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Metals contained and leached from rubber granulates used in synthetic turf areas

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ABSTRACT

The aim of this study was to quantify metals contained in and leached from different types of rubber granulates used in synthetic turf areas. To investigate the total content of metals, ca 0.5 g of material was added with HNO_3, HF and $HClO_4$ and microwave digested with power increasing from 250 W to 600 W. Leachates were prepared by extraction of about 5.0 g of material at room temperature for 24 h in an acidic environment (pH 5). Leaching with deionized water was also performed for comparison. Aluminium, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Fe, Li, Mg, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Tl, V, W and Zn were quantified by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) and ICP optical emission spectrometry (ICP-OES).

Results indicated that the developed method was accurate and precise for the multi-element characterization of rubber granulates and leachates. The total amount and the amount leached during the acidic test varied from metal to metal and from granulate to granulate. The highest median values were found for Zn (10,229 mg/kg), Al (755 mg/kg), Mg (456 mg/kg), Fe (305 mg/kg), followed by Pb, Ba, Co, Cu and Sr. The other elements were present at few units of mg/kg. The highest leaching was observed for Zn (2300 μg/l) and Mg (2500 μg/l), followed by Fe, Sr, Al, Mn and Ba. Little As, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Rb, Sb and V leached, and Be, Hg, Se, Sn, Tl and W were below quantification limits. Data obtained were compared with the maximum tolerable amounts reported for similar materials, and only the concentration of Zn (total and leached) exceeded the expected values.

1. Introduction

Synthetic turf areas are by now well established in almost all sport facilities. Waste automobile tires are being used increasingly as a primary component of playground surfaces and running tracks. In addition to the benefits of recycling, playground surfaces made from waste tires have the potential to reduce users' injury due to falls in the playground. Because recycled tires contain several substances of high concern, such as Polycyclic Aromatic Hydrocarbons (PAHs), phthalates, and certain metals, the environmental and health compatibility of the synthetic turf has to be guaranteed during the use. Environmental and health risks of loading sport areas with used tires might be the possible release of dangerous particles to the air, contamination of soil and groundwater by soluble pollutants of the materials extracted by rain water and the health hazard for residents and users of sport areas by inhalation of pollutants (Swedish Chemicals Inspectorate, 2006).

Automobile tires have been recognized as sources of specific metals in the environment. Analysis showed that the quantity of Zn released by tire wear in USA in the mid-1990s was of the same magnitude as that released from waste incineration and that tire-Zn inputs to watersheds can be greater than atmospheric inputs (Councell et al., 2004).

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Fukuzaki et al. (1986) showed that tire tread contains heavy metals such as Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb, and tire dust pollution contributes to some of these elements in the form of airborne dust. Sadiq et al. (1989) analyzed the metal concentrations in tires and showed that tire dust was a soil pollutant. High zinc ion levels are released in soils from the rubber through weathering (Smolders and Degryse, 2002) and a significant increase in surface soil concentrations of Cd, Pb, and Zn was measured with increasing proximity to a tire dump (Horner, 1996).

In laboratory studies, loadings of Pb, Cd, Cu and Zn were observed in synthetic rain water maintained in contact with tires for 24 h (Davis et al., 2001) and Zn concentration was found to be higher in a leachate collection layer containing tire chips than in that without tire chips (Park et al., 2003).

Zinc may affect water quality for living species and produce toxic effects on cultured cell lines. The degree of toxicity on aquatic organisms was a function of specific surface of the rubber particulate and low pH values favoured the amount of Zn leached (Gualtieri et al., 2005). For example, overlying water from both new and used tires was lethal to rainbow trout and aged tires were more toxic than new tires; more, Zn has been pointed out as the main reason for toxicity to *Ceriodaphnia dubia* (Day et al., 1993; Nelson et al., 1994). Other reports have identified Zn as the major source of eluate toxicity in aquatic environments when automobile tires are used as artificial reefs (Mueller and Liston, 1994). Anthony et al. (1995) suggested that metals are implied in the toxicity of leachates when the tire material is cut or shredded, while toxicity diminished in leachates from whole tires.

In a hazard assessment design applied to the use of recycled tires in playgrounds, hazard to children appeared to be minimal while toxicity to bacteria, invertebrates, fish and green algae was observed; however the activity disappeared with aging of the tire crumb in place in the playground (Birkholz et al., 2003). Even if the question about effects on human health is left unanswered, it has been postulated that children playing on tire crumb could potentially be exposed by ingestion of the product directly, by ingestion of surface water runoff through the product, by inhalation of dust, or by skin contact with the material or surface water runoff (Anderson et al., 2006). Risks may exist in working with the rubber and in tire manufacturing industries; in fact, a study demonstrated hypersensitivity to Ni, Cr, and Co in manufacturers of tires (Rubisz-Brzezińska et al., 1990). Williams et al. (1995) suggested that respirable "tire dust" particles may contribute to the pathogenesis of lung diseases related to air pollution, even if a high amount of energy is required to create smaller crumb rubber particles.

There are currently no common guidelines within the EU for the considerations that must be taken to protect human health and the environment around us when laying and using synthetic turf. The Fédération Internationale de Football Association and the Union Européenne de Football Association have published quality requirements for synthetic turf (Fédération Internationale de Football Association, 2006). These requirements concern principally the technical properties of the surface relevant to playing football, but nothing is reported for human safety or the environment. The German Institute for Standardization (DIN) has published "Sports Grounds Part 7; Synthetic Turf Areas. Determination of Environmental Compatibility" (DIN 18035-7:2002-06). The standard establishes limiting values for the contents of substances in soil and ground water for, among other substances, Pb, Cd, Cr, Hg and Zn depending on the method used to measure the level.

Clearly, more investigation is needed to look at the use of tire crumb and the potential for release of inhalable particles, as well as for contamination of soil and groundwater.

The aim of this study was to determine the total content of 25 chemical elements and the amounts leached under acidic conditions of rubber granulates used in synthetic turf areas for the assessment of possible environmental and human health impacts. Multi-element methods by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) and ICP optical emission spectrometry (ICP-OES) were developed for this purpose.

2. Experimental

2.1. Sample collection

Samples were granulates obtained from the crumbled product of recycled tires. Granulates of 3–4 mm were black, white as well as coloured. A total of 32 samples were analysed and they were collected from 32 different playgrounds located in Italy (50% of them situated in centre, 31% in northern and 19% in southern Italy). Samplings were performed at different positions in the playground to obtain a representative sample for each sporting area. In particular, the playground was divided in 12 sectors (as shown in Fig. 1) and ca. 250 g of granulate were collected from an

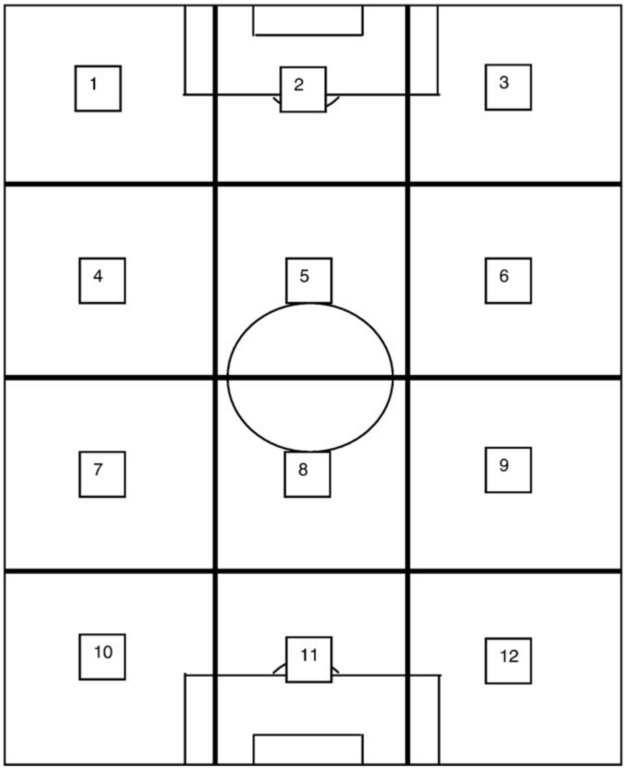

Fig. 1 – Sampling scheme on playgrounds.

Table 1 – HR-ICP-MS and ICP-OES method performances in tire leachates

Metal	Mass (m/z) and wavelength (nm)	LoQ (μg/l)	Precision (%)	Recovery	
				Spiked (μg/l)	Found (%)
Al	27	0.3	4.05	50	97.5
As	75	1	6.12	50	96.3
Ba	138	0.05	5.04	50	98.6
Be	9	0.02	8.04	5	94.6
Cd	111	0.01	7.14	5	93.7
Co	59	0.05	4.55	5	92.4
Cr	52	0.05	8.10	5	90.3
Cu	63	0.4	3.52	50	93.4
*Fe	259.9	2	2.88	2500	101
Hg	202	0.1	5.52	5	97.1
Li	7	0.01	6.65	5	95.1
*Mg	279.5	5	1.54	2500	99.8
Mn	55	0.05	3.24	50	102
Mo	98	0.01	8.88	5	96.9
Ni	60	0.05	6.96	5	94.8
Pb	208	0.05	5.34	5	97.2
Rb	85	0.1	5.68	50	97.5
Sb	121	0.01	4.39	5	95.9
Se	82	1	5.09	50	102
Sn	118	0.5	6.94	5	101
Sr	88	0.1	3.86	50	98.8
Tl	205	0.01	6.78	5	97.3
V	51	0.02	7.07	5	92.2
W	186	0.02	6.44	5	98.8
*Zn	213.8	1	2.46	2500	103

*Performances obtained by the ICP-OES technique.

area of 25 cm^2 placed in the centre of each sector. In this way, 12 samples for playground were obtained. Then, ca. 50 g of granulate were taken from each of the 12 samples and pooled to obtain 1 representative sample per playground. Visible organic matter such as grass, leaves, pine needles and stones was removed by hand.

2.2. *Sample treatment*

2.2.1. *Microwave acidic digestion*

For the determination of total content of the elements, about 0.5 g of rubber were weighed, added with 3 ml of ultrapure HNO_3 (Carlo Erba, Milan, Italy), 1 ml of supra-pure HF (Merck, Darmstadt, Germany) and 1 ml of ultrapure $HClO_4$ (Carlo Erba) and digested in Teflon vessels in a microwave (MW) oven (FKV Milestone, Milan, Italy) through the following cycle of digestion: 10 min at 250 W, 5 min at 400 W and 5 min at 600 W. The solutions were further added with 1 ml of HNO_3, 1 ml of HF and 2 ml of HCO_4 and the MW cycle described above was applied again. The solutions so digested were brought to a final volume of 20 ml with deionised ultra-pure water (EASY-pure, PBI, Milan, Italy) and stored at +4 °C until HR-ICP-MS and ICP-OES analyses. Duplicates were carried out for each rubber sample and digestion also included procedural blanks.

2.2.2. *Extraction with acetic acid*

To determine the fraction extracted, the method described in the Italian Official Journal 183/1986 on the leaching test in acetic acid for organic and inorganic matrices was applied (Italian Interministerial Committee, 1986). In particular, due to the limited quantity of rubber, the amount of sample used for the test was

Table 2 – Total content of metals in tires used in synthetic turf areas

Metal	Median	Min	Max	Legislative Decree 152/2006
Al	755	1.2	6680	
As	0.24	0.10	1.21	20
Ba	22	2.4	4778	
Be	0.04	0.001	0.37	2
Cd	0.37	0.11	1.89	2
Co	15	3.5	234	20
Cr	6.2	0.4	56	150
Cu	12	0.8	60	120
Fe	305	15	4318	
Hg	0.07	0.03	0.16	1
Li	1.5	0.6	11	
Mg	456	123	966	
Mn	5.2	3.0	30	
Mo	0.2	0.04	6.6	
Ni	2.0	0.6	5.8	120
Pb	22	12	46	100
Rb	1.7	0.7	26	
Sb	1.1	0.3	7.7	10
Se	<0.3	<0.3	<0.3	3
Sn	1.2	0.1	3.0	1
Sr	12	3.2	90	
Tl	0.06	0.01	0.21	1
V	2.2	0.4	22	90
W	0.13	0.02	2.0	
Zn	10,229	118	19,375	150

Concentrations in mg/kg.

reduced to about 5.0 g each. The amount of extracting solution was also reduced to approximately 80 ml to keep the liquid/solid ratio at 16, as recommended by the test procedure. Rubber was extracted at pH 5 with ultrapure acetic acid (Carlo Erba) 0.5 M solution by shaking for 24 h at 25 °C. Leachate samples were filtered through Whatman WCN 0.45 mm membranes and stored at +4 °C for further HR-ICP-MS and ICP-OES quantifications. Duplicates were performed for the test on two identical samples, and blanks were prepared by the same sample treatment procedure.

2.2.3. *Extraction with water*

The extraction process was performed according to the German standard method on sludge and sediments for the determination of leachability by water (DIN 38414-4:1984-10). About 5.0 g of granulates were added with 50 ml deionized ultrapure water (sample to water 1:10) and shaken for 24 h at room temperature. Then, the obtained extracts (1st extract 0–24 h) were discarded and the same granulates are treated a second time with fresh water for another 24 h (2nd extract 24–48 h) and filtered through Whatman WCN 0.45 mm membranes. Analyses of the 2nd extract were carried out by HR-ICP-MS and ICP-OES. Extractions were performed in duplicate, and blanks followed the same procedure.

2.3. *Sample analysis*

2.3.1. *ICP-OES*

Iron, Mg and Zn were quantified by ICP-OES. An Optima 3100 XL (Perkin Elmer, Norwalk, CT, USA) was used and the operational settings were the following: radiofrequency (RF), 1.3 kW; nebulizer, cross-flow with Ryton Scott chamber; argon gas flow rates, 13.0 l/min (plasma), 0.5 l/min (auxiliary) and 0.7 l/min (nebulizer). The polychromator was equipped with an echelle grating (ruling density, 79 lines/mm) combined with a Schmidt cross disperser; the detection was achieved by a simultaneous solid-state Segmented-array Charged-coupled device Detector (SCD); maximum resolution, 0.006 nm at 200 nm. The spectral lines (nm) used for the analysis were: Fe, 259.9; Mg, 279.5; Zn, 213.8 and Y (as internal standard, IS), 371.0.

2.3.2. *HR-ICP-MS*

The HR-ICP-MS used for the quantification of elements was an ELEMENT 2 (Thermo Fischer) equipped with Meinhard-type glass nebulizer, water-cooled Scott spray chamber, torch with guard electrode device and platinum interface cones. The following operating conditions were used: RF power, 1.2 kW; gas flow rates, 14.0 l/min (plasma), 1.0 l/min (auxiliary) and 0.90 l/min (nebulizer). The analytical masses (m/z) used for the analysis were: Al, 27; As, 75; Ba, 138; Be, 9; Cd, 111; Co, 59; Cr, 52; Cu, 63; Hg, 202; Li, 7; Mn, 55; Mo, 98; Ni, 60; Pb, 208; Rb, 85; Sb, 121; Sn, 118; Sr, 88; Tl, 205; V, 51; W, 186.

Three different mass resolution settings were adopted (Bocca et al., 2007). The low resolution (LR, 300 m/Δm) was used for the elements such as Ba, Be, Cd, Hg, Li, Mo, Pb, Sb, Sn, Rb, Sr, Tl and W which were not interfered with by any relevant interference. The medium resolution (MR, 4000 m/Δm) was selected for Al, Co, Cr, Cu, Mn, Ni and V quantification because these elements were heavily interfered with by polyatomic ion species produced by a combination of isotopes

Table 3 – A compilation of published data for elements in vehicle tires

Metal	Tires							
	San Miguel et al. (2002)	Kennedy and Gadd (2000)	Legret and Pagotto (1999)	Horner (1996)	MoT (1996)	Hewitt and Rashed (1990)	Sadiq et al. (1989)	David and Williams (1975)
Al	956	20.5					64–3823	
As	<5.0	nd						
Ba		25.8						
Be		0.3						
Cd	2.9	<0.19	2.6	0–3.0	0.77	0.28–4.96		0.13–14.06
Co	38.7	1.05					10.0–997.1	
Cr	49.4	<1						
Cu	68.5	1	1.8			5.5–29.3	1.1–45.9	
Fe	2818	105					9.1–778.1	
Hg		<0.01						
Li		0.2						
Mg	444	11.2						
Mn	13.9	1.2					1.6–11.7	
Mo	10.0	1						
Ni	5.9	1					2.4–17.9	
Pb	59.0	2.72	6.3	8.1–22.3	0.84		2.1–518.6	
Rb		<0.2						
Sb		<0.2						
Se	4.0	nd						
Sn		<0.5						
Sr		0.6						
Tl		nd						
V		nd						
W		nd						
Zn	12,700	8310	10,250	2524–6012	5624			8400–16,600

Concentrations in mg/kg. nd: not detected.

coming from plasma, matrix and reagents. In particular, with the organic matrix containing high quantity of C, the molecular ion $^{40}\mathrm{Ar}^{12}\mathrm{C}$ heavily influenced the $^{52}\mathrm{Cr}$. With concern to the reagents, the addition of HNO_3, HF and $HClO_4$ in digested rubber created interferences that were not negligible, such as $^{12}\mathrm{C}^{15}\mathrm{N}$ which overlapped the signal of $^{27}\mathrm{Al}$, $^{38}\mathrm{Ar}^{14}\mathrm{N}$ on $^{52}\mathrm{Cr}$, $^{40}\mathrm{Ar}^{15}\mathrm{N}$ on $^{55}\mathrm{Mn}$, and $^{36}\mathrm{Ar}^{14}\mathrm{NH}$ on $^{51}\mathrm{V}$; the species $^{35}\mathrm{Cl}^{17}\mathrm{O}$, $^{37}\mathrm{Cl}^{18}\mathrm{O}$ and $^{35}\mathrm{Cl}^{16}\mathrm{O}$ which covered $^{52}\mathrm{Cr}$, $^{55}\mathrm{Mn}$, and $^{51}\mathrm{V}$; and the species $^{44}\mathrm{Ca}^{16}\mathrm{O}$ and $^{23}\mathrm{Na}^{37}\mathrm{Cl}$ which hid $^{60}\mathrm{Ni}$ signal. With regards to fluorine, its argide ($^{40}\mathrm{Ar}^{19}\mathrm{F}$) heavily covered the signal of $^{59}\mathrm{Co}$, while the specie $^{44}\mathrm{Ca}^{19}\mathrm{F}$ interfered with $^{63}\mathrm{Cu}$. The high resolution (HR, 10,000 $m/\Delta m$) was mandatory for $^{75}\mathrm{As}$ and $^{82}\mathrm{Se}$ quantification because it separated the mass 75 from the interfering specie $^{40}\mathrm{Ar}^{35}\mathrm{Cl}$ and the mass 82 from $^{66}\mathrm{Zn}^{16}\mathrm{O}$, $^{38}\mathrm{Ar}^{44}\mathrm{Ca}$ and $^{40}\mathrm{Ar}^{42}\mathrm{Ca}$. In order to correct eventual instrumental drifts and matrix effects, three different ISs were used: $^{115}\mathrm{In}$, $^{195}\mathrm{Pt}$ and $^{45}\mathrm{Sc}$ (Bocca et al., 2007).

3. Results and discussion

3.1. *Method performance*

Table 1 summarizes the HR-ICP-MS and ICP-OES quality performances in the analysis of 25 elements in rubber leachates. The quality control procedure included the calculation of limits of quantification (LoQs), intra-day repeatability and accuracy. It was applied to leachates where concentrations of elements are expected to be lower than those in digested samples and, thus, a high degree of analytical quality was mandatory. Moreover, between duplicate samples prepared in different days was also calculated both for digested rubber and leachate.

The LoQs were expressed as 10 times the standard deviation (SD) of 10 replicated measurements of leachates. The LoQs obtained with HR-ICP-MS were equal or below 0.05 μg/l for most of the elements, and from 0.1 μg/l to 1 μg/l for Al, As, Cu, Hg, Rb, Se and Sr. Iron and Mg (i.e., 2 and 5 μg/l) quantified by ICP-OES had the highest LoQs.

Repeatability was calculated on 10 replicated measurements of a pooled leaching rubber solution and it was satisfactory for all the elements (average relative SD equal to 5.45%).

Recovery tests were performed to determine the accuracy of the method. To this end, one sample of rubber granulates digested in triplicates was added with a multi-element spike which included all the elements determined in this study. Mean recoveries were in the interval 90.3% (Cr)–103% (Zn).

The methods also produced good reproducibility between duplicate samples with deviation from the mean value usually below 12% in digested samples and 10% in leachates.

3.2. *Metal composition of rubber granulates*

The UK Environmental Agency (1998) reported that major and minor elements are used in the manufacture of tires. First of all, Zn-oxide is used as an activator of the vulcanisation reaction, then Mg-oxide is used as an accelerant, and Ca-oxide as a desiccant. Among traces, Pb-oxide seemed to be contained in Zn-oxide additive and Sb-penthasulphide is used as a colorant.

Table 2 provides a summary of the median composition of rubber granulates tested in this study. For comparison, the concentration of metals acceptable in polluted sites according to the Italian regulatory values established by the Legislative Decree 152/2006 is also presented. The Decree reported threshold values of concentration for 15 metals in soils and even if the comparison with the present data was not direct it could give some indications (Legislative Decree 152/2006).

The analysis revealed that rubber granulates contained all the metals under investigation and concentration range for each metal was wide with respect to the different samples analyzed suggesting that metals were not distributed uniformly in the rubber granulates. The samples showed the presence of Zn (10,229 mg/kg) at the highest median concentration. Other inorganic species found at high median concentrations included Al (755 mg/kg), Mg (456 mg/kg) and Fe (305 mg/kg). Also Ba (22 mg/kg), Pb (22 mg/kg), Co (15 mg/kg), Cu (13 mg/kg) and Sr (12 mg/kg) were contained in relatively high amounts. Although there were some significant maximum values among Cr, Mn, Rb, and V, their median values were below 6.0 mg/kg. Elements such as As, Be, Cd, Hg, Li, Mo, Ni, Sb, Se, Sn, Tl and W were present at traces (between 0.04 mg/kg and 1.5 mg/kg).

Comparing the found levels with the maximum concentration allowable for soils, all elements were significantly lower than the limits with the exception of Co, Sn and Zn. With regards to Co and Sn, the ca. 50% of samples exceeded the limit, while, in the case of Zn, all samples except one were above the standard with values ca. 100-times higher.

Table 4 – Leaching (at pH 5) of metals from tires used in synthetic turf areas

Metal	Median	Min	Max	DIN 18035-7:2002-06
Al	67.0	2.00	3940	
As	0.12	<LoQ	2.40	
Ba	27.0	2.00	2050	
Be	<LoQ	<LoQ	<LoQ	
Cd	0.20	<LoQ	0.70	≤5
Co	1.50	<LoQ	41.0	
Cr	0.90	0.20	10.0	≤50
Cu	2.20	0.20	216	
Fe	300	6.00	3220	
Hg	<LoQ	<LoQ	<LoQ	≤1
Li	1.00	<LoQ	440	
Mg	2460	122	28,200	
Mn	33.0	7.00	220	
Mo	0.07	<LoQ	6.00	
Ni	1.40	<LoQ	10.0	
Pb	1.60	<LoQ	27.0	≤40
Rb	0.70	<LoQ	186	
Sb	0.80	<LoQ	18.0	
Se	<LoQ	<LoQ	<LoQ	
Sn	<LoQ	<LoQ	<LoQ	≤50
Sr	77.0	3.00	713	
Tl	<LoQ	<LoQ	<LoQ	
V	0.94	0.14	11.0	
W	<LoQ	<LoQ	<LoQ	
Zn	2300	2.00	62,120	≤3000

Concentrations in μg/l.

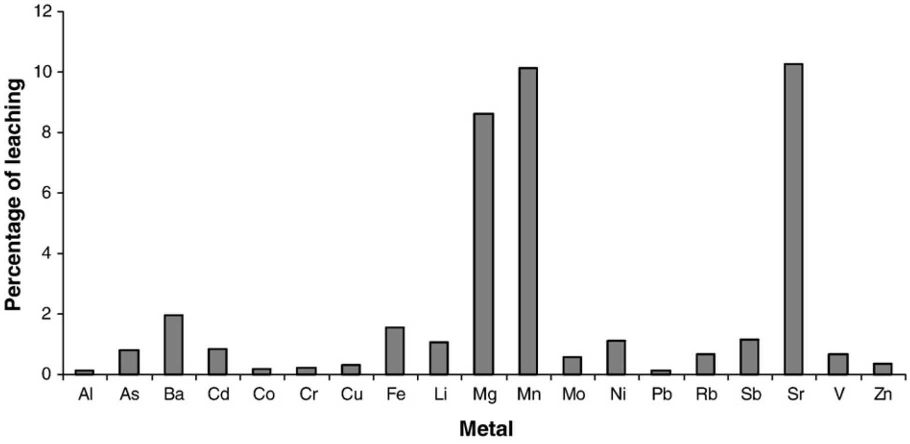

Fig. 2 – Percentage of metals leached from tires used in synthetic turf areas.

In Table 3 a comparison of published data for elements contained in tires is reported. Just as the present findings, rubber from New Zealand tires had elevated contents of Al, Ba, Fe and Zn, and very low or even undetectable levels of As, Be, Cd, Hg, Li, Mo, Ni, Rb, Sb, Se, Sn, Tl, V and W (Kennedy and Gadd, 2000). A low concentration of Cd and a similar range for Zn were identified also in Australian tires (David and Williams, 1975). Another study identified typical concentration of ZnO in tires of 0.7% and Cd and Pb concentration below 1 mg/kg based on data supplied by the tire industry (Ministry of Transport, MoT, 1996). The concentrations of Al, Cu, Co, Mg, Pb and Sr measured in this study may be higher than previously indicated (Kennedy and Gadd, 2000; Legret and Pagotto, 1999), but reflected those reported by other authors in UK tire rubber and in different brands of auto tires (San Miguel et al., 2002; Sadiq et al., 1989). San Miguel et al. (2002) suggested elements concentrated as follows: Zn>Fe>Al>Mg; Sadiq et al. (1989) observed Al as dominant element, but also Co and Pb were highly contained and appreciably contributed to the contamination of the environment. In a tire tread sample, chipped off from a used tire made in Japan, elements more concentrated were Zn and Al, while several other elements as Ba, Fe, Mn, Sr, Cr, Cu, Ni, and V were not detected (Adachi and Tainosho, 2004).

3.3. *Metal leaching from rubber granulates*

The data on the leachates of samples at a constant pH of 5.0 are given in Table 4. The same table reports the limits for some elements found in the regulation for environmental compatibility of synthetic turf areas (DIN 18035-7:2002-06). This regulation sets the maximum content for some metals in soil and ground water. It should be noted that a direct comparison can not be made between the results from leaching tests and the limiting values, since the limiting values were not defined for this purpose. The comparisons do, however, give a certain indication.

The highest leaching was observed for Zn (2300 μg/l) and Mg (2460 μg/l), followed by Fe (300 μg/l), Sr (77.0 μg/l), Al (67 μg/l), Mn (33.0 μg/l) and Ba (27 μg/l). Very little amounts of As, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Rb, Sb and V were leached, and Be, Hg, Se, Sn, Tl and W were under the limits of quantification. The metals that were most frequently found in leachates were those which were more concentrated in the original rubber (i.e., Al, Fe, Mg and Zn); also Ba, Mn and Sr were significantly released from rubber. Comparing the leachate concentration with the DIN standards, median values for Cd, Cr, Hg, Pb, Sn were below the specified amounts. With regards to Zn, a total of 14 samples out of 32 (44%) were above the specified standard.

Data of leaching were also normalized to the amount of solid rubber, and expressed as mg of constituent in the leachate per kg of material. Then, percentages of leaching with respect to the original content were calculated and represented in Fig. 2. Percentages varied from element to element, and in general leaching was less than 1% for most of the elements (Zn included), 1–2% for Ba and Fe, and ca 10% for Mg, Mn and Sr.

Table 5 shows a comparison between the amounts of metals leached under water and those leached under acidic conditions (pH 5). The test was applied to a smaller set of samples and it was limited to those elements regulated by the DIN 18035-7:2002-06. Results showed that leaching gave non-detectable concentrations for Hg and Sn in both conditions, while releases of Cd, Cr, Pb and Zn were lower in water than in acid. The variation was undoubtedly attributed to differences in the experimental procedures and pH conditions. In order to take into account the less aggressive condition, the DIN reported a more stringent limit for Zn in water (≤500 μg/l) and, once again, samples analyzed exceeded the standard. Although Zn is rarely found in natural waters at concentrations above 50 μg/l, tap water concentrations are usually far greater due to leaching

Table 5 – Comparison of leaching of tires in acid and water (median concentrations in μg/l on a set of 5 tires)

Metal	Acid (pH 5)	H_2O*
Cd	0.40	<LoQ
Cr	0.50	0.20
Hg	<LoQ	<LoQ
Pb	4.50	<LoQ
Sn	<LoQ	<LoQ
Zn	2546	966

*Zn≤500 μg/l in water (DIN 18035-7:2002-06).

from galvanised pipes, fittings and water tanks. Health based standards for this element (World Health Organisation, 1996) established a concentration limit of 3000 μg/l in drinking water. The water leaching of Zn here found (i.e., 966 μg/l) was lower than this limit.

Only few studies approached the problem of the leaching of metals from tires and, thus, comparisons with the literature are quite limited. Moreover, experimental conditions such as extracting pH and time, laboratory or field settings, the use of whole tires instead of granules or powder might affect the comparison.

In automobile tire powder sampled in USA, synthetic rain water was able to leach in 24 h a mean concentration of 3400 mg/kg of Zn, 17 mg/kg of Pb, 5 mg/kg of Cu, and 1 mg/kg of Cd (Davis et al., 2001) which were several orders of magnitude higher than the data here obtained. In UK, metals were extracted from tire chip by simulated acid-rain solutions (pH 2.5) and Zn concentration of the leachate ranged from 169–463 mg/l, but Cd and Pb concentrations were negligible (Horner, 1996). Twenty-five tires collected from two different tire retailers leached – under water for 72 h – a Zn concentration range from 110 to 590 μg/l (Wik and Daves, 2006). San Miguel et al. (2002) found, in the water-leaching of rubber-derived activated carbons, levels of Zn (i.e., 578 μg/l) fairly comparable to the present data, but higher leaching concentration for Pb (<33 μg/l), Cd (<5.6 μg/l) and Cr (<11 μg/l). In laboratory tests, new vehicle wheel leached at pH 5 after 24 h-shaking a quantity of Zn equal to 6500 μg/l and the eluted Zn was the 1.5% of the original amount but there was not a linear correlation between the initial particle quantity and the concentration of eluted Zn (Gualtieri et al., 2005).

4. Conclusions

The analytical methods developed can be successfully applied to the multi-element characterization of rubber granulates used in synthetic turf areas.

Rubber granulates varied widely in their metal composition, but a common finding was that Zn was contained at the highest concentration, and other inorganic species at relatively high levels included Al, Fe and Mg. Also Ba, Co, Cu, Pb, and Sr were found in considerable amounts.

Also the quantity of metals leached under the constant pH 5.0 conditions varied from rubber to rubber. The highest leaching was observed for Zn and Mg, followed by Al, Ba, Fe, Mn, and Sr. Very little or undetectable leaching levels were observed for the other elements analyzed. In particular, toxic metals such as As, Hg, Cd and Pb or other severely allergenic metals as Co, Cr and Ni had non-significant releases.

Comparing the results with the standards for the environmental compatibility of synthetic turf areas, and if a risk for humans and ecosystems might exist in the use of recycled rubber in synthetic playgrounds, Zn seemed to be the unique element which contributes most to this risk.

Following the high variability in metallic composition and leaching observed in this study, it should be also considered that factors which include the local ground conditions, the type of drainage, the composition of the filler material might influence the risk. This means that an assessment of risk must be made for each individual case at a local level for the assessment to be reliable. Finally, for an exhaustive risk assessment the determination of inorganic elements in the inhalable PM10 would be desirable.

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