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

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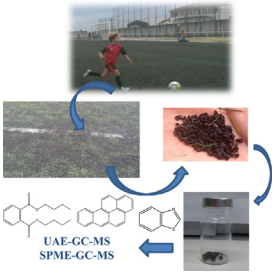
## HIGHLIGHTS

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

## GRAPHICAL ABSTRACT

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## ABSTRACT

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

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

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

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



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## 1. Introduction

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

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

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

Nevertheless, regarding sport surfaces of synthetic turf, such as football fields, specific studies dealing with the composition of the crumb rubber are scarce. Most studies have focused on the human health risk associated with synthetic turf fields (Ginsberg et al., 2011a, 2011b; Menichini et al., 2011), and just few references related to the presence of trace metals, semi-volatiles and volatiles organic compounds (SVOCs and VOCs) or PAHs could be found (Marsili et al., 2015). The bioaccessibility of several organic compounds and metals in different human fluids has also been reported (Han et al., 2008; Pavilonis et al., 2014), including dermal absorption, inhalation or even direct ingestion of the rubber crumb. The presence of a biological exposure marker to PAHs, 1-hydroxypyrene, was detected in human urine after playing over the synthetic turf surface (van Rooij and Jongeneelen, 2010).

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

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

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

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

## 2. Experimental

### 2.1. Reagents and materials

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

Ethyl acetate, methanol and acetone were provided by Sigma-