



Artificial-turf playing fields: Contents of metals, PAHs, PCBs, PCDDs and PCDFs, inhalation exposure to PAHs and related preliminary risk assessment

Edoardo Menichini ^a, Vittorio Abate ^a, Leonello Attias ^b, Silvia De Luca ^a, Alessandro di Domenico ^a, Igor Fochi ^a, Giovanni Forte ^a, Nicola Iacovella ^a, Anna Laura Iamiceli ^a, Paolo Izzo ^b, Franco Merli ^a, Beatrice Bocca ^{a,*}

^a Department of Environment and Primary Prevention, Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy

^b National Centre for Chemical Substances, Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy

ARTICLE INFO

Article history:

Received 18 January 2011

Received in revised form 13 July 2011

Accepted 18 July 2011

Available online 9 September 2011

Keywords:

Ambient air
Benzo[a]pyrene
Carcinogenic risk
Recycled tyres
Rubber waste
Zinc

ABSTRACT

The artificial-turf granulates made from recycled rubber waste are of health concern due the possible exposure of users to dangerous substances present in the rubber, and especially to PAHs. In this work, we determined the contents of PAHs, metals, non-dioxin-like PCBs (NDL-PCBs), PCDDs and PCDFs in granulates, and PAH concentrations in air during the use of the field. The purposes were to identify some potential chemical risks and to roughly assess the risk associated with inhalation exposure to PAHs. Rubber granulates were collected from 13 Italian fields and analysed for 25 metals and nine PAHs. One further granulate was analysed for NDL-PCBs, PCDDs, PCDFs and 13 PAHs. Air samples were collected on filter at two fields, using respectively a high volume static sampler close to the athletes and personal samplers worn by the athletes, and at background locations outside the fields. In the absence of specific quality standards, we evaluated the measured contents with respect to the Italian standards for soils to be reclaimed as green areas. Zn concentrations (1 to 19 g/kg) and BaP concentrations (0.02 to 11 mg/kg) in granulates largely exceeded the pertinent standards, up to two orders of magnitude. No association between the origin of the recycled rubber and the contents of PAHs and metals was observed. The sums of NDL-PCBs and WHO-TE PCDDs + PCDFs were, respectively, 0.18 and 0.67×10^{-5} mg/kg. The increased BaP concentrations in air, due to the use of the field, varied approximately from <0.01 to 0.4 ng/m^3 , the latter referring to worst-case conditions as to the release of particle-bound PAHs. Based on the 0.4 ng/m^3 concentration, an excess lifetime cancer risk of 1×10^{-6} was calculated for an intense 30-year activity.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The use of playing fields with artificial turf is widespread for their claimed advantages relative to natural grass fields: mainly the almost continuous use without periodical closures for maintenance and restoration, but also resistance to atmospheric events, relatively quick installation, lower cost for long-term maintenance, and saving of water (Claudio, 2008). Artificial turfs are made from in-fill granulates constituted by crumbs of elastomeric origin. Several of these fields use crumbs from recycled rubber waste, such as automobile tyres or gaskets of various type, expected to contain dangerous substances usually present in the rubber (IARC, 1982). Such substances may be released to the air, so the users are potentially exposed by inhalation as well as by ingestion and skin contact. PAHs, which are present in carbon black and process oils, like aromatic extender oils, used in the rubber industry, are of major concern due to their well-known carcinogenic activity (IARC, 2010).

According to the literature, no appreciable excess risk due to the use of these fields was observed in studies based on: (a) genotoxicity tests on tyre crumb extracts (Birkholz et al., 2003); (b) measurements of volatile organic compounds (VOCs), PM10, PAHs, PCBs, phthalates and alkylphenols in air at indoor pitches during training sessions (NIPH, 2006); (c) the similarity between the concentration levels of particulate matter, metals and VOCs in air samples collected at the fields and at background levels, and the finding that more than 90% of the lead in tyre crumb material is unavailable for absorption by users (US EPA, 2009); (d) the urinary excretion of 1-hydroxypyrene after playing with intensive skin contact with the rubber in-fill (van Rooij and Jongeneelen, 2010); and (e) a review of the scientific literature (Beausoleil et al., 2009).

In a risk assessment study in children (OEHHA, 2007), the calculated increased cancer risk following ingestion of rubber tyre shreds was less or slightly higher than 1 in a million; besides, no skin sensitization by rubberised surfaces was observed. The inhalation route was not considered since any VOCs volatilizing or fine particles resuspending were considered to quickly disperse in the atmosphere.

A risk assessment of general validity is hindered by the many variables involved: e.g., the type and origin of the rubber, its chemical

* Corresponding author. Tel.: +39 0649902252; fax: +39 0649902011.
E-mail address: beatrice.bocca@iss.it (B. Bocca).

Table 1
Concentrations (mg/kg, dry weight) of metals and PAHs in 13 rubber granulate samples of various origins.

	Virgin thermoplastic		Coated recycled tyres		Recycled tyres (uncoated)				Recycled scrap of vulcanised rubber		Recycled ground gaskets			Median	Soil contamination standards		
	Sample code		2/A	2/B ^a	3/A	3/B	3/C	3/D	4/A	4/B	5/A	5/B	5/C		Italy, ^b "green area" use	NY, ^c unrestricted use	
	1/A	1/B															
Metals																	
Al	1.2	6680	490	1028	164	477	755	230	3260	311	4884	2065	5922	755			
As	0.14	0.94	0.12	0.24	0.41	0.13	0.10	0.10	1.2	0.11	0.54	0.28	0.37	0.24	20	13	
Ba	4.4	3485	741	4.7	2.4	5.3	23	5.0	31	10	4778	28	22	22		350	
Be	0.001	0.11	0.007	0.04	0.01	0.02	0.04	0.008	0.37	0.006	0.15	0.06	0.21	0.04	2	7.2	
Cd	0.11	0.37	1.9	0.12	1.9	1.1	0.62	1.7	0.30	0.17	0.17	1.1	0.34	0.37	2	2.5	
Co	<0.5	27	234	5.0	116	33	8.8	58	4.1	3.5	9.9	8.4	21	15	20		
Cr (total)	49	56	6.2	1.8	<0.3	0.44	4.6	1.2	6.2	<0.3	20	2.5	18	6.2	150	1 + 30 ^d	
Cu	0.82	55	60	12	22	16	8.7	20	5.9	13	6.3	11	3.4	12	120	50	
Fe	15	4318	465	201	199	291	620	305	637	183	460	241	403	305			
Hg	<0.02	0.05	0.07	0.08	0.05	0.16	0.06	0.07	0.06	0.03	0.09	<0.02	0.07	0.07	1	0.18	
Li	4.3	4.1	0.60	7.4	1.4	1.4	1.1	0.87	11	2.7	1.0	1.5	4.4	1.5			
Mg	470	456	966	668	235	280	653	465	518	186	286	253	123	456			
Mn	5.2	30	4.9	5.2	3.0	4.4	3.6	3.8	10	6.2	16	3.8	8.3	5.2			
Mo	0.04	2.1	0.13	0.09	0.12	0.18	0.29	0.18	0.19	0.11	0.34	6.6	0.30	0.18			
Ni	0.67	1.5	5.8	0.67	2.5	1.3	1.9	2.0	4.4	0.61	5.5	2.4	3.3	2.0	120	30	
Pb	46	43	28	<0.7	26	22	12	22	14	<0.7	35	17	14	22	100	63	
Rb	0.65	12	1.8	3.0	3.1	1.3	0.90	1.2	26	0.78	1.7	1.5	2.2	1.7			
Sb	0.34	7.7	6.4	1.6	0.52	1.1	0.46	0.53	1.2	3.6	1.1	0.65	2.7	1.1	10		
Se	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	3	3.9	
Sn	0.12	2.5	1.74	0.58	2.00	0.79	0.65	2.4	3.0	0.32	1.2	0.98	1.4	1.2	1		
Sr	17	90	12	19	3.8	6.0	5.3	3.2	17	9.9	86	6.9	13	12			
Tl	0.02	0.09	0.07	0.03	0.14	0.06	0.04	0.05	0.21	0.01	0.17	0.09	0.03	0.06	1		
V	0.38	2.4	1.5	1.5	2.2	1.3	3.5	1.4	9.6	0.94	22	9.7	22	2.2	90		
W	0.02	0.84	0.07	0.36	0.06	0.06	0.12	0.06	1.8	0.13	0.79	0.15	0.74	0.13			
Zn	118	6813	19,375	1063	17,772	12,274	10,229	13,781	7611	1408	10,910	14,187	9488	10,229	150	109	
PAHs^e																	
Pyrene	PY	0.02	1.51	15.1	0.42	2.77	1.86	9.74	4.48	0.44	0.20	11.2	5.63	0.75	1.86	5	100
Benz[a]anthracene	BaA	0.001	0.29	0.15	0.04	0.21	0.43	0.33	0.36	0.14	0.21	0.09	0.18	0.01	0.18	0.5	1
Chrysene ^f	CHR	0.01	1.43	0.97	0.99	0.80	2.38	0.65	1.51	1.34	0.50	0.46	0.67	0.03	0.80	5	1
Benzo[b]fluoranthene+	BbFA+	0.001	0.03	0.46	0.05	0.44	1.78	0.27	0.39	0.33	0.08	0.23	0.44	0.01	0.30	0.5+	1+
benzo[k]fluoranthene ^f	BkFA															0.5	0.8
Benzo[a]pyrene	BaP	<0.001	0.05	2.30	0.06	3.04	10.7	1.19	1.38	0.77	0.07	0.72	2.83	0.02	0.98	0.1	1
Indeno[1,2,3-cd]pyrene	IP	0.001	0.09	1.08	0.05	nc	nc	3.73	nc	nc	0.07	1.26	nc	0.04	0.08	0.1	0.5
Dibenz[a,h]anthracene ^f	DBaHA	<0.001	nc	nc	0.03	nc	nc	nc	nc	nc	nc	nc	nc	nc	<0.03	0.1	0.33
Benzo[ghi]perylene	BghiP	0.01	0.28	8.36	0.25	nc	nc	29.2	nc	nc	0.46	9.02	nc	0.25	0.37	0.1	100
Σ9 PAHs		0.04	3.67	28.5	1.90	7.25	17.1	45.1	8.11	3.03	1.59	22.9	9.76	1.11	7.25	10 ^g	

<...: not detected (the reported concentration is the estimated limit of detection). nc: not calculable due to interference from the laboratory blank sample.

^a Compound of recycled tyre dust coated by extrusion.

^b Threshold values for soils to be reclaimed for use as "green areas".

^c NY State, soil cleanup legislation: concentrations requiring no use restrictions.

^d Cr (VI) and Cr (III), respectively.

^e Ranked according to increasing GC retention time.

^f CHR co-eluted with triphenylene; DBaHA co-eluted with its isomer DBaCA; the sum BbFA + BkFA also included the unresolved isomer BjFA.

^g Threshold value including also four dibenzopyrenes (DBaEP, DBaHP, DBaIP, DBaLP) not determined in these samples.

composition, the conditions of use of the playing field, its age, and the meteorological and climatic conditions.

There is little data concerning dangerous substances contained in, and released from, rubber granulates. The contents of PAHs and metals were determined by Zhang et al. (2008) in seven samples from fields at different ages, and by Gomes et al. (2010) in one sample within a study concerning the use of coated rubber granulates.

PAHs concentrations in air during normal operating conditions were measured in Norway (together with VOCs, PM10 and PM2.5) inside three indoor artificial-turf halls (Dye et al., 2006). BaP was found at mean concentrations ranging 0.8–1.2 ng/m³; however, the increase in concentration due to the activity in the hall with respect to the background level was not reported.

In this work, we determined the following selected substances in, and released from, recycled rubber granulates: (a) metals and PAHs in 13 granulates of different origins; (b) PCBs, PCDDs, PCDFs and PAHs in an additional granulate obtained from recycled tyres; and (c) PAH concentrations in air at two in-use playing fields whose granulates were obtained from recycled tyres, measured using static and personal samplers, respectively. The purposes were to identify any occurrence of some potential chemical risks consequent to the use of artificial playing fields, and to preliminarily assess the increased carcinogenic risk associated with the inhalation exposure to PAHs released during the use.

To our knowledge, these are the first reported measurements concerning the content of PCBs, PCDDs and PCDFs in a rubber granulate, and the PAH concentrations the users may actually be exposed to.

2. Experimental

The study was developed through four steps.

- Step 1 *Metals and PAHs in 13 granulates of various origins.* Twenty-five metals and nine PAHs were determined in rubber granulates whose origins were (Table 1): virgin thermoplastic, coated recycled tyres, compound of recycled tyre dust coated by extrusion, recycled tyres, recycled technical scrap of vulcanised rubber for uses other than tyres, and recycled ground gasket materials. Samples were collected from 13 playing fields located in 10 Italian towns.
- Step 2 *PAHs, PCBs, PCDDs and PCDFs in a recycled tyre granulate.* To confirm the high PAH levels found in the recycled rubber granulates analysed in Step 1, a granulate obtained from recycled tyres was collected from an additional field and analysed for PAHs. The same sample was also analysed for PCBs, PCDDs and PCDFs.
- Step 3 *PAHs in air, static sampler.* To investigate the inhalation exposure to PAHs by the users of playing fields, PAH concentrations in air were measured in the field whose granulate had shown the highest PAH content in Step 1. Air samples were collected during training activity using a high volume (hi-vol) sampler located within the field.
- Step 4 *PAHs in air, personal samplers.* PAH concentrations in air were measured at the field investigated in Step 2, using personal air samplers worn by the athletes.

2.1. Methods for the analysis of rubber granulates

2.1.1. Sampling

Sampling was performed according to a procedure described in detail elsewhere (Bocca et al., 2009). Briefly, the playing field was divided in 12 sectors of identical area. About 50 g of granulate were collected from the centre of each sector. The 12 samples were pooled to obtain one composite sample per field. Visible organic matter and stones were removed by hand.

2.1.2. Metals

The method for the total content of metals was previously described in Bocca et al. (2009). Briefly, about 0.5-g rubber granulate was added with 3 ml of ultrapure HNO₃ (Carlo Erba, Milan, Italy), 1 ml of supra-pure HF (Merck, Darmstadt, Germany) and 1 ml of ultrapure HClO₄ (Carlo Erba), and microwave (MW) digested (FKV Milestone, Milan, Italy) through the following cycle: 10 min at 250 W, 5 min at 400 W and 5 min at 600 W. The solution was further added with 1 ml of HNO₃, 1 ml of HF and 2 ml of HClO₄ and again subjected to MW irradiation as described above. The high-resolution inductively coupled plasma mass spectrometry was used for the determination of elements according to Bocca et al. (2007). As target metals (Table 1), we selected those required by the Italian legislation concerning soils to be reclaimed for use as “green areas” (Gazz. Uff., 2006; see Section 3.1.1).

2.1.3. PAHs

The method was previously described in detail (Abate et al., 2010a). About 2-g rubber granulate was spiked with a mixture of totally deuterated PAHs (*d*-PAHs), used as internal standards, which were allowed to equilibrate with the matrix overnight (the amount of the extracted granulate was 10-fold larger than the amount successively cleaned up for the analysis, to take into account a poor homogeneity, if any, of the sampled material). PAHs were ultrasonically extracted with three 20-ml portions of dichloromethane and then with one 20-ml portion of *n*-hexane (each extraction time, 30 min). The extracts were combined and concentrated under reduced pressure at 35 °C to about 40 ml. A 10% portion of the combined extract was allowed to sorb onto about 0.5-ml silica gel containing 10% (w/w) of water. After evaporation of the solvent under light nitrogen flow, the extract (appearing as a dry powder) was transferred to the top of a silica gel column (i.d., 1 cm) containing 10% (w/w) of water. The column was pre-washed with 14 ml of *n*-hexane (discarded) and then eluted with *n*-hexane. Two fractions were collected according to a procedure previously published (Turrio-Baldassarri et al., 2003): Fraction I (14 ml), containing light aliphatic hydrocarbons, and Fraction II (70 ml), containing heavy aliphatic hydrocarbons and PAHs. Fraction II was concentrated under reduced pressure, transferred into a conic vial, added with 1 µl of *n*-tetradecane as a solution keeper, and reduced to near dryness under light nitrogen stream.

The sample was taken up with 500 µl of ¹³C-BaP solution at 200 pg/µl as an injection standard, diluted to 1.5 ml with *iso*-octane, and analysed by HRGC-LRMS (EI, 35 eV) in the SIM mode. PAHs were identified using their relative retention time and quantified by monitoring the molecular mass. The target PAHs were selected on the basis of the aforementioned legislation (Section 2.1.2): the set of nine PAHs listed in Table 1 for the analysis of the 13 granulates in Step 1, plus four dibenzopyrenes for the analysis of the recycled tyre granulate in Step 2 (Table 2).

The method performances, as determined for the nine PAHs listed in Table 1 within an intra-laboratory in-house validation, were reported by Abate et al. (2010a). In short: the limit of detection of the method ranged from 0.005 to 0.03 mg/kg; the repeatability standard deviation ($n = 5$ replicate analyses of the same sample) was in the 5–7% range (13% for DBahA); the expanded uncertainty (coverage factor $k = 2$) was in the 14–59% range for the individual PAHs and $\leq 30\%$ for $\Sigma 9$ PAHs. The recovery rates of deuterated standards were in the 40–120% range.

2.1.4. PCBs, PCDDs and PCDFs

The method was adapted from previously published methods (di Domenico et al., 1992; Turrio-Baldassarri et al., 2007), and was described in detail elsewhere (Abate et al., 2010b). About 5-g rubber granulate was spiked with a mixture of ¹³C-labelled PCB, PCDD and PCDF congeners, extracted and concentrated, as above described for

Table 2

Concentrations of PAHs, NDL-PCBs, PCDDs and PCDFs (mg/kg, dw) in the recycled tyre granulate from the playing field No. 2.

PAHs		NDL-PCBs	
PY	14.2	2,2',5'-T ₃ CB [18]	6.16 × 10 ⁻³
BaA	0.51	2,4,4'-T ₃ CB [28]	6.28 × 10 ⁻³
CHR ^a	5.01	2,4',5'-T ₃ CB [31]	7.80 × 10 ⁻³
BbFA + BkFA ^a	2.30	2,3',4',5'-T ₃ CB [33]	<0.10 × 10 ⁻³
BaP	1.81	2,2',4,5'-T ₄ CB [49]	9.27 × 10 ⁻³
IP	1.02	2,2',5,5'-T ₄ CB [52]	8.24 × 10 ⁻³
DBahA ^a	0.36	2,3',4,4'-T ₄ CB [66]	3.97 × 10 ⁻³
BghiP	6.93	2,2',3',4',5'-T ₄ CB [70]	6.16 × 10 ⁻³
DBaIP	<0.05	2,4,4',5'-T ₄ CB [74]	2.36 × 10 ⁻³
DBaEP	0.18	2,2',3,4',6'-P ₅ CB [91]	0.93 × 10 ⁻³
DBaIP	<0.05	2,2',3,5',6'-P ₅ CB [95]	6.78 × 10 ⁻³
DBaHP	<0.06	2,2',4,4',5'-P ₅ CB [99]	3.28 × 10 ⁻³
Σ13 PAHs	32.5	2,2',4,5',5'-P ₅ CB [101]	9.99 × 10 ⁻³
Italian soil legislation ^b	See footnote ^c	2,3,3',4',6'-P ₅ CB [110]	9.62 × 10 ⁻³
		2,2',3,3',4,4'-H ₆ CB [128]	3.52 × 10 ⁻³
		2,2',3,4,4',5'-H ₆ CB [138]	12.9 × 10 ⁻³
PCDDs+PCDFs	× 10 ⁻⁵	2,2',3,4,5,5'-H ₆ CB [141]	3.70 × 10 ⁻³
2,3,7,8-TCDD	<0.08	2,2',3,4',5,5'-H ₆ CB [146]	2.22 × 10 ⁻³
1,2,3,7,8-PeCDD	<0.10	2,2',3,4',5',6'-H ₆ CB [149]	10.2 × 10 ⁻³
1,2,3,4,7,8-HxCDD	<0.15	2,2',3,3',5,5',6'-H ₆ CB [151]	2.98 × 10 ⁻³
1,2,3,6,7,8-HxCDD	<0.11	2,2',4,4',5,5'-H ₆ CB [153]	16.2 × 10 ⁻³
1,2,3,7,8,9-HxCDD	<0.12	2,2',3,3',4,4',5-H ₇ CB [170]	5.34 × 10 ⁻³
1,2,3,4,6,7,8-HpCDD	40.9	2,2',3,3',4,5,6'-H ₇ CB [174]	4.16 × 10 ⁻³
OCDD	288	2,2',3,3',4,5',6'-H ₇ CB [177]	2.29 × 10 ⁻³
2,3,7,8-TCDF	0.26	2,2',3,4,4',5,5'-H ₇ CB [180]	11.6 × 10 ⁻³
1,2,3,7,8-PeCDF	<0.08	2,2',3,4,4',5',6'-H ₇ CB [183]	2.34 × 10 ⁻³
2,3,4,7,8-PeCDF	<0.07	2,2',3,4',5,5',6'-H ₇ CB [187]	4.40 × 10 ⁻³
1,2,3,4,7,8-HxCDF	0.30	2,2',3,3',4,4',5,5'-O ₈ CB [194]	<0.22 × 10 ⁻³
1,2,3,6,7,8-HxCDF	<0.20	2,2',3,3',4,4',5,6'-O ₈ CB [196]	<0.25 × 10 ⁻³
1,2,3,7,8,9-HxCDF	<0.25	2,2',3,4,4',5,5',6'-O ₈ CB [203]	<0.19 × 10 ⁻³
2,3,4,6,7,8-HxCDF	<0.25	Σ30 PCBs	0.18
1,2,3,4,6,7,8-HpCDF	1.49	Italian soil legislation ^b , Σ PCBs ^d	0.06
1,2,3,4,7,8,9-HpCDF	<0.11	NY soil legislation ^f , PCBs ^e	
OCDF	2.92	unrestricted use	0.10
Σ17 PCDDs+PCDFs	334	residential use	1
WHO – TE PCDDs+PCDFs	0.67 ^d		
Italian soil legislation ^b , WHO – TE PCDDs+PCDFs	1		

PAH abbreviations as per Table 1. DBaIP: dibenzo [a,i] pyrene; analogously for DBaEP, DBaIP, DBaHP. <...: see footnote in Table 1.

^a See footnote f in Table 1.

^b Threshold values for soils to be reclaimed for use as “green areas”.

^c See Table 1 (column “Green area use”) for the threshold values of ΣPAHs and individual PAHs. The threshold value for each DBP is 0.1 mg/kg.

^d Medium-bound estimate (<LOD entered in the sum as 1/2 LOD).

^e Congeners unspecified.

^f New York State, soil cleanup legislation. Concentrations requiring no use restriction and concentrations allowed for a residential use.

PAHs. As for PAHs, a 10% portion of the combined extract was diluted with 50 ml of *n*-hexane and allowed to percolate through a glass column (i.d., 4 cm) packed with 20 g of Extrelut[®] impregnated with 20 ml of concentrated sulphuric acid. After eluting the sample with 250 ml of *n*-hexane, the eluate was concentrated to 15 ml under reduced pressure. Clean-up was carried out by using an automated multi-column Power-Prep[™] system equipped with a disposable column set constituted, in sequence, by a multi-layer silica column, a basic alumina column, and a carbon-celite column. The sample was transferred onto the silica column and eluted with 80 ml of *n*-hexane. The eluate was further eluted with 150 ml of a 50:1 (v/v) *n*-hexane/dichloromethane mixture through the alumina column to collect a first fraction containing non-dioxin-like PCBs (NDL-PCBs) (besides mono-*ortho* DL-PCBs not included in this study). The eluate was finally transferred onto the carbon-celite column with 190 ml of a 1:1 (v/v) *n*-hexane/dichloromethane mixture and back-flushed with 70 ml of toluene to collect a second fraction containing PCDDs and PCDFs (besides non-*ortho* DL-PCBs not included in this study).

Each fraction was treated as per Fraction II of PAHs (see above) and finally taken with 50 μl of *iso*-octane containing the injection standards: ¹³C-chlordane for the NDL-PCB fraction, and ¹³C-1,2,3,6,7,8-H₆CDD and ¹³C-1,2,3,7,8,9-H₆CDF for the PCDD + PCDF fraction.

NDL-PCBs were determined by HRGC-LRMS (SIM) and PCDDs and PCDFs by HRGC-HRMS (SIM) with a resolution of 10,000 (both MS: EI, 35 eV). The congener identification was carried out using both the relative retention time and the ratio of the two most intense masses of the molecular multiplet; the latter was also used for quantification.

The method performances, as determined within an intra-laboratory in-house validation, were the following: for most congeners, the limit of detection was about 10–20 ng/kg for NDL-PCBs and ranged 0.3–1.3 ng/kg for PCDDs and PCDFs; the repeatability standard deviation was ≤20% for the individual congeners and the cumulative values; the expanded uncertainty of the method (coverage factor *k*=2) was ≤25% for the individual congeners and ≤20% for the cumulative values. The recovery rates of labelled standards were in the 40–120% range.

2.2. Determination of PAHs in ambient air, playing field No. 1

2.2.1. The playing field

To investigate the inhalation exposure to PAHs under presumed worst-case conditions, samples were collected in the field whose granulate had previously shown (Step 1) the highest content of Σ9 PAHs (Table 1, sample code 3/C).

The field was located in a green area in Rome, approximately 100 m far from the nearest road and 220 m from a traffic road. Apart from vehicular traffic, no PAH source was identified in the neighbouring area. The location could be considered as an urban background site. The field was commonly used approximately 2 to 5 h/day, all year round, for football matches and training activities involving about 20 athletes.

2.2.2. Target PAHs

The samples were analysed for the seven PAHs whose monitoring in ambient air is regulated in the European Union (EU, 2005) (Table 3): the human carcinogen BaP (PAH abbreviations are reported in Tables 1 and 2) and six PAHs “probably” (BaA and DBaA) or “possibly” (BbFA, BkFA, BkFA and IP) human carcinogens (IARC, 2010).

2.2.3. Sampling

The target PAHs are almost exclusively present in ambient air as particle-bound compounds (Menichini and Monfredini, 2003). So, the air samples were collected on glass fibre (GF) filters (Pall, type A/E, 20.3 × 25.4 cm, NY, USA) using three hi-vol samplers (General Works-Sierra Andersen, mod. SAUV-15H) equipped with a PM10 size-selective inlet (mod. SA 1200), operating at a constant flow rate of 1.13 m³/min. Sampling duration was about 2–3 h, i.e., the usual daily duration of a training session. Sampling was performed during 3 days in May. The mean ambient temperature during the three sampling periods ranged 22–24 °C and the mean relative humidity 65–67%.

2.2.4. Sampling strategy

The following measures were taken to collect samples as far as possible representative of the air inhaled by the athletes. Sampling was performed during the training activity, with a sampler located within the playing field. The activities included athletic training, football matches and motionless briefing. The athletes were asked to make their usual activity as far as possible around the sampler, i.e., within some tenths of metres from it.

A second sampler was simultaneously operated outside the field, approximately 40 m from the nearest field border, to estimate the background concentrations in a contiguous area. A third one was operated at the PAH monitoring station of our Institute, located in

Table 3
PAH concentrations in air during the use at the playing field No. 1.

PAHs	1st sampling day				2nd sampling day				3rd sampling day				Mean			
	Concn. (ng/m ³) ^a			Field/ urban %	Concn. (ng/m ³) ^a			Field/ urban %	Concn. (ng/m ³) ^a			Field/ urban %	Concn. (ng/m ³) ^a			Field/ urban %
	Field	BG	Urban		Field	BG	Urban		Field	BG	Urban		Field	BG	Urban	
BaA	0.05	0.04	0.06	82	0.03	0.04	0.08	40	0.03	0.03	0.06	48	0.04	0.04	0.07	57
B(b + j + k)FAs ^b	0.10	0.09	0.14	72	0.11	0.11	0.20	54	0.09	0.08	0.15	57	0.10	0.09	0.16	61
BaP	0.06	0.05	0.08	79	0.05	0.05	0.10	50	0.04	0.04	0.09	46	0.05	0.05	0.09	58
IP	0.06	0.05	0.08	74	0.05	0.05	0.09	54	0.05	0.04	0.09	55	0.05	0.05	0.09	61
DBahA (+ DBacA) ^b	0.01	0.01	0.01	78	0.01	0.01	0.01	64	0.01	0.01	0.01	74	0.01	0.01	0.01	72

^a At the field, outside the field (background, BG) and at an urban site. Results corrected for the recovery rate of the surrogate standard.

^b See footnote f in Table 1.

Rome in a mixed medium traffic-residential area described elsewhere (Menichini et al., 1999), to allow comparing the concentrations measured at the playing field with the simultaneous concentrations at an urban site.

2.2.5. Sample treatment and analysis

After removal from the sampler, filters were stored at -18°C . Before extraction, they were evenly spiked drop by drop with 100 μl of a solution of *d*-BaP in toluene at 0.1 ng/ μl , as a surrogate standard. The total spiked amount was 10.0 ng: for a 2-h hi-vol sampling, this amount is equivalent to an air concentration of 0.07 ng/m³, in the order of magnitude of the expected BaP concentration in May in Rome atmosphere (Menichini and Monfredini, 2006). After solvent evaporation, filters were ultrasonically extracted with dichloromethane, three times for 15 min with 80 + 50 + 50 ml. The extracts were stored at 4 $^{\circ}\text{C}$ without clean-up.

Immediately before the analysis, each sample was concentrated to ca. 400 μl and spiked with 25 μl of a solution of *d*-PE in toluene at 0.40 ng/ μl , as an internal standard. Samples were made up with toluene to 500 μl immediately before the analysis which was performed by GC/LRMS (SIM). Each sample was analysed in duplicate. The recovery rate of the surrogate standard was in the 86–107% range.

A laboratory blank sample was run on each sampling day, by taking a blank filter in parallel to the field samples through the same analytical procedure as field samples. PAHs were detected in the blank samples at not quantifiable levels, i.e., at concentrations lower than 4–8% (24–34% for DBahA) of those measured in the field samples.

Results were corrected for the blank by subtracting a concentration corresponding to half the mentioned percentages on a sample-by-sample basis. The estimated limit of detection of the method was 0.002 ng/m³.

The whole procedure (sampling and analysis) was in agreement with the CEN (2008) method for BaP in ambient air.

2.3. Determination of PAHs in ambient air, playing field No. 2

2.3.1. The playing field

The field was the one whose granulate was previously analysed (Step 2). It was located in Rome. Three sides were near low-traffic roads, whereas the fourth side was close to a high-traffic road. Apart from vehicular traffic, no other PAH source was identified in the neighbouring area. The fill-in material consisted of recycled tyre rubber granulate. The field was commonly used as per field No. 1 (Section 2.2.1).

2.3.2. Target PAHs

Besides the seven PAHs previously determined at the playing field No. 1, six other PAHs were included in the analysis (Table 4), resulting in the same PAH set determined in the rubber granulate of the field. Pyrene, a further target PAH in the granulate analysis, was not determined since in air it is only partially present in the particulate phase, especially during the summer (Menichini and Monfredini, 2003).

Table 4
PAH concentrations (ng/m³) in air during the use at the playing field No. 2.

PAHs	1st sampling day				2nd sampling day			
	In the field	Background	Urban	Urban	In the field	Background	Urban	Urban
	TSP	TSP	TSP	PM10	PM10	TSP	TSP	PM10
Sampler	Personal	Lo-vol	Lo-vol	Hi-vol	Personal	Lo-vol	Lo-vol	Hi-vol
Volume, m ³	1.0	1.5	2.0	82.5	0.6	2.6	2.8	122
BaA	0.05–0.2*	0.05–0.1*	0.02–0.1*	0.02	0.1–0.2*	0.04–0.1*	≤0.04*	0.02
CHR (+ TRI) ^a	0.2–0.3*	0.1–0.2*	0.01–0.1*	0.04	0.3–0.5*	0.2	0.05–0.1*	0.05
B(b + j + k)FAs ^a	0.6–0.7	0.3–0.4	0.1–0.2	0.1	1.0–1.2	0.2	0.1*	0.1
BaP	0.3	0.2	0.1	0.03	0.5	0.1	0.03–0.1*	0.03
IP	0.5	0.2–0.3	0.1	0.03	0.6	0.1	0.1	0.04
DBahA (+ DBacA) ^a	0.1	≤0.04*	≤0.02*	0.003	0.1	0.01–0.02*	≤0.01*	0.003
BghiP	0.3–0.4	0.1	0.1	0.1	0.8–0.9	0.1	0.2	0.1
DBaIP	<0.03	<0.03	<0.02	nc	nc	<0.02	nc	nc
DBaEP	<0.03	<0.03	<0.02	<0.002	<0.1	<0.02	<0.02	nc
DBaIP	<0.03	<0.03	<0.02	<0.001	<0.1	<0.02	<0.02	<0.001
DBaHP	<0.03	<0.03	<0.02	<0.001	<0.1	<0.02	<0.02	<0.001

Ranges refer to the concentrations calculated by applying or not the correction for the laboratory blank (see text, Section 2.3.5).

TSP: Total Suspended Particles; nc = not calculable due to interference; <...: not detected (the reported concentration is the estimated limit of detection).

^a See footnote f in Table 1.

* In at least one laboratory blank, the GC signal was >40% than the signal in the sample.

2.3.3. Sampling

Air samples were collected using: (a) personal samplers for total suspended particles (TSP) of the type commonly used at workplaces (model GilAir-5; Gilian Instr. Corp., NY, USA), equipped with an open-face filter holder and a GF filter (Gelman Instr. Comp., Ann Arbor, MI, USA; type A/E; d, 37 mm), operating at 4.2 L/min; (b) a personal sampler (Leland Legacy, SKC, PA, USA) equipped with a PM10 size-selective inlet PEM (Personal Environmental Monitor, model 200, MSP Corporation, MN, USA) and a GF filter (d, 37 mm), operating at 10 L/min; (c) low volume (lo-vol) samplers (Bravo M, Tecora, Milan, Italy) equipped with an open-face filter holder and a GF filter (d, 47 mm), operating at 25 L/min; and (d) a hi-vol sampler as for the playing field No. 1.

Personal samplers were worn by the athletes to collect air samples as much as possible representative of the actual exposure to particle-bound PAHs. The samplers were fastened on a waist-band, except the heavier PM10 personal sampler which was housed in a small backpack.

Sampling was performed during two days in June, with substantially identical climatic conditions. The mean ambient temperature during the two sampling periods ranged 34–38 °C and the mean relative humidity 34–36%.

2.3.4. Sampling strategy

• *Criteria adopted in selecting the sampling conditions.* We considered that any release of particulate matter is likely consequent to the stress of the ground, namely the stamping of the ground and, in case of football activity, the rebound of the ball. We also wanted the collected samples to be representative of the presumed worst-case conditions. Based on this, the following criteria were adopted.

- (1) Sampling under dry conditions, favourable to the dispersion of particulate matter in air: after nine days from the last rain, with a low relative humidity, in the afternoon, i.e., distant from any night humidity deposited on the ground.
- (2) Sampling in the summer when PAH concentrations in urban air are the lowest in the year (Menichini et al., 1999): the lower the background concentrations outside the playing field are, the more any low increase of concentration in the field can be detected.
- (3) Athletes continuously moving: so the particulate matter was continuously raised from the ground.
- (4) Filter holder fastened on the waist-band at a height of about 1 m above the ground: this height simulated sampling in the respiratory zone of children (while likely overestimated the inhalation of particulate matter by adults).
- (5) The open face of the filter holder turned back: so the particulate matter was collected as close as possible to the point where it was raised consequent to the stamping of the ground.

The athletes, all volunteers, were asked to perform a training activity consisting in a light running. Each athlete ran for about 1 h. During sampling as well as in the preceding morning time, no other activity was performed in the field.

- *Samples collected in the playing field.* Given the limited availability of both the field and the athletes, the following samples could be collected. On the first sampling day, two athletes wore two personal TSP samplers each, with the filter holders distant from one another. The four filters were extracted together resulting in one 4-h composite sample. On the second sampling day, one athlete wore a personal PM10 sampler.
- *Samples collected outside the playing field.* The following samples were collected simultaneously to the samples in the field: (a) a lo-vol TSP sample outside the field, at 25 m from the nearest field-border and at 8 m from a low-traffic street, to estimate the background PAH concentrations in a contiguous area; (b) a lo-vol TSP sample and a hi-vol PM10 sample at the aforementioned PAH monitoring station in Rome, to compare the concentrations in the field with those at an

urban site. Finally, a 24-h hi-vol PM10 sample was collected at the latter monitoring station on the two sampling days.

2.3.5. Sample treatment and analysis

The samples were treated and analysed as reported for the playing field No. 1, with the following differences.

The surrogate standard spiked onto the filters was constituted by 10 µl of the solution of *d*-BaP at 0.1 ng/µl. The ultrasonic extraction of personal and lo-vol samples was performed with 30 + 20 + 20 ml of dichloromethane (Menichini and Monfredini, 1995). The internal standard was constituted by 10 µl of a solution of *d*-PE in toluene at 0.1 ng/µl, added to samples concentrated at about 70 µl (400 µl for the hi-vol samples). The final volume for the analysis was 100 µl (500 µl for the hi-vol samples).

Under the experimental sampling conditions (namely: short sampling durations, low sampling flow-rates and low PAH concentrations in air), low PAH amounts were collected. Consequently, the contribution of interfering ions occurring in blank samples was not negligible in a number of quantifications. In these cases, the result was given as a range referring to the concentrations calculated by correcting or not for the blank: the true value is within the range. The recovery efficiency of *d*-BaP ranged 95–107%.

3. Results and discussion

3.1. Metals and PAHs in the rubber granulates

3.1.1. Analysis of 13 samples of various origins

The contents of metals and PAHs measured in the set of 13 samples (Step 1) are shown in Table 1, where samples were grouped in subsets on the basis of their origin. Summary statistics of metal determinations were previously reported (Bocca et al., 2009).

Table 1 also shows the concentrations set in Italy as threshold values for soils to be reclaimed for use as “green areas” (Gazz. Uff., 2006). These values were chosen for reference in the absence of quality standards for materials to be used in playing fields. For completeness of information, Table 1 also reports the concentrations set in the New York State as “cleanup objectives” for soils which require no use restrictions (NYDEC, 2006) and hence roughly assimilable to playing fields. As to metals, these concentrations are mostly in the order of magnitude of the mentioned Italian soil standards, while for some PAHs they exceed the Italian standards by up to two orders of magnitude.

Of the 25 elements determined, only Zn (an additive used as zinc oxide in rubber compounding; IARC, 1982) was present at concentrations largely exceeding the mentioned standards in almost all the samples, up to over two orders of magnitude. The concentrations of Zn in granulates (except the virgin thermoplastic sample 1/A) ranged from 1.1 to 19 g/kg. The high values within this range were distributed in various subsets of samples: no ranking of the content was evident based on the origin of the granulate. The Italian standards were also exceeded by Co and Sn, approximately in half of the samples.

PAHs generally showed a high variability, even greater than one order of magnitude, for granulates of the same origin. The BaP concentrations ranged from 0.02 to 11 mg/kg (except in sample 1/A), i.e., up to 100-fold the pertinent Italian standard for a “green area” use of a soil. Almost all the measurements of the other PAHs were below the pertinent standards, except BghiP and PY, two substances of minor health concern. The Σ9 PAHs in recycled rubber samples spanned over two orders of magnitude. In the virgin sample 1/A, as expected, such sum was lower (two orders of magnitude lower than the median of all samples); however, the other virgin sample (1/B) was even richer of PAHs than some recycled samples (see here below). As for Zn, no ranking was observed based on the origin of the recycled rubber granulate, for the BaP content and for the content of PAHs as a sum.

These results were consistent with the few ones previously obtained in rubber granulates. Zhang et al. (2008) determined Zn in two samples

at concentrations of 5.7 and 10 g/kg, and BaP in seven samples at concentrations of 0.06 and 8.6 mg/kg. Gomes et al. (2010) determined BaP at 1.2 mg/kg. The metal results are also in agreement with the analyses of two tyre rubbers from New Zealand and UK. The former showed elevated concentrations of Al, Ba, Fe and Zn, and very low or undetectable levels of As, Be, Cd, Hg, Li, Mo, Ni, Rb, Sb, Se, Sn, Tl, V and W (Kennedy and Gadd, 2000). The UK material showed metal contents according to the sequence Zn > Fe > Al > Mg (San Miguel et al., 2002).

In summary, the metal and PAH contents were quite variable, regardless of the origin of the rubber. A granulate constituted by a virgin thermoplastic material (sample 1/B) had Zn and PAH contents similar to, or higher than, the granulates constituted by, respectively, scraps of vulcanised rubber and three granulates of recycled rubber (2/B, 4/B and 5/C). Compared to the other virgin thermoplastic material (sample 1/A), the former one (1/B) contained elements at concentrations even three (Al and Ba) or two (Be, Cu and Mo) orders of magnitude higher, while other elements were in the same order of magnitude (Cd, Co, Cr, Li, Mg, Ni and Pb). We do not have an explanation for that. Moreover, sample 1/B was marketed as virgin but the rubber manufacturing and product traceability were unknown.

The Zn and PAH contents are likely to depend on various factors, such as the brand of the artificial turf, the composition of the waste materials collected to produce the final granulate, the inclusion of inferior waste within the artificial turf. As to PAHs, the content may also largely depend on the weathering of the granulate, i.e., its age in the playing field and the meteorological and climatic conditions during its life. The decline of PAH contents as the field ages was observed by Zhang et al. (2008), who also noticed that the decay was complicated by the refilling with new rubber granules to compensate for the loss of the material. Similarly, VOCs out-gassing from rubber granulates were found to decrease in samples collected at two-year-old fields when compared with a virgin material (Li et al., 2010).

3.1.2. Analysis of a recycled tyre granulate from a further playing field

The PAH concentrations determined in an additional sample of granulate obtained from recycled tyres (Step 2) are reported in Table 2. These results generally confirmed the contents we had previously found in the most contaminated samples out of the 13 analysed at Step 1. The mentioned Italian soil standards were exceeded for the sum of PAHs by a factor of 3 and for BaP by one order of magnitude.

3.2. PCBs, PCDDs and PCDFs in a rubber granulate

Table 2 gives the concentrations of PCBs and PCDDs + PCDFs (Step 2). The sums of 30 ND-L-PCBs and WHO-TE PCDDs + PCDFs were, respectively, 0.18 and 0.67×10^{-5} mg/kg. The mentioned Italian soil standards (Section 3.1.1) were exceeded for the sum of PCBs by a factor of 3, while the sum of WHO-TE PCDDs + PCDFs was equal to 2/3 of the standard.

3.3. PAH concentrations in ambient air, playing field No. 1

The PAH concentrations in air during the use of the field are reported in Table 3, together with the simultaneous background concentrations and the simultaneous concentrations at a urban site in Rome. The air concentrations in the field were substantially constant on the three sampling days, not significantly different from that detected at the background site and lower (~60%, on average) than those of the urban site. BaP reached approximately 5% of the target value in the EU (2005). The concentration ratios of all PAHs vs. BaP lied in the respective ranges observed in urban areas (Menichini et al., 1999). The concentrations measured in the field substantially equalled the urban background concentrations measured close to the field, and the contribution of PAHs released from the granulate was likely negligible. Since target PAHs are present in air as particle-bound, their highest concentrations are expected to occur close to the

points where the turf is stressed causing particles to be released. However, for practical reasons (not to hinder the activity), the hi-vol air sampler was located at some tenths of metres from the athletes, which implies the measurements could underestimate the actual concentrations the athletes were exposed to.

3.4. PAH concentrations in ambient air, playing field No. 2

The PAHs concentrations are reported in Table 4. The results whose accuracy was heavily affected by the laboratory blank (Section 2.3.5) are flagged with an asterisk.

BaA and CHR are expected to be underestimated, since they are also present in the vapour phase, in relevant percentages depending on meteorological conditions: 70% of their concentrations were previously found in the vapour phase in Rome in June (Menichini and Monfredini, 2003).

The BaP atmospheric concentrations in Rome during the two sampling days, as measured by our PAH monitoring station, were among the lowest in the year: 0.07 and 0.11 ng/m³ as daily means in the PM10 fraction.

The BaP concentrations the athletes were exposed to, during the activity in the field on the 2 days of sampling, were 0.3 and 0.5 ng/m³. The simultaneous background concentrations outside the field were 0.2 and 0.1 ng/m³, respectively. The concentration of 0.5 ng/m³ was measured in a PM10 sample while the other three concentrations were measured in TSP samples. There is no data about size distribution of particle-bound PAHs originated from in-fill materials. However, 5- and 6-ring PAHs in urban air are known to be almost exclusively present in the PM10 fraction (Menichini and Monfredini, 1995). As a first approximation, we assumed that PAH contents measured in PM10 and TSP fractions were comparable. Hence, on the first sampling day, we measured a BaP increase approximately in the order of 0.1 ng/m³ relatively to the background concentration outside the field. On the second day, such increase was about 0.4 ng/m³. The other PAHs showed similar behaviours.

3.5. A preliminary risk assessment for the inhalation exposure to BaP

The PAH concentrations measured at the playing field No. 1 were not different (within ± 0.01 ng/m³) from the background concentrations measured outside the field. The samples were collected during a typical training session including also pauses without stamping of the ground. Instead, at the playing field No. 2, close to continuously running athletes, we measured increased concentrations in air of PAHs, relative to background concentrations. Under the worst-case scenario, the increase of BaP, the PAH commonly assumed as a marker of carcinogenicity of PAHs in ambient air (IPCS, 1998; WHO, 2000; EU, 2005), was approximately 0.4 ng/m³. So, the true incremental exposure to BaP most probably ranged between <0.01 ng/m³ and about 0.4 ng/m³.

If as worst-case conditions we assume an exposure to 0.4 ng BaP/m³, for 5 h/day, 5 days/week, all year round, the annual mean concentration an athlete would be exposed to would increase by 0.06 ng/m³ relative to background levels. Such increase corresponds to 6% of the European target value. To calculate the increased lifetime exposure, we conservatively multiplied the concentration of 0.06 ng/m³ by 30 years of athletic activity and averaged over a lifetime of 70 years. As a result, the athlete could be subjected to an increased lifetime concentration of 0.025 ng/m³, which corresponds to 2.5% of the mentioned European target value. This concentration is in the order of magnitude of the BaP concentration of 0.012 ng/m³ estimated by WHO (2000) as associated to an excess lifetime cancer risk of 1 in a million of exposed persons. Such estimated risk is the upper-bound value of a range calculated using the quite conservative multi-stage linearised model.

Due to the limited dataset available, this risk assessment should be regarded as a preliminary study giving a first indication about the

inhalation risk associated with the use of the artificial turf under worst-case conditions.

4. Conclusions

Compared with the Italian limits for “green area” soils, high contents of Zn and PAHs were found in the granulates present in playing fields, whatever the origin of the rubber. Zn and BaP concentrations largely exceeded such limits by up to two orders of magnitude. A high variability was found even within granulates of the same origin, probably mirroring the composition of wastes used as the starting material of granulates. Such variability does not allow predicting the contents of Zn and PAHs on the basis of the rubber origin.

PCBs and PCDDs + PCDFs were found in a recycled tyre granulate, at levels in the order of magnitude of the mentioned limits. The analysis was limited to one sample, so their occurrence needs to be confirmed before drawing conclusions on the potential risks from this contamination. The concentrations of particle-bound PAHs in air during the training activity were measured at two playing fields with recycled-tyre granulate. The increases of BaP concentration in the field with respect to background concentration outside the field, varied from approximately $<0.01 \text{ ng/m}^3$, when measured using a static sampler close to the athletes, up to 0.4 ng/m^3 under the presumed worst-case scenario, using personal samplers worn by the athletes.

Based on the 0.4 ng/m^3 concentration and using a conservative approach, we calculated an excess lifetime cancer risk of 1×10^{-6} for an athlete with an intense 30-year activity. Indeed, the corresponding risk tends to be even less relevant for discontinuous or amateur users.

The use of personal air samplers (preferably equipped with a PM10 size-selective inlet) during a light sport activity like running seems to be a suitable procedure to estimate the actual concentrations the athletes are exposed to.

Further work is needed to assess the actual scenarios of exposure to PAHs by inhalation and the corresponding risks, and to reach more comprehensive conclusions.

References

- Abate V, di Domenico A, De Luca S, Fochi I, Iacovella N, Iamiceli AL. Metodo per la determinazione di idrocarburi policiclici aromatici (IPA) in materiali d'origine elastomerica in forma di pellet. In: Bocca B, di Domenico A, Forte G, Iamiceli AL, Menichini E, editors. Metodi chimici per l'analisi degli intasi in materiale elastomerico impiegati nei campi da gioco in erba sintetica. Rapporti Istisan 10/8. Rome: Istituto Superiore di Sanità; 2010a. p. 1–16. Available at <http://www.iss.it/binary/publ/cont/10ottoWEB.pdf>. accessed on 30 June 2011.
- Abate V, di Domenico A, De Luca S, Fochi I, Iacovella N, Iamiceli AL. Metodo per la determinazione di policlorobifenili (PCB), policlorodibenzodiossine (PCDD) e policlorodibenzofurani (PCDF) in materiali d'origine elastomerica in forma di pellet. In: Bocca B, di Domenico A, Forte G, Iamiceli AL, Menichini E, editors. Metodi chimici per l'analisi degli intasi in materiale elastomerico impiegati nei campi da gioco in erba sintetica. Rapporti Istisan 10/8. Rome: Istituto Superiore di Sanità; 2010b. p. 17–28. Available at <http://www.iss.it/binary/publ/cont/10ottoWEB.pdf>. accessed on 30 June 2011.
- Beausoleil M, Price K, Muller C. Chemicals in outdoor artificial turf: a health risk for users? Public Health Branch, Montreal Health and Social Services Agency; June 2009. Available at http://greylib.pbworks.com/f/Health+Risk_Outdoor_Artificial_Turf_June+2009.pdf. accessed on 30 June 2011.
- Birkholz DA, Belton KL, Guidotti TL. Toxicological evaluation for the hazard assessment of tire crumb for use in public playgrounds. J Air Waste Manage Assoc 2003;53:903–7.
- Bocca B, Forte G, Senofonte O, Violante N, Paoletti L, De Berardis B, et al. A pilot study on the content and the release of Ni and other allergenic metals from cheap earrings available on the Italian market. Sci Total Environ 2007;388:24–34.
- Bocca B, Forte G, Petrucci F, Costantini S, Izzo P. Metals contained and leached from rubber granulates used in synthetic turf areas. Sci Total Environ 2009;407:2183–90.
- CEN. Air quality – standard method for the measurement of the concentration of benzo [a]pyrene in ambient air. European Standard EN 15549:2008. Brussels: CEN; 2008.
- Claudio L. Synthetic turf – health debate takes root. Environ Health Perspect 2008;116: A117–22.
- di Domenico A, De Felip E, Ferri F, Iacovella N, Miniero R, Scotto di Tella E, et al. Determination of the composition of complex chemical mixtures in the soil of an industrial site. Microchem J 1992;46:48–81.
- Dye C, Bjerke A, Schmidbauer N, Manø S. Measurement of air pollution in indoor artificial turf halls. Report NILU OR 03/2006. Norwegian Pollution Control Authority/Norwegian Institute for Air Research; 2006. Available at <http://www.iss.de/conferences/Dresden%202006/Technical/NILU%20Engelsk.pdf>. accessed on 30 June 2011.
- EU. Directive 2004/107/CE of the European Parliament and the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Off J Eur Union, L 23/3 of 26.1.2005.
- Gazz. Uff. Decreto legislativo 3 Aprile 2006, n. 152. Norme in materia ambientale; 2006. Suppl. ord. Gazz. Uff. n. 88 del 14 aprile.
- Gomes J, Mota H, Bordado J, Cadete M, Sarmento G, Ribeiro A, et al. Toxicological assessment of coated versus uncoated rubber granulates obtained from used tires for use in sport facilities. J Air Waste Manage Assoc 2010;60:741–6.
- IARC. The rubber industry. IARC Monogr Eval Carcinog Risk Chem Hum, Vol. 28. Lyon: Int. Agency Res. Cancer; 1982.
- IARC. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC Monogr Eval Carcinog Risks Hum, Vol. 92. Lyon: Int. Agency Res. Cancer; 2010.
- IPCS. Selected non-heterocyclic polycyclic aromatic hydrocarbons. International Programme on Chemical Safety. Environmental Health Criteria 202Geneva: World Health Organization; 1998.
- Kennedy P, Gadd J. Preliminary examination of trace elements in tyres, brake pads and road bitumen in New Zealand. Report prepared for the Ministry of Transport of New Zealand; 2000. rev. 2003.
- Li X, Berger W, Musante C, Mattina MI. Characterization of substances released from crumb rubber material used on artificial turf fields. Chemosphere 2010;80:279–85.
- Menichini E, Monfredini F. A field comparison of ‘total suspended particles’ and ‘PM₁₀’ air samplers in collecting polycyclic aromatic hydrocarbons. Int J Environ Anal Chem 1995;61:299–307.
- Menichini E, Monfredini F. Monitoring of carcinogenic PAHs in air under mild-warm ambient temperatures: relative importance of vapour- and particulate-phase analyses in assessing exposure and risk. Int J Environ Anal Chem 2003;83:897–908.
- Menichini E, Monfredini F. Idrocarburi policiclici aromatici. In: Stazione di rilevamento dell'Istituto Superiore di Sanità per lo studio della qualità dell'aria: anni 2003 e 2004. In: Cattani G, Viviano G, editors. Rapporti Istisan 06/13. Rome: Istituto Superiore di Sanità; 2006. p. 63–8.
- Menichini E, Monfredini F, Merli F. The temporal variability of the profile of carcinogenic polycyclic aromatic hydrocarbons in urban air: a study in a medium traffic area in Rome, 1993–1998. Atmos Environ 1999;33:3739–50.
- NIPH. Artificial turf pitches – an assessment of the health risks for football players. Oslo: Norwegian Institute of Public Health and the Radium Hospital; January 2006. Available at <http://www.iss.de/conferences/Dresden%202006/Technical/FHI%20Engelsk.pdf>. accessed on 30 June 2011.
- NYDEC. Regulations and Enforcements. Subpart 375-6: Remedial Program Soil Cleanup Objectives (Effective December 14, 2006). Tables 375-6.8(a) and 375-6.8(b). New York State Department of Environmental Conservation. Available at <http://www.dec.ny.gov/regs/15507.html> accessed on 30 June 2011.
- OEHHA. Evaluation of health effects of recycled waste tires in playground and track products. Office of Environmental Health Hazard Assessment (OEHHA); January 2007. Available at <http://www.calrecycle.ca.gov/Publications/Tires/62206013.pdf>. accessed on 30 June 2011.
- San Miguel G, Fowler GD, Sollars CJ. The leaching of inorganic species from activated carbons produced from waste tyre rubber. Water Res 2002;36:1939–46.
- Turrio-Baldassarri L, Battistelli CL, Iamiceli AL. Evaluation of the efficiency of extraction of PAHs from diesel particulate matter with pressurized solvents. Anal Bioanal Chem 2003;375:589–95.
- Turrio-Baldassarri L, Abate V, Alivernini S, Battistelli CL, Carasi S, Casella M, et al. A study on PCB, PCDD/PCDF industrial contamination in a mixed urban-agricultural area significantly affecting the food chain and the human exposure. Part I: soil and feed. Chemosphere 2007;67:1822–30.
- US EPA. EPA News Release. Limited EPA study finds low level of concern in samples of recycled tires from ballfield and playground surfaces. Washington: US Environmental Protection Agency; 2009. December 10. Available at <http://yosemite.epa.gov/opa/admpress.nsf/4f88b25ea20ccb985257359003f5345/c8d28e3f9f3-ca0a4852576880053bed41OpenDocument>. accessed on 30 June 2011.
- Van Rooij JGM, Jongeneelen FJ. Hydroxypyrene in urine football players after playing on artificial sports field with tire crumb infill. Int Arch Occup Environ Health 2010;83: 105–10.
- WHO. Air quality guidelines for Europe. WHO Regional Publications, European Series No. 91, 2nd ed. Copenhagen: World Health Organization, Regional Office for Europe; 2000.
- Zhang J, Han I-K, Zhang L, Crain W. Hazardous chemicals in synthetic turf materials and their bioaccessibility in digestive fluids. J Expo Sci Environ Epidemiol 2008;18: 600–7.