns located near Tarragona’s northern industrial complex also showed a higher presence of the VOCs produced and handled in the area.

4. Conclusions

In this study passive sampling in CX tubes was successfully used to determine 70 of the target compounds (including solvents, EOCs, aldehydes and others) in the gas phase of indoor settings at a school in Tarragona and 42 target compounds in outdoor environments around Tarragona, Spain.

With regard to indoor air samples, the $\Sigma$Total values ranged from 343 $\mu$g m$^{-3}$ to 563 $\mu$g m$^{-3}$, with $\Sigma$Solvents contributing 71%–85% of the $\Sigma$Total. Solvents were ubiquitous throughout the school, with ethanol and isopropyl alcohol being the most prevalent. If we compare the current results with those reported by Vallecillos et al. (2020a, 2020b) at the same school two years earlier, we find that the $\Sigma$Total values for 2021 were three times as high as those reported in 2019. Regardless of the indoor setting evaluated, the compounds with the greatest increase in 2021 were $\Sigma$Solvents. This is because of the more intensive cleaning activities and the use of hydroalcoholic gels as anti-COVID-19 measures. Aldehydes were monitored because they are known to be degradation products of primary alcohols. Our results showed that formaldehyde, acrolein and hexanal were the most representative aldehydes, with values comparable to those reported by other authors (Villanueva et al., 2018) also in schools. Overall, no significant differences were detected between the values of $\Sigma$Aldehyde found at the school and the houses evaluated.

The $\Sigma$Total values found at the outdoor sites (ranging from 14.8 $\mu$g m$^{-3}$ to 33.0 $\mu$g m$^{-3}$) were twenty times lower than those found indoors, while EOCs were undetected. The $\Sigma$Others, whose percentage of $\Sigma$Total was 16%–78%, were the most representative compounds, which shows that road traffic is one of the main sources of air pollution in urban areas. Although some peak concentrations of compounds linked to chemical industries were detected in towns close to Tarragona’s northern industrial complex, none of the outdoor settings exceeded the maximum annual average concentrations. Therefore, the concentrations of the target compounds observed do not present a potential health risk. Although the concentrations of VOCs and semi-VOCs in indoor environments were much higher than those outdoors, the most prevalent target compounds, i.e. $\Sigma$Solvents, either do not present a health risk or their reference values for preforming risk assessment are much lower than those of the most common VOCs and semi-VOCs in outdoor atmospheres.

CRediT authorship contribution statement

Nicole Ninyà: Introduction, method development and validation, research, writing of original draft, review, and editing. Laura Vallecillos: Introduction, method development and validation, research, writing of 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 affiliation with any organization that has financial or non-financial interest in the subject matter or materials discussed in this manuscript.

Acknowledgments

The authors wish to thank Col·legi Sant Pau Apòstol in Tarragona and the pupils who participated in this project for their cooperation and support at every stage of the study. We also wish to thank the Department of Territory and Sustainability of the Government of Catalonia in Tarragona for providing access to Government of Catalonia’s XVPCA monitoring cabins.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.155611.
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