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Evaluation of chemicals of environmental concern in crumb rubber and water leachates from several types of synthetic turf football pitches

Maria Celeiro^a, Daniel Armada^a, Nuno Ratola^b, Thierry Dagnac^c, Jacob de Boer^d, Maria Llompart^{a,*}

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

^b LEPABE—Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias S/n, 4200-465, Porto, Portugal

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

^d Vrije Universiteit Amsterdam, Department of Environment & Health, De Boelelaan 1085, 1081HV, Amsterdam, the Netherlands

HIGHLIGHTS

- The presence of 40 hazardous chemicals was evaluated in Portuguese pitches.
- Runoff water was analyzed to assess if an inflow of the target compounds exists.
- Results revealed the presence of PAHs in crumb rubber at concentrations of $57 \mu\text{g g}^{-1}$.
- Continuous chemicals leaching from crumb rubber to the runoff water was demonstrated.
- The transfer of chemicals into runoff water poses a risk for the aquatic environment.

GRAPHICAL ABSTRACT

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ABSTRACT

Nowadays concern exists about the safety for both football players and the environment of recycled tire rubber used as infill in synthetic turf football pitches. In this study 40 target compounds, including polycyclic aromatic hydrocarbons (PAHs), plasticizers, antioxidants and vulcanization agents were determined in 50 synthetic football pitches of diverse characteristics to estimate environmental risks. This is the first study of crumb rubber sport facilities in Portugal. Analyses were performed by ultrasound-assisted extraction followed by gas chromatography-tandem mass spectrometry (UAE-GC-MS/MS). To evaluate the transfer of the target chemicals from the crumb rubber to the runoff water, water leachates collected from several football pitches were analyzed by solid-phase microextraction (SPME-GC-MS/MS). In addition, lab-scale runoff simulation experiments were performed to assess whether a persistent inflow of the target compounds from the football pitches into the runoff water would exist. Results revealed the presence of most of the target PAHs in crumb rubber at total concentrations up to $57 \mu\text{g g}^{-1}$, next to a high number of plasticizers and vulcanization agents. Runoff water collected from the football pitches contained up to 13 PAHs as well as other chemicals of environmental concern. In addition, continuous leaching of chemicals from the crumb rubber to the surrounding water

* Corresponding author.

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

was demonstrated. The transfer of target chemicals into the runoff water poses a potential risk for the aquatic environment.

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1. Introduction

Waste management is a crucial activity for the sustainability of our planet but is also a challenging task. In fact, these measures may have harmful side-effects that need to be addressed and mitigated. One of the examples is the recycling of end-of-life tires (ELTs). Every year, a large volume of used tires enters the waste stream worldwide and most of them are still dumped and not always through the proper channels (Lee and Yoo, 2011). Incineration aiming at the production of energy is one of the options for ELTs valorization, but some contaminants such as polycyclic aromatic hydrocarbons (PAHs), heavy metals, dioxins and furans can be released during the process (Watterson, 2017). Not long ago, recycling was considered a valid alternative. ELTs were ground into granulates of different size and called 'crumb rubber'. Crumb rubber from mechanical or cryogenic grinding of ELTs has been successfully applied in several functions related for instance to construction materials (ECHA, 2017), but about 43% is used as infill material in synthetic turf fields and playgrounds due to its high resistance and lower maintenance needs (Cheng et al., 2014). Currently, the durability and the maintenance needs of such surfaces is under scrutiny as there may be differences between the commercial assessments and the empirical findings about the pitch and playground lifetimes.

Due to the complex manufacturing process of tires, several compounds (accelerators, activators, plasticizers, and vulcanizing agents) and chemicals (benzene, phthalates, and alkylphenols, among others) can generate potential environmental and public health concerns (Bocca et al., 2009). Traces of hazardous pollutants from tire production, such as PAHs, heavy metals, volatile organic hydrocarbons (VOCs) and numerous additives have been found in crumb rubber (Plessner and Lund, 2004; Han et al., 2008; Menichini et al., 2011; Llompart et al., 2013; Ruffino et al., 2013; Celeiro et al., 2014, 2018; Schneider et al., 2020c). The crumb rubber employed as infill in synthetic turf football pitches or playgrounds, is considered a mixture and the maximum individual concentrations for PAHs were initially set at $100 \mu\text{g g}^{-1}$ for benzo[a]pyrene (B[a]P) and dibenzo[ah]anthracene (D[ah]A), and at $1000 \mu\text{g g}^{-1}$ for other six PAHs (benzo[e]pyrene (B[e]P), benzo[a]anthracene (B[a]A), chrysene (CHY), benzo[b]fluoranthene (B[b]F), benzo[j]fluoranthene (B[j]F) and benzo[k]fluoranthene (B[k]F) (ECHA, 2018). However, the regulated levels for the eight ECHA (European Chemicals Agency) PAHs (B[a]P, D[ah]A, B[e]P, B[a]A, CHY, B[b]F, B[j]F, and B[k]F) in rubber consumer products that can come into direct contact with the skin or the oral cavity such as toys are set at $1 \mu\text{g g}^{-1}$ or $0.5 \mu\text{g g}^{-1}$ (Barrero-Moreno et al., 2018). Due to the potential human health risk of the recycled rubber pitches and playgrounds, the European Commission limited, on September 2019, the total concentration of the eight ECHA PAHs to $20 \mu\text{g g}^{-1}$ in granules and mulches used in synthetic turf pitches and playgrounds (ECHA, 2019).

These sport facilities are usually outdoors and exposed to different weather conditions. Already under mild conditions of temperature and leaching, the crumb rubber components can be volatilized into the atmosphere and be leached into water (Celeiro et al., 2014, 2018; Schneider et al., 2020b). This poses an environmental risk since several PAHs, NAP, B[b]F, B[k]F, B[a]P, IND and B

[ghi]P, and plasticizers, such as diethyl hexyl phthalate (DEHP) are considered as priority pollutants in surface waters by the European Union (Regulation, 2008/105/EC), whereas other phthalates such as diethyl phthalate (DEP), dimethyl phthalate (DMP), benzylbutyl phthalate (BBP), dibutyl phthalate (DBP) and di-*n*-octyl phthalate (DnOP), as well as the 16 PAHs are considered as priority substances by the United States Environmental Protection Agency (EPA,). Thus, crumb rubber may constitute a potential chemical hazard for humans and the environment (Oomen and De Groot, 2017; Pronk et al., 2018; Schneider et al., 2020a, 2020b).

The problems that may arise from leaching by rain and irrigation to maintain the infill in synthetic turf football pitches are poorly studied and understood. Chemicals present in the rubber like metals (e.g. zinc and iron) and organic chemicals (like PAHs or benzothiazole) can be released with a potential negative impact on sewage water, groundwater and/or natural surface and even marine waters.

Although there are some studies dedicated to the presence of contaminants in crumb rubber, the last reports available from regulatory bodies (Schneider et al., 2020a, 2020b, 2020c) stress the need for more extensive monitoring for a better assessment of the risks for human health and the environment. Most of the available studies are focused on specific geographical areas and usually include only a few samples and compounds.

To the best of our knowledge, the present study is the first one including crumb rubber samples taken from football pitches in Portugal. Samples from 50 crumb rubber football pitches of diverse characteristics (outdoor/indoor, new/old, public/private access, etc.) were taken and the levels of 40 target compounds, including PAHs, plasticizers, antioxidants and vulcanization agents were determined. Crumb rubber analysis was performed by ultrasound-assisted extraction followed by gas chromatography-tandem mass spectrometry (UAE-GC-MS/MS). In several pitches, runoff water samples were collected and analyzed by solid-phase micro-extraction (SPME-GC-MS/MS). In addition, some leachate experiments were performed. The results obtained in this last experiments are in consonance with those obtained in the real water samples collected from the eight football pitches demonstrating the continuous lixiviation of chemicals from the crumb rubber towards the water including PAHs, phthalates and other agents, and the subsequent threat that can pose to the environment and the water bodies.

2. Experimental

2.1. Reagents and materials

The studied compounds, and their CAS numbers are summarized in Table S1. Ethyl acetate was provided by Sigma-Aldrich (Steinheim, Germany), methanol by Scharlab (Barcelona, Spain), and acetone was provided by Fluka Analytical (Steinheim, Germany).

Individual stock solutions of each compound were prepared in methanol or ethyl acetate. Further dilutions and mixtures were prepared in acetone (spike solutions) or ethyl acetate (calibration studies). Stock solutions were stored in glass vials protected from light at -20°C . All reagents were of analytical grade. Since one of

the studied compound groups were plasticizers that are ubiquitously used, plastic material was replaced by metallic and glass material to avoid possible contamination during the experimental procedure and overestimation in the results. All material was also heated at 230 °C before use.

The SPME manual holder and the 65 mm polydimethylsiloxane-divinylbenzene (PDMS/DVB) fiber were supplied by Supelco (Bellefonte, PA, USA). The fiber was conditioned as recommended by the manufacturer prior to their use (250 °C for 0.5 h).

2.2. Sampling procedure

A total of 50 rubber crumb samples from synthetic turf football pitches (44 from outdoor surfaces, and 6 from indoor pitches) were directly collected from the studied surfaces in Portugal. About 100 g of rubber crumb was collected, placed into a glass vial, sealed with an aluminum cap, stored at room temperature, and protected from light until analysis by UAE-GC-MS/MS.

On rainy days, eight rainwater samples (about 20 mL) were collected from several of the outdoor surfaces (FP11, FP13, FP16, FP17, FP18, FP21, FP28 and FP30) with a glass Pasteur pipette, transferred to amber glass vials, sealed and stored at 4 °C, protected from light until analysis.

To evaluate the possible transfer of the analytes between the crumb rubber of the football pitches and the water in contact with it, 3 g of four crumb rubber samples (FP10, FP11, FP13 and FP30), were placed in contact with 13 mL of both irrigation water (the football pitches are frequently watered, especially in summer), and rainwater for 24 h. Afterwards, the water was collected and analyzed by SPME-GC-MS/MS. In addition, to assess whether a persistent inflow of the target compounds from the football pitches into the runoff water was present, the same rubber crumb was put in contact with a new rainwater aliquot each 24 h for 1 week, analyzing the collected extract each 24 h. Details about the analyzed samples are given in Table S2.

2.3. Ultrasound assisted extraction (UAE)

The experimental conditions were previously optimized by the authors (Celeiro et al., 2018). Briefly, 200 mg of the corresponding sample were placed in a 4 mL glass vial, and 2 mL of ethyl acetate were added. Then, the vial was sealed with an aluminum cap furnished with PTFE-faced septum, and it was immersed into an ultrasound bath (P. Selecta, Barcelona, Spain) for 20 min, at 50 Hz and controlled temperature (25–30 °C). After extraction, the organic supernatant was filtered through 0.22 µm PTFE filters (25 mm diameter), and diluted 1:10, v/v in ethyl acetate prior the injection in the chromatographic system. The overall process comprised a sample dilution factor of 1:100 (w/v).

2.4. Solid-phase microextraction (SPME)

Five mL of water sample was placed in a 10 mL glass vial, sealed with an aluminum cap furnished with PTFE-faced septa, and immersed in a water bath at 100 °C under magnetic stirring. After 5 min of sample equilibration, the PDMS/DVB fiber was exposed to the headspace over the water sample (HS-SPME mode) for 20 min. After that, the fiber was retracted into the needle of the holder syringe and thermally desorbed at 270 °C in the GC injection port for 5 min. Procedure blanks were performed periodically by exposing the fiber in a vial containing 5 mL of ultrapure water, to evaluate the absence of contamination.

2.5. GC-MS/MS analysis

Analyses were carried out employing a Thermo Scientific Trace 1310 gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 8000) with an autosampler IL 1310 from Thermo Scientific (San Jose, CA, USA). Separation was performed on a Zebtron ZB-Semivolatiles (30 m × 0.25 mm i.d. × 0.25 µm film thickness) obtained from Phenomenex (Torrance, CA, USA). Helium (purity 99.999%) was employed as carrier gas at a constant flow of 1.0 mL min⁻¹. The GC oven temperature was programmed from 60 °C (held 2 min) to 210 °C at 15 °C min⁻¹ and to 290 °C at 5 °C min⁻¹ (held 4 min). The total run time was 38 min. Pulsed splitless mode (200 kPa, held 1.2 min) was employed for injection. The injector temperature was set at 270 °C, and the injection volume was 1 µL (for direct injection). The mass spectrometer detector (MSD) was operated in the electron ionization (EI) positive mode (+70 eV). The temperatures of the transfer line and the ion source were set at 290 °C, and 350 °C, respectively. The filament was set at 25 µA and the multiplier voltage was 1460 V. Selected Reaction Monitoring (SRM) acquisition mode was implemented monitoring 2 or 3 transitions per compound (see Table S1) for an unequivocal identification and quantification of the target compounds. The system was operated by Xcalibur 2.2, and Trace Finder™ 3.2 software.

2.6. UAE and SPME-GC-MS/MS performance

UAE and SPME-GC-MS/MS method performance parameters are summarized in Table S3. For UAE-GC-MS/MS, the calibration curves were carried out employing standard solutions prepared in ethyl acetate containing the 40 target compounds covering a concentration range from 0.1 to 1000 µg L⁻¹, with 13 concentration levels (0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500 and 1000 µg L⁻¹) and 3 replicates per level. The specific range for each compound is shown in Table S3. In all cases, the method showed a good linearity, with coefficients of determination (R²) higher than 0.9900. The instrumental precision was evaluated within a day (n = 3) and amongst days (n = 5) for all concentration levels. Relative standard deviation (RSD) values are shown in Table S3 and they were in general lower than 8% and 10% for intra-day and inter-day, respectively. Limits of detection (LODs) were calculated as the concentration giving a signal-to-noise ratio of 3 (S/N = 3). For the three phthalates that were detected in the blanks, DIBP, DBP and DEHP, the LODs were estimated as the average amount of analyte giving a response in the blank plus 3 times the standard deviation. In all cases, they were at the low ng g⁻¹, excluding the two multiple phthalates, DINP and DIDP, and 2 MBTZ.

Regarding the SPME-GC-MS/MS method performance, calibration studies were carried out employing ultrapure water spiked with the target compounds, covering a concentration range from 0.001 to 0.5 µg L⁻¹ (nine levels, and two replicates per level). The method exhibited a direct proportional relationship between the amount of each compound and the chromatographic response, showing R² higher than 0.9900 for all compounds (see specific linear range for each compound in Table S3). The method precision was evaluated within a day (n = 3) and amongst several days (n = 5) at different levels of concentration, and RSD values for 0.1 µg L⁻¹ concentrations were determined (Table S3). Precision lower than 10% was observed in most cases. Recovery studies were performed applying the SPME method to rainwater containing 0.1 µg L⁻¹ of the target compounds. Recoveries were calculated comparing their obtained response (area) with those obtained for ultrapure water. Recoveries ranged between 74 and 120% with RSD values lower than 10% in most cases.

Limits of detection (LODs) were also calculated as the

concentration giving a signal-to-noise ratio of 3 ($S/N = 3$), excluding the phthalates that were detected in the blanks, DIBP, DBP and DEHP. For these compounds, the LODs were estimated as the average amount of analyte giving a response in the blank plus 3 times the standard deviation. In all cases, they were at the low ng L^{-1} .

3. Results and discussion

3.1. Analysis of the crumb rubber samples

In this study, 44 samples from outdoor football pitches and 6 samples from indoor pitches were collected from different locations of Portugal.

As can be seen in Table 1 and Table 2, 30 of the 40 target compounds were detected, including 15 of the 16 PAHs. Table 1 also includes the total concentration of the PAHs (see last row), the concentration ranges in the samples (see individual results in Table S4), as well as the average and median values.

In all outdoor football pitches, seven PAHs, PHEN, FLA, PYR, CHY, B[k]F, B[a]P and B[ghi]P, five plasticizers, DEP, DIBP, DBP, DEHA and DEHP, the antioxidant BHT and all vulcanization agents (BTZ, TBP and MBTZ) were found. NAP and B[a]A were also detected in all samples, excluding one in each case. The total PAH concentration ranged between 6 and 54 $\mu g g^{-1}$. The most abundant one was PYR, that reached concentrations of 30 $\mu g g^{-1}$, followed by FLA with values close to 10 $\mu g g^{-1}$. The PAH distribution per sample for the outdoor football pitches is shown in Fig. 1a. As can be seen, the profile was similar for the 44 analyzed samples, with PYR contributing the most to the total PAH concentration. This result, as well as the Σ PAHs levels agree with those reported in previous studies (Marsili L, 2015; Celeiro et al., 2018; Diekmann A and Schaumann, 2019; Schneider et al., 2020c). However, the PAH concentration measured in the crumb rubber is much higher than that found in urban soils of several North American cities, some of them located in areas close to high-traffic roads (Gao et al., 2019; Liu et al., 2019). In these studies, the concentration range for the $\Sigma 16$ PAHs was between 1.8 and 4.1 $\mu g g^{-1}$ and between 3.2 and 4.6 $\mu g g^{-1}$, in small and large cities respectively.

Regarding the results for indoor football pitches (see Tables 1 and 2), 13 PAHs, NAP, ACY, FLU, PHEN, ANC, FLA, PYR, B[a]A, CHY, B[k]F, B[a]P, IND and B[ghi]P, were detected in all samples, and ACE and B[b]F in four of the six samples. On the other hand, seven plasticizers, DEP, DIBP, DBP, BPA, BBP, DEHA and DEHP, BHT, and all the target vulcanization agents, BTZ, TBP and MBTZ, were found in all indoor samples, and DMP in all samples excluding one. The PAH levels are in general higher in indoor pitches than in outdoor surfaces, and the distribution of the PAHs per sample is similar (Fig. 1b), with PYR as the most abundant congener, followed by FLA. The sum of PAH concentrations (Table 1 and Table S4) was higher than 30 $\mu g g^{-1}$ in four of the five indoor samples. Only seven of the 44 samples taken from outdoor pitches showed a concentration higher than 30 $\mu g g^{-1}$. As can be seen in Table 1, PAH average and median concentrations were 48 $\mu g g^{-1}$ and 53 $\mu g g^{-1}$, respectively, in the indoor football pitches. Thus, they are 3.1 and 2.5 times higher than those observed in the outdoor pitches, in which these values reached 19 $\mu g g^{-1}$ and 17 $\mu g g^{-1}$, respectively. These results are visualized in Box-Whisker charts that include the average, and median concentrations as well as the ranges for the 16 target PAHs (Figures S1a and S1b). These charts highlight the difference between the concentrations of indoor and outdoor synthetic turf football pitches that might be due to the influence of weather conditions (wind, rain, temperature) as well as runoff, making indoor spaces potentially more dangerous than outdoor ones. Five (B[a]A, CHY, B[b]F, B[k]F and B[a]P) of the eight target PAHs regulated

Table 1
PAH concentrations in the crumb rubber samples from synthetic turf football pitches ($\mu g g^{-1}$) and runoff water ($\mu g L^{-1}$). Statistical parameters.

PAHs	Outdoor football pitches (44 samples)				Indoor football pitches (6 samples)				Collected runoff water (8 samples)				Simulated runoff water (8 samples)			
	N ^a	Range ($\mu g g^{-1}$)	Average ($\mu g g^{-1}$)	Median ($\mu g g^{-1}$)	N ^a	Range ($\mu g g^{-1}$)	Average ($\mu g g^{-1}$)	Median ($\mu g g^{-1}$)	N ^a	Range ($\mu g L^{-1}$)	Average ($\mu g L^{-1}$)	Median ($\mu g L^{-1}$)	N ^a	Range ($\mu g L^{-1}$)	Average ($\mu g L^{-1}$)	Median ($\mu g L^{-1}$)
NAP	43	0.05–0.36	0.13	0.10	6	0.08–0.22	0.14	0.14	7	0.007–0.11	0.043	0.032	6	0.02–0.07	0.040	0.041
ACY	32	0.02–0.49	0.071	0.042	6	0.05–0.49	0.18	0.15	7	0.005–0.04	0.021	0.020	8	0.02–0.09	0.052	0.049
ACE	8	0.01–0.122	0.032	0.023	4	0.02–0.09	0.048	0.041	2	0.01–0.02	0.017	0.022	8	0.007	0.012	0.014
FLU	40	0.02–0.40	0.07	0.031	6	0.14–0.28	0.21	0.21	3	0.02–0.05	0.033	0.028	8	0.01–0.09	0.042	0.035
PHEN	44	0.07–4.30	0.63	0.33	6	2.0–5.0	3.1	2.8	8	0.007–0.12	0.055	0.033	8	0.05–0.50	0.15	0.19
ANC	40	0.01–0.62	0.12	0.044	6	0.20–0.77	0.38	0.35	4	0.01–0.03	0.020	0.022	8	0.01–0.12	0.042	0.024
FLA	44	0.3–9.4	2.9	2.6	6	5.1–9.7	7.4	7.7	8	0.03–0.25	0.10	0.078	8	0.05–0.60	0.20	0.18
PYR	44	1.0–30	9.3	8.4	6	18–30	25	27	8	0.05–0.90	0.32	0.24	8	0.2–1.7	0.79	0.50
B[a]A	43	0.06–1.2	0.45	0.32	6	0.22–2.70	1.0	0.74	0				2	0.01–0.04	0.022	0.022
CHY	44	0.4–3.6	1.7	1.7	6	0.80–4.26	2.8	3.1	6	0.02–0.08	0.041	0.040	4	0.02–0.17	0.073	0.038
B[b]F	25	0.05–0.32	0.16	0.14	4	0.11–1.60	0.50	0.13	0				2	0.01–0.02	0.011	0.011
B[k]F	44	0.08–1.40	0.61	0.59	6	0.42–3.65	1.4	1.2	0				0			
B[a]P	n.c.				n.c.				n.c.				4	0.01–0.04	0.02	0.02
B[a]P	44	0.1–2.0	0.76	0.70	6	0.32–5.52	1.8	1.2	0				1	0.022	0.022	0.022
IND	36	0.06–1.23	0.56	0.50	6	0.24–2.44	1.0	0.80	0				0			
B[ghi]P	44	0.3–5.6	2.2	2.1	6	1.0–6.9	3.7	3.7	0				0			
Σ EPA PAHs	44	6–54	19	17	6	29–57	48	53	8	0.2–1.5	0.6	0.5	8	0.3–3.3	1.5	1.0

n.c. Compound not considered.

^a Number of samples containing the compound.

Table 2
Plasticizer and vulcanization agent concentrations in the crumb rubber samples from synthetic turf football pitches ($\mu\text{g g}^{-1}$) and runoff water ($\mu\text{g L}^{-1}$). Statistical parameters.

	Outdoor football pitches (44 samples)				Indoor football pitches (6 samples)				Collected runoff water (8 samples)				Simulated runoff water (8 samples)			
	N ^a	Range ($\mu\text{g g}^{-1}$)	Average ($\mu\text{g g}^{-1}$)	Median ($\mu\text{g g}^{-1}$)	N ^a	Range ($\mu\text{g g}^{-1}$)	Average ($\mu\text{g g}^{-1}$)	Median ($\mu\text{g g}^{-1}$)	N ^a	Range ($\mu\text{g L}^{-1}$)	Average ($\mu\text{g L}^{-1}$)	Median ($\mu\text{g L}^{-1}$)	N ^a	Range ($\mu\text{g L}^{-1}$)	Average ($\mu\text{g L}^{-1}$)	Median ($\mu\text{g L}^{-1}$)
Plasticizers																
BPA	31	0.02–0.9	0.19	0.18	6	0.1–0.6	0.20	0.24	0				8	0.01–0.15	0.070	0.049
DMA	2	0.01–0.02	0.015	0.015	0				0				8	0.04–0.11	0.061	0.054
DMP	21	0.01–0.06	0.02	0.022	5	0.02–0.10	0.12	0.13	6	0.03–1.4	0.53	0.24	8	0.2–2.4	1.6	1.8
DEP	44	0.03–0.70	0.15	0.083	6	0.1–3.8	1.0	0.5	7	0.1–1.5	0.60	0.49	8	0.2–0.5	0.33	0.34
DIBP	44	0.2–2.9	2.8	1.3	6	1.3–17	8.5	6.0	8	0.1–1.2	0.51	0.40	2	0.06–0.10	0.084	0.084
DBP	44	0.1–11	1.4	0.69	6	0.8–14	5.1	4.3	8	0.04–0.6	0.22	0.15	8	0.02–0.52	0.14	0.19
BBP	32	0.04–1.4	0.31	0.19	6	0.2–8.3	2.4	1.0	7	0.01–0.06	0.032	0.019	6	0.02–0.06	0.031	0.030
DEHA	44	0.9–15	3.7	2.31	6	6.7–46	24	21	1	0.012	0.012	0.012	5	0.01–0.04	0.022	0.015
DEHP	44	6.2–59	22	19	6	12–173	56	39	5	0.02–0.06	0.033	0.023	5	0.01–0.04	0.021	0.019
DPhP	1	0.59	0.59	0.59	0				0				0			
DnOP	1	0.51	0.52	0.52	0				0				3	0.03–0.04	0.032	0.044
Antioxidants and vulcanization agents																
BHT	44	0.1–2.0	1.1	1.1	6	1.1–2.2	1.4	1.4	8	0.02–0.7	0.23	0.12	8	0.04–0.13	0.082	0.079
BTZ	44	1.2–62	5.6	2.8	6	5.4–26	13	11	8	0.7–9.4	3.1	1.5	8	9–13	11	11
4 TB P	44	0.02–3.73	0.24	0.08	6	0.3–3.8	1.2	0.73	8	0.1–4.0	1.2	0.33	8	1.8–8.2	5.4	5.5
2MBTZ	44	1–205	51	25	6	16–135	71	68	0				0			

^a Number of samples containing the compound.

by ECHA, and considered carcinogenic substances, were detected at 3-fold higher concentrations in indoor football pitches than in outdoor ones (see Table 1).

Considering regulatory restrictions, crumb rubber, employed as infill in synthetic turf football pitches and other sport or recreational facilities, is considered a mixture, being the individual PAH concentration limited to $100 \mu\text{g g}^{-1}$ for B[a]P and D[ah]A, and to $1000 \mu\text{g g}^{-1}$ for other six PAHs (B[e]P, B[a]A, CHY, B[b]F, B[j]F and B[k]F) (ECHA, 2018). Recently, the European Commission restricted the total concentration of the eight ECHA PAHs to $20 \mu\text{g g}^{-1}$ in granules and mulches used in synthetic turf pitches and playgrounds (ECHA, 2019). However, these levels are still higher than the maximum values set for the eight ECHA PAHs in rubber consumer products, that come into direct contact with the skin or the oral cavity ($1 \mu\text{g g}^{-1}$) or in toys ($0.5 \mu\text{g g}^{-1}$) (ECHA, 2020). It is worth underlining here the intense use of these surfaces by children or young people, which implies repetitive contact with the human skin under normal or reasonably foreseeable conditions of use. As can be seen in Fig. 2 (see also Table S4), many of the detected PAHs in the indoor surfaces reached concentrations above $1 \mu\text{g g}^{-1}$ (upper part of the figure) and even much higher (for example PYR $> 20 \mu\text{g g}^{-1}$ in all samples, or CHY about $3\text{--}4 \mu\text{g g}^{-1}$ in most samples), failing in fulfilling this last restriction regarding rubber components in repetitive contact with the human skin (maximum individual PAH concentration 1 mg kg^{-1}).

Individual results for plasticizers, antioxidants and vulcanization agents are shown in Table S4. An adipate, DEHA, and three phthalates DEHP, DIBP and DBP were the plasticizers showing the highest concentrations in both types of pitches, being up to one order of magnitude higher in the indoor materials, with DEHP even reaching hundreds of $\mu\text{g g}^{-1}$ (Table S4). The above-mentioned phthalates are deemed to be substances of very high concern (SVHC) by ECHA (Regulation, 2020/171), considering them toxic for reproduction and endocrine disruptors.

Attending to vulcanization agents, outdoor and indoor pitches contain BTZ and MBTZ in average concentrations of 5.6 and $51 \mu\text{g g}^{-1}$, and 13 and $71 \mu\text{g g}^{-1}$, respectively. It is important to emphasize that ECHA considers MBTZ as a SVHC (ECHA Europe).

3.2. Runoff water analysis

3.2.1. Samples collected on the football pitches

Meteorological conditions can affect the diffusion of the compounds present in crumb rubber into the environment. Recent studies have demonstrated the effect of rainwater and snowmelt on the mobility of pollutants in urban spaces (Muller et al., 2020). In addition, several studies reported that the leaching of chemicals present in recycled rubber is amplified by the irrigation of these recreational surfaces. Therefore, in this study runoff water from eight different synthetic turf football pitches (samples FP11, FP13, FP16, FP17, FP18, FP21, FP28 and FP30) was collected on rainy days and analyzed by SPME-GC-MS/MS (experimental procedure was described in Section 2.4). The results are summarized in Table 1 (see individual concentrations in Table 3). Fig. 3a and b shows the accumulative graph for PAH concentrations ($\mu\text{g L}^{-1}$) per sample, as well as their individual concentrations, respectively. Regarding PAHs, 9 out of the 16 target were detected in the collected water samples, reaching total concentrations of $1.5 \mu\text{g L}^{-1}$. Three of them, PHEN, FLA and PYR were found in all samples, PYR reaching $0.90 \mu\text{g L}^{-1}$. The other PAHs were found in 7 (NAP, ACY), 6 (CHY), 4 (ANC) and 3 (FLU) runoff water samples, with average concentrations between 0.02 and $0.04 \mu\text{g L}^{-1}$. All these PAHs are included in the EPA priority pollutant lists (EPA). In addition, one of the PAHs found in the real water samples, CHY, is included in the ECHA group of carcinogenic PAHs, and NAP and ANC are in the list of priority

Fig. 1. PAH concentration ($\mu\text{g g}^{-1}$) profiles of the a) outdoor and b) indoor football pitches.

Fig. 2. PAH concentrations in the indoor football pitches.

Table 3

Concentration ($\mu\text{g L}^{-1}$) of the target compounds in the runoff water samples collected over several football pitches.

Compounds	W11	W13	W16	W17	W18	W21	W28	W30
PAHs ($\mu\text{g L}^{-1}$)								
NAP	0.098		0.072	0.111	0.013	0.037	0.007	0.018
ACY	0.044	0.021	0.006	0.005		0.018	0.024	0.017
ACE	0.023							0.010
FLU	0.027						0.017	0.05
PHEN	0.13	0.009	0.010	0.007	0.007	0.050	0.123	0.049
ANC	0.028					0.009	0.017	0.013
FLA	0.25	0.070	0.040	0.028	0.028	0.097	0.152	0.10
PYR	0.9	0.209	0.220	0.094	0.053	0.258	0.392	0.4
CHY	0.04	0.024		0.043	0.036	0.078		0.018
Total PAHs	1.55	0.33	0.35	0.29	0.10	0.55	0.73	0.68
Plasticizers ($\mu\text{g L}^{-1}$)								
DMP		1.445	0.091		0.034	0.234	0.125	1.0
DEP	0.55	0.859		0.485	0.524	0.331	1.460	0.09
DIBP	0.360	0.159	0.389	0.810	1.183	0.147	0.795	0.12
DBP	0.17	0.052	0.085	0.432	0.611	0.076	0.253	0.04
BBP	0.044	0.027	0.010	0.022	0.022		0.058	0.02
DEHA				0.01				
DEHP		0.016		0.018	0.033	0.058	0.016	
Antioxidants and vulcanization agents ($\mu\text{g L}^{-1}$)								
BHT	0.74	0.043	0.021	0.002	0.001	0.067	0.123	0.39
BTZ	1.98	0.703	0.808	0.842	1.117	4.947	9.401	4.8
4 TBP	3.98	0.274	0.204	0.116	0.118	0.416	0.786	3.7

Fig. 3. a) PAH concentration ($\mu\text{g g}^{-1}$) profiles in the runoff water samples (W) and b) Individual PAH concentrations in the runoff water samples (W).

substances in the field of water policy (Regulation, 2008/105/EC).

Regarding plasticizers, two of them, DIBP and DBP, were detected in the eight analyzed water samples at concentrations higher than $0.6 \mu\text{g L}^{-1}$, whereas DEP and DMP were found in 7 and 6 samples, respectively, reaching concentrations higher than $1.4 \mu\text{g L}^{-1}$. Other two phthalates (BBP, DEHP) and the adipate DEHA were detected at concentrations up to $0.2 \mu\text{g L}^{-1}$ in 7, 5 and 1 samples, respectively, whereas the antioxidant BHT, and the vulcanization agents BTZ and 4 TBP were detected in all samples at concentration up to $9.4 \mu\text{g L}^{-1}$. It is important to note that phthalates are considered as endocrine disruptors, and specifically DEHP is catalogued as a priority pollutant in water (Regulation, 2008/105/

EC, Diamanti-Kandarakis et al., 2009).

In view of the results shown above, it is clear that a relation exists between the water pollution and the chemical compositions of the crumb rubber football pitches. These results demonstrate the transfer of many of the target compounds, most of them considered as priority pollutants, into the runoff water, that can easily reach surface waters or ground water, representing a potential risk for the aquatic environment.

3.2.2. Simulated runoff water

To evaluate the transfer of the target compounds from the crumb rubber pitches to the water in contact with the rubber,

Table 4

Individual concentration ($\mu\text{g L}^{-1}$) of the target PAHs in the simulated runoff water on consecutive days.

Football pitches (FP)	Irrigation ($\mu\text{g L}^{-1}$)	Rainwater ($\mu\text{g L}^{-1}$)				
	Day 1	Day 1	Day 2	Day 3	Day 4	Day 7
NAP						
FP10		0.029	0.024	0.049	0.059	0.074
FP11	0.032	0.039	0.046	0.054	0.061	0.109
FP13	0.031	0.029	0.034	0.031	0.048	0.060
FP30	0.050	0.031				0.035
ACY						
FP10	0.023	0.029	0.024	0.027	0.027	0.027
FP11	0.019	0.033	0.029	0.032	0.03	0.031
FP13	0.061	0.089	0.088	0.094	0.087	0.072
FP30	0.049	0.063	0.078	0.097	0.084	0.061
ACE						
FP10	0.007	0.009	0.008	0.009	0.008	0.008
FP11	0.007	0.009	0.008	0.008	0.008	0.008
FP13	0.012	0.026	0.024	0.029	0.021	0.018
FP30	0.015	0.011	0.015	0.02	0.014	0.011
FLU						
FP10	0.009	0.016	0.013	0.015	0.015	0.012
FP11	0.012	0.030	0.015	0.016	0.016	0.013
FP13	0.029	0.085	0.081	0.084	0.059	0.046
FP30	0.031	0.032	0.055	0.07	0.044	0.037
PHEN						
FP10	0.048	0.095	0.081	0.095	0.063	0.077
FP11	0.059	0.081	0.084	0.117	0.077	0.068
FP13	0.240	0.523	0.459	0.512	0.345	0.261
FP30	0.248	0.151	0.331	0.484	0.297	0.203
ANC						
FP10	0.012	0.013	0.011	0.014	0.008	0.006
FP11	0.009	0.010	0.012	0.012	0.009	0.006
FP13	0.039	0.100	0.089	0.098	0.065	0.039
FP30	0.038	0.022	0.052	0.076	0.045	0.028
FLA						
FP10	0.060	0.129	0.118	0.147	0.079	0.043
FP11	0.052	0.085	0.102	0.127	0.106	0.069
FP13	0.562	0.524	0.457	0.462	0.363	0.259
FP30	0.410	0.195	0.43	0.54	0.387	0.299
PYR						
FP10	0.201	0.411	0.382	0.478	0.240	0.092
FP11	0.228	0.268	0.328	0.409	0.332	0.158
FP13	1.290	1.690	1.490	1.492	1.079	0.660
FP30	1.286	0.643	1.409	1.709	1.145	0.763
B[a]A						
FP10				0.009	0.004	
FP11				0.007	0.006	
FP13		0.038	0.036	0.034	0.029	0.021
FP30		0.012	0.014	0.015	0.014	0.009
CHY						
FP10		0.040	0.037	0.045	0.023	0.006
FP11		0.024	0.028	0.036	0.028	0.014
FP13		0.168	0.169	0.157	0.126	0.086
FP30		0.037	0.072	0.076	0.056	0.046
B[b]F						
FP10		0.006	0.003	0.005	0.002	
FP11			0.004	0.005	0.003	
FP13		0.016	0.013	0.011	0.006	0.006
FP30			0.006	0.006	0.005	0.005

Table 4 (continued)

Football pitches (FP)	Irrigation ($\mu\text{g L}^{-1}$)	Rainwater ($\mu\text{g L}^{-1}$)				
	Day 1	Day 1	Day 2	Day 3	Day 4	Day 7
B[e]P						
FP10		0.018	0.015	0.018	0.009	
FP11		0.009	0.014	0.019	0.013	0.006
FP13		0.041	0.039	0.032	0.025	0.024
FP30		0.013	0.023	0.016	0.018	0.015
B[a]P						
FP10				0.006		
FP11				0.019	0.013	0.009
FP13		0.017		0.009	0.013	0.007
FP30						

simulated irrigation and rain runoff water were prepared as described in **Section 2.2**, and analyzed by SPME-GC-MS/MS. Four crumb rubber samples from outdoor pitches, FP10, FP11, FP13 and FP30, were selected for this study. A 3-g sample was weighted in a vial, and 13 mL of irrigation and/or rainwater were added. After being in contact with the water for 24 h, the water was removed, and a new water aliquot was added to the vial. The same process was repeated several times for a week. All the water aliquots were analyzed to assess the amount of leaching of chemicals from the rubber to the water.

Results for the irrigation and rainwater are summarized in **Table 1** and quantification of individual PAHs is shown in **Table 4**. As can be seen, 13 PAHs were detected in the simulated runoff water samples, reaching total PAH concentrations of $3.3 \mu\text{g L}^{-1}$. Seven of them, ACY, ACE, FLU, PHEN, ANC, FLA, and PYR were detected in all analyzed samples, with PYR as the most abundant compound, with concentrations ranging from 0.2 to $1.7 \mu\text{g L}^{-1}$. The PAH concentrations observed in the simulated runoff water for a week is displayed in **Fig. 4** for each individual compound and sample, and summarized in **Table 4**. It is worth noting that each 24 h, fresh rainwater was added to the crumb rubber. As can be seen in **Fig. 4**, most of the 13 compounds were found in the water samples collected at the different days for all the samples. The average concentrations of the most volatile PAHs, ACY, ACE and FLU, was between 0.01 and $0.05 \mu\text{g L}^{-1}$, comparable to those found in the collected real water samples. The concentrations of the heaviest PAHs were higher than those obtained for the most volatiles, ranging between 0.02 and $1.7 \mu\text{g L}^{-1}$, including B[b]F and B[a]P, both considered as priority pollutants in water (Regulation, 2008/105/EC). The similarity between the concentration profiles of the lab leachates and the real run-off water samples demonstrates that the source of the chemical pollution comes from the crumb rubber pitches.

These results revealed that crumb rubber is a continuous source of emission of PAHs into the runoff water. The final fate of the runoff water can be surface waters, marine waters (for football pitches located close to rivers, lakes or the sea), or groundwater through leachate infiltration water. Released PAHs can also be transported to wastewater treatment plants through wastewaters (for some football pitches located in urban areas), where they are not completely removed, being then reintroduced into the aquatic environment.

Regarding the other target compounds, seven phthalates (DMP, DEP, DIBP, DBP, BBP, DEHP and DnOP), two adipates (DMA and DEHA) and BPA were detected in the simulated runoff water at concentrations reaching $2.4 \mu\text{g L}^{-1}$. The results are in consonance with those obtained in the real water samples collected from the eight football pitches. In addition, the antioxidant BHT and the

Fig. 4. Daily PAH concentration monitoring in the simulated runoff water samples.

vulcanizing agents BTZ and 4 TBP were found in all analyzed samples, highlighting the presence of BTZ in concentrations greater than 10 µg L⁻¹.

4. Conclusions

The presence of 40 chemicals of environmental concern, such as PAHs, plasticizers, antioxidants, and vulcanization agents was

evaluated in crumb rubber employed as infill in 50 outdoor and indoor synthetic turf football pitches in Portugal. Runoff water samples collected from several of the studied sport facilities were also analyzed. The continuous leaching of these chemicals from the crumb rubber to the runoff water was simulated at lab-scale, as well. The results showed the presence of 30 of the 40 target compounds in the crumb rubber, including 14 of the 16 EPA PAHs, which reached total concentrations of 57 µg g⁻¹. Many of the PAHs

reach concentrations above the limit of $1 \mu\text{g g}^{-1}$ that should fulfill plastic and rubber components that enter in repetitive contact with human skin, which could pose a health risk. In addition, plasticizers and other substances such as MBTZ that cause human toxicity and are included in the ECHA SVHCs list, were found in the samples.

In the runoff water samples, 13 PAHs were detected reaching concentrations of $3.3 \mu\text{g L}^{-1}$, as well as other hazardous compounds such as various phthalates considered as endocrine disruptors. The results demonstrated a continuous leaching of chemicals from the crumb rubber to surface water or other nearby water bodies, which represents a potential risk for the aquatic environment. In this context, there is a need to perform additional studies to gather more information, to evaluate how can affect aquatic pollution.

It is worth underlining the scarce or no information available about the materials used in these sport facilities. It would be then valuable to ask suppliers to provide more information about the crumb rubber characteristics, which would help to draw conclusions. Definitely, it is essential to have comprehensive information and data on all these aspects for the proper assessment of the not negligible risk posed by these sports field infill materials, both to human health and to the aquatic environment.

Author contribution

Maria Celeiro: Formal analysis, Investigation, Validation, Data discussion, Writing, review & editing, Visualization. Daniel Armada: Formal analysis, Investigation, Data Formal analysis, Writing - review. Nuno Ratola: Sample acquisition, Data discussion, Writing & review. Thierry Dagnac: Conceptualization, Writing - review & editing. Jacob de Boer: Conceptualization, Writing - review & editing. Maria Llompart: Conceptualization, Resources, Data discussion, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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.

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Appendix A. Supplementary data

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