Environmental risk analysis procedure applied to artificial turf sports fields

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RESEARCH ARTICLE

Environmental–sanitary risk analysis procedure applied to artificial turf sports fields

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Abstract Owing to the extensive use of artificial turfs worldwide, over the past 10 years there has been much discussion about the possible health and environmental problems originating from styrene-butadiene recycled rubber. In this paper, the authors performed a Tier 2 environmental–sanitary risk analysis on five artificial turf sports fields located in the city of Turin (Italy) with the aid of RISC4 software. Two receptors (adult player and child player) and three routes of exposure (direct contact with crumb rubber, contact with rainwater soaking the rubber mat, inhalation of dusts and gases from the artificial turf fields) were considered in the conceptual model. For all the fields and for all the routes, the cumulative carcinogenic risk proved to be lower than 10^{-6} and the cumulative non-carcinogenic risk lower than 1. The outdoor inhalation of dusts and gases was the main route of exposure for both carcinogenic and non-carcinogenic substances. The results given by the inhalation pathway were compared with those of a risk assessment carried out on citizens breathing gases and dusts from traffic emissions every day in Turin. For both classes of substances and for both receptors, the inhalation of atmospheric dusts and gases from vehicular traffic gave risk values of one order of magnitude higher than those due to playing soccer on an artificial field.

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Introduction

In recent years, the use of artificial turfs, man-made surfaces manufactured from synthetic materials designed to look like natural grass, has become increasingly popular because fake grass is more resistant to heavy use, such as sports, than natural grass and requires no irrigation or trimming. An artificial turf is made of a mat of fibers filled with small rubber granules or a mixture of rubber granules and sand, to a depth of about 4 cm. The granules currently used in mat layers are made of rubber from exhaust tires (styrene-butadiene recycled rubber (SBRr)). Due to the manufacturing process of tires, several compounds, like vulcanizing agents, accelerators, activators, anti-ozonants, antioxidants, retarders, plasticizers and extenders are present in crumb rubber, as well as various chemicals such as benzene, phthalates, and alkylphenols that may become bonded to tires during use (Denly et al. 2008). Owing to the extensive use of artificial turfs in Europe and North America, over the past 10 years there has been much discussion about the possible health and environmental problems originating from SBRr.

In Europe, the debate arose on the back of a Norwegian study (Plesser and Lund 2004) that analyzed the total content of As, Pb, Cd, Cu, Cr, Hg, PCBs, PAHs, phthalates, and phenols in three SBRr samples and in one presumably not recycled product made of ethylene propylene diene monomer and carried out leaching and degassing tests. Finally, an assessment of the potential risk was performed in a simplified version, comparing the total content of environmentally harmful substances in the source materials to the permitted values for use in the most sensitive areas (gardens, kindergartens, schools). The authors of the study concluded that a

more detailed evaluation and further tests were required to determine whether there is a real risk for the environment and human health. On the other hand, a report published by the Swedish Chemicals Inspectorate (KemI 2006) supported the concern that the use of artificial turf pitches could have an adverse effect on the environment and the health of their users due to the leaching of chemical substances into the soil and water.

Following these reports, several studies have been carried out to enhance knowledge regarding the amount and the types of chemicals in recycled tires (Nilsson et al. 2005; Zhang et al. 2008; Beausoleil et al. 2009; Bocca et al. 2009; EPA 2009; Wik and Dave 2009; Menichini et al. 2011; Sadiktsis et al. 2012), their potential to leach (Birkholz et al. 2003; Nilsson et al. 2005; Verschoor 2007; Bocca et al. 2009; EPA 2009; Lim and Walker 2009; Li et al. 2010) and degas (NILU 2006; Beausoleil et al. 2009; EPA 2009; Lim and Walker 2009; Li et al. 2010), and the subsequent risk to the environment and human health. Concerning the risk to human health, the potential exposure to chemicals in crumb rubber could occur through several pathways. Quite a few researchers focused their attention on dermal contact (Nilsson et al. 2005, 2008; NIPH 2006; CalEPA 2007; Ledoux 2007) and inhalation of particulates and off-gassing volatile organic compounds (VOCs) from rubber (NIPH 2006; Moretto 2007; Nilsson et al. 2008; Menichini et al. 2011). The aforementioned studies followed very different procedures in their characterization of the rubber materials and the assessment of risk. However, each of these publications indicated that the health risk from playing on synthetic turf fields was minimal despite the leaching and volatilization of chemicals from tire granules.

In this work, the authors characterized five samples of crumb rubber and one sample of natural soil from sports facilities, and assessed their capacity to release chemicals on contact with water. The components of the gases and dusts collected from the air just above the sport facilities and from a point located in the centre of the city of Turin were also determined.

Finally, an environmental–sanitary risk assessment was carried out with the aid of the Risk Integrated Software for Clean-ups (RISC4) software (Spence and Walden 2001), in order to evaluate if the rubber granules in artificial turf fields may pose a health risk to child and adult players via direct contact with the infill material, contact with rainwater soaking the rubber mat or inhalation of dusts and gases released from the pitch. The environmental exposure models were developed in an effort to quantify the human exposure to chemicals via contact with the surrounding natural environment. In the international context, the procedure of environmental–sanitary risk assessment has assumed a central role in the management of contaminated sites, mainly with reference to emerging pollutants (Jin et al. 2012; Stasinakis et al. 2012), but the same procedure can be successfully applied to other fields of interest, like foods and toys (Leber 2001; Walden 2005; Fryer et al. 2006; Hang et al. 2009).

Materials and methods

Sample overview

The present study deals with six sports turf fields located in the city of Turin. Barracuda (B), Carrara (C), Pellerina Gomma (PG) and River Mosso (RM) are artificial turf fields whose infill is made of SBRr from shredded tires. C and B are 1.5 years old, PG and RM are 3 years old, respectively. Passo Buole (PB) is a 3-year-old artificial turf field whose infill is made of a thermoplastic elastomer (TPE) specifically produced for turf field applications. Pellerina Terra (PT) is a natural turf field.

For each sporting field, a 1,200-g sample of the infill material was collected using an Electrolux extractor fan at 12 different positions in the playing area (Bocca et al. 2009). Natural soil (1 kg) from the PT field was also collected and used as a blank sample.

Both rubber and soil samples underwent a physical and chemical characterization involving a particle size distribution analysis and the determination of benzene, toluene, xylenes (BTX), PAHs (B(a)A, benz(a)anthracene; B(b)F, benzo(b)fluoranthene; B(k)F, benzo(k)fluoranthene; B(a)P, benzo(a)pyrene; B(g,h,i)P, benzo(g,h,i)perylene; CHR, chrysene; D(a,h)A, dibenz(a,h)anthracene; PYR, pyrene) and metals (Na, K, Ca, Mg, Fe, Mn, Cd, Cu, Ni, Zn, Pb, Ti, Ba, Al, Co, Cr, Sn, As). Rubber and soil samples were subjected to a leaching test, according to the EN 12457/2 compliance test.

Samples of gases and dusts were collected immediately above the ground, close to the sports fields and in a point in the centre of the city, and underwent the determination of BTX (gases) and PAHs (dusts). The samples of gases and dusts from the centre of the city were collected and analysed in order to evaluate the influence of vehicle-emitted contaminants on the composition of dusts and gases from the sporting fields.

Analytical methods

The particle size distribution analysis was performed using Tyler Standard sieves (48, 28, 20, 14, 10, 8 and 6 Tyler meshes for crumb rubber samples and 400, 200, 100, 48, 28, 14, 8 and 4 Tyler meshes for the natural soil sample).

For the determination of BTX and PAHs, crumb rubber and natural soil (three replicates for each sample) underwent a microwave-assisted extraction (MAE, 2-g sample, 20 mL of dichloromethane–Supelco, pesticide grade, 20 min, 600 W,

Milestone 1200 Mega) followed by gas-chromatograph analysis using an Agilent GCD 1800C GC-MS.

For BTX analysis, the GC-MS was equipped with a J&W DB624 capillary column (30 m×0.25 mm×1.4 μm). The initial column temperature was 46 °C for 4 min, and the temperature was risen to 95 °C at a rate of 3 °C/min and then maintained at 95 °C for 1 min. Three replicates (max standard deviation 5 %) of each extract (5 μL) were injected in splitless mode with a solvent delay of 1.80 min. The mass spectrometer was operated in SIM mode, and helium was used as a carrier gas in a constant flow mode. The injector temperature was 200 °C while that of the detector was 230 °C. Calibration curves for each compound were obtained by injecting standard solutions at eight different concentration values, with three replicates for each concentration value, prepared in dichloromethane by weighing from Supelco EPA VOC mix (2,000 μg/mL) and stored at −20 °C until use. Different calibration curves ($0.9935<R^2<0.9996$), referred to specific concentration intervals, were considered depending on the signal given by the samples. A working standard (1 μg/L) in dichloromethane was prepared daily. The method had a detection limit of 0.001 μg/L for each of the three analysed compounds.

For PAH analysis, the GC-MS was equipped with an HP5-MS capillary column (30 m×0.25 mm×0.25 μm). The initial column temperature was 60 °C for 4 min, and the temperature was risen to 280 °C at a rate of 10 °C/min and then maintained at 280 °C for 10 min. Three replicates (max standard deviation 4 %) of each extract (5 μL) were injected in splitless mode with a solvent delay of 3 min. The mass spectrometer was operated in SIM mode, and helium was used as a carrier gas in a constant flow rate mode. The injector temperature was 250 °C while that of the detector was 240 °C. Calibration curves ($0.9886<R^2<0.9997$) for each compound were obtained by injecting standard solutions at 12 different concentration values prepared in dichloromethane by weighing from Supelco TCL PAH mix (2,000 μg/mL) and stored at −20 °C until use. A working standard (1 μg/L) in dichloromethane was prepared daily. The method had a detection limit of 0.001 μg/L for each of the eight analysed compounds.

Metal content was determined using an MAE in a Milestone 1200 Mega following two different procedures depending on the sample material (three replicates for each samples)—for rubber: 0.10 g, 3 mL HNO_3 (65 %, Riedel de Haen, Sigma Aldrich) and 1 mL $HClO_4$ (70 %, Merck); for natural soil: 0.25 g, first digestion stage 2.5 mL H_2SO_4 (95–97 %, Riedel de Haen, Sigma Aldrich) and 2.5 mL H_3PO_4 (85 %, Merck), second digestion stage 5 mL HF (48 %, Merck). All the digested solutions were filtered through Whatman 542 filters, brought to a 100-mL final volume and analysed using a Perkin Elmer Optima 2000 ICP-OES. The detection limits for the metals analysed are shown in Table 1, and the maximum standard deviation was always lower than 3 %.

Determination of in-water extractable compounds (BTX, PAHs, metals) was performed according to the EN 12457/2 compliance test (deionized water, one stage, stirred, 24 h, room temperature batch test at a liquid–solid ratio of 10 L/kg for materials with particle sizes below 4 mm). The extracts obtained were filtered through Whatman 0.45-micron membranes.

BTX in the leachates were determined using a static headspace technique (procedure: 5 mL of filtered leachate and 1 g NaCl in a 10-mL sealed headspace vial warmed for 30 min at 60 °C). The static headspace technique was followed for both samples and standard solutions so as to obtain the same recovery value. BTX were analysed using the Agilent GCD 1800C GC-MS following the previously described method by injecting 200 μL of headspace (solvent delay 1.80 min).

A solid phase extraction (SPE) by means of ENVI-18 tubes (Supelco, 3 mL×0.5 g; procedure: conditioning with 2 mL methanol–Supelco, pesticide grade, and 2 mL deionized water, loading of 300 mL of aqueous samples, elution with two 1.5 mL aliquots of dichloromethane, Supelco, pesticide grade), was used to concentrate PAHs by transferring them from water to CH_2Cl_2. SPE procedure was followed for both samples and standard solutions so as to obtain the same recovery value. The final extracts (5 μL) were injected into the Agilent GCD 1800C GC-MS following the method described for PAH analysis.

A Perkin Elmer Optima 2000 ICP-OES was used for the quantification of metals in the eluate. The detection limits for the metals analysed are shown in Table 1, and the maximum standard deviation was always lower than 3 %.

Anions (chloride, sulfate, nitrates and fluoride) and the chemical oxygen demand content were determined according to standard methods (APHA, AWWA, WEF 2005).

BTX in the outdoor air and PAHs in the dust samples were sampled and analysed by the researchers from the Group of General and Applied Hygiene, University of Turin, according to the methods described in Gilli et al. (2007).

Risk analysis

A risk assessment was carried out through the steps described in the "Site conceptual model" section, "Determination of the concentration values at the point of exposure" section and "Risk quantification" section.

Site conceptual model

The site conceptual model involves the sources of contamination, the migration pathways (also called routes of exposition) and the receptors.

Q3 **Table 1** Concentration of BTX, PAHs, metals and anions in the eluates obtained according to the EN 12457/2 compliance test on the samples of rubber granules and natural soil

		B	C	PB	PG	RM	PT	DL
B	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
	.2.70	1.56	1.15	2.70	2.08	2.56		
T	µg/L	0.43	0.41	0.18	0.29	0.33	0.25	0.001
	.1.09	1.51	1.27	0.723	0.735	681		
X	µg/L	0.36	0.42	0.36	0.45	0.34	0.37	0.001
	.0.477	0.577	1.45	0.462	0.499	8.01		
PYR	µg/L	0.05	0.06	0.07	0.03	0.03	<0.001	0.001
	.2.21E-03	2.32E-03	1.99E-02	1.40E-03	1.50E-03	1.67E-02		
B(a)A	µg/L	<0.001	0.01	0.05	<0.001	<0.001	<0.001	0.001
	.2.12E-04	8.93E-04	2.50E-02	6.54E-05	1.05E-04	3.57E-03		
CHR	µg/L	<0.001	0.04	0.02	<0.001	<0.001	<0.001	0.001
	.6.45E-04	9.50E-03	2.06E-02	3.13E-04	6.94E-04	1.43E-02		
B(b)F	µg/L	<0.001	0.02	<0.001	0.04	<0.001	<0.001	0.001
	.5.46E-04	4.58E-03	2.89E-04	4.54E-03	ND	1.47E-03		
B(k)F	µg/L	<0.001	0.02	0.04	<0.001	<0.001	<0.001	0.001
	.ND	8.23E-03	1.00E-02	1.99E-04	ND	1.96E-03		
B(a)P	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
	.8.70E-04	7.09E-04	3.91E-04	7.94E-04	ND	3.57E-03		
D(a,h)A	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
	.9.80E-04	1.23E-04	1.22E-03	2.49E-04	1.39E-03	1.37E-03		
B(g,h,i)P	µg/L	0.04	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
	%	2.06E-02	2.40E-04	1.15E-03	4.37E-04	5.88E-04	1.19E-03	
As	µg/L	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	5.3
	%	ND	ND	ND	ND	ND	ND	
Co	µg/L	11.9	12.5	4.80	9.41	9.03	3.30	0.60
	.0.103	0.116	0.085	0.075	0.093	0.458		
Cr	µg/L	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	0.71
	%	ND	ND	ND	ND	ND	1.51E-03	
Ni	µg/L	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	1.5
	.ND	ND	ND	ND	ND	ND		
Pb	µg/L	<4.2	<4.2	<4.2	<4.2	<4.2	<4.2	4.2
	.0.014	0.112	0.122	0.210	0.213	0.042		
Sn	µg/L	34.5	25.3	21.2	<9.6	47.7	<9.6	9.6
	%	0.265	0.074	9.42E-03	0.014	0.122	1.33E-03	
Zn	µg/L	1,143	1,525	452	1,530	2,729	<0.18	0.18
	%	0.075	0.122	0.078	0.122	0.224	3.55E-03	
Al	µg/L	11.0	39.8	82.0	10.4	7.97	30.5	2.8
Ba	µg/L	10.9	12.4	88.7	21.3	15.4	<0.13	0.13
Cd	µg/L	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	0.25
Cu	µg/L	16.4	10.5	10.2	6.62	22.1	3.80	0.54
Fe	µg/L	18.3	53.9	25.2	27.4	38.2	68.4	0.46
Mn	µg/L	12.3	29.8	17.2	22.9	42.4	4.37	0.14
Ti	µg/L	1.48	2.88	2.49	0.848	2.28	1.39	0.38
NO_3^-	mg/L	2.24	<0.1	1.50	0.45	2.47	2.84	0.05
F^-	mg/L	<0.1	< 0.1	<0.1	<0.1	<0.1	<0.1	0.05
$SO_4^=$	mg/L	3.98	8.97	3.54	5.36	6.40	19.3	0.5
Cl^-	mg/L	0.735	1.18	0.602	0.847	2.25	2.06	0.05
COD	mg/L	59.4	63.6	50.2	70.2	52.6	22.3	0.5
pH		6.63	6.63	7.36	6.51	6.41	9.86	
CE	µS/cm	71	97	145	68	83	330	

For the compounds involved in the risk analysis the percent accessibility was also calculated

DL detection limit for the determination of each species, *ND* impossible to calculate (both values involved in the percent accessibility calculation were below the detection limits)

Q4 The receptors were adults and children who usually play on the turf. The sources of contamination were the rubber granules from the artificial turf fields and the natural soil used as a reference material. The chemicals of concern (COCs) involved in the risk assessment were: benzene, toluene, xylene, pyrene, B(a)A, B(a)P, B(b)F, B(k)F, B(g,h,i)P, chrysene, D(a,h)A, lead, cobalt, tin and zinc for rubber materials and the soil sample, and arsenic, nickel and chromium for the soil sample only.

Among the possible routes, in this work only dermal contact with the infill material (direct dermal contact (DDC)), dermal contact with the rainwater soaking the infill (rain water contact (RWC)) and inhalation of dusts and gases from the fields (dust and gas inhalation (DGI)) were taken into account. The exposure to contaminants in crumb rubber through ingestion was not evaluated because it was assumed that the potential of this route is greater for little children than older children and adults owing to the mouthing of their hands or objects. Older children and adults using artificial turfs can reasonably be expected to get some inadvertent/unintentional oral exposure to crumb rubber from dusts generated in the routine use of these facilities whose extent may be deemed negligible (Denly et al. 2008).

For each route, a Tier 2 risk assessment was performed. The results from the scenario "outdoor inhalation of dusts and gases from a turf field" were compared with the outcomes of the risk analysis performed on the same route on both adults and children living in the centre of Turin. The latter receptors are exposed for 6 h a day and for 350 days a year to outdoor dusts and gases from traffic and domestic combustion.

Determination of the concentration values at the point of exposure

For the DDC route, the COC concentration at the point of exposure was equal to the amount of chemicals (BTX, PAHs and metals) in the rubber granules or soil shown in Table 2.

For the RWC route, the COC concentration at the point of exposure was calculated by way of the hypothesis that the EN 12457/2 elution test was able to extract the whole leachable amount of each COC from the rubber granules (see Table 1), simulating the transfer into rainwater. Since a risk assessment has to be performed under conservative conditions, the solid/liquid ratio between crumb rubber and the rainwater soaking the rubber granule layer during rainfall was set at 1:2, meaning that the leachable amount of each COC is dissolved in a volume equal to 1/5 of the elution test volume. This hypothesis is conservative because the release of COCs on contact with water decreases as the solid/liquid ratio increases (from 1:10 in test EN 12457/2 to 1:2 in the real case). The ratio of 1:2 came from the remarks about rainfall amounts and artificial turf field constructive features here reported. The daily average rainfall value over the last 10 years in Turin has been 11.7 mm/day (data from ARPA–Agenzia Regionale per la Protezione dell'Ambiente - Piemonte). According to the guidelines for the construction of artificial turfs (The Football Association 2005), from bottom to top, an artificial turf field is made of a 10-mm silica sand layer, with a porosity of 0.4 and a 10-mm crumb rubber layer with a porosity of 0.5. Based on the aforementioned remarks, it can be concluded that the solid/liquid ratio between the infill material and the rainwater soaking the rubber granules is 1:2.

For the DGI route, the COC concentration at the point of exposure was equal to the BTX concentration in the outdoor air and the PAHs in the dusts, sampled at the borders of the sports fields, listed in Table 3.

Risk quantification

For each receptor (child player or adult player), for each source (synthetic or natural turf field) and for each exposure pathway (DDC, RWC, DGI), the risks due to each contaminant were divided into two categories: non-carcinogens and carcinogens.

According to standard EPA methods (NDEQ 2009), for non-carcinogenic chemicals the risk was calculated as in the following equation: Q5

$$\mathrm{THQ} = \frac{\mathrm{ADI}}{\mathrm{RfD}}, \tag{1}$$

where ADI (milligrammes per kilogramme per day), average daily intake, is the estimated dose the receptor is exposed to from an exposure route; RfD (milligrammes per kilogramme per day) is the dose, for a given route, that is believed to be without effect.

For non-carcinogenic compounds, acceptable values of total hazard quotient (THQ) (dimensionless) are less than 1. The same criterion has to be assumed for both individual and cumulative THQ (D.lgs. 152/06). With reference to one field and one route, the cumulative THQ has to be seen as the sum of the THQ calculated as in Eq. (1) for each contaminant.

For carcinogenic chemicals, the risk was calculated as in the following equation: Q6/Q7

$$\mathrm{CR} = \mathrm{LDI} \times \mathrm{CSF}, \tag{2}$$

where CR (dimensionless) is cancer risk, that is, the probability of cancer occurring in the exposed population over a 70-year lifetime; LDI (milligrammes per kilogramme per day), lifetime daily intake, is the dose of contaminants the receptor is exposed to for all their life through an exposure route; CSF (kilogramme per day per milligramme) is the cancer slope factor for each exposure route derived from dose–response studies.

Table 2 Concentration of BTX, PAHs and metals in the samples of rubber granules and natural soil

Turf field/COC		B	C	PB	PG	RM	PT	CTC residential	CTC industrial
B	µg/kg	0.37	0.64	0.87	0.37	0.48	0.39	0.10	2
T	µg/kg	393	272	142	401	449	36.7	0.50	50
X	µg/kg	754	728	248	975	682	46.2	0.50	50
PYR	mg/kg	22.6	25.9	3.51	21.4	20.0	0.06	0.50	50
B(a)A	mg/kg	4.72	11.2	2.00	15.3	9.55	0.28	0.50	10
CHR	mg/kg	1.55	4.21	0.97	3.19	1.44	0.07	5	50
B(b)F	mg/kg	1.83	4.37	3.46	8.81	<0.01	0.68	0.50	10
B(k)F	mg/kg	<0.01	2.43	3.99	5.02	<0.01	0.51	0.50	10
B(a)P	mg/kg	1.15	1.41	2.56	1.26	<0.01	0.28	0.10	10
D(a,h)A	mg/kg	1.02	8.13	0.82	4.01	0.72	0.73	0.10	10
B(g,h,i)P	mg/kg	1.94	4.16	0.87	2.29	1.70	0.84	0.10	10
Na	%	0.039	0.050	0.025	0.036	0.027	4.33	–	–
K	%	0.062	0.075	0.068	0.056	0.052	0.979	–	–
Ca	%	0.885	2.21	9.16	0.284	0.409	2.51	–	–
Mg	%	0.044	0.053	0.095	0.041	0.036	1.66	–	–
Fe	%	0.037	0.092	0.585	0.055	0.105	2.26	–	–
Mn	mg/kg	<0.14	5.50	13.7	<0.14	4.00	421	–	–
Cd	mg/kg	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	2	15
Co	mg/kg	116	108	56.7	125	97.0	7.20	20	250
Cr (tot)	mg/kg	<0.71	<0.71	<0.71	<0.71	<0.71	471	150	800
Cu	mg/kg	34.5	60.5	77.0	29.0	43.7	16.5	120	600
Ni	mg/kg	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	120	500
Zn	%	1.53	1.25	0.578	1.25	1.22	0.005	150	1,500
Pb	mg/kg	308	37.5	34.3	20.0	19.7	99.1	100	1,000
Ti	mg/kg	36.0	48.5	101	47.0	47.3	1,740	–	–
Ba	mg/kg	167	1,325	1,036	1,775	10.7	296	–	–
Al	%	0.094	0.092	0.483	0.077	0.068	3.57	–	–
Sn	%	0.013	0.034	0.225	0.021	0.039	0.687	1	350
As	mg/kg	<5.3	<5.3	<5.3	<5.3	<5.3	324	20	50

Soil quality guidelines (CTC) for residential and industrial areas according to Italian Decree 152/06

For small values of average daily intake, in which the CR is linearly proportional to the exposed contaminant concentration, as in Eq. (2), an additional lifetime cancer risk of 10^{-6} is retained to be acceptable for the individual CR while for

Table 3 Concentrations (milligramme per cubic metre) of BTX and PM10 in the samples of gases and concentrations (nanogramme per cubic metre) of PAHs in the samples of dusts collected above the playgrounds and in the centre of the city (traffic)

		B	C	PB	PG	RM	PT	Traffic
B	µg/m^3	2.2	1.3	3.0	1.8	1.4	1.4	3.0
T	µg/m^3	5.3	5.6	6.9	10.2	4.2	5.0	12.9
X	µg/m^3	8.8	7.9	8.3	20.9	7.6	7.4	6.4
PM10	µg/m^3	62	63	72	33	54	39	31
PYR	ng/m^3	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
B(a)A	ng/m^3	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
CHR	ng/m^3	<0.09	<0.09	0.10	0.10	<0.09	<0.09	<0.09
B(b)F+B(k)F	ng/m^3	<0.09	0.12	<0.09	0.17	0.12	0.15	<0.09
B(a)P	ng/m^3	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
D(a,h)A	ng/m^3	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
B(g,h,i)P	ng/m^3	<0.09	0.09	<0.09	0.12	<0.09	0.10	<0.09

cumulative CR the maximum acceptable value is 10^{-5} (D.lgs. 152/06). As said before, with reference to one field and one route, the cumulative CR is the sum of the CR calculated as in Eq. (2) for each contaminant.

The daily intake, ADI for non-carcinogenics and LDI for carcinogenics, is the product of the specific exposition rate (*E*, daily amount, normalized on the body weight, of crumb rubber or rainwater contacted, or air breathed) and the concentration *C* of COC in the taken media at the point of exposure.

The exposition rate was calculated by RISC4 for each exposition route as in the following equations:

Direct dermal contact

$$E\left[\frac{\mathrm{mg}}{\mathrm{kg}\cdot\mathrm{day}}\right]=\frac{\mathrm{SA}\cdot\mathrm{AF}\cdot\mathrm{ABS}\cdot\mathrm{EF}\cdot\mathrm{ED}\cdot\mathrm{BIO}}{\mathrm{BW}\cdot\mathrm{AT}}$$

Dermal contact with rainwater

$$E\left[\frac{\mathrm{cm}^2}{\mathrm{kg}\cdot\mathrm{day}}\right]=\frac{\mathrm{SA}\cdot\mathrm{PC}\cdot\mathrm{EFg}\cdot\mathrm{EF}\cdot\mathrm{ED}}{\mathrm{BW}\cdot\mathrm{AT}}$$

Inhalation of outdoor dusts and gases

$$E\left[\frac{\mathrm{m}^3}{\mathrm{kg}\cdot\mathrm{day}}\right]=\frac{\mathrm{Bo}\cdot\mathrm{EFg}\cdot\mathrm{EF}\cdot\mathrm{ED}}{\mathrm{BW}\cdot\mathrm{AT}}$$

The parameters utilized to calculate the specific exposition rates are listed in Table 4.

For the non-carcinogenic ADI values, the average time was assumed to be equal to 6 years for children and 30 years for adults (equal to ED), while 70 years (lifetime) was assumed for the calculation of LDI for carcinogenic substances. Pertinent RfD and CSF values are listed in the ISS-ISPESL (Istituto Superiore di Sanità–Istituto Superiore per la Prevenzione e la Sicurezza del Lavoro) Database and are reported in Table 5. For both direct and indirect contact routes, RfD and CSF values for ingestion were considered.

Results and discussion

Sample characterization

All the samples of rubber granules analysed were characterized by sizes ranging from 1 to 3 mm, with the exception of the PG sample, which showed a sharper particle size distribution, from 1 to 2 mm, and the C sample, which had 6 % by weight (b.w.) of 0.6–1 mm material. The PT natural soil sample showed a larger particle size distribution, ranging from 0.01 to 10 mm.

The BTX and PAH content for the six examined samples is shown in Table 2. The PB thermoplastic sample had a lower total content of both BTX and PAHs than the samples made of SBRr. The PT sample showed quite a substantial concentration of BTX and some PAHs. In particular, the concentration of benzene in PT was similar to those found in artificial turf fields (B, PG, RM). The turf field materials originating from recycled tires were characterized by a pyrene concentration of approximately 20 mg/kg. Similarly, B(a)A was contained in all the SBRr samples, with a concentration of about 10 mg/kg (with the exception of the B sample, characterized by a B(a)A concentration which was slightly lower than 5 mg/kg).

Zinc concentrations in the artificial turf materials were substantially higher than any of the other test metals (Table 2). All of the SBRr samples showed a zinc content ranging from 1.22 % b.w. to 1.53 % b.w due to the zinc oxide used as an activator in the vulcanization process. Iron, cobalt and manganese were detected at significant levels in spite of the efforts to separate steel from the crumb rubber. High concentrations of barium are possibly a result of its use to catalyze the synthesis of polybutadiene rubber. Lead was also identified, possibly due to the use of lead oxide as an activator of the vulcanization process (CalEPA 2007; Denly et al. 2008). The PT sample had a considerably high concentration of potentially hazardous metals like nickel, lead, chrome, tin and arsenic.

Figure 1 shows the average value of PAHs from the four SBRr samples, the TPE infill from the PB field, the average value of the dust samples collected from the air just above an SBRr artificial turf field, the dust collected from just above the thermoplastic turf field and the dust collected from just above the natural turf field.

The results in Fig. 1 highlight that the three samples of dust had a very similar composition, but this was remarkably different from the composition of the infill materials made of exhaust tires or non-recycled thermoplastic rubber, in particular with reference to the content of pyrene and B(a)A. This demonstrates that the majority of the dust samples did not come from the infill material but from other sources, like domestic combustion and urban traffic, in line with the outcomes found by Castellano et al. (2008).

The concentration of both organic and inorganic substances in the rainwater after contact with the infill materials was simulated using the EN 12457/2 leaching test. The results of the elution tests are shown in Table 1. For the four SBRr samples, the BTX and PAH concentration in the leachate from the new infill materials (B and C) was higher than in the leachate from the old ones (PG and RM). This is in line with the data from Birkholz et al. (2003) and Moretto (2007), demonstrating that the toxicity of leachate decreases with the age of the infill material in place. The PB sample showed a high capacity for mobilizing PAHs compared to the other infill materials. The results shown in this work are in line with the outcomes from field studies (Moretto 2007), although a laboratory leaching test alone is not able to predict the real concentration in rainwater because it

Table 4 List of parameters utilized for the calculation of the specific exposition rates

Parameter (acronym)	Parameter description	Unit of measurement	Numeric value
BW	Body weight	kg	Adult, 70–child, 25
ATn	Average exposure duration for non-carcinogenic substances	years	ED
ATc	Average exposure duration for carcinogenic substances	years	70
ED	Exposure duration	years	Adult, 30–child, 6
Direct dermal contact			
SA	Amount of exposed skin to crumb rubber	cm^2	Adult, 8,600–child, 4,000
AF	Soil-to-skin adherence	$mg/cm^2/day$	1
ABS	Dermal adsorption factor	Dimensionless	0.1–0.01
EF	Exposure frequency	days/year	100
BIO	Biodisponibility factor	Dimensionless	[a]
Rainwater contact			
SA	Amount of exposed skin to rainwater	cm^2	Adult, 8,600–child, 4,000
PC	Permeability coefficient	cm/h	[b]
EFg	Daily exposure frequency	h/day	$2\times0.05=0.1$[c]
EF	Exposure frequency	days/year	24[d]
Inhalation of outdoor dusts and gases			
Bo	Breathed air rate	m^3/h	Adult, 3.2–child, 1.9
EFg	Daily exposure frequency	h/day	2
EF	Exposure frequency	days/year	100
Inhalation of outdoor dusts and gases: residential scenario			
Bo	Breathed air rate	m^3/h	Adult, 0.9–child, 0.7
EFg	Daily exposure frequency	h/day	6
EF	Exposure frequency	days/year	350

[a] BIO is the amount of contaminant in crumb rubber that may actually be extracted by water thus being absorbed by the skin. It was calculated in a conservative manner, for each family of compounds (BTX, PAHs and metals) from values of Tables 1 and 2. For SBRr and TPE fields, the following BIO values were assumed: BTX BIO, 10^{-1}; PAH BIO, 10^{-3}; metal BIO, 10^{-2}. For the PT field, the following BIO values were assumed: BTX BIO, 10^{-1}; PAH BIO, 10^{-2}; metal BIO, 10^{-3}. The risk calculation for the DDC route keeps into account that a player is in contact with rubber granules for the whole length of his training session (2 h)

[b] PCs for each substance are listed in Table 5 (see Supplementary Material)

[c] The evaluation of the EFg to rainwater soaking the crumbed rubber and leaching from it keeps into account that a player can come in contact with rainwater only in cases of falls on the ground. Accordingly, the EFg was calculated as the product of the number of hours per day (Eq. (2)) sportsmen play on the field and the number of minutes per hour (3 min equals 0.05 h) a player spends on the ground after a fall

[d] The calculation of the EF for the RWC route keeps into account that in the town of Turin, there are, on the average, 85 rainy days per year; that means that a player who trains on the field for 100 days per year may contact rainwater for 24 days per year ($24=85\times100/365$)

produces better contact between the infill material and the contact liquid than what occurs in a real field.

The maximum concentration (C') of each substance in the leachate can be calculated as in the following equation:

$$C'\,(\text{milligramme/litre}) = \text{C(milligramme per kilogramme)}/10, \quad (3)$$

where C is the amount of a given substance found in the solid sample (rubber or soil) and 10 is the b.w. ratio between the liquid and solid phases.

Considering the maximum amount of chemicals that may be mobilized in a leaching test, calculated as in Eq. (3), the per cent accessibility of each compound for each sample can be calculated by dividing the amount of each chemical released into the water from a sample by the maximum concentration (C') of the given chemical in the leachate generated by the given sample and eventually multiplying the result by 100. As shown in Table 1, the per cent accessibility of each PAHs for the PT and PB samples is lower than 10^{-3} (10^{-1}%), and that for all four SBRr samples is lower than 10^{-4}, with the exception of B(g,h,i)P for the B sample. The BTX fraction released in water by all the tested samples, both artificial and natural, is lower than 10^{-1}, and the highest values were detected in the natural soil sample. The higher amount of PAHs and BTX mobilized in the natural soil sample can be explained taking into account that the PAH and BTX content in soil is entirely due to the deposition of atmospheric particulate on the ground. PAHs and BTX in atmospheric dusts are more easily mobilized

Q10/Q11 **Table 5** ISS-ISPESL database

	CAS number	Carcinogen catalogue UE	Carcinogen class EPA	SF ingestion [mg/kg/day]	SF inhalation [mg/kg/day]	RfD ingestion (mg/kg/day)	RfD inhalation (mg/kg/day)	Dermal adsorption factor	Permeability coefficient [cm/h]
Inorganic compounds									
Arsenic	7440-38-2	–	A	1.50E+00	1.50E+01	3.00E-04	3.00E-04	0.01	0.001
Cobalt	7440-48-4	2	–	–	–	6.00E-02	2.90E-04	0.01	0.00121
Total chromium	16065-83-1	–	–	–	–	1.50E+00	1.50E+00	0.01	0.0013
Nickel	7440-02-0	3	A	2.00E-02	8.40E-01	2.00E-02	2.00E-02	0.01	0.001
Lead	7439-92-1	1/3	B2			3.50E-03	3.50E-02	0.01	0.000342
Tin	7440-31-5	–	–			6.00E-01	6.00E-01	0.01	0.00288
Zinc	7440-66-6	–	D			3.00E-01	3.00E-01	0.01	0.0006
Aromatic									
Benzene	71-43-2	1	A	5.50E-02	2.91E-02	4.00E-03	8.55E-03	0.1	0.021
Toluene	108-88-3	–	D			8.00E-02	1.14E-01	0.1	0.045
Xylenes	1330-20-7	–	D			2.00E-01	2.00E-01	0.1	0.08
PAHs									
Benzo(a)anthracene	56-55-3	2	B2	7.30E-01	6.00E-01		2.85E-01	0.1	0.81
Benzo(a)pyrene	50-32-8	2	B2	7.30E+00	7.32E+00		3.14E+00	0.1	1.2
Benzo(b)fluoranthene	205-99-2	2	B2	7.30E-01	6.00E-01		2.85E-01	0.1	1.2
Benzo(g,h,i)perylene	191-24-2	–	D			3.00E-02	3.00E-02	0.1	1.66
Benzo(k)fluoranthene	207-08-9	2	B2	7.30E-02	3.10E-02		2.85E-02	0.1	1.2
Crysene	218-01-9	2	B2	7.00E-03	–	3.00E-02	3.00E-02	0.1	0.81
Dibenzo(a,h)anthracene	53-70-3	2	B2	7.30E+00	6.10E+00		1.14E-01	0.1	2.7
Pyrene	129-00-0	–	D			3.00E-02	3.00E-02	0.1	0.324

than the same compounds fixed in the rubber framework, which leads to the conclusion that the release of chemical compounds in water after leaching tests seems not to depend on the amount of chemicals in the infill material but only on the way they are connected within the rubber framework.

As for the metal concentration in the leachate, the lowest mobilization ($<10^{-3}$) was observed for the natural soil sample and the highest ($\cong 10^{-2}$) for the SBRr granules. The PB sample showed an intermediate behaviour. The better capacity of the soil to retain inorganic substances was due to the inclusion of metals in the soil framework.

Risk assessment

The cumulative risk values from non-carcinogenic substances, THQ, calculated as in Eq. (1) and from carcinogenic substances, CR, calculated as in Eq. (2), for each field and for each receptors (adult player and child player) are shown in Fig. 2. In each diagram, for each turf field (natural or synthetic), the cumulative risk values for each of the three routes are reported. The last bar of the histogram represents the cumulative risk value to what a citizen living in the centre of Turin was exposed through the outdoor inhalation of dusts and gases from traffic and domestic combustion every day.

As shown in Fig. 2, the CR was higher for an adult player than for a child player. This comes from the equation used for the calculation of the specific exposition rate (E). In fact, an adult player is exposed to carcinogenic compounds (ED) for 30 years, a child only for 6.

For all the routes considered, the non-carcinogenic risk was higher for children than for adults, in line with the fact that children are more sensitive to non-carcinogenic substances than adults.

For the DDC route, the highest cumulative THQ value was reported for the B field because its concentration of lead and zinc in the rubber granules was higher than that of other artificial turf fields (see Table 2). The high non-carcinogenic risk value of the B field was not due to the presence of BTX or PAHs because the amount of these compounds was not different from that in other synthetic fields. On the other hand, regarding the CR for the DDC route, the B field showed quite a low value because of its low content of carcinogenic compounds like benzene, B(a)A, B(b)F and B(a)P. The PT field showed the highest carcinogenic risk for the DDC route due to its content of arsenic (not detected in the rubber granules) and D(a,h)A. The presence of nickel showed a negligible effect in the determination of the total CR, in fact the CR due to nickel was two orders of magnitude lower than that due to the most relevant substances.

The PB thermoplastic field showed the lowest cumulative THQ among the sport fields investigated for both DDC and RWC routes. The low cumulative THQ for the DDC route

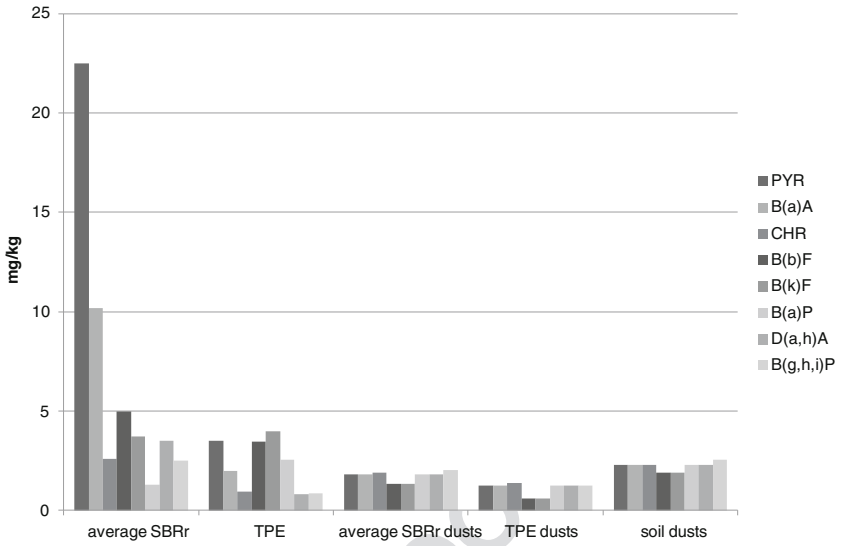

Fig. 1 Average value of PAHs from the four SBRr samples (*first* group of bars), the TPE infill from the PB field (*second* group of bars); average value of the dust samples collected from the air just above an SBRr artificial turf field (*third* group of bars), the dust collected from the air just above the thermoplastic turf field (*fourth* group of bars) and the dust collected from the air just above the natural turf field (*fifth* group of bars)

was due to the low content of cobalt, zinc, toluene, xylene and PAHs (with the exception of B(b)F, B(k)F and B(a)P), so most of the substances considered in the risk analysis. On the other hand, the low THQ for the RWC route (in spite of the capacity of the PB field to release PAH compounds) was mainly due to the remarkably low concentration of zinc in

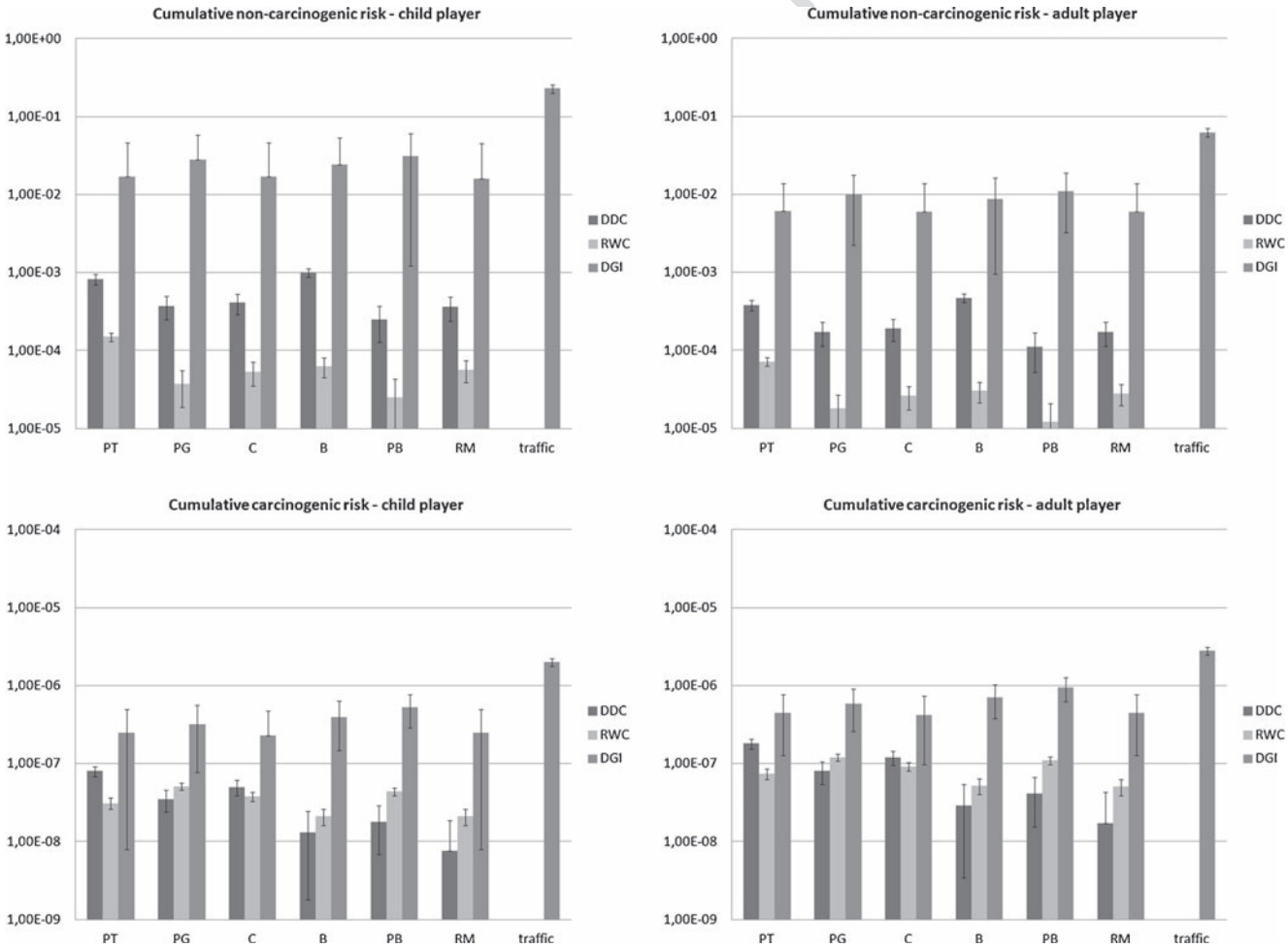

Fig. 2 Results of the calculation of the risk performed for each field and for each route on four scenarios: cumulative non-carcinogenic risk for a child player, cumulative non-carcinogenic risk for an adult player, cumulative carcinogenic risk for a child player, cumulative carcinogenic risk for an adult player

the leachate, of one order of magnitude lower than in the leachates from SBRr granules.

The highest cumulative THQ value for the RWC route was found in the natural soil field; as shown in Fig. 3, this was due to the presence of arsenic. The leaching tests performed on both the rubber granule and natural soil samples showed that arsenic concentration in all the eluates was under the detection limit. However, only for the natural soil sample was the concentration of arsenic in the eluate set to be equal to the detection limit (5 μg/L), owing to quite a substantial concentration of arsenic found in the soil. On the contrary, as shown in Table 2, the arsenic content was under the detection limit in all the rubber granule samples.

Among the artificial turf fields, the highest cumulative THQs for the RWC were observed for the B and C fields. These fields were characterized by being relatively new (1.5 years old) and, according to literature studies (Birkholz et al. 2003; Moretto 2007), rubber materials show the greatest capacity to release BTX and PAH compounds into water in the short term. The same observation could not be made for zinc because, according to Verschoor (2007), the zinc concentration in the leachates increases with age when tires are laboratory-aged, whereas in samples aged under field conditions, the zinc concentration increases with age for car tire crumbs but not for truck tire crumbs.

The outdoor inhalation of dusts and gases was the main exposition route for both carcinogenic and non-carcinogenic substances. The relevance of the inhalation pathway for dusts and gases from artificial turf pitches was compared with the same route for dusts and gases from vehicular traffic. The cumulative CR due to the inhalation of contaminants from traffic was equal to 2.0×10^{-6} for the child receptor and 2.8×10^{-6} for the adult receptor. The non-carcinogenic risk was equal to 0.23 for the child receptor and 0.062 for the adult receptor. For both classes of substances and for both receptors, the inhalation of atmospheric dusts and gases from vehicular traffic gave risk values of one order of magnitude higher than those due to playing soccer on an artificial field.

Conclusions

On the basis of the chemical characterization results, the PB turf field, made of thermoplastic material, shows a BTX and PAH content that is lower than in the samples made of rubber from exhaust tires. The PT field shows a low but not negligible concentration of BTX and some PAHs. As regards heavy metals, zinc was detected at the highest levels. All the samples from exhaust tires show a zinc content ranging from 1.22 % b.w. to 1.53 % b.w. The PB sample is characterized by a zinc content equal to 0.58 % b.w., and the PT sample shows a considerable amount of hazardous metals, like nickel, lead, chromium, tin and arsenic.

On the other hand, the results of the leaching tests show that among the four SBR samples, the concentration of BTX and PAHs is higher in the leachates from the new infill materials than from the old ones. The Passo Buole sample shows the highest leaching release of PAH compounds. This may be due to the different chemical bonds which exist in thermoplastic materials compared to SBRr granules. The higher amount of PAHs and BTX mobilized in the natural soil sample can be explained by taking into account that the soil content of PAHs and BTX is only due to the deposition of atmospheric particulate on the ground.

The characterization of the atmospheric dusts sampled just above the artificial turfs shows that the composition of

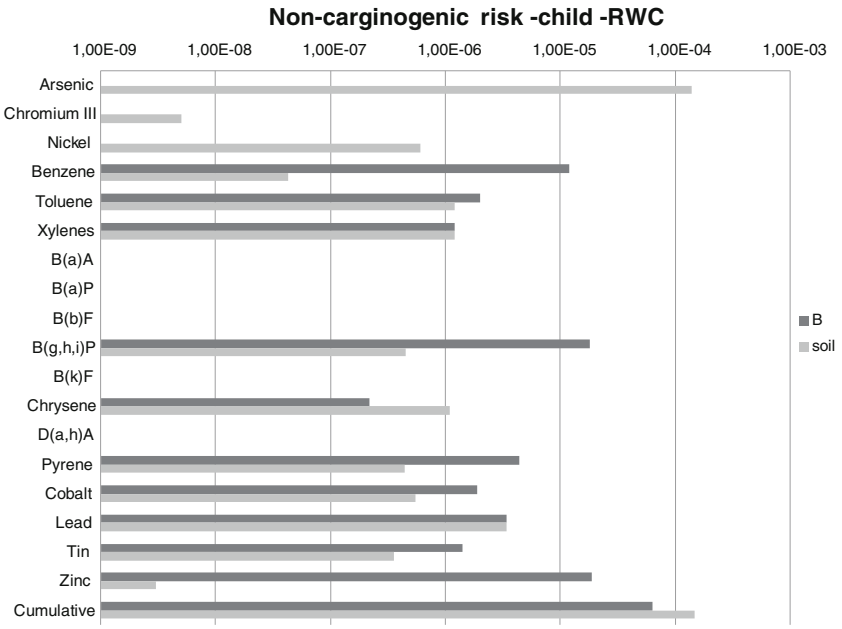

Fig. 3 Non-carcinogenic risk value for each chemical (and cumulative value) for the scenario child player, rainwater contact for the Barracuda field and natural soil

dust samples is very different from that of the infill materials made of exhaust tires or non-recycled thermoplastic rubber, thus implying that these dusts originate from traffic.

The results of the risk analysis performed show that for all the turf fields examined and for all the routes considered, the cumulative CR proved to be lower than 10^{-6} and the non-carcinogenic risk (for the sum of COCs) lower than 1, in line with Italian guidelines.

Outdoor inhalation of dusts and gases is the main exposition route for both carcinogenic and non-carcinogenic contaminants. The relevance of the inhalation pathway—the most dangerous among the three pathways considered—for dusts and gases from artificial turf pitches was compared with the same pathway for dusts and gases from vehicular traffic. For both classes of COCs, carcinogenic and non-carcinogenic, and for both receptors, the inhalation of atmospheric dusts and gases from vehicular traffic gave risk values on average one order of magnitude higher than those due to activity on a turf field.

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