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Artificial Turf Football Fields: Environmental and Mutagenicity Assessment

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Artificial football turf fields: environmental and mutagenicity assessment.

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Corresponding Author:	Tiziana Schiliro University of Torino ITALY
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	University of Torino
Corresponding Author's Secondary Institution:	
First Author:	Tiziana Schiliro
First Author Secondary Information:	
Order of Authors:	Tiziana Schiliro Deborah Traversi Raffaella Degan Cristina Pignata Luca Alessandria Dario Scozia Roberto Bono Giorgio Gilli
Order of Authors Secondary Information:	
Abstract:	<p>The public recently has raised concerns regarding potential human health and environmental risks associated with tire crumb constituents in artificial football turf fields. The aim of the present study was to develop an environmental analysis drawing a comparison between artificial football turf fields and urban areas relative to concentrations of particles PM10 and PM2,5 and related polycyclic aromatic hydrocarbons (PAHs); aromatic hydrocarbons (BTXs); and mutagenicity of the organic PM10 and PM2,5 extracts.</p> <p>No significant differences were found between PM10 concentrations at an urban site and at football turf fields, both in warm and in cold seasons, and neither with or without on-field activity; PM2,5 concentrations were significantly higher in the urban site in cold season as the PM2,5 and PM10 ratio. BTXs were significantly higher in urban sites than in football turf fields both in warm days and in cold ones; the toluene and benzene ratio was always related to normal urban conditions. The concentration of PAHs in the monitored football fields were comparable to urban levels in the two different periods of samplings and the contribution of PAHs released from the granulate was negligible. PM10 organic extract mutagenicity in artificial football turf fields was higher, while PM2,5 organic extract mutagenicity was lower compared to the considered urban site, however both comparable to that reported in literature for urban sites. On the basis of this environmental monitoring are not present more environmental risks on artificial football turf fields than on rest of the city.</p>
Suggested Reviewers:	Elisabetta Carraro Department of Environmental and Life Science, University of Eastern Piedmont "A.

	<p>Avogadro", Alessandria, Italy elisabetta.carraro@unipmn.it extensive experience in research of biological effects of airborne particulates in vitro</p>
	<p>Angelo Cecinato Institute for Atmospheric Pollution, Italian National Research Council (CNR-IIA), Via Salaria km 29.3, P.O. Box 10, I-00015 Monterotondo Stazione, RM, Italy. cecinato@iia.cnr.it extensive experience in research of airborne particulate matter and relates PAHs.</p>
	<p>Maurizio Gualtieri Department of Environmental Science, University of Milano-Bicocca, 1 piazza della Scienza, 20126 Milan, Italy maurizio.gualtieri@unimib.it extensive experience in research of airborne particulate matter.</p>
	<p>F J Jongeneelen IndusTox Consult, PO Box 31070, 6503 CB Nijmegen, The Netherlands joost.vanrooij@industox.nl experience in research on artificial sports field with tire crumb infill.</p>
	<p>Tee L. Guidotti Department of Environmental and Occupational Health, School of Public Health and Health Services, George Washington University, Washington DC 20037 eohtlg@gwumc.edu experience in evaluations for the hazard assessment of tire crumb</p>

Dear Editor,

We are sending the manuscript

“Artificial football turf fields: environmental and mutagenicity assessment”

that we submit for possible publication on *Archives of Environmental Contamination and Toxicology*.

An environmental analysis was performed to determine the contamination levels due to the presence of tire crumb in artificial turf fields and to determine whether an artificial turf field can lead to an additional exposure on the normal exposure levels to pollutants in urban areas.

The aim of the present study was to compare data from artificial football turf fields with urban areas in relation to: 1) concentration of airborne particulates PM10 and PM2,5; 2) concentration of related PAHs; 3) concentration of aromatic hydrocarbons (benzene, toluene and xylenes); and 4) mutagenicity of the organic PM10 and PM2,5 extracts. These analyses were conducted both with or without activity in the turf fields and, in order to understand how natural weather conditions influence levels of chemicals released from turf fields, in two different seasons.

The samplings were conducted in Torino, an industrial north western Italian city, at six different football fields and at two meteorological–chemical control stations located in the urban centre, a background and a traffic one; five of the football fields contained artificial turf.

On the basis of this environmental monitoring there were not present more environmental risks on artificial football turf fields than on rest of the city.

Best regards

Tiziana Schilirò

1 **Artificial football turf fields: environmental and mutagenicity assessment.**

2

3 Tiziana Schilirò^{1*}, Deborah Traversi¹, Raffaella Degan¹, Cristina Pignata¹, Luca

4 Alessandria¹, Dario Scozia², Roberto Bono¹, Giorgio Gilli¹

5

6 ¹*Department of Public Health and Microbiology, University of Torino, Torino, Italy*

7 ²*Multiservice Company Casalese S.p.A., Casale Monferrato (AL), Italy*

8

9 ***Corresponding Author:**

10 Tiziana Schilirò

11 Department of Public Health and Microbiology, University of Torino.

12 Via Santena, 5bis - 10126 Torino – ITALY

13 tel. + 39 011 670 5810

14 Fax + 39 011 236 5810

15 e-mail: tiziana.schiliro@unito.it

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26 **ABSTRACT**

1
2 27 The public recently has raised concerns regarding potential human health and environmental
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4 28 risks associated with tire crumb constituents in artificial football turf fields. The aim of the
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7 29 present study was to develop an environmental analysis drawing a comparison between
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9 30 artificial football turf fields and urban areas relative to concentrations of particles PM10 and
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11 31 PM2,5 and related polycyclic aromatic hydrocarbons (PAHs); aromatic hydrocarbons
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13 32 (BTXs); and mutagenicity of the organic PM10 and PM2,5 extracts.
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17 33 No significant differences were found between PM10 concentrations at an urban site and at
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19 34 football turf fields, both in warm and in cold seasons, and neither with or without on-field
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21 35 activity; PM2,5 concentrations were significantly higher in the urban site in cold season as the
22
23 36 PM2,5 and PM10 ratio. BTXs were significantly higher in urban sites than in football turf
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25 37 fields both in warm days and in cold ones; the toluene and benzene ratio was always related to
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27 38 normal urban conditions. The concentration of PAHs in the monitored football fields were
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29 39 comparable to urban levels in the two different periods of samplings and the contribution of
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31 40 PAHs released from the granulate was negligible. PM10 organic extract mutagenicity in
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33 41 artificial football turf fields was higher, while PM2,5 organic extract mutagenicity was lower
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35 42 compared to the considered urban site, however both comparable to that reported in literature
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37 43 for urban sites. On the basis of this environmental monitoring are not present more
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39 44 environmental risks on artificial football turf fields than on rest of the city.
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48 **INTRODUCTION**

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51 47 Recycled tire material or “tire crumb” is used as a component in many recreational fields,
52
53 48 including artificial turf fields. These crumbs are as much as 90% by weight of the fields. The
54
55 49 tire crumbs are roughly the size of grains of course sand. They are made by shredding and
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57 50 grinding used tires. Tire crumb materials are spread two to three inches thick over the field
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surface and packed between ribbons of green plastic used to simulate green grass (EHHL, 2007). Tire rubber is composed of 40 - 60% rubber polymer, reinforcing agents such as carbon black (20 - 35%), aromatic extender oils (15 - 20%), vulcanization additives (4%, e.g., zinc oxide, benzothiazole and derivatives), antioxidants (1%) and processing aids (<1%, e.g., plasticizers and softeners) (Wik and Dave, 2009) . The use of tire crumbs in applications such as football fields provides several benefits, including reduced sports injury. Non-playground uses include as an asphalt additive in road building and as an aggregate in concrete; tire crumb contributes to the strength of concrete, and the product is reportedly lighter in weight than typical concrete (Pierce and Blackwell, 2003). The public recently has raised concerns regarding potential human health and environmental risks associated with the presence of and potential exposures to tire crumb constituents in recreational fields, especially with regard to children's exposures (US EPA, 2009). Adults, and especially 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. Public health analysis of the health risks from human exposures to the rubber tire crumbs has not been adequately addressed up to this point (Anderson et al., 2006). Concerns have been expressed that toxic chemicals derived from tire rubber could be transferred to the environment and to organisms having direct contact with these products. For example, chemical additives such as Zn and polycyclic aromatic hydrocarbons (PAHs) were widely detected in the leachate from tire rubber (Stephensen et al., 2003; Wik and Dave, 2005; Kanematsu et al., 2009; Menichini et al., 2011). Zhang and collaborators (2008) reported that the levels of PAHs and Zn in tire crumb used as infill for artificial turf were above health-based soil standards, and lead in the tire crumb was highly bioaccessible in synthetic gastric fluid at relatively low levels (Zhang et al., 2008).

75 To examine further the known risks to human from exposure to the playground product,
76 Anderson and colleagues (2006) turned to traditional published scientific literature; one study,
77 done by investigators working in Alberta (Birkholz et al., 2003), examined the human and
78 ecosystem hazard presented by tire crumb using *in vitro* mutagenicity assays. The associated
79 hazard analysis suggested that the risk associated with playground use was very low. Toxicity
80 to all of the aquatic organisms tested was observed in the fresh aqueous extract, but activity
81 disappeared with aging of the tire crumb for 3 months in place on the playground. The
82 investigators concluded that the use of tire crumb in playgrounds results in minimal hazard to
83 children and the receiving environment, assuming intended use of the product, such as
84 exclusive outdoor use and the presence of no solvents other than water. Regarding the central
85 question of potential harm to children, the published literature contained some information
86 about the product, including *in vitro* toxicity models (Gualtieri et al., 2005; Wik and Dave,
87 2006; Mantecca et al., 2007; Gomes et al., 2010). Most previous work has focused on the
88 toxic chemicals in the leachate of tire rubber material. Wik and Dave (2009) reviewed
89 thoroughly the ecotoxicological effects of tire rubber leachate and indicated its potential risks
90 to aquatic organisms in water and sediment (Wik and Dave, 2009). The report went onto
91 indicate that the health aspects associated with the inhalation of rubber particles are largely
92 unknown. Very limited work has been done on the characterization of volatile and semi-
93 volatile organic compounds out-gassing from commercial tire crumbs on artificial turf fields
94 (US EPA, 2009; Li et al., 2010; van Rooij and Jongeneelen, 2010), despite the fact that if tire
95 crumb is used as infill for artificial turf, the inhalation zone over these installations could be a
96 major human exposure source. Really, traditional published resources and networks of
97 environmental health experts could not establish the product's safety in use with children or
98 adults (Anderson et al., 2006). The possible danger for children or adults is from direct
99 contact with chemical compounds contained in the crumbs, which could happen by ingestion

100 or as a result of contact. A qualitative assessment of these risks produced the following
1
2 101 conclusions -ingestion on the ground is unlikely and the gastric juices of the digestive system
3
4 102 are not powerful enough to extract the toxic products from the crumb; - dermatological
5
6
7 103 contact presents a generally very low risk: a more effective solvent than water would be
8
9
10 104 needed to extract toxic compound in quantity, and an adequate (non polar) carrier would be
11
12 105 necessary to penetrate the skin and cause significant absorption; - inhalation is considered
13
14 106 negligible as the crumbs do not contain volatile chemical compounds under pressure,
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16
17 107 although, as the wear of a tire, even the use of an artificial field could generate fine particles
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19 108 and related compounds (Birkholz et al. 2003; LRCCP, 2006).

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22 109 An environmental analysis is needed to determine quantitatively the contamination levels due
23
24 110 to the presence of tire crumb in artificial turf fields. It is also important to determine whether
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26 111 an artificial turf field can lead an additional exposure to the normal exposure levels to
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29 112 pollutants in urban areas. The aim of the present study was to develop an environmental
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31 113 analysis drawing a comparison between artificial football turf fields and urban areas in
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34 114 relation to 1) concentration of particles PM10 and PM2,5, 2) concentration of related PAHs,
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36 115 3) concentration of aromatic hydrocarbons (benzene, toluene and xylenes) and 4)
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39 116 mutagenicity of the organic PM10 and PM2,5 extracts. These analysis were conducted both in
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41 117 presence and absence of use of the turf fields and, in order to understand how natural
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44 118 weathering conditions influence levels of chemicals released from turf fields, in two different
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46 119 seasons.

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50 51 121 **MATERIALS AND METHODS**

52 53 122 Samplings sites

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56 123 The samplings were carried in Torino, an industrial north western Italian city, in six different
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58 124 football fields and in two meteorological–chemical control stations located in the urban
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125 centre, a background and a traffic one; five of the football fields were in artificial turf (Figure
1)
2 126 1). The characteristics of the sampling sites are reported in Table 1. Two different courses of
3
4 127 samplings were carried out: in June (from 12 to 26) without playing and in November (from
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6
7 128 6 to 15) during the course of matches, in order to verify the influences of both meteorological
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10 129 and seasonal conditions and the presence of play.

11 PM analysis

12 130 PM10 and PM2,5 were sampled on glass microfiber filters (Type A/E, 8'' x 10'', Gelman
13
14 131 Sciences, Michigan, USA), with Sierra Andersen High Volume Samplers 1200/VFC
15
16 132 (Andersen Samplers, Atlanta, Georgia, USA) using a flow of approximately 1160 L/min.
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18 133 Sample duration was controlled by a timer accurate to ± 15 min over a 24 hr sample period.
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20 134 The exact flow was calculated daily, corrected for variation in atmospheric pressure and
21
22 135 actual differential pressure across the filter.
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24 136

25
26 137 The filters were pre- and post-conditioned by moving them to a dry and dark environment for
27
28 138 48 h, and they were weighed in a room with controlled temperature and humidity. Procedures
29
30 139 were conducted according to the European Committee for Standardization (CEN, 1998). The
31
32 140 PM10 and PM2,5 concentrations, C ($\mu\text{g}/\text{m}^3$), in the air volume sampled, V (L), was
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34 141 calculated as follows:

$$35 \quad 36 \quad 37 \quad 38 \quad 39 \quad 40 \quad 41 \quad 42 \quad 43 \quad 44 \quad 45 \quad 46 \quad 47 \quad 48 \quad 49 \quad 50 \quad 51 \quad 52 \quad 53 \quad 54 \quad 55 \quad 56 \quad 57 \quad 58 \quad 59 \quad 60 \quad 61 \quad 62 \quad 63 \quad 64 \quad 65$$
$$142 \quad C = [(W2 - W1) - (B2 - B1)] \times 10^3 / V$$

143 where $W1$ is the mean of three tare weights of the same filter before sampling (mg), $W2$ is
144 mean of three post-sampling weights of the same sample-containing filter (mg), $B1$ is mean
145 tare weight of blank filters (mg), $B2$ is mean post-sampling weight of blank filters (mg) and V
146 is volume as sampled at the nominal flow rate. At all football field sampling sites the
147 measurements were carried out at the summit of the penalty area while for urban sampling
148 site the measurements were carried out at the meteorological–chemical stations.

150 Aromatic Hydrocarbons analysis

1
2 151 Measurements of benzene, toluene, and xylenes (BTX) levels were carried out at all sites
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4
5 152 using a sampling line (air flow =1L/min) consisting of a membrane pump (KNF Neuberger,
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7 153 N73 KN 18), a gas meter (SIMBRUNT “Ariete 1”), and a granular activated carbon (GAC)
8
9 154 cartridge (SKC coconut shell charcoal adsorbent sample tubes, inc. catalog number 226-01).
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11
12 155 As reported in the SKC certificate of quality, these cartridges are calibrated at 25 °C. The
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14 156 factors of temperature and humidity are not significant except under the most extreme
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17 157 temperature conditions or over 90% of relative humidity, which did not occur at these sites
18
19 158 during this period. Cold temperatures do not interfere with the collection of chemical
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22 159 substances onto solid sorbents (SKC, Inc.). At all football field sampling sites the
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24 160 measurements were carried out at approximately 2 m of height from street level and
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26
27 161 approximately at the summit of the penalty area while for urban sampling site the
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29 162 measurements were carried out at the meteorological–chemical stations.

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31 163 Air monitor samples were analyzed using a gas chromatograph (GC) Carlo Erba 5300 Mega
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33
34 164 Series equipped with a flame ionization detector (FID) and capillary column DB-624
35
36 165 30m×0.318mm ID, film 1.8µm. Each sample was eluted using 3 mL ultrapure carbon
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39 166 disulfide (CS₂ 99.9% low benzene content, Aldrich 34.227-0). A calibration curve was
40
41 167 prepared from known concentrations of benzene, toluene, and xylenes. GC thermal program
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43
44 168 was: 45 °C for 4min, increase of 10 °C/min, from 45 to 145 °C, then 145 °C for 2 min.

45
46 169 Sampling rates of SKC passive sampler 530-11 were supplied by the manufacturer: benzene
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48
49 170 = 10.26 mL/min, toluene 9.05 mL/min, m-xylene = 8.18 mL/min, o-xylene = 8.18, p-xylene =
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51 171 8.2 mL/min. The detection limit of 0.2 µg/sampler was calculated for the 3 aromatics with a
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54 172 signal-to-noise ratio ranging from 5 to 1. The accuracy of the analysis was determined by
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56 173 repeated analysis of a sample for 20 times. The mean of the 20 injections into GC/FID
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58 174 recorded benzene as 9.4 µg/m⁻³ (SD =0.5) with a coefficient of variation of 4.3%. Recovery
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175 (95%) was determined using previously described techniques (Bono, 2003) . When the signal-
176 to-noise ratio ranged from 5 to 1, there was no apparent benzene contamination of CS₂
177 bottles.

178 Polycyclic Aromatic Hydrocarbons analysis

179 The following PAHs were determined in this study and they were considered pollutants of
180 priority interest as categorized by International Agency for Research on Cancer (IARC) as
181 carcinogenic (Group 1), probable (Group 2A) and possible (Group 2B) carcinogenic to
182 humans: Benzo[a]pyrene (1), Benzo[a]anthracene (2A), Benzo[b]fluoranthene (2B),
183 Benzo[k]fluoranthene (2B), Dibenzo[a,h]anthracene (2A), Indeno[1,2,3-c,d]pyrene (2B),
184 other PAHs determined were: Fluoranthene, Pyrene, Chrysene, Benzo[g,h,i]perylene,
185 Phenanthrene, and Anthracene. The determination of PAHs was performed on each PM₁₀ and
186 PM_{2,5} half filters; they were cut in small pieces and placed in a 50-mL polypropylene sterile
187 tube with 15mL of toluene. The tubes were placed in an ultrasonic water bath for 15 min,
188 followed by 1 min of vortexing. This procedure was repeated 3 times. Toluene extracts were
189 evaporated with a rotary evaporator until 2 mL, than evaporated to 150 µL under a stream of
190 nitrogen. The adopted method consisted of HRGC/ LRMS analysis using the method
191 UT2.M128 R01 2002 (Pereira et al., 2001; Gilli et al., 2007a).

192 Mutagenicity analysis

193 The PM₁₀ and PM_{2,5} half filters were cut in small pieces with stainless steel scissors (about
194 0.5 cm×0.5 cm) and extracted with acetone using a Soxhlet apparatus for at least 85 cycles.
195 Acetone was able to extract moderately polar and highly polar classes of compounds. This
196 polar fraction consistently contributed to the highest percentage of mutagenicity, whereas the
197 neutral non-polar fraction contributed the least (Claxton et al., 2004). Mixture solutions were
198 evaporated with a rotary evaporator and redissolved in dimethyl-3-sulfoxide (DMSO) to
199 obtain a concentration of 0.2 m³/µL. The mutagenic activity of the PM₁₀ extracts was

200 determined using the Salmonella microsome assay (*Ames test*) according to the standard plate
201 method of Maron and Ames (1983). Each sample was evaluated with and without metabolic
202 activation (10% S9 mix), using TA98 Salmonella typhimurium strain. Extracts containing an
203 equivalent of 4, 8 or 16 m³ of sampled air were suspended in DMSO and 2 ml top-agar
204 containing biotin was added and subsequently plated on histidine-free agar plates. Each tester
205 strain was checked routinely to confirm genotypes for optimal response to known mutagens
206 as follows: 2-nitrofluorene (2-NF), 1 µg/plate, were used as positive control for TA98 without
207 S9; 2-aminofluorene (2-AF) at 2 µg/plate was used to assess microsomal fraction efficiency.
208 The appropriate solvent controls were also included in each test to check sample preparation
209 interferences. The plates were incubated for 48 h at 37 °C, before counting the number of
210 revertant colonies.

211 The series of concentrations of PM₁₀ organic extract were tested to generate a concentration-
212 response curve (20, 40 or 80 µL of the DMSO 0.2 m³/mL suspension). The slope of
213 concentration- response curve (revertants/m³) was calculated by least-squares linear
214 regression from the first linear portion of the concentration–response curve. The regression
215 coefficients obtained ranged from 0.67 to 0.99, with mean values of 0.89 ± 0.11 for TA98,
216 0.87 ± 0.14 for TA98 +S9. All experiments were performed in triplicate with at least three
217 concentrations. The results were expressed as net revertants (rev/m³), subtracting the
218 spontaneous revertants, calculated by the concentration–response curve (Buschini et al., 2001;
219 Cassoni et al., 2004; Claxton et al., 2004).

220 Statistical analysis

221 Statistical analyses were performed using the SPSS Package, version 14.0 for Windows.
222 Means were compared with the t-test, and the Spearman rank correlation coefficient (r_S) was
223 used to assess relationships between variables. The mean difference and correlation were
224 considered significant at p < 0.05.

225 **RESULTS and DISCUSSION**

226 PM concentrations

227 A total of 24 PM10 and 24 PM2,5 filters were analysed during the two sampling courses. The
228 temperatures registered during the sampling courses of June were between 16 and 34 °C,
229 while during the sampling course of November between 0 and 18°C. Figure 2 and Figure 3
230 show PM10 and PM2,5 concentrations, respectively, in the sampling sites during the two
231 sampling periods. During the first sampling, in June, the mean PM10 concentrations were 59
232 ± 13 µg/m³ and 54 ± 15 µg/m³ in urban site and in football turf fields respectively; while the
233 mean PM2,5 concentrations were 21 ± 3 µg/m³ and 20 ± 4 µg/m³ in urban site and in football
234 turf fields respectively. During the second sampling, in November, the mean PM10
235 concentrations were 110 ± 18 µg/m³ and 103 ± 17 µg/m³ in urban site and in football turf
236 fields respectively; while the mean PM2,5 concentrations were 83 ± 13 µg/m³ and 54 ± 7
237 µg/m³ in urban site and in football turf fields respectively.

238 No significant differences were found between PM10 concentrations in urban site and in
239 football turf fields both in warm days and in cold ones and neither with or without playing;
240 while for PM2,5 concentrations were significantly higher in the urban site in cold days (p<
241 0.01) while in warm days there was no difference (p= 0.31). Significant differences were
242 found between PM10 and PM2,5 concentrations in June and in November (p< 0.01).

243 The ratio PM2.5/PM10 concentrations in November were between 0.65 and 0.93 with a mean
244 value of 0.76 ± 0.10 in urban sites and between 0.47 and 0.58 with a mean value of 0.53 ±
245 0.04 in football turf fields and the difference was significant (p<0.01); in June the ratios were
246 between 0.27 and 0.43 with a mean value of 0.37 ± 0.06 in urban sites and between 0.29 and
247 0.49 with a mean value of 0.39 ± 0.07 and in football turf fields respectively and the
248 difference was not significant.

249

250 BTX concentrations

1
2 251 A total of 24 GAC cartridges were analysed during the two sampling courses for the
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4
5 252 evaluation of BTX concentrations. In Table 2 are reported BTX concentrations in the
6
7 253 sampling sites during the June and November courses respectively. During the first sampling,
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9
10 254 in June, the mean benzene concentrations were $2.9 \pm 0.1 \mu\text{g}/\text{m}^3$ and $1.9 \pm 0.6 \mu\text{g}/\text{m}^3$; the mean
11
12 255 toluene concentrations were $12.5 \pm 1.6 \mu\text{g}/\text{m}^3$ and $6.2 \pm 2.1 \mu\text{g}/\text{m}^3$, the mean xilenes
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14 256 concentrations were $5.9 \pm 0.4 \mu\text{g}/\text{m}^3$ and $10.1 \pm 5.2 \mu\text{g}/\text{m}^3$ in urban site and in football turf
15
16
17 257 fields respectively. During the second sampling, in November, the mean benzene
18
19 258 concentrations were $6.7 \pm 1.3 \mu\text{g}/\text{m}^3$ and $5.1 \pm 0.9 \mu\text{g}/\text{m}^3$; the mean toluene concentrations
20
21
22 259 were $33.0 \pm 6.5 \mu\text{g}/\text{m}^3$ and $20.4 \pm 6.3 \mu\text{g}/\text{m}^3$, the mean xilenes concentrations were 22.5 ± 7.3
23
24 260 $\mu\text{g}/\text{m}^3$ and $28.5 \pm 5.5 \mu\text{g}/\text{m}^3$ in urban site and in football turf fields respectively. Significant
25
26 261 differences were found between BTXs concentrations in urban site and in football turf fields
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28
29 262 both in warm days and in cold ones, BTXs were mean higher in urban sites ($p < 0.05$).
30
31 263 Significant differences were also found between BTXs concentrations in June and in
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33
34 264 November ($p < 0.01$).

35
36 265 Table 2 also shows ratios between benzene and toluene in the two sampling periods. During
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38
39 266 the first sampling, in June, the mean Toluene/Benzene (T/B) ratios, were 4.3 ± 0.5 and $3.5 \pm$
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41 267 1.2 in urban sites and in football turf fields respectively while during the second sampling, in
42
43
44 268 November, the mean T/B ratios, were 4.9 ± 0.4 and 4.0 ± 0.8 in urban sites and in football turf
45
46 269 fields respectively. The difference between the two sampling sites was significant (paired t-
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48
49 270 test, $p = 0.04$).

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51 PAH concentrations

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54 272 A total of 12 PAHs were analysed from both PM10 and PM2,5 extract in each football fields
55
56 273 and in urban sites, during the two sampling courses. In Table 3 are reported PAHs
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58
59 274 concentrations in the sampling sites during the June and November courses respectively.
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275 These PAHs exhibited effects that were representative of the total PAHs; the health effects of
1
2 276 individual PAHs are not exactly alike. (ATSDR, 1995; Torben, 1996). Benzo[a]pyrene is one
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4
5 277 of the PAHs with demonstrated carcinogenic properties in animals, including humans (Group
6
7 278 1 IARC) (Straif et al., 2005), and it is an excellent indicator of PAHs exposure since it highly
8
9
10 279 correlates with the other major carcinogenic PAHs (Feilberg, 2002). PAHs are products of
11
12 280 incomplete combustion and are widespread in the environment and they may contribute to
13
14 281 human cancer; however, the association between PAH exposure and lung cancer is considered
15
16
17 282 unproven (Nielsen et al., 1996; Farmer et al., 2003). During the first sampling, in June, being
18
19 283 a summer period, concentrations of PAHs, when present, were very low. Among the analysed
20
21
22 284 PAHs the Benzo[a]pyrene is the only ruled by law and it was never present. The only PAHs
23
24 285 with values above the detection limit, although at low concentrations, were:
25
26 286 Benzo[b]fluoranthene + Benzo[k]fluoranthene present in 4 football fields (including the clay
27
28
29 287 field), at least in PM10 fraction, Benzo[ghi]perylene present in 3 football fields (including the
30
31 288 clay field) and Chrysene in 2 football fields only in the PM10 fraction.
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34 289 During the second sampling, in November, PAHs concentrations were higher than in summer
35
36 290 period. Benzo[a]pyrene was always present with a mean value of $1.06 \pm 0.51 \text{ ng/m}^3$ in the
37
38
39 291 football fields, concentration comparable to those reported as annual average according to
40
41 292 current regulation (1 ng/m^3). Except for Anthracene, the other PAHs were often present in
42
43
44 293 every football fields and in urban site; the more abundant compounds are
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46 294 Benzo(b)fluoranthene + Benzo(k)fluoranthene, Chrysene and Benz[a]anthracene, both in
47
48
49 295 football fields and in urban site.
50
51 296 The percentage ratio between the amount of total PAHs and the amount of PM10 or PM2.5 on
52
53 297 which they are adsorbed: $10.4 \pm 5.1 \%$ and $15.8 \pm 7.6 \%$ respectively, confirmed that in
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55
56 298 general, also for the football fields, the highest concentration of PAHs was on the PM 2.5.
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59 299

300 Mutagenicity

1
2 301 Spontaneous reversion of the tester strains to histidine independence is measured in each
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4
5 302 Ames test and was expressed as the number of spontaneous revertants per plate. Spontaneous
6
7 303 reversion is at a frequency that is characteristic of the strain. The data were expressed as the
8
9
10 304 average revertants number per plate from the triplicates. Table 4 summarized the results
11
12 305 obtained from the study tests. Extracts of airborne particulate matters collected in the football
13
14 306 fields and in urban background site of Torino, showed low mean mutagenicity to Salmonella
15
16
17 307 typhimurium strain TA98 with and without metabolic activation (S9 mix). In comparison with
18
19 308 the spontaneous revertants, greater effect was recorded with TA98 without S9 both for PM10
20
21
22 309 and for PM2,5. The mutagenic characteristics show a seasonal trend and were found to be
23
24 310 significantly different for the two sampling periods for both PM2,5 and PM10. In June, in the
25
26
27 311 football fields, mean mutagenicity for PM2,5 was 111.4 ± 40.7 revertants/mg and 77.4 ± 17.0
28
29 312 revertants/mg for TA98 and TA98+S9 respectively; mean mutagenicity for PM10 was $56.6 \pm$
30
31 313 10.8 revertants/mg and 39.5 ± 9.2 revertants/mg for TA98 and TA98+S9 respectively. While
32
33
34 314 in the urban site mutagenicity for PM2,5 was 161.4 and 56.9 revertants/mg for TA98 and
35
36 315 TA98+S9 respectively and for PM10 was 39.7 and 36.9 revertants/mg for TA98 and
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38
39 316 TA98+S9 respectively.

40
41 317 In November, in the football fields, mean mutagenicity for PM2,5 was 490.8 ± 91.9
42
43
44 318 revertants/mg and 328.6 ± 99.7 revertants/mg for TA98 and TA98+S9 respectively; mean
45
46 319 mutagenicity for PM10 was 576.7 ± 268.5 revertants/mg and 333.6 ± 233.5 revertants/mg for
47
48
49 320 TA98 and TA98+S9 respectively. While in the urban site mutagenicity for PM2,5 was 769.8
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51 321 and 373.3 revertants/mg for TA98 and TA98+S9 respectively and for PM10 was 239.2 and
52
53 322 212.5 revertants/mg for TA98 and TA98+S9 respectively.

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325 **CONCLUSIONS**

1
2 326 This environmental analysis showed that the particulate matter fractions in artificial turfs
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5 327 often had concentrations equal to that found in background urban stations, both in warm and
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7 328 in cold periods. In general the monitoring of PM10 and of PM2.5 in Torino showed
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10 329 concentrations that were frequently higher than the daily ($50\mu\text{g}/\text{m}^3$ and $20\mu\text{g}/\text{m}^3$ respectively)
11
12 330 quality targets (Air Quality Directive, 2008/50/CE) especially in winter times. The
13
14
15 331 comparison between artificial field and clay one (P1 and P2) showed slightly higher for the
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17 332 latter especially in cold times, but this situation was also deferred in urban areas in the two
18
19 333 different sampling days; probably the lifting of the clay during the game tends to raise the
20
21
22 334 values of particulates. There were no differences in the concentration of particulate matter
23
24 335 linked to seniority of the fields or the type of fields (black UT or thermoplastic) considering
25
26
27 336 the different sampling days. The PM2.5 and PM10 ratio in football fields was comparable to
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29 337 urban sites, and it was between 0.4 and 0.8 (values closer to 0.8 indicate a situation where it is
30
31
32 338 more important to the respirable fraction), especially in winter times, the situation becomes
33
34 339 more critical in urban sites, reflecting the growing influence of the fine component.
35
36 340 The concentration of BTX in the monitored football fields were constant and were
37
38
39 341 comparable to urban background levels or at least reflect a normal situation related to urban
40
41 342 pollution source of motor vehicles (the only exception is the concentration of xylenes during
42
43
44 343 the first sampling in P1, that was greater than in both the other fields and in urban stations
45
46 344 probably because of in that field had been painted the gates during the days preceding the
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48
49 345 sampling), in general benzene and toluene values were much lower than the urban sites. There
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51 346 were no substantial differences in the concentrations of aromatic hydrocarbons related to
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53
54 347 seniority of the field or the type of fields (black UT or thermoplastic) considering the different
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56 348 sampling days even taking into account the few cases analyzed, the condition of "use" and the
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58 349 temperatures. The T/B ratio was always related to normal urban conditions in all sites
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350 considered; some studies showed that when this ratio takes values greater than two can be
1
2 351 assumed that the pollution comes from traffic (Valerio et al., 2005).
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4
5 352 The concentration of PAH, both on PM10 and on PM2,5, in the monitored football fields
6
7 353 were comparable to urban levels in the two different periods of samplings. About the warm
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9
10 354 sampling, B[b]f + B[k]f were regarded as characteristic of PAH emissions from combustion
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12 355 of gasoline vehicles, B[ghi]pe was considered (after Py) characteristic of emissions from tire
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14 356 wear and asphalt (Pengchai et al., 2005); these PAH were also present on the clay field so
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17 357 probably, since the fields were without on-field activity, these values could be attributable to
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19 358 traffic in surrounding streets. In the cold sampling, B[b]f + B[k]f were present in all fields and
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21
22 359 with the highest percentage compared to others; the same consideration was true for B[a]a
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24 360 (characteristic of PAH emissions from combustion of gasoline vehicles). Py and B[ghi]pe
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26
27 361 were also present on the clay field therefore, as the fields were used, these values could be
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29 362 attributable to traffic in surrounding streets.
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31
32 363 The concentration ratios of all PAHs vs. BaP lied in the respective ranges observed in urban
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34 364 areas (Menichini et al., 1999).
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36
37 365 In Italy, in warm season, the total PAHs concentrations in a traffic site, range between 1 and 4
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39 366 ng/m³ while in a background one between 0.1 and 1 ng/m³ (Menichini et al., 2006, ISPRA,
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41 367 2010); in the monitored fields total PAHs values ranging from <0.1 to 0.6 ng/m³. In cold
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44 368 season, the total PAHs concentrations in a traffic site, range between 3 and 13 ng/m³ while in
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46 369 a background one between 1 and 5 ng/m³; in the monitored fields total PAHs values ranging
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48
49 370 from 2.8 and 15.5 ng/m³ (Menichini et al., 2006, ISPRA, 2010). Therefore also for what
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51 371 concerns the PAHs there was a normal urban profile in the considered periods. The highest
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53
54 372 PAHs concentrations were reported on PM2.5 (70 - 90%), in this regard, in our investigation,
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56 373 the concentration of PAHs could be worse at the city level by considering the relationship
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58 374 between PM10 and PM2,5 in football fields, which turns out to be lower than urban sites. The
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1 375 concentrations measured in the field substantially equalled the urban background
2 376 concentrations measured close to the field, and the contribution of PAHs released from the
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4 377 granulate was likely negligible. There were no differences in the concentration of PAH linked
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6
7 378 to seniority of the fields or the type of fields (black UT or thermoplastic) considering the
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9 379 different sampling days.
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12 380 Since target PAHs were present in air as particle-bound, their highest concentrations were
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14 381 expected to occur close to the points where the turf is stressed causing particles to be released
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17 382 (Menichini et al., 2011). However, the hi-vol air sampler was located at the summit of the
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19 383 penalty area, which implies the measurements could underestimate the actual concentrations
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22 384 the athletes were exposed to. The use of personal air samplers seems to be a suitable
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24 385 procedure to estimate the actual concentrations the athletes are exposed to. However a recent
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26 386 study underline that the uptake of PAH by football players active on artificial grounds with
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29 387 rubber crumb infill is minimal. If there was any exposure, than the uptake is very limited and
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32 388 within the range of uptake of PAH from environmental sources and/or diet (van Rooij and
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34 389 Jongeneelen, 2010).
35
36 390 In the present monitoring the mutagenicity of football field PM10 was higher while the
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39 391 mutagenicity of football field PM2,5 was lower, compared to the urban site. In general in
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41 392 artificial football fields, both in June and in November, there were mean values comparable to
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43
44 393 that reported in other studies in urban sites (Gilli et al., 2007a; Gilli et al., 2007b).
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46 394 In the present study, the concentrations of PM, BTX, PAHs and mutagenicity had a normal
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48
49 395 urban trend in the considered periods and there were no significant differences between
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51 396 football fields and urban sites; moreover no substantial differences were found between
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54 397 artificial football fields and “natural” football field. On the basis of this environmental
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56 398 monitoring there were not present more risks on artificial football turf fields than on rest of
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399 the city, yet, further work will be necessary to assess the actual scenarios of exposure by
1
2 400 inhalation and the corresponding risks.

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4 401

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12
13
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Table 1. Characteristics of the sampling sites.

Football Field (name)	Age (years)	Material	Dimensions (m)	1 st sampling	2 nd sampling
Pellerina 1 (P1)	3	black UT ¹	45 x 90	12 June	6 November
Pellerina 2 (P2)	3	clay	45 x 90	13 June	7 November
Carrara (C)	1.5	black UT ¹	40 x 65	14 June	8 November
Rivermosso (R)	3	black UT ¹	40 x 65	15 June	9 November
Passo Buole (S)	3	thermoplastic	45 x 90	21 June	14 November
Barracuda (B)	1.5	black UT ¹	40 x 65	26 June	15 November
Meteorological–chemical station (name)				1 st sampling	2 nd sampling
Background (1a) Environmental Protection Regional Agency (Piedmont A.R.P.A.)		6 m high, in the central limited traffic zone.		12-26 June	6-15 November
Traffic (1b) Environmental Protection Regional Agency (Piedmont A.R.P.A.)		2 m height, “sandwiched” between two busy streets and bordered with the central limited traffic zone.		12-26 June	6-15 November

¹Used Tires

Table 2. Benzene (B), Toluene (T) and Xilenes (Xs: sum of m-xilene, o-xilene and p-xilene) concentrations ($\mu\text{g}/\text{m}^3$) and Toluene and Benzene (T/B) ratio in the sampling sites during the first period of samplings, 12-26 June (2A) and during the second period of samplings, 6-15 November (2B) (1a: meteorological–chemical background urban station; R: artificial turf, Rivermosso; C: artificial turf, Carrara; P1: artificial turf, Pellerina; P2: football field clay; B: artificial turf, Barracuda; S: artificial turf, Passo Buole).

(2A)	Urban control site (1a)				Football fields				
	B	T	Xs	T/B		B	T	Xs	T/B
12 Jun	2.7	10.4	5.5	3.9	P1	1.8	10.2	20.9	5.7
13 Jun	3.0	11.5	5.8	4.0	P2	1.4	5.1	7.4	3.6
14 Jun	3.0	12.5	6.0	4.2	C	1.3	5.6	7.9	4.3
15 Jun	3.0	12.9	6.4	4.2	R	1.4	4.2	7.2	3.1
21 Jun	3.1	15.3	5.9	5.1	S	3.0	6.9	8.3	2.3
26 Jun	2.7	13.0	6.0	4.2	B	2.2	5.3	8.8	2.4
(2B)									
Date	B	T	Xs	T/B		B	T	Xs	T/B
6 Nov	8.8	41.8	34.4	4.7	P1	6.0	18.9	25.7	3.1
7 Nov	7.4	38.4	25.8	5.2	P2	5.8	23.1	34.7	4.0
8 Nov	5.6	28.2	16.5	5.0	C	4.7	15.4	26.0	3.3
9 Nov	6.2	32.6	22.8	5.2	R	5.7	31.2	33.7	5.5
14 Nov	6.4	33.0	21.6	5.1	S	4.9	20.3	31.1	4.2
15 Nov	5.5	24.0	13.7	4.3	B	3.4	13.6	20.3	4.0

Table 3. Polycyclic Aromatic Hydrocarbons concentrations, from both PM10 and PM2,5 extraction, in the sampling sites during the first period of samplings, 12-26 June (3A) and during the second period of samplings, 6-15 November (3B) (1a: meteorological–chemical background urban station; R: artificial turf, Rivermosso; C: artificial turf, Carrara; P1: artificial turf, Pellerina; P2: football field clay; B: artificial turf, Barracuda; S: artificial turf, Passo Buole). PAH: Benzo[a]pyrene (B[a]p), Benzo[a]anthracene (B[a]a), Benzo[b]fluoranthene (B[b]f), Benzo[k]fluoranthene (B[k]f), Dibenzo[a,h]anthracene (Db[ah]a), Indeno[1,2,3-c,d]pyrene (I[cd]p), Fluoranthene (Fl), Pyrene (Py), Chrysene (Ch), Benzo[g,h,i]perylene (B[ghi]pe), Phenanthrene (Fe), Anthracene (A). LOD (limit of detection) = 0.09 ng/m³.

(3A)	PAH ng/m ³	B[a]p	B[a]a	B[b]f + B[k]f	Db[ah]a	I[cd]p	Fl	Py	Ch	B[ghi]pe	Phe	A
12 June 1a	PM10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	PM2,5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
12 June P1	PM10	<LOD	<LOD	0.17	<LOD	<LOD	<LOD	<LOD	0.10	0.12	<LOD	<LOD
	PM2,5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.10	<LOD	<LOD
13 June P2	PM10	<LOD	<LOD	0.15	<LOD	<LOD	<LOD	<LOD	<LOD	0.10	<LOD	<LOD
	PM2,5	<LOD	<LOD	0.13	<LOD	<LOD	<LOD	<LOD	<LOD	0.09	<LOD	<LOD
14 June C	PM10	<LOD	<LOD	0.12	<LOD	<LOD	<LOD	<LOD	<LOD	0.09	<LOD	<LOD
	PM2,5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
15 June R	PM10	<LOD	<LOD	0.12	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	PM2,5	<LOD	<LOD	0.10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
21 June S	PM10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.10	<LOD	<LOD	<LOD
	PM2,5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
26 June B	PM10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	PM2,5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
(3B)	PAH ng/m³											
15 November 1a	PM10	0.78	0.62	1.98	<LOD	0.70	0.34	0.48	0.62	0.78	<LOD	<LOD
	PM2,5	0.70	na	na	na	na	na	na	na	na	na	na
6 November P1	PM10	0.77	0.76	1.81	<LOD	0.50	0.57	0.69	1.00	0.65	0.17	<LOD
	PM2,5	0.70	0.57	1.61	<LOD	0.49	0.43	0.55	0.77	0.64	0.14	<LOD
7 November P2	PM10	0.34	0.44	1.06	<LOD	0.26	0.25	0.32	0.57	0.29	0.10	<LOD
	PM2,5	0.29	0.26	0.78	<LOD	0.23	0.15	0.19	0.31	0.27	<LOD	<LOD

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8 November C	PM10 PM2,5	1.19 1.09	1.20 1.04	2.53 2.37	0.12 0.11	0.69 0.64	0.45 0.35	0.62 0.44	1.53 1.33	0.87 0.81	0.12 0.11	<LOD <LOD
9 November R	PM10 PM2,5	1.75 1.64	2.13 1.79	3.98 4.00	0.19 0.18	1.03 0.98	0.56 0.40	0.71 0.54	2.24 2.11	1.22 1.16	0.15 0.14	<LOD <LOD
14 November S	PM10 PM2,5	1.49 1.04	1.53 1.1	3.18 2.23	0.25 0.14	1.01 0.67	0.94 0.54	1.32 0.71	1.98 1.37	1.31 0.88	0.24 0.16	<LOD <LOD
15 November B	PM10 PM2,5	0.82 0.72	0.95 0.62	2.08 1.70	<LOD <LOD	0.56 0.49	0.55 0.31	0.79 0.39	1.31 0.82	0.71 0.67	0.17 0.12	<LOD <LOD

Table 4. Mutagenicity of PM10 (4A) and PM2,5 (4B) organic extracts. Summary of the *Ames test* results: mean spontaneous *Salmonella* revertants and mean net revertants *per m*³ of sampled air and *per μg* of particles; (1a: meteorological–chemical background urban station; 1b: meteorological–chemical traffic urban station; R: artificial turf, Rivermosso; C: artificial turf, Carrara; P1: artificial turf, Pellerina; P2: football field clay; B: artificial turf, Barracuda; S: artificial turf, Passo Buole).

(4A) PM10	TA 98 revertants/m³	TA 98 +S9 revertants/m³	TA 98 revertants/mg	TA 98 +S9 revertants/mg	Sampling sites
Spontaneous	19	24	19	24	
12 June	1.2	1.0	39.7	36.9	1a
15 November	56.0	42.0	239.2	212.5	
12 June	2.7	1.8	59.3	39.3	P1
6 November	28.8	18.7	261.9	169.8	
13 June	3.0	1.9	62.0	39.0	P2
7 November	73.7	21.7	562.4	165.5	
14 June	2.7	.2	45.1	37.4	C
8 November	29.7	13.9	312.1	146.1	
15 June	3.2	3.0	56.8	53.6	R
9 November	60.6	38.1	555.9	349.2	
21 June	3.5	3.4	44.0	42.8	S
14 November	76.0	62.4	1036.1	751.8	
26 June	4.7	1.6	72.7	25.1	B
15 November	75.8	37.3	852.1	419.1	
(4B) PM2,5					
12 June	3.4	0.6	161.4	56.9	1b
15 November	63.9	31.0	769.8	373.3	
12 June	1.4	1.5	77.8	80.7	P1
6 November	25.0	15.6	480.8	300.4	
13 June	2.2	1.5	111.7	77.4	P2
7 November	27.5	10.9	416.1	165.7	
14 June	2.2	2.1	100.0	95.36	C
8 November	22.1	17.9	401.7	325.8	
15 June	3.9	1.7	164.0	69.1	R
9 November	36.1	24.9	645.1	443.9	
21 June	1.5	2.3	61.6	93.0	S
14 November	24.7	19.0	548.5	422.6	
26 June	2.6	0.8	153.6	49.0	B
15 November	22.1	15.3	452.6	313.2	

FIGURE CAPTIONS

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Figure 1. Sampling sites are placed in north-western Italy, in Piedmont Region, in the chief town: Torino. Seven different sampling sites, two urban control sites and six football field sites (1a: meteorological–chemical background station; 1b: meteorological–chemical traffic station; R: artificial turf, Rivermosso; C: artificial turf, Carrara; P1: artificial turf, Pellerina; P2: football field clay; B: artificial turf, Barracuda; S: artificial turf, Passo Buole).

Figure 2. PM10 concentrations in the sampling sites during the two sampling periods, 12 – 26 June (grey bars and striped bars) and 6-15 November (black bars and dotted bars). 1a: meteorological–chemical background urban station; R: artificial turf, Rivermosso; C: artificial turf, Carrara; P1: artificial turf, Pellerina; P2: football field clay; B: artificial turf, Barracuda; S: artificial turf, Passo Buole.

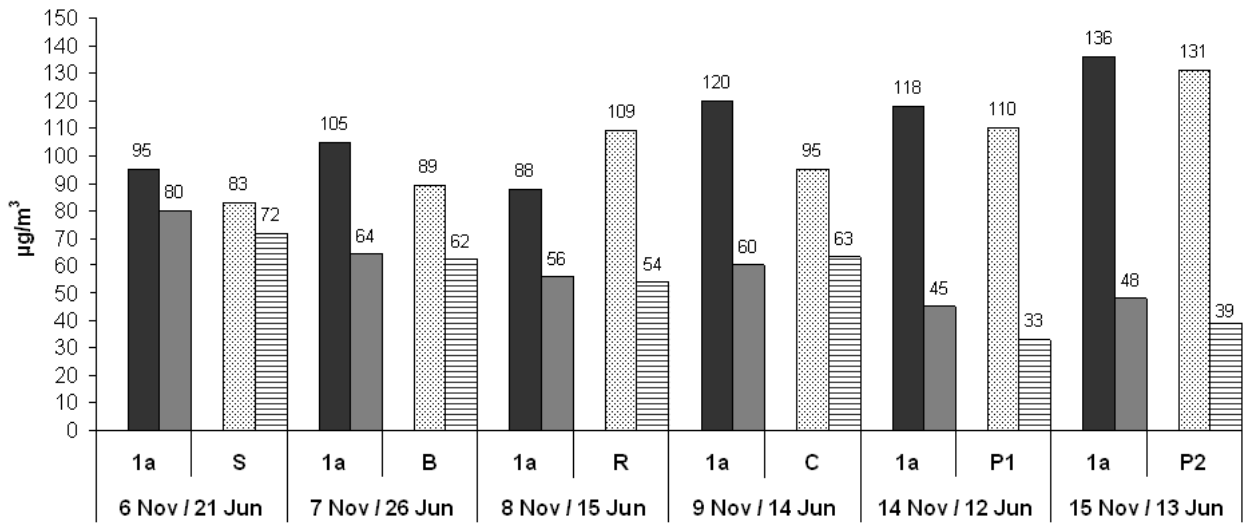
Figure 3. PM2.5 concentrations in the sampling sites during the two sampling periods, 12 – 26 June (grey bars and striped bars) and 6-15 November (black bars and dotted bars). 1b: meteorological–chemical traffic urban station; R: artificial turf, Rivermosso; C: artificial turf, Carrara; P1: artificial turf, Pellerina; P2: football field clay; B: artificial turf, Barracuda; S: artificial turf, Passo Buole.

Figure 1.



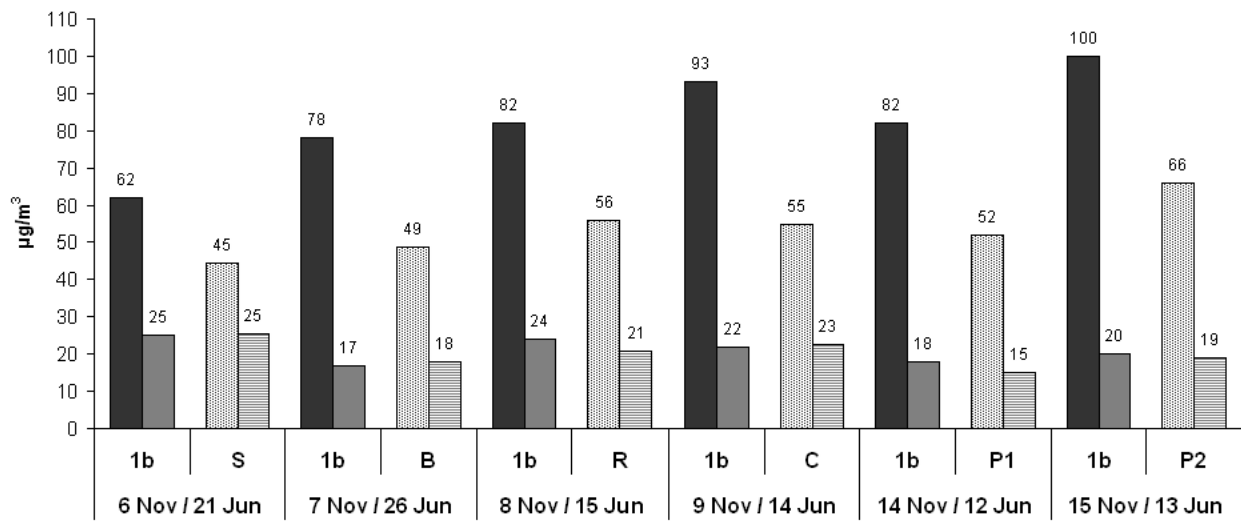
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Figure 2.



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Figure 3.



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