



Hazardous organic chemicals in rubber recycled tire playgrounds and pavers

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HIGHLIGHTS

- ▶ A large number of recycled tire playgrounds and commercial pavers have been analysed.
- ▶ The occurrence of numerous harmful compounds at high levels was confirmed.
- ▶ Thirty-one targets (PAHs, vulcanisation additives, antioxidants, plasticizers) were selected.
- ▶ Total PAH concentration was remarkable. Contribution of B[a]P must be highlighted.
- ▶ Target analytes were detected in the headspace SPME experiments at room temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the presence of hazardous organic chemicals in surfaces containing recycled rubber tires is investigated. Direct material analyses using solvent extraction, as well as SPME analysis of the vapour phase above the sample, were carried out. Twenty-one rubber mulch samples were collected from nine different playgrounds. In addition, seven commercial samples of recycled rubber pavers were acquired in a local store of a multinational company. All samples were extracted by ultrasound energy, followed by analysis of the extract by GC–MS. The analysis confirmed the presence of a large number of hazardous substances including PAHs, phthalates, antioxidants (e.g. BHT, phenols), benzothiazole and derivatives, among other chemicals. The study evidences the high content of toxic chemicals in these recycled materials. The concentration of PAHs in the commercial pavers was extremely high, reaching values up to 1%. In addition, SPME studies of the vapour phase above the samples confirm the volatilisation of many of those organic compounds. Uses of recycled rubber tires, especially those targeting play areas and other facilities for children, should be a matter of regulatory concern.

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1. Introduction

Disposal of used tires has been a major problem in soil waste management (Birkholz et al., 2003; Lee and Yoo, 2011). The

indestructible nature of discarded tires makes them persist in the environment indefinitely, creating long-lasting piles of toxic, synthetic waste.

Tire wastes have been valorised for energy recovery through different processes as scrap tyres have a comparable energy value to coal. Gasification, pyrolysis, plasma or combustion in cement kilns are the main examples of these technologies (Huang and

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Tang, 2007; Huang et al., 2007). Furthermore, used tires have also been applied as raw material for the production of asphalt or other pavements applications in road construction (Kumaran et al., 2008). Although technically viable, in this case it needs to be subsidised to be competitive with conventional aggregates for asphalt pavements (Huang et al., 2007).

Today, one of the most valuable applications of used tires is the transformation in recycling products such as rubber mulch and recycled rubber pavers that are used for sidewalks, animal flooring, fitness centre flooring, playground surface, and sport fields.

Rubber mulch is a product that consists of granular rubber particles. It is available in array of lively colours and it is extensively used in playgrounds along the world. The number of this kind of playground flooring is significantly increasing in the last years. This material constitutes a slip resistant, cushioned floor that prevents injuries in sporting activities and playgrounds and it is a visually attractive choice.

Nevertheless, and although few investigations of the organic content of tires have been reported, it is well known that rubber tire debris contains toxic compounds such as highly aromatic oils and other reactive additives (Zhang et al., 2008; Kanematsu et al., 2009; Aatmeeyata, 2010; van Rooij and Jongeneelen, 2010). Tire rubber is composed of 40–60% rubber polymer, reinforcing agents such as carbon black (20–35%), aromatic extender oil (up to 28%), vulcanisation additives, antioxidants, antiozonants, and processing aids (plasticizers and softeners) (Wik and Dave, 2008; Li et al., 2010). One of the main components of extender oil is highly aromatic oil, which contains polycyclic aromatic hydrocarbons (PAHs) in the range of 300–700 mg kg⁻¹ (Aatmeeyata, 2010). In this sense, the accessibility of heavy metals and organic chemicals originated from reused tire rubber must be a subject of concern.

Several studies about the chemical risk toxicity of tire rubber recycled products have been conducted (Birkholz et al., 2003; Plesser and Lund, 2004; Anderson et al., 2006; Crain and Zhang, 2006; Roels, 2006; Mattina et al., 2007; Moretto, 2007; RAMP, 2007; Kanematsu et al., 2009; Li et al., 2010). Most previous works have focused on the toxic chemicals in the leachate of tire rubber material whereas direct studies about the chemical composition of ground rubber products are scarce. Nevertheless, the chemical exposure pathways, especially in the case of infants, can include dermal absorption, inhalation, and even ingestion, directly from the material.

An interesting research on the presence of hazardous chemicals in synthetic turf material from recycled tires concludes that PAH levels are above health-based soil standards (Zhang et al., 2008). Previously, a study conducted by the Norwegian Building Research Institute had concluded that the total concentration of PAH in the recycled rubber granulates exceeded the Norwegian Pollution Control Authority's normative values for most sensitive land use (Plesser and Lund, 2004).

A recent study dealing with the characterisation of substances released from crumb rubber material of artificial turf fields implemented solid-phase microextraction (SPME) to obtain vapour phase composition profiles. Ten organic compounds were detected in the vapour phase over all commercial tested samples, including benzothiazole, antioxidants and three PAHs (Li et al., 2010).

The objective of the present study is to investigate the presence of hazardous organic chemicals in recycled tire playground surfaces. With this purpose, direct material analysis, using solvent extraction, as well as SPME analysis of the vapour phase above the sample will be conducted.

2. Material and methods

2.1. Reagents and material

The studied compounds, their chemical names and CAS numbers are summarised in Table 1. Ethyl acetate and acetone (analytical grade) were provided by Sigma–Aldrich (Steinheim, Germany). Sand (50–70 mesh particle size) was purchased from Sigma–Aldrich. The SPME manual holders and 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibres were supplied by Supelco (Bellefonte, PA, USA). Prior to first use, fibres were conditioned as recommended by the manufacturer. Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA).

Individual stock solutions of each compound were prepared in acetone. Further dilutions and mixtures were prepared in ethyl acetate and then stored in amber glass vials at –20 °C.

2.2. Sampling and sample treatment

Seventeen samples from nine different urban playgrounds in Northwest of Spain have been manually collected and immediately placed into clean glass bottles and tightly capped. The samples consisted of two different types of ground covers of diverse colours: floor tiles compositions and carpet covers. In some cases (in 4 of them), the coloured upper part of the tiles or the carpets was attached to a black base, which was also sampled and analysed. These samples were washed with Milli-Q water to remove particles of soil or dust and dried overnight at room temperature.

Seven commercial samples were acquired in a local store of a multinational company. Two of them were puzzle pavers while the rest were recycled rubber tire tiles of different colours. Two of the floor tiles had a black base, which was also analysed. The upper part of the samples was constituted by smaller grains highly compacted whereas the black base was in all cases formed by bigger grains with a lower compaction degree. All samples were cut into small particles (around 0.3 cm of diameter) and stored in clean glass vials.

2.3. Ultrasound-assisted extraction (UAE)

Five millilitres of ethyl acetate was added to a 10-mL glass vial containing 500 mg of sample, and sealed with a headspace aluminium cap furnished with PTFE-faced septum. The analytes were extracted from the samples to the organic solvent using ultrasonic energy (J.P. Selecta ultrasound bath, Barcelona, Spain) at 40 kHz frequency and 110 W power, for 15 min. Afterwards, the supernatant was filtered through 0.45 µm Uptidiscs™ PTFE filters (25 mm diameter) (Interchim, Montluçon, F). When it was convenient, extracts were diluted prior to the injection in the chromatographic system.

2.4. Pressurised solvent extraction (PSE)

Extractions were performed on an ASE 150 (Dionex, Co., Sunnyvale, CA, USA), equipped with 10-mL stainless steel cells and 60-mL collection vials. One cellulose filter (Dionex) was placed at each end of the PSE cell. 500 mg of sample was introduced into the cell, where 1 g of clean sand was previously placed. Finally, the dead volume of the cell was filled up with sand. The cell was tightly closed and placed into the PSE system.

Extractions were performed by preheating the cell before filling with solvent (preheat method). The extraction pressure was set at 1700 psi, the flush volume was 60% and the purge time was 60 s.

Table 1
Target compounds: chemical names and GC–MS detection and performance characteristics.

Key	Compound	CAS number	Retention time (min)	Qualifiers and quantifiers (relative ion abundances, %) ^e	Linearity (R) ^f	RSD (%)	IDLs (ng mL ⁻¹)
<i>PAHs^a</i>							
NAP	Naphthalene	91-20-3	7.58	102 (8), 127 (13), <u>128</u> (100), 129 (11)	1.000	<3.3	0.30
ACY	Acenaphthylene	208-96-8	10.12	76 (9), 150 (14), <u>151</u> (20), <u>152</u> (100)	1.000	<6.0	0.30
ACE	Acenaphthene	83-32-9	10.42	76 (17), 152 (47), <u>153</u> (100), 154 (95)	1.000	<10	0.30
FLU	Fluorene	86-73-7	11.23	82 (11), 165 (91), <u>166</u> (100), 167 (14)	1.000	<7.0	0.15
PHN	Phenanthrene	85-01-8	12.80	152 (9), 176 (18), <u>178</u> (100), 179 (15)	1.000	<3.7	0.15
ANC	Anthracene	120-12-7	12.89	152 (7), 176 (18), <u>178</u> (100), 179 (15)	0.999	<4.5	0.20
FLA	Fluoranthene	206-44-0	15.42	101 (11), 200 (20), <u>202</u> (100), 203 (17)	0.999	<3.7	0.15
PYR	Pyrene	129-00-0	16.00	101 (13), 200 (20), <u>202</u> (100), 203 (18)	0.999	<3.7	0.15
B[a]A	Benz[a]anthracene	56-55-3	19.96	114 (11), 226 (26), <u>228</u> (100), 229 (19)	0.997	<5.5	0.40
CHY	Chrysene	218-01-9	20.10	113 (11), 226 (28), <u>228</u> (100), 229 (20)	0.998	<6.5	0.40
B[b]F	Benzo[b]fluoranthene	205-99-2	23.97	126 (13), 250 (22), <u>252</u> (100), 253 (22)	0.998	<4.4	0.60
B[k]F	Benzo[k]fluoranthene	207-08-9	24.06	126 (14), 250 (22), <u>252</u> (100), 253 (22)	0.996	<4.7	0.70
B[a]P	Benzo[a]pyrene	50-32-8	25.11	126 (13), 250 (23), <u>252</u> (100), 253 (22)	0.997	<7.8	1.0
IND	Indeno[1,2,3-cd]pyrene	193-39-5	29.02	138 (18), 274 (20), <u>276</u> (100), 277 (24)	0.999	<7.9	2.0
D[ah]A	Dibenz[a,h]anthracene	53-70-3	29.20	139 (14), 276 (26), <u>278</u> (100), 279 (24)	0.998	<9.2	3.0
B[ghi]P	Benzo[ghi]perylene	191-24-2	29.93	138 (20), 274 (21), <u>276</u> (100), 277 (24)	0.998	<7.2	2.0
<i>Vulcanisation additives, antioxidants and plasticizers</i>							
BTZ	Benzothiazole ^b	95-16-9	8.00	69 (15), 108 (30), <u>135</u> (100)	0.997	<3.0	13
TBP	4-tert-Butylphenol ^b	98-54-4	8.58	107 (36), <u>135</u> (100), 150 (21)	1.000	<0.75	10
MBTZ	2-Mercaptobenzothiazole ^b	149-30-4	14.26	108 (18), 135 (32), <u>167</u> (100)	0.994	<11	1000
BHA	Butylated hydroxyanisole ^b	121-00-6	10.31	137 (64), <u>165</u> (100), 180 (51)	1.000	<9.3	25
BHT	Butylated hydroxytoluene ^b	128-37-0	10.57	177 (7), <u>205</u> (100), 220 (25)	1.000	<12	3.5
DMP	Dimethyl phthalate ^c	131-11-3	10.07	77 (16), <u>163</u> (100), 164 (10), 194 (6)	0.999	<5.4	20
DEP	Diethyl phthalate ^c	84-66-2	11.22	105 (8), <u>149</u> (100), 177 (23)	1.000	<7.8	5.0
DIBP	Diisobutyl phthalate ^b	84-69-5	13.36	104 (7), <u>149</u> (100), 223 (7)	1.000	<3.5	2.0
DBP	Dibutyl phthalate ^b	84-74-2	14.21	104 (4), <u>149</u> (100), 223 (5)	1.000	<7.2	2.0
BBP	Benzylbutyl phthalate ^b	85-68-7	18.38	91 (55), <u>149</u> (100), 206 (24)	1.000	<6.4	16
DEHA	Di(2-ethylhexyl) adipate ^d	103-23-1	19.08	112 (25), <u>129</u> (100), 147 (19)	1.000	<6.7	12
DEHP	Di(2-ethylhexyl) phthalate ^c	117-81-7	21.04	<u>149</u> (100), 167 (32), 279 (11)	1.000	<4.9	11
DOP	Di-n-octyl phthalate ^c	117-84-0	23.45	<u>149</u> (100), 279 (8)	1.000	<5.3	11
DINP	Diisononyl phthalate ^b	28553-12-0	24.73	149 (100), 167 (7), <u>293</u> (17)	1.000	<1.0	500
DIDP	Disodecyl phthalate ^b	26761-40-0	25.98	149 (100), 167 (10), <u>307</u> (20)	1.000	<8.4	1000

^a 16 PAHs mixture (2000 µg mL⁻¹ in dichloromethane/benzene, 1:1) purchased from Ultra Scientific Analytical Solutions (Kingstown, USA).

^b Sigma-Aldrich Chemie GmbH, Steinheim, Germany.

^c Fluka Chemie GmbH (Steinheim, Germany).

^d ChemService (West Chester, USA).

^e Numbers in italics correspond to the selected ions monitored in the SIM method for PAHs.

^f PAHs: 2–1000 ng mL⁻¹, other targets: 20–10000 ng mL⁻¹, with the exception of DINP, DIDP and MBTZ (5–500 µg mL⁻¹).

Ethyl acetate was employed as extraction solvent. The extraction temperature was 120 °C and extraction time was 15 min. PSE extracts (~15 mL) were made up to 20 mL with ethyl acetate and directly analysed by gas chromatography–mass spectrometry (GC–MS). When it was convenient, extracts were diluted prior to the injection in the chromatographic system.

2.5. SPME procedure

500 mg of sample were transferred to a 10-mL glass vial. Then, vials were sealed with aluminium caps furnished with Teflon-faced septa and immersed in a thermostated water bath (25 °C or 60 °C). Samples were let to equilibrate for 5 min before the exposition of a DVB/PDMS fibre took place in the headspace over the sample (20 min). Once finished the exposition period, the fibre was retracted into the needle of the holder syringe and immediately inserted into the GC injector. Desorption was carried out at 270 °C for 5 min and under the selected conditions, carryover was not observed. Blanks were periodically run during the analysis to confirm the absence of contamination.

2.6. GC–MS analysis

The GC–MS analysis was performed using an Agilent 7890A (GC)–Agilent 5975C inert mass spectra detector (MSD) with triple axis detector and an Agilent 7693 autosampler from Agilent Technologies (Palo Alto, CA, USA). The temperatures of the transfer line, the quadrupole, and the ion source were set at 290, 150, and 230 °C, respectively. The system was operated by Agilent MSD ChemStation E.02.00.493 software. Separation was carried out on a HP5-MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). Helium (purity, 99.999%) was employed as carrier gas at a constant column 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 a final ramp to 290 °C (held 17 min) at 5 °C min⁻¹. Splitless mode was used for injection. After 2 min, the split was opened at a flow of 75 mL min⁻¹ and the injector temperature was kept at 270 °C. The injection volume was 1 µL.

In the full scan method, the MSD was operated in the scan mode and the mass range varied from 40 to 700 *m/z*, starting at 4 min and ending at 38 min. The electron multiplier was set at a nominal

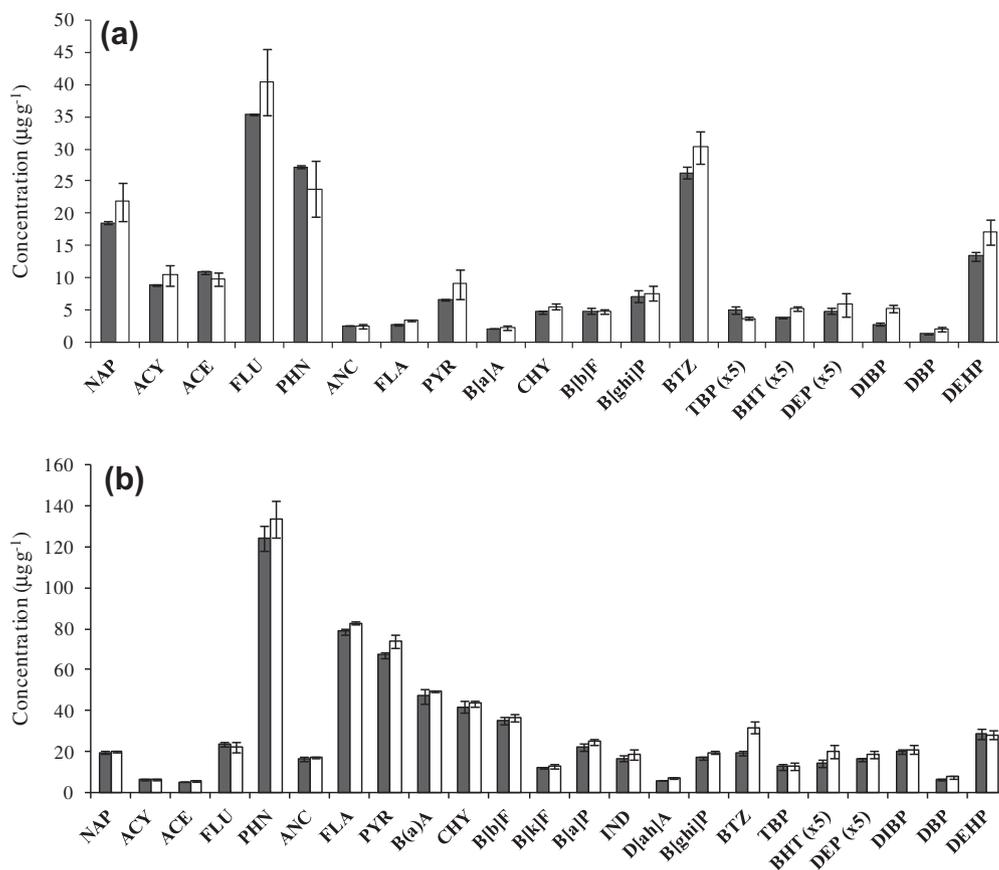


Fig. 1. Extraction of real samples by UAE (black) and PSE (white): (a) playground sample and (b) commercial paver.

Table 2

Concentration of the targets in the samples ($\mu\text{g g}^{-1}$). Statistic parameters.

Compound	Playgrounds samples					Commercial pavers				
	N out of 21	Average	Median	Minimum	Maximum	N out of 9	Average	Median	Minimum	Maximum
<i>PAHs</i>										
NAP	20	1.93	0.55	0.060	24.2	9	186	134	10.8	595
ACY	11	1.37	0.11	0.037	13.4	9	50.0	37.1	3.89	167
ACE	8	1.75	0.14	0.045	12.8	9	56.0	50.6	2.62	135
FLU	14	3.98	0.61	0.056	47.7	9	326	303	11.3	900
PHN	20	2.31	1.04	0.082	25.5	9	1205	860	66.2	3388
ANC	3	1.80	0.53	0.14	4.72	9	271	176	11.0	816
FLA	20	1.83	1.32	0.17	8.24	9	855	384	65.7	2851
PYR	21	7.73	3.80	0.77	29.5	9	632	286	65.6	2088
B[a]A	6	0.95	0.92	0.12	2.02	9	399	156	32.0	1311
CHY	20	1.88	0.77	0.13	9.16	9	368	150	34.5	1210
B[b]F	4	2.82	2.64	1.67	4.32	9	326	84.8	29.1	1182
B[k]F	4	0.83	0.68	0.27	1.69	9	246	77.5	13.8	872
B[a]P	5	2.23	1.96	0.42	4.66	9	346	97.5	23.1	1244
IND	6	1.37	1.40	0.31	2.77	9	243	27.0	10.2	958
D[ah]A	1	0.97	0.97	0.97	0.97	9	51.5	8.95	4.60	238
B[ghi]P	8	4.94	4.28	0.22	11.9	9	183	26.6	11.6	743
Total PAHs	21	23.4	8.42	1.25	178	9	5744	2812	396	18699
<i>Vulcanisation additives, antioxidants and plasticizers</i>										
BTZ	21	9.60	6.16	0.47	39.9	9	95.6	107	19.6	158
TBP	11	0.43	0.39	0.12	0.78	9	14.8	16.8	8.60	21.0
MBTZ	10	195	185	72	398					
BHT	21	7.08	1.78	0.11	23.9	9	19.2	20.8	0.74	39.1
DMP						3	1.08	1.09	0.86	1.30
DEP	13	0.41	0.37	0.082	1.13	5	3.25	2.63	0.41	7.68
DIBP	18	0.97	0.76	0.40	2.45	8	58.4	35.3	7.48	221
DBP	15	0.59	0.43	0.29	1.97	7	43.6	10.1	4.18	151
BBP						2	48.0	48.0	21.9	74.1
DEHA						3	13.1	12.4	7.74	19.3
DEHP	21	20.0	15.6	3.95	63.8	9	359	184	22.4	1205
DINP	8	5415	4179	16.0	20615					
DIDP	1	1284	1284	1284	1284					

value of 1176 V. The target analytes were positively identified by comparison of their mass spectra and retention times to those of the standards. Table 1 summarises their retention times as well as the qualification and quantification ions. A selected ion monitoring (SIM) method was used for the determination of PAHs. Monitored ions are shown in italics in Table 1. The electron multiplier was set at a nominal value of 1376 V.

2.7. Statistical analysis

Basic and descriptive statistics were performed using Statgraphics Centurion XV, Version 15.1.02 (Manugistics, Rockville, MD, USA).

3. Results and discussion

The UAE and PSE procedures, as well as the GC conditions for PAHs and other target compounds analysis, are described in the experimental section. The GC method performance parameters are summarised in Table 1. The data corresponding to PAHs were obtained using the SIM method. Regarding the instrumental linearity, the method exhibited a direct proportional relationship between the amount of each analyte and the chromatographic response (evaluated in different ranges of concentration depending on the family of compounds as it is indicated in Table 1) with correlation coefficients $R \geq 0.996$ for PAHs and $R \geq 0.994$ for the rest of the targets.

Method precision was studied at two concentration levels for each group of compounds: 10 and 500 ng mL⁻¹ for PAHs; 100

and 5000 ng mL⁻¹ for BTZ, TBP, BHA and BHT; 100 and 10000 ng mL⁻¹ for all the plasticizers with the exception of DINP and DIDP (10 and 500 µg mL⁻¹); and 10 and 100 µg mL⁻¹ for MBTZ. Relative standard deviation (RSD) values are shown in Table 1 with an average about 5%.

Instrumental detection limits (IDLs) were calculated as the concentration giving a signal-to-noise ratio of three ($S/N = 3$) in all cases since any of the target compounds were detected in the blanks. The obtained values are included in Table 1 and they were, in general, in the low ng per mL.

3.1. Analysis of recycled tire rubber samples

Several samples collected in urban playgrounds were analysed by GC–MS in the full scan mode. The samples were previously extracted by ultrasound energy (15 min) with ethyl acetate. The screening of these samples showed the presence of a large number of volatile and semi-volatile organic compounds, including persistent organic pollutants (POPs) as well as other chemicals considered toxic or suspected toxic. All these compounds were identified using the NIST Mass Spectral Search Program. Among them, the presence of a large number of PAHs at apparent high concentrations must be stood out. Other compounds identified were vulcanisation additives, antioxidants, and plasticizers, and many other chemicals.

These initial screening experiments, as well as the availability of standards in our lab, allowed selecting 31 targets including 16 priority PAHs (Gan et al., 2009), vulcanisation additives, antioxidants, and plasticizers (Table 1). The retention times and the mass spectra

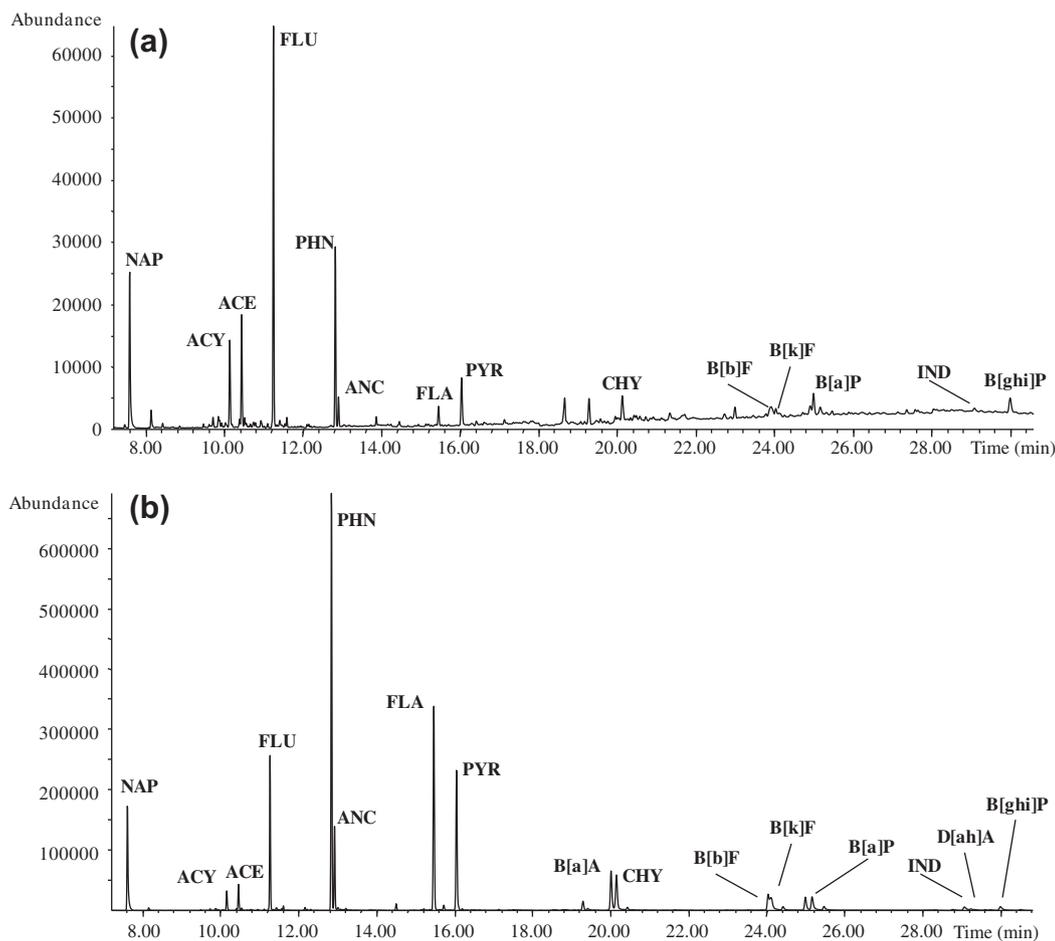


Fig. 2. SIM chromatograms obtained for: (a) a playground sample (PG3, extract dilution 1:10) and (b) a commercial paver (CP4, extract dilution 1:50).

of authentic standards confirmed the presence of the analytes in the samples.

To evaluate the efficiency of the extraction method, UAE was compared with the powerful PSE technique (see conditions in the experimental section) obtaining equivalent results for the extraction of real samples as can be seen in Fig. 1. Statistical hypothesis test (*t*-test) demonstrated no significant differences between the results obtained by both techniques at 95% significant level, with very few exceptions (data not shown). In addition, recovery studies were also carried out for the 16 priority PAHs. Recoveries were satisfactory and ranged from 83.5% to 105%, with a total PAH mean recovery of 93.5%.

The study was extended including a total of 21 samples from nine different urban playgrounds. In addition, seven commercial pavers made from recycled rubber tires were also analysed.

3.2. Polycyclic aromatic hydrocarbons

The individual and total PAH contents in the playground samples are displayed in Table 2. All samples contained PAHs, and their total amount was between $1.25 \mu\text{g g}^{-1}$ and $70.4 \mu\text{g g}^{-1}$. One of the samples showed a higher PAHs content of $178 \mu\text{g g}^{-1}$. The most abundant congener was pyrene (PYR), found in all samples, with an average concentration of $7.7 \mu\text{g g}^{-1}$. Other abundant congeners found in 20 out of 21 samples were naphthalene (NAP), phenanthrene (PHN), fluoranthene (FLA), and chrysene (CHY), with average individual concentrations about $2 \mu\text{g g}^{-1}$. The considered most toxic PAH, benzo[a]pyrene (B[a]P) was found in five samples at values ranging from 0.4 to $5.0 \mu\text{g g}^{-1}$. Both total and individual PAHs levels are quite in agreement with the levels published in

other studies on crumb rubber samples (Crain and Zhang, 2006; Zhang et al., 2008), especially with those reported by Plesser and Lund (Plesser and Lund, 2004). The presence of other PAHs (non-targets) detected in most samples would increase the total PAH content. Considering that these compounds are priority POPs regulated at lower levels in agricultural and even industrial soils, the use of this kind of materials on fields or playgrounds for children should be reconsidered.

The analysis of the commercial pavers (recycled rubber tire tiles) showed surprising results. All samples gave considerably higher PAHs concentration than the playground samples (see Table 2). In 5 out of 7 samples, the total PAHs concentration was extremely high, between 2000 and $8000 \mu\text{g g}^{-1}$. The internal face of the paver (in black colour in all cases) was analysed for 2 of the samples giving even higher concentrations above $10000 \mu\text{g g}^{-1}$. In those cases, the amount of PAHs was then superior to 1%. The other two commercial samples (puzzle pavers) exhibited although high, lower PAH contents (average content at about $500 \mu\text{g g}^{-1}$). All the 16 priority PAHs were found in all the samples with average concentrations of PHN and FLA around $1000 \mu\text{g g}^{-1}$ (excluding the two puzzle pavers). The important contribution of B[a]P on the total PAH content must be highlighted, with a mean concentration above $500 \mu\text{g g}^{-1}$ ($\sim 40 \mu\text{g g}^{-1}$ in the puzzle pavers).

Fig. 2 shows, as example, the SIM chromatograms obtained for a playground sample (a) and for a commercial paver (b). Total PAHs contents in playground samples (a) and commercial pavers (b) are displayed in Fig. 3. Some of both types of samples (playground surface and commercial pavers) were analysed in another laboratory, fulfilling quality control requirements. The extremely high concentration values of PAHs in the commercial pavers were confirmed.

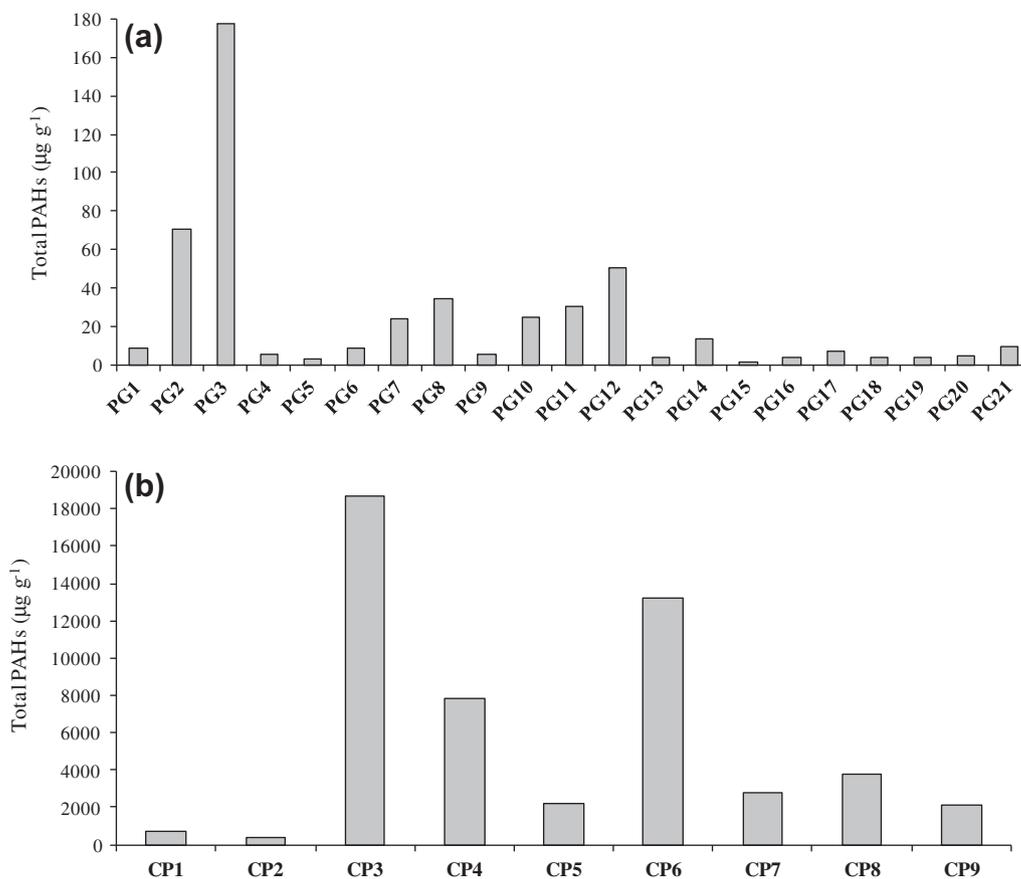


Fig. 3. Total PAH content in playground samples (a) and commercial pavers (b).

3.3. Vulcanisation additives, antioxidants and plasticizers

Fig. 4 shows the distribution of vulcanisation additives, antioxidants and plasticizers in playground samples (a) and commercial pavers (b). The statistical parameters are summarised in Table 2.

Benzothiazole (BTZ) was found in all playground samples. The mean concentration was of $10 \mu\text{g g}^{-1}$ and three samples reached values higher than $20 \mu\text{g g}^{-1}$. The highest found concentration was $40 \mu\text{g g}^{-1}$. Regarding the commercial pavers, two of them presented concentrations around $20 \mu\text{g g}^{-1}$. Nevertheless, the other 7 samples showed considerably higher values with average concentration close to $120 \mu\text{g g}^{-1}$.

2-Mercaptobenzothiazole (MBTZ) was found in playgrounds, but it was not detected in the commercial pavers. The quantitative results for this analyte are tentative, since we have had problems

with the chromatographic determination. Nevertheless, we could confirm that the concentration in some of the samples was high, above $100 \mu\text{g g}^{-1}$.

4-*tert*-Butylphenol (TBP) was found at low concentrations in half of the playground samples (mean concentration of $0.43 \mu\text{g g}^{-1}$) but it was present in all pavers at significantly much higher concentrations ($8.6\text{--}21 \mu\text{g g}^{-1}$) (Table 2).

Butylated hydroxytoluene (BHT) was found in all playgrounds and commercial pavers with mean concentrations of 7.1 and $19 \mu\text{g g}^{-1}$, respectively (Table 2). Butylated hydroxyanisole (BHA) was not found in the samples but a possible by-product, which had ions at m/z 236, 221, 205, 180, 165 and 137, was found in many of the samples (including both types, playgrounds and pavers). This compound was previously found and tentatively identified as 2,6-di-*tert*-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-

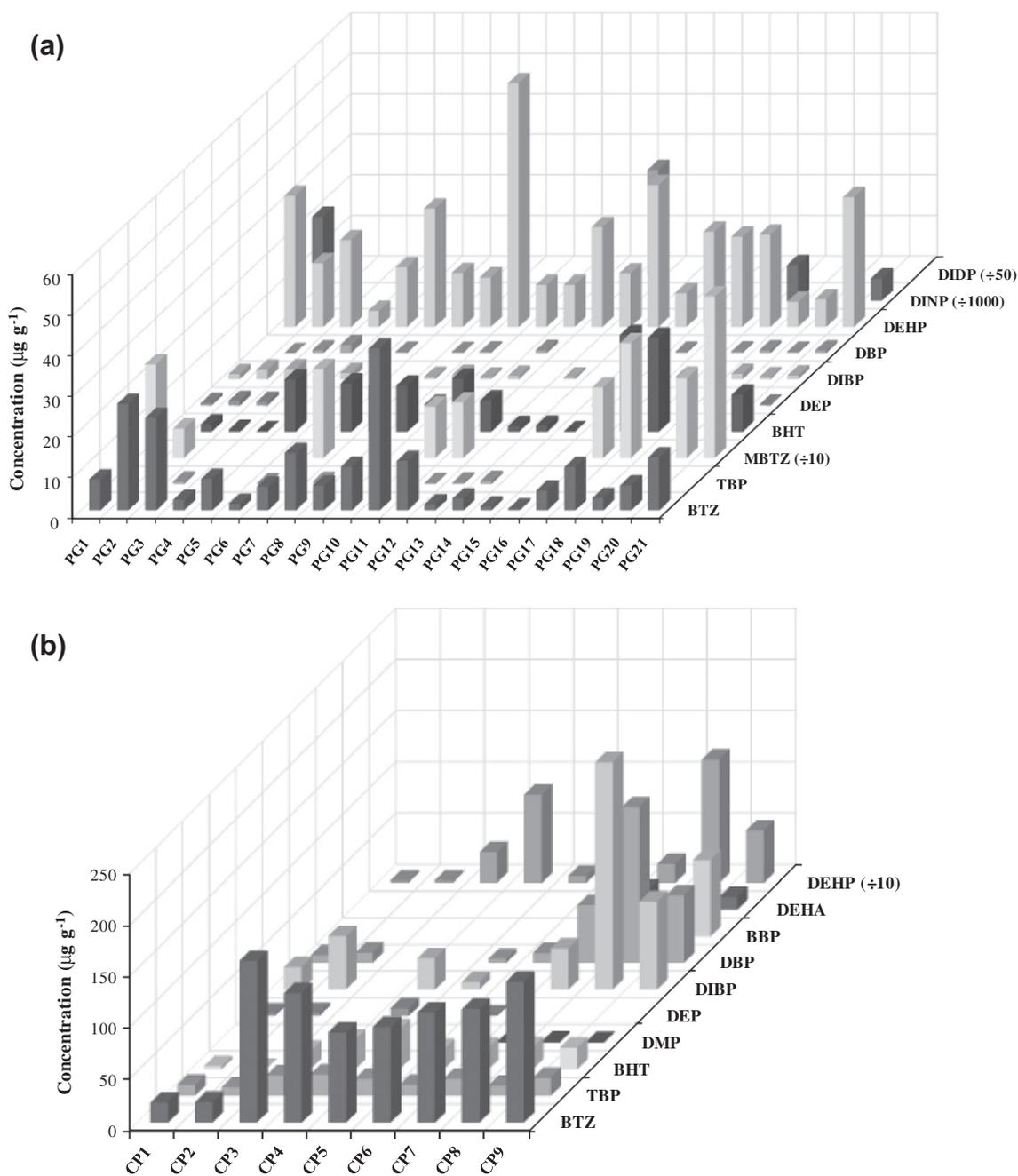


Fig. 4. Vulcanisation additives, antioxidants and plasticizers in playgrounds (a) and commercial pavers (b).

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