Chemosphere 90 (2013) 423–431

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Hazardous organic chemicals in rubber recycled tire playgrounds and pavers

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HIGHLIGHTS

- A large number of recycled tire playgrounds and commercial pavers have been analysed.
- The occurrence of numerous harmful compounds at high levels was confirmed.
- Thirty-one targets (PAHs, vulcanisation additives, antioxidants, plasticizers) were selected.
- Total PAH concentration was remarkable. Contribution of B[a]P must be highlighted.
- Target analytes were detected in the headspace SPME experiments at room temperature.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 23 April 2012
Received in revised form 20 July 2012
Accepted 25 July 2012
Available online 22 August 2012

Keywords:
Scrap tires
Recycled rubber
Playgrounds
Polycyclic aromatic hydrocarbons (PAHs)
Plasticizers
Benzothiazole

ABSTRACT

In this study, the presence of hazardous organic chemicals in surfaces containing recycled rubber tires is investigated. Direct material analyses using solvent extraction, as well as SPME analysis of the vapour phase above the sample, were carried out. Twenty-one rubber mulch samples were collected from nine different playgrounds. In addition, seven commercial samples of recycled rubber pavers were acquired in a local store of a multinational company. All samples were extracted by ultrasound energy, followed by analysis of the extract by GC–MS. The analysis confirmed the presence of a large number of hazardous substances including PAHs, phthalates, antioxidants (e.g. BHT, phenols), benzothiazole and derivatives, among other chemicals. The study evidences the high content of toxic chemicals in these recycled materials. The concentration of PAHs in the commercial pavers was extremely high, reaching values up to 1%. In addition, SPME studies of the vapour phase above the samples confirm the volatilisation of many of those organic compounds. Uses of recycled rubber tires, especially those targeting play areas and other facilities for children, should be a matter of regulatory concern.

1. Introduction

Disposal of used tires has been a major problem in soil waste management (Birkholz et al., 2003; Lee and Yoo, 2011). The indestructible nature of discarded tires makes them persist in the environment indefinitely, creating long-lasting piles of toxic, synthetic waste.

Tire wastes have been valorised for energy recovery through different processes as scrap tyres have a comparable energy value to coal. Gasification, pyrolysis, plasma or combustion in cement kilns are the main examples of these technologies (Huang and

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http://dx.doi.org/10.1016/j.chemosphere.2012.07.053

Tang, 2007; Huang et al., 2007). Furthermore, used tires have also been applied as raw material for the production of asphalt or other pavements applications in road construction (Kumaran et al., 2008). Although technically viable, in this case it needs to be subsidised to be competitive with conventional aggregates for asphalt pavements (Huang et al., 2007).

Today, one of the most valuable applications of used tires is the transformation in recycling products such as rubber mulch and recycled rubber pavers that are used for sidewalks, animal flooring, fitness centre flooring, playground surface, and sport fields.

Rubber mulch is a product that consists of granular rubber particles. It is available in array of lively colours and it is extensively used in playgrounds along the world. The number of this kind of playground flooring is significantly increasing in the last years. This material constitutes a slip resistant, cushioned floor that prevents injuries in sporting activities and playgrounds and it is a visually attractive choice.

Nevertheless, and although few investigations of the organic content of tires have been reported, it is well known that rubber tire debris contains toxic compounds such as highly aromatic oils and other reactive additives (Zhang et al., 2008; Kanematsu et al., 2009; Aatmeeyata, 2010; van Rooij and Jongeneelen, 2010). Tire rubber is composed of 40–60% rubber polymer, reinforcing agents such as carbon black (20–35%), aromatic extender oil (up to 28%), vulcanisation additives, antioxidants, antiozonants, and processing aids (plasticizers and softeners) (Wik and Dave, 2008; Li et al., 2010). One of the main components of extender oil is highly aromatic oil, which contains polycyclic aromatic hydrocarbons (PAHs) in the range of 300–700 mg kg^{-1} (Aatmeeyata, 2010). In this sense, the accessibility of heavy metals and organic chemicals originated from reused tire rubber must be a subject of concern.

Several studies about the chemical risk toxicity of tire rubber recycled products have been conducted (Birkholz et al., 2003; Plesser and Lund, 2004; Anderson et al., 2006; Crain and Zhang, 2006; Roels, 2006; Mattina et al., 2007; Moretto, 2007; RAMP, 2007; Kanematsu et al., 2009; Li et al., 2010). Most previous works have focused on the toxic chemicals in the leachate of tire rubber material whereas direct studies about the chemical composition of ground rubber products are scarce. Nevertheless, the chemical exposure pathways, especially in the case of infants, can include dermal absorption, inhalation, and even ingestion, directly from the material.

An interesting research on the presence of hazardous chemicals in synthetic turf material from recycled tires concludes that PAH levels are above health-based soil standards (Zhang et al., 2008). Previously, a study conducted by the Norwegian Building Research Institute had concluded that the total concentration of PAH in the recycled rubber granulates exceeded the Norwegian Pollution Control Authority's normative values for most sensitive land use (Plesser and Lund, 2004).

A recent study dealing with the characterisation of substances released from crumb rubber material of artificial turf fields implemented solid-phase microextraction (SPME) to obtain vapour phase composition profiles. Ten organic compounds were detected in the vapour phase over all commercial tested samples, including benzothiazole, antioxidants and three PAHs (Li et al., 2010).

The objective of the present study is to investigate the presence of hazardous organic chemicals in recycled tire playground surfaces. With this purpose, direct material analysis, using solvent extraction, as well as SPME analysis of the vapour phase above the sample will be conducted.

2. Material and methods

2.1. Reagents and material

The studied compounds, their chemical names and CAS numbers are summarised in Table 1. Ethyl acetate and acetone (analytical grade) were provided by Sigma–Aldrich (Steinheim, Germany). Sand (50–70 mesh particle size) was purchased from Sigma–Aldrich. The SPME manual holders and 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibres were supplied by Supelco (Bellefonte, PA, USA). Prior to first use, fibres were conditioned as recommended by the manufacturer. Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA).

Individual stock solutions of each compound were prepared in acetone. Further dilutions and mixtures were prepared in ethyl acetate and then stored in amber glass vials at −20 °C.

2.2. Sampling and sample treatment

Seventeen samples from nine different urban playgrounds in Northwest of Spain have been manually collected and immediately placed into clean glass bottles and tightly capped. The samples consisted of two different types of ground covers of diverse colours: floor tiles compositions and carpet covers. In some cases (in 4 of them), the coloured upper part of the tiles or the carpets was attached to a black base, which was also sampled and analysed. These samples were washed with Milli-Q water to remove particles of soil or dust and dried overnight at room temperature.

Seven commercial samples were acquired in a local store of a multinational company. Two of them were puzzle pavers while the rest were recycled rubber tire tiles of different colours. Two of the floor tiles had a black base, which was also analysed. The upper part of the samples was constituted by smaller grains highly compacted whereas the black base was in all cases formed by bigger grains with a lower compaction degree. All samples were cut into small particles (around 0.3 cm of diameter) and stored in clean glass vials.

2.3. Ultrasound-assisted extraction (UAE)

Five millilitres of ethyl acetate was added to a 10-mL glass vial containing 500 mg of sample, and sealed with a headspace aluminium cap furnished with PTFE-faced septum. The analytes were extracted from the samples to the organic solvent using ultrasonic energy (J.P. Selecta ultrasound bath, Barcelona, Spain) at 40 kHz frequency and 110 W power, for 15 min. Afterwards, the supernatant was filtered through 0.45 μm Uptidiscs™ PTFE filters (25 mm diameter) (Interchim, Montluçon, F). When it was convenient, extracts were diluted prior to the injection in the chromatographic system.

2.4. Pressurised solvent extraction (PSE)

Extractions were performed on an ASE 150 (Dionex, Co., Sunyvale, CA, USA), equipped with 10-mL stainless steel cells and 60-mL collection vials. One cellulose filter (Dionex) was placed at each end of the PSE cell. 500 mg of sample was introduced into the cell, where 1 g of clean sand was previously placed. Finally, the dead volume of the cell was filled up with sand. The cell was tightly closed and placed into the PSE system.

Extractions were performed by preheating the cell before filling with solvent (preheat method). The extraction pressure was set at 1700 psi, the flush volume was 60% and the purge time was 60 s.