



Recycled tire rubber materials in the spotlight. Determination of hazardous and lethal substances

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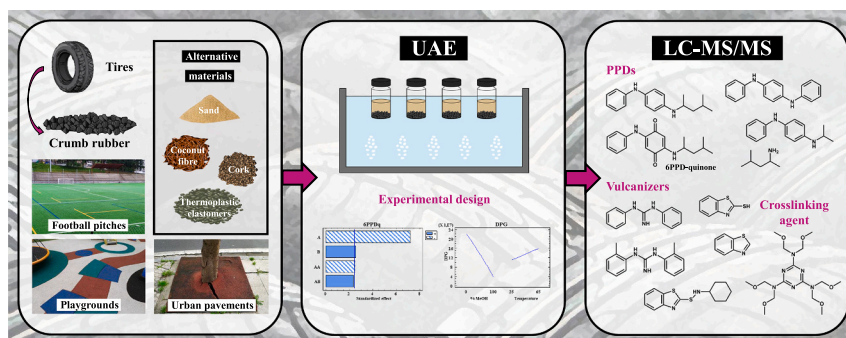
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HIGHLIGHTS

- Tire crumb rubber of different origin (playgrounds or sports fields) is analysed.
- An UAE-LC-MS/MS method is optimized for the analysis of 11 new emerging pollutants.
- Emerging hazardous chemicals (PPDs, vulcanizers) found in all rubber playing surfaces.
- 6PPD reaches concentrations up to 0.2 % w/w in new synthetic fields.
- Infill alternative materials are free of the target compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

One way of recycling end-of-life tires is by shredding them to obtain crumb rubber, a microplastic material (<0.5 mm), used as infill in artificial turf sports fields or as playground flooring. There is emerging concern about the health and environmental consequences that this type of surfaces can cause. This research aims to develop an analytical methodology able to determine 11 compounds of environmental and health concern, including antiozonants such as N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine (6PPD) or N, N'-diphenyl-1,4-phenylenediamine (DPPD), and vulcanization and crosslinking agents, such as N-cyclohexylbenzothiazole-2-sulfenamide (CBS), 1,3-di-o-tolylguanidine (DTG) or hexamethoxymethylmelamine (HMMM) from tire rubber. Ultrasound assisted extraction followed by liquid chromatography coupled to tandem mass spectrometry (UAE-LC-MS/MS) is validated demonstrating suitability. The methodology is applied to monitor the target compounds in forty real crumb rubber samples of different origin including, football pitches, outdoor and indoor playgrounds, urban pavements, commercial samples, and tires. Several alternative infill materials, such as sand, cork granulates, thermoplastic elastomers and coconut fibres, are also collected and analysed. All the target analytes are identified and quantified in the crumb rubber samples. The antiozonant 6PPD is present at the highest concentrations up to 0.2 % in new synthetic fields. The tire rubber-derived chemical 6PPD-quinone (2-((4-methylpentan-2-yl)amino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione), recently linked to acute mortality in salmon, is found in all types of crumb rubber samples attaining concentrations up to 40 $\mu\text{g g}^{-1}$ in football pitches. The crosslinking agent HMMM is detected in most of the playing surfaces, at concentrations up to 36 $\mu\text{g g}^{-1}$.

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g^{-1} . The tested infill alternatives are free of most of the target compounds. To the best of our knowledge, this study is the largest study considering the target compounds in tire rubber particles and the first to focus on these compounds in playgrounds including the analysis of HMMM, 6PPD-quinone and DTG in crumb rubber used as an infill material.

1. Introduction

Tire rubber is a polymeric material containing hundreds of chemicals. This material reaches the environment due to the generation of tire wear particles (TWP) (Luo et al., 2021), as well as, due to recycled tire crumb rubber (RTCR), a material obtained from the recycling of end-of-life tires (ELTs) in sports and leisure surfaces (Celeiro et al., 2021a), representing the main source of intentionally added microplastics in the environment (ECHA granules and mulches, 2023). In recent years, several studies revealed the presence of various hazardous compounds in RTCR such as heavy metals, metalloids, plasticizers, polycyclic aromatic hydrocarbons (PAHs), flame retardants, among others (Kubota et al., 2022; Graça et al., 2022; Llompert et al., 2013; Celeiro et al., 2014; Celeiro et al., 2018; Schneider et al., 2020; Gomes et al., 2021; Moreno et al., 2023). The global dimension of the use of this material as infill in synthetic turf pitches was demonstrated (Armada et al., 2022), as well as the bioaccessibility of some PAHs and other hazardous chemicals was recently revealed (Armada et al., 2023). The European legislation only limits the content of 8 PAHs to $20 \mu\text{g g}^{-1}$ in such materials, and 4 plasticizers (bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and diisobutyl phthalate (DIBP)) to $1000 \mu\text{g g}^{-1}$ in plastic materials, including rubber (Commission Regulation (EU), 2018; Zuccaro et al., 2022). However, in September of 2023, the European Commission announced the ban for the use of crumb rubber as infill in artificial turf fields, allowing a transitional period of 8 years to ensure that a great number of synthetic sport surfaces that use this type of product can reach their natural end-of-life (Commission Regulation (EU), 2023). This prohibition shows the importance of alternative infill materials, some of which have been the subject of studies that have shown them to be free of PAHs and plasticizers (Celeiro et al., 2021b).

Some of the above-mentioned compounds, such as PAHs (Celeiro et al., 2018), are well-known hazardous chemicals, whilst other compounds, such as N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and related compounds, are of recent concern. 6PPD is part of N, N'-substituted-p-phenylenediamines (PPDs), which include, for example, N,N'-diphenyl-p-phenylenediamine (DPPD) and 4-isopropylaminodiphenylamine (IPPD) (Zhao et al., 2023). This family of antioxidants is overlooked in tire crumb rubber, and a deeper characterization appears necessary. The environmental hazard that 6PPD can cause was showed only very recently. Tian et al. (Tian et al., 2021) associated the death of coho salmon with TWP leachates and specifically with a 6PPD derivative, 6PPD-quinone (2-((4-methylpentan-2-yl)amino)-5-(phenylamino) cyclohexa-2,5-diene-1,4-dione, 6PPDq). 6PPD is estimated to be present between 0.4 % and 2 % in passenger and commercial vehicle tires (Tian et al., 2021).

The presence of these substances has been recently studied in a prepared mixture sample of TWP from new and used tires, generated through physical abrasion (Zhao et al., 2023). 6PPD was found at a concentration of $2300 \mu\text{g g}^{-1}$ while 6PPDq at a much lower concentration ($12 \mu\text{g g}^{-1}$), and other compounds of the same family, DPPD, IPPD and the transformation product (TP) of 6PPD 1,3-Dimethylbutylamine (DMBA), were also found in this sample. In addition, crumb rubber from artificial turf fields from public parks ($n = 3$) and schools ($n = 6$) were also analysed. The median values for 6PPD were much lower ($1.2 \mu\text{g g}^{-1}$) while 6PPDq appeared at similar levels ($9.8 \mu\text{g g}^{-1}$). Masset et al., (Masset et al., 2022) analysed a single sample of cryogenically milled tire tread (CMTT) obtained from 3 tires and reported values of $31,000 \mu\text{g g}^{-1}$ for 6PPD and $14 \mu\text{g g}^{-1}$ for 6PPDq. In 2022, another study

addressed the analysis of 6PPD, DPPD and IPPD in commercial samples of tire crumb rubber. 6PPD was found between 62 and $2916 \mu\text{g g}^{-1}$, DPPD between 0.63 and $83 \mu\text{g g}^{-1}$ while 6PPDq was not reported (Kawakami et al., 2022).

Other main chemical agents added to rubber are vulcanizers, such as 1,3-diphenyl guanidine (DPG), 1,3-di-o-tolylguanidine (DTG), benzothiazole (BTZ), 2-mercaptobenzothiazole (MBTZ) or N-cyclohexylbenzothiazole-2-sulfenamide (CBS) (Müller et al., 2022; Kawakami et al., 2022; Li and Kannan, 2023). These compounds are also overlooked in tire and tire particles, especially in RTCR, and some of them could pose environmental and health hazards (Ichihara et al., 2023; Kim et al., 2023; Li and Kannan, 2023). BTZ and MBTZ study is quite difficult due to their ubiquity (BTZ) and the complexity of the analysis (MBTZ) (Skoczyńska et al., 2021; Celeiro et al., 2021b). These chemical agents have been determined in real samples of crumb rubber ($n = 10$) and ELTs ($n = 3$) using UAE and a clean-up step with SPE (Solid Phase Extraction) (Skoczyńska et al., 2021). The BTZ concentrations in artificial football fields and in tires were between 4.2 and 40 and 12–114 $\mu\text{g g}^{-1}$, respectively. As the authors say, MBTZ could only be quantified in 2 samples, highlighting that GC analysis was less suitable for this vulcanizer. In the above-mentioned study of Kawakami et al. (Kawakami et al., 2022), MBTZ and DPG were analysed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS), while the PPDs, BTZ and CBS were analysed by GC-MS. The extraction method consisted of UAE (Ultrasound Assisted Extraction) with 20 mL of solvent (acetone: dichloromethane, 1:1 v/v) for 2 h. Schneider et al. (Schneider et al., 2020) studied crumb rubber samples (commercial and sports fields). The extraction method consisted of using a standardized method where methanol was the extraction solvent and 2 g of sample were employed. 6PPD, DPG and BTZ were some of the chemical compounds detected at the highest concentrations (571, 51 and $48 \mu\text{g g}^{-1}$, respectively).

The crosslinking agent hexamethoxymethylmelamine (HMMM) was only quantified in rubber particles in one study (Zhao et al., 2023), showing a maximum concentration of $3.1 \mu\text{g g}^{-1}$. This compound is more studied in water along with its large number of by-products (Johannessen et al., 2021; Alhelou et al., 2019).

The purpose of this study is the characterization of tire particles, mainly recycled tire crumb rubber, regarding several emerging pollutants of environmental and health concern. To achieve this, an analytical method has been developed, able to isolate and successfully determine eleven compounds including 6PPD, 6PPDq, BTZ, CBS, DMBA, DPG, DPPD, DTG, HMMM, IPPD and MBTZ. To perform that, a methodology based on Ultrasound Assisted Extraction (UAE) followed by LC-MS/MS analysis was developed and validated in terms of main analytical parameters. After that, forty rubber samples of different origin including, football pitches, playgrounds, urban pavements, commercial samples, and tires from different vehicles, among others, were analysed. In addition, several alternative materials were also analysed with comparative purposes ($n = 6$). To the best of our knowledge, this study is the first to focus on these analytes in pavement of playgrounds and to determine DTG in crumb rubber samples, and there is only a single study that includes the analysis of HMMM, 6PPDq and DMBA in crumb rubber used as infill. Moreover, this work stands out for the great amount and variety of real crumb rubber samples collected *in situ*, as well as for the comparison with alternative materials.

2. Materials and methods

2.1. Reagents and materials

The studied compounds, names, CAS numbers, purity, retention time, ionization mode and MS/MS transitions are depicted in **Table S1**. Benzothiazole (BTZ) and 2-mercaptobenzothiazole (MBTZ) were purchased from Sigma-Aldrich Chemie. *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD), 4-isopropylaminodiphenylamine (IPPD), *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS) and hexamethoxymethylmelamine (HMMM) were provided by TCI Europe N.V. (Zwijndrecht, Belgium). *N,N*-diphenyl-*p*-phenylenediamine (DPPD) and 1,3-dimethylbutylamine (DMBA) were purchased from Dr. Ehrenstorfer (Ausborg, Germany). 1,3-di-*o*-tolylguanidine (DTG) was provided by ThermoScientific (San José, California), 1,3-diphenyl guanidine (DPG) by Alfa Aesar (Ward Hill, Massachusetts) and *N*-(1,3-Dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine-quinone (6PPDq) by Toronto Research Chemicals Inc. (North York, Canada). Ethyl acetate (EtAc, 99.5 %), methanol (MeOH, 99.9 %) and ultrapure water were provided by Scharlab (Barcelona, Spain). Nitrogen (> 99.981 %) was produced by a Peak Scientific generator. All reagents and solvents were of analytical grade.

2.2. Samples and sampling procedure

Thirty-two crumb rubber samples from indoor and outdoor sport, leisure and urban tire rubber surfaces, were collected and analysed. In addition, six samples of alternative infill materials in football pitches and playgrounds were also collected and analysed. Most of the samples are from Galicia (NW Spain). An amount between 2 and 100 g of sample were taken from the studied surfaces, transferred to a glass container, sealed with an aluminium cap, stored at room temperature, and protected from light until analysis. Besides, 3 commercial rubber products were marketed and analysed, including two crumb rubber samples and one rubber tile. Finally, since the origin of these materials are ELTs, several tire samples were also acquired and analysed. A detailed description is given in **Table S2**.

2.3. Ultrasound assisted extraction (UAE)

200 mg of sample transferred to a 4 mL vial and 2 mL of solvent were added. The vial was sealed and immersed into an ultrasound bath (*P. Selecta*, Barcelona, Spain) for 15 min, at 50 kHz and 25 °C or 65 °C depending on the experiment. After the UAE extraction, the organic supernatant was filtered through 0.22 µm PTFE filters (25 mm diameter), and 200 µL of the extract were evaporated under nitrogen stream to dryness. Then, it was reconstituted in 1 mL of MeOH and diluted in a proportion of 40:60 aqueous phase (H₂O, 0.1 formic acid and 3 mM of ammonium formate) and organic phase (MeOH, 0.1 formic acid and 3 mM of ammonium formate) resulting in a 1:100 (*w/v*) dilution prior liquid chromatography coupled to tandem mass spectrometry analysis (LC-MS/MS). In some cases, different dilutions factors were employed.

2.4. Chromatographic and mass spectrometry analysis

Analysis was performed employing a Thermo Scientific (San José, CA, USA) instrument based on a TSQ Quantum Ultra™ triple quadrupole mass spectrometer equipped with a HESI-II (heated electrospray ionization) source and an Accela Open autosampler with a 20 µL loop. The chromatographic separation was achieved on a Kinetex C18 column (2.6 µm, 100 × 2.1 mm) obtained from Phenomenex (Torrance, CA, USA). The injection volume was 10 µL and the column temperature was set at 40 °C. The mobile phase consisted of water (A) and methanol (B), both containing 0.1 % formic acid and 3 mM of ammonium formate. The elution program started with 50 % of B held for 1 min; then it was increased up to 90 % of B in 9 min, and held for 1 min. Then, initial

conditions of 50 % of B were reached in 7 min. Finally, the last 2 min, the gradient remains isocratic at 50 % of B. The mobile phase flow rate was 200 µL min⁻¹. The total run time for each injection was 19 min. The mass spectrometer and the HESI-II source were working in the positive mode. The acquisition mode was Selected reaction monitoring (SRM), including 2 or 3 transitions per compound (see **Table S1**), for an unequivocal identification and quantification of the target analytes. The system was operated employing Xcalibur 2.2 and Trace Finder™ 3.2 software.

2.5. Statistical analysis

Statistical analysis and design of experiments (DOE) were performed using Statgraphics Centurion XVIII (Manugistics, Rockville, MD, USA) as software package. A multi-factor categorical experimental design and a mixed level fraction experimental design were selected to optimize the extraction procedure.

Analysis of variance and some graphical tools used in the optimization process are described below.

Analysis of variance (ANOVA) describes the variation of the studied factors on the responses. The F-ratio indicates the contribution of each factor (or interaction) on the variance of the response obtained, while the p-values indicates the statistical significance. Factors with p-values < 0.05 indicate statistically significance at the 95 % confidence level. ANOVA graphs show scaled effects of each factor by comparing the natural variance of the plot with that of the residuals, which are displayed at the bottom of the plot. In the mixed level fraction experimental design, three types of graphic tools are displayed. Pareto charts are bar graphs in which each bar length is proportional to the effect of the corresponding factor or interaction while the vertical line represents the statistical significance bound at 95 % confidence level. In main effect plots, the variation in responses when varying from the low to the high level is represented. The steeper the slope of the line, the greater the effect of the factor. Finally, interaction plots are illustrations of the variation in responses when one factor is affected by the level of other factor and allow visualizing the more favourable conditions.

All graphs were constructed employing Microsoft Office 365 and the abovementioned software.

3. Results and discussion

3.1. Optimization of LC-MS/MS

The target analytes were directly introduced into the ion source and SRM transitions and collision energies were optimized and contrasted with bibliography. All SRM transitions were acquired in only one segment with a scan time of 0.020 s for each transition.

The chromatographic solvent gradient was optimized to achieve a suitable resolution in a short time. Final conditions are indicated in **Section 2.4**. The percentage of aqueous phase (AP) and organic phase (OP) injected can affect both peak shape and chromatographic response. First, the injection of 5 of the compounds (50 µg L⁻¹ see **Fig. 1a**) was compared in different mixtures, from 100 % AP to 100 % OP, varying the proportions 10 by 10. As can be seen, better responses were obtained in the medium AP and OP fractions. For example, HMMM showed higher responses in the 40:60 and 30:70 AP and OP percentages. For the AP/OP 70:30, 60:40, 50:50, 40:60 and 30:70 mixtures, similar chromatographic responses (area counts) were obtained. In addition, the peak shape can also be affected by the percentage of phases. Mostly, better peak shape was observed for the previous mentioned 5 AP/OP mixtures. These mixtures were selected to repeat the tests, this time including BTZ and MBTZ (see **Fig. 1b**). Similar chromatographic responses were observed for the 5 AP/OP mixtures and non-statistical differences were observed, except for CBS, which showed much higher chromatographic response for 40:60 and 30:70 AP/OP. Since DPG peak was unfolded in injection conditions of 30:70 AP/OP (**Fig. S1**), the selected conditions were 40:60

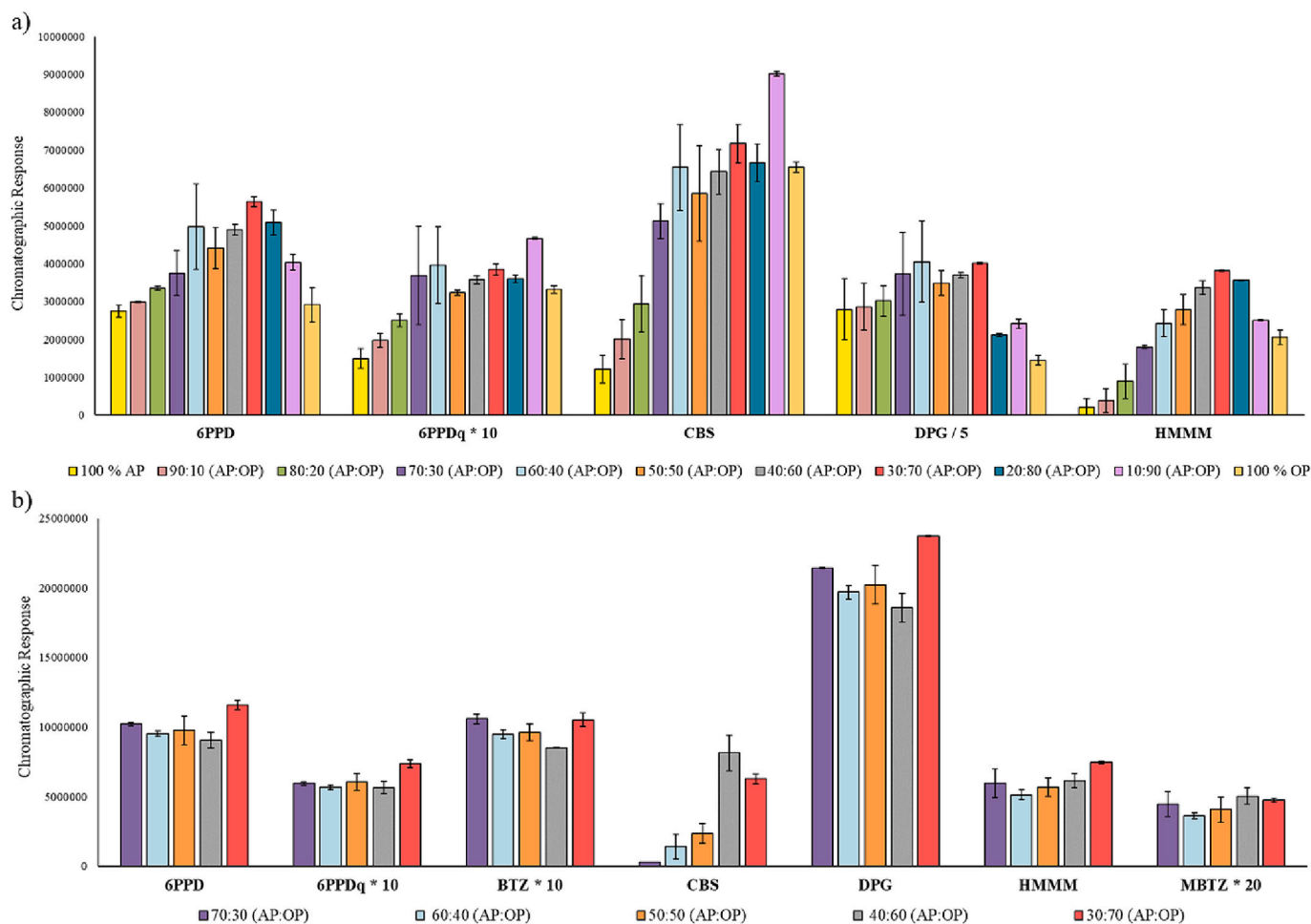


Fig. 1. a) Chromatographic responses for 6PPD, 6PPDq, CBS, DPG and HMMM in different AP:OP mixtures, from 100 % AP to 100 % OP, varying the proportions 10 by 10, b) Chromatographic responses for 6PPD, 6PPDq, BTZ, CBS, DPG, HMMM and MBTZ in AP/OP 70:30, 60:40, 50:50, 40:60 and 30:70 mixtures. AP: aqueous phase, OP: organic phase. For the composition of each phase, see Section 2.4.

Table 1

ANOVA table for a) the multi-factor categorical experimental design, and b) the mixed-level factorial experimental design. Values in bold indicate statistical significance (p -value < 0.05).

a.					
Compound	Solvent		Temperature		
	F	P	F	P	P
6PPD	15.30	0.0253	0.05		0.8445
6PPDq	4.13	0.1373	0.17		0.7107
BTZ	1.77	0.3248	4.21		0.1327
CBS	3.98	0.1434	0.44		0.5563
DPG	2.09	0.2803	1.07		0.3766
HMMM	9.47	0.0487	13.66		0.0344
MBTZ	2.52	0.2342	45.53		0.0066

b.								
Compound	Solvent (% MeOH) (A)		Temperature (°C) (B)		AB		AA	
	F	P	F	P	F	P	F	P
6PPD	215.28	0.0000	2.94	0.1374	20.22	0.0041	6.22	0.0469
6PPDq	51.63	0.0004	6.46	0.0440	5.52	0.0571	6.17	0.0475
BTZ	17.89	0.0055	11.64	0.0143	2.34	0.1766	1.23	0.3091
CBS	17.52	0.0058	18.69	0.0050	23.02	0.0030	17.97	0.0054
DPG	39.65	0.0007	4.43	0.0800	16.62	0.0065	0.05	0.8234
HMMM	12.93	0.0114	24.79	0.0025	0.59	0.4715	22.94	0.0030
MBTZ	50.73	0.0004	134.68	0.0000	9.37	0.0222	3.91	0.0954

AP/OP for further experiments.

3.2. Optimization of sample extraction solvent and temperature via experimental design

To achieve the most favourable extraction conditions, an experimental design optimization using a crumb rubber sample from a synthetic turf field containing the target compounds (non-spiked) was performed. In this way, the real interactions between the matrix and the analytes are fully considered. A multi-factor categorical experimental design (n° of experiments = 2 \cdot 4, see **Table S3**), was employed to observe trends of the extraction conditions (screening design). The extraction solvent was evaluated at four levels: ethyl acetate (EtAc), methanol (MeOH), a mixture EtAc/MeOH (50:50 v/v) and a mixture MeOH/H₂O (50:50 v/v). These levels were selected considering both the chromatographic mobile phase employed (MeOH, H₂O) and previous studies

in which the extraction efficiency of EtAc in this type of matrices was observed (Celeiro et al., 2018). Besides, the temperature was evaluated at two levels: ambient temperature (25 °C) and 65 °C (high temperature but below the boiling point at atmospheric pressure of the solvents). Interactions between factors were not included.

ANOVA results are indicated in **Table 1a**. Temperature is significant for HMMM and MBTZ, while solvent is for 6PPD and HMMM. **Fig. 2a** includes the ANOVA graphs for these compounds. As can be seen, the extraction at 65 °C attained a higher chromatographic response (right part of the graph). In addition, higher response is obtained with the mixture EtAc/MeOH and EtAc. In general, the extraction with MeOH/H₂O was inefficient. For 6PPD, 6PPDq, DPG and HMMM, EtAc and the mixture EtAc/MeOH show similar and higher responses than the other two solvent levels. These similarities between each extraction with each solvent can be seen in **Table S4** where the results of a multiple comparison procedure are shown (multiple range test, see supplementary

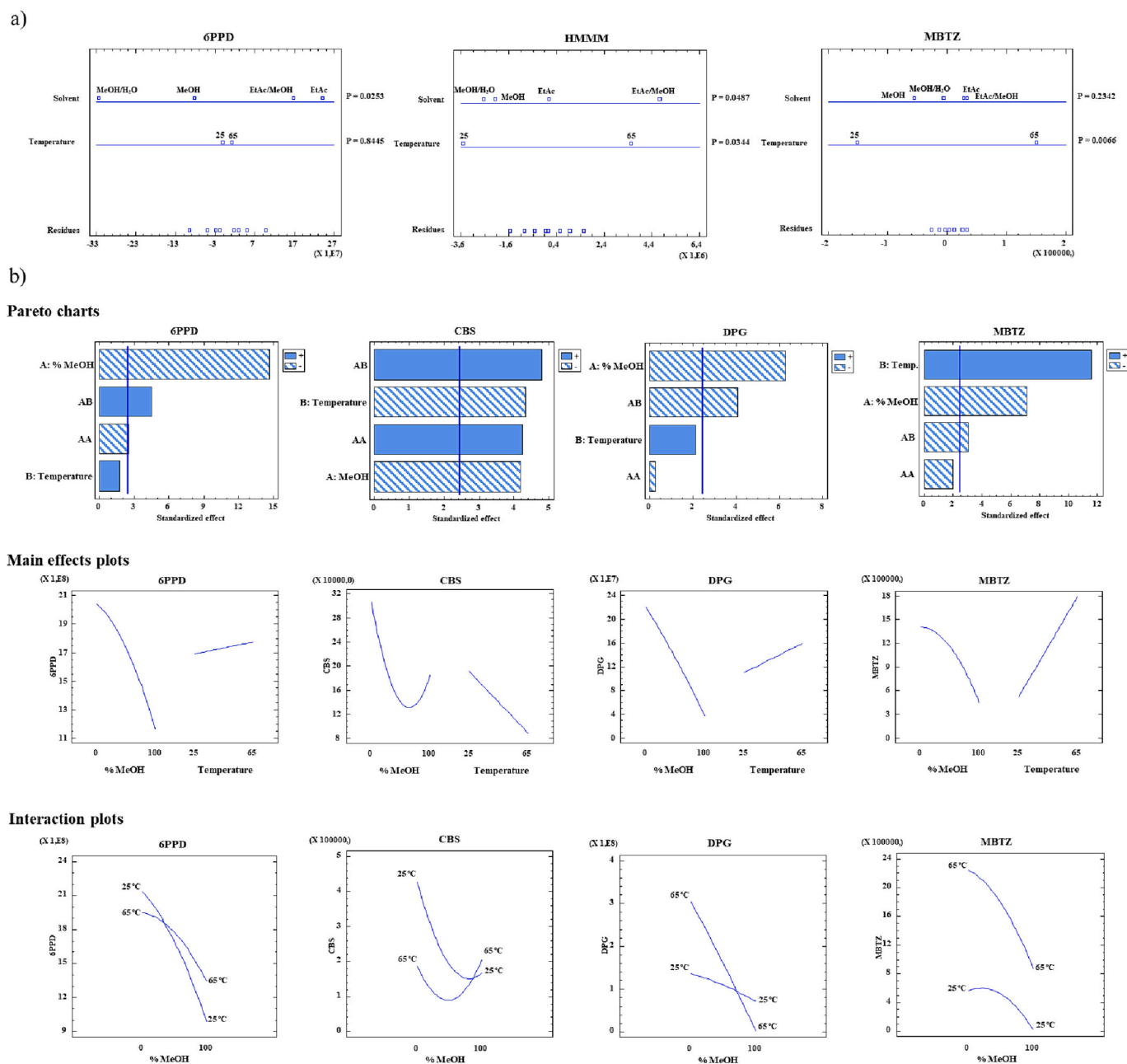


Fig. 2. a) ANOVA charts for 6PPD, HMMM and MBTZ in the multi-factor categorical experimental design, b) pareto charts, main effects plots, and interaction plots for 6PPD, CBS, DPG and MBTZ in the mixed-level factorial experimental design.

material).

Since the more favourable conditions were not clear at this stage, a second design mixed-level factorial experimental design was performed, and the experiments involved are included in **Table S5**. Replicates were carried out giving rise to 12 experiments. The factors and the levels included were the same but excluding this time the use of MeOH/H₂O. The solvent MeOH/EtAc (factor A) was studied at three levels (0 %, 50 % and 100% of MeOH) and the temperature (factor B) at two levels (25 °C and 65°C). Now the interaction between factors were considered, as well.

Table 1b shows F-ratio and p-values from the ANOVA analysis. The results of this experimental design can be visualized in the Pareto charts provided by the statistical software (see **Fig. 2b** and **Fig. S2**).

Solvent extraction is a statistically significant factor, for all analytes, while temperature is significant for all of them except 6PPD and DPG. Besides, the interaction between temperature and solvent is statistically significant for 6PPD, DPG, MBTZ and CBS.

Fig. 2b and **Fig. S2** displays the main effect plots. As can be seen, EtAc is the most favourable solvent for most analytes, excluding BTZ. Regarding temperature, 65 °C is the most suitable, excluding CBS. **Fig. 2b** includes the interaction plots for 6PPD, CBS, DPG and MBTZ. Once again, we can see that the most favourable conditions are EtAc and 65 °C (excluding 25 °C for CBS and MeOH for BTZ). **Table S6** summarizes the most favourable extraction conditions for each analyte.

The proposed methodology includes only a single extraction step. The possibility of performing a second extraction was evaluated in real samples. This experiment showed that the amount of extracted target analytes was below 10 % in all cases, and therefore a second extraction step was not considered necessary. In this way, the proposed method remains simple and more sustainable (less time, less solvent, less energy, etc.). The comparison of the responses obtained after the first and second round extraction is given in **Fig. S3**.

To confirm that the amount of solvent used (2 mL) was enough to efficiently extract the analytes, two real samples were extracted using a double amount of solvent (4 mL). The results were completely equivalent in both cases, confirming the selection of 2 mL as optimal solvent volume (for more information see Supplementary material, **Fig. S4**).

Finally, the extraction time was studied with the objective of

evaluating if lower extractions times were efficient (**Fig. S5**). In general, for most of the compounds the extraction times of 5 and 10 min showed lower extraction efficiency than 15 min. Therefore, 15 min were selected as the most suitable extraction time.

3.3. Method performance

Once the UAE-LC-MS/MS method was optimized, it was validated regarding main analytical quality parameters such as linearity, accuracy, sensitivity, and precision. Results are shown in **Table 2**.

The linearity study was performed with standard solutions (40:60 AP/OP) containing the target compounds covering a concentration range from 0.2 to 1000 µg L⁻¹ (thirteen levels by triplicate). Chromatographic responses were proportional to the concentrations of the studied compounds, with coefficients of determination (R²) higher than 0.990, except for DPPD (0.980).

Instrumental precision was evaluated intra-day ($n = 3$) and inter-day ($n = 6$) obtaining a relative standard deviation (RSD) values between 2 % and 15 %, and 7 % and 16 %, respectively.

IDLs and IQLs were calculated as the concentration of the standard giving a signal-to-noise ratio equal to 3 and 10, respectively. The values are shown in **Table 2**. IDLs are below 0.1 µg L⁻¹, excluding BTZ and MBTZ (< 0.8 µg L⁻¹).

The best way to evaluate the method extraction accuracy/efficiency would have consisted of analysing a certified reference material. But this kind of material was not available at the moment we performed our study. The method accuracy was then assessed employing fortification with the target compounds in real crumb rubber at three concentration levels (2.5, 25 and 250 µg g⁻¹) and subsequent recovery studies. The experiments were carried out by triplicate. Lower concentrations than 2.5 µg g⁻¹ were not considered since some compounds were present in all raw samples and this did not enable to conduct recovery studies at lower levels. The initial concentrations in raw materials were considered to calculate the final recoveries.

As can be seen in **Table 2**, recoveries were satisfactory for all compounds and the mean recovery values were in most cases between 85 and 100 %. Method precision was also evaluated, with RSD values between 1.8 % and 13 %, except for DPG.

Table 2

UAE-LC-MS/MS method performance: linearity, precision, accuracy, instrumental detection limits (IDLs) and quantification (IQLs), limits of detection (LODs) and quantification limits (LOQs).

Compound	Linearity		Precision (RSD, %)		IDL (µg L ⁻¹)	IQL (µg L ⁻¹)	LOD ^a (ng g ⁻¹)	LOQ ^a (ng g ⁻¹)	Accuracy (%)				
	R ²	Linear range (µg L ⁻¹)	Intra-day (n = 3)	Inter-day (n = 6)					0.25 µg g ⁻¹	2.5 µg g ⁻¹	25 µg g ⁻¹	Mean recovery	RSD (%)
6PPD	0.9950	0.2–1000	3	16	0.052	0.174	2.6	8.7	93 ± 24	79.5 ± 1.0	78.5 ± 4.9	83.7	11
6PPDq	0.9954	0.2–1000	1	14	0.071	0.235	3.55	11.8	98.5 ± 2.1	93.5 ± 1.0	85.5 ± 2.1	92.5	1.8
BTZ	0.9901	5–1000	4	7	0.790	2.63	39.5	132	99.1 ± 3.2	101 ± 28	88.5 ± 7.8	96.2	13
CBS	0.9982	0.2–100	15	15	0.032	0.108	1.6	5.4	91.5 ± 1.0	92.5 ± 9.2	80.0 ± 1.4	88.0	4.2
DMBA	0.9920	0.2–1000	8	13	0.025	0.08	1.25	4	87.9 ± 9.7	97 ± 11	100 ± 11	95.0	11
DPG	0.9916	0.2–1000	2	16	0.071	0.236	3.55	11.8	84 ± 21	105 ± 15	70 ± 17	86.3	18
DPPD	0.9801	0.2–250	13	11	0.043	0.14	2.15	7.0	97.0 ± 2.8	99 ± 14	88.5 ± 2.1	94.8	6.5
DTG	0.9989	0.2–1000	5	16	0.017	0.057	0.85	2.9	76 ± 15	106.0 ± 4.2	73 ± 14	85.0	7.2
HMMM	0.9943	0.2–500	8	15	0.031	0.102	1.55	5.1	99.5 ± 7.8	102 ± 14	99.0 ± 4.2	100	8.7
IPPD	0.9970	0.2–1000	9	16	0.009	0.031	0.45	1.6	61.4 ± 6.2	79 ± 11	105 ± 10	81.7	9.5
MBTZ	0.9944	5–1000	12	16	0.424	1.414	21.2	70.7	–	107.5 ± 6.4	93 ± 11	100	9.0

^a Calculated considering a sample dilution of 1:50 (w/v). Lowest values can be achieved by injecting 1:10 (w/v) dilution.

3.4. Analysis of crumb rubber samples

The method was applied to the analysis of the 11 tire rubber chemicals in a high number of recycled rubber samples of different origin collected from synthetic turf football pitches, children's outdoor and indoor playgrounds, urban pavements, as well as commercial rubber products. In addition, several tire samples, including car tires, tractor tires and one bike tire were analysed to check whether hazardous compounds could be found in different types of tires and thus facilitate their release in different environment compartments. Finally, some alternative materials used as flooring in playgrounds and sports fields were also analysed, to find out if they could be considered as a safer alternative regarding these chemicals. A detailed description of the tire rubber and alternative samples is given in **Table S2**.

3.4.1. Synthetic turf infill

A total of thirteen synthetic turf football pitch infills, eight recycled crumb rubber samples (from FP-1 to FP-8) and five alternative infill materials, including coconut fibre (FP-9), cork (FP-10), sand (FP-11 and FP-12), and thermoplastic elastomers (FP-13) were taken and analysed. Individual concentrations of the target substances are summarized in **Table 3a**. Statistical figures including frequency, concentration range, mean and median for each analyte in crumb rubber football pitches are shown in **Table 4**. To simplify visualization, the frequency and mean concentrations of the analytes are also depicted in **Fig. 3a**.

All 11 target compounds were found in the crumb rubber samples and 4 out of the 8 samples contained all compounds. On the other hand, the compounds were not present in the alternative material, excluding very low concentrations of 6PPD ($< 0.08 \mu\text{g g}^{-1}$). FP-9 is an exception since this sample consists of a mix material containing crumb rubber and coconut fibres, and, therefore, the compounds were also found.

Table 3

Analysis of real samples. Concentration ($\mu\text{g g}^{-1}$) of the target compounds in the crumb rubber samples from a) synthetic turf football pitches (FP); b) children's playgrounds. OP: outdoor playground, IP: indoor playground; c) urban pavements and tires. CT: car tire, BT: bike tire, TT: tractor tire, BIT: bike inner tube, CIT: car inner tube, UP: urban pavement, CR: commercial rubber granulate, Ctile: commercial rubber tile.

a.													
$\mu\text{g g}^{-1}$	Crumb Rubber								Alternative Materials				
	FP-1	FP-2	FP-3	FP-4	FP-5	FP-6	FP - 7	FP - 8	FP-9	FP-10	FP-11	FP-12	FP-13
6PPD	0.47	0.37	2085	59	1359	5.1	1.1	3.8	0.14	0.022	0.080	–	0.033
6PPDq	0.60	0.68	13	40	19	11	0.26	0.50	3.2	< LOD	–	–	< LOQ
BTZ	4.0	5.3	63	22	47	–	1.4	1.6	2.1	–	–	–	< LOQ
CBS	0.037	0.074	0.16	0.19	0.32	–	0.030	0.030	0.049	–	–	–	–
DMBA	0.80	0.21	73	25	21	2.1	1.2	2.8	n.a.	–	–	–	–
DPG	1.6	0.52	47	5.9	2.4	5.8	–	–	11	–	–	–	–
DPPD	0.23	–	23	15	26	0.52	0.35	0.71	n.a.	–	–	–	–
DTG	0.060	–	0.56	0.22	0.16	–	0.13	0.030	n.a.	–	–	–	–
HMMM	0.81	–	27	9.5	2.4	0.77	0.63	0.030	0.11	–	–	–	–
IPPD	0.090	–	9.1	2.3	0.73	–	0.030	–	n.a.	–	–	–	–
MBTZ	1.5	–	23	11	18	2.5	1.9	2.2	0.25	–	–	–	–

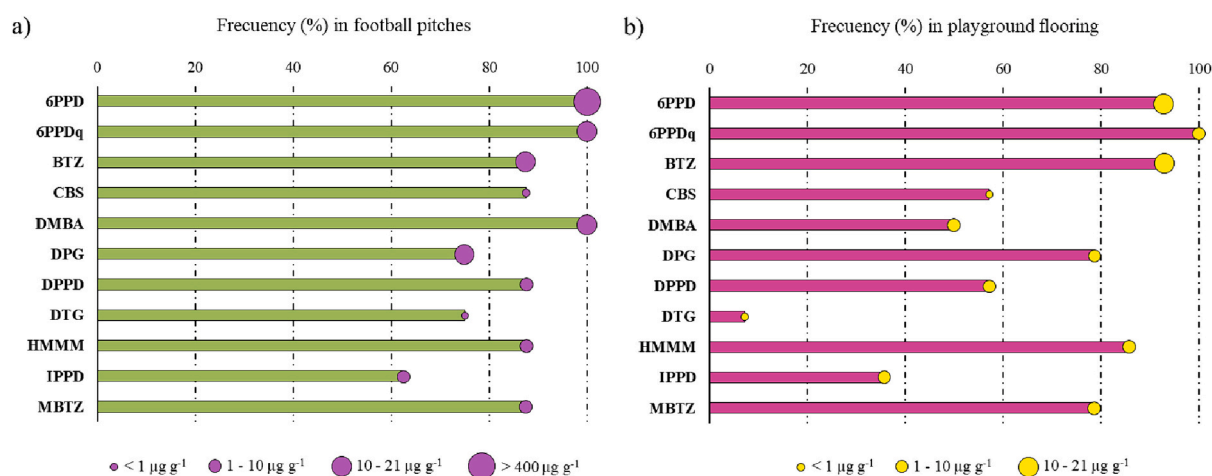
b.															
$\mu\text{g g}^{-1}$	Outdoor playground								Indoor playground						
	OP-1	OP-2	OP-3	OP-4	OP-5	OP-6	OP-7	OP-8	IP-1	IP-2	IP-3	IP-4	IP-5	IP-6	IP-7
6PPD	–	8.6	12	12	0.26	0.63	35	36	22	–	13	0.29	7.8	140	0.25
6PPDq	–	7.1	12	5.4	0.45	0.63	6.4	11	9.8	0.059	3.8	0.052	1.3	21	0.19
BTZ	–	7.5	15	5.0	–	1.0	12	4.6	23	0.27	12	0.23	29	38	11
CBS	–	0.82	1.7	0.31	–	–	–	0.056	0.053	–	–	–	< LOQ	0.099	0.028
DMBA	–	–	6.9	5.8	0.91	n.a.	7.0	0.80	n.a.	–	n.a.	–	–	0.78	5.3
DPG	–	7.5	22	9.6	0.083	< LOD	3.0	1.9	2.1	< LOD	0.083	0.031	0.013	20	–
DPPD	–	0.18	3.3	3.7	0.034	n.a.	5.0	1.1	n.a.	–	n.a.	–	0.14	5.1	–
DTG	–	–	–	–	–	n.a.	–	–	n.a.	–	n.a.	0.0060	–	–	–
HMMM	–	0.58	0.84	0.33	–	–	1.3	0.061	19	0.021	3.1	0.012	1.5	36	0.11
IPPD	–	0.0063	–	4.4	–	n.a.	0.87	0.90	n.a.	–	n.a.	–	–	3.8	–
MBTZ	–	2.0	4.2	3.0	0.90	0.27	30	2.6	14	–	13	–	–	26	0.25

c.																
$\mu\text{g g}^{-1}$	Urban pavements							Commercial products			Tires					
	UP-1	UP-2	UP-3	UP-4	UP-5	UP-6	UP-7	CR - 1	CR - 2	Ctile	CT-1	CT-2	BT	TT	BIT	CIT
6PPD	7.0	72	13	17	0.42	7.3	2.6	1633	268	0.20	1974	4.3	43	7.5	0.48	0.58
6PPDq	2.4	13	1.6	2.3	0.065	2.4	0.11	8.2	22	< LOQ	30	26	11	2.4	–	0.23
BTZ	11	11	3.5	6.6	–	1.4	–	88	75	0.094	32	4.9	–	–	10	5.5
CBS	–	0.063	0.024	0.036	–	0.020	0.0020	0.66	0.34	–	1.1	0.54	0.36	–	–	1.0
DMBA	–	–	–	–	–	–	–	23	12	–	36	9.0	13	n.a.	2.2	–
DPG	–	–	0.12	< LOQ	< LOQ	3.2	–	–	–	0.15	147	0.29	–	–	130	–
DPPD	–	1.6	0.49	0.26	–	0.36	0.021	83	32	–	0.47	–	–	n.a.	–	–
DTG	–	0.067	–	–	–	–	–	0.040	0.050	–	–	–	–	n.a.	–	–
HMMM	–	–	0.024	0.069	0.010	0.048	< LOQ	30	51	0.017	270	0.81	–	–	0.091	–
IPPD	–	–	0.62	0.026	–	0.079	–	0.61	1.8	–	0.44	–	0.069	n.a.	–	1.3
MBTZ	2.0	–	–	6.1	0.42	–	–	18	–	–	0.64	–	0.95	–	16	–

n.a.: not analysed.

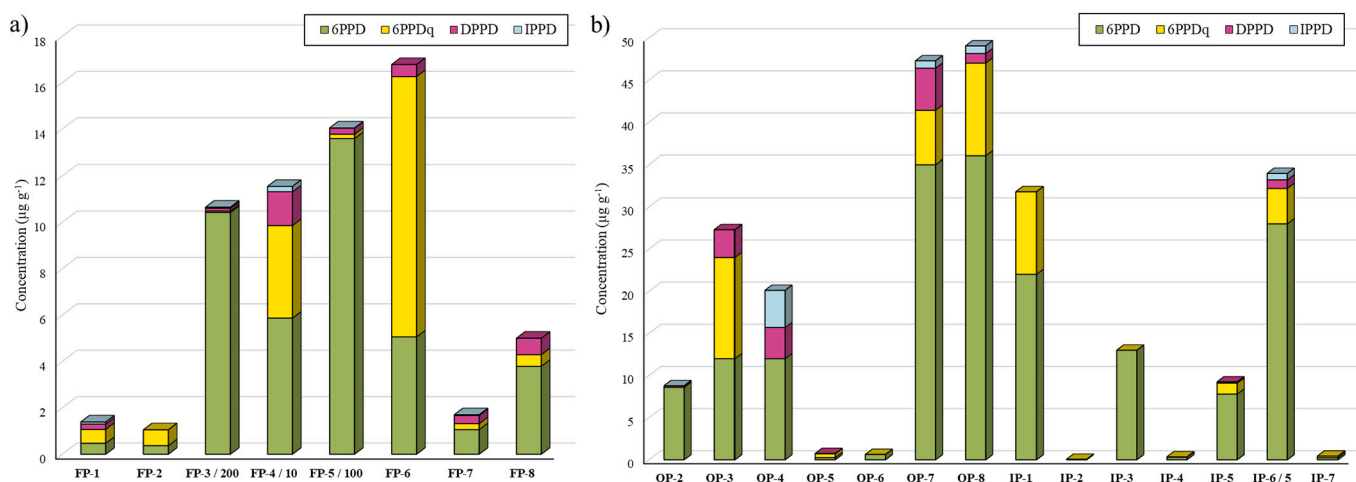
Table 4Analysis of real samples, statistical parameters: detection frequency (N), concentration range ($\mu\text{g g}^{-1}$), mean and median concentrations ($\mu\text{g g}^{-1}$).

$\mu\text{g g}^{-1}$	Football pitches (n ^a =8)				Playground flooring (n ^a =14)			
	N ^b	Range	Mean	Median	N ^b	Range	Mean	Median
6PPD	8	0.37–2085	439	4.4	13	0.25–140	22	12
6PPDq	8	0.26–40	11	5.9	14	0.052–21	5.7	4.6
BTZ	7	1.4–63	21	5.3	13	0.23–38	12	11
CBS	7	0.03–0.32	0.12	0.074	8	0.028–1.7	0.44	0.099
DMBA	8	0.21–73	16	2.4	7	0.78–7.0	3.9	5.3
DPG	6	0.52–48	11	4.1	11	0.013–22	6.0	2.1
DPPD	7	0.23–26	9.4	0.71	8	0.034–5.1	2.3	2.2
DTG	6	0.03–0.56	0.19	0.15	1	–	0.0060	–
HMMM	7	0.03–27	5.8	0.81	12	0.012–36	5.2	0.71
IPPD	5	0.03–9.1	2.5	0.73	5	0.0063–4.4	2.0	0.90
MBTZ	7	1.5–23	8.6	2.5	11	0.25–30	8.7	3.0

^a n: Number of samples collected.^b N: Number of samples containing the compound.**Fig. 3.** Frequency (%) and mean concentration ($\mu\text{g g}^{-1}$) for the target compounds in a) football pitches and b) playground flooring.

The antiozonant 6PPD was the target compound found at the highest concentrations in the crumb rubber infill samples from new synthetic fields, obtaining values of 2085 and 1359 $\mu\text{g g}^{-1}$ in FP-3 and FP-5 (between 0.14 and 0.21 % w/w). These values are in consonance with those reported in literature for several commercial samples (Schneider et al., 2020; Kawakami et al., 2022). A sample collected in a partially covered pitch (FP-4) registered a 6PPD concentration of 59 $\mu\text{g g}^{-1}$. In these 3

samples the other target analytes also showed the highest concentrations although much lower than 6PPD concentrations in the case of FP-3 and FP-5. The TP DMBA was detected at concentrations between 21 and 73 $\mu\text{g g}^{-1}$ in these samples, being higher concentrations than the values obtained in other recent study for 9 real crumb rubber samples (Zhao et al., 2023). 6PPDq and DPPD were detected at concentrations up to 40 and 26 $\mu\text{g g}^{-1}$, respectively, while IPPD is the compound from the family

**Fig. 4.** PPDs concentration ($\mu\text{g g}^{-1}$) profiles of a) football pitches and b) playground flooring. To improve visualization, some of the values were scaled (FP-3 divided by 200, FP-4 divided by 10, FP-5 divided by 100 and IP-6 divided by 5).

of PPDs found at lower concentrations, between 0.73 and 9.1 $\mu\text{g g}^{-1}$. The values in the other samples (FP-1, FP-2, FP-6, FP-7, and FP-8) ranged between 0.37 and 5.1 $\mu\text{g g}^{-1}$ for 6PPD and between 0.6 and 11 $\mu\text{g g}^{-1}$ for 6PPDq, in line with the values recently reported (Zhao et al., 2023). In these 5 samples, DMBA was detected between 0.21 and 2.8 $\mu\text{g g}^{-1}$, DPPD between 0.23 and 0.71 $\mu\text{g g}^{-1}$ in all samples except FP-2, while IPPD was only detected in two samples (0.03 and 0.09 $\mu\text{g g}^{-1}$).

6PPD, as well as its TPs 6PPDq and DMBA, were found in all samples. The other 2 compounds of the same family were found in 60–80 % of the samples. Regarding concentrations, 6PPD was at higher concentrations than DPPD and IPPD (see Fig. 3a and Fig. 4a). Regarding 6PPDq, in crumb rubber from new synthetic fields, the distribution between 6PPDq and 6PPD concentrations revealed much higher values for 6PPD, but in “aged” fields this distribution was quite different and, in several samples, 6PPDq showed higher concentrations than 6PPD (see Fig. 4a and Fig. S6, representation of Table 3a results).

DPG, DTG, BTZ, MBTZ and CBS were found in most crumb rubber samples from football pitches (see Fig. 3a). BTZ and MBTZ reached concentrations up to 63 and 23 $\mu\text{g g}^{-1}$, respectively, while CBS reached only 0.32 $\mu\text{g g}^{-1}$, and DPG and DTG, 47 and 0.56 $\mu\text{g g}^{-1}$, respectively (see Table 4). As it is described in bibliography, BTZ is in general present at higher concentrations than MBTZ (Schneider et al., 2020). DPG value range is similar to that found in Zhao et al. study (Zhao et al., 2023), while CBS values are lower than those reported by Kawakami et al. in commercial samples (4.4–7.6 $\mu\text{g g}^{-1}$) (Kawakami et al., 2022).

Regarding HMMM, it was detected in all samples except one, at concentrations between 0.03 and 27 $\mu\text{g g}^{-1}$ (see Table 4), values higher than the maximum concentration (3.1 $\mu\text{g g}^{-1}$) reported in the only study covering its analysis in crumb rubber samples (Zhao et al., 2023).

Regarding alternative infill materials, cork granulates, sand and thermoplastic elastomers only 6PPD was detected above the LOQ, in any case below 0.1 $\mu\text{g g}^{-1}$. The low concentrations registered for 6PPD and 6PPDq, as well as the absence of the other studied compounds, makes these alternative infills a good substitute as infill in artificial football pitches (Armada et al., 2022). The 6PPD concentrations are likely residues since crumb rubber was used as infill on these fields before they were replaced by the alternative materials. However, due to the particle size and plastic based composition of the thermoplastic elastomers, this infill also contributes to microplastic pollution. As mentioned, FP-9 is a sample composed by 30 % of crumb rubber and 70 % of coconut fibre. The crumb rubber portion can explain the values obtained for some of the target compounds.

3.4.2. Children's playgrounds

Recycled rubber employed as flooring in fourteen children's playgrounds was analysed, as well as a sand sample (OP-1) used with the same purpose. In Table 3b the obtained results of the studied samples are displayed. As it is shown, none of the target compounds were detected in the sand sample. The concentration range, mean and median for each analyte for the rest of the samples are shown in Table 4. To simplify visualization the frequency and mean concentrations of the target analytes in these samples are also depicted in Fig. 3b.

There were varied results in the crumb rubber playground flooring. In the outdoor playgrounds (OP) ($n = 7$), five samples (OP-2, OP-3, OP-4, OP-7, and OP-8) showed the highest values for all compounds. 6PPD and 6PPDq, which were detected in all outdoor recycled rubber samples, reached concentrations up to 36 and 12 $\mu\text{g g}^{-1}$. DMBA, DPPD, and IPPD reached concentrations up to 7.0, 5.9 and 4.4 $\mu\text{g g}^{-1}$, respectively. BTZ was detected in all samples except one (OP-5) at concentrations up to 14.6 $\mu\text{g g}^{-1}$ while MBTZ was detected in all samples between 0.273 and 30 $\mu\text{g g}^{-1}$. CBS was quantified in three samples (OP-2, OP-3, and OP-4). Finally, DTG was not detected, and DPG reached concentrations up to 22 $\mu\text{g g}^{-1}$.

Regarding the indoor samples (IP) ($n = 7$), IP-1, IP-3, IP-5, and IP-6 registered the highest values for all detected compounds. 6PPD and 6PPDq reached concentrations up to 140 and 21 $\mu\text{g g}^{-1}$ in IP-6, probably

because this sample comes from a newly built playground. In the other samples, 6PPD was detected in two samples at low concentrations (0.3 $\mu\text{g g}^{-1}$). BTZ, CBS and MBTZ concentrations reached 38 $\mu\text{g g}^{-1}$. The highest concentrations for DPG and HMMM were 20 and 36 $\mu\text{g g}^{-1}$. DTG was detected in one sample (IP-4) at very low concentration (0.0060 $\mu\text{g g}^{-1}$). As was the case for football pitches, 6PPD was detected in more samples and at higher concentrations than DPPD in playground flooring. (see Fig. 3b and Fig. 4b).

As it was above-mentioned, among playground flooring samples, IP-6 showed the highest concentrations for almost all analytes. Although indoor are not exposed to meteorological factors (such as rain, wind or high and low temperatures, etc.) there is not a significant difference between indoor and outdoor samples, excluding this sample and IP-1, which presented higher values for BTZ, HMMM and MBTZ.

3.4.3. Comparison between football pitches and playground flooring

In general, it is worth mentioning that the target compounds show a higher frequency (except for BTZ and IPPD), and higher concentrations (except for CBS, HMMM and MBTZ), in football pitches than in playground flooring (see Fig. 3a, Fig. 3b and Table 4). 6PPDq was detected in all samples and 6PPD was also found in all samples except in one playground sample. The highest concentrations of the target analytes in both types of samples were obtained for 6PPD. DTG was detected in 75 % of the analysed football pitches, while it was only detected in one playground flooring sample (see Fig. 3a and Table 4).

In general, the results obtained cannot be compared with those published in the bibliography, since data referring to the target analytes from football pitches and playground flooring are scarce. For some of these compounds no data (DTG) or only a single study (DMBA, CBS or HMMM) in RTCR is available (Zhao et al., 2023). As it was mentioned before, in new synthetic fields, 6PPD reached concentrations up to 0.14 and 0.21 % w/w, values in consonance with several commercial samples analysed in literature (Schneider et al., 2020; Kawakami et al., 2022). In our samples, DMBA was detected at higher concentrations than those reported by Zhao et al. for real crumb rubber samples, while DPPD, 6PPDq and DPG concentration ranges in all football pitch samples are in consonance with this study (Zhao et al., 2023). On the other hand, CBS values are lower than those reported in commercial samples (Kawakami et al., 2022) and HMMM concentrations are higher than Zhao et al. values (Zhao et al., 2023).

3.4.4. Other kind of samples

In addition to the granulate from the fields and the playgrounds, other samples were analysed: urban pavements including tree RTCR roots retainers, commercial rubber products including two crumb rubber samples and one rubber tile, car tires (two samples) and other vehicles tires from a bicycle and a tractor, and the inner tubes from a bike tire (BIT) and a car tire (CIT). One of the tree protectors was divided into two sub-samples: a red surface part in contact with the air (UP-1) and a black surface part in contact with the roots (UP-2). The results for the target chemicals detected in these samples are presented in Table 3c.

The analysis of five tree roots protector samples (from UP-1 to UP-5) revealed the presence of all target analytes except DMBA, and DTG was only detected in one sample. As it was mentioned for football pitches and playground flooring, 6PPD is the compound that was detected at the highest concentration in all samples, with a mean concentration of 22 $\mu\text{g g}^{-1}$. It is important to emphasize that 6PPD and 6PPDq showed higher concentrations (72 and 13 $\mu\text{g g}^{-1}$, respectively) in UP-2 than in UP-1. This, alongside with the detection of most of the target analytes, is concerning since the take up and bioaccumulation of several of these hazardous compounds was recently demonstrated in vegetation (Castan et al., 2022), as well as their possible diffusion to the soil via water leachates. In the other two urban pavements (UP-6 and UP-7), the same compounds were found like in tree root protectors. DPG reached concentrations up to 3.2 $\mu\text{g g}^{-1}$ in UP-6. For all urban pavements, the concentrations were generally lower than those detected in playground

flooring.

Regarding commercial products, and a tile, all target analytes were detected in 2 granulated rubber samples (except DPG, and MBTZ in CR-2). 6PPD showed very high concentrations of 1633 and 268 $\mu\text{g g}^{-1}$ and, as it was observed in crumb rubber infill samples from new synthetic fields, these values are in consonance with those reported for commercial samples in literature (Schneider et al., 2020; Kawakami et al., 2022). Finally, the commercial tile showed low concentrations of 6PPD, 6PPDq, BTZ, DPG and HMMM ($< 0.2 \mu\text{g g}^{-1}$).

Since the origin of these materials are ELTs, it was decided to analyse 4 tires available in some of the author's home. Regarding car tires (2 samples), sample CT-1 presented higher concentrations for all target compounds. 6PPD, 6PPDq, DMBA and IPPD showed values of 2000, 30, 36 and $0.44 \mu\text{g g}^{-1}$, respectively, in accordance with the concentrations reported by Zhao et al. analysing a sample of TWP from new and used tires (Zhao et al., 2023). These results also agree with those obtained in this work from the analysis of commercial products and new synthetic fields. It can be emphasized that HMMM and DPG reached a concentration of 270 and $147 \mu\text{g g}^{-1}$ in CT-1 sample.

In the tire samples from a bike and a tractor, 6PPD and 6PPDq were detected at concentrations up to 43 and $11 \mu\text{g g}^{-1}$, respectively. Results for 6PPDq are similar to the values obtained in car tires. To the best of our knowledge, this is the first time that information is reported regarding these hazardous compounds present in agricultural tires. This is very important since, as above-mentioned, recent research informed about the uptake and accumulation of tire derived chemicals such as 6PPD, HMMM, DPG, or 6PPDq in lettuce (Castan et al., 2022). The presence of these compounds in agricultural vehicle tires may facilitate their entry into various plants and crops intended for food or feed.

Furthermore, the inner tubes from a bike tire (BIT) and a car tire (CIT) were studied quantifying several of the target substances in their composition at concentrations up to $10 \mu\text{g g}^{-1}$ for BTZ, $16 \mu\text{g g}^{-1}$ for MBTZ and $130 \mu\text{g g}^{-1}$ for DPG. DPPD and DTG were not detected in these two samples.

4. Conclusions

An analytical method, requiring small amounts of sample and solvent, based on UAE followed by LC-MS/MS was successfully developed and validated for the determination of new chemicals of emerging concern issued from tire rubber materials.

A total of forty rubber materials and six alternative materials were analysed. In the recycled rubber samples all studied compounds were detected, including 6PPD, 6PPDq, BTZ, CBS, DMBA, DPG, DPPD, DTG, HMMM, IPPD and MBTZ, which represent a risk to the environment and human health.

The antiozonant 6PPD was the chemical found at the highest concentrations, up to 0.1–0.2 % in new synthetic turf fields, values similar to those detected in commercial samples and in a car tire sample. 6PPDq reached concentrations up to dozens of $\mu\text{g g}^{-1}$. IPPD was the compound from the family of PPDs found at the lowest concentrations. BTZ was in general present at higher concentrations than MBTZ in crumb rubber samples from infill football pitches. The crosslinking agent HMMM was detected in most of the analysed football pitches and playground flooring, with concentrations up to 27 and $36 \mu\text{g g}^{-1}$, respectively.

Regarding playgrounds, no significant difference appeared between indoor and outdoor samples. In general, it can be mentioned that a higher frequency and concentrations of the target compounds were observed in football pitches compared with playground flooring.

The analysed infill alternatives are free of most of the target compounds, and any identified trace of them can be regarded as residues issued from a previous crumb rubber surface.

All these chemicals are ubiquitous since they are present in samples from different environments (sport, leisure, traffic and agricultural), which facilitates dispersion towards different environmental compartments.

CRedit authorship contribution statement

Andres Duque-Villaverde: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Daniel Armada:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Thierry Dagnac:** Writing – review & editing, Funding acquisition. **Maria Llompарт:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.172674>.

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