

PIXE Analysis of Synthetic Turf

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Abstract We performed a proton-induced X-ray emission (PIXE) analysis of synthetic turf blade and crumb rubber infill samples to search for heavy metals and other possibly toxic substances. Samples were collected from eight FieldTurf athletic fields installed in the Capital District of New York between 2009 and 2016. The samples were bombarded with proton beams from the 1.1-MV tandem Pelletron accelerator in the Union College Ion-Beam Analysis Laboratory and the emitted X-rays were measured using a silicon drift detector with an energy resolution of about 130 eV. All of the infill samples contained Zn at levels above soil standards. Approximately 17% of the infill samples contained measurable concentrations of Pb and one had a level (110 ± 10 ppm) exceeding soil standards. Bromine was detected in approximately 42% of the infill samples with a maximum concentration of 1500 ± 200 ppm and may be due to the presence of brominated flame retardants. The distributions and relative concentrations of elements measured in synthetic turf blade samples of different colors are indicative of the metal-oxide pigments used to color the blades. For example, V and Bi observed in yellow blade samples are from the environmentally friendly, yellow pigment bismuth vanadate.

Keywords PIXE, Synthetic Turf, Heavy Metals, Bromine

Of particular concern is the crumb rubber infill from recycled tires that is used to cushion the surfaces and support the synthetic turf blades.

High levels of volatile organic compounds and heavy metals have been measured in crumb rubber infill in a number of recent studies. Zhang et al. [2] performed a small-scale study in which they analyzed seven samples of crumb rubber and one sample of artificial grass fiber for polycyclic aromatic hydrocarbons (PAHs) using high-performance liquid chromatography (HPLC) and several heavy metals (Zn, Cr, As, Cd, and Pb) using an inductively-coupled plasma mass spectrometer (ICP-MS) after acid digestion. Their results showed that the crumb rubber samples contained PAHs at levels above soil standards, Zn concentrations far exceeding soil standards, and a maximum Pb level of 53 ppm. Low concentrations of Cr, As, Pb, and a few PAHs were measured in the artificial grass fiber sample. In a larger-scale study by Menichini et al. [3], crumb rubber samples were collected from 13 fields in Italy and analyzed for nine metals using ICP-MS and 25 PAHs using a high resolution gas chromatograph-low resolution mass spectrometer (HRGC-LRMS). They found high levels of PAHs, Zn concentrations well above soil standards, and a maximum Pb concentration of 46 mg/kg. Marsili et al. [4] examined nine samples of crumb rubber for seven heavy metals by microwave mineralization and 14 PAHs using HPLC. Their results also show high levels of Zn and PAHs, and a maximum Pb level of about 39 mg/kg.

1 Introduction

There are at least tens of thousands of synthetic turf athletic fields and playgrounds in use throughout the world. The popularity of artificial turf is due to a number of advantages over natural turf fields. They have lower maintenance costs, don't require treatment with pesticides and fertilizers, provide increased playing time, and save water. However, there have been considerable concerns in recent years about potential health effects associated with chemicals that may be released from synthetic turf (see for example Ref. [1]).

In a recent review [5] of health and environmental impacts of synthetic turf, the authors point out that more data and research are needed to assess the risk presented by crumb rubber infill on the environment and human health. Last year, the U.S. Environmental Protection Agency (EPA), the Centers for Disease Control and Prevention/Agency for Toxic Substances and Disease Registry (ATSDR), and the Consumer Product Safety Commission (CPSC) launched a multi-agency study on the environmental and health effects of recycled tire crumb used on playing fields and playgrounds.

In this paper, we report the results of a proton-induced X-ray emission (PIXE) [6] analysis of synthetic turf infill and blade samples. Concentrations were measured for elements heavier than Ca to search for the presence of heavy metals and toxic chemicals. Proton-induced X-ray emission is a powerful tool for the study of environmental samples because it can provide information on a broad range of elements with high sensitivity and low detection limits, and is non-destructive. Also, it often requires little or no sample preparation, unlike many chemical techniques.

2 Materials and Methods

2.1 Sample Collection and Preparation

Crumb rubber infill samples were collected at eight FieldTurf athletic fields installed in the Capital District of New York between 2009 and 2016. The samples were collected at random locations and stored in a single, clean plastic bag for each field. The crumb rubber infill typically consists of small ($\lesssim 2\text{-}3\text{ mm}$) granules of shredded, recycled tires. Three pellets were prepared from the samples for each field by pressing 1 g of crumb rubber with approximately 1 g of 5-minute epoxy. The flat surfaces of the pellets were sanded and cleaned to remove epoxy from the surfaces and expose the crumb rubber infill. The pellets were mounted on a target ladder with double-sided tape for the PIXE measurements. Shown in Fig. 1 is a photograph of 1 g of loose infill (left) and a pellet (right).



Figure 1. A photograph of 1 g of loose crumb rubber infill (left) and a pellet made by pressing 1 g of infill with approximately 1 g of 5-minute epoxy (right).

Samples of eight different colored synthetic grass blades were also collected from two of the athletic fields. Blades of each color were mounted on glass slides and coated with a thin layer of Al in a vacuum evaporator to prevent the samples from charging during the PIXE measurements. The blade samples were removed from the glass slides and taped to a target ladder for the measurements. A photograph of some of the synthetic turf blades before they were coated with a thin layer of Al is shown in Fig. 2.

2.2 PIXE Experiments

The PIXE measurements were performed with the 1.1-MV tandem Pelletron accelerator in the Union College Ion-Beam Analysis Laboratory. Proton beams with an energy

of 2.2 MeV, currents of 5-15 nA, and diameters of 1-2 mm were incident on the infill pellets and blade samples positioned in the center of a multipurpose scattering chamber. Each target was irradiated for 15-30 minutes in 5 minute intervals and the accumulated charge was estimated by removing the sample from the beam and integrating the beam current in a Faraday cup periodically for 5 minute intervals. The total charge incident on the samples ranged from 9 to 25 μC with an uncertainty of less than 10%. Also, a charge of 1 μC was collected on Ti, Cr, Fe, Cu, Ge, Au, and Pb MICROMATTER standards. The X-rays emitted from the samples were detected at an angle of 135° from the beam direction with an Amptek XR-100SDD silicon drift detector with a resolution of about 130 eV and an effective solid angle of approximately 2.0 msr. An approximately 79- μm thick Al foil was placed in front of the detector to suppress X-rays from light elements. The X-ray energy spectra were analyzed using GUPIX software [7].

3 Results

3.1 Infill Samples

A typical PIXE spectrum of one of the infill samples is shown in Fig. 3. The concentrations of elements measured by fitting the spectra for the 24 infill samples with GUPIX are listed in Table 1. Concentrations are reported only for elements that are present in each sample at a 95% confidence level. The quoted uncertainties were determined by adding in quadrature the estimated uncertainty in charge integration and the fit error reported by GUPIX. All of the samples contained detectable concentrations of Fe and Zn. The Fe concentrations ranged from 43 ± 5 to 800 ± 80 ppm, while those for Zn spanned from 510 ± 50 to 4700 ± 500 ppm. A third of the samples contained Ti at concentrations ranging from 110 ± 30 to 640 ± 90 ppm. Measurable concentrations of Co at the level of 15 ± 2 to 64 ± 6 ppm were found in approximately 42% of the samples. Approximately 42% of the samples contained Ni at concentrations of 4 ± 1 to 18 ± 3 ppm. Concentrations of Cu were measured in approximately 71% of the samples at levels of 8 ± 2 to 180 ± 20 ppm. Approximately 42% of the samples contained Br at concentrations from 13 ± 3 to 1500 ± 200 ppm. Finally, Pb was measured in about 17% of the samples at levels of 26 ± 6 to 110 ± 10 ppm.



Figure 2. A photograph of some of the synthetic turf blades before they were coated with a thin layer of Al.

Table 1. Concentrations of heavy elements measured in the infill samples.

Sample #	Concentration in ppm							
	Ti	Fe	Co	Ni	Cu	Zn	Br	Pb
1	640 ± 90	250 ± 20		10 ± 2		4700 ± 500	110 ± 10	
2		86 ± 9	29 ± 4			1600 ± 200		
3		79 ± 8	23 ± 3			1100 ± 100	33 ± 6	29 ± 8
4	230 ± 60	800 ± 80		18 ± 3	17 ± 4	1900 ± 200	1500 ± 200	
5		290 ± 30				920 ± 90	550 ± 60	
6		280 ± 30				810 ± 80		
7	110 ± 24	240 ± 20	17 ± 3	12 ± 2	120 ± 10	1300 ± 100	90 ± 10	49 ± 8
8		310 ± 30	31 ± 3	12 ± 2	110 ± 10	1000 ± 100	20 ± 4	
9		230 ± 20	43 ± 5		17 ± 5	2000 ± 200		
10	280 ± 30	210 ± 20	15 ± 2		25 ± 3	1600 ± 200	13 ± 3	
11		130 ± 10	64 ± 6		19 ± 3	3500 ± 400	14 ± 4	
12	500 ± 50	190 ± 20			76 ± 8	4000 ± 400		
13		190 ± 20			9 ± 2	1000 ± 100		
14	110 ± 30	330 ± 30	53 ± 5	12 ± 2	180 ± 20	3100 ± 300		
15	280 ± 40	120 ± 10			51 ± 5	1200 ± 100		
16		120 ± 10		4 ± 1	10 ± 2	510 ± 50		26 ± 6
17		190 ± 20		5 ± 1	18 ± 2	1400 ± 100		
18		160 ± 20		5 ± 1	10 ± 3	1100 ± 100		
19		43 ± 5	46 ± 5		16 ± 3	1600 ± 200		
20		49 ± 5			8 ± 2	780 ± 80		
21		200 ± 20		8 ± 2	20 ± 4	1100 ± 100		110 ± 10
22		120 ± 10	22 ± 4			2600 ± 300		
23		230 ± 20		4 ± 1		2800 ± 300	29 ± 5	
24	230 ± 40	160 ± 20			12 ± 3	840 ± 80	42 ± 6	

3.2 Blade Samples

A PIXE spectrum from the irradiation of the yellow blade sample is shown in Fig. 4. Shown in Figure 5 is a bargraph of the elemental concentrations measured in the analysis of the synthetic blade samples. Concentrations are reported only for elements that are present in each sample at a 95% confidence level. The quoted uncertainties were determined by adding in quadrature the estimated uncertainty in charge integration and the fit error reported by GUPIX. The black blade sample contained Fe (75 ± 8 ppm), Cu (500 ± 50 ppm), and Zn (21 ± 4 ppm). Concentrations of Ti (2800 ± 300 ppm), Fe (230 ± 20 ppm), Cu (800 ± 80 ppm), and Zn (18 ± 4 ppm) were measured in the blue blade sample. The garnet blade sample had measurable levels of Ti (2400 ± 200 ppm), Fe (6100 ± 600 ppm), Cu (26 ± 3 ppm), and Zn (16 ± 3 ppm). Levels of Fe (11000 ± 1000 ppm), Cu (210 ± 20 ppm), and Zn (15 ± 4 ppm) were detected in green blade sample. The purple blade sample contained Ti (3600 ± 400 ppm), Mn (50 ± 10 ppm), Fe (150 ± 20 ppm), Cu (17 ± 3 ppm), Zn (770 ± 80 ppm), As (16 ± 2 ppm), and Sr (37 ± 6 ppm). Concentrations of Ti (11000 ± 100 ppm), Fe (180 ± 20 ppm), Cu (9 ± 2 ppm), and Zn (19 ± 3 ppm) were measured in the red blade sample. The white blade sample contained Ti (19000 ± 2000 ppm), Fe (180 ± 20 ppm), and Zn (22 ± 4 ppm). Finally, levels of Ti (10000 ± 1000 ppm), V (1300 ± 200 ppm),

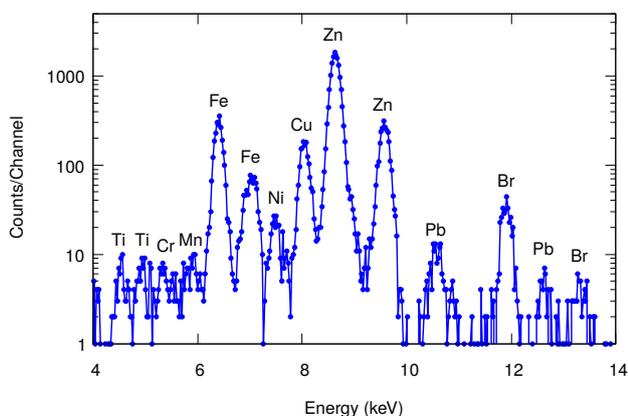


Figure 3. A PIXE spectrum taken on infill sample 7. The X-ray lines are identified. An Al filter with a thickness of $79 \mu\text{m}$ was placed between the target and the detector to suppress X-rays from lighter elements.

Fe (110 ± 10 ppm), Zn (2100 ± 200 , and Bi (2900 ± 300 ppm) were measured in the yellow blade sample.

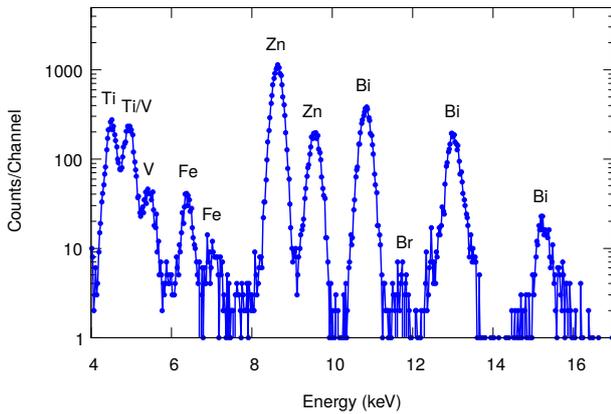


Figure 4. A PIXE spectrum taken on the yellow blade sample. The X-ray lines are identified. An Al filter with a thickness of $79 \mu\text{m}$ was placed between the target and the detector to suppress X-rays from lighter elements.

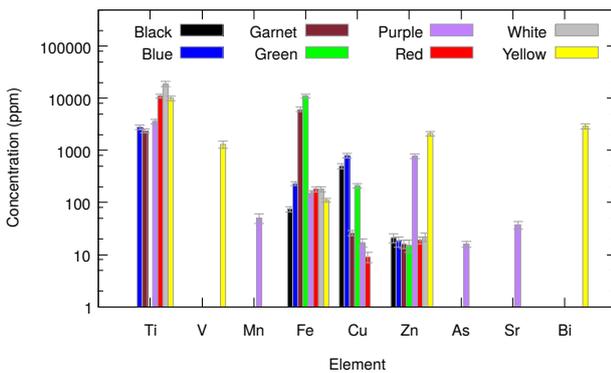


Figure 5. A bargraph of the concentrations of heavy elements measured in the turf blade samples.

4 Discussion

4.1 Infill Samples

It is clear from the broad range of measured elemental concentrations that the infill samples are not homogeneous. This is probably due to the fact that the crumb rubber infill is produced from recycled tires and other rubber from many different sources and distributed randomly over the fields.

The high concentrations of Zn measured in many of our infill samples are consistent with the results of other studies [2, 3, 4]. All of the infill samples had Zn levels exceeding the New York State Department of Conservation (NYDEC) unrestricted use soil standard of 109 ppm and six of them exceeded the residential restricted use standard of 2200 ppm [8]. These high levels of Zn are not surprising since tires contain approximately 1-2% Zn by weight [9]. Zinc is not nearly as toxic to humans as other heavy metals such as Pb, but long-term, high-dose Zn intoxication

can interfere with the uptake of Cu and other essential trace elements [10]. Also, runoff with elevated levels of Zn may have adverse effects on aquatic wildlife and plants [11].

The range of Pb concentrations measured in our samples are in agreement with those reported in earlier investigations [2, 3, 4]. Only one of the four infill samples that contained measurable levels of Pb had a concentration above the NYDEC unrestricted use soil standard of 63 ppm [8]. However, due to the acute toxicity of Pb, there is no known level of exposure that is considered safe and the addition of new Pb to the environment should be avoided [12].

An initially surprising result is the Br that was detected in approximately 42% of the infill samples with a maximum concentration of 1500 ± 200 ppm. These levels are consistent with those reported in a non peer-reviewed analysis of crumb rubber infill samples using a hand-held X-ray fluorescence analyzer [13]. The bromine may be from flame retardants that were added to some of the tires used to make the crumb rubber or used to treat the fields [14]. Some brominated flame retardant chemicals have been linked to adverse health effects in humans. For example, polybrominated diphenyl ethers (PBDEs) are commonly used flame retardants that have been shown to reduce fertility [15] and have hormone-disrupting effects, in particular, on estrogen and thyroid hormones [16].

The concentrations of Co measured here in approximately 42% of the samples were low ($\leq 64 \pm 6$ ppm) and in agreement with those reported in a recent study by the European Chemicals Agency [17]. The NYDEC does not report a soil standard for Co.

All of the concentrations of Ni measured in this study were below the NYDEC unrestricted use soil standard of 30 ppm [8]. Copper levels found in approximately 21% of the infill samples are above the NYDEC unrestricted use soil standard of 50 ppm, but all the measured concentrations were below the NYDEC restricted residential use soil standard of 270 ppm. Finally, the concentrations of Ti and Fe measured in the infill samples are much lower than what is typically found in soil [18].

The high levels of Zn and Br, and the presence of Pb in some of the infill samples raises concerns about potential health risks. A recent, non peer-reviewed study of airborne particulate matter above artificial turf playing fields suggests that some of the infill particles are small enough to be inhaled [19]. Also, athletes playing on these fields often come into contact with the infill and it is possible that the particles can be ingested or that the chemicals can be absorbed through the skin.

4.2 Blade Samples

The distribution and relative concentrations of elements in the synthetic turf blade samples are indicative of the pigments used to color the blades. These are typically mixed metal-oxide pigments (e.g. titanium dioxide) that are mixed with the plastic polymers (nylon, polypropylene or polyethylene) before they are extruded to make the blades [20].

An interesting example is the V and Bi observed in the yellow blade sample that are from the yellow pigment bismuth vanadate (BiO_4V).

We did not detect Pb in any of the blade samples, unlike the results on some samples from older generation artificial turf fields [2, 21]. The elements with high concentrations all have relatively low toxicity. Even Bi has unusually low toxicity for a heavy metal [22]. Because the pigments are mixed with the plastic polymers before the blades are extruded, the only way these chemicals could enter the body is through ingestion or if the blades deteriorate forming dust that could be inhaled.

5 Conclusions

We have performed a PIXE analysis of synthetic turf blade and crumb rubber infill samples collected from eight athletic fields in the Capital District of New York to search for heavy metals and other possibly toxic substances. All of the infill samples had Zn levels above the NYDEC unrestricted use soil standard and a quarter of them exceeded the residential restricted use standard. Bromine was detected in approximately 42% of the infill samples with a maximum concentration of 1500 ± 200 ppm. Approximately 17% of the infill samples contained measurable concentrations of Pb and one had a level (110 ± 10 ppm) above the NYDEC unrestricted use soil standard of 63 ppm. Copper levels found in approximately 21% of the infill samples are above the NYDEC unrestricted use soil standard, but all the measured concentrations were below the NYDEC restricted residential use soil standard. The concentrations of Ti and Fe measured in the infill samples are much lower than what is typically found in soil. Trace amounts of Co and Ni were also found in nearly half of the samples.

The distributions and relative concentrations of elements measured in the synthetic turf blade samples of different colors are indicative of the metal-oxide pigments used to color the blades. Significant concentrations of Ti, Fe, Cu, and Zn were measured in many of the samples. The yellow blade sample contained V and Bi from the yellow pigment bismuth vanadate. Also, trace amounts of Mn, As, and Sr were found in the purple blade sample.

The high concentrations of Zn and Br, and the presence of Pb measured in the infill samples in this study validate concerns about the health risks associated with modern synthetic turf fields. Some of the infill particles may be small enough to be inhaled and transport these chemicals into the bloodstream. Also, athletes playing on these fields often come into contact with the infill and it is possible that the particles can be ingested or that the chemicals can be absorbed through the skin. The presence of these toxic elements points to the need for more in-depth health risk and environmental assessment studies to better understand the potential negative impacts of crumb rubber infill.

Acknowledgements

We would like to thank the Union College Department of Physics and Astronomy, the Union College Undergraduate Research Program, and the New York NASA Space Grant for the continued support of undergraduate research and the Union College Ion-Beam Analysis Laboratory. We also thank John Sheehan for his support in the design and fabrication of a number of instruments, and Heather Watson for help preparing the infill samples.

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