A new look at rubber recycling and recreational surfaces: The inorganic and OPE chemistry of vulcanised elastomers used in playgrounds and sports facilities

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HIGHLIGHTS

- Colours used in playground crumb rubbers influence their trace element chemistry.
- Zinc concentrations can be ×10 lower in some crumb rubber samples than others.
- Many different OPE flame retardants and plasticisers are present in crumb rubbers.
- Detailed chemical data on these materials should be made easily available to buyers.

GRAPHICAL ABSTRACT

Zn, S, Cu, Co, Bi, Cd, Nd, La/Ce, OPEs.....

ABSTRACT

We revisit current understanding of the chemical complexity of different kinds of particulate vulcanised elastomers widely used in playgrounds and sports fields, adding new data on trace element and organophosphate ester contents of used tyre and EDPM crumb rubber. Enrichments in elements such as Zn, S, Co, Bi and Nd relate to the vulcanised mixtures created during manufacture. Zinc concentrations vary across an order of magnitude, being highest in our used tyre particulate samples (up to 2.4 %). In contrast, other trace element variations are due to coloured pigments causing increases in Cu and Zr (blue), Cr (green), and Fe and Sn (red and yellow) concentrations. The use of pale fillers such as $CaCO_3$ and clay minerals (rather than carbon black) strongly influences Ca and Al concentrations, which are much higher in the coloured EPDM than in black used tyre crumb rubber. Representatives from all three of the main organophosphate ester (OPE) groups, namely chlorinated (e.g. TCEP, TCIPP, TDCPP), alkyl (e.g. TEHP, TEP, TNBP, TBOEP) and aryl (e.g. TPHP, EHDPP, TCP) were identified, confirming how these chemicals are commonly used in modern rubber compounding as flame retardants and plasticisers. Elevated concentrations of TEHP (up to 117 μg/g) in coloured-coated used tyre turf infill crumb rubbers were traced to the coating rather than the crumb rubber itself. The presence and weathering behaviour of OPEs in recreational crumb rubber materials deserve closer investigation. The ecological "onehealth" impact of potentially toxic substances present in recreational crumb rubbers will depend on if and how they are released during play and sports activities, maintenance procedures, and natural weathering. We argue that detailed chemical data on these materials should be available to buyers, as manufacturers strive to reduce ecotoxin content as part of the quest towards sustainable use and recycling of vulcanised elastomers.

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1. Introduction

Granulated vulcanised elastomeric materials such as crumb rubber sourced from used tyres present both a serious environmental challenge and new technological opportunities. The challenge stems from the fact that these microplastic mixtures are chemically complex and therefore difficult to recycle, they are environmentally persistent and contain toxins, and they are present in huge quantities: *there are probably more waste tyres on the surface of the planet than people* (Bowles et al., 2020). In contrast, modern opportunities offered by waste rubber reprocessing encompass new "circular economy" sustainable applications in fields such as pyrolytic reclamation of feedstocks (e.g. Dabic-Miletic et al., 2021), high-tech devulcanization (Markl and Lackner, 2020), or the production of environmentally friendly adsorbents for use in water purification (e.g. Battista et al., 2021; Zedler et al., 2022). Despite such promising ongoing research and future potential, however, the reality has been that over the years most waste vulcanised rubber has been disposed of via the more prosaic options of landfill, combustion for energy recovery, asphalt modification, incorporation into new rubber products, or for recreational use in sports facilities and playgrounds (e.g. Makoundou et al., 2021; Valentini and Pegoretti, 2022).

Of all the many applications of these waste vulcanised elastomers, it is the widespread use of crumb rubber installed as synthetic turf infill and cushioning surfaces where children run and play that has proven to be the most publicly sensitive and hotly debated issue. Vulcanised rubber, especially in the form of tyre compounds, contains chemicals toxic to humans and ecosystems. The most attention has been paid to the presence of carcinogenic polycyclic aromatic hydrocarbons (PAHs), but other potential toxins detected in crumb rubber include volatile organic compounds, phthalate and adipate plasticisers, vulcanisation accelerators such as benzothiozoles, chlorinated paraffins, antioxidants and antiozonates such as *p*-phenylenediamines, as well as metals, most notably zinc (e.g. Llompart et al., 2013; Avagyan et al., 2014; Marsili et al., 2014; Brandsma et al., 2019; Diekmann et al., 2019; Schneider et al., 2020; Celeiro et al., 2021; Gomes et al., 2021; Menichini et al., 2011; Skoczyńska et al., 2021; Armada et al., 2022a, 2022b; Cao et al., 2022; de Boer et al., 2022; Fořt et al., 2022; Graça et al., 2022; Grynkiewicz-Bylina et al., 2022). As a result, there has been considerable concern expressed regarding the presence of these chemicals in recreational settings (e.g., Brown, 2007; Claudio, 2008; Marsili et al., 2014; Watterson, 2017; Britton, 2019; Perkins et al., 2019; Massey et al., 2020; Zuccaro et al., 2022). This concern has been countered by a series of published papers, overviews and reports that have concluded that no significant health threat is present for those playing on these synthetic materials (e.g. Bleyer, 2017; Rijksinstituut voor Volksgezondheid en Milieu (RIVM), 2017; Janes et al., 2018; Peterson et al., 2018; Eykelbosh, 2019; Pronk et al., 2020; Verschoor et al., 2021): *Evaluation of these data with a conservative approach to risk characterisation, leads us to conclude that there are no relevant health risks associated with the use of synthetic turfs with end-of-life-tyre (ELT)-derived infill material* (Schneider et al., 2020). Other studies have reached less definitive conclusions, with for example the detailed US Environmental Protection Agency report (EPA &amp and CDC/ATSDR, 2019) concluding that *these findings support the premise that while many chemicals are present in the recycled tire crumb rubber, exposure may be limited based on what is released into air or biological fluids.*

Given this situation, the debate over the chemical safety of recreational crumb rubber has become polarised (see for example de Boer et al., 2022 versus de Vries et al., 2021). Reassuring statements from government bodies, industry and institute researchers (some funded by the ELT industry) have been challenged by those unconvinced by the data published so far (*Rubber Crumb - Is it the new asbestos?* Britton, 2016; *How the "Syn-Turf" Industry Pulled the Wool over the Public's Eyes on Crumb Rubber*: Burch, 2020). To complicate matters further, this lack of consensus coincides with a modern recycled rubber industry that is evolving in response to increasing demands for more environmentally friendly solutions. In this context, for example, the European Chemicals Agency has defined new limits to allowable concentrations of eight PAHs known to be carcinogenic (ECHA European Chemicals Agency, 2019) and, in the case of toxic metals, efforts are being made to reduce the traditionally high zinc content in vulcanised rubbers (Heideman et al., 2007; Maciejewska et al., 2019; Mostoni et al., 2019).

To this moving target of evolving industrial practice and changes in the chemistry of tyre materials can be added the fact that recreational surfaces these days commonly use crumb rubber not sourced from tyres. In the case of playgrounds, for example, the most popular system currently comprises a "poured-in-place" layered structure involving different rubber-based products bonded by polyurethane resin. In a typical 2-layer system a shock absorbent base layer, granulated from used tyres with an elastomer mix including mainly styrene-butadiene rubber (SBR), is overlain by a colourful "wear layer" of bonded ethylene propylene diene monomer (EPDM) rubber or thermoplastic vulcanizates (TPV). Thus, if installed correctly and maintained undamaged, children using such surfaces are not in direct exposure to used tyre materials but instead play on granulated, coloured and bonded "virgin" (or recycled) synthetic rubbers. Using another approach, sports fields can now utilise colour-coated rather than traditional black crumb rubber infills, offering a more aesthetically acceptable image. Perhaps surprisingly, however, there remains a paucity of freely available published data on the chemical differences between all these materials: *there is very limited characterisation of waste rubber prior to use in research works* (Formela, 2021).

In this context, the primary objective of this paper is to revisit our understanding of the chemical complexity and variety of different kinds of particulate rubber materials currently used in playgrounds and sports fields. In particular, we focus on the trace element chemistry of playground base-layer tyre crumb rubber ("traditional" black SBR) and compare this with variously coloured playground EPDM wear layer granulates. To this database we add analyses of the inorganic chemistry of colour-coated sports field infill crumb rubber derived from used tyres. We demonstrate how some elements and element ratios in a given rubber compound can be used as tracers to reveal something of the chemical mix used in vulcanisation. Finally, we investigate the presence in these granulated elastomers of organophosphate esters (OPEs), a diverse and environmentally ubiquitous group of chemical pollutants used as plasticizers and flame retardants that until now has been almost entirely overlooked in crumb rubber studies.

2. Methodology

Samples of pristine (unused) crumb rubbers (0.8-3 mm particle size) representative of those widely used in playgrounds, athletic tracks and synthetic grass sports fields were selected for analysis. The playground/athletic track materials included both wear (top) layer coloured EPDM rubbers and underlying base layer black crumb rubber produced by granulating used tyres containing SBR. The sports field materials comprised two types of colour-coated crumb rubber infill derived from a mix of used tyre elastomers listed by the suppliers as comprising natural rubber, SBR, polybutadiene rubbers, butyl rubber and halogenated butyl rubber.

A total of ten EPDM samples (four red, three green, two yellow and one blue), three black SBR loose crumb rubber samples, and three loose synthetic turf infill granulates (two brown and one green) were analysed for inorganic elements and OPEs, along with a blank sample to correct possible contamination during the extraction process (Fig. S1 in Supplementary information). The coloured EPDM samples included both loose (unbonded) granular material (Red 1, Green 1, Yellow 1, Blue 1) as well as polyurethane-bonded examples which represent the finished product on the recreational surface (Red 2,3,4; Green 2,3; Yellow 2). Most of the crumb rubber samples (with two exceptions, for comparison: Red 4 and Green 3) were initially cryogenically ground using a 6775 Freezer/Mill® (SPEX SamplePrep, LLC). This equipment allows the grinding of samples using liquid nitrogen, reducing their grain size depending on the number of cycles used. In this case, 15 cycles of 1 min were applied to the samples. After this, it was found that in practically all cases the average grain size achieved was between 200 and 300 μm. The reason why we did not

crush all samples for the inorganic analysis was that uncrushed crumb rubber proved difficult and time consuming to fully acid digest, and the two uncrushed samples that we analysed were not clearly different in their inorganic chemistry (compare, for example, samples Red 3 and 4, or Green 2 and 3 on Supplementary Table S1).

For the inorganic chemical analysis, a dried portion of the sample was acid-digested using a special two-step digestion method devised by Querol et al. (1992, 1997) to retain volatile elements. This protocol can be summarized as follows: 1) Digestion in a closed system for retaining the volatile elements: 2 ml of concentrated supra-pure nitric acid was added to 100 mg of sample and heated at 90 °C in a closed bomb for 4 h. After water addition (18.2 Mohmsxcm), the mixture was centrifuged (3000 rpm for 15 min) and the solution obtained was transferred to a volumetric flask. The residue was water washed and centrifuged twice before adding the washing solution to the graduated flask. 2) Digestion of non-volatile elements: The residue was transferred to the PFA bomb with the addition of 7 ml of supra-pure hydrofluoric acid and heated at 90 °C in a closed bomb for 3 h, 2 ml of supra-pure perchloric acid was then added before the mixture was driven to dryness after adding 2 ml of supra-pure nitric acid and the solution transferred to the graduated flask (with the solutions obtained from the first stage) to make a volume of 100 ml.

The concentrations of major inorganic elements in the acid digests were determined using Inductively-Coupled Plasma Atomic-Emission Spectrometry (ICP-AES, Thermo iCAP 6500 Radial view device from Thermo Scientific). The acid digest solutions were pumped with a peristaltic pump (50 rpm) through an automatic sampler and injected into the plasma compartment with a pneumatic concentric nebulizer (Argon 1.5 l/min) through a quartz spray chamber and a quartz torch. All instrument parameters are entered and controlled by appropriate software (iTEVA). The instrument is calibrated with the mixture of monoelemental standard solutions of 1000 ppm and 10,000 ppm of CPI International and checked with appropriate Certified Reference Materials (CRMs).

Trace elements were analysed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS, iCAP RQ from Thermo Scientific). Digestion of international reference materials (SARM19, results shown in Table S2) and blanks were prepared following the same procedure. The samples are pumped with a peristaltic pump (40 rpm) through an autosampler and injected into the plasma compartment with a pneumatic nebulizer (Argon 0.85 l/min) through a thermostatized quartz spray chamber (2.7 °C) and a quartz concentric torch (2.5 mm). At the interference region, the nickel sampling and skimmer cones operate a low vacuum (1–2 mbar). The quadrupole mass spectrometer analyzer has a resolution of 1 amu. All instrument parameters are entered and controlled by appropriate software (Qtegra). The instrument is calibrated with a mixture of Multielement standard solution 5 for ICP 10 ppm, transition metal mix 2 for ICP 100 ppm and Periodic table mix 3 for ICP all of Sigma-Aldrich. These standards cover the full range of expected concentrations forming calibration curves. Frequent tuning and calibration of the mass spectrometer insures the proper operation of the detector. Work has been done by applying an internal correction using an internal standard (In 10 ppb) for monitoring and correcting the signal fluctuations in both, short and long term and to correct for unspecified matrix effects. We work in kinetic energy discrimination (KED) mode using the Helium gas collision cell to minimize matrix interferences (presence of Cl). Detection limit for all elements analysed by ICP was 0,01 ppm, except for Ca and Mg (0,1 ppm), Al (0,2 ppm) and Fe, K and Na (0,5 ppm).

With regard to the OPE analyses, these were applied in all cases to both the coarse "parent" uncrushed materials as well as the cryogenically ground samples. Targeted analysis of the additive OPEs was performed using turbulent flow chromatography-liquid chromatography-tandem mass spectrometry (TFC-LC-MS/MS). For the unground samples rubber, 1 g of sample was spiked with 40 ng of internal standard solution (d_{15}-TDCIPP, d_{27}-TNBP, d_{12}-TCEP, d_{15}-TPHP, d_{15}-TEP, d_{21}-TPP and d_{15}-TEHP) at 1 ng/ μl, whereas the cryogenically ground rubber 0.5 g was spiked with 15 ng of the same internal standard solution (see Supplementary Information for the whole name of the OPEs analysed). After equilibration, samples were loaded

into a 22 ml extraction cell previously loaded with 8 g of hydromatrix. Dead volume was filled with hydromatrix. The extraction solvent used was hexane:acetone (1:1), with a temperature of 50 °C and a pressure of 1500 psi. Two static extractions of 10 min at constant pressure and temperature were developed after an oven heat-up time of 5 min under these conditions. Extracts were concentrated with a purified nitrogen stream to a small volume (around 2 ml) and transferred to 2 ml chromatography vial, to evaporate to incipient dryness with a gentle nitrogen stream. Immediately after evaporation, it was reconstituted with 500 μl of methanol, being ready for instrumental analysis.

Samples were subjected to an online sample purification and analysis with a Thermo Scientific TurboFlow™ system consisting of a triple quadrupole (QqQ) MS with a heated-electrospray ionisation source (H-ESI), two LC quaternary pumps and three LC columns, two for purification and one for separation (Giulivo et al., 2016). The TurboFlow™ purification columns employed were: Cyclone™-P (0.5 × 50 mm) and C18-XL (0.5 × 50 mm). Chromatographic separation was subsequently achieved using an analytical column: Purosphere Star RP-18 (125 mm × 0.2 mm) with a particle size of 5 μm. Selective reaction monitoring (SRM) mode was used for all compounds with two transitions monitored for each analyte. The most intense transition was used for quantification, while the second provided confirmation. Quantification was carried out by isotopic dilution method based on the use of labelled OPE standards in calibration curves previously determined. Nine different calibration standards were injected, containing each all the analytes at 9 different concentration levels and the internal standards (labelled compounds). A calibration curve was built from the ratio of areas between the analyte and the internal standard versus the ratio of injected nanograms for each analyte, selecting the 5 points that adjusted better to the relationship found in the real samples.

During the entire analysis process, plastic material was avoided in order to prevent contamination of the samples, since the analytes are used as plasticizers. They have only been in contact with the plastic bag in which they were shipped. Blank signals have been minimized as much as possible, for example, by heating all non-volumetric material to 340 °C and washing all material with ethanol and hexane:acetone (1:1) before use. The corresponding levels of the blank have been subtracted from each sample. Recoveries from the method ranged between 48 and 112 %, with relative standard deviation (RSD) (%) values going from 1 to 14 %, these values together with limits of detection (LODs) and limits of quantification (LOQs) are resumed in Table S3.

3. Results

3.1. Inorganic elements

Table 1 summarises the inorganic chemical analyses of the samples investigated and reveals notable differences between the various crumb rubber materials (note Supplementary Table S1 presents full details of all 10 individual samples analysed). The black SBR tyre samples are strongly enriched in Zn, S, and Co compared to the EPDM samples, and show relatively higher values of Na, P, Bi, Cd, and Pb. The three brown/green colour-coated turf infill particulate samples are chemically similar to the black samples although with relatively higher concentrations of Al, Ca, Ba and several trace elements such as Cu, Ga, Li, Mn, Sn, Sr and Zr. A notable chemical difference likely due to the colour coating of these infill rubber particles is indicated by the brown samples being richer in Fe and V, whereas the green sample records the highest concentrations of Cr (157 μg/g) in all samples analysed (Table 1).

With the exception of Na, the EPDM samples have higher concentrations of major and minor elements than the tyre rubbers, especially Ca (13–18 %) and Al (4–5 %), but also (in lower amounts) Fe, K, and Ti (Table 1). They are also relatively enriched in most trace elements, notably Ba, Li, Ce (and the lanthanoids in general). The most extreme differences in elemental concentrations between the used tyre base layer and EPDM wear layer of the playground materials (Table 1) are displayed by Ca (>x100 higher in EPDM wear layer), Co (> x100 higher in tyre base layer), Al

Table 1

Summary of ICP-AES and -MS chemical analyses of crumb rubber samples used in playgrounds and sports fields. The coloured samples from the upper surface of the playground ("Wear layer" Red, Green, Yellow, Blue) are all EPDM rubber. The underlying cushioning (Black) "base layer" below the playground EPDM comprises black crumb rubber sourced from used tyres. The colour-coated Brown and Green crumb rubber used as synthetic turf infill in sports fields is also sourced from used tyres. Note that all samples presented in this table were cryogenically crushed prior to analysis. The full chemical data on all individual samples is given in Table S1 (In Table 1 Red = average of Red 2 and Red 3 on Table S1. Similarly Black = average of Black 1–3 on Table S1, and Brown = average of Brown 1 and 2 on Table S1). This averaging has been performed so that Tables 1 and 3 may be more easily compared. LOD: limit of detection.

µg/g	Playgrounds								Sports	
	Wear layer - EPDM							Base layer - used tyre	Turf infill - used tyre	
	Red	Red	Green	Green	Yellow	Yellow	Blue	Black	Brown	Green
	Unbonded	Bonded	Unbonded	Bonded	Unbonded	Bonded	Unbonded	Unbonded		
Al	47,001	38,667	47,462	39,342	47,996	43,456	49,729	632	1262	1205
Ca	165,872	137,114	178,706	142,218	171,300	154,375	155,850	898	3425	4404
Fe	32,512	27,282	2778	2468	19,396	17,892	3021	275	5886	565
K	1964	1979	1793	1447	1627	1550	2004	531	609	638
Mg	871	797	881	679	990	911	847	405	416	397
Na	122	133	126	110	158	145	151	310	554	494
Ti	2294	1532	2303	2130	1812	2041	2307	44.5	97	68
Zn	2541	2102	1151	2104	1169	1051	1069	23,416	17,622	17,100
P	213	176	208	162	176	153	209	271	181	179
S	3631	3067	3749	3075	3448	3250	3329	16,555	15,405	14,854
As	4.2	2.9	2.9	2.7	3.8	3.4	2.2	0.7	1.0	1.1
Ba	65.5	54.2	57.9	52.9	56.8	51.7	66.3	3.4	16.4	7.6
Be	0.9	0.7	0.9	0.7	1.2	0.9	1.4	0.9	<LOD	<LOD
Bi	0.5	0.5	0.7	0.6	0.5	0.5	0.5	0.9	0.7	0.8
Cd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.5	0.6	0.5
Ce	29.9	28.2	25.8	27.4	24.4	24.3	24.1	0.7	1.0	1.1
Co	2.5	2.5	1.7	1.9	2.2	2.3	1.6	210.9	114.0	116.8
Cr	63.9	54.9	121.8	93.6	75.1	83.6	53.6	5.7	9.6	157.3
Cs	1.3	1.5	1.3	1.1	0.9	0.8	1.6	0.8	<LOD	<LOD
Cu	47.8	50.5	4.5	4.6	5.7	5.8	1319	48.9	68.4	71.1
Dy	1.6	1.3	1.5	1.5	1.1	1.1	1.2	1.1	<LOD	<LOD
Er	0.7	0.6	0.7	0.7	0.5	0.5	0.6	0.5	<LOD	<LOD
Eu	0.4	0.3	0.4	0.4	0.3	0.3	0.3	0.3	<LOD	<LOD
Ga	11.3	8.7	11.5	9.6	10.2	9.1	12.2	0.3	0.9	0.8
Gd	1.6	1.4	1.5	1.5	1.1	1.1	1.1	1.1	<LOD	<LOD
Ge	0.5	0.4	0.6	0.4	0.6	0.2	0.5	0.2	<LOD	<LOD
Hf	1.1	0.6	1.1	1.0	1.0	0.9	1.3	0.9	<LOD	<LOD
Ho	0.3	0.2	0.3	0.3	0.3	0.3	0.3	<LOD	<LOD	<LOD
La	19.6	17.5	16.2	17.1	15.1	15.1	16.1	1.6	1.4	1.5
Li	21.0	15.9	23.6	17.2	30.2	25.5	28.0	0.9	1.9	1.6
Mn	70.1	47.8	47.9	40.1	58.0	52.9	40.9	4.4	13.3	6.8
Mo	4.3	3.6	1.0	0.9	5.8	4.9	1.8	0.3	0.5	0.7
Nb	11.8	6.6	7.5	7.5	8.4	8.1	8.9	8.1	0.5	0.3
Nd	9.9	9.2	9.5	9.1	8.1	7.8	7.8	2.7	9.7	9.8
Ni	15.7	15.7	13.2	13.8	13.3	16.4	11.4	5.7	7.2	10.2
Pb	22.0	17.6	18.8	17.8	15.2	15.3	20.0	25.9	21.2	21.1
Pr	3.0	2.7	2.6	2.7	2.4	2.4	2.4	2.4	<LOD	<LOD
Rb	12.4	14.1	11.3	9.2	8.6	7.9	14.1	2.3	1.9	2.0
Sb	0.9	0.8	1.1	0.8	1.7	1.4	1.0	0.5	0.7	0.4
Sc	4.3	3.7	4.6	4.0	4.9	4.4	4.9	4.4	<LOD	<LOD
Se	0.6	0.6	0.7	0.5	0.5	0.4	0.4	0.4	<LOD	<LOD
Sm	2.0	1.8	1.9	1.9	1.6	1.5	1.5	1.5	<LOD	<LOD
Sn	8.4	7.6	4.2	4.0	3.4	3.2	4.1	1.4	3.2	2.3
Sr	45.6	39.7	49.2	37.8	55.2	49.2	47.7	1.7	4.2	4.1
Ta	0.6	0.5	0.6	0.6	0.5	0.4	0.8	0.4	<LOD	<LOD
Th	5.3	3.5	5.3	4.4	5.8	5.3	4.9	5.3	<LOD	<LOD
U	5.2	4.8	3.2	3.8	2.5	2.4	2.5	2.4	<LOD	<LOD
V	31.0	21.9	38.6	27.0	48.6	42.8	38.8	1.7	2.9	8.2
W	2.8	2.2	2.1	2.0	2.0	2.0	2.9	2.0	<LOD	<LOD
Y	6.9	5.4	7.0	6.7	5.0	5.0	5.3	5.0	<LOD	<LOD
Yb	0.7	0.5	0.7	0.7	0.5	0.5	0.6	0.5	<LOD	<LOD
Zr	34.8	19.8	36.8	31.1	31.9	28.1	44.4	1.3	3.2	2.8

(>x50 in wear), Ti and Ce (>x30 in wear), Zn (>x20 in base) and Ba (>x10 in wear). As with the used-tyre infill particulates, the EPDM data indicate that the colouring pigments used in these materials can be observed in their cation chemistry, with red colour favouring Fe and Sn, blue colour resulting in high Cu (and Zr) content, green colour once again being associated with Cr, and yellow colouring coinciding with higher Fe and Sb (Fig. 1). The presence of a polyurethane sealant (or crushing the sample) has little impact on the cation chemistry, apart from a dilution effect which can exceed 15–20 % (in Ca for example: Table S1).

Table 2 compares nine metals and metalloids known to be toxic if present at high enough concentrations in the appropriate chemical form and oxidation state, especially in sensitive environments such as aquatic conditions contaminated by leaching. The dataset compares our cryogenically crushed EPDM and used-tyre crumb rubbers with other tyre-sourced particulate infills (Bocca et al., 2009; Halsband et al., 2020) and a recent paper reporting on tyre compositions (Jeong, 2022). Concentrations of these elements in all these materials are generally low, with the notable exception of Zn which is present at levels of 0.1–0.25 % in all EPDM samples and ten times higher than this in all used tyre samples (1.2–2.4 %: Table 2).
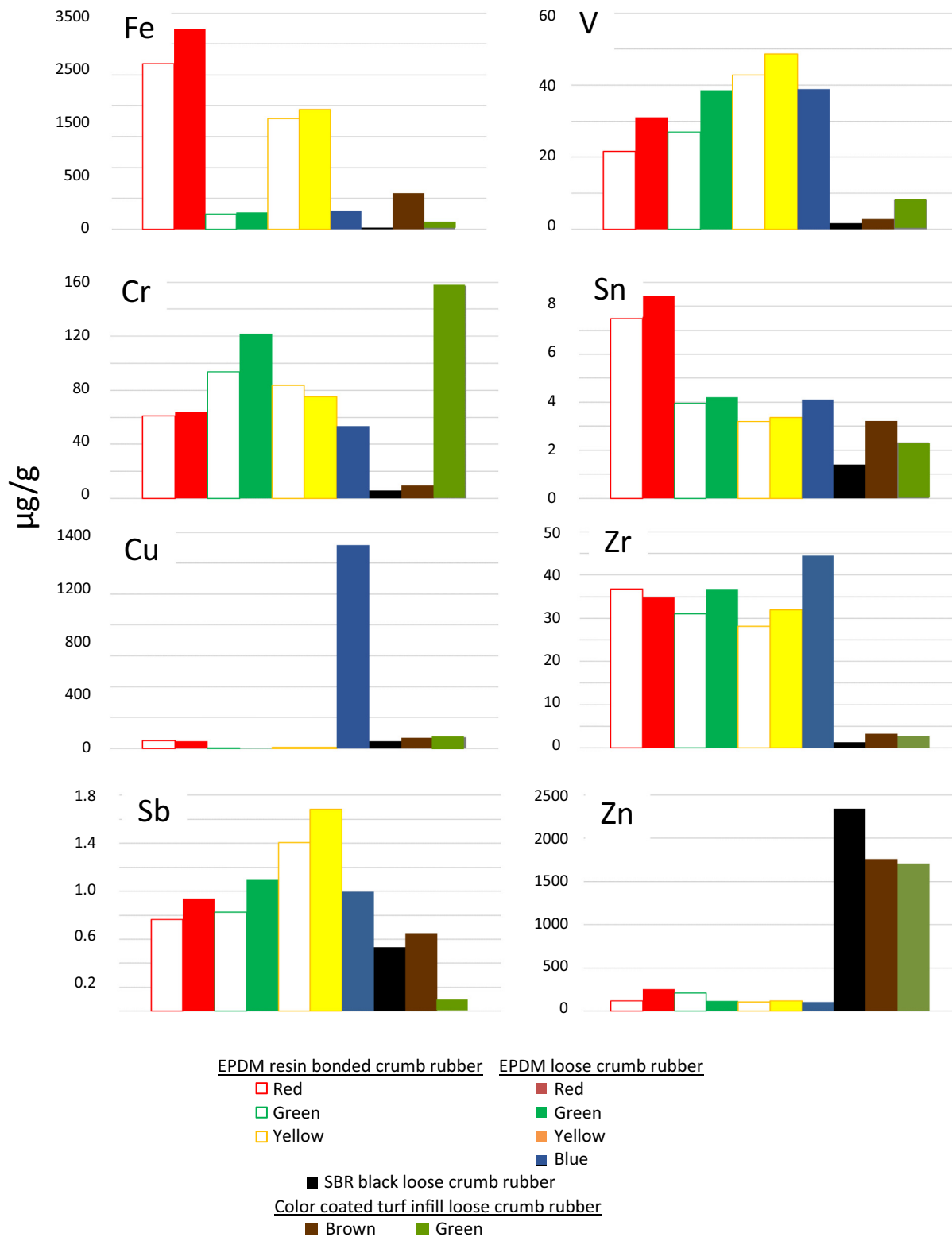
Fig. 1. Histograms demonstrating the chemical influence of colouring pigments mixed with EPDM crumb rubber. The most obvious influences are red and yellow on Fe content, green on Cr content, red on Sn content, and, most strikingly, blue on Cu content. In addition, the Zn histogram illustrates the bimodal difference in the concentrations of this metal in EPDM (lower Zn) and used tyre (higher Zn) samples.

Copper concentrations are highly variable, rising to an exceptional 1319 μg/g in the blue EPDM sample and 771 μg/g in the tyre sample from France, but otherwise lying in the much more subdued range of 5–212 μg/g. Arsenic concentrations are higher in the EPDM samples (2.2–4.2

μg/g) than in the tyre turf infill materials (<1.3 μg/g), with highest levels found in the red coloured EPDM (Table 2). In contrast, unlike in the tyre materials, the EPDM samples all have such a low Cd content that it is below detection level (Table 2).

Table 2
Comparisons between concentrations of metals and metalloids reported in this paper with published examples of those in other used tyre crumb rubbers and tyres. All data from this paper and Bocca et al. (2009) show maximum μg/g values; Halsband et al. (2020), and Jeong (2022) report only average values. <dl = below detection limit.

μg/g				As	Cd	Cr	Cu	Ni	Pb	Sb	Sn	Zn
Playground crumb rubbers	WEAR LAYER - EPDM	Red	This paper	4.2		63.0	51.6	17.8	22.0	0.9	8.4	2541
		Green	This paper	2.9		122	4.6	13.8	18.8	1.1	4.2	2104
		Yellow	This paper	3.8		83.6	5.8	16.4	15.3	1.7	3.4	1169
		Blue	This paper	2.2		53.6	1319	11.4	20.0	1.0	4.1	1069
	BASE LAYER - USED TYRE	Black	This paper	0.8	0.5	5.9	50.3	6.3	26.6	0.7	1.4	23,755
Sports field crumb rubbers	TURF INFILL - USED TYRE	Brown	This paper	1.0	0.6	908	68.7	7.2	21.5	0.7	3.3	17,692
		Green	This paper	1.1	0.5	157	71.1	10.2	21.1	<LOD	2.3	17,100
		Old	Plesser and Lund, 2004	<3	1.0	<2	35.0	<2	20.0			7500
		Old	Plesser and Lund, 2004	<3	1.0	<2	20.0	<1	15.0			7300
		Old	Plesser and Lund, 2004	<2	2.0	<2	70.0	<5	17.0			17,000
		EPDM	Plesser and Lund, 2004	<2	<0.5	5200	<3	<5	8.0			9500
		Old	Bocca et al.. 2009	1.2	1.9	56.0	60.0	5.8	46.0	7.7	3.0	19,375
		Old	Halsband et al., 2020		0.7	5.5	17.7	4.3	17.8	4.4		12,544
		New	Halsband et al., 2020		1.8	1.9	85.0	2.6	24.9	0.2		22,601
		Pristine	Halsband et al., 2020		0.7	2.1	22.6	2.8	16.6	6.7		14,136
Tyres	S Korea 1		Jeong, 2022	0.4	0.3	2.7	157	8.8	13.4	3.6	46.8	12,194
	S Korea 2		Jeong, 2022	1.1	0.6	8.7	212	5.3	33.2	23.7	10.2	13,322
	S Korea 3		Jeong, 2022	0.3	0.1	2.2	202	7.3	9.5	1.3	24.1	12,367
	France		Jeong, 2022	2.2	0.5	9.7	771	2.0	15.9	1.1	21.3	10,128
	China		Jeong, 2022	0.9	0.7	2.5	11.6	6.4	55.4	2.9	2.8	10,032

Taking a geological approach to place the chemistry of these materials in an earth science perspective one can graphically normalise the compositions of the used tyre and EPDM granulates with that of the average upper continental crust (UCC; values from Wedepohl, 1995; Fig. 2). This immediately highlights the distinctive anthropogenic chemistry of these vulcanised crumb rubbers. Samples derived from used tyres clearly demonstrate their artificial richness in Zn (up to 2.4 % > x10^5 UCC), S (up to 1.7 % > x10^4 UCC) and Co (up to 224 μg/g: >x10^4 UCC), as well as up to 71 μg/g Cu, 0.9 μg/g Bi and 0.6 μg/g Cd (all >x10^3 UCC). Other cations that are present in above average UCC concentrations are Pb, Sb and (in some samples) Sn (Table 1). In comparison, the EPDM granulate samples are notably less enriched in Zn (0.25 %) and S (0.37 %), although these are nevertheless

values >x10^4 UCC and > x10^3 UCC respectively (Fig. 2b). Calcium is by far the dominant major element in the EPDM samples (13–18 %; >10^3 UCC) but is present in concentrations of only around 0.1 % or less in the used tyre materials. Both Se and Bi in the EPDM are also notably enriched over average UCC levels, and Cu and Fe provide special cases due to the effects of colouring, as noted above (Table 1, Fig. 1). Most of the remaining cations analysed in the EPDM are present at concentrations of 1–10^{-1} UCC. Thus, in comparison to the used tyre granulates the EPDM materials show no Co enrichment, and are very depleted in Cd but much richer in Se (below detection limit in used tyres, Fig. 2a, b).

More subtle geochemical differences between the tyre-derived and EPDM crumb rubber sample groups are revealed by their lanthanoid or
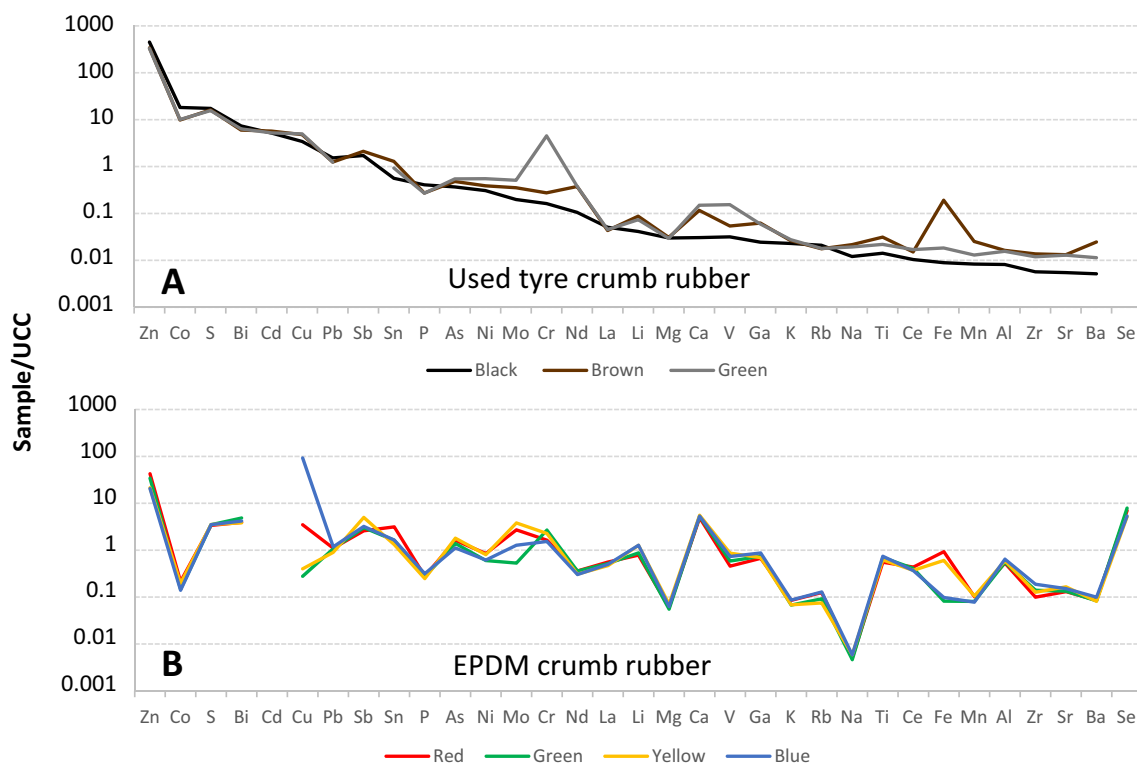
Fig. 2. UCC normalised metal concentrations in the samples analysed from turf infill used tyres for sport fields (A) and EPDM and base layer used tyre for children playgrounds (B). UCC values from Wedepohl (1995).

"rare earth element" signature. Compared to UCC, lanthanoid concentrations are extremely low in the samples, especially in the used tyre crumb rubbers (e.g. Ce 10^{-2} UCC) in which most of them are below detection (Fig. 2b). An interesting anomaly however is provided by Nd in the EPDM samples and brown and green infill granulates, all of which contain concentrations approaching 10 μg/g Nd as opposed to <3 μg/g in the black base layer tyre particulates (Table 1). The likely reasons for these various geochemical cation distributions are considered later in the Discussion and conclusions section.

3.2. Organophosphate esters

Concentration levels and percentage contributions of OPEs present in the EPDM and used tyre crumb rubber samples are shown in Table 3 and Figs. 3 and 4. Of the 20 OPEs targeted for analysis, only B4IPPPP, IDPP, and THP were undetected in all samples, and TPrP was present at very low concentrations (<1 ng/g). Within the remaining 16 detected OPEs

concentration levels were variable and marked by high outlier values in some samples, most notably TEHP in the used tyre turf infill materials (Table 3). Average ΣOPE contents were higher in used tyre crumb rubber than in EPDM, and higher in most polyurethane bonded EPDM than unbonded EPDM (Table 3). The histograms in Fig. 3 compare cryogenically crushed samples of the three main crumb rubber groups (unbonded EPDM, bonded EPDM and used tyre). Further details are provided below.

3.2.1. Used tyre crumb rubbers

By far the highest ΣOPE concentrations of all samples analysed were found in the used tyre turf infill crumb rubbers (brown and green on Table 3 and Fig. 3), due to exceptional levels of TEHP (52,307 ng/g and 116,990 ng/g in the uncrushed samples, 6242 and 11,900 in the crushed samples respectively: Table 3). Less extreme, but still unusually elevated, concentrations were registered by TCEP in the crushed black sample (1742 ng/g), EHDPP in the uncrushed black sample and TCEP in the crushed brown sample (1497 ng/g in both). The commonest nine OPEs in

Table 3
OPE concentrations (ng/g) of uncrushed and crushed samples analysed for playgrounds and sport field facilities.

ng/g	Uncrushed									
	Playgrounds								Sports field	
	Wear layer (unbonded)				Wear layer (polyurethane bonded)			Base layer - used tyre	Turf infill - used tyre	
	Red	Green	Yellow	Blue	Red	Green	Yellow	Black	Brown	Green
TEP	17.6	118	79.5	172	15.3	9.28	36.4	134	709	591
TCEP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TPPO	3.67	9.74	14.2	4.82	22.6	11.3	14.4	21.7	26.1	63.8
TCIPP	7.63	21.7	44.3	14.1	58.3	114	59.1	48.0	104	102
TPrP	0.18	0.34	0.33	0.75	0.53	0.51	0.31	0.39	0.47	0.41
TDCIPP	nd	3.70	6.36	1.26	8.07	4.54	6.51	2.73	4.60	1.70
TPHP	1.85	4.94	6.40	1.93	93.6	968	66.2	5.27	26.1	32.7
TNBP	4.23	nd	10.3	0.18	28.4	18.1	16.2	48.4	60.5	55.2
DCP	9.32	25.6	38.2	7.74	54.9	36.0	55.8	14.7	53.2	47.2
TBOEP	nd	0.69	0.50	nd	0.67	0.95	0.47	30.1	132	90.9
2IPPDPP	nd	2.79	1.68	0.13	5.08	4.54	6.53	0.94	6.52	6.41
RDP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4IPPDPP	1.19	3.95	2.83	1.66	4.74	4.42	4.48	3.23	3.93	4.23
TCP	nd	nd	nd	nd	8.63	8.26	1.76	nd	40.5	41.3
EHDPP	20.7	49.5	26.3	18.2	42.6	36.2	57.9	1497	220	150
B4IPPPP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IDPP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
T2IPPP	0.25	nd	nd	1.68	nd	nd	nd	5.26	7.47	6.24
THP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TEHP	5.07	nd	nd	nd	nd	42.0	nd	192	52,307	116,990

| ng/g	Crushed									
	Playgrounds								Sports field	
	Wear layer (unbonded)				Wear layer (polyurethane bonded)			Base layer - used tyre	Turf infill - used tyre	
	Red	Green	Yellow	Blue	Red	Green	Yellow	Black	Brown	Green
TEP	80.8	31.7	40.8	40.0	883	181	606	43.9	367	503
TCEP	1659	93.8	21.5	64.9	414	363	1062	1742	1497	83.9
TPPO	3.98	3.84	4.02	4.18	5.1	4.2	5.26	10.4	24.7	36.0
TCIPP	42.0	23.1	13.2	20.7	37.2	52.8	20.9	34.4	67.8	86
TPrP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TDCIPP	11.4	7.35	4.62	5.40	3.53	6.20	1.52	7.30	12.3	11.1
TPHP	1.45	333	4.49	0.92	41.7	448	39.1	1.42	30.0	27.1
TNBP	180	124	138	100	127	143	72.0	96.7	90.8	101
DCP	2.89	24.3	4.69	0.31	0.92	1.60	nd	3.39	10.2	10.3
TBOEP	1.59	0.97	1.01	1.05	1.60	2.73	3.61	30.7	421	119
2IPPDPP	3.73	55.1	4.96	3.01	3.08	6.91	2.97	3.05	8.64	14.9
RDP	0.36	18.0	0.80	0.34	0.55	0.81	0.97	nd	nd	nd
4IPPDPP	0.31	14.8	0.80	0.19	0.31	1.48	0.27	0.40	1.74	3.84
TCP	1.64	1.94	1.45	0.82	4.73	5.19	0.93	10.9	26.8	43.0
EHDPP	12.1	13.3	7.40	15.5	15.1	14.8	11.3	460	88.7	119
B4IPPPP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IDPP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
T2IPPP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
THP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TEHP	nd	nd	nd	nd	10.1	25.2	5.77	17.0	6242	11,900
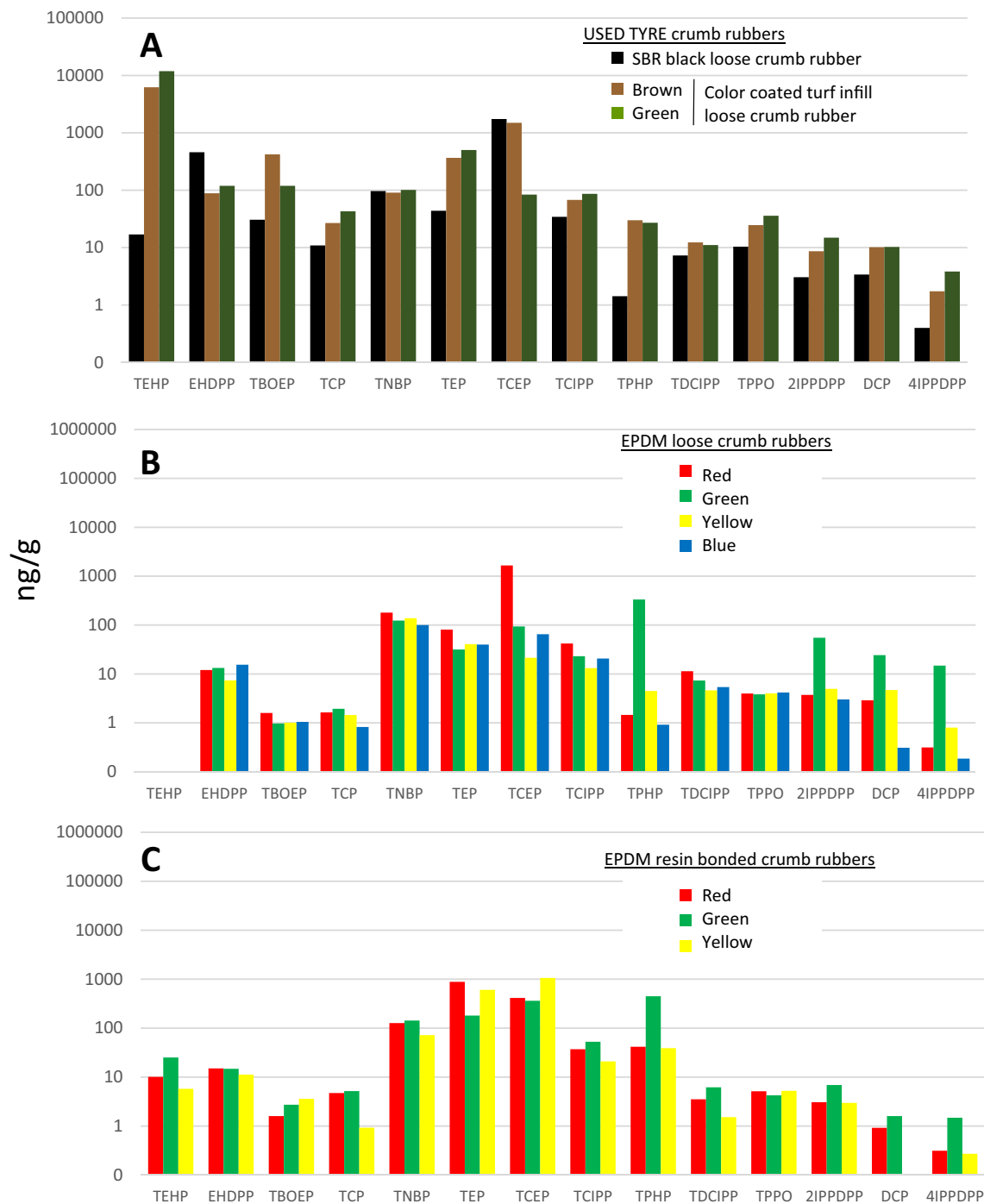
Fig. 3. OPEs concentrations (ng/g) in crushed materials analysed, separating used tyre crushed crumb rubber (A), playground wear layer red, green, yellow and blue unbonded (loose) EPDM crushed crumb rubber (B), and playground wear layer red, green and yellow EPDM bonded crushed crumb rubber samples (C).

these samples are TEHP, TCEP (in crushed samples), EHDPP, TEP, TNBP, TCIPP, TBOEP, TPPO, and DCP. The black base layer SBR rubber is chemically quite different from the turf infill rubbers, containing less TEP, TPPO, TCIPP, TPHP, TBOEP, 2IPPDPP, TCP, and TEHP, but much higher amounts of EHDPP (Table 3). The used tyre samples contain notably more TEHP, EHDPP, TBOEP and TCP than the EPDM samples (left side of Fig. 3).

3.2.2. EPDM crumb rubbers

The lowest ΣOPE concentrations of all samples analysed were found in the uncrushed unbonded EPDM crumb rubbers (ΣOPE = 72–241 ng/g).

Within these samples just four OPE compounds contribute 78–95 % of ΣOPE (Fig. 4): TEP (18–172 ng/g; 25–77 %), EHDPP (18–50 ng/g; 8–29 %), TCIPP (8–44 ng/g; 6–19 %) and DCP (8–38 ng/g; 4–17 %). The three uncrushed but bonded EPDM samples not only have higher ΣOPE than the unbonded samples, but they have a contrasting OPE chemical signature, with six OPEs present in notably higher concentrations. These six OPEs with an apparent preference for the polyurethane bonded samples are: TPHP (66–968 ng/g; 20–77 %, as compared to 2–6 ng/g in unbonded samples), TCIPP (58–114 ng/g as compared to 8–44 ng/g), TNBP (16–28 ng/g as compared to 0–11 ng/g), TCP (2–9 ng/g, undetected in unbonded
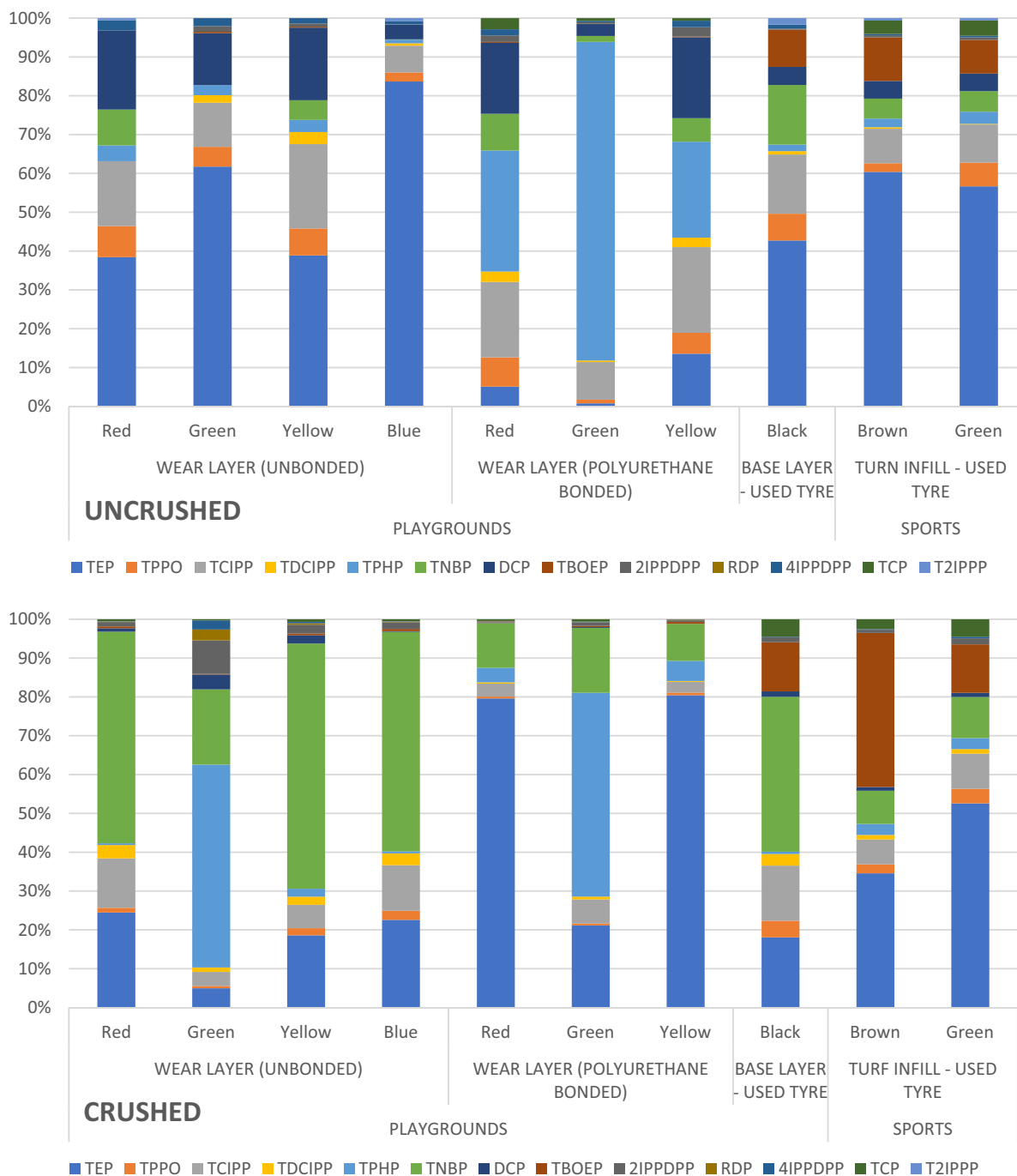
Fig. 4. Main OPEs contribution in % for all uncrushed (top) and crushed (bottom) samples.

samples), 2IPPDPP (4–7 ng/g as compared to 0–3 ng/g), and 4IPPDPP (4–5 ng/g as compared to 2–4 ng/g). The exceptionally high concentration of TPHP (968 ng/g) in the uncrushed bonded green sample is the only unusual data spike outlier (Table 3). The crushed EPDM samples also record the lowest levels of ΣOPE in most of the unbonded samples. In the crushed bonded group, the five dominant OPEs are TEP (181–883 ng/g; 14–57 %), TCEP (363–1062 ng/g; 27–58 %), TPHP (39–448 ng/g; 2–36 %), TNBP (72–143 ng/g; 4–11 %) and TCIPP (21–53 ng/g; 1–4 %) (Fig. 3). A notable aspect of the crushed sample data is the presence of more outlier spikes of relatively exceptional concentrations: 1659 ng/g (TCEP red unbonded), 1062 ng/g (TCEP yellow bonded), 448 ng/g (TPHP green bonded: compare with the 968 ng/g uncrushed bonded spike), plus four OPE outliers in the green unbonded sample (333 ng/g TPHP; 55 ng/g 2IPPDPP; 24 ng/g DCP; 18 ng/g RDP; 15 ng/g 4IPPDPP).

4. Discussion and conclusions

The most characteristic inorganic geochemical signature of all these vulcanised materials is their enrichment in Zn and S. High levels of Zn and S (Σ2–5 %: Baensch-Baltruschat et al., 2020) are typical of tyre elastomers such as SBR and polyisoprene (natural rubber) because these elements are central to the most common vulcanisation (or "curing") process. The sulfur crosslinks the polymer chains, irreversibly toughening the rubber, and the addition of ZnO acts as a chemical activator, reducing reaction time and enhancing the final product. The much lower concentrations of Zn in the EPDM samples presumably reflect differences in the vulcanisation method applied during rubber manufacture. For example, nanoparticulated ZnO and other alternatives have been shown to be capable of curing rubber using one-tenth or less of the Zn concentrations that characterise in

conventional systems (Heideman et al., 2005, 2007; Gujel et al., 2018; Mostoni et al., 2019).

The relatively high concentrations of Co can also be attributed to the rubber manufacturing methodology because this element is used as a cohesion agent that does not slow the vulcanisation rate. Bismuth is similarly involved in the curing process, with compounds such as bismuth dimethyl dithiocarbamate used for many years as a vulcanisation accelerator (Brooks et al., 1955). Copper is used in tyre bead alloys, helping improve bonding between bead and rubber, and the presence of Cd in the used tyre materials is likely to be as a by-product contaminant of Zn refining. Other trace metals (in addition to Co, Cd and Bi) that are more highly concentrated in the tyre crumb rubber samples compared to the EPDM samples include Sn and Pb (Table 1). Finally, the higher Na concentrations in the used tyre granulates may be due to the presence of small amounts (e.g. 1.5 %) of sodium sulphate in the precipitated silica used as a filler in tyre manufacture (Wypych, 2016).

The higher levels of Nd observed in the EPDM samples and brown and green infill granulates are attributed to the fact that this element is used as a catalyst both in EPDM and polybutadiene manufacture (Walter, 2014; TCGR (The Catalyst Group Resources), 2018). Polybutadiene is listed as a rubber compound ingredient by the supplier of the infill samples (Nd = 9–10 μg/g) but not in the black base layer samples (Nd <3 μg/g). Another lanthanoid-based geochemical tracer is the La/Ce ratio, which is higher in the tyre crumb rubbers (1.4–2.5) than in the EPDM samples (0.6–0.9) (Table 1). We attribute this relative enrichment of La in the tyre crumb rubbers either to the use of La-bearing vulcanisation accelerators such as lanthanum diethyldithiocarbamate (Ajiboye et al., 2022), and/or to the presence of carbon black, a manufactured product that has been central to the tyre industry for its value as a reinforcing filler. Carbon black is a by-product of hydrocarbon production and is most commonly made from residual oil feedstocks resulting from catalytic cracking processes. Such processes use La-concentrates (Moreno et al., 2008a, 2008b) which contaminate the residual oils. This would be expected to increase La/Ce values in tyre compounds using carbon black manufactured from such oils.

The manufacturers of our EPDM samples will have avoided the use of black fillers in order to allow the application of colouring agents in these children's recreational rubber materials. This presumably explains not only the low La/Ce values but also the strongly enhanced content of Ca in EPDM samples because $CaCO_3$ can be added to EPDM dispersed with ZnO as a white-coloured reinforcing filler that reduces Zn content while enhancing the vulcanisation process (e.g. Shokrzadeh et al., 2014; Gujel et al., 2018). The presence of abundant carbonate in the EPDM samples explains the presence of elevated amounts (relative to the tyre rubbers) of several other trace elements such as Sr and Mn (Table 1). Similarly, the relatively high concentrations of Al likely owe their origin to the use of EPDM fillers such as Al_2O_3 or and/or clay minerals (e.g. Wang et al., 2011; Babu et al., 2013).

With regard to OPEs our study of these vulcanised rubber materials reveals, to our knowledge for the first time, the presence of a broad range of compounds that encompasses representatives from all three main OPE flame retardant groups, namely chlorinated (e.g. TCEP, TCIPP, TDCPP), alkyl (e.g. TEHP, TEP, TNBP, TBOEP) and aryl (e.g. TPHP, EHDPP, TCP) phosphates. Several of these, such as TEP, TCIPP, and TCEP, are currently among the most commonly manufactured OPEs on the world market (Huang et al., 2022) and they are ubiquitous in the environment (Kung et al., 2022). Concentration values of individual OPEs approaching or exceeding 1000 ng/g were observed both in some of our EPDM samples (TCEP, TPHP) as well as in the used tyre materials (TCEP, TEHP, EHDPP). Several OPEs increased in concentration in the polyurethane bonded samples, presumably due to the use of these chemicals (such as TPHP) as a flame retardant in resins.

The most striking of our observations on OPE levels in crumb rubber samples however was the presence of TEHP at concentrations of 52 μg/g and 117 μg/g in the uncrushed brown and green colour-coated turf infill materials. Interestingly, the same crumb rubber samples lost much of their TEHP content on crushing (reducing to 6.2 μg/g and 11.9 μg/g respectively: Table 3). We suggest that this concentration loss of TEHP (by an

order of magnitude) is linked directly to the fact that these samples also lost their colour during crushing, returning to the "carbon black" aspect typical of used tyre crumb rubber. Thus, TEHP is likely to be present more in the colourant applied to coat the crumb rubber rather than the crumbs themselves, an interpretation that needs to be verified by separate analysis of the coloured coating. Such coatings can be manufactured by mixing elastomeric latex-based binding materials (typically a mix of natural and synthetic rubbers) with coloured pigments (e.g. see patent application https://patents.google.com/patent/US20020193501A1/en) and will themselves influence the final chemical composition and weathering characteristics of the crumb rubber being employed. Even if there was not found a pattern of OPE between crushed and uncrushed samples, these results are interesting as when these materials are used initially they will have a behaviour similar to uncrushed samples, but over time the material will suffer abrasion and behave as the crushed material. With this, it can be considered that uncrushed samples can represent the new material, and could be used to evaluate the exposure to OPE through dermal contact that would be the main exposure route when material is recently used. While crushed samples represent the material after abrasion for its use and sun, that can be used to evaluate the exposure through ingestion and inhalation.

We attribute the presence of these OPEs in crumb rubber mainly to the fact that this group of chemicals is widely used as flame retardant plasticisers in elastomer compounding, especially since the ban on persistent organic pollutant alternatives such as chlorinated paraffins (Babu et al., 2013). When TEHP is used, for example, it can be introduced into the rubber compound at anything between 10 and 80 parts per hundred of rubber (Coste et al., 2015), demonstrating that, despite having been generally overlooked, OPEs can potentially be important components of these elastomer materials.

Given a rapidly increasing realisation of how pervasive and commonplace these chemicals are in the anthroposphere, the ecological impacts of OPEs have become a focus of ongoing pollutant research, although as yet no clear risk assessment picture with regard to human exposure has emerged (e.g. Blum et al., 2019; Li et al., 2019; Pelletier et al., 2020; Fernández-Arribas et al., 2021; Patisaul et al., 2021; Kung et al., 2022; Sala et al., 2022; Xie et al., 2022). Several of these organophosphate compounds, such as TCEP, TEHP, TNBP and TCIPP, pose potential risks to human health by inhalation, ingestion or dermal contact (USEPA, 2022). Their presence and weathering behaviour in recreational crumb rubber materials therefore deserves closer investigation.

In the light of our study, then, we return to the polarised debate over the use of crumb rubber in playgrounds and sports fields. Those in favour will emphasise safer and more reliable playing surfaces, less injuries to children, employment opportunities offered by what is a globalised multi-million-dollar industry, as well as the key environmental advantages of avoiding toxic and pestilential tyre landfilling and incineration (and therefore CO_2 emissions and other atmospheric pollutants). To these advantages can be added less irrigation water use, pesticide applications, and no grass mowing emissions. Those against use of crumb rubber will argue that synthetic surfaces sourced ultimately from the petroleum and tyre industries are intrinsically linked to global climate change and, on a more local level, can cause heat stress to individual players and cities (with sports fields creating urban "heat islands"). In contrast, natural materials may instead absorb CO_2, cool and filter water, and avoid the polluting release of potentially toxic chemicals and long-lived microplastics into the aquatic and atmospheric environments. With regard to human health effects, those in favour of synthetic recreational surfaces will emphasise the studies that have concluded that there is negligible risk. Those against will point to the proven presence of toxins and their ecotoxicological effects, the paucity of human epidemiological data, the uneven nature of global regulatory controls (Zuccaro et al., 2022), and argue that when in doubt the precautionary principle should govern our behaviour.

This paper does not attempt to take sides in these arguments but hopes to move the subject forward. Our study was conceived as applying "fishing expedition" research principles to a subject about which much has been written while easily accessible chemical data on specific products remain

relatively few. We asked ourselves what, exactly, is in these materials, starting with inorganic elements and OPEs, and how easy is it for the buyer to access this chemical information? It is obvious from our study, for example, that the concentrations of Zn in different recreational crumb rubbers can vary at least by an order of magnitude. The city councillors responsible for applying the black base layer used-tyre crumb rubber layer were unlikely to be aware that this material contains up to 2.4 % Zn, as opposed to the top wear layer EPDM which contains just 0.1–0.25 % Zn, or that the blue coloured EPDM in the wear layer contains unusually high concentrations of Cu.

The environmental health impact of potentially toxic substances present in recreational crumb rubbers will depend on if and how they are released during play and sports activities, maintenance procedures, and natural weathering. Soluble components will be most subject to environmental loss, as suggested by the Norwegian data on Table 2 (Halsband et al., 2020) where "old" weathered crumb rubber collected from a sports field shows lower Zn and Cu concentrations than in its unused "new" equivalent prior to exposure outdoors (Table 2). A similar observation was made by the US EPA (EPA-CDC 2019 pg. 22). We consider that buyers of newly installed playground and sports surfaces should have access to certified details regarding the inorganic and organic chemistries of the materials they are purchasing. This would undoubtedly encourage competition and good practice in a direction likely to achieve reductions in the ecotoxins present in vulcanised rubbers. At the same time there needs to be more effort directed towards sustainable recycling of vulcanised elastomers within the concept of a circular economy (e.g. Campbell-Johnston et al., 2020: *How circular is your tyre?*). This will likely involve advanced devulcanisation methods successful enough to recapture the original rubber compounds and thus reduce the exploitation of natural resources.

CRediT authorship contribution statement

Teresa Moreno: Conceptualization, writing, funding acquisition. Aleix Balasch: Data curation, writing and validation for OPEs. Rafael Bartrolí: Data curation and validation for inorganics. Ethel Eljarrat: review, writing, editing and supervision.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Teresa Moreno reports financial support was provided by Fundacion ACS.

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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.2023.161648.

References

Ajiboye, T.O., Ajiboye, T.T., Marzouki, R., Onwudiwe, D.C., 2022. The versatility in the applications of dithiocarbamates. Int. J. Mol. Sci. 23 (3), 1317. https://doi.org/10.3390/ijms23031317.

Armada, D., Celeiro, M., Dagnac, T., Llompart, M., 2022a. Green methodology based on active air sampling followed by solid phase microextraction and gas chromatography-tandem mass spectrometry analysis to determine hazardous substances in different environments related to tire rubber. J.Chromatogr.A 1668, 462911. https://doi.org/10.1016/j.chroma.2022.462911.2022.

Armada, D., Llompart, M., Celeiro, M., Garcia-Castro, P., Ratola, N., Dagnac, T., de Boer, J., 2022b. Global evaluation of the chemical hazard of recycled tire crumb rubber employed on worldwide synthetic turf football pitches. Sci. Total Environ. 812, 152542. https://doi.org/10.1016/j.scitotenv.2021.152542.

Avagyan, R., Sadiktsis, I., Bergvall, C., Westerholm, R., 2014. Tire tread wear particles in ambient air—a previously unknown source of human exposure to the biocide 2-mercaptobenzothiazole. Environ. Sci. Pollut. Res. 21, 11580–11586. https://doi.org/10.1007/s11356-014-3131 (2014).

Babu, R.R., Shibulal, G.S., Chandra, A.K., Naskar, K., 2013. Compounding and vulcanization. In: Visakh, P.M., Thomas, S., Chandra, A.K. (Eds.), Advances in Elastomers I. Blends and Interpenetrating Networks. Springer. ISBN: 978-3-642-20924-6, pp. 83–136.

Baensch-Baltruschat, B., Kocher, B., Stock, F., Reifferscheid, G., 2020. Tyre and road wear particles (TRWP) - a review of generation, properties, emissions, human health risk, ecotoxicity, and fate in the environment. Sci. Total Environ. 733, 137823. https://doi.org/10.1016/j.scitotenv.2020.137823.

Battista, M., Gobetti, A., Agnelli, S., Ramorino, G., 2021. Post-consumer tires as a valuable resource: review of different types of material recovery. Environ. Technol.Rev. 10 (1), 1–25. https://doi.org/10.1080/21622515.2020.1861109.

Bleyer, 2017. Synthetic turf fields, crumb rubber, and alleged cancer risk. Sports Med. 47, 2437–2441. https://doi.org/10.1007/s40279-017-0735-x (2017).

Blum, A., Behl, M., Birnbaum, L., Diamond, M.L., Phillips, A., Singla, V., Sipes, N., Stapleton, H., Venier, M., 2019. Organophosphate ester flame retardants: are they a regrettable substitution for polybrominated diphenyl ethers? Environ. Sci. Technol. Lett. 6 (11), 638–649. https://doi.org/10.1021/acs.estlett.9b00582.

Bocca, B., Forte, G., Petrucci, F., Costantini, S., Izzo, P., 2009. Metals contained and leached from rubber granulates used in synthetic turf areas. Sci. Total Environ. 407 (7), 2183–2190. https://doi.org/10.1016/j.scitotenv.2008.12.026 Epub 2009 Jan 19.

Bowles, A.J., Fowler, G.D., O'Sullivan, C., Parker, K., 2020.. Sustainable rubber recycling from waste tyres by waterjet: a novel mechanistic and analysis. Sustain. Mater. Technol. 25, e00173. https://doi.org/10.1016/j.susmat.2020.e00173 ISSN 2214-9937.

Brandsma, S., Brits, M., Groenewoud, Q., van Velzen, M., Leonards, P., de Boer, J., 2019. Chlorinated paraffins in car tires recycled to rubber granulates and playground tiles. Environ. Sci.Technol. 53, 7595–7603.

Britton, P., 2016. Rubber crumb – is it the new asbestos? https://www.pitchcare.com/news-media/rubber-crumb-is-it-the-new-asbestos.html

Britton, P., 2019. The Rubber Crumb Debate - blinding us with science? Pitchcare.com. https://www.pitchcare.com/news-media/the-rubber-crumb-debate-blinding-us-with-science.html

Brooks, L.A., Tronson, J.L., Rowley, A.C., 1955. Ultra Accelerators in CV Vulcanization. Ft. Belvoir Defense Technical Information Center 32pp.

Brown, D., 2007. Artificial turf: exposures to ground-up rubber tires in athletic fields, gardens, and playgrounds. Environment and Human Health, Inc.. http://www.ehhi.org/turf_report07.pdf.

Burch, L.W., 2020. "Syn-Turf" Industry Pulled the Wool over the Public's Eyes on Crumb Rubber. Clean Water Action. https://www.cleanwateraction.org/2018/01/31/how-%E2%80%9Csyn-turf%E2%80%9D-industry-pulled-wool-over-public%E2%80%99s-eyes-crumb-rubber.

Campbell-Johnston, K., Calisto Friant, M., Thapa, K., Lakerveld, D., Vermeulen, W.J.V., 2020. How circular is your tyre: experiences with extended producer responsibility from a circular economy perspective. J.Clean.Prod. 270, 122042. https://doi.org/10.1016/j.jclepro.2020.122042.

Cao, G., Wang, W., Zhang, J., Wu, P., Zhao, X., Yang, Z., Hu, D., Cai, Z., 2022. New evidence of rubber-derived quinones in water, air, and soil. Environ. Sci.Technol. 56 (7), 4142–4150. https://doi.org/10.1021/acs.est.1c07376.

Celeiro, M., Armada, D., Ratola, N., Thierry, D., de Boer, J., Llompart, M., 2021. Evaluation of chemicals of environmental concern in crumb rubber and water leachates from several types of synthetic turf football pitches. Chemosphere 270, 128610. https://doi.org/10.1016/j.chemosphere.2020.128610.

Claudio, L., 2008. Synthetic turf: health debate takes root. Environ. Health Perspect. 116 (3), A116–A122. https://doi.org/10.1289/ehp.116-a116.

Coste, N., Lemasson, G., Schach, R., 2015. Tyre tread (World Intellectual Property Organization: WO 2015/007575). https://patents.google.com/patent/WO2015007575A1/en.

Dabic-Miletic, S., Simic, V., Karagoz, S., 2021. End-of-life tire management: a critical review. Environ. Sci. Pollut. Res. 28, 68053–68070. https://doi.org/10.1007/s11356-021-16263-6.

de Boer, J., Llompart, M., Massey, R., Dinan, W., Clapp, R., Watterson, A., 2022. Letter to the Editor of Risk Analysis on the de Vries et al. Article (2021) on the Role of the media in communicating about risks linked to crumb rubber. Risk Anal. 41 (12), 2179–2182.

de Vries, M., Claassen, L., Te Wierik, M., Das, E., Mennen, M., Timen, A., Timmermans, D., 2021. The role of the media in the amplification of a contested health risk: rubber granulate on sport fields. Risk Anal. 41 (11), 1987–2002.

Diekmann, A., Giese, U., Schaumann, I., 2019. Polycyclic aromatic hydrocarbons in consumer goods made from recycled rubber material: a review. Chemosphere 220, 1163–1178. https://doi.org/10.1016/j.chemosphere.2018.12.111.

ECHA European Chemicals Agency, 2019. Polycyclic-aromatic hydrocarbons (PAH). ECHA/RAC/RES-O-0000001412-86-279/F. https://echa.europa.eu/documents/10162/0a91bee3-3e2d-ea2d-3e33-9c9e7b9e4ec5.

EPA & CDC/ATSDR, 2019. Synthetic Turf Field Recycled Tire Crumb Rubber Research Under the Federal Research Action Plan Final Report: Part 1 - Tire Crumb Characterization (Volumes 1 and 2). (EPA/600/R-19/051). U.S. Environmental Protection Agency, Centers for Disease Control and Prevention/Agency for Toxic Substances and Disease Registry.

Eykelbosh, A., 2019. Artificial turf: the contributions and limits of toxicology in decision-making. Environ. Health Rev. 62 (4), 106–111. https://doi.org/10.5864/d2019-026.

Fernández-Arribas, J., Moreno, T., Bartrolí, R., Eljarrat, E., 2021. COVID-19 face masks: a new source of human and environmental exposure to organophosphate esters. Environ. Int. 154, 106654. https://doi.org/10.1016/j.envint.2021.106654.

Formela, K., 2021. Sustainable development of waste tires recycling technologies: recent advances, challenges and future trends. Adv.Ind.Eng.Polym.Res. 4 (3), 209–222. https://doi.org/10.1016/j.aiepr.2021.06.004.

Fořt, J., Kobetičová, K., Böhm, M., Podlesný, J., Jelínková, V., Vachtlová, M., Bureš, F., Černý, R., 2022. Environmental consequences of rubber crumb application: soil and water pollution. Polymers (Basel) 30;14 (7), 1416. https://doi.org/10.3390/polym14071416.

Giulivo, G., Capri, E., Eljarrat, E., Barceló, D., 2016. Analysis of organophosphorus flame retardants in environmental and biotic matrices using on-line turbulent flow chromatography-liquid chromatography-tandem mass spectrometry. J.Chromatogr. A 1474, 71–78. https://doi.org/10.1016/j.chroma.2016.10.042.

Gomes, F.O., Rocha, M.R., Alves, A., Ratola, N., 2021. A review of potentially harmful chemicals in crumb rubber used in synthetic football pitches. J. Hazard. Mater. 5 (409), 124998. https://doi.org/10.1016/j.jhazmat.2020.124998.

Graça, C.A.L., Rocha, F., Gomes, F.O., Rocha, M.R., Homem, V., Alves, A., Ratola, N., 2022. Presence of metals and metalloids in crumb rubber used as infill of worldwide synthetic turf pitches: exposure and risk assessment. Chemosphere 299, 134379. https://doi.org/10.1016/j.chemosphere.2022.134379.

Grynkiewicz-Bylina, B., Rakwic, B., Słomka-Słupik, B., 2022. Tests of rubber granules used as artificial turf for football fields in terms of toxicity to human health and the environment. Sci. Rep. 12, 6683. https://doi.org/10.1038/s41598-022-10691-1.

Gujel, A.A., Bandeira, M., Menti, C., Perondi, D., Guégan, R., Roesch-Ely, M., Giovanela, M., Crespo, J.S., 2018. Evaluation of vulcanization nanoactivators with low zinc content: characterization of zinc oxides, cure, physico-mechanical properties, Zn 2+ release in water and cytotoxic effect of EPDM compositions. Polymer Engineering and Science58 (10). Wiley-Blackwell, pp. 1800–1809.

Halsband, C., Sørensen, L., Booth, A.M., Herzke, D., 2020. Car tire crumb rubber: does leaching produce a toxic chemical cocktail in coastal marine systems? Front.Environ. Sci. 8, 125. https://doi.org/10.3389/fenvs.2020.00125.

Heideman, G., Datta, R., Noordermeer, J.W.M., van Baarle, B., 2005. Influence of zinc oxide during different stages of sulfur vulcanization. Elucidated by model compound studies. J. Appl.Polym.Sci. 95 (6), 1388–1404. https://doi.org/10.1002/app.21364.

Heideman, G., Noordermeer, J.W.M., Datta, R., van Baarle, B., 2007. Various ways to reduce zinc oxide levels in S-SBR rubber compounds. Macromol. Symp. 245–246 (1), 657–667. https://doi.org/10.1002/masy.200651393.

Huang, J., Ye, L., Fang, M., Su, G., 2022. Industrial production of organophosphate flame retardants (OPFRs): big knowledge gaps need to be filled? Bull. Environ. Contam. Toxicol. 108, 809–818. https://doi.org/10.1007/s00128-021-03454-7.

Janes, C., Rodriguez, J., Kelly, C., White, T., Beegan, C., 2018. A review of the potential risks associated with chemicals present in poured-in-place rubber surfacing. Environ. Health Rev. 61 (1), 12–16. https://doi.org/10.5864/d2018-001.

Jeong, H., 2022. Toxic metal concentrations and Cu–Zn–Pb isotopic compositions in tires. J. Anal. Sci. Technol. 13, 2. https://doi.org/10.1186/s40543-021-00312-3.

Kung, H.C., Hsieh, Y.K., Huang, B.W., Cheruiyot, N.K., Chang-Chien, G.P., 2022. An overview: organophosphate flame retardants in the atmosphere. Aerosol Air Qual. Res. 22, 220148. https://doi.org/10.4209/aaqr.220148.

Li, R., Wang, H., Mi, C., Feng, C., Zhang, L., Yang, L., Zhou, B., 2019. The adverse effect of TCIPP and TCEP on neurodevelopment of zebrafish embryos/larvae. Chemosphere 220, 811–817. https://doi.org/10.1016/j.chemosphere.2018.12.198.

Llompart, M., Sanchez-Prado, L., Pablo Lamas, J., Garcia-Jares, C., Roca, E., Dagnac, T., 2013. Hazardous organic chemicals in rubber recycled tire playgrounds and pavers. Chemosphere 90 (2), 423–431. https://doi.org/10.1016/j.chemosphere.2012.07.053.

Maciejewska, M., Sowińska, A., Kucharska, J., 2019. Organic zinc salts as pro-ecological activators for sulfur vulcanization of styrene-butadiene rubber. Polymers (Basel) 21;11 (10), 1723. https://doi.org/10.3390/polym11101723.

Makoundou, C., Johansson, K., Wallqvist, V., Sangiorgi, C., 2021. Functionalization of crumb rubber surface for the incorporation into asphalt layers of reduced stiffness: an overview of existing treatment approaches. Recycling 6, 19. https://doi.org/10.3390/recycling6010019.

Markl, E., Lackner, M., 2020. Devulcanization technologies for recycling of tire-derived rubber: a review. Materials 13, 1246. https://doi.org/10.3390/ma13051246.

Marsili, L., Coppola, D., Bianchi, N.P., Maltese, S., Bianchi, M., Fossi, M.C., 2014. Release of polycyclic aromatic hydrocarbons and heavy metals from rubber crumb in synthetic turf fields: preliminary hazard assessment for athletes. J. Environ.Anal.Toxicol. 5, 1–9.

Massey, R., Pollard, L., Jacobs, M., Onasch, J., Harari, J., 2020. Artificial turf infill: a comparative assessment of chemical contents. New Solut. 30 (1), 10–26. https://doi.org/10.1177/1048291120906206.

Menichini, E., Abate, V., Attias, L., De Luca, S., di Domenico, A., Fochi, I., Forte, G., Iacovella, N., Iamiceli, A.L., Izzo, P., Merli, F., Bocca, B., 2011. Artificial-turf playing fields: contents of metals, PAHs, PCBs, PCDDs and PCDFs, inhalation exposure to PAHs and related preliminary risk assessment. Sci. Total Environ. 1;409 (23), 4950–4957. https://doi.org/10.1016/j.scitotenv.2011.07.042.

Moreno, T., Querol, X., Alastuey, A., Gibbons, W., 2008a. Identification of FCC refinery atmospheric pollution events using lanthanoid- and vanadium-bearing aerosols. Atmos. Environ. 42, 7851–7861. https://doi.org/10.1016/j.atmosenv.2008.07.013.

Moreno, T., Querol, X., Alastuey, A., Pey, J., Minguillón, M.C., Pérez, N., Bernabé, R., Blanco, S., Cárdenas, B., Gibbons, W., 2008b. Lanthanoid geochemistry of urban atmospheric particulate matter. Environ. Sci. Technol. 42 (17), 6502–6507.

Mostoni, S., Milana, P., Di Credico, B., D'Arienzo, M., Scotti, R., 2019. Zinc-based curing activators: new trends for reducing zinc content in rubber vulcanization process. Catalysts 9, 664. https://doi.org/10.3390/catal9080664.

Patisaul, H.B., Behl, M., Birnbaum, L.S., Blum, A., Diamond, M.L., Rojello Fernández, S., Hogberg, H.T., Kwiatkowski, C.F., Page, J.D., Soehl, A., Stapleton, H.M., 2021. Beyond cholinesterase inhibition: developmental neurotoxicity of organophosphate ester flame retardants and plasticizers. Environ. Health Perspect. 129 (10), 105001. https://doi.org/10.1289/EHP9285.

Pelletier, G., Rigden, M., Wang, G.S., Caldwell, D., Siddique, S., Leingartner, K., Kosarac, I., Cakmak, S., Kubwabo, C., 2020. Comparison of tris(2-ethylhexyl) phosphate and di(2-ethylhexyl) phosphoric acid toxicities in a rat 28-day oral exposure study. J. Appl. Toxicol. 40 (5), 600–618. https://doi.org/10.1002/jat.3930.

Perkins, A., Inayat-Hussain, S., Deziel, N., Johnson, C., Ferguson, S., Garcia-Milian, R., Thompson, D., Vasiliou, V., 2019. Evaluation of potential carcinogenicity of organic chemicals in synthetic turf crumb rubber. Environ. Res. 169, 163–172.

Peterson, M.K., Lemay, J.C., Pacheco Shubin, S., Prueitt, R.L., 2018. Comprehensive multipathway risk assessment of chemicals associated with recycled ("crumb") rubber in synthetic turf fields. Environ. Res. 160, 256–268.

Plesser, T., Lund, O., 2004. Potential health and environmental effects linked to artificial turf systems - final report. Report from the Norwegian Building Research Institute. Available online https://www.knvb.nl/downloads/bestand/7065/noorwegen-2004–potential-health-and-environmental-effects-linked-to-artificial-turf-systems.

Pronk, M.E.J., Woutersen, M., Herremans, J.M.M., 2020. Synthetic turf pitches with rubber granulate infill: are there health risks for people playing sports on such pitches? J. Expo. Sci. Environ. Epidemiol. 30 (3), 567–584. https://doi.org/10.1038/s41370-018-0106-1.

Querol, X., Fernandez Turiel, J.L., Lopez Soler, A., Duran, M.E., 1992. Trace elements in high-S subbituminous coals from the Teruel Mining District, Northeast Spain. Appl. Geochem. 7, 547–561. https://doi.org/10.1016/0883-2927(92)90070-J.

Querol, X., Whateley, M.K.G., Fernández-Turiel, J.L., Tuncali, E., 1997. Geological controls on the mineralgy and geochemistry of the Beypazari lignite, central Anatolia, Turkey. Int. J. Coal Geol. 33, 255–271. https://doi.org/10.1016/S0166-5162(96)00044-4.

Rijksinstituut voor Volksgezondheid en Milieu (RIVM), 2017. Evaluation of health risks of playing sports on synthetic tuf pitches with rubber granulate: scientific background document. Report No.: 2017-0017. Available at:National Institute for Public Health and the Environment (RIVM), Netherlands. https://www.rivm.nl/bibliotheek/rapporten/2017-0017.pdf.

Sala, B., Giménez, J., Fernández-Arribas, J., Bravo, C., Lloret-Lloret, E., Esteban, A., Bellido, J.M., Coll, M., Eljarrat, E., 2022. Organophosphate ester plasticizers in edible fish from the Mediterranean Sea: marine pollution and human exposure. Environ. Pollut. (ISSN: 0269-7491) 292 (Part B), 118377. https://doi.org/10.1016/j.envpol.2021.118377.

Schneider, K., Bierwisch, A., Kaiser, E., 2020. ERASSTRI - European risk assessment study on synthetic turf rubber infill - part 3: exposure and risk characterisation. Sci. Total Environ. 718, 137721. https://doi.org/10.1016/j.scitotenv.2020.137721.

Shokrzadeh, A., Naderi, G., Esmizadeh, E., 2014. Mechanical and rheological properties of calcium carbonate-filled ethylene propylene diene elastomer reinforced by metallic acrylate salt. Fibers Polym. 15 (8), 1691–1700. https://doi.org/10.1007/s12221-014-1694-6.

Skoczyńska, E., Leonards, P.E.G., Llompart, M., de Boer, J., 2021. Analysis of recycled rubber: development of an analytical method and determination of polycyclic aromatic hydrocarbons and heterocyclic aromatic compounds in rubber matrices. Chemosphere 276, 1–10. https://doi.org/10.1016/j.chemosphere.2021.130076 [130076].

TCGR (The Catalyst Group Resources), 2018. Catalysts and processes for the rubber & elastomer industries: technology advances and commercial/strategic implications. https://www.catalystgrp.com/wp-content/uploads/2018/05/PROP-Catalysts-and-Processes-for-The-Rubber-Elastomer-Industries.pdf.

USEPA, 2022. Regional screening levels (RSLs) - Generic Tables. https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables.

Valentini, F., Pegoretti, A., 2022. End-of-life options of tyres. A review. Adv.Ind.Eng.Polym. Res. 5, 203–213.

Verschoor, A.J., van Gelderen, A., Hofstra, U., 2021. Fate of recycled tyre granulate used on artificial turf. Environ. Sci. Eur. 33, 27. https://doi.org/10.1186/s12302-021-00459-1.

Walter, J., 2014. Tire material effects. Tire Technology International. https://www.tiretechnologyinternational.com/opinion/tire-material-effects.html.

Wang, Z.-H., Lu, Y.-H., Liu, J., Dang, Z.-M., Zhang, L.-Q., Wang, W., 2011. Preparation of nanoalumina/EPDM composites with good performance in thermal conductivity and mechanical properties. Polym. Adv. Technol. 22 (12). https://doi.org/10.1002/pat.1761.

Watterson, A., 2017. Artificial turf: contested terrains for precautionary public health with particular reference to Europe? Int. J. Environ. Res. Public Health 12;14 (9), 1050. https://doi.org/10.3390/ijerph14091050.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta 59, 1217–1232.

Wypych, G., 2016. Fillers – origin, chemical composition, properties and morphology. Handbook of Fillers, Fourth edition ChemTec Publishing. ISBN: 978-1-895198-91-1, pp. 13–266.

Xie, Z., Wang, P., Wang, X., Castro-Jiménez, J., Kallenborn, R., Liao, C., Mi, W., Lohmann, R., Vila-Costa, M., Dachs, J., 2022. Organophosphate ester pollution in the oceans. Nat. Rev. Earth Environ. 3, 309–322. https://doi.org/10.1038/s43017-022-00277-w.

Zedler, Ł., Wang, S., Formela, K., 2022. Ground tire rubber functionalization as a promising approach for the production of sustainable adsorbents of environmental pollutants. Sci. Total Environ. 836, 155636. https://doi.org/10.1016/j.scitotenv.2022.155636.

Zuccaro, P., Thompson, D., de Boer, J., Watterson, A., Wang, Q., Tang, S., Shi, X., Llompart, M., Ratola, N., Vasiliou, V., 2022. Artificial turf and crumb rubber infill: an international policy review concerning the current state of regulations. Environ.Chall. 9. https://doi.org/10.1016/j.envc.2022.100620.