



Green methodology based on active air sampling followed by solid phase microextraction and gas chromatography-tandem mass spectrometry analysis to determine hazardous substances in different environments related to tire rubber

Daniel Armada^a, Maria Celeiro^a, Thierry Dagnac^b, Maria Llompart^{a,*}

^aCRETUS, Department of Analytical Chemistry, Nutrition and Food Science, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain

^bAgronomic Research Centre (AGACAL-CIAM), Unit of Organic Contaminants, Apartado 10, E-15080, A Coruña, Spain

ARTICLE INFO

Article history:

Received 13 December 2021

Revised 9 February 2022

Accepted 16 February 2022

Available online 24 February 2022

Keywords:

Air analysis

Crumb rubber

Gas chromatography-tandem mass spectrometry

Hazardous compounds

Solid-phase microextraction

Tire rubber materials

ABSTRACT

A fast, efficient, and simple air sampling methodology was developed to study a high number of volatile and semivolatile organic compounds in air above tire rubber materials and surfaces made of recycled tire rubber. The proposed method, based on active sampling (solid-phase extraction, SPE) using a small quantity of sorbent material (25 mg) followed by solid-phase microextraction (SPME) and gas chromatography-tandem mass spectrometry analysis, was developed with the aim of determining 40 organics substances including polycyclic aromatic hydrocarbons (PAHs), plasticizers, antioxidants, and vulcanization agents. An experimental design was carried out to study the influence of main factors such as type of SPME fibre, solvent addition, headspace volume, stirring, as well as the factor interactions. Method performance showed good linearity in a broad concentration range (0.05 to 200 ng m⁻³, for most compounds), with coefficients of determination (R²) higher than 0.9900. Whole method precision (≤ 16 %) and accuracy were also satisfactory, obtaining quantitative recoveries (mean values between 80 and 110 % in most cases). Limits of detection and quantification have also been calculated, yielding values of sub ng m⁻³ for most compounds. The validated method was applied to outdoor and indoor air environments including playgrounds, football pitches and warehouses showing the presence of most target compounds in the samples achieving high levels for some PAHs (concentrations up to 51 ng m⁻³), benzothiazole (BTZ), diisobutyl- dibutyl- and di-(2-ethylhexyl)- phthalate, among others, reaching concentrations up to hundreds of ng m⁻³ (BTZ). This is the first time that the combination of techniques SPE and SPME is applied for these families of chemicals, and it is also the first time that this approach is proposed for the simultaneous multiclass compound extraction of substances of different chemical families. The whole sampling and extraction procedure is performed in a short period of time (61 min) allowing high throughput. The elimination of the use of organic solvents and waste generation by using only 25 mg of sorbent and a SPME fibre than are both reused makes the method sustainable and in consonance with the principles of the green chemistry. The method can be implemented in any routine lab and easily automated using a SPME autosampler.

© 2022 The Author(s). Published by Elsevier B.V.

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

1. Introduction

Tire waste management is a problem in most developed societies due to the increasing number of tires discarded each year and the environmental problems associated with them [1]. As example, in 2019, 3.45 million tonnes of end-of-life tires (ELTs) were generated in Europe (27 European Union countries plus Norway,

Serbia, Switzerland, Turkey and United Kingdom) [2]. For this reason, in last years, diverse ways of recycling ELTs have been implemented to give old tires a second useful life [3]. In 2019, 94% of ELTs were collected and treated for material recycling and energy recovery [2]. The most common and easy way to reuse ELTs is the transformation in crumb rubber, a material that is employed to construct new facilities such as childrens' playgrounds or to be used as infill in synthetic turf football pitches [4]. These recycled products contain many substances, which can be harmful to the environment and to human health such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), alkylphe-

* Corresponding author.

E-mail address: maria.llompart@usc.es (M. Llompart).

nols, plasticizers, antioxidants, vulcanisation additives, benzothiazoles, chlorinated paraffins, heavy metals, among others [5–11]. PAHs are considered as persistent organic pollutants, and present adverse properties such as carcinogenic, bioaccumulative, or toxic, among others according to the European Chemicals Agency (ECHA) [12]. Recent studies have demonstrated the diffusion of these and other compounds from car tires and recycled crumb rubber to the aquatic environment and to the atmosphere [13–15], where they can be taken up through inhalation. Several individual PAHs (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene and indene[1,2,3-cd]pyrene), total PAHs), as well as polychlorinated biphenyls (PCBs) are monitored in air by the European Union Member States, and results are provided in the Annual Emission Report for Atmospheric Pollutants Directive [16]. Benzo[a]pyrene, which is carcinogenic and toxic for reproduction, is regulated by European Union with a maximum concentration level of 1 ng m^{-3} in particulate matter (PM_{10}) ambient air [17].

Air analysis is a difficult task that usually comprises a sampling step using solid sorbents. Active and passive sampling strategies can be carried out [18]. The number of studies intended to measure the pollutants spread out by car tires and recycled crumb rubber into the surrounding air is very scarce. Several sampling methods, including lab-scale studies and *in-situ* sampling have been employed. Some approaches based on SPME [13,19,20], active air sampling [21–24] and passive sampling using common sorbents (polyurethane foam, silicone samplers), have been reported for monitoring PAHs, plasticizers and other compounds nearby artificial pitches [7,25]. However, there is not much information about the composition of the air above rubber playgrounds and these qualitative studies have been only performed at lab-scale using SPME. The studies that include real sample analysis employed multistep extraction procedures based on Soxhlet extraction, liquid-liquid and solid-liquid extraction requiring quite large volumes (hundreds of mL) of organic solvents (hexane, dichloromethane, etc.) [22,23,25] and long extraction times (from 45–120 min). In addition, there is not much information about the composition of the air above rubber playgrounds since only lab-scale qualitative studies have been reported [6,26]. Active air sampling followed by SPME was successfully applied for the determination of organic compounds such as synthetic musks and fragrance allergens in air [27,28]. In a previous study performed by the authors, a simple, fast and sustainable methodology for the analysis of PAHs, plasticizers, antioxidants and vulcanisation additives present in air adjacent to tire rubber and crumb rubber materials was developed [14].

Therefore, the main goal of this study is to develop a green SPE-SPME procedure followed by GC-MS/MS analysis, for the analysis of PAHs, plasticizers, antioxidants and vulcanisation additives present in air samples from tire rubber environments. To the best of our knowledge, this is the first time that SPE followed by SPME is proposed for the extraction and enrichment of these families of hazardous compounds. The elimination of waste generation and the use of negligible volumes of organic solvent make this method a green and sustainable alternative. Critical SPME parameters (i.e., type of fibre, solvent addition, headspace volume, stirring) were optimized by design of experiments (DOE) strategy to obtain the highest extraction efficiency. The validated method was applied to the analysis of real air samples collected in different environments related to tire rubber or recycled tire rubber.

2. Experimental

2.1. Reagents and materials

The 40 target compounds, their CAS numbers, retention times, and MS/MS transitions are summarized in Table 1. Their inhala-

tion reference doses [29] are also included in Table 1. Ethyl acetate (EtAc, 99.5%), methanol (MeOH, 99.9%), and acetone (99.9%) were supplied by Sigma-Aldrich Chemie (Stenheim, Germany). A 16 EPA PAH solution ($2000 \mu\text{g mL}^{-1}$) was provided by Supelco (Bellefonte, USA), B[j]F ($2000 \mu\text{g mL}^{-1}$) and B[e]P ($100 \mu\text{g mL}^{-1}$) solutions prepared in dichloromethane were provided by Sigma-Aldrich. For plasticizers, antioxidants and vulcanisation additives individual stock solutions ($10000\text{--}25000 \mu\text{g mL}^{-1}$) were prepared in methanol. Purity of the 40 target compounds ranged between 95 and 99%. Working mixtures were prepared in acetone. All solutions were stored in amber glass vials at $-20 \text{ }^\circ\text{C}$. Glass wool and Tenax TA porous polymer sorbent (mesh size: 60/80) was purchased from Supelco (Stenheim, Germany). All reagents and solvents were of analytical grade.

Commercial $100 \mu\text{m}$ polydimethylsiloxane (PDMS), $65 \mu\text{m}$ polydimethylsiloxane/divinylbenzene (PDMS/DVB), $50/30 \mu\text{m}$ divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), and $85 \mu\text{m}$ polyacrylate (PA) SPME fibres and a manual SPME holder were provided by Supelco. Before use, the fibres were conditioned following manufacturer recommended instructions, inserting them in the GC injector under helium flow at $250 \text{ }^\circ\text{C}$ (PDMS and PDMS/DVB), $270 \text{ }^\circ\text{C}$ (DVB/CAR/PDMS) and $280 \text{ }^\circ\text{C}$ (PA) for 30 min.

Since one of the studied families was plasticizers, the plastic material was replaced by glass and metallic material to avoid possible contamination and overestimation in the results. All material was also maintained at $230 \text{ }^\circ\text{C}$ for 12 h before use.

The Telstar S-8 vacuum pump was purchased from Telstar (Tarasa, Spain). A flowmeter was used for the analyses in order to measure the volume of air pumped. The pump was operated to the maximum flow ($3.6 \text{ m}^3 \text{ h}^{-1}$).

2.2. Samples

Air sampling was performed at 8 different locations in several municipalities of Galicia (NW Spain), comprising indoor, children's playground, tire warehouses and a warehouse containing some recycled rubber material, and outdoor, synthetic turf football pitches and playgrounds, environments. A detailed description of the sampling areas is included in Supplementary Table S1. Air samples from outdoor children's playgrounds were collected in outdoor playgrounds in sunny days, both located in places where there is almost no vehicle traffic. In the case of the outdoor playgrounds, air of the surrounding area (approx. 25 m of distance to the playground) was sampled to discard other potentially source of pollution which could affect the assessment. In addition, one indoor playground was collected in a shopping centre. Air from football pitches was collected in areas with a low traffic density. In addition, air of the surrounding area (in the stands of the pitch, approx. 15 m, OP2) was sampled to check whether exposure can affect not only players, referees and technical staff, but also spectators. Two tire warehouses without ventilation were also sampled. One of them stored new car tires (TW1) and the other ELTs (TW2).

In addition, crumb rubber samples (0.2 g) employed as flooring in the outdoor playgrounds (OP1, OP2) were subjected to UAE (2 mL ethyl acetate, ultrasound bath at 50 kHz) during 20 min and at $25 \text{ }^\circ\text{C}$. The extracts were filtered through $0.22 \mu\text{m}$ PTFE filters and diluted ($1:10$, *v/v*) in ethyl acetate prior the analysis by GC-MS/MS.

2.3. SPE procedure

Active air sampling conditions based on SPE, were adapted from those previously optimized by the authors [14]. Briefly, 1 m^3 of air was pumped through 25 mg of sorbent (Tenax TA) packed on a 2 mL polypropylene cartridge employing a vacuum pump (Telstar

Table 1
Target compounds, CAS number, retention time, MS/MS transitions and inhalation reference dose values.

| Code | Compound | CAS | RetentionTime (min) | Quantification and identificationTransitions (CE, eV) ^a | Inhalation reference value for general population ($\mu\text{g m}^{-3}$) | Inhalation reference value for workers ($\mu\text{g m}^{-3}$) |
|---------------------|----------------------------|----------|---------------------|--|--|---|
| PAHs | | | | | | |
| NAP | Naphthalene | 91-20-3 | 7.81 | 128→102(30), 128→78(25) | - | - |
| ACY | Acenaphthylene | 208-96-8 | 10.40 | 152→151(10), 152→126(10), 152→102(30) | - | - |
| ACE | Acenaphthene | 83-32-9 | 10.68 | 154→152(30), 154→153(30), 153→126(40) | - | - |
| FLU | Fluorene | 86-73-7 | 11.52 | 166→165(10), 166→163(10), 165→139(30) | - | - |
| PHN | Phenanthrene | 85-01-8 | 13.19 | 178→176(30), 178→152(30) | - | - |
| ANC | Anthracene | 120-12-7 | 13.28 | 178→176(30), 178→152(30) | - | - |
| FLA | Fluoranthene | 206-44-0 | 16.01 | 202→200(30), 202→201(30), 202→176(30) | - | - |
| PYR | Pyrene | 129-00-0 | 16.65 | 202→200(30), 202→201(30), 202→176(30) | - | - |
| B[a]A | Benzo[a]anthracene | 56-55-3 | 20.85 | 228→202(20), 228→226(30) | - | - |
| CHY | Chrysene | 218-01-9 | 20.98 | 228→226(30), 228→202(20) | - | - |
| B[b]F | Benzo[b]fluoranthene | 205-99-2 | 25.00 | 252→250(30), 250→248(30), 252→226(30) | - | - |
| B[j]F | Benzo[j]fluoranthene | 205-82-3 | 25.01 | 250→248(30), 250→249(30), 252→250(30) | - | - |
| B[k]F | Benzo[k]fluoranthene | 207-08-9 | 25.10 | 252→250(30), 252→226(30), 250→248(30) | - | - |
| B[e]P | Benzo[e]pyrene | 192-97-2 | 26.00 | 252→250(30), 250→224(25), 250→248(30) | - | - |
| B[a]P | Benzo[a]pyrene | 50-32-8 | 26.15 | 252→250(35), 252→226(30) | 1•10 ^{-3b} [1] | - |
| IND | Indeno[1,2,3-cd]pyrene | 193-39-5 | 30.33 | 276→274(40), 276→250(35), 276→248(40) | - | - |
| D[ah]A | Dibenzo[ah]anthracene | 53-70-3 | 30.55 | 278→276(35), 278→252(30), 278→226(35) | - | - |
| B[ghi]P | Benzo[ghi]perylene | 191-24-2 | 31.41 | 276→274(35), 276→248(40) | - | - |
| Plasticizers | | | | | | |
| DMA | Dimethyl adipate | 627-93-0 | 8.19 | 111→83(10), 114→71(15), 114→113(10) | - | - |
| DEA | Diethyl adipate | 141-28-6 | 9.59 | 157→111(5), 157→83(15), 128→99(10) | - | - |
| DMP | Dimethyl phthalate | 131-11-3 | 10.24 | 163→77(20), 163→133(10), 163→135(10) | - | - |
| DEP | Diethyl phthalate | 84-66-2 | 11.40 | 176→149(10), 149→121(10) | - | - |
| DiBP | Diisobutyl phthalate | 84-69-5 | 13.64 | 149→65(25), 149→93(15), 149→121(15) | 25 ^c [2] | - |
| DBP | Dibutyl phthalate | 84-74-2 | 14.55 | 149→65(20), 149→93(15), 149→121(10) | 20 ^c [3] | 130 ^c [3] |
| DMEP | Di(methoxyethyl) phthalate | 117-82-8 | 14.91 | 149→65(20), 149→121(10), 104→76(10) | - | - |

(continued on next page)

Table 1 (continued)

| Code | Compound | CAS | RetentionTime (min) | Quantification and identification Transitions (CE, eV) ^a | Inhalation reference value for general population ($\mu\text{g m}^{-3}$) | Inhalation reference value for workers ($\mu\text{g m}^{-3}$) |
|--------------------------------------|----------------------------|------------|---------------------|---|--|---|
| DIPP | Diisopentyl phthalate | 605-50-5 | 15.70 | <u>149</u> →93(15), <u>149</u> →121(15), <u>237</u> →149(10) | - | - |
| DPP | Dipentyl phthalate | 131-18-0 | 16.64 | <u>149</u> →65(25), <u>149</u> →93(15), <u>149</u> →121(15) | - | - |
| BBP | Benzylbutyl phthalate | 85-68-7 | 19.20 | <u>206</u> →149(10), <u>149</u> →93(15), <u>149</u> →65(20) | 1700 ^c [3] | 9900 ^c [3] |
| DEHA | Di(2-ethylhexyl) adipate | 103-23-1 | 19.72 | <u>129</u> →101(5), <u>129</u> →83(10), <u>147</u> →101(10) | - | - |
| DIHP | Diisooheptyl phthalate | 41451-28-9 | 20.58 | <u>265</u> →149(30), <u>149</u> →121(30), <u>149</u> →65(30) | - | - |
| DCHP | Dicyclohexyl phthalate | 84-61-7 | 21.44 | <u>167</u> →149(10), <u>149</u> →65(25), <u>149</u> →93(15) | 630 ^c [2] | - |
| DEHP | Di(2-ethylhexyl) phthalate | 117-81-7 | 21.64 | <u>167</u> →149(10), <u>149</u> →121(15), <u>149</u> →93(15) | 120 (child) ^c [4] 160 (adult) ^c [4] | 880 ^c [4] |
| DPhP | Diphenyl phthalate | 84-62-8 | 21.79 | <u>225</u> →77(20), <u>225</u> →115(30), <u>225</u> →153(10) | - | - |
| DnOP | Di-n-octyl phthalate | 117-84-0 | 24.31 | <u>149</u> →93(15), <u>149</u> →121(15), <u>279</u> →149(10) | - | - |
| DiNP | Diisononyl phthalate | 28553-12-0 | 24.94 | <u>293</u> →149(30), <u>149</u> →93(30), <u>149</u> →65(30) | 870 (child) ^b [2] 1160 (adult) ^b [2] | - |
| DiDP | Diisodecyl phthalate | 26761-40-0 | 26.80 | <u>307</u> →149(30), <u>149</u> →65(30), <u>149</u> →93(30) | 380 (child) ^b [2] 900 (adult) ^b [2] | - |
| Vulcanizants and antioxidants | | | | | | |
| BTZ | Benzothiazole | 95-16-9 | 8.26 | <u>135</u> →108(15), 135 →91(10) | - | - |
| TBP | 4-tert-butylphenol | 98-54-4 | 8.77 | <u>150</u> →107(30), <u>150</u> →135(30) | - | - |
| BHA | Butylated hydroxyanisole | 121-00-6 | 10.53 | <u>165</u> →137(10), <u>180</u> →165(10), <u>137</u> →77(20) | - | - |
| BHT | Butylated hydroxytoluene | 128-37-0 | 10.72 | <u>220</u> →205(10), <u>205</u> →145(15), <u>205</u> →177(10) | - | - |

^a CE: Collision energy, expressed in electron volts (eV). Underlined MS/MS transition was the selected for quantification. ^b For benzo[a]pyrene as a marker for PAH mixture. ^c Limit for a derived no-effect level (DNEL) [1]. European Commission. Ambient air pollution by Polycyclic Aromatic Hydrocarbons (PAH). Position Paper, [2] A.G. Oomen, G.M. de Groot, G. M. Evaluation of health risks of playing sports on synthetic turf pitches with rubber granulate. National Institute for Public Health and the Environment, 2017 [3]. ECHA, 24th Meeting of the committee for risk assessment 5 - 8 MARCH 2013. RAC/24/2013/09 [4]. ECHA, 24th Meeting of the committee for risk assessment 5 - 8 MARCH 2013. RAC/24/2013/08.

model S-8; Tarrasa, Spain) at a controlled flow of 3.6 m³ h⁻¹). After SPE, the sorbent with the retained compounds was placed into a 10 mL glass vial and sealed with an aluminium cap furnished with a PTFE-faced septum. Finally, SPME (see Section 2.4) and ultrasound assisted extraction (UAE) were performed under the optimized conditions (see Section 2.4). For UAE, the obtained extract was filtered through polytetrafluoroethylene (PTFE 0.22 μm) filter, and directly analyzed by GC-MS/MS.

2.4. SPME procedure

After SPE, the vial containing the sorbent with the retained compounds was immersed in a controlled temperature water bath (100 °C) for 5 min. Then, the PDMS/DVB coating fibre was exposed to the headspace of the vial for 45 min without stirring (see optimal conditions in Section 3.1.2). To promote the extraction of the analytes, 100 μL of acetone were added. After the extraction time, the SPME fibre was desorbed at 270 °C in the GC injection port and GC-MS/MS analysis was carried out.

Optimization experiments, as well as the comparison with the UAE procedure, were performed spiking the sorbent at 25 ng g⁻¹ with the 40 target compounds.

To validate the method different concentrations of the target compounds were employed to spike the sorbent (Tenax TA). Linearity was assessed covering a concentration range from 0.05 to 200 ng g⁻¹, with 12 concentration levels (0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25, 50, 100 and 200 ng g⁻¹) and 3 replicates per level. In the case of DINP and DIDP concentration levels were 25, 50, 100, 250, 500, 750, 1000 and 1250 ng g⁻¹. Calibration curves were obtained by SPME. As the volume of air pumped in the experiments is 1 m³, the concentrations in ng m⁻³ are equivalent to ng g⁻¹ in the sorbent.

Limits of detection (LODs) and limits of quantification (LOQs) of the whole SPE-SPME-GC-MS/MS method were calculated as the compound concentration giving a signal-to-noise ratio (S/N) = 3 and (S/N) = 10, respectively. For the compounds that were detected in the SPME and procedure blanks, LODs and LOQs were calculated as the average concentration corresponding to the sig-

nal of the blank plus three and ten times its standard deviation, respectively.

The method precision was evaluated within a day ($n = 3$) and amongst several days ($n = 6$) at three concentration levels for the 40 target compounds.

Accuracy of the method was calculated by recovery experiments carried out by SPME-GC-MS/MS employing Tenax TA spiked at 2 concentration levels (7.5 and 75 ng m⁻³). Quantification was accomplished using calibration curves.

To prevent contamination and assess background levels and interferences, SPME fibre blank and whole procedure blanks (1 m³ of air sampled through 25 mg of Tenax TA and SPME for 45 min) were daily carried out.

2.5. GC-MS/MS analysis

The GC-MS/MS analysis was performed employing a Thermo Scientific Trace 1310 gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 8000) with an autosampler IL 1310 from Thermo Scientific (San Jose, CA, USA). Target compounds separation was achieved employing a Zebron ZB-Semivolatiles (30 m × 0.25 mm id × 0.25 μm film thickness) column supplied by Phenomenex (Torrance, CA, USA). Helium (purity 99.999%) was employed as carrier gas at a constant flow of 1.0 mL min⁻¹. The GC oven temperature was programmed from 60 °C (held 2 min) to 210 °C at 15 °C min⁻¹ and to 290 °C at 5 °C min⁻¹ (held 8 min). The total run time was 36 min. The injector was operated in pulsed split/splitless mode (200 kPa, held 1.2 min). Injector temperature was set at 270 °C, and the injection volume was 1 μL (UAE). The mass spectrometer was operated in the electron ionization positive mode (+70 eV). Temperatures of the transfer line and the ion source were maintained at 290 and 350 °C, respectively. The filament was set at 25 μA and the multiplier voltage was 1850 V. Selected reaction monitoring (SRM) acquisition mode was implemented, monitoring two or three transitions per compound for an unequivocal identification and quantification of the target compounds (see Table 1). The software employed for the operation of the equipment and the identification and quantification of the compounds were Xcalibur 2.2, and Trace Finder 3.2 software.

2.6. Chemometric analysis

Statistical analysis and design of experiments (DOE) were performed using Statgraphics Centurion XVIII (Manugistics, Rockville, MD, USA) as software package. An experimental design methodology (mixed level fraction experimental design) was applied for the SPME optimization to evaluate the experimental parameters affecting extraction efficiency. This type of experimental design has resolution V, which implies that it can assess all factors main effects and all interactions between factors.

In the analysis of variance (ANOVA) the *F-ratio* evaluates the influence of each factor and interaction on the variation of the response, and the *p-value* tests the statistical significance of every factor and interaction. If the *p-value* is lower than 0.05%, the factor or the interaction has a statistically significant effect at a 95% confidence level.

To easily visualize the influence of the factors and interactions Pareto figures were provided by the software package. The length of the bar is proportional to the absolute value of its associated standardized effect of each factor or interaction. Vertical line in the figures represents the statistically significant bound at a 95% level and, if the bar exceeds the vertical line, it denotes statistical significance.

Main effects figures represent the variation, employing a line, of the signal among the low (-) and the high (+) level of the corresponding factors. The length of the line is proportional to the

magnitude of the effect for each factor, and the sign (negative or positive) of the slope indicates the most favourable level of the factor. Finally, interaction figures allow the visualization of the effects relationships and synergies, as well as the most favourable conditions. These figures are employed to examine the behaviour of a variable that may or may not depend on the value of another variable. Interaction occurs when two or more factors take effect together in a process. In this type of figure, two or more lines are drawn, each representing a factor. If the lines are kept parallel to each other, no interaction occurs, but if the lines are not parallel, there is interaction between the factors. If the interaction is very strong, the lines cut each other or are very non-parallel.

3. Results and discussion

An active sampling approach based on SPE-SPME followed by GC-MS/MS analysis was selected with the objective of quantifying the target contaminants in different rubber air environments (including playgrounds and football pitches) with high sensibility and expending a short sampling time. In fact, at the beginning of this study, SPME alone was tested as passive sampler, but sensitivity was very low. Most compounds identified and quantified with the SPE-SPME method were hardly detected by passive SPME sampling.

3.1. SPME preliminary experiments

One of the most critical steps of the SPE-SPME extraction is the transfer of the compounds from the sorbent to the SPME fibre. For this reason, the selection of the most suitable type of SPME fibre coating is an essential parameter affecting the extraction efficiency. Since most of the target compounds present different physico-chemical properties, the effectiveness of four types of SPME fibre was evaluated: PA (high polarity), PDMS/DVB (medium polarity), DVB/CAR/PDMS (wide polarity range) and PDMS (non-polar) Fig. 1. shows the obtained results with all tested fibres for PAHs (Fig. 1a and b) and some other representative compounds (Fig. 1c and d). As can be seen, DVB/CAR/PDMS fibre attained the highest chromatographic response for most volatile compounds from all families (BTZ, TBP, DMA, DEA, NAP), but for the heavier ones, such as PHN, PYR, DBP, DEHP, among others, this coating fibre showed a very low response. This behaviour may be attribute to the presence of carboxen in the composition of the coating. This material due to its small micropores is very efficient for the retention of small molecules but this material fails for the retention of higher molecular size compounds [30,31]. In view of the results, DVB/CAR/PDMS fibre was discarded for further experiments. PDMS coating achieved lower responses for most compounds than PA and PDMS/DVB fibres, excluding the heaviest PAHs (IND, D[ah]A and B[ghi]P) that showed higher responses than PA coating. The obtained results were in concordance with those previously reported, demonstrating that PDMS shows a lower extraction efficiency in comparison with PDMS/DVB coating [13]. In view of these results, PDMS/DVB was included in the further experimental design, as well as PA, that showed a high efficiency in the extraction of low-polar chemical compounds.

3.2. Experimental design for SPME optimization

To achieve the most effective extraction a mixed level fraction experimental design was performed. Based on previous studies focused on air sampling [27,28], four factors (see Supplementary Table S2) were evaluated: solvent addition (Factor A), type of fibre (Factor B), headspace volume (Factor C) and extraction stirring (Factor D). The solvent (acetone) addition was studied at three levels (0, 50 and 100 μL). The other three factors were studied at two levels. The pre-selected coating fibres PA and PDMS/DVB (see

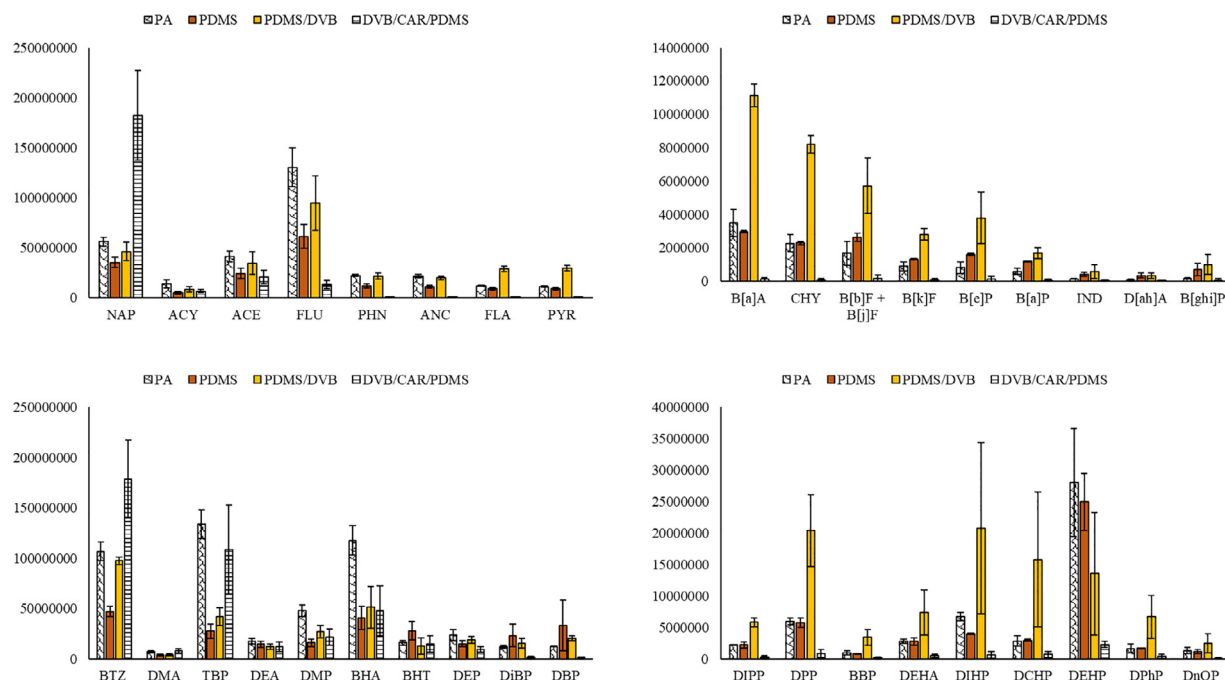


Fig. 1. Comparison of the chromatographic responses obtained for the different fibre coatings (PA, PDMS, PDMS/DVB and DVB/CAR/PDMS).

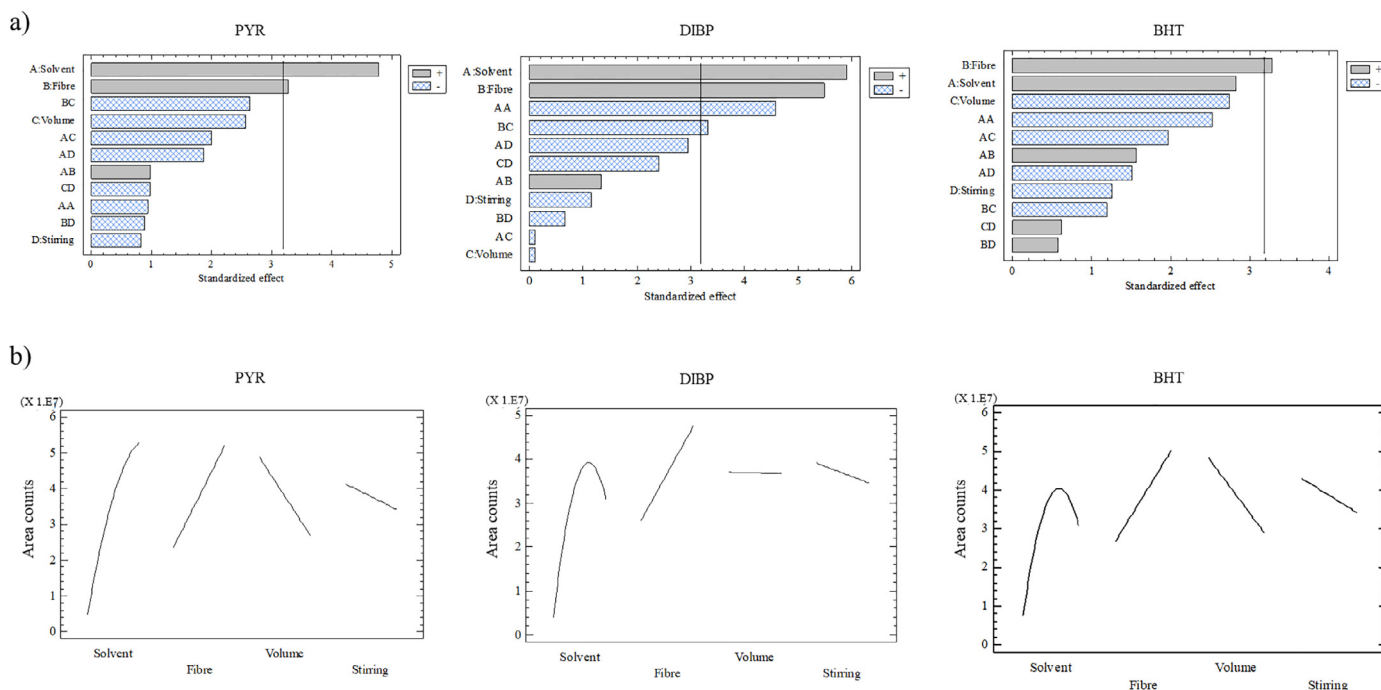


Fig. 2. a) Pareto figures showing the significant factors at 95 % confidence level, and b) main effects figures for some selected compounds (PYR, DIBP and BHT).

Section 3.1.) were also included in the experimental design. Stirring or not stirring during the SPME was also assessed. Finally, the headspace volume, which could be an important parameter in SPME was evaluated employing 2 mL and 10 mL glass vials to perform the SPME extraction. All these factors were included in a mixed level fraction experimental design, involving 15 experiments defined in $3 \cdot 2^{3-1} + 3$ central points. Supplementary Table S3 summarized the experimental design matrix. The ANOVA obtained results for the main factors and most relevant interactions are summarized Table 2. Pareto figures for some compounds are shown in

Fig. 2a. As can be seen, in Table 2, the most relevant factors were the type of fibre (factor B) and the addition of solvent (0–100 μ L, factor A). Factor A was statistically significant for 10 compounds including 4 PAHs (FLA, PYR, B[a]A, CHY) and 6 phthalates (DIBP, DBP, DMEP, DIPP, DPP, BBP).

The type of fibre (B) was statistically significant for 14 compounds, including 5 PAHs (NAP, FLA, PYR, B[a]A and CHY), 7 plasticizers (DEHA, DIBP, DBP, DMEP, DIPP, DPP, DEHP and DIDP) and 1 antioxidant (BHT). Otherwise, headspace volume (factor C) was only statistically significant for 3 compounds (BBP, DIHP and

Table 2

Analysis of variance (ANOVA) table for the main factors and statistically significant interactions, and optimum extraction conditions. Values in bold denote statistical significance (p-value < 0.05).

| Compound | Solvent (A) | | Fibre (B) | | Volume (C) | | Stirring (D) | | AA | | AC | | AD | | BC | | CD | | Optimum conditions |
|--|-------------|-------------|-----------|-------------|------------|-------------|--------------|------|------|-------------|------|-------------|-------|-------------|------|-------------|------|-------------|-------------------------------|
| | F | P | F | P | F | P | F | P | F | P | F | P | F | P | F | P | F | P | |
| <i>PAHs</i> | | | | | | | | | | | | | | | | | | | |
| NAP | 2.24 | 0.23 | 11.44 | 0.04 | 0.37 | 0.58 | 0.53 | 0.52 | 5.18 | 0.11 | 0.12 | 0.75 | 2.23 | 0.23 | 0.01 | 0.92 | 0.00 | 0.99 | 0 µL, DVB, 2 mL and stirring |
| ACY | 1.34 | 0.33 | 2.25 | 0.23 | 1.07 | 0.38 | 0.85 | 0.42 | 1.15 | 0.33 | 0.91 | 0.41 | 1.19 | 0.35 | 0.09 | 0.79 | 0.69 | 0.47 | 100 µL, DVB and 2 mL |
| ACE | 1.69 | 0.28 | 3.99 | 0.14 | 1.81 | 0.27 | 1.14 | 0.36 | 1.58 | 0.30 | 1.47 | 0.31 | 1.26 | 0.34 | 0.10 | 0.77 | 0.74 | 0.45 | 100 µL, DVB and 2 mL |
| FLU | 3.93 | 0.14 | 2.14 | 0.24 | 1.87 | 0.27 | 1.56 | 0.30 | 1.27 | 0.34 | 1.50 | 0.31 | 1.29 | 0.34 | 0.40 | 0.57 | 0.77 | 0.45 | 100 µL, DVB and 2 mL |
| PHN | 6.63 | 0.08 | 2.38 | 0.22 | 0.93 | 0.41 | 1.21 | 0.35 | 0.97 | 0.40 | 1.20 | 0.35 | 1.53 | 0.30 | 1.15 | 0.36 | 0.11 | 0.76 | 100 µL, DVB and 2 mL |
| ANC | 6.51 | 0.08 | 2.28 | 0.23 | 0.95 | 0.40 | 1.21 | 0.35 | 0.91 | 0.41 | 1.18 | 0.36 | 1.49 | 0.31 | 1.16 | 0.36 | 0.12 | 0.75 | 100 µL, DVB and 2 mL |
| FLA | 19.8 | 0.02 | 10.1 | 0.04 | 4.95 | 0.11 | 0.84 | 0.43 | 1.23 | 0.34 | 2.95 | 0.18 | 3.55 | 0.16 | 6.26 | 0.09 | 0.75 | 0.45 | 100 µL, DVB and 2 mL |
| PYR | 22.8 | 0.02 | 10.8 | 0.04 | 6.63 | 0.08 | 0.68 | 0.47 | 0.89 | 0.42 | 4.00 | 0.14 | 3.51 | 0.16 | 6.94 | 0.08 | 0.95 | 0.40 | 100 µL, DVB and 2 mL |
| B[a]A | 135 | 0.00 | 24.4 | 0.02 | 1.21 | 0.35 | 0.93 | 0.41 | 1.15 | 0.36 | 33.4 | 0.01 | 14.9 | 0.03 | 86.5 | 0.00 | 97.3 | 0.00 | 100 µL, PA and 10 mL |
| CHY | 138 | 0.00 | 38.1 | 0.01 | 4.15 | 0.13 | 0.11 | 0.76 | 0.72 | 0.46 | 28.6 | 0.01 | 14.5 | 0.03 | 102 | 0.00 | 125 | 0.00 | 100 µL, PA and 10 mL |
| B[b]F | 3.55 | 0.16 | 2.22 | 0.23 | 4.03 | 0.14 | 1.60 | 0.29 | 1.34 | 0.33 | 8.81 | 0.06 | 1.43 | 0.32 | 6.64 | 0.08 | 9.93 | 0.05 | 100 µL, PA and 10 mL |
| B[j]F | 3.27 | 0.17 | 1.68 | 0.29 | 3.23 | 0.17 | 1.19 | 0.36 | 0.80 | 0.44 | 7.04 | 0.08 | 1.38 | 0.33 | 5.61 | 0.10 | 8.35 | 0.06 | 100 µL, PA and 10 mL |
| B[k]F | 3.23 | 0.17 | 2.43 | 0.22 | 4.04 | 0.14 | 1.51 | 0.31 | 1.46 | 0.31 | 9.58 | 0.05 | 1.70 | 0.28 | 6.07 | 0.09 | 9.51 | 0.05 | 100 µL, PA and 10 mL |
| B[e]P | 1.75 | 0.28 | 2.42 | 0.22 | 3.08 | 0.18 | 1.53 | 0.31 | 1.47 | 0.31 | 6.21 | 0.09 | 0.61 | 0.49 | 5.61 | 0.10 | 9.22 | 0.06 | 100 µL, PA and 10 mL |
| B[a]P | 2.91 | 0.19 | 3.96 | 0.14 | 3.92 | 0.14 | 1.87 | 0.27 | 2.25 | 0.23 | 9.59 | 0.05 | 1.94 | 0.26 | 7.57 | 0.07 | 11.5 | 0.04 | 100 µL, PA and 10 mL |
| IND | 2.20 | 0.23 | 4.17 | 0.13 | 4.15 | 0.13 | 3.04 | 0.18 | 3.65 | 0.15 | 2.98 | 0.18 | 0.42 | 0.56 | 6.72 | 0.08 | 10.5 | 0.04 | 0 µL, PA and 10 mL |
| D[ah]A | 2.61 | 0.20 | 3.41 | 0.16 | 2.57 | 0.21 | 1.51 | 0.31 | 1.34 | 0.33 | 0.45 | 0.55 | 0.83 | 0.43 | 2.47 | 0.21 | 4.98 | 0.11 | 0 µL, PA and 10 mL |
| B[ghi]P | 3.41 | 0.16 | 2.25 | 0.23 | 1.29 | 0.34 | 2.19 | 0.24 | 1.86 | 0.27 | 0.17 | 0.71 | 1.71 | 0.28 | 2.30 | 0.23 | 5.04 | 0.11 | 0 µL, PA and 10 mL |
| <i>Plasticizers</i> | | | | | | | | | | | | | | | | | | | |
| DMP | 2.45 | 0.21 | 0.95 | 0.40 | 0.79 | 0.44 | 0.80 | 0.44 | 1.60 | 0.29 | 0.43 | 0.56 | 1.08 | 0.37 | 0.50 | 0.53 | 0.54 | 0.51 | 100 µL, DVB and 2 mL |
| DEP | 8.74 | 0.06 | 2.87 | 0.19 | 0.85 | 0.42 | 1.07 | 0.38 | 3.73 | 0.15 | 0.46 | 0.55 | 1.82 | 0.27 | 2.35 | 0.22 | 0.23 | 0.67 | 100 µL, DVB and 2 mL |
| DIBP | 35.0 | 0.01 | 30.2 | 0.01 | 0.01 | 0.93 | 1.31 | 0.33 | 21.1 | 0.02 | 0.01 | 0.93 | 8.69 | 0.06 | 11.0 | 0.04 | 5.84 | 0.09 | 100 µL, DVB and 2 mL |
| DBP | 70.6 | 0.00 | 55.9 | 0.01 | 0.83 | 0.43 | 0.84 | 0.43 | 28.5 | 0.01 | 2.40 | 0.22 | 10.96 | 0.04 | 27.4 | 0.01 | 16.6 | 0.03 | 50 µL, DVB, 2 mL and stirring |
| DMEP | 33.2 | 0.01 | 38.5 | 0.01 | 5.36 | 0.10 | 0.69 | 0.47 | 8.87 | 0.06 | 27.6 | 0.01 | 6.48 | 0.08 | 23.1 | 0.02 | 31.1 | 0.01 | 100 µL, DVB and 10 mL |
| DIPP | 144 | 0.00 | 144 | 0.00 | 2.74 | 0.20 | 0.97 | 0.40 | 54.8 | 0.01 | 18.9 | 0.02 | 33.29 | 0.01 | 65.3 | 0.00 | 75.5 | 0.00 | 50 µL, DVB, 2 mL and stirring |
| DPP | 26.2 | 0.01 | 25.4 | 0.02 | 1.70 | 0.28 | 0.42 | 0.56 | 4.08 | 0.14 | 12.3 | 0.04 | 5.77 | 0.10 | 16.0 | 0.03 | 19.7 | 0.02 | 100 µL, DVB and 10 mL |
| BBP | 11.7 | 0.04 | 2.64 | 0.21 | 23.8 | 0.02 | 5.94 | 0.09 | 2.26 | 0.23 | 42.5 | 0.01 | 2.12 | 0.24 | 13.9 | 0.03 | 29.0 | 0.01 | 100 µL, PA and 10 mL |
| DIHP | 5.41 | 0.10 | 2.67 | 0.20 | 10.4 | 0.04 | 4.14 | 0.13 | 2.79 | 0.19 | 58.5 | 0.00 | 2.56 | 0.21 | 9.46 | 0.05 | 10.9 | 0.04 | 100 µL, PA and 10 mL |
| DCHP | 7.46 | 0.07 | 4.28 | 0.13 | 11.7 | 0.04 | 5.70 | 0.10 | 2.47 | 0.21 | 48.9 | 0.01 | 1.29 | 0.34 | 18.6 | 0.02 | 19.3 | 0.02 | 100 µL, PA and 10 mL |
| DEHP | 5.15 | 0.11 | 30.9 | 0.01 | 9.30 | 0.06 | 0.38 | 0.58 | 0.20 | 0.68 | 6.85 | 0.08 | 0.84 | 0.43 | 3.24 | 0.17 | 0.33 | 0.61 | 100 µL, PA, 2 mL and stirring |
| DPhP | 3.01 | 0.18 | 0.45 | 0.55 | 5.86 | 0.09 | 0.51 | 0.53 | 0.54 | 0.51 | 29.5 | 0.01 | 4.70 | 0.12 | 3.23 | 0.17 | 3.76 | 0.15 | 100 µL, PA and 10 mL |
| DnOP | 0.43 | 0.56 | 2.14 | 0.24 | 0.37 | 0.59 | 0.16 | 0.71 | 1.79 | 0.27 | 20.6 | 0.02 | 1.89 | 0.26 | 1.42 | 0.32 | 2.71 | 0.20 | 100 µL, PA and 10 mL |
| DINP | 0.00 | 0.98 | 6.53 | 0.08 | 0.70 | 0.46 | 0.01 | 0.94 | 0.43 | 0.56 | 3.66 | 0.15 | 2.23 | 0.23 | 1.44 | 0.32 | 0.95 | 0.40 | 100 µL, PA and 10 mL |
| DIDP | 2.63 | 0.20 | 18.6 | 0.02 | 0.00 | 0.98 | 0.20 | 0.68 | 0.59 | 0.50 | 3.05 | 0.18 | 1.29 | 0.34 | 0.07 | 0.81 | 0.00 | 0.98 | 100 µL, PA and 10 mL |
| DMA | 0.46 | 0.55 | 2.94 | 0.19 | 0.26 | 0.64 | 0.29 | 0.63 | 0.61 | 0.49 | 0.14 | 0.73 | 1.70 | 0.28 | 0.00 | 0.96 | 0.01 | 0.94 | 100 µL, DVB and 2 mL |
| DEA | 1.31 | 0.34 | 2.35 | 0.22 | 2.88 | 0.19 | 0.43 | 0.56 | 2.22 | 0.23 | 1.46 | 0.31 | 0.59 | 0.50 | 0.57 | 0.50 | 0.54 | 0.52 | 100 µL, DVB and 2 mL |
| DEHA | 6.73 | 0.08 | 1.84 | 0.27 | 5.56 | 0.10 | 1.02 | 0.39 | 0.11 | 0.76 | 17.8 | 0.02 | 1.16 | 0.36 | 1.10 | 0.37 | 3.49 | 0.16 | 100 µL, PA and 10 mL |
| <i>Antioxidants and vulcanization agents</i> | | | | | | | | | | | | | | | | | | | |
| BTZ | 0.91 | 0.41 | 6.92 | 0.08 | 1.41 | 0.32 | 0.03 | 0.88 | 1.18 | 0.36 | 0.10 | 0.77 | 1.48 | 0.31 | 0.02 | 0.90 | 0.85 | 0.43 | 50 µL, DVB and 2 mL |
| 4TBP | 0.00 | 0.99 | 0.20 | 0.69 | 0.00 | 0.99 | 0.00 | 0.99 | 0.89 | 0.42 | 0.00 | 0.98 | 0.52 | 0.52 | 0.04 | 0.85 | 0.30 | 0.62 | 50 µL, DVB and 2 mL |
| BHA | 2.09 | 0.24 | 0.23 | 0.67 | 0.09 | 0.78 | 0.05 | 0.84 | 2.23 | 0.23 | 0.11 | 0.76 | 0.75 | 0.45 | 1.00 | 0.39 | 0.06 | 0.82 | 50 µL, DVB and 2 mL |
| BHT | 7.97 | 0.07 | 10.8 | 0.04 | 7.55 | 0.07 | 1.58 | 0.30 | 6.37 | 0.09 | 3.85 | 0.14 | 2.27 | 0.23 | 1.41 | 0.32 | 0.39 | 0.58 | 100 µL, DVB and 2 mL |

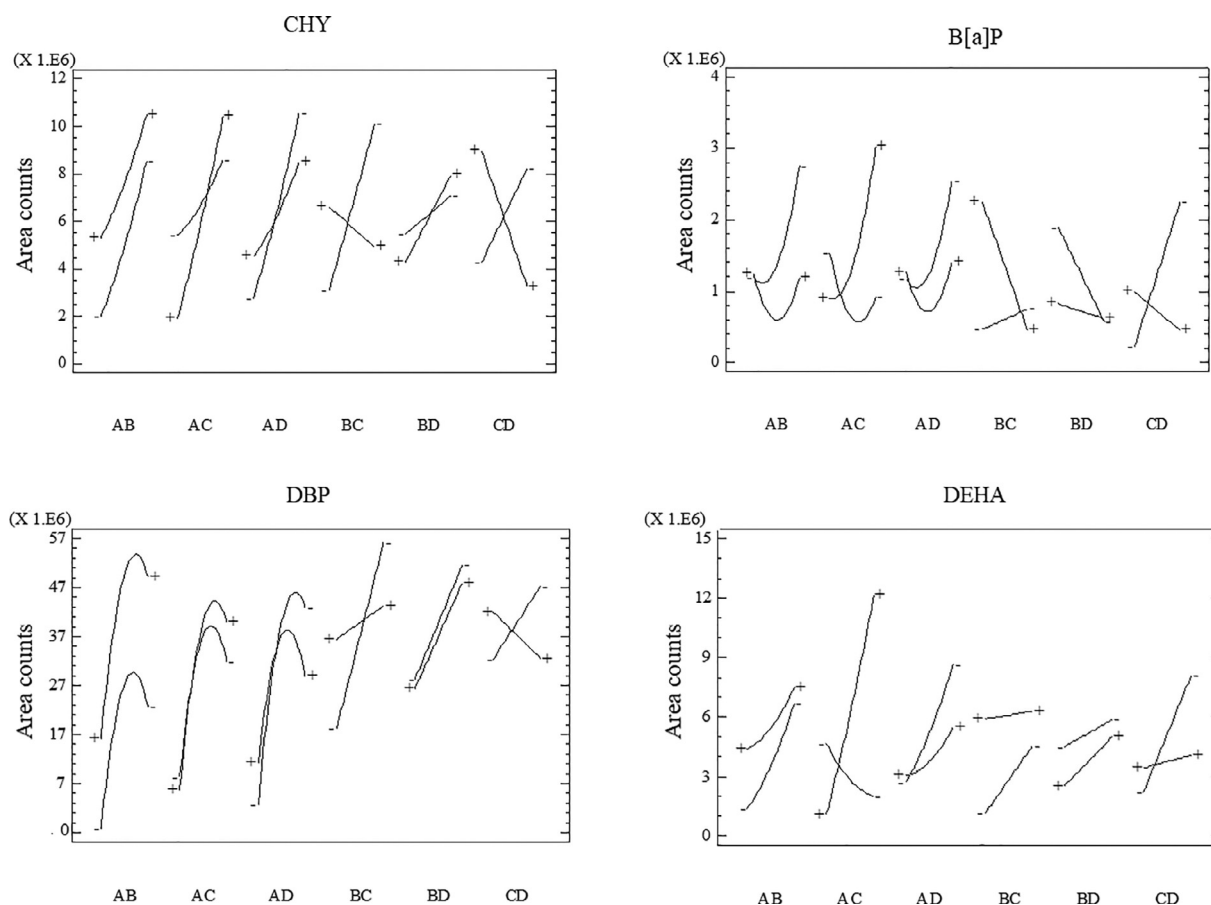


Fig. 3. Interaction figures for CHY, B[a]P, DBP, DCHP and DEHA.

DCHP), whereas stirring (factor D) was no significant for any compound.

Main effect figures for PYR, DIBP and BHT can be seen in Fig. 2b. For PAHs, only two of the four evaluated factors were statistically significant, solvent addition (A) and type of fibre (B), obtaining a higher response with the addition of 100 μ L of acetone employing the PDMS/DVB fibre (see main effects figure for PYR). Regarding plasticizers, factors A, B and C were statistically significant for 6, 7 and 3 phthalates, respectively (see Table 2). For factor A (solvent addition), higher responses were obtained by adding 50 μ L (DBP and DIPP) or 100 μ L (DIBP, DMEP, DPP and BBP) of acetone. Regarding the fibre coating, PDMS/DVB showed the highest responses for 5 phthalates (DIBP, DBP, DMEP, DIPP and DPP), whereas for DEHP and DIDP, higher responses were achieved employing the PA fibre. The most favourable headspace volume (factor C), that was significant for BBP, DIHP and DCHP, was obtaining employing the highest (10 mL vial). Taking into account the 40 studied substances, the extraction (Factor D) was more effective for 31 compounds (14 PAHs, 16 plasticizers and 1 antioxidant) with the addition of 100 μ L acetone.

To easily visualize the optimal conditions, the statistical software includes the interaction figures Fig. 3. shows some examples for CHY, B[a]P, DBP and DEHA. It is important to note that although factors were no significant or only statistically significant for a few compounds, their interactions can be statistically significant. For example, headspace volume (factor C) was only significant for 4 compounds and stirring (factor D) for none, but their interaction (CD) was statistically significant for 11 compounds (B[a]A,

CHY, B[a]P, IND, DBP, DMEP, DIPP, DPP, BBP, DIHP and DCHP). The most relevant interactions were solvent volume-headspace volume (AC), type of fibre-headspace volume (BC) and headspace volume-stirring (CD). Interaction AC was statistically significant for 11 compounds (B[a]A, CHY, DEHA, DMEP, DIPP, DPP, BBP, DIHP, DCHP, DPhP, and DnOP) being the addition of 100 μ L of acetone employing a 10 mL vial to perform SPME the best conditions as can be seen in Fig. 3. Furthermore, interaction BC was statistically significant for 9 compounds including 2 PAHs (B[a]A, CHY) and 7 plasticizers (DIBP, DBP, DMEP, DIPP, DPP, BBP and DCHP) being the most favourable conditions for PAHs the use of PDMS/DVB fibre in combination with the 2 mL vial. By contrast, for the 7 plasticizers PDMS/DVB fibre can be used regardless the vial head-space volume or PA fibre employing the 10 mL vial. Interaction CD was statistically significant for 11 compounds including 4 carcinogenic PAHs (B[a]A, CHY, B[a]P and B[e]P) and 7 phthalates (DBP, DMEP, DIPP, DPP, BBP, DIHP and DCHP). For 5 of the 11 compounds, optimal conditions were no stirring employing a 10 mL vial, and for the other 6 similar results were obtained using a 2 mL vial stirring the sorbent or a 10 mL vial without stirring. On the other hand, interaction AD (solvent addition volume-stirring) had statistical significance only for 4 compounds (B[a]A, CHY, DBP and DIPP), obtaining as best conditions adding 100 μ L of acetone in a 10 mL vial. Additionally, from a practical point of view, employing a 10 mL vial makes this experimental procedure easier than using a 2 mL vial.

Therefore, in view of the experimental design results, the optimized experimental conditions for the SPME of the target com-

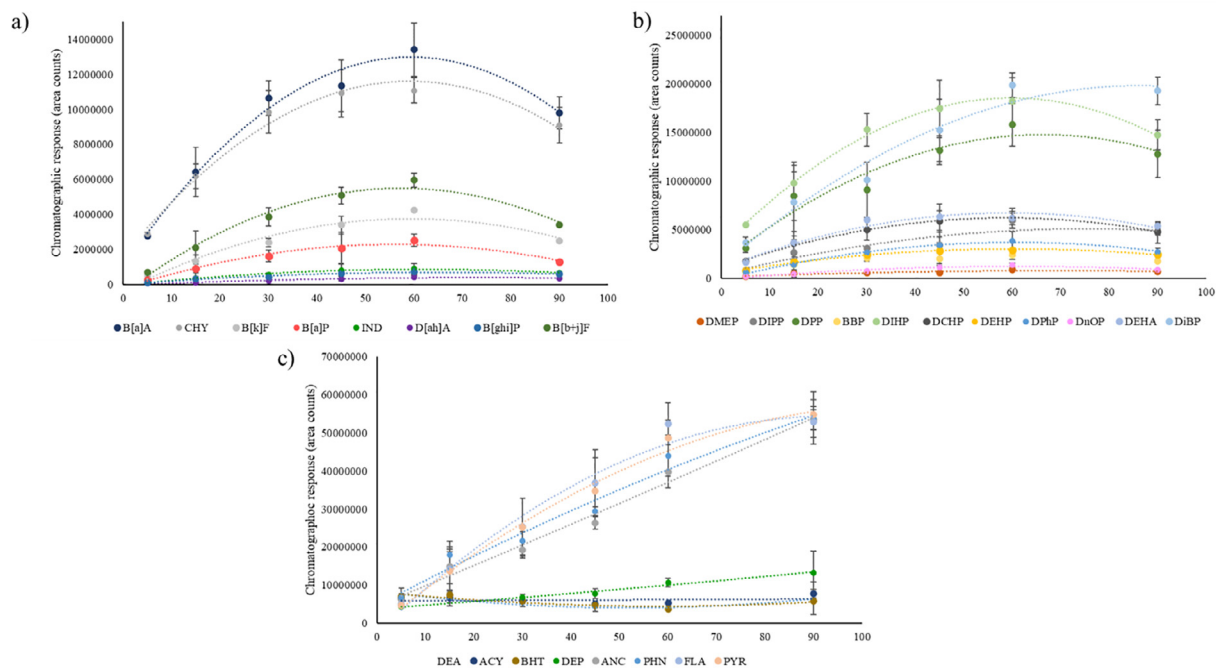


Fig. 4. Time profile curves for the target analytes (area counts). Extraction times: 5, 15, 30, 45, 60 and 90 min.

pounds comprise the addition of 100 μL of acetone to 25 mg of Tenax TA, employing a PDMS/DVB fibre in a 10 mL vial without stirring, although the use of PA fibre is also suitable. Similar results were obtained using PDMS/DVB (medium polar) and PA (high polar) fibre coatings for some poorly polar compounds (B[a]A, CHY, DMEP, and DPP).

3.3. SPME extraction time profile

The time required to attain equilibrium in SPME is conditioned by the physicochemical properties of the target analytes, the matrix nature and the physicochemical properties of the fibre coating, among others [32]. To assess the extraction time, under the optimal conditions, six different extraction times (5, 15, 30, 45, 60 and 90 min) were considered. These studies were performed employing Tenax TA spiked at 25 ng g^{-1} with the 40 target compounds. Extraction time profiles are depicted in Fig. 4. As can be seen, the optimal extraction time is highly depended on the compound. Overall, for most target analytes studied, equilibrium was reached fairly rapid, between 45 and 60 min (see in Fig. 4a and b). Otherwise, compounds with higher molecular weight such as PAHs B[a]A, CHY, B[b]F+B[j]F, B[k]F, IND, D[ah]A and B[ghi]P; and plasticizers DPP, DIHP, DCHP, DEHP, DPhP and DnOP, did not attain up the equilibrium until 45 min. Only a few compounds (FLU, PHN, ANC, FLA, PYR and DEP) did not reach stability at the maximum extraction time studied (90 min), see Fig. 4c. On the other hand, as can be seen in Fig. 4, for several compounds an extraction time of 90 min may result in a slight loss of sensitivity. This may be due to a desorption of the compounds from the SPME fibre into the headspace. Therefore, to obtain a sensitive and high throughput extraction, 45 min was selected as the optimum extraction time.

3.4. SPE-SPME-GC-MS/MS method performance

Once the SPE-SPME-GC-MS/MS method was optimized, its analytical quality parameters, including linearity, accuracy, and preci-

sion were evaluated. LODs and LOQs were also calculated. Results are shown in Table 3.

The linearity study was performed spiking the Tenax TA with an acetic solution of the 40 compounds covering a concentration range from 0.05 to 200 ng m^{-3} (DINP and DIDP, 25 to 1250 ng m^{-3}). A more detailed description is included in section 2.4. Chromatographic response was proportional to the concentration of target compounds, with coefficients of determination (R^2) higher than 0.9900. Individual linear range for each compound is shown in Table 3.

LODs and LOQs of the whole SPE-SPME-GC-MS/MS method were calculated. For those compounds found in the procedure blanks were taking into account to calculate them (see in section 2.4). The values were at the sub ng m^{-3} for most compounds, ranged from 0.010 to 4.6 ng m^{-3} (LODs) and from 0.033 to 15 ng m^{-3} (LOQs), showing the suitability of the proposed methodology to quantify trace levels of the target compounds in air.

The method precision was evaluated within a day ($n = 3$) and amongst several days ($n = 6$) obtaining a relative standard deviation (RSD) mean values for the 40 target compounds about 14% and 16%, respectively.

To demonstrate the accuracy of the method, recovery experiments were carried out by SPE-SPME-GC-MS/MS employing Tenax TA spiked at 2 concentration levels. Recovery values were satisfactory, showing accuracy and precision, with average recoveries between 80 and 110 % in most cases and RSD values lower than 12 % (excluding some plasticizers with values lower than 19 %).

3.5. Comparison with other methodologies

Until now, there are not much research studying the influence of these recycled rubber surfaces on the surrounding air. The proposed methodology has been compared with other methods reported in the literature (see Table 4), including a previous one based on SPE-UAE developed by the authors [6,7,14,19–

Table 3
Method performance: Linearity, precision, recoveries, limits of detection (LOD) and limits of quantification (LOQ).

| Compounds | Linearity | Linear range (ng g ⁻¹)* | Precision, RSD (%) | | Recoveries and Precision (%) | | | LOD (ng m ⁻³) | LOQ (ng m ⁻³) |
|--|----------------|--|--------------------|-----------|------------------------------|-----------------------|------------|------------------------------|------------------------------|
| | R ² | | Intra-day | Inter-day | 7.5 ng m ⁻³ | 75 ng m ⁻³ | Mean RSD** | | |
| PAHs | | | | | | | | | |
| NAP | 0.9997 | 0.25-200 | 4.7 | 11 | 117 | 104 | 18 | 0.04 | 0.13 |
| ACY | 0.9959 | 0.1-200 | 8.3 | 12 | 91.1 | 104 | 7 | 0.022 | 0.073 |
| ACE | 0.9948 | 0.05-200 | 1.7 | 15 | 94.1 | 128 | 11 | 0.017 | 0.056 |
| FLU | 0.9954 | 0.05-100 | 3.8 | 15 | 82.5 | 95.8 | 8.2 | 0.011 | 0.036 |
| PHN | 0.9984 | 0.1-100 | 16 | 19 | 55.4 | 87.9 | 8.5 | 0.02 | 0.066 |
| ANC | 0.9978 | 0.25-100 | 15 | 16 | 97.5 | 79.8 | 19 | 0.031 | 0.1 |
| FLA | 0.9903 | 0.25-100 | 5 | 20 | 74.1 | 94.3 | 9.9 | 0.07 | 0.23 |
| PYR | 0.9991 | 0.1-200 | 7.6 | 10 | 75 | 89 | 11 | 0.027 | 0.089 |
| B[a]A | 0.9939 | 0.25-200 | 11 | 11 | 89.8 | 94.1 | 1.3 | 0.063 | 0.21 |
| CHY | 0.9939 | 0.25-200 | 12 | 7.5 | 90.9 | 113 | 14 | 0.087 | 0.29 |
| B[b]F+B[j]F | 0.9918 | 2.5-200 | 10 | 19 | 112 | 61.2 | 1.6 | 0.62 | 2 |
| B[k]F | 0.9949 | 0.1-200 | 8.3 | - | 119 | 68.6 | 2.4 | 0.026 | 0.086 |
| B[e]P | 0.99 | 0.1-200 | 1.2 | 19 | 102 | 78.7 | 1.9 | 0.027 | 0.089 |
| B[a]P | 0.9905 | 0.1-200 | 9.8 | 19 | 96.5 | 74.5 | 12 | 0.045 | 0.15 |
| IND | 0.9995 | 0.25-200 | 16 | 19 | 90.2 | 92.1 | 15 | 0.077 | 0.25 |
| D[ah]A | 0.999 | 0.5-200 | 18 | 16 | 93.6 | 79.5 | 3.8 | 0.095 | 0.31 |
| B[ghi]P | 0.9975 | 0.5-200 | 11 | 19 | 98.7 | 76.4 | 7.1 | 0.17 | 0.56 |
| Plasticizers | | | | | | | | | |
| DMA | 0.9998 | 5-200 | 4.1 | 15 | 114 | 109 | 13 | 1.7 | 5.6 |
| DEA | 0.9993 | 0.05-200 | 6.3 | 10 | 110 | 93.8 | 17 | 0.01 | 0.033 |
| DMP | 0.9883 | 0.1-100 | 3.7 | 12 | 76 | 89 | 15 | 0.034 | 0.11 |
| DEP | 0.997 | 1-100 | 1.9 | 20 | 71 | 85.6 | 1.7 | 0.39 | 1.3 |
| DIBP | 0.9952 | 2.5-200 | 2.3 | 15 | 66.8 | 103 | 8.3 | 0.73 | 2.4 |
| DBP | 0.9924 | 10-200 | 18 | 18 | 80.3 | 103 | 18 | 2.6 | 8.6 |
| DMEP | 0.9973 | 2.5-200 | 2 | 8 | 54.5 | 99.9 | 4.2 | 0.78 | 2.6 |
| DIPP | 0.9972 | 0.25-200 | 18 | 18 | 66.4 | 98.7 | 1.6 | 0.066 | 0.22 |
| DPP | 0.9973 | 0.25-200 | 1.9 | 15 | 64.3 | 94.4 | 19 | 0.085 | 0.28 |
| BBP | 0.9979 | 2.5-200 | 6.1 | 14 | 84 | 104 | 9.8 | 0.51 | 1.7 |
| DEHA | 0.99 | 10-200 | 9 | 12 | 105 | 76.2 | 14 | 2.6 | 8.7 |
| DIHP | 0.9978 | 2.5-200 | 5 | 19 | 101 | 109 | 16 | 0.96 | 3.2 |
| DCHP | 0.9961 | 2.5-200 | 3 | 22 | 70.6 | 97 | 17 | 1.2 | 3.9 |
| DEHP | 0.9993 | 10-200 | 14 | 19 | - | 102 | 18 | 2.2 | 7.4 |
| DPhP | 0.9987 | 2.5-200 | 13 | 20 | 99.2 | 86.2 | 8.2 | 0.45 | 1.5 |
| DnOP | 0.9951 | 5-200 | 12 | 18 | 61.3 | 113 | 9.6 | 1.7 | 5.5 |
| DINP | 0.9967 | 25-1250 | 14 | 20 | - | 78.6 | 6.4 | 3.3 | 11 |
| DIDP | 0.9945 | 25-1250 | 8.1 | 19 | - | 99.6 | 12 | 4.6 | 15 |
| Antioxidants and vulcanization agents | | | | | | | | | |
| BHA | 0.9913 | 0.05-100 | 11 | 14 | 61.3 | 90.4 | 8.6 | 0.01 | 0.033 |
| BHT | 0.9959 | 2.5-200 | 10 | 14 | 95.9 | 113 | 13 | 0.14 | 0.46 |
| BTZ | 0.9959 | 10-200 | 0.7 | 20 | 100 | 121 | 11 | 2 | 7.2 |
| 4TBP | 0.995 | 0.1-200 | 4.9 | 7 | 85.1 | 97.1 | 11 | 0.029 | 0.096 |

*Equivalent to ng m⁻³ in the air sampling 1 m³. **Mean value for the two concentration levels tested.

26]. Different techniques comprising passive or active air sampling have been used. In the passive studies, the most commonly used technique has been SPME [6,19,20,26]. SPME was only used on a laboratory scale, evaluating the compounds released into the headspace above crumb rubber samples, but not real air samples were analyzed. Donald et. al [25] employed low-density polyethylene (LDPE) and silicone passive samplers to evaluate the presence of volatile and semivolatile compounds in air above synthetic turf pitches. In addition, several active sampling methods were employed to perform real air sampling above synthetic turf football pitches [14,21–24]. Afterwards, the compounds retained in the sorbent were generally desorbed by solvation using organic solvent such as hexane, dichloromethane, and diethyl ether. Some of the proposed method required the use of hundreds of mL of organic solvents to isolate the compounds retained in the sorbent [22,23,25]. Regarding sampling time during real air sampling, most studies involve more than 2 h. The method proposed in the present research allowed a faster air sampling (16 min) avoiding the use of organic solvents as well as residue generation since the sorbent and the SPME fibre are reused. Regarding analytical performance, in most studies, accuracy was not evaluated. In addition, some of the methods were only proposed to identify the presence or absence of the studied compounds [22,24,25].

The main advantages of using SPME after SPE air sampling is that the use of organic solvents is not required and the high concentration capacity. In Fig. 5 the results obtained for SPE-UAE and SPE-SPME methods using enriched Tenax TA (25 ng g⁻¹) (Fig. 5a), and for a real playground air sample (Fig. 5b) are depicted. As can be seen in Fig. 5a, the chromatographic response for the most volatile PAHs was up to 20 times higher employing SPME. This behaviour was also observed for other of the studied compounds reaching up to 35 times higher chromatographic response (see Fig. 5a). Similar results were observed for real samples (see Fig. 5b), demonstrating that the use of SPME significantly increased method sensitivity that constitutes a great benefit for the analysis of real air samples.

3.6. Application to real samples

The validated methodology was applied to 7 real air samples collected from indoor and outdoor places. Results are summarized in Table 5.

3.6.1. Football pitches and playgrounds

Air samples from three childrens' playgrounds and two synthetic turf football pitches were analyzed. For a detailed sample description see Section 2.2 and Supplementary Table S2.

Table 4

Comparison of SPE-SPME-GC-MS/MS with other methods to determine organic compounds in air adjacent to rubber playgrounds, synthetic turf football pitches and other tire rubber materials.

| Type of air sample | Analyte families | N ^o of analytes | Sampling Method | Sampling time (min) | Sample preparation | Solvent and volume | Extraction time (min) | Analysis | LOD/LOQ | Recovery (%) | RSD (%) | Real samples concentrations | References |
|--|---|----------------------------|--|---------------------|--------------------------------|--|-----------------------|------------------|---|---------------------|---------|---|------------|
| Indoor artificial football pitches | PAHs, BTZ, toluene, 4-methyl-2-Pentanone, phthalates | 45 | Active sampling using Tenax TA | Approx. 300 | Soxhlet, LLE, thermodesorption | Hundreds of mL | - | GC-MS | - | > 90 | - | 0.01-58 ng m ⁻³ (PAHs) 0.01-0.38 ng m ⁻³ (phthalates) | [20] |
| Lab-scale | BTZ, hexadecane, 4-t-OP, BHA, BHT alteration product | 4 | - | - | SPME | - | 42 | GC-MS | - | - | - | - | [17] |
| Lab-scale | PAHs, BTZ, BHT, BHA, 4-t-OP | 10 | - | - | SPME | - | 20 | GC-MS | 0.2-0.6 ng m ⁻³ (LOQs) | - | - | - | [18] |
| Football pitches | PAHs | 5 | Active sampling | 120-180 | SLE | Dozens of mL of dichloromethane and n-hexane | 45 | GC-LRMS | 0.002 ng m ⁻³ (LOD) | 86-107 ^a | <7 | 0.01-0.11 ng m ⁻³ (PAHs) | [19] |
| Football pitches | Vulcanisers, antioxidants, PAHs and 93 SVOCs | 120 (22 PAHs) | Polyurethane foam samplers according to U.S. EPA Method TO-13A | 120 | Soxhlet | 700-750 mL diethyl ether/hexane (10:90, v/v) | 120 | GC-MS | - | 75-125 | < 25 | 0.04-113 ng m ⁻³ (PAHs) | [21] |
| Lab-scale | PAHs, vulcanisation additives, antioxidants and plasticizers | 31 | - | - | SPME | - | 25 | GC-MS | - | - | - | - | [6] |
| Lab-scale | B[a]A, Chy, B[a]P, 4 B[ghi]P | 4 | - | - | Florisil trap | - | 300 | HPLC-FL | - | - | - | - | [7] |
| Lab-scale | PAHs, vulcanisation additives, antioxidants and plasticizers | 30 | - | - | SPME | - | 35 | GC-MS | - | - | - | - | [24] |
| Indoor and outdoor synthetic turf football pitches | PAHs and oxygenated PAHs | > 70 | LDPE and silicone passive sampling | - | Thermal desorption and SLE | 100 mL hexane | 120 | GC-/MS | < 0.001- 0.64 ng m ⁻³ (LOQs) | - | < 21 | 0.001-600 ng m ⁻³ (PAHs) | [23] |
| Indoor and outdoor football pitches | PAHs, BTZ, tert-butylamine, cyclohexanone and 2-heptanone. ^a | 20 | Active sampling | 120-180 | Soxtherm® extraction system | Hexane | - | GC-MSD and LC-MS | Approx. 3 ng m ⁻³ - (LOQ) | - | - | 2-190 ng m ⁻³ (PAHs) | [22] |
| Indoor and outdoor locations | PAHs, vulcanisation additives, antioxidants and plasticizers | 40 | Active sampling using Tenax TA | 16 | SPE-UAE | 1 mL ethyl acetate | 2 | GC-MS/MS | 0.01-20 ng m ⁻³ (LOQs) | 71-110 | < 7 | 0.08-528 ng m ⁻³ (PAHs) 0.8-264 ng m ⁻³ (phthalates) 7.1-226 ng m ⁻³ (others) | [13] |
| Indoor and outdoor locations | PAHs, vulcanisation additives, antioxidants and plasticizers | 40 | Active sampling | 16 | SPE-SPME | 100 µL acetone | 45 | GC-MS/MS | 0.01-4.6 ng m ⁻³ (LOQs) | 54-128 | < 10 | 0.05-80 ng m ⁻³ (PAHs) 0.03-81 ng m ⁻³ (phthalates) 0.09-1213 ng m ⁻³ (others) | This work |

PAHs: polycyclic aromatic hydrocarbons, BTZ: benzothiazole, LLE: liquid-liquid extraction, SLE: solid-liquid extraction, SPME: solid-phase microextraction, SPE: solid-phase extraction, UAE: ultrasound assisted extraction, SVOCs: semivolatiles organic compounds, BHA: butylated hydroxyanisole, BHT: butylated hydroxytoluene, GC: gas chromatography, LC: liquid chromatography, MS: mass spectroscopy, LDPE: low-density polyethylene, LRMS: low resolution mass spectrometry, FL: fluorescence detector, 4-t-OP: 4-(t-octyl) phenol.

^a Recovery value referred for the internal standard.

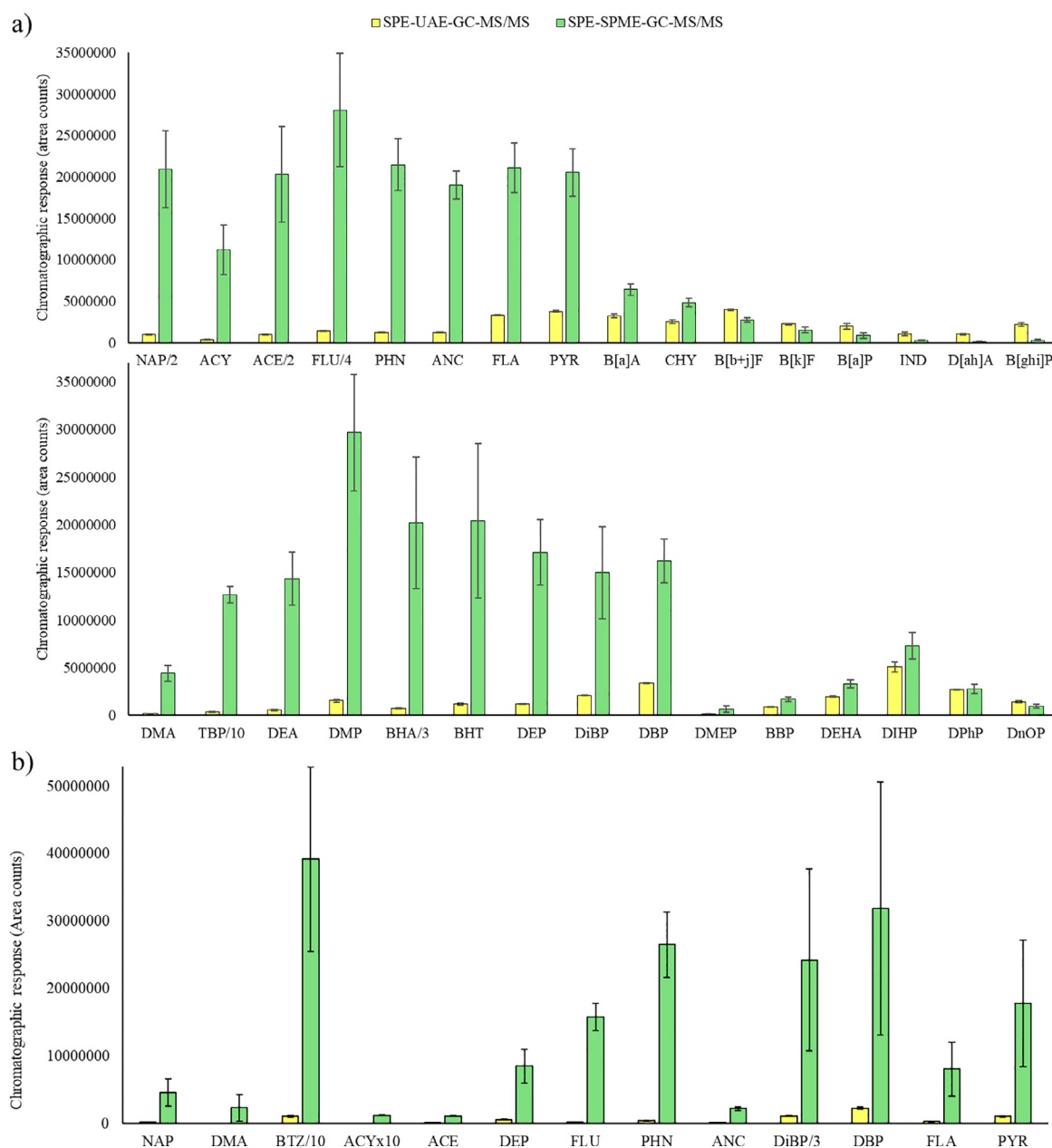


Fig. 5. Comparison of the chromatographic response (area counts) obtained employing SPE-UAE-GC-MS/MS and SPE-SPME-GC-MS/MS methods: a) enriched Tenax TA spiked with target compounds and b) real playground air sample.

Between 8 and 10 PAHs were found in all the samples, being 8 of the PAHs (NAP, ACY, ACE, FLU, PHN, ANC, FLA and PYR) detected in all air samples at concentrations between 0.1 and 10.9 ng m⁻³. The sum of PAH ranged between 7.3 and 27 ng m⁻³. These PAH levels are similar to those reported in the literature for football pitches [23,24]. OP2 achieved the highest concentrations, probably due to the high temperatures during the air sampling (aprox. 30 °C, see Supplementary Table S1). A chromatogram of this sample is depicted in Supplementary Fig. S1. Regarding the surrounding air samples of OP1 and OP2, fewer PAHs were detected at much lower concentrations (sum of PAH 2.7 and 1.2 ng m⁻³ respectively). In addition, concentrations were lower in the stands than in the pitch (see Supplementary Fig. S2), although people watching the matches are also exposed to these compounds. B[a]A and CHY, both considered as carcinogenic by the European Chem-

icals Agency (ECHA), were detected at levels above 1 ng m⁻³ (the ECHA limit for B[a]P) in sample OP1. The PAHs concentration profiles are depicted in Fig 6a. As can be seen, the concentrations and distributions were similar in playgrounds and football pitches, except for sample OP1 in which FLA, B[a]A and CHY reached a similar concentration to PYR.

Regarding plasticizers (see Table 5), DIBP and DBP, both considered toxic for reproduction and endocrine disruptors [33], were detected in all samples, reaching concentrations up to 28 and 17 ng m⁻³, respectively. Other hazardous compound, BTZ, a demonstrated substance that is dangerous if inspired and might produce damage to organs through prolonged or repeated exposure [34], was found in the 5 samples, at concentrations up to 65 ng m⁻³. In general the concentration values were similar to those obtained employing SPE-UAE-GC-MS [14]. However, Dye et.

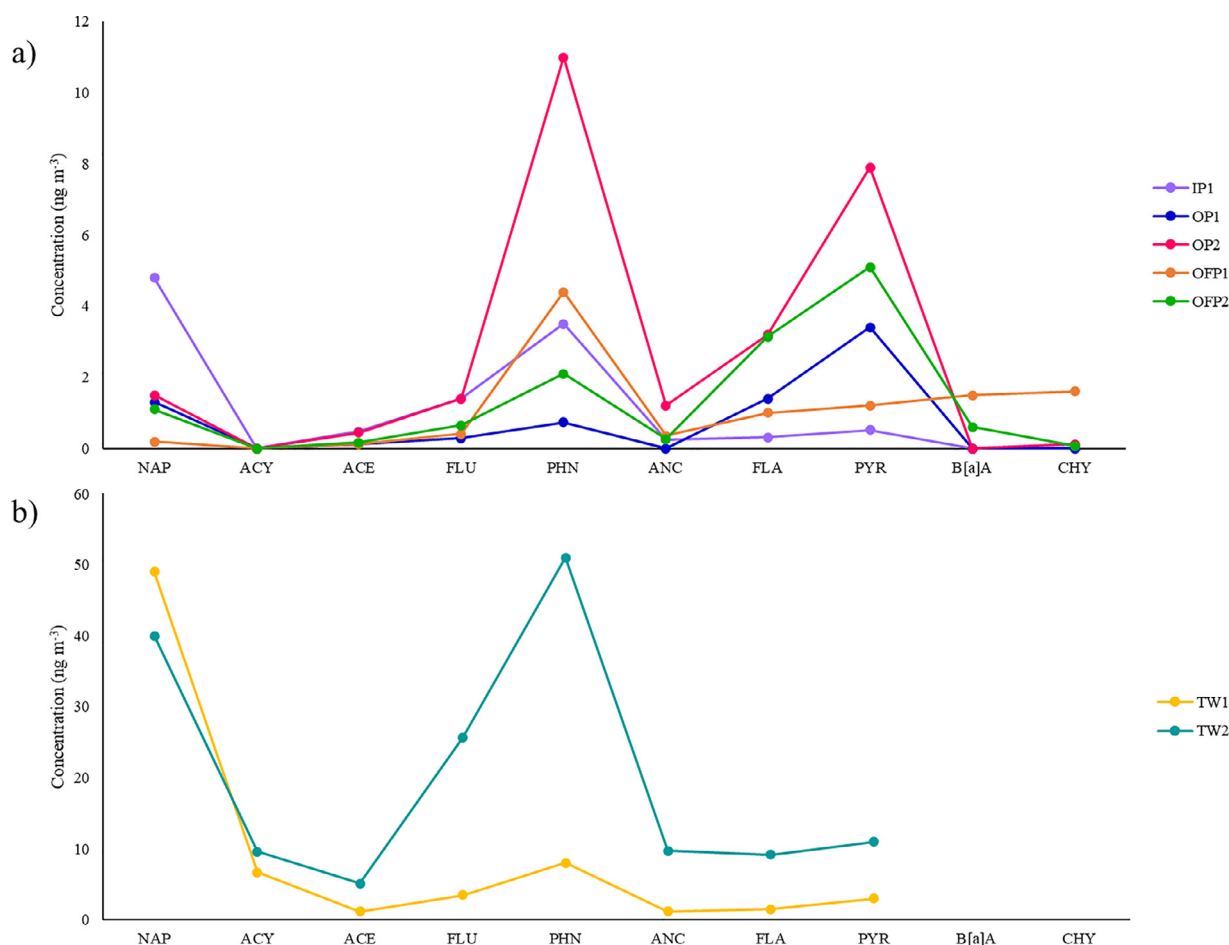


Fig. 6. Concentration profiles (ng m^{-3}) for individual PAHs in the eight real samples: a) football pitches and playgrounds and b) tire warehouses. (IP: indoor playground; OP: outdoor playground; OFP: outdoor football pitch; TW: tire warehouse). To facilitate visualization, the response for some compounds have been multiplied or divided by a factor.

al [22], reported higher concentrations for DEP, DBP and DIBP, although in indoor football pitches.

Only one plasticizer and two vulcanisation additives (DPP, BTZ and TBP) have been detected in the playgrounds surrounding air at much lower concentrations, showing that the presence of these chemicals in the air of the rubber playgrounds is due to the use of this material as flooring. To establish a relationship between the presence of the target compounds in the air samples and in crumb rubber flooring, Supplementary Fig. S3 shows the concentration profile in the outdoor air and in the crumb rubber used as flooring in the same playgrounds. As can be seen, a relationship between air contamination and the chemical compositions of the recycled crumb rubber tiles employed in these surfaces is clear.

3.6.2. Warehouses

Two warehouses without ventilation, which store new (TW1) and old (TW2) car tires, were also sampled. Most volatile PAHs (NAP, ACY, ACE, FLU, PHN and ANC) achieved higher concentrations in these spaces than in playgrounds and football pitches, especially the old tire warehouse and the recycled rubber tiles storage warehouse, reaching concentrations up to 51 ng m^{-3} (PHN) (see Fig. 6a and b). The sum of PAHs was 74 and 160 ng m^{-3} in TW1 and TW2, respectively. The PAHs concentrations obtained in the old tire store (TW2) were higher than those in the new tires (TW1), being up to 8 times higher for some compound (see Table 5). It is important to emphasise the high concentrations detected for BTZ with val-

ues of 994 and 1213 ng m^{-3} . Plasticizers DIBP, DBP, BBP and DEHA reached concentrations up to 81 , 28 , 2.6 and 20 ng m^{-3} , respectively. The presence of these compounds in unventilated spaces can be harmful for workers in the rubber tire industry [35]. The other target compounds were similar in TW1 and TW2 excluding BHT, which showed significantly higher concentrations in TW1. In contrast, TW2 showed higher PAH concentration although the profiles were completely analogous (see Fig. 6b).

In summary, much higher PAH concentrations were found in the tire warehouses whereas the concentrations were similar in playgrounds and football pitches, as can be seen in Fig. 6a and b. It is interesting to notice that B[a]A and CHY that appears in the football pitches and playgrounds were not detected in the tire warehouses. By contrast, plasticizers, antioxidants and vulcanizers concentrations were slightly higher in playgrounds than in football pitches, except for DMA, DMP, BTZ, TBP and BHT, which were significantly higher in the playgrounds (Table 5). The vulcanizers BTZ and TBP, as well as the antioxidant BHT, were found in much higher concentrations in the air of the tire warehouses (see Table 5). It has been shown that the presence of these pollutants in the adjacent air is due to the presence of these recycled rubber materials and their dispersion can reach several tens of metres, harming not only the people who use these surfaces. It is important to remark that tire rubber workers including those installing playgrounds and pitches are exposed to these pollutants for long periods of time [36].

Table 5
PAHs, plasticizers, antioxidants and vulcanisation additives concentration (ng m⁻³) in the seven real air samples (total number of samples 10). IP: indoor playground; OP: outdoor playground; OPF: outdoor football pitch; TW: tire warehouse.

| Compound | IP1 | Surrounding air OP1 | OP1 | Surrounding air OP2 | OP2 | OPF1 | Stands air OP2 | OPF2 | TW1 | TW2 |
|----------|---------------|---------------------|---------------|---------------------|---------------|---------------|----------------|-----------------|------------------------|-------------------------|
| NAP | 4.78 ± 0.59 | 0.75 | 1.28 ± 0.47 | 1.1 | 1.54 ± 0.51 | 3.51 ± 0.40 | 3.0 | 1.1 ± 1.0 | 48.7 ± 4.8 | 40 ± 15 |
| ACY | < LOQ | | < LOQ | < LOQ | < LOQ | < LOQ | < LOQ | < LOQ | 6.69 ± 0.72 | 9.6 ± 2.2 |
| ACE | 0.481 ± 0.030 | | 0.133 ± 0.083 | 0.10 | 0.441 ± 0.010 | 0.123 ± 0.017 | 0.24 | 0.173 ± 0.017 | 1.16 ± 0.11 | 5.1 ± 1.0 |
| FLU | 1.43 ± 0.22 | 0.21 | 0.279 ± 0.092 | 0.048 | 1.41 ± 0.19 | 0.413 ± 0.078 | 0.63 | 0.649 ± 0.059 | 3.47 ± 0.24 | 25.71 ± 0.14 |
| PHN | 3.50 ± 0.93 | 0.23 | 0.73 ± 0.16 | < LOQ | 10.9 ± 2.0 | 4.4 ± 1.3 | 1.0 | 2.08 ± 0.40 | 8.0 ± 2.0 | 51 ± 13 |
| ANC | 0.253 ± 0.021 | | < LOQ | | 1.16 ± 0.13 | 0.357 ± 0.076 | 0.12 | 0.262 ± 0.075 | 1.16 ± 0.29 | 9.7 ± 1.6 |
| FLA | 0.31 ± 0.11 | 0.56 | 1.36 ± 0.30 | < LOQ | 3.22 ± 0.40 | 1.05 ± 0.47 | 0.60 | 3.14 ± 0.10 | 1.51 ± 0.62 | 9.2 ± 4.7 |
| PYR | 0.51 ± 0.24 | 0.39 | 3.45 ± 0.87 | | 7.94 ± 0.82 | 1.16 ± 0.54 | 1.1 | 5.15 ± 0.40 | 3.0 ± 1.2 | 11.0 ± 5.4 |
| B(a)A | | | | | | 1.53 ± 0.95 | 0.49 | 0.60 ± 0.18 | | |
| CHY | | | | | | 1.61 ± 0.46 | 0.050 | 0.064 ± 0.030 | | |
| ΣPAHs | 12 | 2.1 | 7.3 | 1.2 | 27 | 11 | 7.3 | 13 | 74 | 160 |
| DMA | 33.7 ± 5.6 | | | < LOQ | 5.9 ± 3.5 | | < LOQ | < LOQ | < LOQ | < LOQ |
| DEA | < LOQ | | | < LOQ | | | | | < LOQ | < LOQ |
| DMP | 9.91 ± 0.96 | | 0.129 ± 0.010 | < LOQ | 0.289 ± 0.037 | < LOQ | 0.18 | 0.114 ± 0.010 | 1.183 ± 0.012 | 0.034 ± 0.020 |
| DEP | 2.53 ± 0.46 | | 1.71 ± 0.38 | < LOQ | 4.9 ± 1.6 | 1.81 ± 0.39 | 5.2 | 3.38 ± 0.90 | 4.79 ± 0.63 | 2.4 ± 1.0 |
| DiBP | 17.43 ± 0.64 | | 20.8 ± 3.5 | | 27.8 ± 4.1 | 19.4 ± 3.9 | 6.2 | 16.1 ± 4.3 | 42 ± 13 | 81 ± 26 |
| DBP | 17.0 ± 3.5 | | 13.8 ± 1.9 | | 11.0 ± 2.2 | 13.3 ± 1.3 | < LOQ | < LOQ | 28 ± 24 | 10.6 ± 2.6 |
| DPP | < LOQ | 0.22 | 0.140 ± 0.066 | | | | 2.3 | 11.18 ± 0.86 | | |
| BBP | | | | | < LOQ | < LOQ | < LOQ | 2.47 ± 0.23 | < LOQ | 2.6 ± 2.3 |
| DEHA | | | | | < LOQ | < LOQ | < LOQ | < LOQ | | 20 |
| DnOP | | | | | | | | | | |
| BTZ | 65.1 ± 8.9 | < LOQ | < LOQ | < LOQ | 62 ± 22 | 10.2 ± 2.0 | < LOQ | < LOQ | 994 ± 103 ^a | 1213 ± 245 ^a |
| TBP | 0.789 ± 0.029 | 0.09 | 0.176 ± 0.010 | < LOQ | 1.34 ± 0.22 | < LOQ | 0.13 | 0.0872 ± 0.0013 | 11.5 ± 1.1 | 13.3 ± 2.3 |
| BHT | 2.05 ± 0.33 | | < LOQ | < LOQ | 0.99 ± 0.65 | | 0.25 | | 125 ± 28 | 30.1 ± 4.2 |

^a Estimated values (above calibration range).

4. Conclusions

A miniaturized method based on SPE-SPME-GC-MS/MS was successfully developed to determine 40 compounds, including PAHs, plasticizers, antioxidants and vulcanisation additives in indoor and outdoor air samples above tire rubber materials. SPME experimental conditions were performed by a mixed level fraction experimental design. The optimal conditions involve the use of a PDMS/DVB fibre in a 10 mL vial containing the enriched sorbent (Tenax TA, 25 mg) at 100 °C. Quantification was possible preparing matrix matched standards in Tenax TA. The whole SPE-SPME-GC-MS/MS methodology was validated in terms of linearity, precision and accuracy. RSD values for most compounds were lower than 16 % and recoveries were around 109 %. Additionally, the method provided low limits of detection (0.01–4.6 ng m⁻³). Finally, the methodology was applied to a wide range of air samples including childrens' playgrounds, synthetic turf football pitches, and tire warehouses. Results demonstrated the ubiquity and diffusion of these hazardous compounds from the tire rubber facilities to the adjacent air, which can suppose a health risk for the users of these surfaces, as well as for workers of the tire industry and those laying the recycled rubber surfaces.

The proposed miniaturized methodology is fast and sensitive, allowing a high throughput (total analysis time 61 min including the sampling step), and can be easily implemented in any laboratory due to the simple and minimal instrumentation and equipment required. Once the samples reach the lab, the analytical process can be easily automatized using a SPME autosampler.

Declaration of Competing Interest

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

CRedit authorship contribution statement

Daniel Armada: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Maria Celeiro:** Writing – review & editing, Visualization. **Thierry Dagnac:** Conceptualization, Writing – review & editing, Funding acquisition. **Maria Llompert:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Acknowledgements

This research was supported by projects RETOS [PID2019-104336RB-I00](#) and [UNST10-1E-491](#) (Ministry of Science and Innovation, Spain) and [ED431 2020/06](#) and [IN607B 2019/13](#) (Xunta de Galicia). The authors belong to the National Network for the Innovation in miniaturized sample preparation techniques, [RED2018-102522-T](#). This study is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society and upon work from the IUPAC project No. [2021-015-2-500](#) 'Greenness of official standard sample preparation methods'. All these programs are co-funded by FEDER (EU). The authors would like to thank all the people who have allowed sampling in private establishments, as well as the Concello de Guitiriz and Concello de Vilalba (Lugo, Spain) for collaborating in sampling in public places.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2022.462911](https://doi.org/10.1016/j.chroma.2022.462911).

References

- [1] U. Arachchige, G.M. Sithari, T. Tgahr, G.M. Tharakie, K.V.H. Tharuka, Environmental pollution by tire manufacturing industry, *Int. J. Sci. Technol. Res.* 8 (2018) 80–81.
- [2] Europe 94% of all End of Life Tyres were collected and treated in 2019, European Tyre & Rubber manufacturers association (ETRma), 2021 https://consorciocaucho.es/documentos/20210511_etрма_press-release_elt-2019.pdf (accessed 10 October 2021).
- [3] K. Formela, Sustainable development of waste tires recycling technologies—recent advances, challenges and future trends, *Adv. Ind. Eng. Pol. Res.* 4 (3) (2021) 209–222.
- [4] M. Celeiro, D. Armada, T. Dagnac, J. de Boer, M. Llompart, Hazardous compounds in recreational and urban recycled surfaces made from crumb rubber. Compliance with current regulation and future perspectives, *Sci. Total Environ.* 755 (2021) 142566.
- [5] B. Bocca, G. Forte, F. Petrucci, S. Costantini, P. Izzo, Metals contained and leached from rubber granulates used in synthetic turf areas, *Sci. Total Environ.* 407 (7) (2009) 2183–2190.
- [6] M. Llompart, L. Sanchez-Prado, J.P. Lamas, C. Garcia-Jares, E. Roca, T. Dagnac, Hazardous organic chemicals in rubber recycled tire playgrounds and pavers, *Chemosphere* 90 (2) (2013) 423–431.
- [7] L. Marsili, D. Coppola, N. Bianchi, S. Maltese, M. Bianchi, M.C. Fossi, Release of polycyclic aromatic hydrocarbons and heavy metals from rubber crumb in synthetic turf fields: preliminary hazard assessment for athletes, *J. Environ. Anal. Tox.* 5 (2) (2015) 1.
- [8] S.H. Brandsma, M. Brits, Q.R. Groenewoud, M.J.M. Van Velzen, P.E.G. Leonards, J. De Boer, Chlorinated paraffins in car tires recycled to rubber granulates and playground tiles, *Environ. Sci. Technol.* 53 (13) (2019) 7595–7603.
- [9] K. Schneider, M. de Hoogd, M.P. Madsen, P. Haxaire, A. Bierwisch, E. Kaiser, ERASSTRI-European risk assessment study on synthetic turf rubber infill-part 1: analysis of infill samples, *Sci. Total Environ.* 718 (2020) 137174.
- [10] E. Skoczynska, P.E.G. Leonards, M. Llompart, J. de Boer, Analysis of recycled rubber: development of an analytical method and determination of polycyclic aromatic hydrocarbons and heterocyclic aromatic compounds in rubber matrices, *Chemosphere* 276 (2021) 130076.
- [11] D. Armada, M. Llompart, M. Celeiro, P. Garcia-Castro, N. Ratola, T. Dagnac, J. de Boer, Global evaluation of the chemical hazard of recycled tire crumb rubber employed on worldwide synthetic turf football pitches, *Sci. Total Environ.* 812 (2022) 152542.
- [12] Candidate List of substances of very high concern for Authorisation, European Chemicals Agency (ECHA), 2021 <https://echa.europa.eu/candidate-list-table> (accessed 10 October 2021).
- [13] M. Celeiro, T. Dagnac, M. Llompart, Determination of priority and other hazardous substances in football fields of synthetic turf by gas chromatography–mass spectrometry: A health and environmental concern, *Chemosphere* 195 (2018) 201–211.
- [14] D. Armada, M. Celeiro, A. Martinez-Fernandez, P. Nurerk, T. Dagnac, M. Llompart, Miniaturized active air sampling method for the analysis of tire rubber pollutants from indoor and outdoor places, *J. Sep. Sci.* 44 (8) (2021) 1694–1705.
- [15] M. Celeiro, D. Armada, N. Ratola, T. Dagnac, J. de Boer, M. Llompart, Evaluation of chemicals of environmental concern in crumb rubber and water leachates from several types of synthetic turf football pitches, *Chemosphere* 270 (2021) 128610.
- [16] European Chemicals Agency (ECHA), Atmospheric pollutants directive, annex I – annual emission reporting, 80 Substances, 2021.
- [17] Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, *Eur. Off. J.* 23 (2005) 3.
- [18] M.R. Ras, F. Borrull, R.M. Marcé, Sampling and preconcentration techniques for determination of volatile organic compounds in air samples, *TrAC-Trend, Anal. Chem.* 28 (3) (2009) 347–361.
- [19] M.I. Mattina, M. Isleyen, W. Berger, S. Ozdemir, Examination of crumb rubber produced from recycled tires, The Connecticut Agricultural Experiment Station, New Haven, 10 October 2021 <https://www2.teamlogic.com/userfiles/file/154/11%20CT%20Examination%20of%20Crumb%20Rubber%20AUG2007.pdf> (accessed).
- [20] X. Li, W. Berger, C. Musante, M.I. Mattina, Characterization of substances released from crumb rubber material used on artificial turf fields, *Chemosphere* 80 (3) (2010) 279–285.
- [21] E. Menichini, V. Abate, L. Attias, S. De Luca, A. Di Domenico, I. Fochi, G. Forte, N. Iacovella, A.L. Iamiceli, P. Izzo, Artificial-turf playing fields: contents of metals, PAHs, PCBs, PCDDs and PCDFs, inhalation exposure to PAHs and related preliminary risk assessment, *Sci. Total Environ.* 409 (23) (2011) 4950–4957.
- [22] C. Dye, A. Bjerke, N. Schmidbauer, S. Mané, Measurement of air pollution in indoor artificial turf halls, Report Number NILU OR 3 (2006).
- [23] N.J. Simcox, A. Bracker, G. Ginsberg, B. Toal, B. Golembiewski, T. Kurland, C. Dye, A. Bjerke, N. Schmidbauer, S. Mané, Measurement of air pollution in indoor artificial turf halls, Report Number NILU OR 3 (2006).
- [24] K. Schneider, M. de Hoogd, P. Haxaire, A. Philipps, A. Bierwisch, E. Kaiser, ERASSTRI-European risk assessment study on synthetic turf rubber infill-part 2: migration and monitoring studies, *Sci. Total Environ.* 718 (2020) 137173.
- [25] C.E. Donald, R.P. Scott, G. Wilson, P.D. Hoffman, K.A. Anderson, Artificial turf: chemical flux and development of silicone wristband partitioning coefficients, *Air Qual. Atmos. Health* 12 (5) (2019) 597–611.
- [26] M. Celeiro, J.P. Lamas, C. Garcia-Jares, T. Dagnac, L. Ramos, M. Llompart, Investigation of PAH and other hazardous contaminant occurrence in recycled tire rubber surfaces. Case-study: restaurant playground in an indoor shopping centre, *Int. J. Environ. Anal. Chem.* 94 (12) (2014) 1264–1271.
- [27] J. Regueiro, C. Garcia-Jares, M. Llompart, J.P. Lamas, R. Cela, Development of a method based on sorbent trapping followed by solid-phase microextraction for the determination of synthetic musks in indoor air, *J. Chromatogr. A* 1216 (14) (2009) 2805–2815.
- [28] J.P. Lamas, L. Sanchez-Prado, M. Lores, C. Garcia-Jares, M. Llompart, Sorbent trapping solid-phase microextraction of fragrance allergens in indoor air, *J. Chromatogr. A* 1217 (33) (2010) 5307–5316.
- [29] M.E.J. Pronk, M. Woutersen, J.M.M. Herremans, Synthetic turf pitches with rubber granulate infill: are there health risks for people playing sports on such pitches? *J. Expo. Sci. Env. Epidemiol.* 30 (3) (2020) 567–584.
- [30] J.N. Bianchini, G. Nardini, J. Merib, A.N. Dias, E. Martendal, E. Carasek, Simultaneous determination of polycyclic aromatic hydrocarbons and benzene, toluene, ethylbenzene and xylene in water samples using a new sampling strategy combining different extraction modes and temperatures in a single extraction solid-phase microextraction-gas chromatography-mass spectrometry procedure, *J. Chromatogr. A* 1233 (2012) 22–29.
- [31] A.N. Dias, V. Simao, J. Merib, E. Carasek, Cork as a new (green) coating for solid-phase microextraction: determination of polycyclic aromatic hydrocarbons in water samples by gas chromatography-mass spectrometry, *Anal. Chim. Acta* 772 (2013) 33–39.
- [32] M. Llompart, M. Celeiro, C. Garcia-Jares, T. Dagnac, Environmental applications of solid-phase microextraction, *TrAC-Trend, Anal. Chem.* 112 (2019) 1–12.
- [33] Commission Implementing Decision (EU) 2017/1210 of 4 July 2017 on the identification of bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and diisobutyl phthalate (DIBP) as substances of very high concern according to Article 57(f) of Regulation (EC) No 1907/2006 of the European Parliament and of the Council (notified under document C 4462), 2017.
- [34] European Chemicals Agency (ECHA), Substance information for Benzothiazole. <https://echa.europa.eu/es/substance-information/-/substanceinfo/100.002.179> (accessed 10 October 2021).
- [35] A. Watterson, Artificial turf: contested terrains for precautionary public health with particular reference to Europe? *Int. J. Environ. Res. Pub. Health* 14 (9) (2017) 1050.
- [36] R. Moretto, Environmental and health assessment of the use of elastomer granulates (virgin and from used tyres) as filling in third-generation artificial turf, Report. ALIAPUR in partnership with Fieldturf Tarkett and the ADEME (Environmental French Agency). <https://www.groundsmartrubbermulch.com/docs/resources/Environmental-and-health-assessment-of-the-use-of-elastomer-granulates-virgin-and-from-used-tyres-as-infill-in-third-generation-artificial-turf.pdf> (accessed 13 October 2021).