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Off-gassing of Rubber Particles Used for Athletic Fields using Automated Dynamic Headspace Sampling

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Abstract
Rubber particles, sometimes derived from used tires, are used on artificial turf athletic fields, on playgrounds and as mulch. These particles can off-gas and leach compounds into the environment and may present a contact or inhalation hazard. Recent news reports in the US and Europe indicate a growing concern regarding potential health effects in athletes using these artificial turf fields.

This study describes the use of the GERSTEL Dynamic Headspace Sampler (DHS) for the collection and analysis of compounds off-gassing from samples of rubber particles collected from local athletic fields and playgrounds. The DHS can be configured to analyze a single sample under set conditions, or collect samples from a single sample over time. Quantitative and qualitative results will be shown in this study.

Introduction
The GERSTEL Dynamic Headspace Sampler (DHS) is an accessory for the Multi Purpose Sampler (MPS) which allows dynamic purging of the headspace above a sample. Analytes in the purged headspace are trapped onto 2 cm sorbent beds in compact glass tubes. The thermal desorption tube is then placed into the Twister Desorption Unit (TDU) and analytes thermally desorbed into the gas chromatograph. The analytes are cryofocused in the CIS 4 inlet to improve peak shape. Figure 1 shows a schematic of the trapping and desorption process. GERSTEL Maestro software also allows the samples to be extracted by dynamic headspace independent of the thermal desorption step. This mode allows nearly continuous sampling of a specimen over a set time period for later analysis.

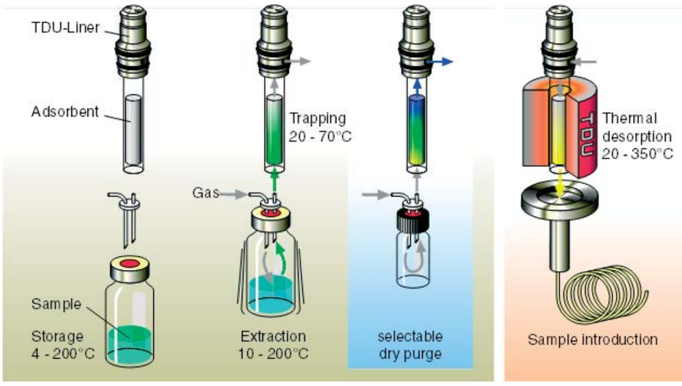

Figure 1. Schematic view of DHS process.

This study examines analysis of compounds off-gassed from rubber crumbs used on synthetic turf athletic fields. Samples were analyzed directly using dynamic headspace extraction. The DHS was also used to look at off-gassing of the crumbs over an extended time at various temperatures.

Experimental

Instrumentation. GERSTEL MPS sampler with TDU option, GERSTEL Dynamic Headspace Station, GERSTEL CIS 4 Cooled Inlet System with CCD[2] Option, and Agilent Technologies 7890B GC/ 5977A MSD.

Figure 2. GERSTEL MPS-DHS-TDU Agilent 7890/5977 system.

Analysis conditions.

TDU:	splitless
	40°C (0 min); 720°C/min;
	280°C (3 min)
PTV:	Tenax TA liner,
	split 1:20
	-20°C (0 min); 12°C/s; 280°C (5 min)
Column:	30 m Rxi-5ms (Restek)
	d_i = 0.25 mm d_f = 0.25 µm
Pneumatics:	He, constant flow = 1 mL/min
Oven:	40°C (2 min); 15°C/min; 280°C (2 min)
	40°C (2 min); 5°C/min; 280°C (2 min)
MSD:	Scan, 30 - 350 amu

Analysis conditions DHS.

Trap:	Tenax TA
Incubation:	60°C (10 min)
Agitation:	750 rpm
Sampling:	Sample 60°C
	Trap 25°C
	Volume 1000 mL (100 mL/min)
Transferline:	100°C

Analysis conditions DHS, off-gassing experiment.

Trap:	Tenax TA
Incubation:	30, 40, 50, 60°C (5 min)
Agitation:	750 rpm
Sampling:	Sample 60°C
	Trap 25°C
	Volume 600 mL (20 mL/min)
Transferline:	100°C

Sample Description. Rubber crumb samples were collected from local athletic fields. A sample of unused rubber crumbs was obtained from a site with a recently completed field.

Sample Preparation. Samples of rubber crumbs (0.25 g ± 0.01g) were weighed into a 20 mL screw capped vial.

Standard Preparation. Standards of Benzothiazole were prepared in Methanol. Two microliters of standard were spiked onto the fritted end of a TDU tube filled with Tenax-TA®. Dry nitrogen was passed through the tube for 3 minutes at a flow rate of 50 mL/min to purge the solvent.

Results and Discussion

Figure 3 shows the total ion chromatogram (TIC) for dynamic headspace extraction of the unused rubber crumb sample. Table 1 lists compounds identified in the sample. The two largest peaks are 2-Ethyl-1-hexanol and Benzothiazole. Benzothiazole and 2-Mercaptobenzothiazole, also present in the chromatogram, are byproducts of accelerators used for vulcanization of rubber [1]. 2-Ethyl-1-hexanol is a solvent used in rubber production. A wide variety of compounds are found in the sample, including a series of C4 and C5 Benzene isomers. Figure 4 shows extracted ion chromatograms for Naphthalene and C2-C4 substituted Naphthalenes, which were also found in the sample.

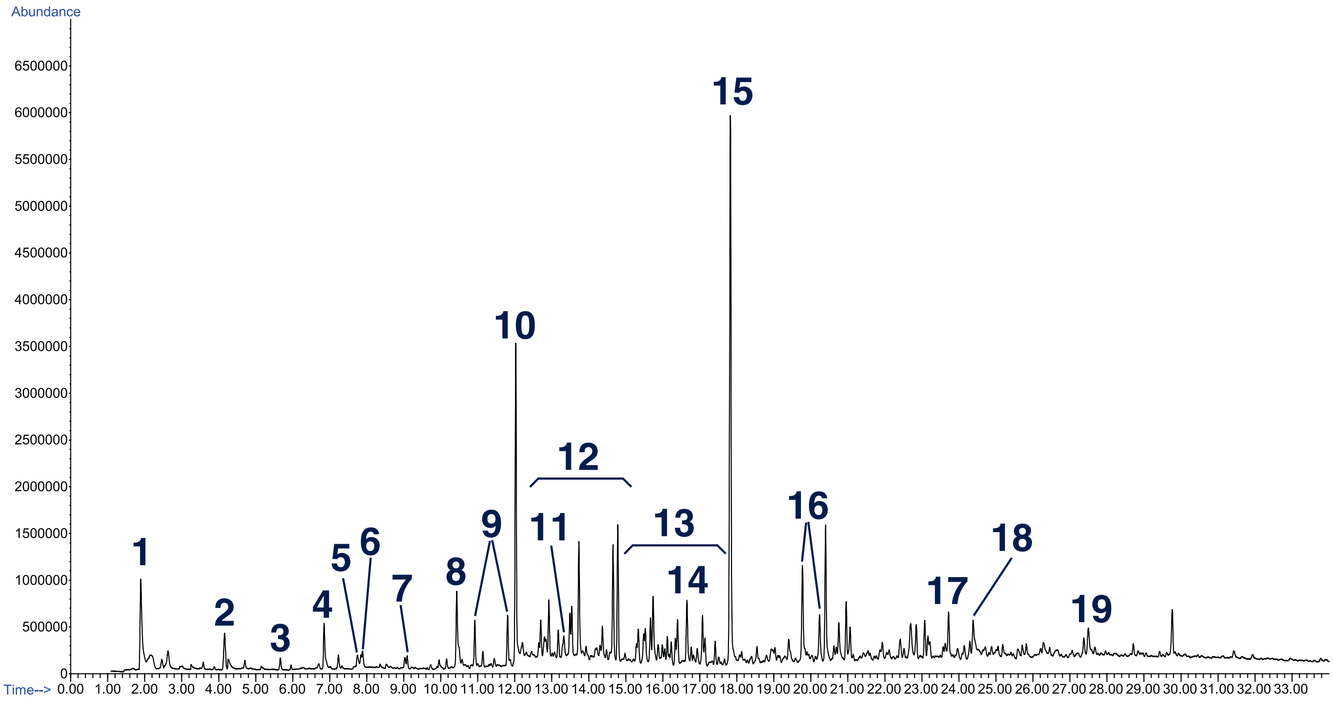

Figure 3. Total Ion Chromatogram (TIC) for DHS extraction of unused rubber crumb sample.

Table 1. Peak identities for figure 3.

No.	Compound	No.	Compound	No.	Compound
1	t-Butylamine	8	Aniline	15	Benzothiazole
2	Methyl Isobutyl Ketone	9	Trimethylbenzene Isomer	16	Methyl Naphthalenes
3	Tetrachloroethylene	10	2-Ethyl-1-hexanol	17	1,2-Dihydro-2,2,4-trimethylquinoline
4	3,3-Dimethyl Butanamide	11	o-Toluidine	18	4-t-Butyl-4-hydroxyanisole
5	N-t-Butylformamide	12	C4-Benzene Isomers	19	2-Mercaptobenzothiazole
6	Styrene	13	C5-Benzene Isomers		
7	N-t-Butylpyrrole	14	Naphthalene		

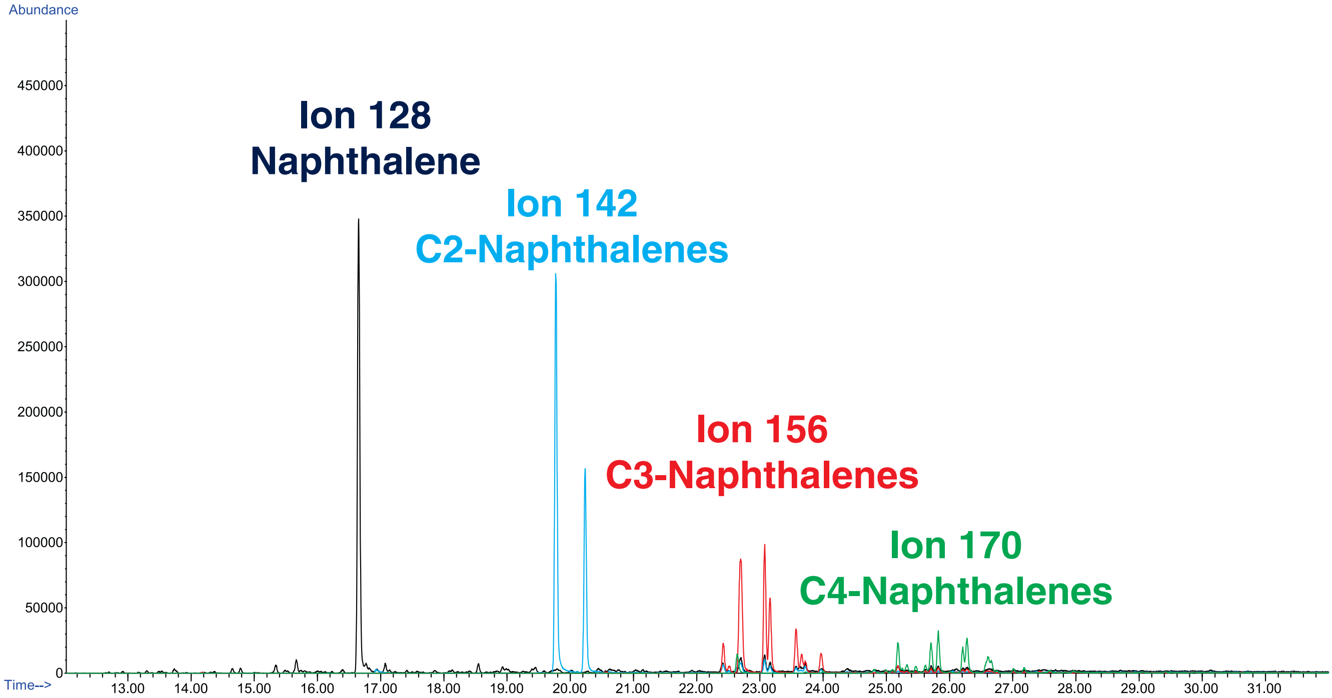

Figure 4. Extracted Ion Chromatograms showing Napthalenes in unused rubber crumb sample.

Figure 5 shows a stacked view of TICs for the unused rubber crumbs and a sample from an athletic field. The used sample was gathered in March of 2016, it has been weathered over several months during the winter. The chromatograms show much reduced levels for compounds emitted from the used rubber crumb sample, as one would expect in a weathered sample. A series of n-Alkanes, Limonene and Benzothiazole are seen in the sample from the athletic field.

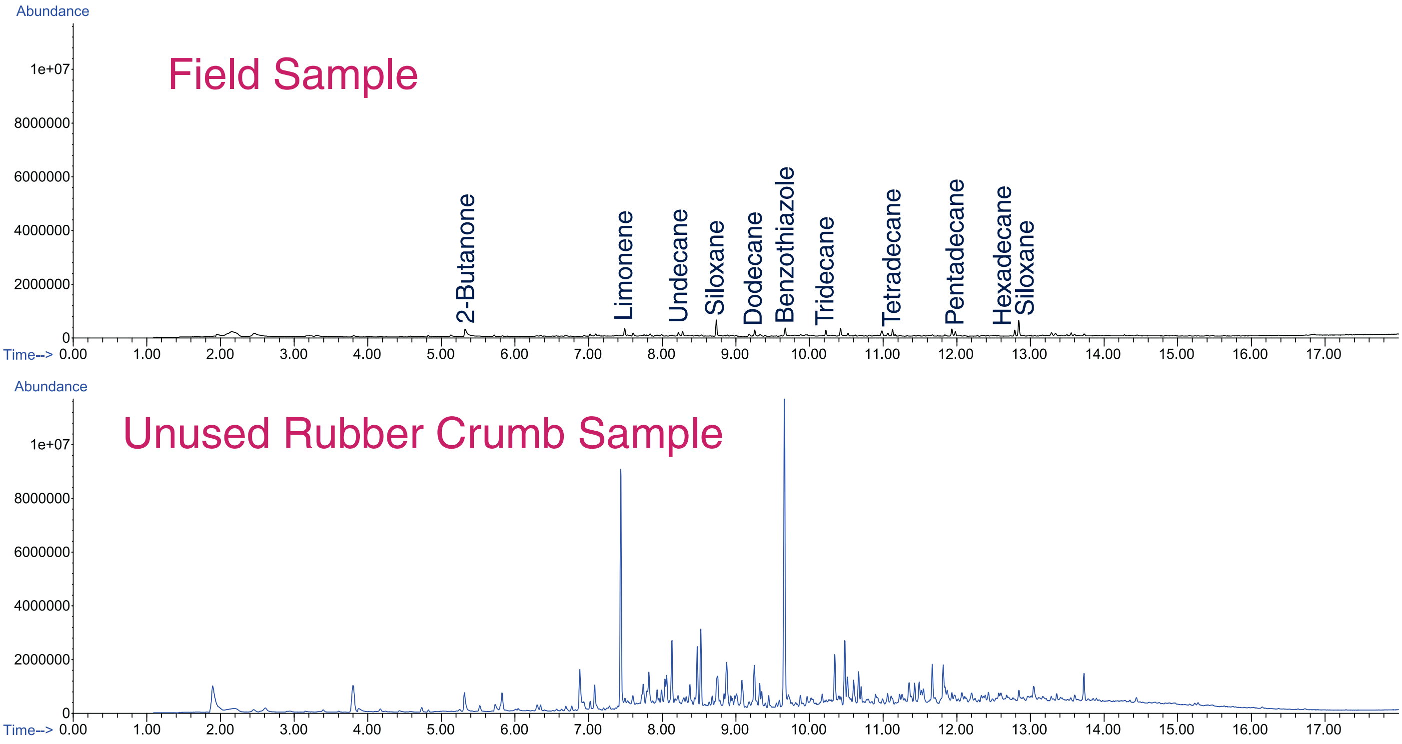

Figure 5. Stacked view of TICs for a field sample and unused rubber crumb sample.

In order to quantify the amount of Benzothiazole, an external calibration curve was constructed using standards spiked onto sorbent tubes. The results of the quantification are shown in Table 2. The amounts shown do not represent the total amount in the sample, as an exhaustive extraction was not performed. The amounts represent what was given off during the experimental conditions used for this extraction. The unused rubber sample was analyzed in triplicate. The average value found was 1390 ng of Benzothiazole per gram of rubber with good reproducibility (2.6% RSD). The field samples show values ranging from 2-20 ng/g. The field samples show an average level of 0.75% relative to the unused rubber indicating significant off-gassing of this compound during weathering.

Table 2. Quantitative results for Benzothiazole extracted from the samples.

Sample	Benzothiazole [ng/g]
Field 1	3.31
Field 2	2.31
Field 3	12.9
Field 4	11.5
Field 5	13.8
Field 6	18.7
Unused Rubber 1	1420
Unused Rubber 2	1400
Unused Rubber 3	1350
Average	1390
%RSD	2.6

The next set of experiments examined off-gassing of the unused rubber crumb sample over an extended time at different temperatures. The Maestro software allows the samples to be extracted by dynamic headspace without thermal desorption. This mode allows nearly continuous sampling of a sample over a set time period. The temperatures used for this study were 30, 40, 50, and 60°C. The time period chosen was three hours. Six Tenax-TA® tubes were used in series at each temperature, each tube collecting analytes from a total volume of 600 mL over 30 minutes (extraction flow of 20 mL/min). Figure 6 shows the Maestro Scheduler for this experiment. The yellow boxes show the extraction of the sample. The dark yellow boxes indicate the transfer of tubes from the MPS tray to the DHS station. The time required for transfer of the tubes is approximately 3 minutes. The red boxes indicate thermal desorption of the TDU tubes. The beige boxes are the GC run and cooldown times. The overall processing time for the conditions used for this study, is 6 hours and 20 minutes for each temperature level.

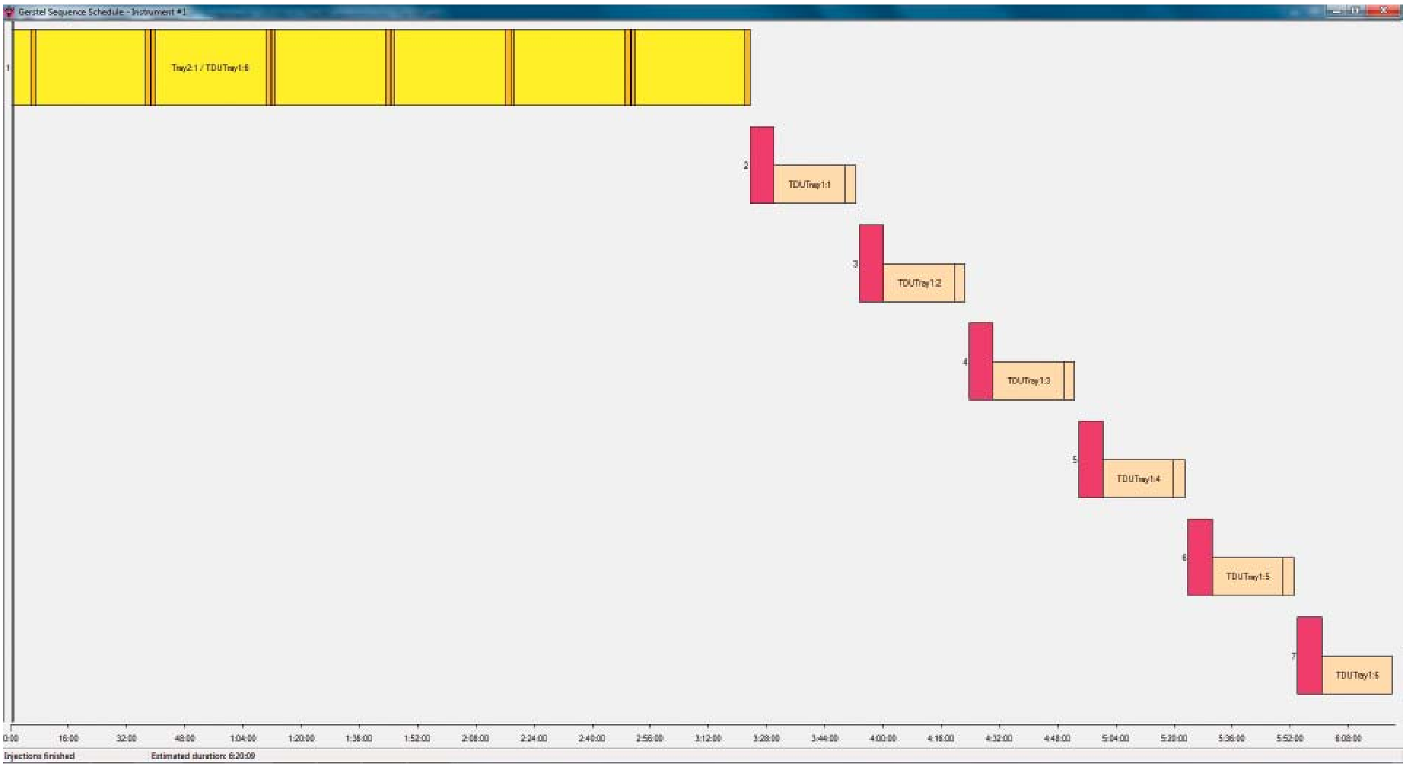

Figure 6. Maestro Scheduler for off-gassing experiments.

Table 3 shows the data for these experiments. Figure 7 shows a plot of the data in Table 3. At 60°C, the plot shows the amount of Benzothiazole off-gassing drops quickly in the first two hours and gets close to reaching a steady state at 180 minutes. At the other temperatures, the off-gassing of Benzothiazole also levels off after about 2 hours. The total amount of Benzothiazole emitted divided by the total extraction volume ranged from 97-744 ng/g of sample per liter of gas for the temperature range studied.

Table 3. Quantitative results for Benzothiazole off-gassed from the unused sample in ng/g.

Time [min]	30°C	40°C	50°C	60°C
30	93.5	215	385	812
60	64.4	159	295	571
90	56.7	133	241	477
120	49.0	115	203	293
150	45.5	107	169	268
180	41.1	90.7	152	256
Total Over 3 hrs	350	820	1440	2680
Total Per Liter	97.3	228	401	744

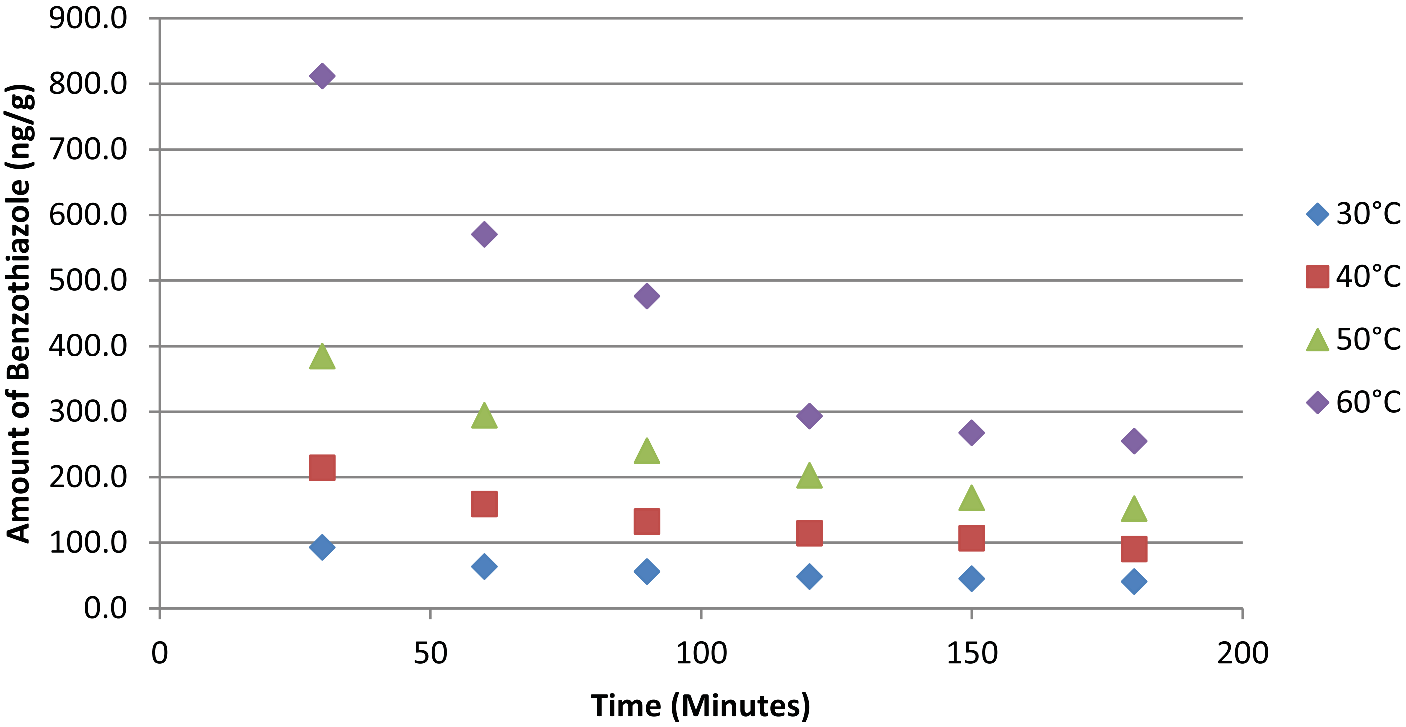

Figure 7. Amount of Benzothiazole versus time for off-gassing experiments.

Conclusions

The results showed several classes of organic compounds off-gassing from new and used rubber crumbs. The amount of Benzothiazole off-gassed from the field samples was very low relative to the unused crumbs showing that weathering of the crumbs substantially lowered the emission of volatiles. The time and temperature experiments show that the amount of Benzothiazole decreased faster in the first two hours, then reached a steady state. Thermal treatment of the crumbs prior to field application may be one approach to reducing the amount of chemical off-gassing from this product limiting athletes' exposure to these chemicals.

The GERSTEL Dynamic Headspace Accessory for the MPS allows trace level detection of analytes from solid or liquid matrices. GERSTEL Maestro software allows for multiple dynamic headspace extractions of the same vial which can be used to monitor off-gassing from different sample types.

References

[1] Hans-Wilhelm Engels, Herrmann-Josef Weidenhaupt, Manfred Pieroth, Werner Hofmann, Karl-Hans Menting, Thomas Mergenhagen, Ralf Schmoll, Stefan Uhrlandt. Rubber, 4. Chemicals and Additives in *Ullmann's Encyclopedia of Industrial Chemistry* **2004**, Wiley-VCH, Weinheim.

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