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Global evaluation of the chemical hazard of recycled tire crumb rubber employed on worldwide synthetic turf football pitches

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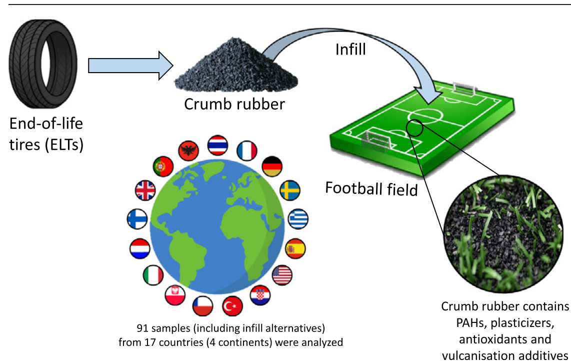
HIGHLIGHTS

- 91 infill football field samples from 17 countries on 4 continents were analyzed.
- Hazardous compounds (PAHs, plasticizers and vulcanizers) were found in all samples.
- Some samples exceeded the recently established 8 ECHA PAH limit (20 μg g^{-1}).
- Cork appears to be a good alternative in line with circular economy.
- Plastic and crumb rubber infills are microplastics considered emerging contaminants.

GRAPHICAL ABSTRACT



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ABSTRACT

Social and environmental concern about the use of crumb rubber from end-of-life car tires in the construction of different sport and recreational facilities is increasing due to the presence of hazardous compounds. The aim of this research was the assessment of 42 organic chemicals, including polycyclic aromatic hydrocarbons (PAHs), phthalates, adipates, antioxidants and vulcanisation agents in a large number of infill samples (91) from synthetic turf football pitches of diverse characteristics and geographical origin. Samples were taken worldwide, in 17 countries on 4 continents, to show the global dimension of this problem. Ultrasound assisted extraction was employed to extract the target compounds, followed by gas chromatography coupled to tandem-mass spectrometry (UAE-GC–MS/MS). Seventy-eight crumb rubber samples as well as thirteen samples of alternatives materials, such as cork granulates, thermoplastic elastomers and coconut fibre, were analyzed. The results highlight the presence of all target PAH in most rubber samples at concentrations up to μg g^{-1}, including the eight ECHA (European Chemicals Agency) PAHs considered as carcinogenic, and anthracene (ANC), pyrene (PYR) and benzo[*ghi*]perylene (B[*ghi*]P), catalogued as substances of very high concern (SVHC). Endocrine disruptors such as some plasticizers (mainly phthalates), and other compounds like benzothiazole (BTZ) and 2-mercaptobenzothiazole (MBTZ) were found reaching the mg g^{-1} level. This confirms the presence of the hazardous substances in the recycled crumb rubber samples collected all around the world. Three crumb rubber samples exceeded the limit of 20 μg g^{-1} for the sum of the eight ECHA PAHs. Regarding the chemical composition of other infill alternatives, cork appears to be adequate, while the thermoplastic elastomers contained

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high levels of some plasticizers. In addition, the plastic infill as well as the crumb rubber both are microplastics. Microplastics are considered contaminants of emerging concern since they do not biodegrade and remain in the environment for a long time.

1. Introduction

Due to the increasing number of discarded tires every year, the management of tire waste is a problem in most developed societies. This product has a high environmental impact since it is not biodegradable. The problematic associated to landfills of end-of-life tires (ELTs) induced governments and institutions to look for alternatives for their re-use. Until a few years ago, incineration processes were the most common solution, employed to obtain energy from ELTs with the consequent release and spreading of harmful substances present in tire rubber into the atmosphere (Watterson, 2017). Recent studies have in depth explored pyrolysis as an alternative for using the heat capacity of ELTs, a process strongly influenced by temperature (Nisar et al., 2018; Nisar et al., 2020). Alternative solutions were needed, and one of the most useful and attractive applications of ELTs seemed their conversion into crumb rubber (Formela, 2021), to be employed as infill in synthetic turf football pitches, among other uses (Celeiro et al., 2021a).

However, recycled tire rubber employed as infill in synthetic turf football fields is on the spotlight for the presence of hazardous substances in its composition (Wik and Dave, 2009, Gomes et al., 2021). Several studies demonstrated the presence of heavy metals (Cd, Pb, Cr, Ni, Cu, Zn, Fe, etc.) in crumb rubber at concentration up to thousands of μg g^{-1} (Bocca et al., 2009; Menichini et al., 2011; Marsili et al., 2015). Organic compounds such as polycyclic aromatic hydrocarbons (PAHs), plasticizers, antioxidants, vulcanisation additives, benzothiazoles, chlorinated paraffins, polychlorinated biphenyls (PCBs) or alkylphenols, among others, were detected in this infill material (Llompart et al., 2013; Brandsma et al., 2019; Schneider et al., 2020a; Skoczyńska et al., 2021), potentially posing a problem for human and environmental health.

For some years now, the possible release of some of these substances into the environment and the effects on human health have been cause of concern and several studies assessing the risk of using these surfaces have been carried out (Oomen and De Groot, 2017, Peterson et al., 2018, Pronk et al., 2020). Synthetic football pitches are often used in outdoor environments and are consequently exposed to a multitude of weather conditions. Recent studies demonstrated the diffusion of hazardous compounds present in crumb rubber into the air (Celeiro et al., 2014; Schneider et al., 2020b; Armada et al., 2021), as well as to water leachates (Rhodes et al., 2012; Celeiro et al., 2018; Halsband et al., 2020; Celeiro et al., 2021b). Bioaccessibility studies (dermal, ingestion and inhalation) carried out with crumb rubber reported that heavy metals and several compounds such as PAHs or semivolatile organic compounds (SVOCs) were bioaccesible in the gastrointestinal fluids (Zhang et al., 2008; Pavilonis et al., 2014). In addition, it was recently found that the cancer risk for children is up to 10 times higher if exposed to recycled rubber surfaced playgrounds in comparison with classical uncovered surfaces (Tarafdar et al., 2020).

Taking this evidence into account, in December of 2020 the European Union approved a restriction of 20 μg g^{-1} in granules or mulches used as infill material in synthetic turf pitches or in loose form on playgrounds or sport applications for eight PAHs considered as carcinogenic (benzo[*a*]anthracene (B[*a*]A), chrysene (CHY), benzo[*b*]fluoranthene (B[*b*]F), benzo[*j*]fluoranthene (B[*j*]F), benzo[*k*]fluoranthene (B[*k*]F), benzo[*a*]pyrene (B[*a*]P), benzo[*e*]pyrene (B[*e*]P) and dibenzo[*ah*]anthracene (D[*ah*]A)) to protect human health (ECHA, 2019; ECHA, 2021). It is important to note that the maximum level allowed by European Commission for these compounds in plastic and rubber consumer goods and materials with prolonged or short-term repetitive contact with the human skin or the oral cavity is 1 μg g^{-1}. Regarding toys and childcare products this limitation is 0.5 μg g^{-1} (Off. J. Eur. Union, 2013). In addition, the United States Environmental Protection Agency (EPA) had already catalogued sixteen PAHs (naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHN), anthracene (ANC), pyrene (PYR), fluoranthene (FLA), B[*a*]A, CHY, B[*b*]F, B[*k*]F, B[*a*]P, indene (IND), D[*ah*]A and benzo[*ghi*]perylene (B[*ghi*]P)) as priority pollutants in the 1970s (EPA, 2014).

So far, most studies based on the analysis of pollutants in crumb tire rubber are generally focused on specific countries such as Spain, Portugal, the Netherlands, among others, with all samples collected in the same country (Celeiro et al., 2021a; Celeiro et al., 2021b; Skoczyńska et al., 2021). However, it is also important to assess the problem of these surfaces from a global point of view, including a variety of samples from different countries and continents. Until now, to the best of our knowledge, only Schneider et al., 2020a have evaluated crumb rubber employed in synthetic football pitches from several European countries, including migration and monitoring studies, and exposure and risk assessment (Schneider et al., 2020b; Schneider et al., 2020c).

In previous studies accomplished by the authors, a protocol based on ultrasound assisted extraction (UAE) followed by gas chromatography-tandem mass spectrometry (GC–MS/MS) has demonstrated a high effectiveness and sensitivity to isolate and determine trace levels of organic compounds in crumb rubber (Celeiro et al., 2018; Celeiro et al., 2021a), and was again used this time.

The aim of this study is to evaluate the presence of hazardous compounds, including 18 PAHs, 19 plasticisers (phthalates, adipates and bisphenol A), two antioxidants and three vulcanisation agents, in 78 crumb rubber samples from synthetic turf football pitches with different characteristics (outdoor/indoor, new/old, public/private access, etc.) and 13 samples from alternative materials such as cork crumb, coconut fibre and thermoplastic elastomers for comparison. To our knowledge, this is the first study including such a high number of samples (91) collected from football pitches from a large number of different countries such as, for example, Chile, Poland or Thailand, and others. Statistical tools were used to attempt to relate the geographical origin of the recycled crumb rubber based on its chemical profile.

2. Experimental

2.1. Reagents and materials

The 42 target compounds studied, their CAS numbers, retention times and MS/MS transitions are summarized in Table S1. Ethyl acetate (EtAc, 99.5%) was provided by Sigma-Aldrich (Steinheim, Germany), methanol (MeOH, 99.9%) by Scharlab (Barcelona, Spain), and acetone (99.9%) by Fluka Analytical (Steinheim, Germany).

A 16 EPA PAHs solution (2000 μg mL^{-1}) was provided by Supelco (Bellefonte, USA), B[*j*]F (2000 μg mL^{-1}) and B[*e*]P (100 μg mL−1) solutions prepared in dichloromethane were provided by Sigma-Aldrich. For plasticizers, antioxidants and vulcanisation additives, individual stock solutions (10.000–25.000 μg mL^{-1}) were prepared in methanol. Purity of the 42 target compounds ranged between 95 and 99%. Further mixtures were prepared in ethyl acetate (calibration studies). All solutions were stored in amber glass vials at −20 °C. Since one of the studied families were plasticizers, plastic material was replaced by metallic and glass material to prevent possible contamination during the experimental procedure and overestimation in the results. All material was also baked at 230 °C before use.

2.2. Sampling procedure

A total of 91 samples, 78 crumb rubber samples (71 outdoor and 7 indoor) and 13 alternative materials, were directly collected from football pitches at different locations in 17 countries around the world (Albania, Chile, Croatia, Finland, France, Germany, Greece, Italy, Netherlands, Poland, Portugal, Spain, Sweden, Thailand, Turkey, United Kingdom and United States). The alternative materials included plastic polymer materials (7 samples), cork crumb (5 samples), and coconut fibre (1 sample). Details about the collected and analyzed real samples are given in Table S2. Between 2 and 100 g of sample were collected from the studied surfaces, transferred to a glass container, sealed with an aluminium cap, stored at room temperature, and protected from light until analysis.

2.3. UAE procedure

The experimental UAE procedure was previously optimized (Celeiro et al., 2018). Briefly, 200 mg of the corresponding sample were placed in a 4 mL glass vial, and 2 mL of EtAc were added. Then, the vial was sealed with an aluminium cap furnished with PTFE-faced septum, and it was immersed into an ultrasound bath (*P. Selecta*, Barcelona, Spain) for 20 min, at 50 kHz 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 EtAc prior to injection in the chromatographic system.

2.4. GC–MS/MS analysis

The GC–MS/MS analysis were performed on 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). The chromatographic separation was performed employing a Zebron ZB-Semivolatiles (30 m × 0.25 mm i.d. × 0.25 μm film thickness) column provided by Phenomenex (Torrance, CA, USA). Helium (purity 99.999%) was employed as carrier gas at a constant flow of 1.0 mL min^{-1}. The GC oven temperature was programmed from 60 °C (held 2 min) to 210 °C at 15 °C min^{-1} and to 290 °C at 5 °C min^{-1} (held 8 min), with a total run time of 36 min. Pulsed splitless mode injection (200 kPa, held 1.2 min) was employed, with the injector temperature at 270 °C and 1 μL of injection volume. The mass spectrometer detector (MSD) was operated in electron ionization (EI) positive mode (+70 eV) and the temperatures of the transfer line and the ion source were 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 (Thermo Fisher Scientific Inc., San Jose, CA, USA), and Trace FinderTM 3.2 (Thermo Fisher Scientific Inc., San Jose, CA, USA) software packages.

2.5. UAE-GC–MS/MS performance

The UAE-GC–MS/MS methodology employed was previously optimized (Celeiro et al., 2018) and its accuracy demonstrated in crumb rubber from different surfaces, including synthetic football fields (Celeiro et al., 2021a). The analytical quality parameters are shown in Table S3. The calibration curves were built employing standard solutions including the 42 studied compounds prepared in EtAc and covering a concentration range from 0.1 to 1000 mg L^{-1} for most compounds, 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 three replicates per level. For all compounds, the method showed good linearity with a direct proportional relationship between compound concentration and chromatographic response, and R^2 values higher than 0.9900. The method instrumental precision was assessed for intra-day ($n = 3$) and inter-day ($n = 6$) assays at three concentration levels (1, 10 and 100 μg L^{-1}) obtaining relative standard deviation values (RSD) lower than 8.7% and 16% for intra-day and inter-day, respectively. To assess the precision for MBTZ and multiple phthalates DINP and DIDP (a complex mixture of isomers), standard solutions of 500 μg L^{-1} were employed, obtaining satisfactory RSD values around 9.5%. The instrumental detection and quantification limits (IDLs and IQLs, respectively) were calculated as the compound concentration giving a signal-to-noise ratio of three (S/N = 3) for IDLs and ten (S/*N* = 10) for IQLs, employing standards containing low concentration of the target compounds prepared in EtAc. In most cases, they were in the low μg L^{-1} range.

2.6. Statistical analysis

Statistical analysis of the results was performed with the Statgraphics Centurion XVIII (Manugistics, Rockville, MD, USA) software package.

3. Results and discussion

3.1. Crumb rubber analysis and applicable legislation

One of the main objectives of the present work was to reveal if the problematic of crumb rubber containing several toxic substances would only be found in a few countries or, in contrast, would be observed globally. Crumb rubber samples from 78 synthetic turf football pitches of different characteristics from 17 countries of four continents (North and South America, Europe, Asia and Africa) were analyzed. The results were compared with other infill materials such as cork granulates, coconut fibre and different types of thermoplastic elastomers (plastic) also collected from 13 synthetic turf football fields. The total number of football fields including in this project was 91. A detail description of the samples is included in Table S2 and the concentrations of the individual target compounds (42 substances) in each sample are depicted in Table S4.

3.1.1. Polycyclic aromatic hydrocarbons

The concentration range, mean and median of the target compounds in the 78 crumb rubber samples are given in Table 1. Table 2 shows the individual PAHs, sum of 8 ECHA, sum of 16 EPA and sum of total PAH concentrations per country. As can be seen, at least 12 PAHs were detected in all crumb rubber samples. PYR and FLA were found in all samples at the highest concentrations up to 34 μg g^{-1} (SE 2) and 46 μg g^{-1} (CL 8), respectively (see Table S4). It is very important to note that FLA is considered as a very toxic substance to aquatic life with long lasting effects and harmful by ingestion, as well as persistent and bioaccumulative (ECHA FLA, 2021). B[*a*]P, considered the most carcinogenic PAH, was detected at concentrations up to 5 μg g^{-1} (SE 2) in EU samples and 15 μg g^{-1} (CL 8) in non-EU samples. Volatile PAH such NAP, ACY and ACE, were detected at concentrations up to 0.11, 0.52 and 0.97 μg g^{-1}, respectively. These lower concentrations for most volatile PAHs could be attributed to their volatilization from the pitch to the surrounding atmosphere. Other PAHs of high concern such as PHN and CHY were found at concentrations up to 42 μg g^{-1} (SE 2), and 29 μg g^{-1} (CL 8), respectively. The results for PAHs concentrations were in concordance with those obtained by Celeiro et al. (2021b) in which crumb rubber from Portuguese outdoor synthetic turf football pitches were analyzed. In addition, the concentrations detected for several PAHs were in agreement with Menichini et al. (2011), Schneider et al. (2020a) and Skoczyńska et al. (2021) findings.

In order to compare the country distribution, the individual PAH profiles are shown in Fig. 1 and reflect similar trends in most cases. Results were in consonance with individual PAH data, since PYR was the most abundant PAH in all countries, followed by FLA. It should be noted that PHN, considered toxic to aquatic life with long lasting effects and harmful if swallowed (ECHA PHN, 2021), was the most abundant PAH after PYR in samples from Albania, Poland and Sweden, reaching individual concentrations up to 11 μg g^{-1}. Likewise, carcinogenic PAHs CHY and B[*e*]P were found in high concentrations (up to 6 μg g^{-1}), in Chile, France, United Kingdom and Albania samples.

As regards the total sum of PAHs, sample CL 8 from Chile reached concentrations up to 230 μg g^{-1}, followed by samples SE 2 (Sweden) and PL 3 (Poland) (135 and 87 μg g^{-1}, respectively). All these samples are from newly constructed fields, between 0.5 and 2 years (see Table S2), and probably their rubber infill was unused and not subject to too much weathering.

Table 1
Concentration (μg g^{-1}; range, mean, median) of the target compounds in 78 crumb rubber samples. Sum of 8 ECHA PAH, 16 EPA PAH, Total PAH, and the 4 ECHA plasticizers are included.

PAHs					Plasticizers					Antioxidants and vulcanisation additives				
Compound	N[a]	Range	Mean	Median	Compound	N[a]	Range	Mean	Median	Compound	N[a]	Range	Mean	Median
NAP	74	0.008–0.50	0.048	0.035	DMA	1	0.011	0.011	0.011	BHA	3	0.05–0.1	0.08	0.08
ACY	57	0.01–0.52	0.085	0.036	DMP	24	0.024–0.21	0.081	0.061	BHT	73	0.037–85	3.7	0.82
ACE	48	0.007–0.97	0.071	0.020	DEP	19	0.050–12	1.4	0.42	BTZ	67	0.030–36	7.1	5.5
FLU	75	0.004–4.0	0.14	0.025	DiBP	60	0.28–90	4.1	1.7	4TBP	59	0.030–6.4	0.63	0.13
PHN	78	0.029–42	1.9	0.35	DBP	61	0.13–56	6.1	1.5	2MBTZ	8	40–146	86	82
ANC	73	0.005–15	0.36	0.037	BBP	61	0.014–6.3	0.51	0.19					
FLA	78	0.05–46	3.4	2.1	DEHA	59	0.076–39	8.5	3.7					
PYR	78	0.12–34	8.5	5.0	DCHP	62	0.024–1.1	0.24	0.16					
B[*a*]A	73	0.017–17	0.71	0.29	DEHP	78	0.90–9470	253	28					
CHY	78	0.021–29	1.8	1.2	DnOP	11	1.4–142	21	3.3					
B[*b*]F + B[*j*]F	76	0.024–17	0.94	0.52	DIDP	1	955	955	955					
B[*k*]F	73	0.022–8.0	0.29	0.12	DINP	4	36–10,130	3607	2132					
B[*e*]P	75	0.18–18	2.2	1.8	Σ4 ECHA	78	1.1–9527	262	36					
B[*a*]P	77	0.025–15	0.90	0.51										
IND	71	0.037–12	0.61	0.34										
D[*ah*]A	17	0.089–3.0	0.52	0.28										
B[*ghi*]P	78	0.20–12	2.0	1.7										
8 ECHA	78	0.25–107	6.8	4.4										
16 EPA	78	0.63–212	22	15										
Total PAHs	78	0.81–230	24	17										

[a] N: Number of samples containing the compound.

Several articles reported a reduction in PAH content over time (Marsili et al., 2015; Diekmann et al., 2019). However, the crumb rubber is in most cases refilled, periodically, due to wear and tear caused by intended use, meteorological conditions and leaching. For this reason, it is difficult to associate the year that the pitch was built with the actual age of the crumb, particularly in older facilities. This makes the correlation of concentration of chemicals and age of the crumb a challenging task. This correlation was performed for PAHs and all other studied substances detected in the crumb rubber samples.

Focusing on the potential carcinogenic Σ8 ECHA PAHs (see Table 2), the average highest concentration was found in two EU countries: Finland (6.3 μg g^{-1}) and Sweden (11.8 μg g^{-1}). This can represent an increased environmental danger since it was demonstrated the spread of these compounds, among others (plasticizers, metals, etc.), in runoff water leachates (Celeiro et al., 2021b) and both Nordic countries are characterized by heavy rainfall and snowmelt.

Fig. 2a and b shows the box and whiskers plots for Σ8 ECHA and Σ16 EPA PAHs, respectively, in EU and non-EU countries, including the average, median and concentration range for PAH in the analyzed samples per country. In EU countries, only one Swedish sample (SE 2) exceed the proposed EU limitation of 20 μg g^{-1} in granules or mulches employed as infill material in synthetic turf pitches or in loose form on playgrounds and sports facilities. This legislation was recently approved by the EU to protect users from potential carcinogenic and reproductive toxicity effects of PAHs (ECHA, 2021). This result was in concordance with the estimation of the National Institute for Public Health and the Environment (RIVM) that 5% of actual crumb rubber used as infill in synthetic turf football fields may not respect the proposal limit (RIVM, 2017; ECHA, 2018). Although, the non-EU countries are not covered by this legislation, two samples from Chile (CL 8 and CL 9) also exceed the mentioned limits. In addition, most crumb rubber samples exceed the individual limit of 1 μg g^{-1} for some of the eight ECHA PAHs in consumer goods and in materials 'with intensive contact' with the human skin or the oral cavity (Off. J. Eur. Union, 2013).

Regarding the sum of the 16 PAH catalogued as emerging priority pollutants by United States EPA (see Fig. 2b), as well as to the sum of the 18 PAH including in this study (see Table S4), 25 and 29 of the 78 crumb rubber samples (one third of the samples) ranged between 20 and 42 μg g^{-1}, respectively. Three samples (CL8, PL3 and SE2) achieved higher concentrations up to 247 μg g^{-1}. It is important to underline the presence in the samples of other PAHs (not included among the 8 ECHA PAHs) as NAP, PHN, ANC, FLA, PYR and B[*ghi*]P, considered persistent, bioaccumulative, toxic and/or SVHC (see as examples (ECHA NAP, 2021; ECHA PYR, 2021) in references).

3.1.2. Plasticizers

Plasticizers were detected in all crumb rubber samples. The concentration range, mean and median of the target compound in all crumb rubber samples are shown in Table 1. Table 3 shows the concentrations of individual plasticizers for each country (for individual concentrations and sum of the four ECHA plasticizers DIBP, DBP, BBP and DEHP per sample, see also Table S4). As can be seen, the plasticizer DEHP was detected in all the 78 crumb rubber samples, BBP and DBP in 61, and DIBP in 60 (see also Table 1). These four chemicals are included in the ECHA SVHC list. All of them are catalogued as toxic for reproduction and are endocrine disruptors (ECHA plasticizers, 2021). DIBP reached concentrations up to 90 μg g^{-1} in CL 8, BBP 6.2 μg g^{-1} in PT 5 and the phthalates DBP and DEHP were found in concentrations up to 56 and 9470 μg g^{-1}, respectively. Besides, other plasticizers, DEHA and DNOP, were detected in concentrations up to 39 μg g^{-1} (CI 2) and 142 μg g^{-1} (IT 2). The presence of multiple phthalate DINP at high-level concentrations of 2400 and 5300 μg g^{-1} in samples TH 1 and IT 2, respectively, is also noteworthy. For most detected target plasticizers, median concentrations were in concordance to the data reported by Celeiro et al. (2021a). DIBP concentrations were similar to those obtained by Schneider et al. (2021a).

The results by country for the sum of the four ECHA-targeted plasticizers (DIBP, DBP, BBP and DEHP) are depicted in Fig. 3. Only one EU sample exceeded the legal EU limit by ECHA: a maximum concentration of 1000 μg g^{-1} in plasticised materials, including rubber among others (childcare articles, adhesives, different polymers, etc.), for each of these individual phthalates or the sum of them (Commission Regulation (EU), 2018, ECHA Annex XVII to REACH, 2021). Sample IT 5 fails to fulfil this regulation since the concentration of DEHP was 1665 μg g^{-1}. As regards to non-EU samples (shown in Fig. 3), two samples (CL 9 and TH 1) surpassed this limit (2669 and 9470 μg g^{-1}, respectively). It is important to note that these four phthalates are toxic for reproduction (B1 category) and the ECHA has notified their risks and consequences (ECHA plasticizers, 2021).

3.1.3. Antioxidants and vulcanisation additives

As can be seen in Table 1, in which the concentration range, mean and median of the compounds in the 78 crumb rubber samples are included, and for each country in Table 3, the three target vulcanisation agents, BTZ, 4TBP and 2MBTZ were detected in 67, 59 and 8 samples, reaching

Table 2
Concentration (μg g^{-1}; range, mean, median) of the target PAHs in the 17 countries. Sum of 8 ECHA PAH, 16 EPA PAH and Total PAH are included.

	Thailand (n[a] = 5)				Netherlands (n[a] = 5)				Italy (n[a] = 7)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
NAP	5	0.03–0.06	0.039	0.036	5	0.02–0.04	0.032	0.032	7	0.032–0.057	0.041	0.037
ACY	1	0.005–0.02	0.02	0.02	5	0.02–0.52	0.15	0.07	7	0.012–0.05	0.028	0.03
ACE	0	–	–	–	5	0.01–0.05	0.019	0.012	4	0.008–0.024	0.016	0.016
FLU	4	0.005–0.006	0.006	0.006	5	0.006–0.12	0.041	0.025	7	0.009–0.028	0.016	0.013
PHN	5	0.04–0.40	0.17	0.139	5	0.14–1.9	0.97	0.94	7	0.058–0.59	0.17	0.07
ANC	5	0.007–0.09	0.033	0.026	5	0.02–0.13	0.071	0.071	7	0.006–0.06	0.021	0.009
FLA	5	0.05–3.0	1.2	1.3	5	1.3–4.2	3.5	3.9	7	0.13–3.2	0.86	0.4
PYR	5	0.12–6.5	3.3	4.5	5	2.9–15	11	13	7	0.33–12	2.5	1
B[*a*]A	5	0.02–0.73	0.22	0.069	5	0.12–0.29	0.21	0.22	5	0.017–0.7	0.22	0.14
CHY	5	0.04–1.0	0.33	0.11	5	0.26–1.0	0.68	0.77	7	0.08–2.5	0.67	0.45
B[*b*]F + B[*j*]F	5	0.06–0.32	0.17	0.16	5	0.17–0.49	0.36	0.39	7	0.075–1.2	0.44	0.26
B[*k*]F	5	0.02–0.11	0.052	0.04	4	0.030–0.097	0.065	0.067	5	0.022–0.24	0.08	0.04
B[*e*]P	5	0.21–0.70	0.45	0.4	5	0.78–1.9	1.3	1.3	7	0.38–1.8	1.2	1.1
B[*a*]P	5	0.10–0.30	0.19	0.19	5	0.35–0.55	0.47	0.5	7	0.081–0.5	0.27	0.31
IND	5	0.06–0.21	0.11	0.1	5	0.24–0.41	0.32	0.31	7	0.07–0.8	0.31	0.24
D[*ah*]A	0	–	–	–	1	0.08–0.12	0.12	0.12	2	0.06–0.24	0.18	0.18
B[*ghi*]P	5	0.49–1.0	0.60	0.5	5	1.4–2.1	1.7	1.6	7	0.38–2.2	1.2	1.3
Σ8 ECHA PAH	5	0.56–4.0	1.4	1.4	5	1.4–6.3	3.1	3.1	7	0.98–10	2.8	2.2
Σ16 EPA PAH	5	1.3–12	6.4	8.6	5	11–24	20	22	7	2.1–20	6.8	5.1
ΣTotal PAH	5	1.6–13	7.0	9.0	5	14–25	21	24	7	2.6–21	8.5	7.1

μg g^{-1}	Chile (n[a] = 11)				Croatia (n[a] = 2)				Finland (n[a] = 10)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
NAP	11	0.018–0.05	0.031	0.031	2	0.010–0.014	0.012	0.012	10	0.033–0.065	0.047	0.045
ACY	11	0.017–0.3	0.069	0.035	2	0.027–0.034	0.031	0.031	7	0.029–0.12	0.055	0.05
ACE	9	0.007–0.11	0.036	0.03	2	0.009–0.016	0.013	0.013	9	0.015–0.13	0.057	0.036
FLU	11	0.007–0.44	0.11	0.057	2	0.023–0.025	0.024	0.024	9	0.014–0.21	0.066	0.05
PHN	11	0.1–19.5	2.7	0.2	2	0.25–0.27	0.26	0.26	10	0.26–4.0	1.6	1.5
ANC	11	0.17–1.7	0.27	0.09	2	0.029–0.037	0.033	0.033	9	0.022–0.32	0.15	0.12
FLA	11	0.36–46	6.5	1.624	2	1.78–2.56	2.2	2.2	10	1.5–7.1	5.3	5.3
PYR	11	1.0–31	8.85	4.6	2	3.6–8.5	6.05	6.05	10	3.5–22	15	15
B[*a*]A	11	0.06–17	2.2	0.28	2	0.33–0.48	0.40	0.40	10	0.37–0.79	0.58	0.59
CHY	11	1.2–29	5.7	2.5	2	1.05–1.45	1.2	1.2	10	1.06–2.41	1.7	1.6
B[*b*]F + B[*j*]F	11	0.22–17	2.5	0.4	2	0.5–1.0	0.75	0.75	10	0.48–1.5	0.84	0.84
B[*k*]F	11	0.04–8.0	1.0	0.09	2	0.13–0.39	0.261	0.261	10	0.09–0.28	0.15	0.13
B[*e*]P	11	1.0–18.0	3.6	1.4	2	1.5–2.2	1.85	1.85	10	1.8–3.3	2.5	2.4
B[*a*]P	11	0.194–15	2.1	0.4	2	0.6–0.8	0.7	0.7	10	0.54–1.1	0.86	0.87
IND	10	0.08–12	1.7	0.20	2	0.25–0.50	0.38	0.38	10	0.39–0.90	0.65	0.7
D[*ah*]A	5	0.08–3	0.88	0.3	0	–	–	–	1	–	0.28	0.28
B[*ghi*]P	11	0.2–12	1.9	0.89	2	1.3–1.70	1.5	1.5	10	1.8–3.6	2.6	2.6
Σ8 ECHA PAH	11	2.9–107	18	5.2	2	5.1–7.4	5.2	5.2	10	6.5–13	6.6	6.6
Σ16 EPA PAH	11	4.5–212	36	14	2	13–17	14	14	10	16–41	30	30
ΣTotal PAH	11	5.8–247	42	19	2	16–19	17	17	10	20–43	33	33

μg g^{-1}	Turkey (n[a] = 2)				France (n[a] = 5)				Poland (n[a] = 3)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
NAP	2	0.022–0.027	0.025	0.025	5	0.021–0.035	0.026	0.024	3	0.030–0.55	0.041	0.040
ACY	0	–	–	–	5	0.010–0.023	0.014	0.013	2	0.36–0.50	0.43	0.43
ACE	2	0.014–0.02	0.017	0.017	0	–	–	–	3	0.008–0.27	0.11	0.029
FLU	2	0.037–0.077	0.057	0.057	5	0.009–0.023	0.014	0.011	3	0.016–1.1	0.38	0.05
PHN	2	0.11–0.43	0.27	0.27	5	0.07–0.72	0.23	0.14	3	0.22–23	7.9	0.54
ANC	2	0.013–0.015	0.014	0.014	5	0.015–0.073	0.028	0.017	3	0.015–3.5	1.2	0.035
FLA	2	0.59–0.76	0.675	0.675	5	0.25–2.9	1.4	1.1	3	2.3–19	7.9	2.6
PYR	2	0.89–3.58	2.235	2.235	5	0.5–10	4.7	3.6	3	4.0–26	12	5.2
B[*a*]A	1	0.22	0.22	0.22	5	0.08–0.30	0.19	0.22	3	0.44–3.1	1.4	0.64
CHY	2	0.08–1.35	0.72	0.72	5	0.24–1.2	0.72	0.531	3	1.0–2.9	1.7	1.1
B[*b*]F + B[*j*]F	2	0.06–1.08	0.57	0.57	5	0.16–0.61	0.41	0.42	3	0.44–0.87	0.70	0.80
B[*k*]F	2	0.09–0.63	0.36	0.36	5	0.06–0.12	0.093	0.1	3	0.16–0.25	0.21	0.22
B[*e*]P	2	0.7–2.4	1.6	1.6	5	0.6–2.6	1.6	1.5	3	1.0–2.2	1.6	1.6
B[*a*]P	2	0.19–0.75	0.47	0.47	5	0.2–0.7	0.4	0.4	3	0.30–1.3	0.77	0.72
IND	0	–	–	–	5	0.14–0.55	0.37	0.33	3	0.11–0.52	0.36	0.45
D[*ah*]A	0	–	–	–	2	0.089–0.18	0.17	0.17	0	–	–	–
B[*ghi*]P	2	0.70–0.93	0.82	0.82	5	0.80–2.9	2.0	1.8	3	0.7–1.7	1.2	1.2
Σ8 ECHA PAH	2	1.7–8.4	3.8	3.8	5	1.6–6.7	3.5	3.0	3	4.3–11	6.4	5.1
Σ16 EPA PAH	2	6.3–9.0	6.3	6.3	5	5.4–18	11	11	3	11–84	36	14
ΣTotal PAH	2	7.0–13	8.5	8.5	5	7.3–20	13	14	3	12–87	38	16

μg g^{-1}	Greece (n[a] = 3)				Sweden (n[a] = 5)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
NAP	3	0.024–0.029	0.027	0.027	5	0.060–0.11	0.079	0.075

(continued on next page)

Table 2 (*continued*)

μg g−1	Greece (n[a] = 3)				Sweden (n[a] = 5)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
ACY	0	–	–	–	5	0.072–0.41	0.17	0.13
ACE	0	–	–	–	5	0.069–0.97	0.33	0.27
FLU	3	0.006–0.007	0.007	0.007	5	0.12–4.0	1.2	0.78
PHN	3	0.077–0.11	0.093	0.092	5	0.63–42	11	4.7
ANC	0	–	–	–	5	0.03–15	3.2	0.55
FLA	3	0.45–0.78	0.567	0.46	5	1.7–9.9	5.7	5.4
PYR	3	0.84–2.4	1.4	0.99	5	3.1–34	17	16
B[*a*]A	3	0.14–0.24	0.17	0.147	5	0.35–4.4	1.3	0.44
CHY	3	0.75–0.91	0.85	0.87	5	1.2–4.3	2.2	1.7
B[*b*]F + B[*j*]F	3	0.44–0.72	0.59	0.61	5	0.67–3.0	1.7	1.5
B[*k*]F	3	0.11–0.18	0.13	0.12	5	0.08–0.5	0.24	0.15
B[*e*]P	3	1.6–2.6	2.1	2.1	5	2.4–5.9	4.0	4.2
B[*a*]P	3	0.34–0.64	0.52	0.57	5	0.92–4.6	2.0	1.2
IND	3	0.36–0.72	0.54	0.53	5	0.53–2.0	1.2	1.0
D[*ah*]A	0	–	–	–	3	0.21–1.4	0.83	0.62
B[*ghi*]P	3	1.4–3.0	2.2	2.3	5	2.3–4.6	3.2	3.0
Σ8 ECHA PAH	3	4.4–6.7	4.4	4.4	5	6.4–23	12	9.7
Σ16 EPA PAH	3	6.0–9.7	7.1	8.0	5	17–129	51	35
ΣTotal PAH	3	8.2–13	9.9	11	5	23–137	57	38

μg g−1	Spain (n[a] = 7)				Canary Islands (n[a] = 4)				Portugal (n[a] = 5)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
NAP	6	0.031–0.5	0.16	0.08	1	0.055	0.055	0.055	5	0.008–0.042	0.030	0.033
ACY	5	0.024–0.49	0.13	0.04	3	0.016–0.039	0.026	0.023	4	0.032–0.054	0.041	0.038
ACE	3	0.013–0.080	0.04	0.01	1	0.012	0.012	0.012	3	0.010–0.017	0.013	0.011
FLU	6	0.019–0.22	0.07	0.05	4	0.004–0.020	0.009	0.006	5	0.011–0.11	0.054	0.046
PHN	7	0.12–3.07	0.96	0.15	4	0.029–0.73	0.25	0.12	5	0.29–2.4	1.3	1.5
ANC	6	0.013–0.33	0.12	0.09	4	0.005–0.97	0.035	0.019	5	0.023–0.035	0.15	0.13
FLA	7	0.5–7.4	2.8	2.4	4	0.071–3.0	1.1	0.71	5	1.0–4.6	3.5	4.0
PYR	7	1.3–24.6	9.1	7.1	4	0.20–11	4.1	2.6	5	4.0–18	13	14
B[*a*]A	6	0.16–0.6	0.34	0.28	2	0.23–0.31	0.27	0.27	5	0.078–0.42	0.26	0.28
CHY	7	0.47–3.6	1.6	1.5	4	0.02–1.4	0.55	0.38	5	0.32–2.1	1.3	1.3
B[*b*]F + B[*j*]F	5	0.17–1.8	0.96	1.2	4	0.024–0.53	0.28	0.27	5	0.26–1.1	0.67	0.70
B[*k*]F	6	0.048–0.73	0.31	0.25	3	0.046–0.12	0.079	0.074	5	0.061–0.22	0.14	0.15
B[*e*]P	4	0.90–3.5	1.9	1.7	4	0.18–2.3	1.4	1.5	5	1.0–4.3	2.6	2.9
B[*a*]P	7	0.29–1.4	0.69	0.48	4	0.025–0.42	0.25	0.27	5	0.35–1.3	0.83	0.88
IND	7	0.15–0.8	0.38	0.27	4	0.037–0.29	0.17	0.18	5	0.14–0.58	0.32	0.34
D[*ah*]A	0	–	–	–	1	0.19	0.19	0.19	2	0.11–0.41	0.36	0.36
B[*ghi*]P	7	1.20–4.6	2.3	1.5	4	0.21–2.6	1.4	1.4	5	1.2–4.8	2.8	3.0
Σ8 ECHA PAH	7	2.1–10.4	4.6	3.3	4	0.25–5.3	2.7	2.6	5	2.1–9.8	5.9	6.2
Σ16 EPA PAH	7	8.2–42.4	19	17	4	0.048–18	8.5	7.8	5	7.7–35	24	28
ΣTotal PAH	7	8.2–42.4	21	20	4	0.048–19	10	10	5	8.9–40	28	32

[a] n: Number of samples collected per country.
[b] N: Number of samples containing the compound.

concentrations of 36, 6.4 and 146 μg g^{-1}, respectively (Table S4). These concentrations were similar to those reported by Celeiro et al. (2018) and (2021a). 4TBP is catalogued as endocrine disruptor and toxic for aquatic life with long lasting effects (ECHA 4TBP, 2021). In addition, the transfer of 4TBP from crumb rubber to runoff water was recently demonstrated (Celeiro et al., 2021b). On the other hand, 2MBTZ is considered very toxic to aquatic life with long lasting effects. It is also a skin sensitizer. Some authors suggested that BTZ may cause serious health risks after a high exposure such as, among others, central nervous depression, pulmonary irritation, and liver and kidney damage (Ginsberg et al., 2011).

Regarding the antioxidants BHA and BHT, both compounds are currently under evaluation as endocrine disruptors and were included in the Community Rolling Action Plan (CoRAP) (ECHA BHA, 2021; ECHA BHT, 2021). BHT was present in 68 crumb rubber samples, at concentrations up to 85 μg g^{-1}, similar concentrations as Celeiro et al. (2018), whereas BHA was only detected in one sample (FR 4) at a much lower concentration (0.05 μg g^{-1}). Both were considered as very harmful to the aquatic ecosystem with long term impacts.

The profiles per country for BHA, BHT, BTZ and 4TBP are depicted in Fig. 4. BHT showed an average level of 21 μg g^{-1} in crumb rubber from Finland, while in the rest of countries the concentrations ranged between 0.07 and 2.8 μg g^{-1} except in the Canary Islands samples, where it was not found. On the other hand, vulcanisation additive BTZ was detected at concentrations up to 18 μg g^{-1} in samples from Sweden, whereas 4TBP oscillated between 0.05 and 1.5 μg g^{-1}. This randomness in the profiles is probably due to the lack of knowledge of the origin of the rubber used as infill in the different countries.

3.1.4. Microplastic consideration

Crumb rubber infill is a microplastic material, which contains substances that can be distributed into the environment (propagate to the air or leaching) with a potential negative ecological risk (Luo et al., 2021; ECHA hot topic 1, 2021). The presence of hazardous chemicals in the crumb rubber around the world have been shown in previous sections (Sections 3.1.1, 3.1.2 and 3.1.3). Most crumb rubber samples studied in this research have been characterized regarding the particle size and the information is included in Table S2. All of them meet the size of microplastics (less than 5 mm in length). Microplastics as such are considered contaminants of emerging concern since they do not biodegrade and remain in the environment for a long time. Microplastics may bioaccumulate in animals, including fish and seafood, and can consequently, be consumed by humans. According to ECHA, around 42,000 t of microplastics end up intentionally in the environment each year because of the use of products containing them. An important source of this microplastic contamination is crumb rubber material employed in artificial turf pitches with emissions up to 16,000 tonnes (ECHA ANNEX XV, 2021; ECHA hot topic 2, 2021).

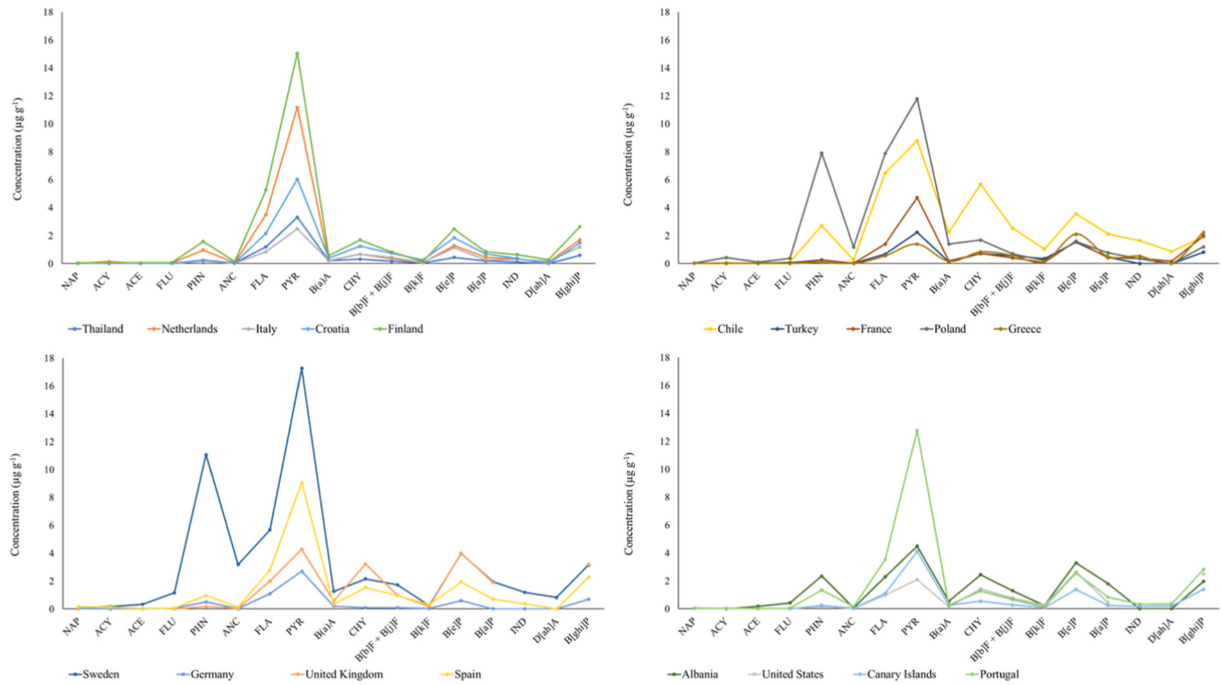


Fig. 1. Mean concentration profiles (μg g^{-1}) per country for individual PAHs.

3.2. *Infill alternatives: cork, coconut fibre and thermoplastic elastomers*

Currently, alternative materials are being used to replace crumb rubber as infill in synthetic turf football fields (Watterson, 2017). In this study, three types of materials, cork, thermoplastic elastomers and coconut fibre, were included. Results are shown in Fig. 5, which illustrates the comparison between crumb rubber (mean values for each country) and the other materials. Individual concentrations for each sample are also included in Table S4.

As can be seen in Fig. 5a (see also Table S4), natural organic backfill materials such as cork (5 samples) and synthetic alternatives as thermoplastic elastomers (7 samples) also contain some PAHs, although at much lower levels (ng g^{-1}) than crumb rubber. The presence of some residual PAHs could be explained as "memory" contamination since most of the pitches where these materials are installed were previously filled with crumb rubber, and some residues may have remained on site. A sample collected in Spain CR/CF (ES 5) is a mixture of 70% of coconut fibre and 30% of crumb rubber, which explained its high concentration compared with the other alternative samples.

On the other hand, see Fig. 5b (and Table S4), it is important to mention that high concentrations of some plasticizers were detected in some thermoplastic elastomers, which could be expected given their plastic-based composition. DBP and DEHA were found in two green thermoplastic elastomers samples at 100 and 1728 μg g^{-1} (IT 3 and FI 8, respectively). Additionally, the phthalates DINP and DIDP were quantified at concentrations of 149 and 20 mg g^{-1}, respectively, in an Italian sample (IT 3). Although

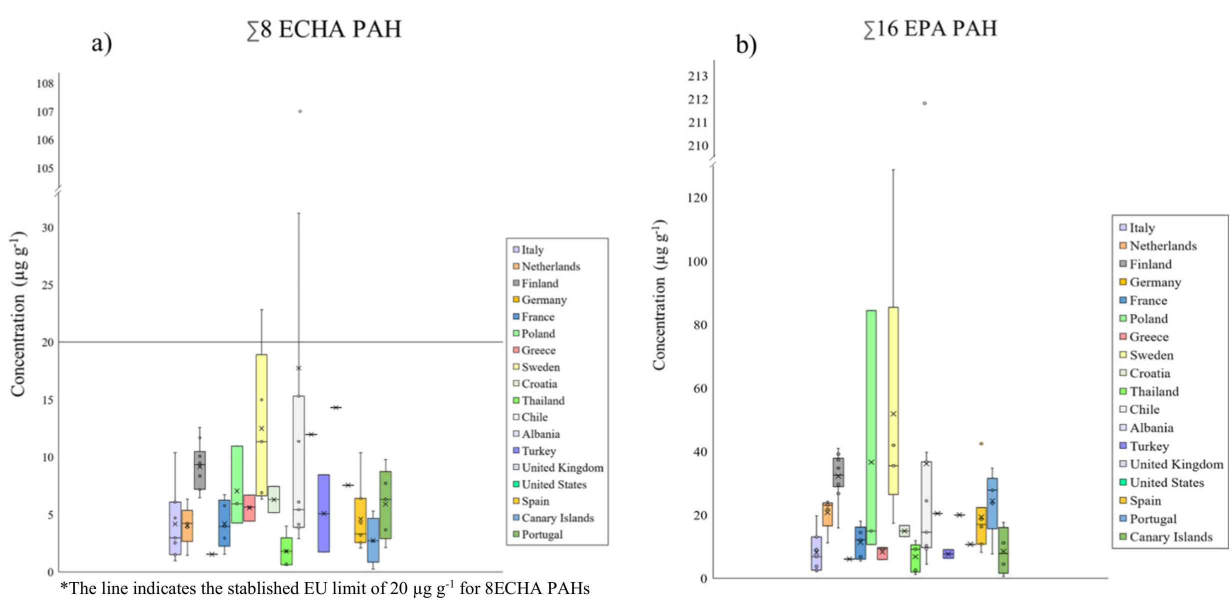


Fig. 2. Box-and-Whisker charts for crumb rubber samples by country for: a) 8 ECHA PAHs and b) 16 EPA PAHs.

Table 3
Concentrations (μg g^{-1};range, mean, median) of target plasticizers, antioxidants and vulcanisation agents in the 17 countries.

μg g^{-1}	Thailand (n[a] = 5)				Netherlands (n[a] = 5)				Italy (n[a] = 7)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
DMA	0	–	–	–	1	–	0.011	0.011	0	–	–	–
DEA	0	–	–	–	0	–	–	–	0	–	–	–
DMP	0	–	–	–	1	–	0.148	0.148	7	0.04–0.1	0.064	0.055
DEP	0	–	–	–	0	–	–	–	7	0.19–0.42	0.39	0.38
DiBP	4	0.49–1.2	1.3	0.9	5	0.5–1.8	1.18	1.2	7	0.6–11	3.2	1.7
DBP	5	0.6–56	14	0.8	5	0.13–0.64	0.374	0.26	7	0.82–46	18.5	9
BBP	2	0.08–0.27	0.18	0.18	5	0.02.0.2	0.087	0.09	6	0.07–0.6	0.24	0.13
DEHA	5	0.14–22	6.964	0.53	5	0.11–10	3.83	0.6	3	0.38–16	5.5	0.64
DCHP	3	0.05–0.68	0.296	0.16	5	0.16–0.24	0.206	0.22	7	0.02–0.2	0.094	0.087
DEHP	5	20–9470	2189.6	494	5	5.3–12	9.7	10.9	7	16–1666	341	40
DnOP	3	2.0–44	16	3.0	0	–	–	–	3	1.9–142	49	3.5
DINP	1	2398	2398	2398	1	8.5	8.5	8.5	1	5295	5295	5295
DIDP	0	–	–	–	0	–	–	–	0	–	–	–
BHA	0	–	–	–	0	–	–	–	0	–	–	–
BHT	5	0.79–1.3	0.94	0.88	5	0.9–9.4	2.8	1.4	7	0.08–0.24	0.16	0.14
BTZ	0	–	–	–	5	1.3–23	7.1	3.6	6	0.03–0.44	0.19	0.12
4TBP	5	0.04–0.13	0.07	0.053	5	0.07–3.4	0.92	0.28	0	–	–	–
2MBTZ	1	146	146	146	2	74–123	98	98	0	–	–	–

μg g^{-1}	Chile (n[a] = 11)				Croatia (n[a] = 2)				Finland (n[a] = 10)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
DMA	0	–	–	–	0	–	–	–	0	–	–	–
DEA	0	–	–	–	0	–	–	–	0	–	–	–
DMP	2	0.07–0.12	0.098	0.098	0	–	–	–	0	–	–	–
DEP	4	0.54–12	4.0	1.7	0	–	–	–	0	–	–	–
DiBP	11	1.3–90	12	2	0	–	–	–	10	0.3–5.5	2.0	1.9
DBP	11	1.2–29	9.0	2.9	0	–	–	–	10	0.2–2.9	1.1	0.93
BBP	11	0.15–0.82	0.34	0.19	1	0.086	0.086	0.086	10	0.12–1.2	0.53	0.41
DEHA	11	0.4–24	4.5	1.3	0	–	–	–	10	0.11–33	6.7	4
DCHP	11	0.05–0.5	0.20	0.14	2	0.13–0.31	0.22	0.22	8	0.08–0.37	0.19	0.17
DEHP	11	26–2669	371	89	2	38–39	39	39	10	11–79	34	29
DnOP	6	0.22–6	6	6	0	–	–	–	2	2–25	14	14
DINP	1	81	81	81	0	–	–	–	0	–	–	–
DIDP	0	–	–	–	0	–	–	–	0	–	–	–
BHA	0	–	–	–	0	–	–	–	0	–	–	–
BHT	11	0.12–0.89	0.37	0.18	2	0.6–0.8	0.715	0.715	10	2.5–85	21	5.6
BTZ	11	1.7–20	7.41	5	2	3–3.7	3.35	3.35	10	4.4–14	7.6	6.4
4TBP	11	0.03–6	0.75	0.15	2	0.05–0.07	0.064	0.064	5	0.2–3.1	1.0	0.6
2MBTZ	1	51	51	51	0	–	–	–	1	40	40	40

μg g^{-1}	Turkey (n[a] = 2)				France (n[a] = 5)				Poland (n[a] = 3)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
DMA	0	–	–	–	0	–	–	–	0	–	–	–
DEA	0	–	–	–	0	–	–	–	0	–	–	–
DMP	0	–	–	–	2	0.08–0.09	0.088	0.088	0	–	–	–
DEP	1	1.8	1.8	1.8	0	–	–	–	0	–	–	–
DiBP	1	0.52	0.52	0.52	2	1.0–2.7	1.9	1.9	2	1.7–3	2.4	2.4
DBP	0	–	–	–	2	2.2–3.2	2.7	2.7	2	1.4–14	7.7	7.7
BBP	0	–	–	–	3	0.12–0.25	0.19	0.2	2	0.13–0.15	0.14	0.14
DEHA	0	–	–	–	3	2.7–14	5.6	2.7	1	7.3	7.3	7.3
DCHP	0	–	–	–	5	0.11–0.61	0.37	0.36	3	0.14–0.3	0.20	0.16
DEHP	2	67–807	437	437	5	6.3–25	16	16	3	15–27	19	16
DnOP	0	–	–	–	0	–	–	–	0	–	–	–
DINP	0	–	–	–	0	–	–	–	0	–	–	–
DIDP	0	–	–	–	0	–	–	–	0	–	–	–
BHA	0	–	–	–	1	0.05	0.05	0.05	0	–	–	–
BHT	2	1.3–1.4	1.4	1.4	5	0.10–0.17	0.13	0.12	3	0.74–0.91	0.82	0.82
BTZ	2	1.4–1.5	1.5	1.5	5	5.5–12	7.2	5.8	3	2.3–7.2	4	2.5
4TBP	0	–	–	–	5	0.03–0.12	0.057	0.044	3	0.03–0.98	0.35	0.04
2MBTZ	0	–	–	–	0	–	–	–	0	–	–	–

μg g^{-1}	Greece (n[a] = 3)				Sweden (n[a] = 5)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
DMA	0	–	–	–	0	–	–	–
DEA	0	–	–	–	0	–	–	–
DMP	0	–	–	–	0	–	–	–
DEP	0	–	–	–	0	–	–	–
DiBP	0	–	–	–	3	2.3–5.5	3.3	3.4
DBP	0	–	–	–	3	1.5–4.4	2.5	1.6
BBP	3	0.09–0.1	0.098	0.10	4	0.4–1.0	0.69	0.7
DEHA	0	–	–	–	4	2.7–38	14	8.3

Table 3 (*continued*)

μg g⁻¹	Greece (n[a] = 3)				Sweden (n[a] = 5)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
DCHP	3	0.08–0.3	0.08	0.075	5	0.10–0.16	0.13	0.13
DEHP	3	29–68	45	39	5	15–35	25	25
DnOP	0	–	–	–	0	–	–	–
DINP	0	–	–	–	1	16	16	16
DIDP	0	–	–	–	0	–	–	–
BHA	0	–	–	–	0	–	–	–
BHT	3	1.1–1.9	1.5	1.4	5	1.3–2.1	1.6	1.5
BTZ	3	1.02–1.7	1.3	1.0	5	7.2–36	18	15
4TBP	1	0.049	0.049	0.049	5	0.12–6.4	1.5	0.42
2MBTZ	0	–	–	–	2	90–107	99	99

μg g⁻¹	Spain (n[a] = 7)				Canary Islands (n[a] = 4)				Portugal (n[a] = 5)			
	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median	N[b]	Range	Mean	Median
DMA	0	–	–	–	0	–	–	–	0	–	–	–
DEA	0	–	–	–	0	–	–	–	0	–	–	–
DMP	3	0.024–0.081	0.053	0.055	4	0.06–0.22	0.097	0.059	4	0.04–0.10	0.059	0.048
DEP	4	0.05–0.32	0.17	0.15	0	–	–	–	3	0.25–0.56	0.41	0.42
DiBP	6	0.28–3.8	1.5	1.5	1	0.90	0.90	0.90	5	0.28–4.5	2.3	2.7
DBP	7	1.2–1.4	1.3	1.2	2	0.7–0.8	0.74	0.74	5	0.25–5.4	2.9	3.8
BBP	3	0.18–0.27	0,208	0,185	4	0.04–0.05	0.20	0.11	5	0.31–6.3	2.9	2.5
DEHA	7	0.17–32	13,229	3700	3	0.7–39	18	14	5	2.6–29	17	21
DCHP	3	0.24–1.1	0,715	0,769	4	0.09–0.79	0.46	0.49	2	0.25–0.41	0.33	0.33
DEHP	7	0.9–13	6104	4655	4	5.9–28	14	11	5	4.9–114	67	75
DnOP	0	–	–	–	2	1.4–3.3	2.4	2.4	0	–	–	–
DINP	1	14	14	14	0	–	–	–	0	–	–	–
DIDP	0	–	–	–	1	4.7	4.7	4.7	0	–	–	–
BHA	1	0.10	0.10	0.10	1	0.078	0.078	0.078	0	–	–	–
BHT	7	0.06–2.2	0.70	0.34	0	–	–	–	4	0.04–0.11	0.067	0.060
BTZ	6	0.8–26	11	9.5	1	13	13	13	5	1.1–18	9.1	9.2
4TBP	6	0.048–3.6	0.91	0.44	4	0.04–0.21	0.10	0.083	5	0.12–2.2	0.74	0.30
2MBTZ	1	62	62	62	0	–	–	–	0	–	–	–

[a] n: Number of samples collected per country.
[b] N: Number of samples containing the compound.

DINP, DIDP and DNOP are not regulated in plastic materials or rubber, the legislation restricted their concentrations as substances or in mixtures to 1000 μg g^{-1} in toys and childcare products which can be ingested by children (hand to mouth) (ECHA Annex XVII to REACH, 2021). In addition, DIDP is classified as a compound very toxic to aquatic life and with long lasting effects (ECHA DIDP, 2021). In reference to the other chemicals, the antioxidant BHT showed the highest concentration in the green pellets of sample FI 8 at 322 μg g^{-1}.

In view of these results, the concentrations of the hazardous organic compounds studied were much higher for crumb rubber samples, especially

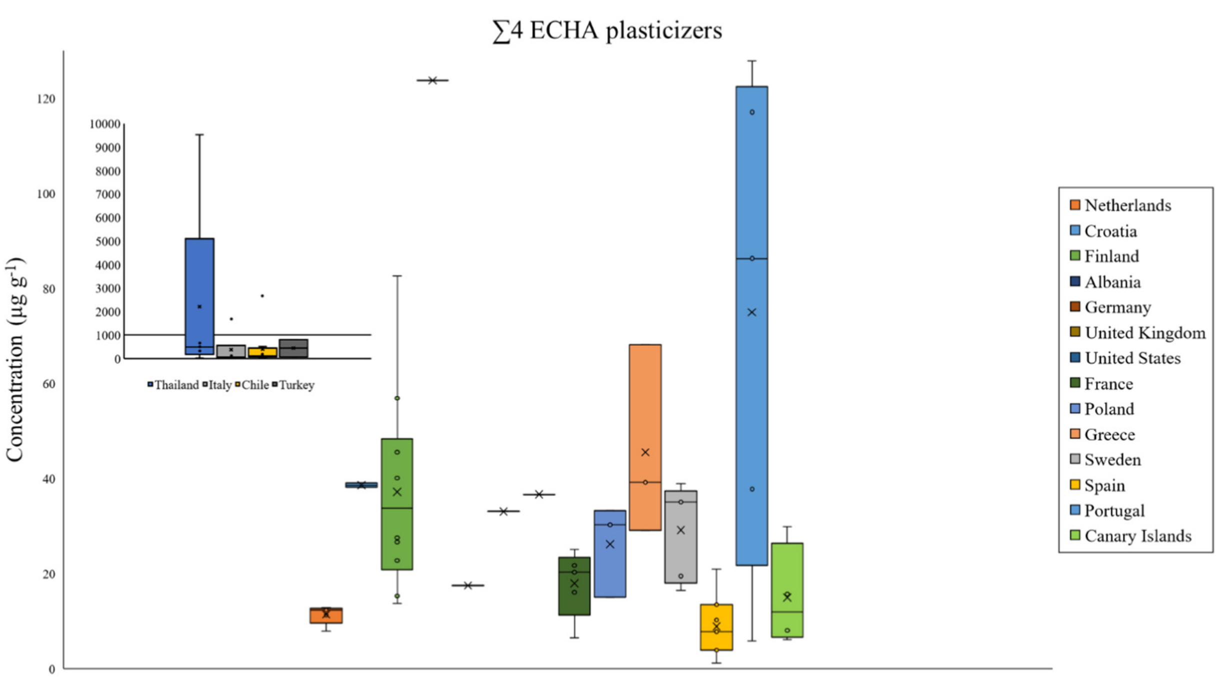


Fig. 3. Box-and-Whisker charts for the 4 ECHA plasticizers by country in the crumb rubber samples.

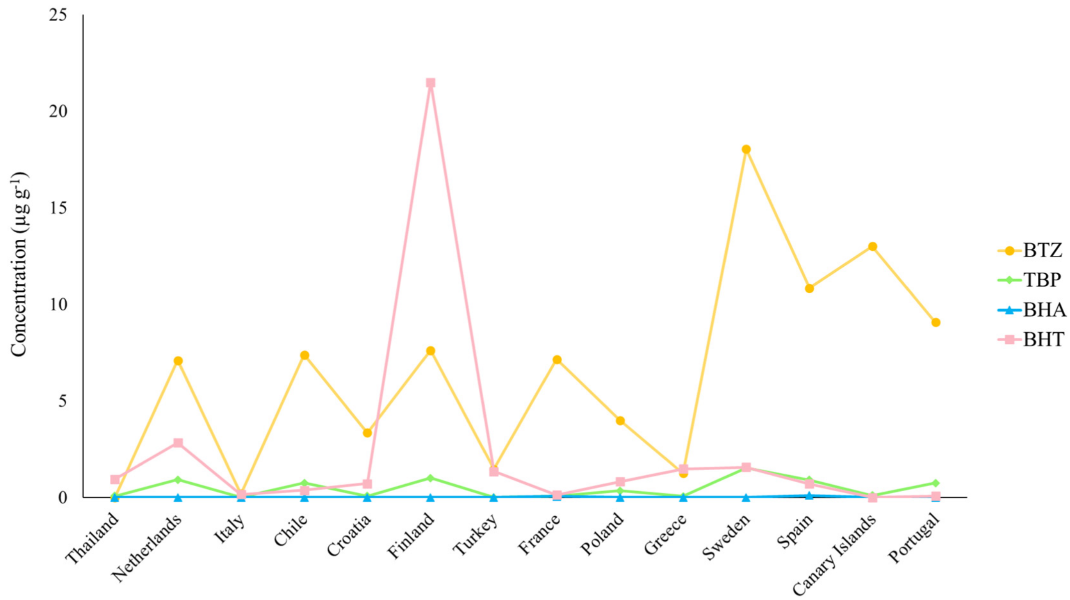
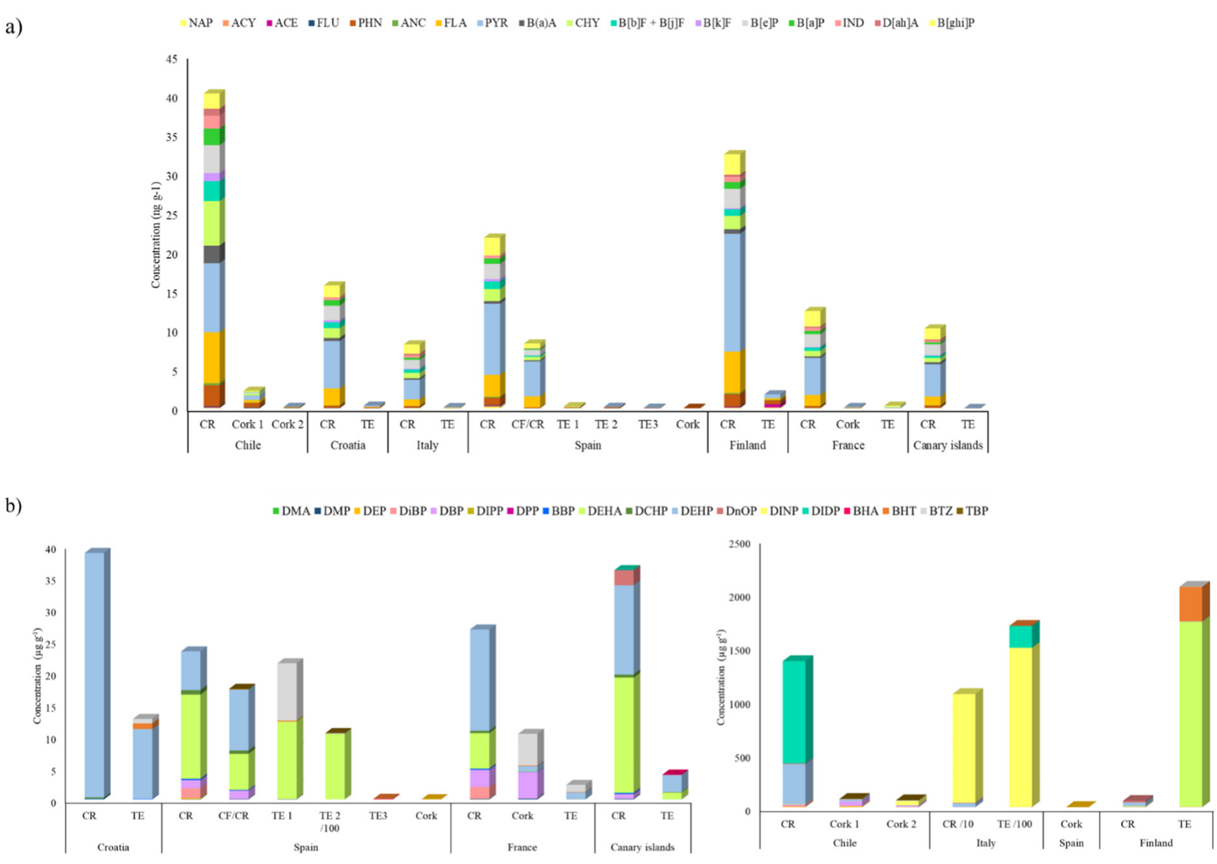


Fig. 4. Mean concentration profiles (µg g^{-1}) per country for the antioxidants BHA and BHT and vulcanisation additives BTZ and 4TBP.

considering PAH content. Nevertheless, some thermoplastic materials shown high concentrations of plasticizers. Indeed, these infill materials, as well as the crumb rubber, are microplastics itself and can be easily released to the environment contributing to microplastic pollution.

On the other hand, cork infill appears to be a good substitute regarding hazardous chemicals content. The absence of PAHs and other compounds was also reported by Celeiro et al. (2021a), proposing this material as safer and sustainable alternative. This natural and biodegradable material



*CR: Crumb rubber; TE: Thermoplastic elastomer; CF/CR: 70 % coconut fiber: 30 % crumb rubber

Fig. 5. Comparison of compounds concentration (µg g^{-1}) per country in green alternatives and crumb rubber (mean value per country): a) PAHs and b) plasticizers, antioxidants and vulcanisation additives. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is also a by-product of the cork industry that proves to be an environmentally and public health-friendly alternative. Furthermore, the use of cork by-products as infill gives this waste material a second life, fitting in a transition to a sustainable circular economy.

3.3. Analysis of variance (ANOVA)

One-way analysis of variance (ANOVA) was performed to determine if significant differences existed between crumb rubber from different football fields considering the geographical origin of the field, age of the field and indoor/outdoor location. The concentration of the target compounds was designated as the dependent variable, and country of origin as a studied factor. ANOVA analysis was carried out individually for all target compounds as well as for sum of the 8 ECHA PAH, sum of 16 EPA PAH and sum of the 4 toxic plasticizers DIBP, DBP, BBP and DEHP. The results for *F-ratio* and *p-value* are summarized in Table 4.

As can be seen, for 8 of the 42 studied compounds (NAP, ACY, ACE, PYR, DMP, BBP, DEHP and BTZ), significant differences between the mean compounds (PAHs) concentration and the country were observed. These differences could be attributed to the fact that samples from Poland and Sweden, which contained higher PAH concentrations than samples from other countries, were included in the statistical study. As mentioned in Section 3.1.2. some of the pitches of these countries were recently build (Table S2), so the higher presence of the most volatile PAHs, such as NAP, ACY and ACE, may be influenced by the young age of the field, and then declining as the field ages.

Mean concentration of PYR per country, is depicted in Fig. S1a. Besides, a comparison of the PYR concentration detected in indoor and outdoor facilities is displayed in Fig. S1b. Results revealed higher concentrations of this compound in indoor pitches, which is in consonance with previous studies (Celeiro et al., 2021a). On the other hand, values obtained for BBP reached higher concentrations in the samples from Portugal (4 of the 5 analyzed samples were from indoor fields) (Fig. S1c). For this reason, a comparison of BBP between indoor and outdoor scenarios was carried out (Fig. S1d), showing also higher concentrations in indoor fields, in line with other studies (Celeiro et al., 2021a; Gomes et al., 2021). The same trend was found for DMP, as shown in Fig. S2a. This is also true for the vulcanising additive BTZ (Fig. S2b), although the latter also reached high concentrations outdoors. This can be another problem for the environment and aquatic life since this compound has high water solubility and teratogenic properties (Celeiro et al., 2018; Capolupo et al., 2020; Halsband et al., 2020; Celeiro et al., 2021b). As already discussed in Section 3.1.3, Fig. S2c shows that Spain and Sweden were the countries with the highest concentrations of BTZ.

In view of the results, it is clear that, although some differences were found between countries, it very difficult to determine the geographical origin of the crumb rubber employed as football pitches infill and establish accurate correlations. The crumb rubber employed in various countries can be provided by the same commercial company or manufactured from the same end-of-life tires (ELTs).

The influence of the football pitch age was assessed to determine whether a relationship with the concentration of the target chemicals exists. Fig. S3 illustrates the distribution of the values of the total PAHs concentration per sample obtained and the pitch age. The concentrations ranged between 0.8 and 50 μg g^{-1}, except for three samples (CL 8, PL 3 and SE 2) with values above 50 μg g^{-1}. Several authors have demonstrated a decrease in the concentration of the PAHs over time (Marsili et al., 2015; Diekmann et al., 2019), but in this case it was not possible to confirm such a correlation. As previously commented, we should bear in mind that the fields are periodically refilled with fresh crumb rubber. To be more specific, the traceability of the ELTs origin and type of tires used to produce the crumb rubber must be implemented and enforced in the recycling facilities.

4. Conclusions

Forty-two organic compounds, including PAHs, plasticizers, antioxidants and vulcanisation additives, in 91 synthetic turf football pitches from 17 different countries were analyzed. This is the largest study evaluating hazardous chemicals in real crumb rubber samples and alternative materials. Most target compounds were detected in the crumb rubber samples, highlighting the presence of all studied PAH, including the eight ECHA PAH, and the plasticizers (DIBP, DBP, BBP and DEHP) that have been regulated by ECHA. Almost all crumb rubber samples complied (only three exceeded) with the limit of 20 μg g^{-1} for the sum of the eight ECHA PAHs. Overall, most samples exceed the limit of 1 μg g^{-1} for eight ECHA PAHs in consumer goods and in materials 'with intensive contact' with the human skin or the oral cavity. This study shows the global dimension of this problem. Therefore, different stakeholders (legislators, environmental agencies, academia, etc.) must work on a consensus to protect not only human health but also the environment, since there is evidence that crumb rubber hazardous chemicals can reach the environment and affect wildlife (Tian et al., 2021).

Table 4
ANOVA study; *F-ratio* and *p-value* for the target compounds, and for the sum of 8 ECHA PAH, 16 EPA PAH, Total PAH, and the 4 ECHA plasticizers. Statistically significant values are in bold.

PAHs			Plasticizers			Antioxidants and vulcanisation additives		
Compound	*F-ratio*	*p-Value*	Compound	*F-ratio*	*p-Value*	Compound	*F-ratio*	*p-Value*
NAP	**6.11**	**0.0000**	**DMA**	0.75	0.735	**BHA**	1.81	0.0505
ACY	**2.36**	**0.0085**	**DMP**	**3.92**	**0.001**	**BHT**	1.49	0.1317
ACE	**2.66**	**0.0032**	**DEP**	0.63	0.8558	**BTZ**	**3.56**	**0.0002**
FLU	1.76	0.0594	**DIBP**	0.52	0.9303	**4TBP**	0.59	0.8883
PHN	1.08	0.3958	**DBP**	1.52	0.1215	**2MBTZ**	1.05	0.4257
ANC	0.90	0.5795	**BBP**	**5.16**	**0.0000**			
FLA	0.63	0.8552	**DEHA**	1.75	0.0599			
PYR	**2.66**	**0.0032**	**DCHP**	**4.21**	**0.0000**			
B[*a*]A	0.47	0.9559	**DEHP**	0.92	0.5523			
CHY	1.05	0.4274	**DNOP**	0.49	0.9457			
B[*b*]F + B[*j*]F	0.53	0.9257	**DINP**	0.49	0.9471			
B[*k*]F	0.45	0.9628	**DIDP**	1.02	0.4531			
B[*e*]P	0.92	0.5538	**4 ECHA**	0.93	0.5486			
B[*a*]P	0.57	0.9002						
IND	0.42	0.9748						
D[*ah*]A	0.69	0.7959						
B[*ghi*]P	0.88	0.594						
8 ECHA	0.65	0.8337						
16 EPA	0.91	0.5690						
Total PAHs	0.87	0.6105						

In terms of the alternative infills, cork seems to be a good substitute regarding hazardous chemicals content. On the other hand, although thermoplastic elastomers appear a good alternative regarding to PAH content, they contained high concentrations of plasticizers.

In addition, thermoplastic and crumb rubber infill are considered as microplastics, since their particle size is lower than 5 mm. In this way, they can be easily released to the environment contributing to the environmental microplastic pollution, which is nowadays an emerging concern.

Finally, after a statistical analysis of all crumb rubber samples, and although differences were found between countries, it is difficult to relate the geographical origin of the sample to its chemical composition. Countries receive tires from all parts of the world and the recycling factories are unable to distinguish when they receive ELTs from this or that country or from car or truck tires, for example. This kind of tracing is (unfortunately) virtually impossible nowadays and this can justify some randomness in the country profiles.

CRediT authorship contribution statement

Daniel Armada: Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Maria Llompart:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Maria Celeiro:** Writing – review & editing, Visualization. **Pablo Garcia-Castro:** Validation, Formal analysis, Investigation, Data curation. **Nuno Ratola:** Investigation, Conceptualization, Writing – review & editing. **Thierry Dagnac:** Conceptualization, Writing – review & editing. **Jacob de Boer:** Conceptualization, Writing – review & editing.

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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.152542.

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