



Characterization of substances released from crumb rubber material used on artificial turf fields

Xiaolin Li, William Berger, Craig Musante, MaryJane Incorvia Mattina*

The Connecticut Agricultural Experiment Station, 123 Huntington Street, New Haven, CT 06511, United States

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ABSTRACT

Crumb rubber material (CRM) used as infill on artificial turf fields can be the source of a variety of substances released to the environment and to living organisms in the vicinity of the CRM. To assess potential risks of major volatilized and leached substances derived from CRM, methods were developed to identify organic compounds and elements, either in the vapor phase and/or the leachate from CRM. A qualitative method based on solid phase micro-extraction (SPME) coupled with gas chromatography/mass spectrometry (GC–MS) was developed to identify the major volatile and semi-volatile organic compounds out-gassing from CRM samples under defined laboratory conditions. Direct vapor phase injection into the GC–MS was applied for the quantitative analysis. Ten organic compounds were identified in the vapor phase by the SPME method. Volatile benzothiazole (BT) was detected at the highest level in all commercial CRM samples, in the range 8.2–69 ng g⁻¹ CRM. Other volatile PAHs and antioxidants were quantified in the vapor phase as well. A decrease of volatile compounds was noted in the headspace over CRM samples from 2-years-old fields when compared with the virgin CRM used at installation. An outdoor experiment under natural weathering conditions showed a significant reduction of out-gassing organic compounds from the CRM in the first 14 d; thereafter, values remained consistent up to 70 d of observation. Zinc was the most abundant element in the acidified leachate (220–13 000 µg g⁻¹), while leachable BT was detected at relatively low amounts.

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1. Introduction

There is growing concern in the US and other countries regarding the reuse and disposal of scrap tires. Such environmental and public health concerns were intensified by the accessibility of heavy metals and organic chemicals originating from reused tire rubber (Gualtieri et al., 2005; Wik and Dave, 2006; Mantecca et al., 2007; Zhang et al., 2008; Kanematsu et al., 2009). The potential magnitude of the issue was underscored in a report from the US Rubber Manufacturers Association (RMA) that over 299 million scrap tires were generated in 2005 and 260 million scrap tires were consumed in the end-use market, including 38 million tires recycled for ground rubber applications in new rubber products, playgrounds, other sports venues, and rubber-modified asphalt (RMA US, 2006).

Production of crumb rubber material (CRM), prepared by shredding tires and other sources of used rubber, is an attempt to recycle these wastes. The CRM so prepared has been widely used as infill for artificial turf installations in the US since 1960. As of 2008, there are 3500 full-size artificial fields in the US with 900–1000

new fields being installed annually, a number which does not include small surfaces like practice fields and playgrounds (McCarthy and Berkowitz, 2008).

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). Concerns have been expressed that toxic chemicals derived from tire rubber could be transferred to the environment and to organisms having direct contact with recycled products, tire wear particles or illegal dumps. For example, chemical additives such as Zn and PAHs were widely detected in the leachate from tire rubber (Stephensen et al., 2003; Wik and Dave, 2005; Zhang et al., 2008; Kanematsu et al., 2009). Zhang et al. (2008) reported that the levels of PAHs and Zn in CRM used as infill for artificial turf were above health-based soil standards, and lead in the CRM was highly bioaccessible in synthetic gastric fluid at relatively low levels (Zhang et al., 2008). Benzothiazole (BT) and its derivatives, derived primarily from tire wear particles, were detected ubiquitously in environmental samples (Reddy and Quinn, 1997; Kumata et al., 2000; Kloefer et al., 2005; Ni et al., 2008). Indeed, this class of compounds has been cited as a tracer for street run-off in highly urbanized environments (Kumata et al., 2002).

* Corresponding author. Tel.: +1 203 974 8449; fax: +1 203 974 8502.
E-mail address: MaryJane.Mattina@ct.gov (M.J. Mattina).

Most previous work has focused on the toxic chemicals in the leachate of tire rubber material. Wik and Dave (2009) reviewed thoroughly the ecotoxicological effects of tire rubber leachate and indicated its potential risks to aquatic organisms in water and sediment (Wik and Dave, 2009). The report went on to indicate that the health aspects associated with the inhalation of rubber particles are largely unknown. Very limited work has been done on the characterization of volatile and semi-volatile organic compounds out-gassing from commercial CRMs on artificial turf fields (EPA US, 2009; Lim and Walker, 2009), despite the fact that if CRM is used as infill for artificial turf, the inhalation zone over these installations could be a major human exposure source.

Due to the complexity of the matrix and its highly sorbent properties, a robust analytical method is needed to determine qualitatively the trace level organic chemicals released from CRM. It is also important to understand how natural weathering conditions influence levels of organic chemicals in the vapor phase. The aim of the present study was to develop robust analytical methods for both qualitative and quantitative assessments of volatile organic compounds from commercial CRM products and aged CRM used on artificial turf fields. For the qualitative screening and identification of volatile and semi-volatile organic compounds in the headspace of CRM samples under well defined laboratory conditions, solid phase micro-extraction (SPME) coupled with GC-MS detection was used. Analysis of the vapor phase above the CRM samples via direct gas phase injection was used to quantify the volatilized compounds from CRM samples. The alteration of the pattern of volatile compounds with time after installation was assessed for both laboratory and field-aged samples under natural weathering conditions. And finally, the accessibility of substances in the CRM to leaching by aqueous solutions was also examined.

2. Experimental

2.1. Standards

Individual standards of benzothiazole (BT), 2-methylbenzothiazole (MBT), 1-methylnaphthalene (1-MeNA), 2-methylnaphthalene (2-MeNA), fluoranthene (Flu), naphthalene (NA), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), 4-tert-octylphenol (4-t-OP), were purchased from Sigma Aldrich (St. Louis, MO). Phenanthrene (Phe) and pyrene (Pyr) were purchased from Acros Organics (Geel, Belgium). Deuterated NA and Pyr were purchased from Cambridge Isotope Laboratories Inc. (Andover, MA).

2.2. Samples

All samples were received in pre-cleaned Qorpak[®] jars as finely ground particles (0.84–2.0 mm diameter) made from either recycled tire rubber (T) or other alternative rubber materials (A). A total of 15 commercial CRM samples, that were ready to be used as infill material on artificial turf fields, were supplied to the laboratory at The Connecticut Agricultural Experiment Station by the Connecticut Department of Environmental Protection (DEP); one was purchased by Environment and Human Health Inc. (EHHI). Five CRM samples (T1–T5) were collected from the sealed storage bags at five different installations at local schools in Connecticut. The other eleven samples, including eight recycled tire CRMs (T6–T12, Te) and three alternative rubber materials (A1–A3) were obtained from five different commercial suppliers. This permitted monitoring of CRM produced by a particular supplier at different times. Aged field CRM samples (F2 and F4) were collected from the artificial turf fields of two local schools at which the virgin CRM T2 and T4 had been installed 2 years earlier. As mentioned above T2 and T4 were collected at local schools from the storage bags that were

used to refill the field over time. In other words all T samples were never exposed to natural weathering conditions.

2.3. Sample preparation

2.3.1. Volatile organic compounds

A method was developed to evaluate the volatile and semi-volatile organic compounds out-gassing from CRM samples under the operational conditions used in our laboratory. A 1 g CRM sample was transferred to a 10 mL headspace injection vial (Sun Sri, Rockwood, TN), sealed, and warmed for 20 min at 60 °C. (CombiPal Auto Sampler, CTC Analytics, Switzerland). This temperature has been shown to be reached at the surface of artificial turf fields during summer (Lim and Walker, 2009). Heating times from 1 to 60 min were evaluated and 20 min was chosen because there was no significant difference in the organic compounds detected at 20 versus 60 min (Supplementary content, Appendix A).

For the qualitative screening of volatile organic compounds, SPME fibers (30 µm PDMS coating, Supelco, Bellefonte, PA) were used with the CombiPal auto sampler. The SPME fiber was exposed in the headspace over the CRM sample for 20 min at 60 °C, and the fiber was then desorbed in the inlet of the GC system (Varian 3800) at 260 °C for 20 min. Sample amount, headspace volume, and fiber exposure time were optimized to achieve better sensitivity and reproducibility for the SPME injection.

SPME is a reliable method for concentrating and measuring relative amounts of volatile organic chemicals in environmental samples (Zeng and Noblet, 2002). However, the present study also included the quantitation of total amounts of volatilized organic chemicals in the headspace over CRM samples by direct vapor phase injection of the headspace gas. The SPME fiber was replaced by a gas tight syringe; after incubating the CRM under the same conditions described above, a 1 mL gas sample was injected directly into the GC-MS.

2.3.2. Leachable substances

Leaching studies of the CRM were conducted by modification of EPA 1312 method, Synthetic Precipitation Leaching Procedure, designed to determine the mobility of organic and inorganic analytes present in soils and wastes. Briefly, a 2 g CRM sample was weighed into a 40 mL glass vial, fitted with a screw cap with Teflon[®] liner, and filled with 40 mL of extraction fluid 1 (distilled water) or extraction fluid 2 (acidified water pH 4.2 ± 0.5 prepared from a 60/40 wt.% mixture of sulfuric and nitric acids). The sample was agitated on a wrist action shaker at ambient temperature for 18 h. The quantitative analysis for leachable organics focused on the most abundant of the volatile and leachable compounds, benzothiazole. Twenty mL leachate was filtered through GF/F filters and spiked with 5 µg MBT as surrogate standard (not detected in any CRM leachate). Solid phase extraction (SPE) (Oasis 20 mg HLB cartridges, Waters, Taunton, MA) was modified from a previous report to concentrate BTs (Kloepfer et al., 2004). Briefly, 5 mL 1:1 methanol:acetone mixture was used to precondition the column, followed by 5 mL distilled water. Aqueous sample was then loaded on the column at a speed of 2.5–3.0 mL min⁻¹. The column was left under vacuum for 20 min before elution with 5 mL 1:1 methanol:acetone. Three µL of final sample extract was injected into GC-MS. The average recovery of the surrogate standards for all samples ($n = 22$) was 100 ± 17%.

2.3.3. Content analysis of CRM samples

To determine the total amount of substances present in the CRM samples, one CRM sample (Te) and one alternative rubber material sample (A1) were analyzed. One gram of sample was spiked with deuterated NA and Pyr, and Soxhlet extracted for 8 h using methanol (Reddy and Quinn, 1997). The extract was concentrated by Kuderna-Danish evaporation and solvent exchanged to

1–10 mL toluene under nitrogen gas. No further clean-up steps (Reddy and Quinn, 1997) were needed before injection. Two additional sequential Soxhlet extractions were repeated with the CRM from the previous extraction and the combined two sequential extractions showed less than 1% of total extractables remaining for all 10 compounds of interest.

2.4. Laboratory weathering experiment

To monitor the volatile and leachable chemicals from the CRM under natural weathering conditions, several glass funnels, each filled with the EHHI CRM sample (Te), were placed outdoors. Each funnel rested on top of 250 mL glass bottle for collection of the rain water leachate. CRM from this experimental setup was sub-sampled once a week and examined using the headspace injection and the leaching extraction techniques described above. All glassware used for the setup was baked over night at 565 °C.

2.5. Gas chromatographic system

Separations were performed with a FactorFour™ capillary column (VF-5 ms, 30 m × 0.25 mm I.D., Varian, Lake Forest, CA). The initial temperature was held at 40 °C for 5 min and the temperature ramped to 50 °C in 5 min. Temperature was then ramped to 160 °C in 22 min and finally 300 °C in the next 24 min giving a analysis time of 56 min total.

2.6. Mass spectrometry conditions

A Varian 4000 ion trap mass spectrometer with electron impact ionization (EI) was employed. The transfer line was set at 200 °C. Full scan was acquired under the following conditions: mass range 35–420 *m/z*, scan time average 1.3 s, manifold temperature 60 °C, trap and ion source temperature 180 °C, emission current 25 μA.

2.7. Quantitation of volatile organic compounds

A six-point series of standards were prepared in hexane and analyzed daily for calibration. The standard curves were used to calculate the concentration of compounds in the vapor phase injections (*C*, μg mL⁻¹); total amounts of volatile compounds in the headspace per gram CRM (*M*, μg g⁻¹) were calculated by the formula: $M = (C \times V)/m$, where *V* is the volume of headspace, *m* is the mass of CRM sample. In this study *V* was ~8 mL for all measurements.

2.8. Elemental analysis

CRM materials were leached with extraction fluid 2 using a slightly modified US EPA Method 1312. Approximately 1.0 g of material was leached with 20 mL of fluid 2 in a 50 mL polypropylene centrifuge tube. The tubes were agitated for about 18 h on a wrist action shaker at ambient temperature. The samples were centrifuged at 3000 rpm for 10 min and a 5 mL aliquot was withdrawn for ICP-MS analysis. Aliquots were acidified so as to contain 5% nitric acid prior to ICP-MS analysis. Concentrations of metals were determined using an Agilent 7500ce ICP-MS fitted with an Octopole Reaction System (ORS), using conditions recommended by the manufacturer (Agilent Technologies Inc., Santa Clara, CA).

3. Results and discussion

3.1. Identification of volatile chemicals from CRM samples

Volatile and semi-volatile organic compounds in the headspace of CRM samples were adsorbed and concentrated on the SPME fi-

ber. Desorption in the GC inlet was followed by mass spectral identification. Spectra were compared with those from authentic standards analyzed by the same GC-MS method. Ten compounds, known to be added or produced as impurities during rubber manufacture, were chromatographically well-separated and identified in the vapor phase over CRM samples (Fig. 1A), including the vulcanization accelerator (BT), PAHs (NA, Phe, 1-MeNA, 2-MeNA, Flu, Pyr) typically found in extender oil, and three antioxidants (BHA, BHT and 4-t-OP). These are listed in Table 1 along with retention times, primary quantitation ions and physicochemical properties. These 10 compounds were detected by the SPME method in all commercial CRM products ready to be used as infill on artificial turf.

An aged field sample (F2) from 2 years of natural weathering (derived from the virgin material identified as CRM (T2) that was applied to the field in 2007) was also examined. SPME analysis of the field sample showed significantly reduced signal for the volatile compounds (BT, 1-, 2-MeNA, and NA) having vapor pressures (VP) > 2.0 Pa at 25 °C (Table 1). Other relatively less volatile compounds (VP < 2.0 Pa, Table 1), including BHA, BHT, 4-t-OP, Phe, Flu and Pyr, were detected at 20–90% of the signals from the virgin CRM (Table 1). Of this latter group, residuals of BHA, BHT, and 4-t-OP with medium VP (0.2 Pa < VP < 2.0 Pa) were 19%, 32%, and 67%, respectively, of their original amounts, while Flu and Pyr with much lower vapor pressure (VP < 0.02 Pa) remained at 93% and 89% respectively of their original amounts. We hypothesize that reduction of volatile organic chemicals from CRM in the field depends both on the diffusion of the volatile compounds from the interior to the surface of the CRM particles, followed by evaporation from the surface of CRM particles to the gas phase. It is interesting to point out that BHT and 4-t-OP with VP similar to or larger than BHA were detected in higher amounts in the field sample as compared to BHA. This might be because BHT and 4-t-OP are more tightly adsorbed to the rubber polymer within the CRM particles than BHA, as suggested by the octanol/water partition coefficient (*K*_{ow}) in Table 1.

Although SPME was an extremely sensitive technique for concentrating the hydrophobic volatile and semi-volatile compounds in the vapor phase, it provides only a qualitative profile. Given the current experimental conditions, we could not prepare vapor phase standards and extrapolate the concentrations of each compound in the headspace from its desorption off the SPME fiber. Without knowing the partition coefficient between vapor phase and SPME fiber for each compound under current experimental conditions, the response produced from the SPME injection in the GC inlet (Fig. 1) does not necessarily correspond to the relative levels of each compound in the headspace. To quantitatively evaluate the major volatile organic compounds in the vapor phase under the operational conditions used, we needed to evaluate all samples by direct vapor phase injection. Using this approach, seven compounds (1-MeNA, 2-MeNA, 4-t-OP, BT, BHT, BHA, and NA) were detected and quantified for each CRM sample with excellent precision and limit of quantitation (LOQ; *S/N* = 10) (Table 2). LOQ could be improved in future experiments by analyzing more CRM to produce a lower headspace volume.

Volatilized BT was detected in all CRM samples and was the most abundant volatile chemical with a range of 15–69 ng g⁻¹ for all virgin recycled tire CRMs and 8.2–10 ng g⁻¹ in the samples made of other alternative rubber materials. Volatile BT was much lower for the two aged field CRMs (0.76 and 0.86 ng g⁻¹); there was no detection of 1-, 2-MeNA and NA which agreed with what was found by the SPME injections (Fig. 1 and Table 1), while two less volatile compounds (4-t-OP and BHA) were still detected at over 40% of that in the virgin CRMs. Volatile BHA, NA, and 4-t-OP were detected in all virgin CRM products with ranges of 2.6–6.0 ng g⁻¹, 0.41–3.4 ng g⁻¹, and 0.46–4.1 ng g⁻¹, respectively.

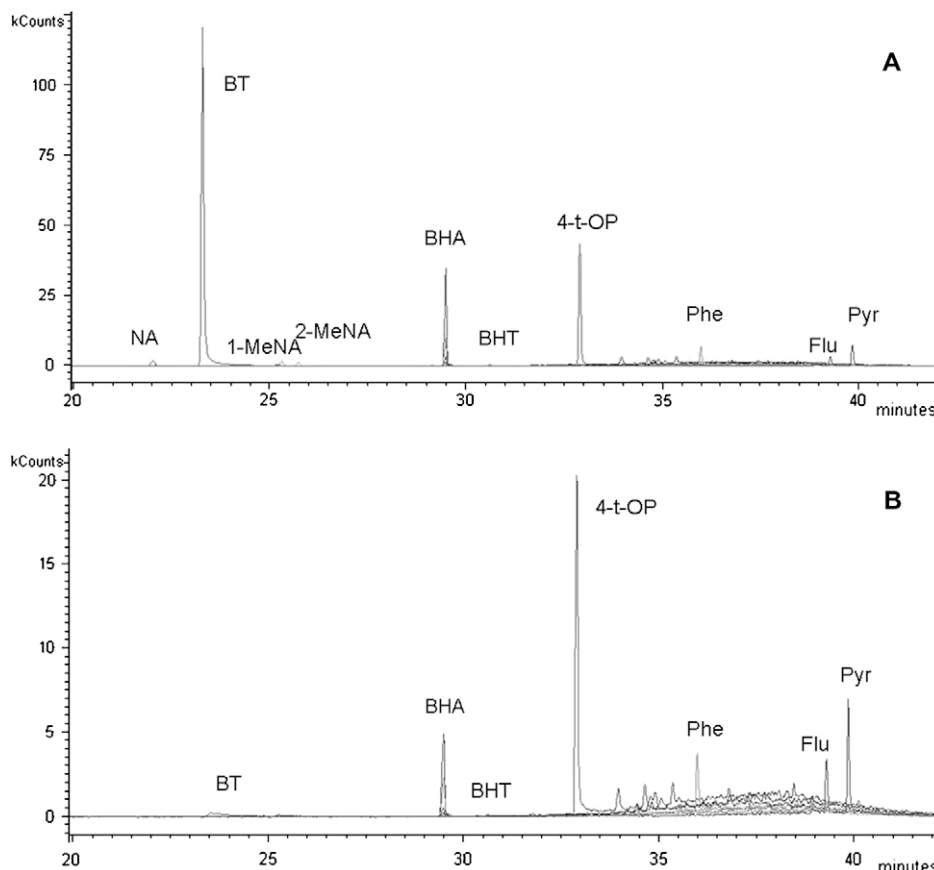


Fig. 1. Overlaid reconstructed ion chromatograms of volatile organic compounds by SPME injections for the (A) commercial CRM T2 and the (B) field CRM sample F2 collected from a 2-years-old synthetic turf field installed with virgin CRM T2. Note the different ordinate scales in the two panels.

Table 1

Primary quantitation ions, gas chromatographic retention times, physicochemical properties of the 10 organic compounds detected in the vapor phase over CRM.

Compounds	Quantitation ion (<i>m/z</i>)	Retention time (min)	Boiling point (°C) ^a	Log (Kow) ^a	Vapor pressure at 25 °C (Pa) ^a	Fraction remaining in field sample ^b
NA	128	22.04	218	3.30	11	n.d. ^c
BT	135	23.30	231	2.01	2.0	<0.01
2-MeNA	142	25.34	241	3.86	9.1	n.d. ^c
1-MeNA	142	25.78	245	3.87	7.2	n.d. ^c
BHA	165	29.52	268	3.50	0.33	0.19
BHT	205	30.64	265	5.10	1.3	0.32
4-t-OP	135	32.92	282	5.28	0.23	0.67
Phe	178	35.98	340	4.46	0.016	0.65
Flu	202	39.29	384	5.16	0.0012	0.93
Pyr	202	39.87	404	4.88	0.00060	0.89

^a Chemical properties for each compounds were obtained from the United States National Library of Medicine. <<http://chem.sis.nlm.nih.gov/chemidplus/chemidlite.jsp>>.

^b Fractions were calculated on the peak areas of each compounds by SPME injections for virgin CRM (A2) and the 2-years-old field CRM (F2).

^c Not detected.

There is a different profile for volatile chemicals in the vapor phase over CRM samples versus alternative rubber products. 1-MeNA and 2-MeNA were detected in all recycled tire CRMs ranging from 0.23 to 1.1 ng g⁻¹ and 0.48–1.6 ng g⁻¹ respectively, but were not detected in the alternative rubber CRMs. However, BHT was not detected in seven out of 13 recycled tire CRMs (see Table 2). In the other five samples, it was found at a range of 0.9–1.2 ng g⁻¹ and was detected relatively higher in all three alternative CRMs (3.2, 3.9 and 5.4 ng g⁻¹). There could be preferential usage of BHT, BHA and 4-t-OP as antioxidants in rubber manufacture for tire rubber and other rubber products. To the best of our knowledge this is the first report of detection these three antioxidants in the vapor phase released from any tire rubber materials.

3.2. Total organic chemicals in CRM

Total amounts of 10 selected organic chemicals in two CRMs (Te and A1) were determined by the Soxhlet method described above (Table 3). The recoveries for the standards, deuterated NA and Pyr, were 74 ± 7% and 84 ± 4%, respectively, for all measured samples and extraction blank (*n* = 5). BT was still found at the highest detected level (48 μg g⁻¹ and 10 μg g⁻¹) among all 10 compounds (Table 3). BT in the tire CRM sample was comparable to a previous report on total BT (171 μg g⁻¹) in the CRM used in modified asphalt (Reddy and Quinn, 1997). Similar levels of 4-t-OP were also detected in the Te tire CRM (48 μg g⁻¹) and A1 alternative CRM (5.4 μg g⁻¹). Generally, the volatilized compounds found in the va-

Table 2
Volatile organic compounds (ng g⁻¹) in the headspace of CRM samples (RSD%).^a

Sample ID	Supplier	Collection time	1-MeNA	2-MeNA	4-t-OP	BT	BHT	NA	BHA
T1	School 1 storage bag	August-09	0.52(16)	0.78(2)	1.4(22)	15(3)	n.d.	1.8(1)	3.4(3)
T2	School 2 storage bag	March-09	0.26(1)	0.54(3)	1.6(8)	69(3)	n.d.	0.78(7)	5.4(3)
T3	School 3 storage bag	September-09	0.66(13)	1.1(3)	3.7(7)	22(1)	1.1(3)	2.2(2)	5.2(4)
T4	School 4 storage bag	March-09	0.85(6)	1.2(4)	2.5(14)	45(2)	n.d.	2.5(3)	4.9(1)
T5	School 5 storage bag	March-09	1.0(10)	1.5(5)	2.2(3)	32(2)	n.d.	3.4(1)	4.0(3)
T6	Company A	August-09	0.23(7)	0.48(7)	1.0(18)	23(6)	1.0(3)	0.61(3)	4.0(5)
T7		September-09	0.78(2)	1.2(3)	3.9(4)	34(1)	n.d.	2.5(1)	5.2(5)
T8	Company B	March-09	0.32(5)	0.54(3)	2.5(1)	52(2)	1.2(1)	1.3(3)	5.6(5)
T9		September-09	0.29(1)	0.49(3)	2.4(6)	32(1)	1.3(4)	0.90(6)	5.0(3)
T10	Company C	March-09	0.64(3)	1.1(3)	2.5(9)	39(2)	0.94(7)	1.9(3)	6.0(6)
T11		August-09	0.53(1)	0.89(1)	1.8(9)	39(2)	1.1(6)	1.6(5)	5.1(3)
T12	Company D	April-09	1.1(6)	1.6(4)	4.1(14)	28(3)	n.d.	1.9(2)	5.5(11)
Te	Company E	August-07	0.74(1)	1.1(1)	2.1(7)	16(1)	n.d.	2.4(1)	3.6(7)
A1	Company A	August-09	n.d.	n.d.	0.58(6)	10(1)	3.9(1)	0.46(7)	2.8(5)
A2	Company B	March-09	n.d.	n.d.	3.5(15)	9.7(2)	5.4(2)	0.68(2)	2.9(1)
A3		September-09	n.d.	n.d.	0.46(7)	8.2(3)	3.2(3)	0.41(1)	2.7(4)
F2	School 2 field	October-09	n.d.	n.d.	1.4(1)	0.86(7)	n.d.	n.d.	2.6(1)
F4	School 4 field	October-09	n.d.	n.d.	1.1(7)	0.76(2)	n.d.	n.d.	3.0(5)
LOQ ^b	-	-	0.2	0.4	0.4	0.6	0.1	0.2	0.02

^a Relative standard deviation (RSD) given in percent on the basis of duplicate samples measurements.

^b The limit of quantification (LOQ) was determined in the lowest standard when $S/N = 10$.

Table 3
Total amounts of the organic chemicals in two CRM samples (μg g⁻¹).

CRMs	NA	BT	2-MeNA	1-MeNA	BHA	BHT	4-t-OP	Phe	Flu	Pyr
Recycled tire rubber (Te)	1.1	48	2.1	1.0	24	0.36	48	4.6	19	9.0
Alternative rubber (A1)	0.16	10	n.d.	0.07	2.4	11	5.4	4.1	16	8.1

por phase (Table 2) were three to four orders lower than the total amounts in the CRMs.

3.3. Leachable chemicals from CRM

All commercial CRM samples were extracted by the modified standard method (EPA 1312, 1994) as a surrogate for rigorous conditions in natural storm events. Distilled water (fluid 1) and acidified water (fluid 2) were employed to show the effect of normal and acid rain water for leaching of organics and metals off CRM in the field.

The SPE method was applied to concentrate the most abundant volatile compound, benzothiazole and its derivatives including ABT, MBT, and MTBT (Kloepfer et al., 2004). Excellent recoveries were achieved for both fortified blank ($85 \pm 6\%$ BT, $87 \pm 10\%$ ABT, $96 \pm 3\%$ MBT; $94 \pm 5\%$ MTBT; $n = 4$) and sample extractions spiked with MBT ($92 \pm 6\%$; $n = 25$). There was no significant difference between two extraction fluids for the organic chemicals (Table 4). BT was in a range of 0.03 – $0.27 \mu\text{g L}^{-1}$ in all CRM samples (Table 4). During the natural weathering experiment leachable BT reduced from 0.18 to $0.02 \mu\text{g L}^{-1}$ after 70 d (Supplementary content, Appendix C) which may be due to loss through evaporation (described in next section). ABT, MBT and MTBT were not detected in any extractions which agree with a previous report showing that MBT and MTBT were negligible for the total contribution of benzothiazoles in street run-off (Kloepfer et al., 2005). More work needs to be done for the other major leachable benzothiazole derivatives (e.g., benzothiazole-2-sulfonic acid BTSA, 2-mercapto benzothiazole MCBT and 2-hydroxybenzothiazole OHBT) detected with higher or similar level as BT in the CRM leachate and wastewater samples as reported previously (Reddy and Quinn, 1997; Kloepfer et al., 2004, 2005).

Zinc was the highest leachable metal (0.7 – $3.6 \mu\text{g L}^{-1}$) in the extraction fluid of all CRM samples (Table 4) due to the use of zinc oxide in tire rubber manufacture as a vulcanization activator (1.2%)

(Wik and Dave, 2009). Surprisingly, Zn in the leachates for two field-aged CRM samples was 4–5 times higher than the virgin CRM samples and relatively higher levels of Ni and Pb were also found in the leachate of field-aged samples. Both field samples were collected right after large rain events. Notably bigger particle size (swollen by soaking in storm water) was found for both field samples compared to the dry virgin CRM. Further work is needed to better understand the leaching mechanism of Zn and other metals from CRM in field samples under different weathering conditions.

Similar to the volatile compounds, there were different profiles for the leachable metals (e.g., Mn, Ni, Zn) in recycled tire and alternative rubber CRMs. Significantly lower Mn and Zn were found in alternative rubber CRMs (0.11 – 0.14 ng g^{-1} and 700 – 900 ng g^{-1} respectively) compared to most of recycled tire CRMs (5 – 72 ng g^{-1} and 220 – 3500 ng g^{-1} respectively), while Ni in the extraction fluid was higher for the alternative rubber CRMs (1.9 – 2.9 ng g^{-1}) than for most of tire rubber CRMs (0.43 – 1.4 ng g^{-1}).

3.4. Reduction of volatile organic compounds under natural weathering conditions

Virgin CRM (Te) was exposed to the outdoor environment from August 3, 2009 to October 12, 2009 to mimic weathering of CRM after the initial field installation. Concentrations of all six compounds (BT, 1-MeNA, 2-MeNA, NA, 4-t-OP, BHA) in the vapor phase were determined weekly (Supplementary content, Appendix B) and showed generally reduced levels over 70 d. Four compounds (BT, 1-MeNA, 2-MeNA, NA) with relatively higher vapor pressure ($>2.0 \text{ Pa}$ at $25 \text{ }^\circ\text{C}$) were reduced to about 20–30% of their initial amounts and reached a consistent level of out-gassing within 2 weeks (Fig. 2). However, slightly more than 50% of BHA remained after 14 d and more than 60% of 4-t-OP was still present after 70 d. Combined with the data from the aged field sample (Table 1), the fraction remaining for all 10 compounds upon natural weathering

Table 4
Leachable BT and heavy metals in the extraction fluids of all CRM samples (g L^{-1}).

	BT (fluid 1)	BT (fluid 2)	Cr ^a	Mn ^a	Ni ^a	Cu ^a	Zn ^a	As ^a	Cd ^a	Ba ^a	Pb ^a
T1	0.14	0.15	1.6	15	1.2	4.3	3600	0.33	n.d. ^c	13	2.7
T2	0.23	0.26	0.10	10	0.58	0.59	1500	n.d.	n.d.	14	0.20
T3	0.17	0.17	n.d.	13	0.85	n.d.	1500	n.d.	n.d.	22	0.19
T4	0.19	0.19	0.05	5.0	0.45	0.28	2900	n.d.	n.d.	13	0.15
T5	0.12	0.12	1.2	72	1.4	7.2	2500	1.4	n.d.	21	3.5
T6	0.18	0.19	n.d.	20	0.80	1.0	2200	n.d.	n.d.	23	0.05
T7	0.18	0.21	n.d.	5.0	0.43	0.71	2500	n.d.	n.d.	6.5	0.12
T8	0.22	0.21	0.07	18	0.55	0.97	420	n.d.	n.d.	8.3	0.08
T9	0.20	0.21	0.18	18	0.65	1.4	220	n.d.	n.d.	11	1.8
T10	0.15	0.11	0.07	14	0.84	0.43	1900	n.d.	n.d.	23	0.44
T11	0.27	0.27	n.d.	12	0.51	0.31	2600	n.d.	n.d.	13	0.14
T12	0.09	0.12	n.d.	13	0.65	0.69	2500	n.d.	n.d.	13	0.19
Te	0.16	0.19	0.19	21	1.6	3.4	2000	n.d.	0.05	11	0.55
A1	0.09	0.09	0.59	0.14	2.3	n.d.	850	n.d.	n.d.	25	n.d.
A2	0.03	0.06	0.66	0.11	2.9	n.d.	930	n.d.	n.d.	24	n.d.
A3	0.08	0.08	0.48	0.14	1.9	n.d.	690	n.d.	0.85	23	n.d.
F2	n.d.	n.d.	2.3	12	6.0	9.5	7500	n.d.	0.06	31	1.9
F4	n.d.	n.d.	0.42	10	2.0	5.0	13 000	n.d.	n.d.	6.4	2.9
LOQ ^b	0.01	0.05	0.05	0.05	0.3	5	0.2	0.05	0.05	0.03	

^a All metals were analyzed in the acidified extraction fluid (fluid 2).

^b LOQ were calculated as three times the standard deviation of seven replicates of a blank standard solution.

^c Not detected.

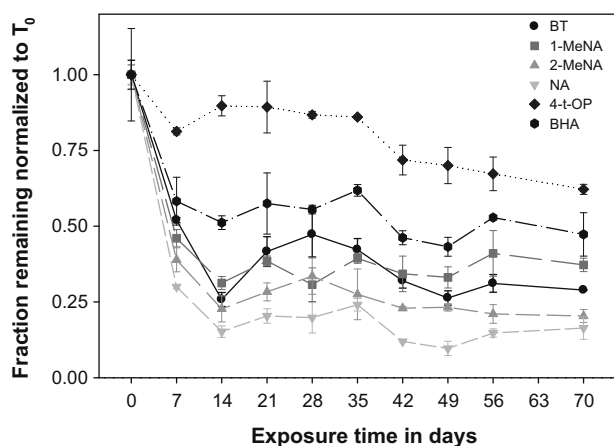


Fig. 2. Reduction of volatilizable organic compounds out-gassing from commercial CRM sample (Te) under natural weathering conditions. Fraction remaining of each time point was normalized to day zero. Standard deviations of duplicate samples are shown as error bars.

is in the order: Flu/Pyr > Phe/4-t-OP > BHT > BHA > 1-MeNA > BT > 2-MeNA > NA.

4. Conclusions

Ten volatile compounds were identified in the vapor phase over all commercial CRM samples and two aged field CRM samples by SPME coupled with GC–MS. Six volatile compounds were quantitated by direct vapor phase injection.

In all 16 virgin commercial CRM samples, BT was the most abundant volatile compound. Different profiles of the volatile compounds were noted between CRM samples made from recycled tire rubber and other alternative rubber products.

Significant reduction of more volatile compounds (BT, NA, 1-MeNA, and 2-MeNA) were found in the 2-years-old field CRM samples.

Leaching experiments showed BT in the leachate with no difference between two extraction fluids. Zinc was the highest of all extractable metals in the acidified extraction fluid.

Reduction of volatile organic compounds under natural weathering conditions occurred mostly within 14 d and reached consistent levels thereafter.

While there appears to be some variability in the out-gassing profile of CRM produced by a given manufacturer as a function of time of year (Table 2), more data are required to determine if this variability is significant.

The data from these experiments can serve as guidelines for field studies. They may also provide suggestions for future study of the mechanisms by which volatile organics are transferred from the CRM particles to the ambient vapor phase over artificial turf installations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2010.04.021](https://doi.org/10.1016/j.chemosphere.2010.04.021).

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