



The Connecticut Agricultural Experiment Station

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5/5/10

Brian Golembiewski
Environmental Analyst
Connecticut Department of Environmental Protection
79 Elm Street
Hartford, CT 06106

Dear Brian,

Please find attached our revised 2009 Crumb Rubber Final Report. The changes made to the document are highlighted in point one below. In addition, our second point relates to the interpretation of our weathering data from section 5 of the report.

1. For the revised report, the following changes have been made. In section 4, entitled "Leaching Study", of our original report, the units provided on page 10 in Table 8 should read "ug/mL" rather than "ng/mL." In addition on pages 11 and 12 in Tables 9 and 10 the units should read "ng/g" rather than "ng/mL." We regret any confusion that this may cause.

2. It is necessary to emphasize that Section 5, entitled "Weathering Study," of our original report is not an exhaustive examination of outgassing of volatile substances from crumb rubber material exposed to natural weathering. One sample of CRM was examined, as reported in Section 5.A, and two samples analyzed, as reported in Section 5.B. Given the number of samples examined, these data must be used with considerable caution.

Please let me know if you have any additional questions. Thank you.

Sincerely,

A handwritten signature in blue ink that reads "Jason C. White".

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**DEPARTMENT OF ANALYTICAL CHEMISTRY
CONNECTICUT AGRICULTURAL EXPERIMENT STATION**

**2009 STUDY OF CRUMB RUBBER DERIVED FROM RECYCLED TIRES
FINAL REPORT**

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Revised 5/4/10

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1. PROJECT OVERVIEW

As part of a broad, State of Connecticut-funded study of several issues associated with artificial turf fields, including components such as crumb rubber infill derived from recycled tires (CRM, crumb rubber material), the Department of Analytical Chemistry at the Connecticut Agricultural Experiment Station (CAES) was charged with conducting a number of laboratory-based studies which are enumerated below:

1. Develop laboratory leaching protocols and simulated crumb rubber aging protocols
2. Develop protocols to identify comprehensively substances which volatilize and leach from crumb rubber and alternative infill materials under laboratory conditions
3. Conduct the laboratory analysis in accordance with submitted procedures
4. Compile data and provide written data report to DEP, DPH and UCHC by November 30, 2009.

We are submitting this report, as required, by 30 November 2009 to the Connecticut Department of Environmental Protection. The report contains the data from the experiments outlined above and conducted in our laboratory. This final report supersedes all previous reports. The timeline associated with the CAES portion of the project is provided here:

- March 2009: purchase of (using study funds), installation of, and familiarization with CombiPal automatic injector for the Varian 3800 gas chromatograph/4000 mass spectrometer in our laboratory.
- March-May 2009: development of solid phase microextraction procedure to identify compounds volatilizing from crumb rubber.
- June 2009: arrival of post-doctoral affiliate, Dr. Xiaolin Li.
- June-July 2009: continued identification of volatile compounds derived from crumb rubber and alternate infill products. Development of rigorous analytical method for quantitation of volatile compounds using direct injection of headspace gas.
- July 2009: initial weathering experiments
- July 2009: preliminary work on leaching study
- August-September 2009: weathering experiments in progress
- August-September 2009: leaching experiments in progress
- August-September 2009: additional samples from Connecticut DEP analyzed
- October-November 2009: leaching and weathering experiments conducted

In sections 2 and 3 of the report we provide the data related to the volatilization of compounds from the all the crumb rubber and alternative infill samples submitted to our laboratory by Connecticut Department of Environmental Protection. In addition, data are included in Sections 4 and 5 which relate to the aqueous leaching experiments and the weathering study of the CRM.

2. VOLATILE COMPOUNDS FROM CRUMB RUBBER

Identification of Volatile Compounds

Step one was to identify comprehensively the volatile organic compounds issuing from the crumb rubber material. This section provides information on this set of experiments.

The Department of Analytical Chemistry provided Connecticut DEP with amber QorPak™ jars fitted with Teflon™ lined lids for sample collection. These containers had been cleaned according to our standard procedures prior to being supplied to DEP. DEP submitted all samples to the laboratory identified solely by DEP codes. Unless noted, the samples consisted of virgin material, unexposed to all field conditions.

To identify the volatile compounds issuing from CRM, a 1 gram subsample of crumb rubber was transferred to a 10mL autosampler vial, capped, and subjected to specific conditions. Experiments in our laboratory determined that this subsample size was reproducible over 5 replicates for each of two different CRM samples and for each of eleven different compounds. See Figure 1A in Appendix A for these data (relative standard deviations were <15%). The 1 gram subsample size is therefore representative of the bulk sample. The vial septum was then pierced with a solid phase microextraction fiber. Following specific adsorption conditions stated in Appendix A, the SPME fiber was removed from the vial and desorbed in the inlet of a gas chromatograph interfaced to a mass spectrometer for analysis. Extensive details of the method are provided in Appendix A at the end of this report.

The following volatile compounds were identified using this approach. Confirmation of each compound was accomplished with authentic standards, retention time, and mass spectral matches.

Table 1. Compounds Volatilizing from Crumb Rubber Samples Analyzed at CAES

	Compound Name	Abbreviation
1	1-methylnaphthalene (PAH)	1-MeNaph
2	2-methylnaphthalene (PAH)	2-MeNaph
3	4-t-(octyl)-phenol	4-t-OP
4	Benzothiazole	BT
5	butylated hydroxytoluene	BHT
6	naphthalene (PAH)	Naph
7	butylated hydroxyanisole	BHA
8	fluoranthene (PAH)*	Flu
9	hexadecane*	Hex
10	phenanthrene (PAH)*	Phen
11	pyrene (PAH)*	Pyr

*Identified but not quantified.

Some comments pertaining to the information in the above table are appropriate. Table 1 lists eleven compounds, each of which was present in every crumb rubber sample analyzed by SPME in our laboratory. Note in Table 1 that the last four compounds listed were identified in the gas

phase over the crumb rubber material using the SPME method, but were not quantitated using the direct headspace injection method referenced below, since these four compounds were present below the limit of quantitation (LOQ) for headspace analysis. It should also be noted that six of the eleven compounds identified in Table 1 are polyaromatic hydrocarbons (PAHs).

Concentrations of Volatile Compounds in the Headspace over the Infill Materials

Consistent quantitation could not be achieved using the SPME technique. Therefore, in step two, we developed a direct injection technique, specifics of which are provided in Appendix B, for sampling and analyzing the headspace gas over the crumb rubber samples for compound quantitation. This method uses 1 gram of the sample in a 10mL vial; as mentioned above this subsample size was shown to be representative of the bulk sample. Using the headspace method, the data in Tables 2 and 3 provide concentration values (and standard deviations) in the headspace for the operational conditions used. Since 1 gram of sample was used and the headspace volume available in the vial was 8 mL (allowing for the volume occupied by the sample), the concentrations in Table 2 can be multiplied by 8 to provide the ng of compound outgassed from one gram of CRM under these specific operational conditions. It should be noted that seven of the eleven compounds listed in Table 1 may be quantitated using the headspace injection method. The LOQs for the compounds in the direct headspace method were (all in ng/mL): 1-methylnaphthalene, 0.03; 2-methylnaphthalene, 0.05; 4-t-octyl-phenol, 0.07; benzothiazole, 0.08; butylated hydroxytoluene, 0.02; naphthalene, 0.02; butylated hydroxyanisole, 0.003.

Table 2. Concentration (ng /ml) of Volatile Compounds in Headspace Over Crumb Rubber Samples Analyzed at CAES (average of two analyses per sample)

DEP Sample ID	1-methyl naphthalene	2-methyl naphthalene	4-(t-octyl)-phenol	benzothiazole	butylated hydroxytoluene	naphthalene	butylated hydroxyanisole
A1001	0.13	0.19	0.28	3.98	n.d.	0.42	0.50
A1002	0.11	0.15	0.31	5.59	n.d.	0.31	0.61
A1003	0.03	0.07	0.19	8.67	n.d.	0.10	0.68
A1004	0.04	0.07	0.31	6.52	0.15	0.16	0.69
A1005	0.08	0.09	0.23	2.35	0.09	0.23	0.46
A1006	0.08	0.14	0.31	4.89	0.12	0.23	0.75
A1007	0.13	0.20	0.52	3.50	n.d.	0.23	0.69
A1008	0.06	0.10	0.18	1.93	n.d.	0.22	0.43
A1009	0.03	0.06	0.13	2.89	0.13	0.08	0.50
A1010	0.07	0.11	0.22	4.91	0.13	0.20	0.64
A1011	0.04	0.06	0.30	3.94	0.16	0.11	0.62
A1012	0.08	0.14	0.46	2.70	0.13	0.28	0.64
A1013	0.09	0.12	0.45	4.45	n.d.	0.30	0.65
A1014	0.10	0.15	0.49	4.25	n.d.	0.31	0.65
B1002	n.d.	n.d.	0.43	1.21	0.67	0.09	0.36
B1009	n.d.	n.d.	0.07	1.29	0.48	0.06	0.35
B1010	n.d.	n.d.	0.06	1.03	0.40	0.05	0.34

The standard deviations associated with these data are provided in Table 3 and the relative standard deviations are provided in Table 4.

Table 3. Standard Deviations (ng/mL) of Concentration Values Provided in Table 2

DEP Sample ID	1-methyl naphthalene	2-methyl naphthalene	4-(t-octyl)-phenol	benzothiazole	butylated hydroxytoluene	naphthalene	butylated hydroxyanisole
A1001	0.013	0.008	0.008	0.091	n.d.	0.002	0.015
A1002	0.006	0.006	0.042	0.104	n.d.	0.008	0.006
A1003	0.000	0.002	0.015	0.269	n.d.	0.006	0.019
A1004	0.002	0.002	0.004	0.123	0.000	0.004	0.036
A1005	0.004	0.004	0.038	0.028	0.004	0.002	0.008
A1006	0.002	0.004	0.028	0.117	0.008	0.006	0.047
A1007	0.008	0.008	0.072	0.089	n.d.	0.004	0.072
A1008	0.011	0.002	0.038	0.064	n.d.	0.002	0.015
A1009	0.002	0.004	0.023	0.187	0.004	0.002	0.025
A1010	0.000	0.000	0.019	0.100	0.008	0.011	0.021
A1011	0.000	0.002	0.017	0.030	0.006	0.006	0.017
A1012	0.011	0.004	0.032	0.019	0.004	0.006	0.023
A1013	0.017	0.006	0.023	0.085	n.d.	0.002	0.011
A1014	0.002	0.004	0.021	0.019	n.d.	0.004	0.030
B1002	n.d.	n.d.	0.066	0.025	0.015	0.002	0.004
B1009	n.d.	n.d.	0.030	0.019	0.006	0.004	0.019
B1010	n.d.	n.d.	0.004	0.028	0.013	0.000	0.013

Table 4. Relative Standard Deviations of Concentration Values Provided in Table 2.

DEP Sample ID	1-methyl naphthalene	2-methyl naphthalene	4-(t-octyl)-phenol	benzothiazole	butylated hydroxytoluene	naphthalene	butylated hydroxyanisole
A1001	9.87%	4.49%	3.04%	2.29%		0.50%	2.96%
A1002	5.98%	4.12%	13.60%	1.86%		2.75%	1.04%
A1003	0.00%	3.14%	7.67%	3.11%		6.53%	2.82%
A1004	5.24%	3.14%	1.36%	1.89%	0.00%	2.72%	5.19%
A1005	5.66%	4.71%	16.53%	1.17%	4.88%	0.94%	1.84%
A1006	2.67%	3.14%	8.97%	2.39%	7.25%	2.74%	6.20%
A1007	6.43%	4.35%	13.98%	2.55%		1.84%	10.50%
A1008	16.44%	2.18%	21.57%	3.29%		0.95%	3.47%
A1009	7.44%	7.07%	18.30%	6.45%	3.37%	2.77%	5.05%
A1010	0.00%	0.00%	8.54%	2.03%	6.43%	5.32%	3.30%
A1011	0.00%	3.45%	5.71%	0.75%	3.89%	5.66%	2.72%
A1012	12.86%	3.07%	6.91%	0.71%	3.21%	2.27%	3.63%
A1013	19.51%	5.24%	5.20%	1.91%		0.70%	1.64%
A1014	2.18%	2.89%	4.36%	0.45%		1.37%	4.56%
B1002			15.17%	2.11%	2.21%	2.48%	1.18%
B1009			5.89%	1.48%	1.31%	7.44%	5.42%
B1010			7.44%	2.68%	3.21%	0.00%	3.72%

In all but 6 cases the relative standard deviations are <15%.

The graphical representation of the data in Table 2 are provided in Figure 1 with the concentrations shown on a logarithmic scale due to the wide range of the concentrations. From this graph it is immediately apparent that benzothiazole (black bar) is present in the largest amount, by an order of magnitude, in the headspace above all the samples, both those coded “A” and those coded “B”. Of particular note, samples B1002, B1009, and B1010 differ from the “A” samples in that butylated hydroxytoluene (green bar) is found in the gas phase at the second highest concentration (after benzothiazole) for all three of these samples.

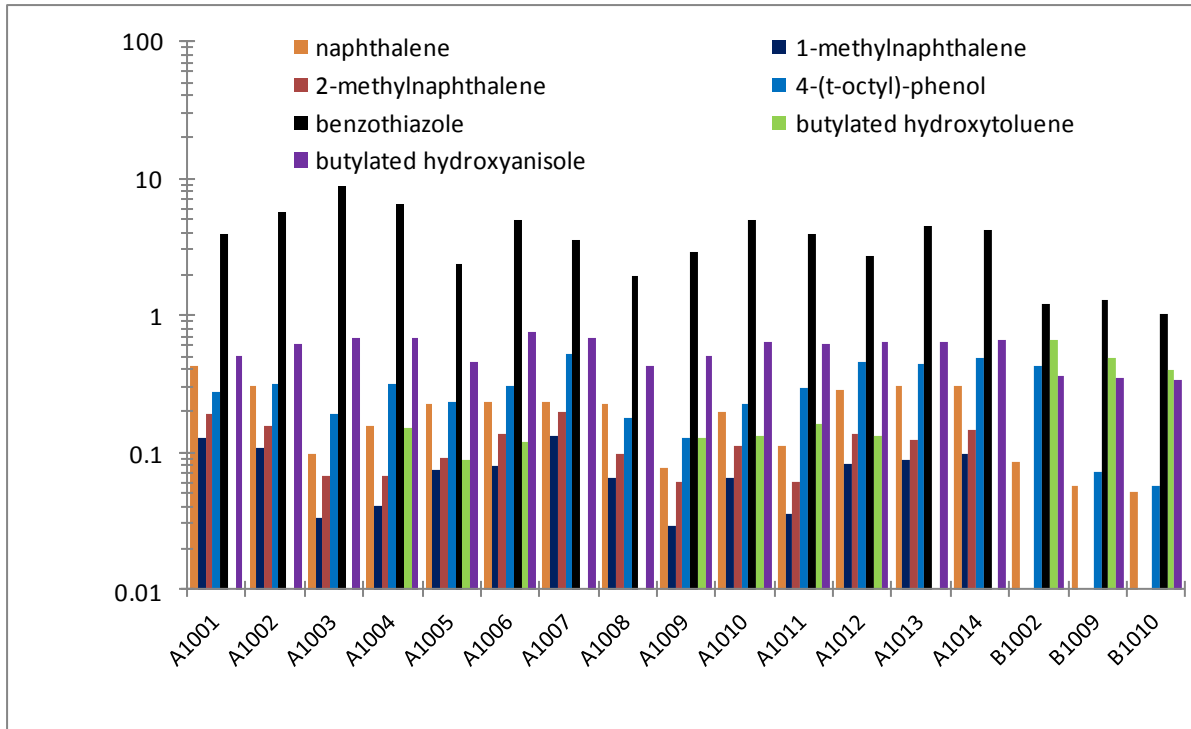


Figure 1.

We also treated the data by principal component analysis and provide a graphical representation of the results in Figure 2. It is not surprising, given the data in Figure 1, that, although there is divergence among the samples, the butylated hydroxytoluene drives all three “B” samples to locations on the PCA plot that are notably different from the other samples. The oval surrounding the “B” samples is for purposes of illustration only.

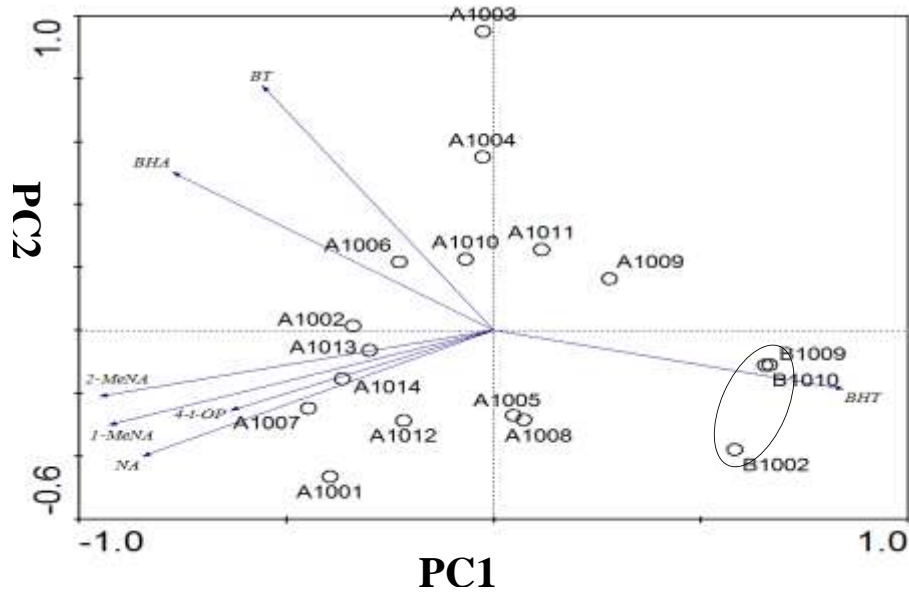


Figure 2.

3. VOLATILE COMPOUNDS FROM ALTERNATE INFILL PRODUCTS

Alternate infill samples (products not derived from crumb rubber) were also provided by DEP for analysis in our laboratory. The samples were run using the same headspace method, specified in Appendix B, as was used for the crumb rubber samples. The volatile organic compounds detected in the headspace over the alternative infill materials—xylenes and styrenes—were different and fewer in number than what was observed for the volatile compounds in the headspace over the CRM. The concentration values for the vapor phase compounds over the alternate infills are given in Table 5. It should be noted that none of the compounds identified in the headspace was detected in the blanks.

Three samples contain all four of the detected volatiles, with the highest amounts in sample B1001. In eight samples none of the volatile compounds was detected. The vapor phase concentrations over sample B1001 are generally an order of magnitude higher than those over the remaining thirteen samples.

Table 5. Concentrations (ng/ml) in Headspace Over Alternate Infills, Average of Two Analyses per Sample

DEP Sample ID	p, m-xylene	o-xylene	styrene	α-methylstyrene
B1001	13.72	1.47	6.35	2.39
B1003	0.39	0.30	0.50	0.27
B1004	n.d.	n.d.	n.d.	n.d.
B1005	0.38	0.31	1.38	0.62
B1006	n.d.	n.d.	n.d.	n.d.
B1007	n.d.	n.d.	n.d.	n.d.
B1008	n.d.	n.d.	n.d.	n.d.
B1011	1.18	1.07	n.d.	n.d.
B1012	n.d.	n.d.	n.d.	n.d.
B1013	n.d.	n.d.	n.d.	n.d.
B1014	n.d.	n.d.	n.d.	n.d.
B1015	n.d.	n.d.	n.d.	n.d.
B1016	1.24	0.99	1.62	n.d.
B1017	1.20	n.d.	n.d.	n.d.

The very small standard deviations and the relative standard deviations for these concentrations are given in Tables 6 and 7.

Table 6. Standard Deviations of Concentration Values in Table 5.

DEP Sample ID	p, m-xylene	o-xylene	styrene	α -methylstyrene
B1001	0.319047	0.024607	0.217435	0.044548
B1003	0.005091	0.000849	0.000424	0.001273
B1004				
B1005	0.001273	0.007637	0.072761	0.03585
B1006				
B1007				
B1008				
B1011	0.035355	0.077782		
B1012				
B1013				
B1014				
B1015				
B1016	0.001414	0.000707	0.06364	
B1017	0.004243			

Table 7. Relative Standard Deviations of Concentration Values in Table 5

DEP Sample ID	p, m-xylene	o-xylene	styrene	α -methylstyrene
B1001	2.326%	1.675%	3.425%	1.865%
B1003	1.294%	0.280%	0.084%	0.469%
B1004				
B1005	0.336%	2.450%	5.272%	5.738%
B1006				
B1007				
B1008				
B1011	1.179%			
B1012	2.263%	10.292%		
B1013	3.009%	7.303%		
B1014				
B1015				
B1016				
B1017				

4. LEACHING STUDY

In the experiments presented in sections 2 and 3 above we report on compounds detected in the gas phase, under the operational conditions employed, associated with crumb rubber and alternate infill materials. We were also charged with examining substances accessible via leaching of the infill materials by aqueous solutions. In section 4 we report our data from the leaching experiments.

To determine major organic compounds and heavy metals which may be leached from CRM when the material is exposed to rain, our experiments relied on EPA Method 1312, Synthetic Precipitation Leaching Procedure (SPLP). At the time of submission of this report, this method is available at (<http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/1312.pdf>). This laboratory-based procedure is a method "...designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes."

The major organic compound observed to leach from the majority of the CRM samples, benzothiazole, was concentrated using solid phase extraction (SPE) of the aqueous leachate, followed by GC/MS analysis of the concentrated extract. For details of the method please see Appendix D. The results are presented in Table 8. The LOQ for benzothiazole in the leachate is 0.007 ng/ml.

Table 8. Benzothiazole ($\mu\text{g}/\text{mL}$) in Leachate from CRM Samples

DEP Sample Code	distilled water	acidified (pH=4.2) water
A1001	0.120	0.120
A1002	0.190	0.190
A1003	0.230	0.260
A1004	0.220	0.210
A1005	0.060	0.070
A1006	0.150	0.110
A1007	0.090	0.120
A1008	0.144	0.150
A1009	0.183	0.185
A1010	0.270	0.268
A1011	0.203	0.206
A1012	0.165	0.169
A1013	0.116	0.095
A1014	0.178	0.213
B1002	0.030	0.060
B1009	0.086	0.090
B1010	0.077	0.080

From the analysis of the tabulated data it may be shown that there is no significant difference between the amount of benzothiazole leached by simulated rainwater versus what is leached by non-pH adjusted water ($\alpha < 0.05$). The data do confirm, however, that BT is accessible by exposure of the CRM to aqueous solution.

Concentrations of several elements were determined directly in the leachate using ICP-MS. Specifics of the method are provided in Appendix C. The data are presented in Table 9 for the CRM and in Table 8 for some of the alternate infill products. It is not surprising that the zinc concentration in every CRM sample exceeds that of the other elements listed by two to six orders of magnitude. This observation is consistent with what has been reported in the literature. (Councill TB, Duckenfield KU, Landa ER, Callender E. “Tire-wear particles as a source of zinc to the environment” ENVIRON SCI TECH, **38**: 4206-4214 (2004).)

Table 9. Elemental Analytes in pH Adjusted Leachate from CRM (ng/g)

DEP Sample ID	Cr	Mn	Ni	Cu	Zn	As	Cd	Ba	Pb
A1001	23.96	1443.19	28.57	143.32	50505.40	27.94	< MDL	415.99	69.90
A1002	1.04	98.24	8.94	5.65	58484.65	< MDL	< MDL	263.82	2.94
A1003	1.94	205.83	11.62	11.86	29536.66	< MDL	< MDL	281.43	3.91
A1004	1.46	361.49	10.94	19.33	8345.73	< MDL	< MDL	165.01	1.63
A1005	2.71	48.88	10.39	6.19	3168.71	< MDL	< MDL	146.27	1.34
A1006	1.44	286.52	16.84	8.66	37429.42	< MDL	< MDL	469.71	8.73
A1007	< MDL	258.13	13.00	13.84	48992.89	< MDL	< MDL	262.87	3.76
A1008	31.47	296.29	23.14	85.97	71535.52	6.57	< MDL	268.76	54.65
A1009	< MDL	404.28	15.90	20.68	43592.73	< MDL	< MDL	464.51	1.01
A1010	< MDL	243.32	10.13	6.16	51270.19	< MDL	< MDL	261.71	2.71
A1011	3.57	365.89	13.06	27.24	4395.81	< MDL	< MDL	210.53	36.66
A1012	< MDL	258.08	17.07	< MDL	30330.14	< MDL	< MDL	431.63	3.74
A1013	1.56	94.17	8.11	6.25	44580.42	< MDL	2.61	124.73	2.55
A1014	< MDL	101.61	8.65	14.15	49327.55	< MDL	< MDL	129.24	2.46
B1002	13.17	2.24	57.15	< MDL	18507.39	< MDL	< MDL	476.78	< MDL
B1009	11.72	2.70	45.99	< MDL	17033.16	< MDL	< MDL	502.91	< MDL
B1010	9.54	2.85	38.54	< MDL	13861.07	< MDL	17.01	460.04	< MDL

The leachate from several of the alternate infill materials was also examined for comparison with the CRM. These data are provided in Table 10. It should be noted that the zinc concentration does not dominate these data as it does for CRM. Particular note should be taken of the chromium concentrations. Several of these alternate infill products are colored green and the source of the chromium may be the colorant.

Table 10. Elemental Analytes in pH Adjusted Leachate from Alternate Infill Products (ng/g)

DEP Sample ID	Cr	Mn	Ni	Cu	Zn	As	Cd	Ba	Pb
B1001	8.10	45.28	19.02	< MDL	117.18	< MDL	< MDL	161.24	< MDL
B1003	27.27	49.16	6.56	< MDL	< MDL	4.51	< MDL	317.68	14.29
B1004	1577.36	60.24	4.52	< MDL	< MDL	8.73	< MDL	204.41	6.97
B1005	100.50	25.06	9.28	6.38	175.02	< MDL	< MDL	427.56	< MDL
B1006	534.20	5.09	8.00	5.12	< MDL	10.61	< MDL	26.15	4.77
B1007	7.15	21.99	382.50	7.86	269.15	12.64	< MDL	24.02	0.74
B1008	455.24	5.21	10.96	13.69	< MDL	7.38	< MDL	21.07	4.09
B1011	< MDL	4.17	1.31	30.50	1114.55	< MDL	< MDL	5.21	< MDL
B1012	1028.23	56.14	3.26	< MDL	< MDL	< MDL	< MDL	11.32	2.13
B1013	2.36	398.68	6.93	5.97	161.91	< MDL	< MDL	6.68	< MDL
B1014	54.65	24.36	5.43	< MDL	< MDL	8.64	< MDL	31.74	0.59
B1015	13.09	26.28	348.75	7.44	226.71	8.88	< MDL	17.27	0.67
B1016	< MDL	14.73	6.54	< MDL	< MDL	< MDL	< MDL	180.45	< MDL
B1017	< MDL	969.01	60.07	349.73	479.49	< MDL	< MDL	471.17	< MDL

Table 11. Minimum Detection Level in the Leachate

	Cr	Mn	Ni	Cu	Zn	As	Cd	Ba	Pb
MDL in ppb	1	1	1	5	100	3	1	1	0.5

5. WEATHERING STUDY

In addition to the determination of substances outgassing (section 2) and leaching (section 4) from virgin CRM and the alternate infills, the laboratory was also asked to examine how the profiles of these substances alter under conditions of weathering, that is, exposure of the CRM to sunlight, heat, rain, and mechanical abrasion. Three different approaches were considered:

A. Controlled exposure of CRM to outdoor environmental conditions.

This experiment was conducted on the New Haven campus of CAES. Four glass powder funnels were fitted with glass wool plugs so as to block the stem. Each funnel was then filled with 50g of virgin CRM (sample purchased and sent directly to CAES by Environment and Human Health Inc. in 2007). Each funnel containing a CRM sample was placed atop a 250mL amber glass Qorpak jar. This set-up was placed in a secure location outside the laboratory building. The CRM in two of the funnels was sampled weekly; for each sample, two 1g portions were analyzed via the headspace method provided in Appendix B. Two different 2g portions were leached and extracted by the SPE method, see Appendix D. The CRM in the other two funnels was not sampled; however, if available, 80mL of rainwater, which leached through these two CRM samples, was collected from the Qorpak jar and analyzed by the SPE method in Appendix D.

In Table 12 we provide the data from the headspace analysis of the CRM exposed to these controlled, outdoor environmental conditions. Please note that in the unweathered sample purchased by EHHI, no butylated hydroxytoluene was detected, in contrast to the data from the samples listed in Table 2.

Table 12. Concentrations (ng /ml) of Volatile Compounds in Headspace Over Crumb Rubber Samples Aged at CAES (average of two analyses per sample)

Sample ID (week)	benzothiazole	1-methyl naphthalene	2-methyl naphthalene	naphthalene	4-(t-octyl)-phenol	butylated hydroxyanisole
T0	3.75	0.12	0.24	0.40	0.35	0.77
T1	1.95	0.05	0.09	0.12	0.28	0.45
T2	0.97	0.04	0.06	0.06	0.31	0.40
T3	1.56	0.04	0.07	0.08	0.31	0.44
T4	1.77	0.04	0.08	0.08	0.30	0.43
T5	1.59	0.05	0.07	0.10	0.30	0.48
T6	1.20	0.04	0.06	0.05	0.25	0.36
T7	0.99	0.04	0.06	0.04	0.24	0.33
T8	1.17	0.05	0.05	0.06	0.23	0.41
T10	1.08	0.04	0.05	0.06	0.22	0.37

The standard deviations for these data are given in Table 13.

Table 13. Standard deviations for data listed in Table 12 (ng/mL)

Sample ID (week)	benzothiazole	1-methyl naphthalene	2-methyl naphthalene	naphthalene	4-(t-octyl)-phenol	butylated hydroxyanisole
T0	0.026	0.006	0.008	0.012	0.016	0.118
T1	0.032	0.003	0.010	0.002	0.004	0.061
T2	0.087	0.003	0.010	0.008	0.012	0.017
T3	0.184	0.002	0.007	0.009	0.030	0.078
T4	0.279	0.006	0.014	0.020	0.004	0.011
T5	0.138	0.002	0.020	0.008	0.001	0.015
T6	0.091	0.007	0.002	0.000	0.017	0.018
T7	0.089	0.004	0.003	0.009	0.021	0.024
T8	0.110	0.009	0.007	0.006	0.019	0.005
T10	0.007	0.003	0.005	0.015	0.006	0.055

We have also plotted the data from Table 12 in Figure 3.

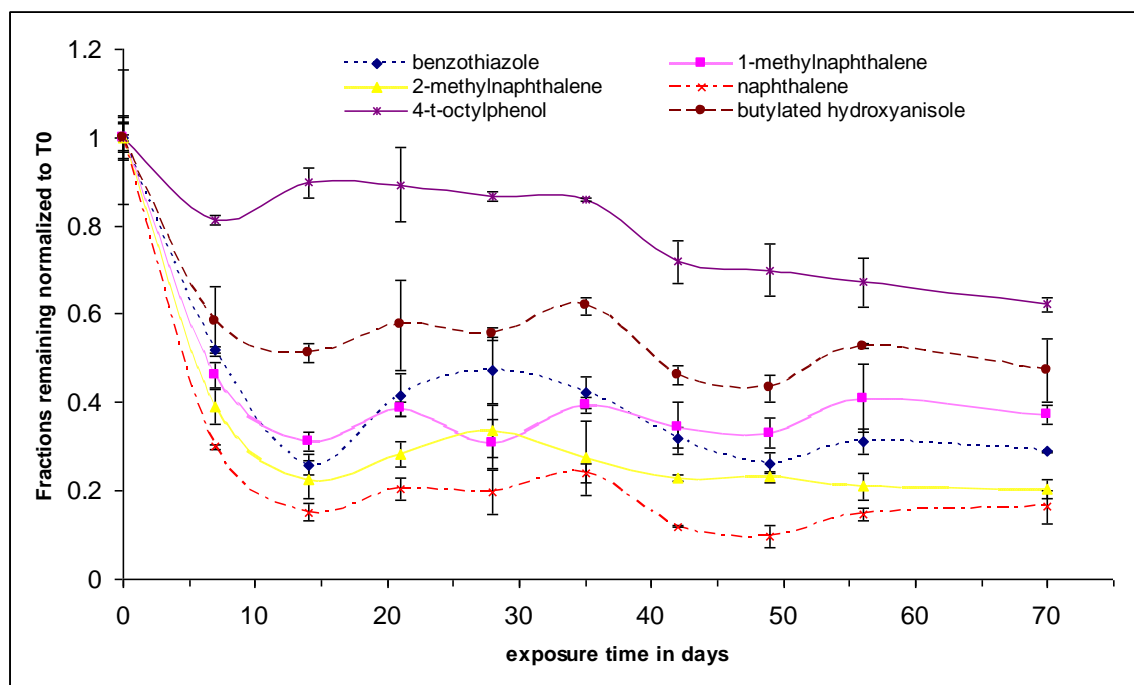


Figure 3.

Several comments are in order relative to the data in Figure 3. First, although there is a decrease in the amounts of all six compounds which outgas over the ten weeks of this experiment, the decrease is the least for 4-t-octylphenol. Second, at approximately 20 days of weathering under the conditions in this experiment, the five compounds appear to reach a consistent level of outgassing, reduced to about 20% of the amount at T0 (naphthalene) to about 80% for 4-t-octylphenol. The order of the remaining fraction is noted here for reference in the next topic: 4-t-OP > BHA > 1-meNaph > BT > 2-meNaph > Naph. It must be emphasized that these observations pertain to the conditions under which this experiment was conducted.

B. Exposure of CRM to real-world, on-field conditions

From Brian Golembewski of Connecticut DEP we learned that for at least two of the fields on which air-sampling was conducted in 2009, the DEP had supplied the CAES laboratory with virgin infill, designated as Sample A1002 and Sample A1003 (see Table 2 in section 2), in the first set of samples submitted for analysis. It was therefore possible to sample these infills from the fields after two years of natural weathering.

Table 14. Data from CRM under On-field Weathering Conditions

DEP Sample ID	1-methyl naphthalene	2-methyl naphthalene	4-(t-octyl)-phenol	benzothiazole	butylated hydroxytoluene	naphthalene	butylated hydroxyanisole
A1002 (T0)	0.107	0.155	0.312	5.59	n.d.	0.309	0.611
A1002 Field (T two years)	n.d.	n.d.	0.179	0.108	n.d.	n.d.	0.323
A1002 Field Normalized to T0			0.58	0.010			0.52
A1003 (T0)	0.033	0.068	0.194	8.669	n.d.	0.098	0.677
A1003 Field (T two years)	n.d.	n.d.	0.143	0.095	n.d.	n.d.	0.375
A1003 Field Normalized to T0			0.74	0.01			0.55

It is of interest to compare these data with those from the experiment described in topic B, above. Interestingly, the normalized order noted in Table 14, 4-t-OP > BHA > BT, is strikingly similar to those in Figure 3, despite the considerably different samples and experimental conditions.

C. Simulated weathering protocol

It was intended that the simulated weathering experiment would be designed using the Xenon Light Stability and Weathering Tester (Q-SUN, Q-Lab Corporation in Arizona) to simulate weathering by sunlight, heat, rain, and likely mechanical stress. However, as of the submission of this report it was not possible for CAES to coordinate with Q-Lab Corporation to schedule a demonstration trial use agreement. Given the information provided above, it is questionable whether it is either desirable or feasible for CAES to obtain and operate a Q-SUN tester for a period of 60 days to conduct the acceleration weathering examination of crumb rubber material. Purchase of this equipment is not possible within the budget allotted for this project.

6. APPENDIX A

METHOD FOR THE IDENTIFICATION OF VOLATILE COMPOUNDS OUTGASSING FROM CRUMB RUBBER DERIVED FROM RECYCLED TIRES

Preparation:

CTC Analytics 10mL headspace vials: PTFE/silicone septa 1.3mm thick

Samples: 1g crumbs/coated sand

To establish that the 1g subsample is a consistent representation of the bulk CRM, multiple analyses using the SPME procedure described in this appendix were conducted on two different CRM samples. The results are provided in the following figure.

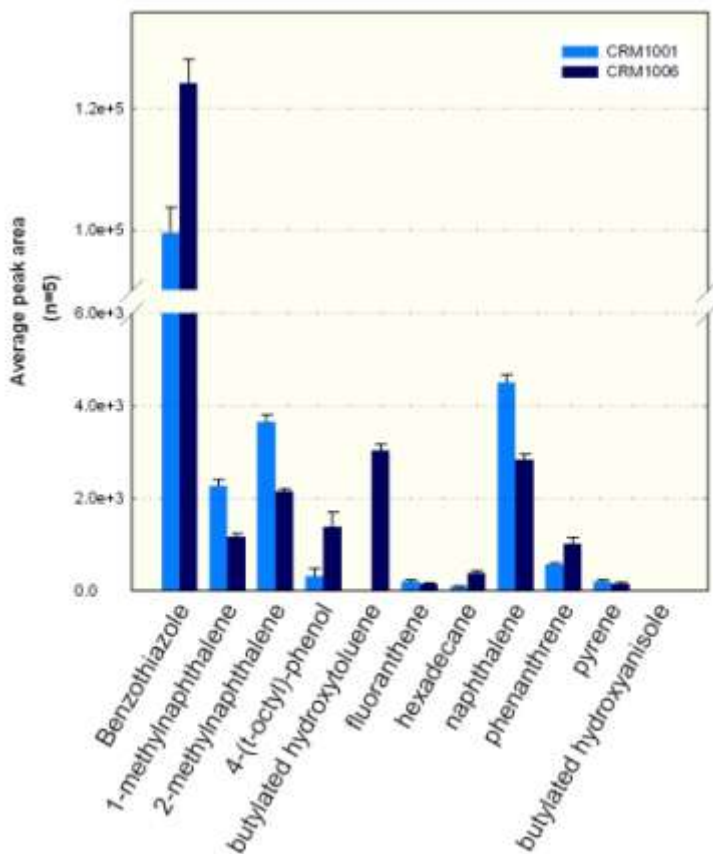


Figure 1A.

The very consistent and small standard deviations for eleven of the compounds, as shown in Figure 1A, justify the assertion that a one gram subsample is representative of the bulk sample.

Analysis: tire_crumb_current.mth

Extraction:

CTC Analytics CombiPAL Model #MXY02-01B w/ MH01-00B Agitator & MB01-00A Controller

Supelco 57289-U PDMS SPME fiber, 30um, 23ga

Agitator 60° C
Pre-Incubation time 0min
Extraction rpm 0
Fiber depth to bottom 25mm
Extrn time 40min
Desorb time 20min
Prep ahead time 60min
No bakeout

Gas Chromatography:

Varian 3800GC
1177 Injector with Supelco 22609-U Merlin Microseal
Injector temp: 260° C
Injector conditions

Time (min)	Condition	Split (%)
0.00	On	50
0.01	off	0
0.75	on	100
3.00	on	20

Constant flow 1.0mL/min
Column: Varian FactorFour VF5-MS 30m x 0.25mm ID x 0.25um film
GC Oven Program

Temp	Rate	Hold	Total
40		5	5
50	2		10
160	5		32
300	10	10	56

Mass Spectrometry:

Varian 4000MS Ion Trap

Source Config: External EI

Trap Temp: 180° C
Manifold Temp: 60° C
Transfer Line Temp: 200° C
Ion Source Temp: 180° C

Fil/Mul Delay: 6min
EI/Auto-Full: 6-56min

Low mass 35m/z
High mass 420m/z

Mult offset=0
Avg 3u scans
Target TIC 20000cts
Max Ion Time 65000us
Emission Current 25uA

External Standard Quantitation: tire_crumb_current_es.mth

RT (min)	Compound	Primary Ion (m/z)
22.053	naphthalene	128.1
23.307	benzothiazole	135.0
25.322	2-methylnaphthalene	142.1
25.750	1-methylnaphthalene	142.1
30.301	butylated hydroxyanisole	165.0
30.648	butylated hydroxytoluene	205.2
32.820	hexadecane	57.0
32.915	4-(t-octyl)-phenol	135.0
36.002	phenanthrene	178.0
39.321	fluoranthene	202.3
39.873	pyrene	202.3

6. APPENDIX B

METHOD FOR THE DETERMINATION OF CONCENTRATION OF VOLATILE COMPOUNDS OUTGASSING FROM CRUMB RUBBER DERIVED FROM RECYCLED TIRES Revised 7-16-09

Samples

1g tire crumbs into 10mL headspace vial with silicone/PTFE-lined septum

Varian 4000MS w/CTC Combipal: tire_crumb_headspace_60deg.mth

Injection mode: GC headspace

Syringe: 1mL gas-tight

Syringe temp: 60° C

Agitator temp.: 60° C

Incubation time: 20min

Agitation speed: 250rpm (must enter a value)

Agitation cycle: 0 sec on, 0 sec off (no agitation)

Plunger fill speed: 100uL/sec

Fill strokes: 0

Injection volume (set in sample list):

Viscosity delay: 1.00 sec

Pre-injection delay: 0.50 sec

Plunger inject speed: 250uL/sec

Post-injection delay: 0.50 sec

Syringe flush time: 30sec

GC cycle time (for Prep Ahead): 1hr

Injector temp: 260° C

Injector liner: Agilent 5181-3316 "5XK"

Injector Conditions

Time (min)	Split State	Split Ratio
Initial	On	50
0.01	Off	Off
0.75	On	100
3	On	20

Constant column flow: 1.0mL/min

GC Oven Program

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
40	0	5	5
50	2	0	10
160	5	0	32
300	10	10	56

Filament/Multiplier Delay: 6.00min
Mass range: 35:420
Target TIC: 20,000 counts
Max ionization time: 65,000 usec
Emission current: 25uA
Scans averaged: 3uscans
Multiplier offset: 0 volts

Calibration Standards:

Five calibration standards at a range of concentrations (ug/mL in hexane) appropriate for each of seven compounds were prepared. For all the calibration curves $r^2 \geq 0.99$.

Varian 4000MS w/CTC Combipal: tire_crumb_solvent inj.mth

Injection mode: GC liquid
Syringe: 10uL liquid
Pre-Inj washes solvent 1: 2
Pre-Inj washes solvent 2: 0
Sample flush volume pct: 50% syringe volume
Sample vial penetration depth pct: 95%
Plunger fill speed: 5ulSec
Fill strokes: 5
Viscosity delay: 0.30sec
Air volume below sample: 1.00uL
Pre-injection delay: 0.50 sec
Plunger inject speed: 5.00uL/sec
Post-injection delay: 0.50sec
Post-inj washes solvent 1: 5
Post-inj washes solvent 2: 0
GC cycle time (for prep ahead): off

All other parameters as in tire_crumb_headspace_60deg.mth

6. APPENDIX C

DETERMINATION OF ELEMENTS LEACHED BY AQUEOUS SOLUTION FROM CRUMB RUBBER DERIVED FROM RECYCLED TIRES (based on EPA Method 1312)

Purpose:

This method provides a description for the leaching of Synthetic Turf Infill Materials (STIM) with acidified water followed by analysis for trace metals using ICP-MS.

Equipment:

pH meter
50 ml centrifuge tubes
15 ml centrifuge tubes
Centrifuge
Wrist action shaker
Agilent 7500ce ICP-MS

Reagents:

Concentrated Nitric Acid (reagent grade)
Concentrated Sulfuric Acid (reagent grade)
Distilled Deionized Water (DDW)
ICP-Standards

Preparation of the acidified water:

The acidified water is intended to simulate acid rain east of the Mississippi River in North America. A mixture of sulfuric and nitric acid (60/40 w/w) is added to DDW to lower the pH to 4.2. This process requires a minute amount of the acid mixture.

Method:

Accurately weigh 1 gram of STIM directly into a 50 ml centrifuge tube.
Accurately add 20 ml of acidified water and tighten cap securely.
Shake for 18 hours using the wrist action shaker.
Remove from shaker and centrifuge at 3000 rpm for 10 minutes.
Carefully withdraw an aliquot of appropriate volume and transfer to a 15 ml centrifuge tube.
Acidify this aliquot (analytical solution) to 5% by volume with nitric acid.
Analyze the analytical solution on the ICP-MS.

Notes:

Use the Crumb Rubber Material (CRM) received in 2007 (purchased by EHHI from manufacturer and sent directly to CAES) as a reference material (RM) for QC and matrix fortification.

Fortify the blank and matrix aliquots after the leaching procedure and transfer from the 50 ml centrifuge tube (fortification before the leaching procedure changes the pH of the leaching solution).

6. APPENDIX D

METHOD FOR DETERMINATION OF BENZOTHAIAZOLE LEACHED BY AQUEOUS SOLUTION FROM CRM

The procedure described here is a modification of EPA method 1312, which is designed to determine the mobility of organic and inorganic analytes present in soils and wastes. Quantitative analysis focused on benzothiazole which is the most abundant compound of all the volatile and leachable chemicals from the majority of the CRM samples as determined in the present work.

- 2g CRM sample was weighed in a 40ml glass vial fitted with screw cap and filled with 40 ml of extraction fluid 1 (distilled water) or extraction fluid 2 (acidified water pH=4.2±0.5 achieved by adding the 60/40 weight percent mixture of sulfuric and nitric acids). The tubes were agitated on a wrist action shaker at ambient temperature for 18 hours.
- Leachate was filtered by Whatman qualitative filter papers, pore size 20-25 microns and 20ml of filtered sample was spiked with 5 µg 2-methylbenzothiazole as surrogate standard.
- Solid phase extraction (SPE) was conducted using Oasis 20mg HLB cartridges to concentrate BT based on previously reported studies (Kloepfer, et al. 2004). Briefly, 5ml 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. Column was left under vacuum for 20 mins before elution with 5ml 1:1 methanol:acetone.
- 3 µl of final sample extract was injected into GC-MS.
- The average recovery of the surrogate standards for 38 samples measured in this study was 100+/-17%.