Determination of priority and other hazardous substances in football fields of synthetic turf by gas chromatography-mass spectrometry: A health and environmental concern

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HIGHLIGHTS

- 40 target compounds were analysed in several football fields of synthetic turf.
- The presence of PAHs and other hazardous substances was confirmed in the rubber crumb.
- The runoff water and the air above the fields were analysed by SPME.
- Partial compounds transfer from the field to the water and air has been demonstrated.
- The environmental risk arising from the incineration of scrap tires was assessed.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Due to the high concern generated in the last years about the safety of recycled tire rubber used for recreational sports surfaces, this study aims at evaluating the presence of forty organic compounds including polycyclic aromatic hydrocarbons (PAHs), phthalates, adipates, vulcanisation additives and antioxidants in recycled tire crumb of synthetic turf football fields.

Ultrasound Assisted Extraction (UAE) was successfully employed to extract the target compounds from the crumb rubber, and analysis was performed by gas chromatography-mass spectrometry (GC-MS).

The transfer of the target chemicals from the crumb rubber to the runoff water and to the air above the rubber surface has also been evaluated employing solid-phase microextraction (SPME).

Samples from fifteen football fields were analysed, and the results revealed the presence of 24 of the 40 target compounds, including 14 of the 16 EPA PAHs, with total concentrations up to $50 \, \mu g \, g^{-1}$. Heavy metals such as Cd, Cr and Pb were also found. A partial transfer of organic compounds to the air and runoff water was also demonstrated. The analysis of rain water collected directly from the football field, showed the presence of a high number of the target compounds at concentrations reaching above $100 \, \mu g \, L^{-1}$. The environmental risk arising from the burning of crumb rubber tires has been assessed, as well, analysing the crumb rubber, and the air and water in contact with this material, showing a substantial increase both of the number and concentration of the hazardous chemicals.

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1. Introduction

Europe generates about six hundred thousands of tonnes of scrap tires per year and most of them are stored in uncontrolled landfills. Their recycling is an alternative that places value on this material, being the most common recycling treatment through mechanical grinding. The recycled crumb rubber is usually employed in all types of indoor surfaces such as floor tiles used in gyms or nurseries, and outdoor surfaces like paving stones in children playgrounds and sport fields. One specific surface is football fields of synthetic turf, where natural grass or sand have been replaced by synthetic turf due to their low cost, easy maintenance, and weather resistance. The so-called third generation turf is the most employed in outdoor football fields, where the artificial grass is supported by a thin layer of sand and by an infill of crumb rubber (Bjørneboe et al., 2010), which is disaggregated and then easily comes to the surface being accessible for players. Besides, these outdoor surfaces are exposed to different climatic conditions, reaching temperatures of 60 °C or even above 80 °C in summer days.

In last years, concern about the safety of football fields of synthetic turf is increasing (Watterson, 2017). Research has looked at potential risks to users from hazardous substances such as metals, volatile organic compounds, or polycyclic aromatic hydrocarbons that may act as endocrine disruptors with developmental reproductive effects, and even carcinogenic. The development of several lymphomas and leukemia cases in football players created suspicions about the health risk engendered by playing on these surfaces (Jason Williams and Maguire, 2015). In fact, recently (October 2016), thirty amateur Dutch clubs decided not to play onto football fields of synthetic turf until there is a guarantee that playing on these surfaces does not endanger players health. Due to the social worrying about the use of recycled tires to build playgrounds, football fields and other sport surfaces, the United States Environmental Protection Agency (EPA), in collaboration with other Agencies, are studying the characterization of several chemicals, and also the potential emissions and toxicity of these surfaces (EPA, 2016). Other European Agencies are also conducting studies to propose restrictions related to granules used in synthetic turf surfaces regarding PAH contents (ECHA, 2017). Several United States cities, such as Los Angeles or New York, even banned the use of recycled tires on their synthetic turf fields due to health concerns, choosing to use 'Green' alternatives like cork or coconut fibres (Jason Williams and Maguire, 2015).

It is worth mentioning that, in the last key FIFA guidance (2015), it is stipulated that: 'the manufacturer should be asked to supply to the purchaser an assurance that the sports surface together with its supporting layers, does not contain in its finished state any substance which is known to be toxic, mutagenic, teratogenic or carcinogenic when in contact with the skin. Furthermore that no such substances will be released as a vapour or dust during normal use' (Annex F4:26) (Football, 2015). Several studies reported the presence of different hazardous organic chemicals including priority pollutants such as polycyclic aromatic hydrocarbons (PAHs), vulcanisants, plasticizers and antioxidants in recycled tires crumb employed in both outdoor and indoor surfaces intended for children activities (playgrounds, pavers …), showing total PAHs concentrations up to worrying levels of 19000 μg g^{-1} (Llompart et al., 2013; Celeiro et al., 2014).

Nevertheless, regarding sport surfaces of synthetic turf, such as football fields, specific studies dealing with the composition of the crumb rubber are scarce. Most studies have focused on the human health risk associated with synthetic turf fields (Ginsberg et al., 2011a, 2011b; Menichini et al., 2011), and just few references related to the presence of trace metals, semi-volatiles and volatiles

organic compounds (SVOCs and VOCs) or PAHs could be found (Marsili et al., 2015). The bioaccessibility of several organic compounds and metals in different human fluids has also been reported (Han et al., 2008; Pavilonis et al., 2014), including dermal absorption, inhalation or even direct ingestion of the rubber crumb. The presence of a biological exposure marker to PAHs, 1-hydroxypyrene, was detected in human urine after playing over the synthetic turf surface (van Rooij and Jongeneelen, 2010).

Another point to keep in mind is that these surfaces are periodically watered to maintain their physical properties. This type of practice, together with rainwater may favour the leaching of metals and hazardous organic compounds from the crumb rubber, whose final fate are sewage waters, groundwater and/or natural surface waters, thereby implying an environmental risk (Krüger et al., 2012a; Krüger et al., 2012b; Rhodes et al., 2012; Kalbe et al., 2013). On the other hand, volatile and semivolatile compounds may be also transferred to the air above the surfaces (Menichini et al., 2011; Simcox et al., 2011; Marsili et al., 2015), especially in summer when the surfaces can reach very high temperatures being the hazardous chemicals more accessible to players by inhalation. In this way, children are the most potentially affected by playing over these surfaces, since their breathing rate is higher than adults and the entrance of potentially toxic substances in their organism may be easier, and the consequence more dangerous.

The objective of this work was to simultaneously determine the presence of a large number of hazardous organic compounds including priority pollutants, such as PAHs, and other hazardous chemicals like phthalates, adipates, vulcanisation additives and antioxidants in recycled tire crumb rubber directly taken from synthetic turf football fields. To the best of our knowledge this study is the first conducted in Spain regarding these sport facilities. The target compounds were selected according to our previous studies on playgrounds (Llompart et al., 2013; Celeiro et al., 2014) and on the information available in literature about tires and crumb rubber compositions.

Seven out of the 16 target PAHs (B[a]A, CHY, B[aa]P, B[b]F, B[k]F, IND and D[ah]A) are considered carcinogen or likely carcinogen according to different international evaluation institutions/programs, such as the International Agency for Research on Cancer (IARC), the National Toxicology Program (NTP) or the World Health Organization (WHO) (NRCC, 1983; ICPS, 1998; NTP, 2005). The heavy metal content was assessed in several samples, as well.

Another goal of this study was to demonstrate the release of hazardous organic chemicals from the football field to the water and the air in contact with these surfaces, which may suggest environmental contamination risk as well as health risk (inhalation of pollutants though breathing air). Besides, the increased risk induced by the burning of this material was evaluated using a real rubber sample from a football field. Based on previous studies, and considering its simplicity and possibility of miniaturization, Ultrasound Assisted Extraction (UAE) was selected as extraction technique of the target analytes from the crumb rubber, whereas solid-phase microextraction (SPME) was employed for the runoff water and air analysis. The experimental parameters were optimized in order to obtain the highest extraction efficiency, and the analytical determinations were carried out by gas chromatography-mass spectrometry (GC-MS).

2. Experimental

2.1. Reagents and materials

The studied compounds, their chemical names, retention times, and selected MS ions are summarised in Table 1.

Ethyl acetate, methanol and acetone were provided by Sigma-

Aldrich Chemie GmbH (Steinheim, Germany). Nitric acid (65%) and sulfuric acid (96%) were purchased from Merck (Darmstadt, Germany).

Individual stock solutions of each compound were prepared in methanol. Further dilutions and mixtures were prepared in ethyl acetate or acetone. All solutions were stored in amber glass vials at −20 °C. All reagents and solvents were of analytical grade. Since one of the studied compound family is plasticizers, plastic material was substituted for metallic and glass material to avoid possible contamination during the experimental procedure and overestimation in the results. All material was also maintained at 230 °C before use, and allowed to cool down wrapped with aluminium foil.

The SPME manual holders and commercially available fibres:

65 μm polydimethylsiloxane-divinylbenzene (PDMS/DVB) and 100 μm polydimethylsiloxane (PDMS) were supplied by Supelco (Bellefonte, PA, USA). The fibres were conditioned as recommended by the manufacturer prior to their use (250 °C for 0.5 h).

2.2. Sampling and sample treatment

Crumb rubber samples were collected from 15 different football fields of synthetic turf from Santiago de Compostela (Northwest of Spain) and its metropolitan area, covering an area of about 260 km². All the studied football fields were built between 2009 and 2011, and they are periodically gravelling with more rubber crumb since part of this material is lost every day as a consequence

Table 1
Studied compounds: chemical names, retention time, selected MS ions and method performance parameters.

Code	Key	Compound	Retention time (min)	Quantification and identification ions (relative ion abundance, %)	Direct injection			SPME	
					R^2	IDL (μg L^{-1})	RSD, %[e]	R^2	RSD, %[e]
PAHs[a]									
1	NAP	Naphthalene	7.68	127 (13), **128** (100), 129 (11)	0.9993	0.16	1.2	0.9914	3.2
7	ACY	Acenaphthlylene	10.24	150 (14), 151 (20), **152** (100)	0.9980	0.16	4.3	0.9979	6.9
9	ACE	Acenaphthene	10.52	152 (47), **153** (100), 154 (95)	0.9995	0.16	5.9	0.9976	3.8
12	FLU	Fluorene	11.36	165 (91), **166** (100), 167 (14)	0.9991	0.11	2.3	0.9987	1.0
13	PHN	Phenanthrene	12.98	176 (18), **178** (100), 179 (15)	0.9998	0.22	6.3	0.9984	0.40
14	ANC	Anthracene	13.07	176 (18), **178** (100), 179 (15)	0.9987	0.17	7.2	0.9955	2.7
20	FLA	Fluoranthene	15.66	200 (20), **202** (100), 203 (17)	0.9989	0.17	7.4	0.9997	3.5
21	PYR	Pyrene	16.28	200 (20), **202** (100), 203 (18)	0.9986	0.17	3.4	0.9992	0.52
27	B[a]A	Benz[a]anthracene	20.33	226 (26), **228** (100), 229 (19)	0.9988	0.33	10	0.9920	0.21
28	CHY	Chrysene	20.35	226 (28), **228** (100), 229 (20)	0.9980	0.33	6.0	0.9999	1.3
33	B[b]F	Benzo[b]fluoranthene	24.27	250 (22), **252** (100), 253 (22)	0.9974	0.67	6.7	0.9999	2.1
34	B[k]F	Benzo[k]fluoranthene	24.40	250 (22), **252** (100), 253 (22)	0.9972	0.67	4.6	0.9992	3.6
35	B[a]P	Benzo[a]pyrene	25.54	250 (23), **252** (100), 253 (22)	0.9984	1.67	5.5	0.9920	1.1
38	IND	Indeno[1,2,3-cd]pyrene	29.52	274 (20), **276** (100), 277 (24)	0.9993	1.67	5.8	0.9900	3.5
39	D[ah]A	Dibenz[a,h]anthracene	29.72	276 (26), **278** (100), 279 (24)	0.9994	3.0	3.4	0.9952	2.4
40	B[ghi]P	Benzo[ghi]perylene	30.51	274 (21), **276** (100), 277 (24)	0.9996	1.6	3.6	0.9961	4.5
Plasticizers									
3	DMA	Dimethyl adipate[b]	8.10	59 (100), **114** (90), 143 (53)	0.9970	1.6	5.4	0.9991	2.9
5	DEA	Diethyl adipate[b]	9.44	**111** (100), 157 (95), 115 (57)	0.9956	1.6	5.7	0.9996	5.7
6	DMP	Dimethyl phthalate[c]	10.12	77 (16), **163** (100), 164 (10)	0.9977	0.67	4.7	0.9991	8.6
11	DEP	Diethyl phthalate[c]	11.24	105 (8), **149** (100), 177 (23)	0.9968	0.17	10	0.9980	3.8
15	DIBP	Diisobutyl phthalate[b]	13.40	104 (7), **149** (100), 223 (7)	0.9939	0.17	0.79	0.9950	0.36
17	DBP	Dibutyl phthalate[b]	14.27	104 (4), **149** (100), 223 (5)	0.9929	0.17	0.23	0.9997	4.4
18	DMEP	Di(methoxyethyl) phthalate[b]	14.62	**59** (100), 149 (11), 104 (15)	0.9912	3.3	2.9	0.9989	9.0
19	DIPP	Diisopentyl phthalate[b]	15.38	71 (16), **149** (100), 237 (11)	0.9984	0.33	0.32	0.9983	7.9
22	DPP	Dipentyl phthalate[b]	16.28	**149** (100), 150 (10), 237 (6)	0.9962	1.9	1.9	0.9907	2.8
23	BPA	Bisphenol A[b]	16.64	119 (20), **213** (100), 228 (25)	0.9953	0.50	1.7	0.9912	3.4
24	BBP	Benzylbutyl phthalate[b]	18.73	91 (55), **149** (100), 206 (24)	0.9923	3.3	1.8	0.9963	4.8
25	DEHA	Di(2-ethylhexyl)adipate[d]	19.24	112 (25), **129** (100), 147 (19)	0.9921	3.0	4.5	0.9964	1.6
26	DIHP	Diisoheptyl phthalate[b]	20.30–20.68	**149** (100), 265 (52), 167 (10)	0.9949	300	7.6	0.9968	12
29	DCHP	Dicyclohexyl phthalate[b]	20.91	**149** (100), 167 (18), 55 (19)	0.9972	3.0	4.8	0.9982	12
30	DEHP	Di(2-ethylhexyl)phthalate[c]	21.13	**149** (100), 167 (32), 279 (11)	0.9945	0.33	2.8	0.9969	15
31	DPhP	Diphenyl phthalate[b]	21.26	**225** (100), 77 (36), 226 (16)	0.9961	0.33	5.1	0.9965	4.9
32	DOP	Di-*n*-octyl phthalate[c]	23.75	**149** (100), 223 (22), 279 (8)	0.9956	1.7	4.9	0.9997	5.0
36	DINP	Diisononyl phthalate[b]	26.21–28.35	149 (100), 167 (7), **293** (17)	0.9982	600	5.6	0.9990	10
37	DIDP	Diisodecyl phthalate[b]	25.01–26.58	149 (100), 167 (10), **307** (20)	0.9987	600	5.8	0.9985	12
Antioxidants and vulcanisation additives									
2	BTZ	Benzothiazole[b]	8.10	69 (15), 108 (30), **135** (100)	0.9989	0.33	3.1	0.9981	7.9
4	TBP	4-*tert*-butylphenol[b]	8.64	107 (36), **135** (100), 150 (21)	0.9941	0.66	1.2	0.9998	1.1
16	MBTZ	2-mercaptobenzothiazole[b]	14.47	69 (14), 109 (16), **167** (100)	0.9980	1000	4.3	0.9900	1.0
8	BHA	Butylated hydroxyanisole[b]	10.38	137 (64), **165** (100), 180 (51)	0.9940	0.66	2.2	0.9999	1.2
10	BHT	Butylated hydroxytoluene[b]	10.56	177 (7), **205** (100), 220 (25)	0.9962	0.33	3.4	0.9990	3.1

See codes in Fig. S2.
[a] 16 PAHs mixture (2000 μg mL^{-1} in dichloromethane/benzene, 1:1, v/v) 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] RSD, n = 6.

of the use. Samples were manually collected and immediately placed into glass vials, sealed with an aluminium cap, and stored at room temperature protected from light until their analysis. The shape and size of the particles of the rubber crumb samples are heterogeneous, including particles of less than 1×1 mm to about 5×5 mm (see Fig. S1). The average density of the samples is 0.6 g mL^{-1}.

Runoff water (about 20 mL) was collected over the football field in a rainy day with a glass Pasteur pipette, transferred to amber glass vials, sealed and stored at $4\,°C$ protected from light until their analysis.

2.3. Ultrasound Assisted Extraction (UAE)

UAE was employed to extract the target compounds from the crumb rubber infill. The corresponding amount of crumb rubber (0.05, 0.1 or 0.2 g) and solvent volume (0.5, 1, or 2 mL of ethyl acetate), depending on the experiment, were placed into a 10 mL glass vial and sealed with an aluminium cap furnished with PTFE-faced septum. The vial was then placed into an ultrasound bath (Hoyer Handel GmbH, Germany) at 50 W during 20 min and at $25\,°C$. Afterwards, the supernatant was filtered through $0.20\,\mu m$ PTFE microporous filters (25 mm diameter). The obtained extract was diluted (1:10, v/v) in ethyl acetate and directly analysed by GC-MS.

2.4. Solid-phase microextraction (SPME)

Water analysis was performed by SPME followed by GC-MS. 5 mL of water were placed in a 10 mL glass vial, sealed with aluminium caps furnished with PTFE-faced septa, and immersed in a water bath at $100\,°C$. After 5 min of sample equilibration, the corresponding fibre (PDMS or PDMS/DVB) was exposed to the headspace over the water sample (HS-SPME mode) for 20 min.

Regarding the analysis of the air above the crumb rubber, 0.2 g of rubber crumb sample were weighted into a 10 mL glass vial and the vial, sealed with aluminium cap furnished with PTFE-faced septa and immersed in a water bath maintained at the chosen working temperature ($25\,°C$ or $60\,°C$, depending on the experiment). Samples were let to equilibrate for 5 min and, then, the SPME fibre was exposed to the headspace over the sample for 20 min.

To perform the burning case-study, 0.2 g of rubber crumb from a football field were exposed to a flame during 30 s. Afterwards, the water and air put in contact with the burnt sample were analysed following the procedure described above.

In all cases, after the extraction, the corresponding fibre was retracted into the needle of the holder syringe and immediately thermally desorbed at $270\,°C$ in the GC injection port for 5 min. To confirm the absence of contamination, fibre blanks and procedure blanks were performed periodically by exposing the corresponding fibre in an empty vial (air analysis) and to the headspace over 5 mL of ultrapure water (water analysis). These two experiments confirmed the absence of the target analytes.

2.5. GC-MS analysis

The GC-MS analysis was performed using an Agilent 7890 A coupled to an 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 to 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 ZB-Semivolatiles (30 m $\times$ 0.25 mm i.d., $0.25\,\mu m$ film thickness) obtained from Phenomenex (Torrance, CA, USA). 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 10 min) at $5\,°C$ min^{-1}. Splitless mode was used for injection. After 1 min, the split valve was opened at a flow of 75 mL min^{-1}. The injector temperature was kept at $270\,°C$. The injection volume was $1\,\mu L$. The electron multiplier was set at a nominal value of 1600 V.

The mass spectral detector (MSD) was operated in the selected ion monitoring (SIM) mode, monitoring 3 ions per compound to achieve an unequivocal identification of the analytes (see Table 1). Full Scan mode was also employed for screening of non-target compounds. In this case, the mass range was $40–700$ *m/z*, from 4-–32 min.

2.6. Microwave digestion and ICP-MS analysis

Microwave digestion (Ethos Plus from Milestone, Sorisole (BG), Italy) was employed for the extraction of metals and metalloids from two crumb rubber samples.

0.1 g of sample were weighted in a Teflon tube and a mixture consisting of 10.5 mL of nitric acid and 1.5 mL of sulfuric acid were added. Microwave digestion was then carried out at 1000 W starting at $100\,°C$ (5 min) and reaching $220\,°C$ (15 min) after two intermediate steps of 5 min at $145\,°C$ and $190\,°C$. After cooling them, the final extracts were adjusted to 50 mL with deionized water.

The metal contents of two crumb rubber samples were determined by ICP-MS analysis. Two different instruments were used: a Magnetic Sector ELEMENT 2 (Thermo Fisher Scientific, San Jose, CA, USA) for Cadmium (Cd), Arsenic (As) and Chromium (Cr) determinations and a XSERIES 2 (Thermo Fischer Scientific, San Jose, CA, USA) Quadrupole for analysing the rest of metals and metalloids.

For the quantitative determinations, calibration standards were prepared in nitric acid (4%) and external calibrations (weighted linear regressions) were used.

3. Results and discussion

3.1. GC-MS analysis

The chromatographic conditions were optimized to achieve an efficient separation of the 40 target compounds: 16 PAHs, 15 phthalates, 3 adipates, Bisphenol A, 2 antioxidants, and 3 vulcanisation additives. GC-MS calibration studies were carried out both for the direct injection and the SPME mode. In both cases, they showed a direct proportional relationship between the amount of each analyte and their chromatographic responses (see Table 1). For the direct injection mode, calibration standards were prepared in ethyl acetate covering a range from 1-–1000 $\mu g\,L^{-1}$ (ten levels, and three replicates per level) for all compounds (excepted for DIHP, 2MBTZ, DINP, DIDP: 1000–10000 $\mu g\,L^{-1}$). Water calibration studies by SPME were carried out covering a concentration range between 0.01 $\mu g\,L^{-1}$ and 2 $\mu g\,L^{-1}$ (seven levels, and three replicates per level). The method precision was evaluated within a day and amongst days. Table 1 summarizes the inter-day precision (n = 6) achieved for direct injection (100 $\mu g\,L^{-1}$) and SPME (0.1 $\mu g\,L^{-1}$). As can be seen, the mean Relative Standard Deviation (RSD) values were lower than 5%. In all cases, Instrumental Detection Limits (IDLs) were calculated as the concentration giving a signal-to-noise of three (S/N = 3) since any of the target compounds were detected in the solvent or in the fibre blanks (see Table 1). These IDLs were at the low $\mu g\,L^{-1}$ for most compounds.

Fig. S2 shows a SIM chromatogram of a 1000 $\mu g\,L^{-1}$ (DIHP, DINP,

DIDP: 4000 μg L^{-1}) standard solution containing the 40 target compounds in ethyl acetate. As can be seen, a complete separation and identification of the target compounds is achieved in less than 33 min.

3.2. Optimization of the UAE conditions for the crumb rubber analysis

The extraction efficiency of different solvents (MeOH, ethyl acetate, mixtures of both (1:1, v/v) and acetone), volumes (0.5, 1 and 2 mL) and amount of sample (0.05, 0.1 and 0.2 g) were studied. The experimental procedure has been described in Section 2.3. A real rubber crumb sample of a football field containing 14 of the studied compounds was selected to carry out the optimization of the experimental UAE conditions instead of a spiked sample, thereby allowing taking into account the real interactions between the matrix and the analytes, and then, obtaining more realistic results. As can be seen in Fig. 1, MeOH (experiments D, E) provided the lowest extraction efficiency for all compounds. On the other hand, the highest extraction efficiency was achieved employing ethyl acetate (experiments A, B, C) and acetone (experiment H) for most compounds. In view of these results, ethyl acetate was selected as extraction solvent due to its compatibility with the chromatographic system. Regarding the ratio amount of sample/solvent volume, no significant differences were observed between experiments A (0.05 g sample and 0.5 mL ethyl acetate), B (0.1 g sample and 1 mL ethyl acetate) and C (0.2 g sample and 2 mL ethyl acetate) for most compounds. Therefore, the UAE procedure can be successfully carried out working in the range 0.05–0.2 g of sample with the correspondent volume of ethyl acetate. The possibility of working with very small sample size (due to the homogeneity of the material) combined with the extraction efficiency achieved employing low solvent volume, enable the miniaturization of the UAE technique which complies with the Green Chemistry Principles. Although the final extract could be directly injected into the GC-MS instrument, an aliquot of this extract was diluted before GC analysis (1:10, v/v in ethyl acetate).

3.3. Optimization of the SPME conditions for the analysis of the runoff water and air above the samples

The sensitivity of the selected extraction technique is an important parameter to consider for the analysis of trace levels of priority pollutants in environmental samples (water and air) such as those studied in this work. In this way, SPME was selected as extraction and preconcentration technique to analyse the runoff water samples. Based on previous studies (Llompart et al., 2013), several parameters were kept constant (100 °C, headspace mode, and 20 min as extraction time). In contrast, the type of fibre, one of the most influential SPME parameters, was studied in order to obtain the highest extraction efficiency, and a high selectivity and sensitivity for the 40 studied compounds, especially for the heaviest PAHs. In this case, the extraction efficiencies of PDMS/DVB and PDMS fibres were compared. Experiments were carried out employing 5 mL of ultrapure water spiked with 0.1 μg L^{-1} of the target compounds, and GC-MS analysis was performed. The experimental procedure has been previously detailed in Section 2.4. Fig. 2 shows the comparative responses for PDMS/DVB and PDMS fibres. For the 16 studied PAHs (Fig. 2a), PDMS/DVB offered the highest extraction efficiency in most cases, especially for the most volatile PAHs. For these compounds, the responses were up to one order of magnitude higher employing PDMS/DVB fibre. As can be seen in Fig. 2b, the plasticizer responses were more variable, due to the different polarities and chemical behaviour of these compounds. As regards the antioxidants and vulcanisation additives

(Fig. 2c), the extraction efficiency employing PDMS/DVB was clearly higher. In view of these results, PDMS/DVB was the selected fibre.

Further experiments were carried out to compare the efficiency of both SPME fibres (PDMS/DVB and PDMS) for the extraction of the studied compounds from the air above the crumb rubber. The experimental procedure has been previously detailed in Section 2.4. In this case, the fibres were exposed to the headspace of a crumb rubber sample from a synthetic turf football field containing 24 of the 40 studied compounds. Higher extraction efficiency was again obtained employing PDMS/DVB as fibre coating, which was then selected for the analysis of the air above the recycled material.

3.4. Analysis of real samples

The recycled crumb rubber of 15 football fields of synthetic turf from Santiago de Compostela and its metropolitan area (Northwest Spain) was analysed by direct injection mode. In addition, the presence of the 40 target compounds in two real runoff waters collected from two football fields, and in the air above two rubber crumb samples (lab scale experiments, see experimental section) was assessed by SPME.

3.4.1. Analysis of the recycled crumb rubber

Table 2 shows the concentrations (μg g^{-1}) of the target compounds in 15 crumb rubber samples.

As can be seen, 24 out of the 40 studied compounds were found in the analysed diluted extracts.

The presence of PAHs could be due to the use of mineral oils employed for the processing and manufacturing of rubber. Besides, their presence might be increased as a consequence of thermal treatment. In this way, fourteen of the 16 target PAHs were found in the samples. Their concentrations and statistical distributions in the samples is also visualized in the Box-and-Whisker chart in Fig. 3a, which includes the average, median and concentration range for each analyte. Fig. 3b (cumulative bar chart) depicts the concentration profile (μg g^{-1}) per sample and the total PAH concentration in each sample.

FLA, PYR and CHY were detected in all the samples, and PYR, FLA and B[ghi]P were the most abundant PAHs with concentrations between 2 and 18 μg g^{-1} (see Table 2 and Fig. 3a and b), highlighting the presence of PYR at very high concentration (>10 μg g^{-1}) in several samples. It is also important to note the presence of B[a]P, considered as the most toxic PAH, at concentrations up to 2 μg g^{-1}. On the other hand, the most volatile PAHs, NAP, ACY, and ACE were found at lower concentrations (<0.5 μg g^{-1}), probably due to volatilization from the football fields. Sample 5 contained all the studied PAHs, reaching a total PAH concentration of 50 μg g^{-1} (see Fig. 3b). The total target PAH concentration per sample was between 5 μg g^{-1} and 50 μg g^{-1}.

If the crumb rubber material were considered as an article and not as a mixture (part of an infrastructure), these high PAH levels would lead manufacturers, in most cases, to consider them as non-compliant material. Actually, the placing on the market for supply to the general public of articles containing PAHs is restricted by the entry 50 of Annex XVII to REACH Regulation (EC) No 1907/2006 (Directive 1907/2006, 2006), paragraphs 5 and 6. Articles placed on the market for supply to the general public will contravene the restriction if any of their rubber or plastic components, that come into direct as well as prolonged contact or short-term repetitive contact with human skin or the oral cavity (under normal or reasonably foreseeable conditions of use), contain more than 1 mg kg^{-1} (0.0001% w/w) of any of the eight PAHs that are identified in Column 1 of the entry. Regarding specific products, such as toys, they should not contain more than 0.5 mg kg^{-1} (0.00005%) of any of the listed PAHs. Guidance for the interpretation of entry 50.5
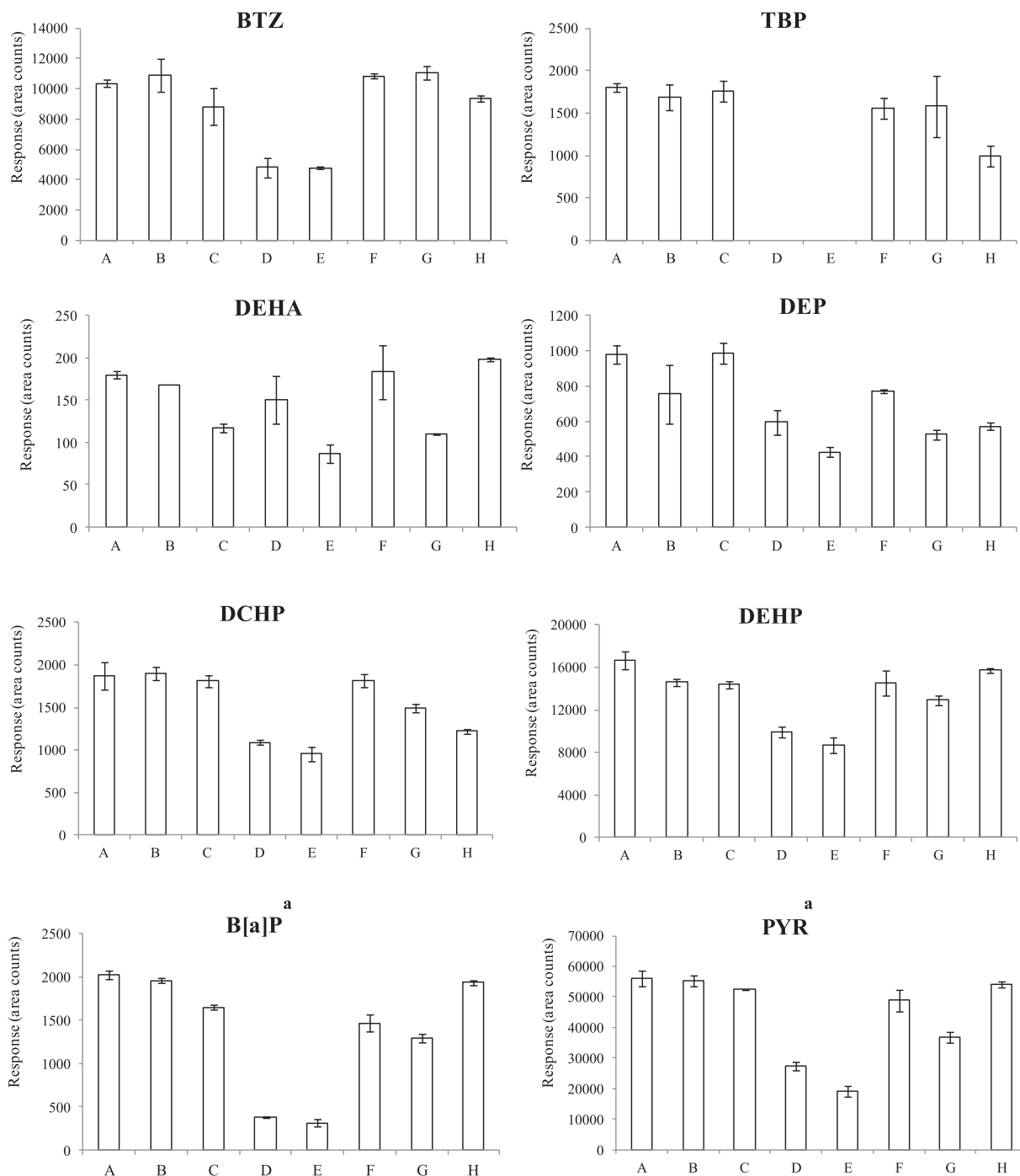
Fig. 1. Optimization of the UAE experimental conditions. A: 0.2 g sample +2 mL ethyl acetate, B: 0.1 g sample +1 mL ethyl acetate, C: 0.05 g sample +0.5 mL ethyl acetate, D: 0.1 g sample +1 mL MeOH, E: 0.1 g sample +0.5 mL MeOH, F: 0.1 g sample +1 mL MeOH/ethyl acetate (1:1, v/v), G: 0.1 sample + 0.5 mL MeOH/ethyl acetate (1:1, v/v), H: 0.2 g + 2 mL acetone. [a] The other PAHs present in the sample (PHN, FLA, B[a]A, CHY, B[b]F and B[ghi]P) exhibit similar behaviour.

and 50.6 is under development. RIVM (National Institute for Public Health and the Environment) in cooperation with the ECHA (European Chemicals Agency) are currently working on the restriction on rubber granules used as infill material in synthetic turf pitches. The proposal is expected to be submitted by April 13, 2018 (ECHA, 2017).

Although the crumb rubber samples were collected from fields located quite close each other (maximum linear distance 15 km), the PAH concentrations differ up to one order of magnitude (see

ranges in Table 2 and Fig. 3a). These concentrations are in concordance with those reported in Italian artificial-turf playing fields, where PYR reached the highest concentrations, and the human carcinogen B[a]P was also detected (Menichini et al., 2011; Marsili et al., 2015). In these surfaces (football fields), the rubber material is equivalent to that employed for playgrounds (Llompart et al., 2013), but the crumb material is disaggregated over the surface being more accessible for players, especially children, thereby constituting a higher potential health risk.
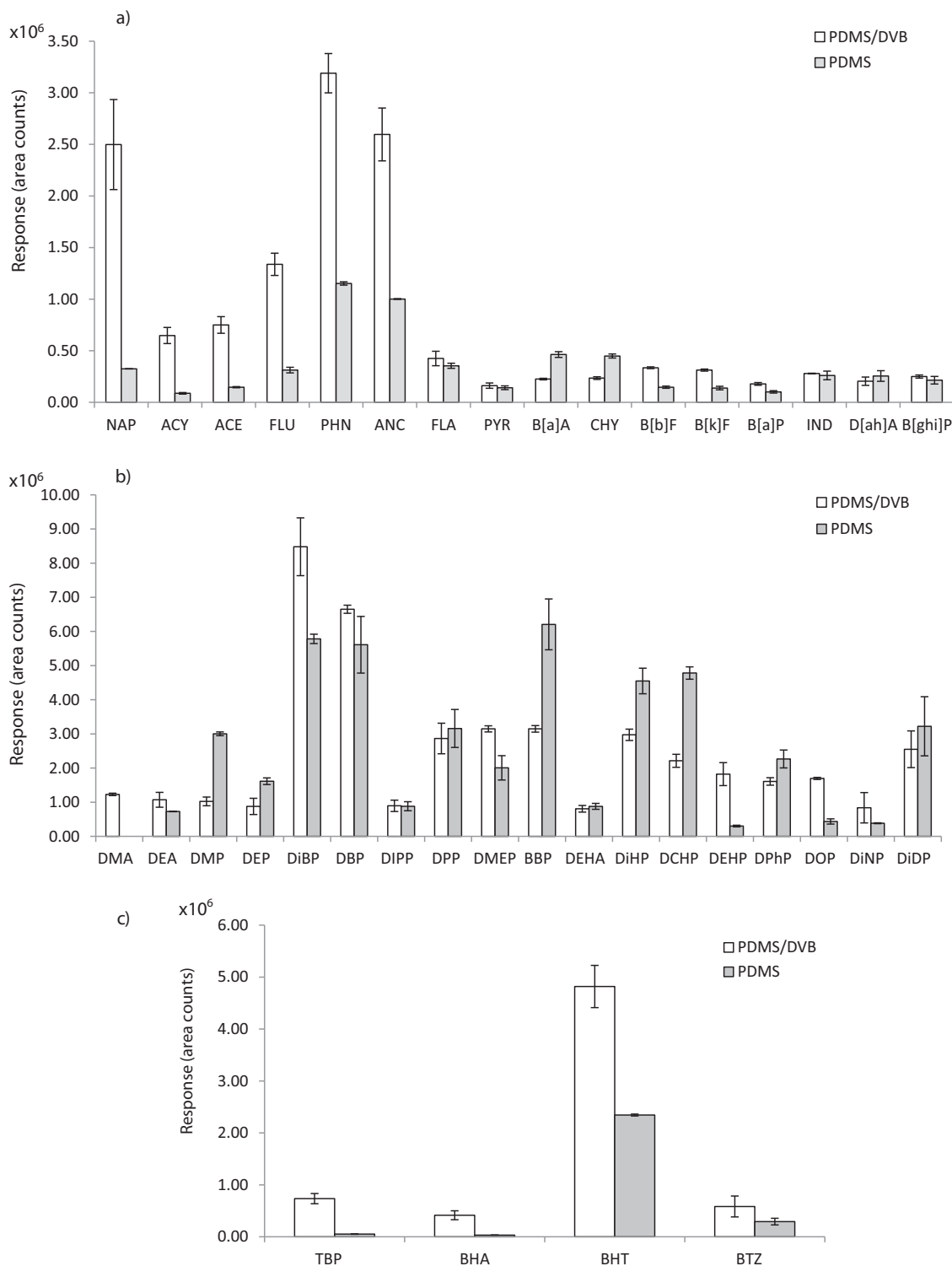
Fig. 2. Selection of the SPME fibre to be employed for water analysis.

Regarding plasticizers, seven of the target compounds were found in the football field samples (5 phthalates, 1 adipate and the endocrine disruptor BPA), as can be seen in Table 2. All samples contained between 3 and 6 plasticizers, highlighting sample 3 with a total plasticizer concentration of 283 µg g^{-1}, mainly due to the high DEHA concentration. The most frequently found plasticizer was DEHP, which was detected in all the samples at a concentration ranging between 5 and 17 µg g^{-1}. It is important to point out that DEHP is considered as an endocrine disruptor and it is included in the list of priority substances in the field of water policy (Annex I of the Directive, 2008/105/EC) (2008/105/EC, 2008). Besides, its use, together with other 5 phthalates, has been banned due to its harmful effects in cosmetics, and it is restricted in several consumer products such as toys. Bisphenol A (BPA), another recognized

Table 2
Concentrations (μg g^{-1}) of target compounds in the crumb rubber.

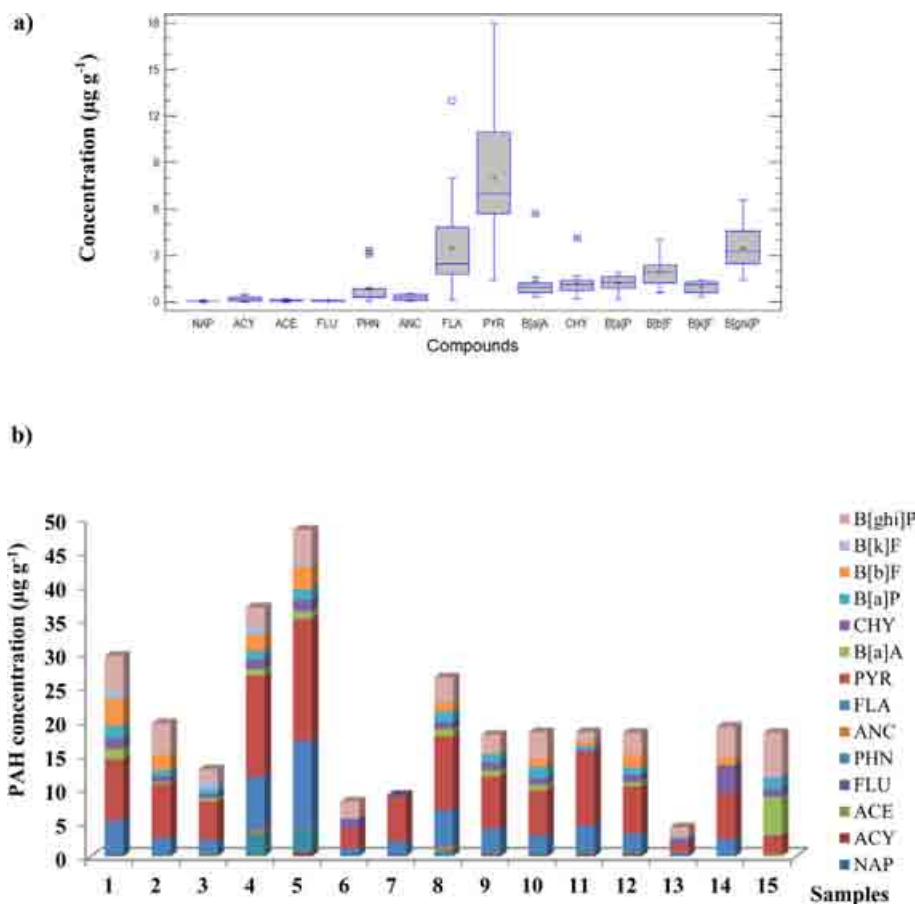| Samples	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Average	Median	Range
PAHs																		
NAP	0.032	0.060	0.014	0.047	0.050		0.021		0.051	0.067	0.089	0.10				0.053	0.051	0.014−0.10
ACY	0.17		0.15		0.46	0.019	0.036		0.16	0.17	0.33	0.33			0.024	0.18	0.16	0.019−0.46
ACE		0.033	0.18	0.17	0.062		0.021		0.090		0.050	0.045			0.15	0.089	0.062	0.021−0.18
FLU					0.073		0.040		0.082							0.065	0.073	0.040−0.082
PHN	0.30	0.27	0.29	3.1	3.3	0.12	0.31	0.87	0.80	0.38	0.83	0.42	0.045	0.26		0.81	0.345	0.045−3.3
ANC		0.050		0.48	0.18			0.56	0.076						0.34	0.28	0.26	0.050−0.56
FLA	4.8	2.4	1.8	8.0	13	0.99	1.8	5.4	2.9	2.5	3.3	2.5	0.43	2.3	0.12	3.5	2.5	0.12−13
PYR	9.1	7.9	5.7	15	18	3.1	6.6	11	7.7	6.7	11	7.0	1.4	6.9	2.5	8.0	7.0	1.4−18
B[a]A	1.6	0.34	0.52	1.0	1.2			1.1	0.88	0.81		0.63			5.7	1.4	0.94	0.34−5.7
CHY	1.5	0.84	0.59	1.4	1.7	1.4	0.28	1.0	1.2	1.0	0.20	1.1	0.75	4.1	1.2	1.2	1.1	0.20−4.1
B[a]P	1.9	0.96	0.78	1.2	1.6			1.6	1.3	1.7	0.63	1.1	0.20		1.7	1.2	1.2	0.20−1.9
B[b]F	4.0	2.3		2.4	3.3			1.4		1.2	0.62	1.9		1.1		2.0	1.9	1.1−4.0
B[k]F	1.3		1.1	1.4	0.63			0.31								0.95	1.1	0.31−1.4
B[ghi]P	5.0	4.6	1.8	2.7	4.8	2.5		3.3	2.8	3.9	1.4	3.2	1.5	4.6	6.6	3.5	3.2	1.4−6.6
Total	**29.7**	**19.8**	**12.9**	**36.9**	**48.4**	**8.1**	**9.1**	**26.5**	**18.0**	**18.4**	**18.4**	**18.3**	**4.3**	**19.3**	**18.3**	**23.2**	**19.9**	**0.014−18**
Plasticizers																		
BPA			1.7					0.054								0.87	0.87	0.054−1.7
BBP				0.19		0.12	0.10					0.13				0.14	0.12	0.10−0.19
DBP	0.42	0.87	2.7			0.45		16	0.44		0.27	1.1	0.27	0.051	0.43	2.1	0.44	0.051−16
DEHP	8.2	8.7	17	9.8	5.6	7.2	7.9	11	8.0	4.6	7.4	15	7.4	4.6	8.0	8.7	8.0	4.6−17
DEHA			251	0.4				0.4				1.9				63	1.2	0.4−251
DEP	0.22		11	2.4	3.0	4.9	0.76	2.2	1.7	0.12	0.50	3.5	0.50		1.7	2.5	1.7	0.12−11
DIBP	0.86	2.4	1.7	1.9	1.6	1.3		5.3	7.1	0.91	1.1	3.8	1.0	0.91	7.2	2.6	1.6	0.86−7.2
Antioxidants and vulcanisation additives																		
BTZ	1.9	2.3	5.2	2.0	1.6	2.6	1.7	2.1	0.90	1.3	1.9	0.96	1.9	1.3	0.92	1.9	1.9	0.90−5.2
TBP	0.083		0.074	0.039	0.037	0.076	0.030	0.047	0.059			0.046			0.060	0.051	0.053	0.030−0.076
BHT	0.097		56	1.3	2.6		4.5	0.12	1.8	0.20		0.57				7.5	1.3	0.097−56

Fig. 3. a) Box-and-Whisker plot for PAH distribution. b) Concentration (μg g^{-1}) profile of the analysed samples for PAHs.

endocrine disruptor, was also found in several samples at concentrations up to $2 \, \mu g \, g^{-1}$.

As regards the other target compounds, BTZ was found in all the analysed samples, with an average concentration of $2 \, \mu g \, g^{-1}$. TBP was detected in 67% of the samples, at low concentration ($<0.1 \, \mu g \, g^{-1}$), whereas the antioxidant BHT was found in 9 samples, highlighting again the sample 3 with a very high concentration of $56 \, \mu g \, g^{-1}$.

3.4.1.1. Metal content analysis.

Many metals (Zn, Mg, Al, Cr, Mn, Fe, Co, Cu, Cd, Ba and Pb) and one metalloid (As) were found in the two rubber granule samples analysed (See Table S1). Zn concentrations were extremely high, between 13 and $15 \, mg \, g^{-1}$, whereas Cd, Pb and Cr concentrations ranged from 0.6 to $1.1 \, \mu g \, g^{-1}$, 17 to $24 \, \mu g \, g^{-1}$ and 1.2 to $1.5 \, \mu g \, g^{-1}$, respectively. As reached a concentration of $0.7 \, \mu g \, g^{-1}$.

Mg and Al concentrations were close to $500 \, \mu g \, g^{-1}$, whereas those of Cu and Co were between 20 and $200 \, \mu g \, g^{-1}$.

These metal concentrations are comparable with those found in other studies (Han et al., 2008; Menichini et al., 2011; Marsili et al., 2015) conducted on this type of recycled rubber material, excepted Co (average $185 \, \mu g \, g^{-1}$) which shows a concentration higher of one order of magnitude in our present study. The high levels of Zn may be due to zinc oxide, which is used as a vulcanisation additive during the rubber production.

3.4.2. Analysis of the runoff water (SPME)

Rainwater may produce the leaching of the chemical compounds present in the crumb rubber infill of the synthetic fields (see Table 2) and their entry in the different environmental compartments. In addition, football fields of synthetic turf are frequently watered in order to maintain their physical properties and to lower the surface temperature, which can reach up to $80 \, °C$ in hot sunny days. Several studies have demonstrated that the watering of these sport surfaces contributes to the compound leaching from the rubber material (Penn State, 2010). In order to evaluate the transfer degree of the compounds from the football fields to the runoff water, two water samples, directly collected from 2 football fields (samples 4 and 5 in Table 2) in a rainy day, were analysed (see experimental procedure in Section 2.4). As it is shown in Fig. 4a, 8 target PAHs (NAP, ACE, FLU, PHN, ANC, FLA, PYR and CHY) were found in the two samples, reaching a total concentration at the $\mu g \, L^{-1}$ level. Three phthalates DMP, DEP, and DIBP, the antioxidant BHT and the vulcanizing BTZ were also found, this last one at a very high concentration of $120 \, \mu g \, L^{-1}$ in both samples. Considering the BTZ concentration in the crumb rubber from these fields (see samples 4 and 5 in Table 2), the transfer rate of this compound to the water media is remarkable.

These results demonstrate that organic hazardous chemicals, including a high number of PAHs, are transferred from the football field to the runoff water. It is worth noting that these water leachates are either incorporated to the sewage water in urban areas or directly discharged in nearby superficial waters, or other environmental compartments.

3.4.3. Analysis of the air above the crumb rubber

The transfer of the target compounds from the rubber crumb material to the air above the football field was evaluated at different temperatures, at lab-scale by SPME, employing samples from two football fields (the experimental procedure has been detailed in Section 2.4). Fig. 4b shows the detected target compounds in the air above the samples 4 (Fig. 4b1) and 5 (Fig. 4b2), at $25 \, °C$ and $60 \, °C$. As can be seen, a largest number of analytes was found and higher chromatographic responses were obtained at $60 \, °C$. The response for BTZ was very high, showing the easy transfer of this compound

to the air. It should be underlined again that these outdoor surfaces can reach this temperature or even higher in summer, making easier the volatilization of the organic chemical compounds and, therefore, their bio-accessibility through inhalation. To this respect, Ginsberg et al. (2011a, 2011b). studied the human health risk assessment of these surfaces. They reported the presence of PAHs and BTZ in the air above the synthetic turf surfaces of football fields, highlighting the presence of high BTZ concentration in the air.

Screening studies (Full Scan mode) were also carried out in order to detect other non-target compounds in the air in contact with the crumb rubber. Several compounds were tentatively identified by comparing the mass fragments and ratio abundances between the experimental mass spectra and those provided by the NIST library. Among others, the presence of several persistent pollutants (POPs), including other non-target PAHs and alkylated PAHs, was observed.

3.5. Case-study: incineration of recycled crumb rubber

It has been demonstrated that football fields of synthetic turf are between 20 and $30 \, °C$ hotter than natural grass surfaces (Penn State, 2010). Although the risk of fire of synthetic turf football field is low, recently, the burning of this type of surfaces due to vandalism has been reported in several American cities. Besides, the landfill burning in which scrap tires are accumulated is very frequent, increasing the toxic substances transfer to the air and runoff water.

In this way, a case-study was carried out in order to evaluate the environmental risk derived from the recycled tire burning (see experimental procedure in Section 2.4). The chromatographic profile comparison between the air above the burnt and the non-burnt samples is showed in Fig. S3a. The relative abundance of the detected target compounds was clearly higher in the air in contact with the burnt sample (see Fig. S3b), where almost half of the target compounds were identified, highlighting again the strong presence of BTZ in comparison with the other compounds.

Rain water was brought into contact with the non-burnt and the burnt crumb rubber and analysed by SPME-GC-MS (see experimental procedure in Section 2.4). As it is clearly depicted in Fig. S3c, the analyte concentrations were much higher for the water in contact with the burnt crumb rubber. Here again, the high concentration ($250 \, \mu g \, L^{-1}$) of BTZ in the water put in contact with the burnt sample must be highlighted.

High concentrations of hazardous organic compounds, including priority pollutants, are proved to be released both to the atmosphere and runoff water. Subsequently, they can be easily moved to different environmental compartments generating tricky environmental issues.

4. Conclusions

This study reveals the presence of priority organic compounds such as PAHs, and other hazardous substances including phthalates, adipates, vulcanizing agents and antioxidants in synthetic turf football fields. The leaching of these chemicals from these synthetic play surfaces to the runoff water and their direct transfer to the air above the crumb rubber has also been demonstrated.

It should be also noted that high concentrations of heavy metals such as Cd, Pb and Cr, were found in two crumb rubber samples.

A miniaturized UAE procedure followed by GC-MS analysis, was successfully employed to analyse the crumb rubber from 15 football field surfaces. The results showed the presence of 24 of the 40 target compounds, including 14 of the 16 EPA PAHs, with total concentration up to $50 \, \mu g \, g^{-1}$.

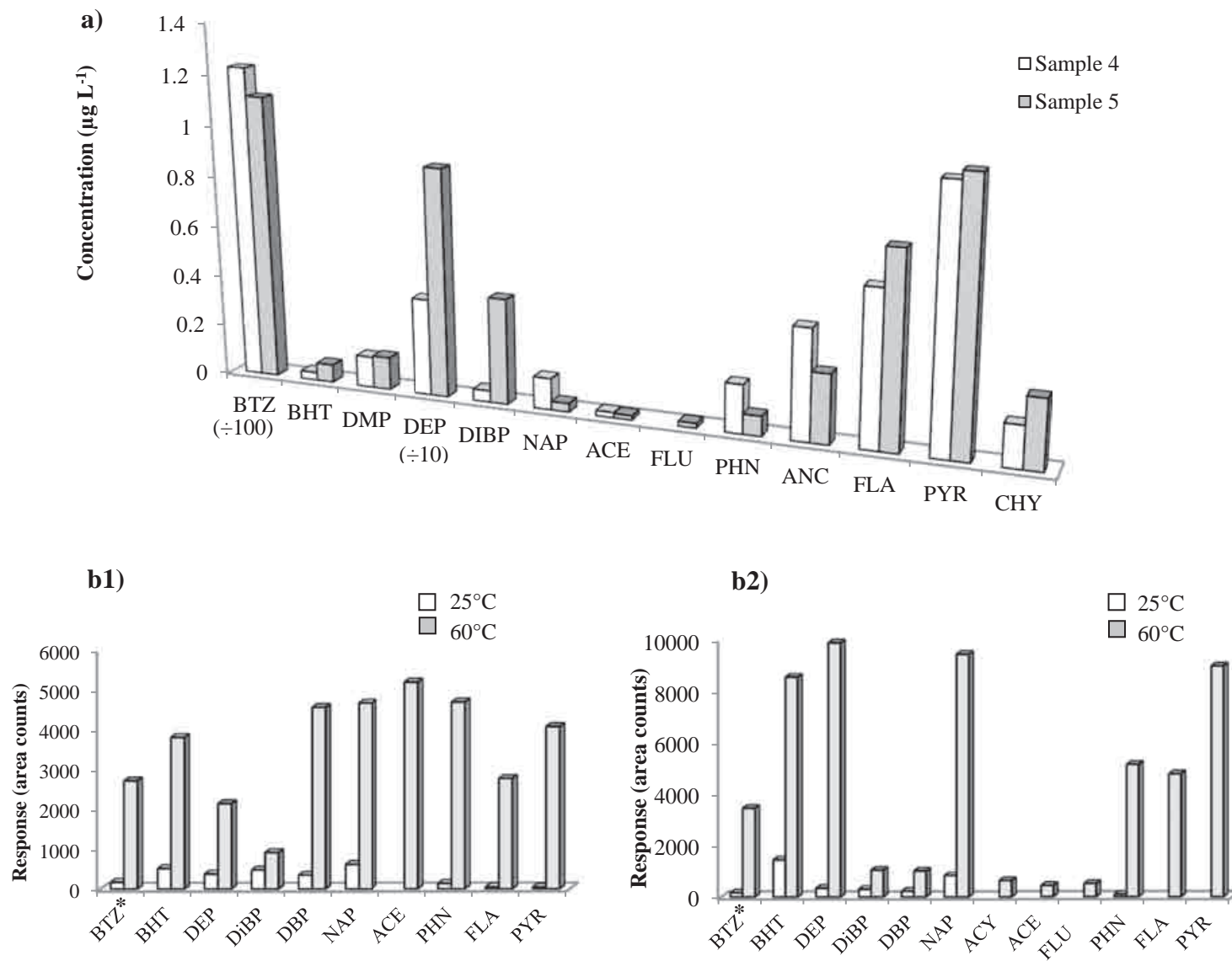The SPME conditions were optimized to achieve the highest

Fig. 4. Runoff water and air analysis. a) Concentration (μg L^{-1}) of the target compounds in the runoff water. b) Comparison between the responses obtained by HS-SPME at 25 °C and at 60 °C for the target compounds identified in the air above the surface. * Response divided by 100 (BTZ).

extraction efficiency of the compounds from the runoff water. Target compounds, including 8 PAHs, BTZ and some phthalates, were detected at μg L^{-1} level. These compounds were also detected after performing SPME analysis of the air above the playing surfaces, underlining the inhalation risk, especially to children.

Therefore, PAHs and other organic substances were proved to quickly transfer into the air and water, suggesting that they could easily reach different environmental compartments. The environmental and health risks derived from the use of these surfaces have to be considered and some regulations should be adopted.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2017.12.063.

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