

## ENGINEERING & GINNING

### Comparison of Emission Profiles for Volatile Organic Compounds from Cotton and Polypropylene-based Tarp

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#### INTERPRETIVE SUMMARY

Contamination of cotton supplies with plastic waste occurs during harvesting and creates losses of more than \$5 million yr<sup>-1</sup> through inadvertent production of blemished finished items that are rejected or discounted for sale. The number of sources and routes for contamination by plastics suggests that future supplies of cotton nationally will contain plastic wastes, and methods are not available to detect or to remove plastics early in production, that is, as cotton enters a gin. One distinguishing feature of synthetic polymers versus natural fibers may be volatile organic compounds emitted by the materials when heated, for example, during the drying step of ginning. Such vapors, if sufficiently characteristic of plastics in a large background of cotton, may be detected by chemical sensors and used to disclose the presence of plastic waste in cotton. In this investigation, cotton and polypropylene-based tarp were heated, and volatile organic compounds in headspace atmospheres were quantitatively determined using a gas chromatograph-mass spectrometer. Samples were treated under temperature and atmospheric pressure conditions that are comparable to those in a cotton gin drying system. At 100 and 150°C, polypropylene-based tarp released volatile organic compounds that differed from those of cotton in both quantity and identity. Aging of plastics was measured by prolonged heating of polypropylene-based tarp and repeated sampling of the vapors emitted. Also, volatile organic compounds were seen

to arise from both thermal desorption and thermal decomposition. These findings suggest that vapor sensors will need to have selective response to alkanes and alkenes with C numbers from ~15 to 20.

#### ABSTRACT

Volatile organic compounds were determined in headspace atmospheres over samples of cotton (*Gossypium hirsutum* L.) and polypropylene {[CH<sub>2</sub>CH(CH<sub>3</sub>)]<sub>n</sub>} at 100 and 150°C in He and air. A small number of volatile organic compounds were released from cotton at 100°C in He with comparatively low emission rates of 0.2 to 0.3 µg g<sup>-1</sup> per component. These components had C numbers below 21. In contrast, emission rates for volatile organic compounds from polypropylene-based tarp were 0.6 to 9 µg g<sup>-1</sup> at 100°C in He, and constituents were predominantly alkanes with C numbers of 14 to 19. Increases in emission rates were observed for components with low vapor pressures (i.e., C numbers >16) though little increase was observed for components with high vapor pressures (i.e., C numbers <16). Exposing cotton to an air atmosphere at 150°C created dramatically new chromatographic profiles for volatile organic compounds versus those from inert atmospheres, and emission rates per compound increased to 0.4 to 1.3 µg g<sup>-1</sup>. Changes in volatile organic compound emissions for polypropylene-based tarp in air were less noticeable at 150°C, though emission rates per compound increased to 0.8 to 11 µg g<sup>-1</sup>. Some compounds produced in air at this higher temperature were suggestive of oxidative decompositions. Prolonged heating of polypropylene-based tarp resulted in thermal desorption of residual solvents or impurities followed by thermal decomposition.

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Contaminants in U.S. cotton result in blemished fabrics and flawed garments or other finished goods, causing economic losses of ~\$5 million annually to the U.S. cotton and garment industry (National Cotton Council, 1997). A major source of contamination is plastic waste, which was found in

nearly 40% of 331 samples of cotton (RFMF, 1999). Such waste is introduced into cotton during harvesting as strands of discarded bale twine and as fragments of plastic tarp used to cover cotton modules. In addition, plastic shopping bags can enter the supply as ordinary litter, driven by wind into crops before harvest. Once plastic waste is introduced into the cotton supply, fragments of plastics can be shredded and widely dispersed throughout a large amount of cotton in highly automated production in modern cotton gins. Eventually, shreds of plastic become entrained in fabric, creating blemishes in finished products such as shirts and linen; this can be evident particularly with dyed fabrics. At present, these flaws are found only during the final inspection of a manufactured item; thus, impurities in cotton are first noticed in the value-added product when the economic impact is worst.

Since plastic use will persist in a technical and consumer-oriented society and control of sources of contamination is unlikely, methods are needed for detecting and removing plastics from the cotton supply. Remediation should occur early in the production process, that is, as the raw material enters a gin and before the contaminating plastic is shredded and dispersed. At present, there are no methods to detect the presence of plastics in seed cotton. Challenges in detecting contaminating plastics in cotton are the high rate of cotton flow into a cotton gin and the random distribution of small plastic contaminants in the cotton. Complicating any intention to measure plastic waste in a cotton supply are the mechanical similarities between the materials and the optical masking of small bits of plastic by the cotton. Differences do exist, however, in the chemical composition of cotton and plastic and these differences may be exploited to detect plastics in cotton feedstock.

A first step in the ginning process is to dry the cotton at  $\sim 100$  to  $150^\circ\text{C}$  for 10 to 30 s; plastics generally release volatile organic compounds when warmed to as low as  $50^\circ\text{C}$ . Substances released from the plastics can arise from desorption of residues in the plastic or from thermal decomposition of the polymer and such vapors might provide chemical markers of plastic contamination in a cotton, particularly in the drier. The plastics commonly found in cotton supplies are polyethylene

$[(\text{CH}_2\text{CH}_2)_n]$  and polypropylene (National Cotton Council, 1997), and volatile organic compounds from these plastics have been identified under inert gas conditions. Relevant to interests here, was delineation of both thermal desorption and decomposition in polypropylene heated from 20 to  $400^\circ\text{C}$  under vacuum conditions (Lattimer, 1993). Residual chemicals from polymer production were emitted at temperatures  $<300^\circ\text{C}$ , while volatile organic compounds from thermal decomposition were created and emitted at temperatures  $>300^\circ\text{C}$ . The vapors from thermal desorption were comparatively simple compared with thermal decomposition, which was attributed to a free radical decomposition mechanism.

The kinetics of decomposition of polyethylene and polypropylene were also described for ambient pressure in the temperature range of 200 to  $450^\circ\text{C}$  (Westerhout et al., 1997) and showed that the energy of activation was  $\sim 200 \text{ kJ mol}^{-1}$ . The volatile organic compounds from thermal decomposition of polypropylene were identified as hydrocarbons with C numbers from 1 to 7, and principal constituents were propylene ( $\text{C}_3\text{H}_6$ ), pentanes ( $\text{C}_5\text{H}_{12}$ ), and hexanes ( $\text{C}_6\text{H}_{14}$ ) (Hedrick and Chuang, 1998); however, an inert gas atmosphere of N was used in these studies and findings cannot be extended directly to conditions in the drier of a cotton gin where plastics encounter a heated air atmosphere. Other volatile organic compounds were created under steam treatment from 275 to  $300^\circ\text{C}$  and included aldehydes, alcohols, and acids in the C number range of 7 to 18 (Rebeyrolle-Bernard and Etievant, 1993). Finally, the rate of emission of volatile organic compounds from thermal desorption ( $70^\circ\text{C}$ ) was time-dependent, with time of persistence up to 15 h; the weathering of plastics increased the complexity of decomposition products (Cunko, 1999).

In summary, heated polypropylene and polyethylene release a mixture of volatile organic compounds, and the composition of these vapors depends upon temperature. The volatile organic compounds that arise from desorption appear to persist for extended periods and should be characteristic of a synthetic plastic (i.e., residuals from the manufacturing processes). Thus findings from existing studies generally support the concept that vapor emissions may serve as a means of

detecting plastics in cotton. However, more than a few variables are unclear or undetermined and are needed to create chemical sensors for plastics in cotton. For example, the quantities and identities of volatile organic compounds emitted from polypropylene and polyethylene in air at elevated temperatures have not been reported, and the effect of air in promoting oxidative decomposition is unclear. Finally, plastics in the drier of a gin will be heated in a large matrix of cotton. The emission profile of volatile organic compounds from cotton under such conditions has not been reported. Volatiles from cotton could interfere chemically with any attempt to use airborne volatile organic compounds as an indicator of plastic contamination of cotton. Estimates of feasibility for detecting plastic in cotton will need both chemical identities and emission rates of volatile organic compounds from cotton vis-à-vis volatile organic compounds in plastic.

A goal for these studies was to obtain chemical identities and emission rates for volatile organic compounds released from polypropylene-based tarp and from cotton under the conditions expected inside the drier of a cotton gin - that is, ambient pressure in air atmosphere and temperatures of 100 to 150°C. A second interest was to identify volatile organic compounds released from commercial plastics with time in accelerated weathering with plastic exposed to high temperatures up to 120 min. Such measurements are relevant here as a measure of aging of plastics in hot environments common to the southwestern states of California, New Mexico, and Arizona. Studies with an air atmosphere were made in parallel with identical determinations for an inert He atmosphere to measure any reactivity from air on the materials and to measure volatile organic compounds released from plastic and cotton.

## EXPERIMENT

### Instrumentation

The gas chromatograph-mass spectrometer used was a model 5890A gas chromatograph and a model 5971A mass selective detector (Hewlett-Packard, Palo Alto, CA) equipped with a 30-m capillary column (50% phenyl, 50% methypolysiloxane stationary, i.d. 0.25 mm,  $d_f$  0.25  $\mu\text{m}$ , Restek,

Bellefonte, PA) and a six-port two-way switching valve (Valvco, Houston, TX) maintained at 200°C. The operating parameters of the gas chromatograph-mass spectrometer were injector temperature, 250°C; interface temperature, 280°C; initial temperature, 10°C; initial time, 5 min; final temperature, 250°C; final time, 0; temperature program rate, 6°C min<sup>-1</sup>; column pressure, 6 psi; carrier gas, He at 2 mL min<sup>-1</sup>; purge flow, 1.5 mL min<sup>-1</sup>; split flow, 20 mL min<sup>-1</sup>. Conditions for the mass spectrometer were mass range, 45 to 550 Da; threshold, 500; scan rate, ~200 Da s<sup>-1</sup>; 70 eV EI-MS, electron multiplier voltage, 2100-2300 V according to the automated calibration routine. A sample oven was fashioned to heat conductively a sample container (a stainless-steel tube, 6 cm long  $\times$  6 mm o.d.) and to heat samples isothermally at 100 or 150°C.

## MATERIALS AND METHODS

A blue plastic tarp, manufactured in China, was purchased at a national discount store in Las Cruces, NM, and was a polypropylene-based commercial product. The cotton lint and seed came from 'Acala 1517' grown locally. Samples of new plastic tarp and cotton lint were gravimetrically assayed and heated for 10 min at either 100 or 150°C in the presence of air or He. After the heating period, a heated switching valve was used to sweep headspace vapors from the sample for 3 min to the gas chromatograph-mass spectrometer for characterization. Then the switching valve was reset to an original position where the sample was isolated from the chromatographic system and the portable oven was removed from the tube containing the sample; the sample was allowed to cool to ambient temperature (~25°C). This procedure of heat treatment and analysis of headspace vapors over a sample was repeated for 12 consecutive cycles, each with a 10-min treatment at a 100 or 150°C. When air rather than He was used as the gas atmosphere, all processes of heating and sampling of the headspace were made using an auxiliary gas flow of bottled air (99.9% purity); the carrier gas for the gas chromatograph-mass spectrometer was always He. To obtain a measure of the repeatability of the experimental methods, five replicate determinations were made on fresh samples of plastic and cotton

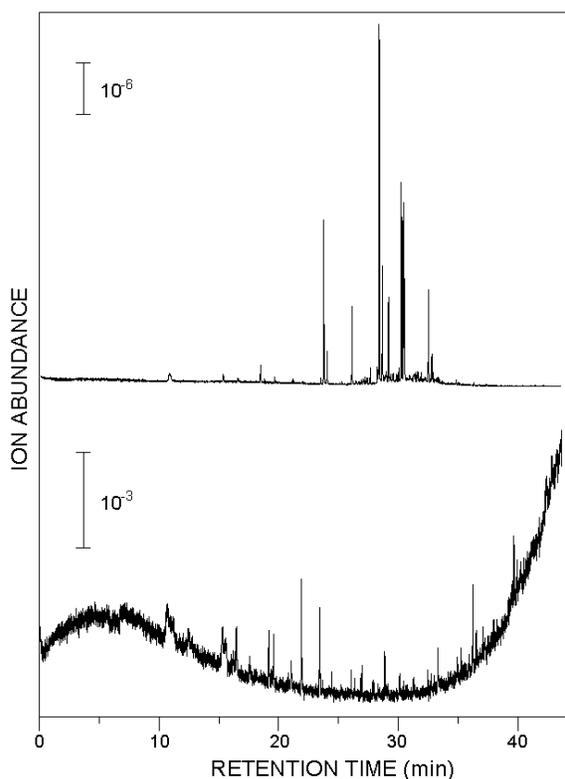
throughout the entire cycle of heatings. Each sample (~100 mg) was weighed before a study to establish a gravimetric ratio of volatile organic compounds to sample. At the beginning of all experiments, measurements were made using blank controls (i.e., a measurement with all steps excepting any sample). All controls were clean at limits of detection before any experiments were made.

Emission rates for volatile organic compounds were determined from gas chromatograph-mass spectrometer measurements. The gas chromatograph-mass spectrometer was calibrated using standard solutions created from serial dilutions of a mixture of alkanes with C numbers from 10 to 16. An initial stock solution was prepared gravimetrically in methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) solvent and subsequent dilutions were made volumetrically. One to two microliters of each solution were analyzed using scanning gas chromatograph-mass spectrometer methods. Chromatograms from each analysis were extracted into spreadsheets and reduced using standard software packages. Conversions of abundance to mass were made using calibration curves from results from gas chromatograph-mass spectrometer determinations of standard solutions.

## RESULTS AND DISCUSSION

### Emission of Volatile Organic Compounds from Polypropylene-based Tarp and Cotton in Inert Gas at 100°C

Results from gas chromatograph-mass spectrometer determination of volatile organic compounds released from polypropylene-based tarp are shown in Fig. 1 (top frame) for a temperature-programmed analysis (10 to 250°C at 6°C min<sup>-1</sup>) after the polypropylene-based tarp was heated in He at 100°C for 10 min. Few peaks were detected in the chromatogram before 20 min (elution temperatures of 10 to 100°C) and this suggested only minor emission of relatively volatile organic compounds, that is, C numbers of 1 to 10 [i.e., methane ( $\text{CH}_4$ ) to decane ( $\text{C}_{10}\text{H}_{22}$ )]. Significant amounts of components are seen in peaks that appear at retention times of 25 to 30 min (130 to 160°C elution temperatures) and were found as a complex mixture of more than 35 components with ~nine major constituents. Mass



**Fig. 1.** Total ion chromatograms from gas chromatograph-mass spectrometer analysis of vapors from new polypropylene (top frame) and cotton (bottom frame) in He atmosphere at 100°C.

spectral results are summarized in Table 1 and components were identified as normal alkanes from tetradecane ( $\text{C}_{14}\text{H}_{30}$ ) to nonadecane ( $\text{C}_{19}\text{H}_{40}$ ) and two alkylated benzenes (2, 6-di-*t*-butylphenol and 2, 6-di-*t*-butyl-*p*-cresol). The rates of emission of individual components were 0.7 to 9  $\mu\text{g g}^{-1}$  of polyethylene and the total rate for principal constituents was ~35  $\mu\text{g g}^{-1}$ .

Figure 1 (bottom frame) shows a chromatogram for volatile organic compounds released from cotton using identical amounts and procedures for plastics. Results can be directly compared with those described above for the polypropylene-based tarp. Although 20 to 30 peaks can be seen above the level of experimental noise in the chromatogram, the amounts of volatile organic compounds (0.2 to 0.3  $\mu\text{g g}^{-1}$ ) were low compared with those from the tarp. The large baseline distortion, magnified due to scaling, suggested some amount of unresolved volatile organic mass. The identities of the volatile organic compounds released from cotton in He were difficult or impossible to determine, given the insufficient mass released by the cotton, though

**Table 1. Chemical identity and abundances for major volatile components released from plastic and cotton at 100°C in He.**

<b>Blue plastic new (17.4 mg)</b>					
Retention time	Base peak	Abundance	MW†	Chemical identity	Emission rate
min		$\times 10^6$			$\mu\text{g g}^{-1}$
26.26	57	2.5	198	tetradecane, $\text{C}_{14}\text{H}_{30}$	4.5
30.64	57	5.3	226	hexadecane, $\text{C}_{16}\text{H}_{34}$	9.3
30.89	55	1.5	224	hexadecene, $\text{C}_{16}\text{H}_{32}$	2.8
32.37	205	3.0	220	unknown aromatic hydrocarbon	5.3
32.53	191	2.7	206	unknown aromatic hydrocarbon	4.8
32.62	57	1.5	240	heptadecane, $\text{C}_{17}\text{H}_{36}$	2.8
34.52	57	1.4	254	octadecane, $\text{C}_{18}\text{H}_{38}$	2.6
34.78	55	1.4	252	octadecene, $\text{C}_{18}\text{H}_{36}$	2.6
36.34	57	0.3	268	nonadecane, $\text{C}_{19}\text{H}_{40}$	0.7
<b>Cotton (19.1 mg)</b>					
		$\times 10^4$			
22.00	44	4.5	168	unidentified hydrocarbon	0.22
22.37	73	4.0		unidentified hydrocarbon	0.21
24.56	44	10.0	128	unidentified hydrocarbon	0.31
26.00	73	8.0		unidentified hydrocarbon	0.28
38.04	57	9.0	282	eicosane, $\text{C}_{20}\text{H}_{42}$	0.29
41.27	43	8.0	296	heneicosane, $\text{C}_{21}\text{H}_{44}$	0.28

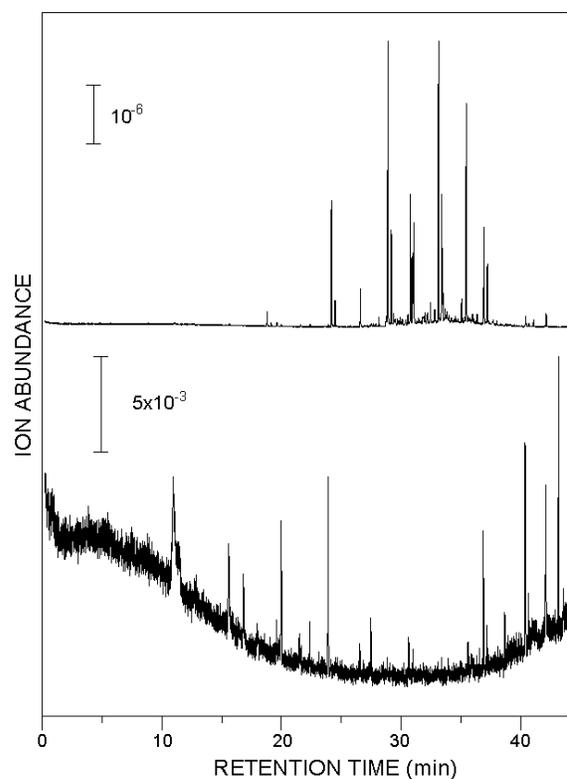
† MW is molecular weight in atomic mass units.

spectra were not recognizable as saturated hydrocarbons.

In summary, significant differences existed in the emission rates of volatile organic compounds from plastics versus cotton in an inert atmosphere at 100°C. Results from gas chromatograph-mass spectrometer analysis demonstrate that polypropylene-based tarp released volatile organic compounds at a rate 10 times that of cotton on a per-gram basis. The volatile organic compounds are released in complex mixtures, and a comparison of retention times illustrates the differences in vapor signatures between cotton and plastics under inert gas conditions. The differences in the results were outside of ordinary variance of the method, which was determined as 15 to 30% relative standard deviation (see below).

#### Effect of Increases in Temperature Under Inert Atmospheres on Volatile Organic Compounds Emission Rate and Composition

Figure 2 shows gas chromatograph-mass spectrometer-generated chromatograms of volatile organic compounds from polypropylene-based tarp and cotton heated under He for 10 min at 150°C.



**Fig. 2. Total ion chromatograms from gas chromatograph-mass spectrometer analysis of vapors from new polypropylene (top frame) and cotton (bottom frame) in He atmosphere at 150°C.**

**Table 2. Chemical identity and abundances for major volatile components released from plastic and cotton at 150°C in He.**

<u>Blue plastic new (16 mg)</u>					
Retention time	Base peak	Abundance	MW†	Chemical identity	Emission rate
min		x10 <sup>6</sup>			µg g <sup>-1</sup>
26.26	57	2.0	198	tetradecane, C <sub>14</sub> H <sub>30</sub>	3.9
30.65	57	5.0	226	hexadecane, C <sub>16</sub> H <sub>34</sub>	9.6
30.89	55	1.4	224	hexadecene, C <sub>16</sub> H <sub>32</sub>	2.8
32.37	205	2.0	220	methyl aromatic hydrocarbon	3.9
32.55	191	1.3	206	methyl aromatic hydrocarbon	2.6
32.62	57	1.5	240	heptadecane, C <sub>17</sub> H <sub>36</sub>	3.0
34.56	57	4.0	254	octadecane, C <sub>18</sub> H <sub>38</sub>	7.7
34.78	55	1.8	252	octadecene, C <sub>18</sub> H <sub>36</sub>	3.6
36.34	57	0.3	268	nonadecane, C <sub>19</sub> H <sub>40</sub>	0.74
36.71	43	3.4	270	unidentified hydrocarbon	6.6
38.08	57	1.4	282	eicosane, C <sub>20</sub> H <sub>42</sub>	2.8
41.30	57	0.2	296	heneicosane, C <sub>21</sub> H <sub>44</sub>	0.56
42.90‡	149	0.3	278	dibutyl phthalate	0.74
<u>Cotton (14 mg)</u>					
		x10 <sup>4</sup>			
22.37	73	8.0		unidentified hydrocarbon	0.38
26.00	73	9.0		unidentified hydrocarbon	0.40
38.05	57	7.0	282	eicosane, C <sub>20</sub> H <sub>42</sub>	0.36
41.28	57	9.0	296	heneicosane, C <sub>21</sub> H <sub>44</sub>	0.40
42.87‡	149	0.7	278	dibutyl phthalate	0.22

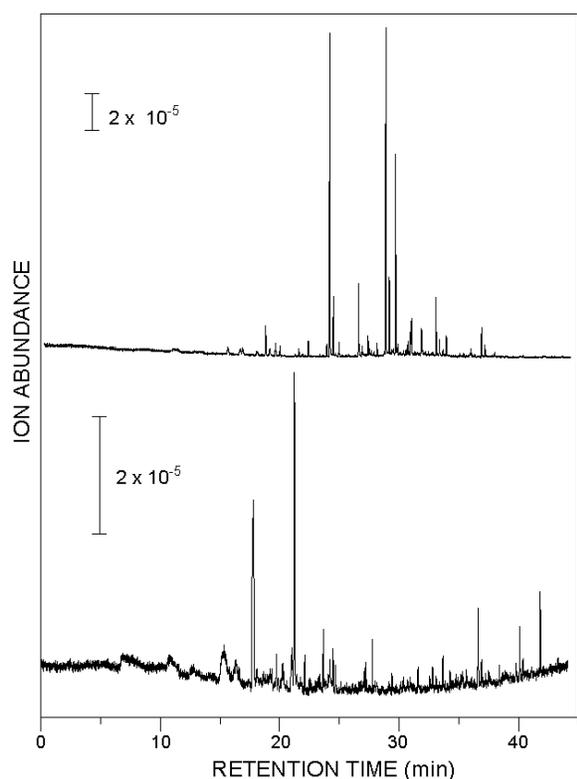
† MW is molecular weight in atomic mass units.

‡ A sporadic procedural artifact.

These chromatograms can be directly compared to those in Fig. 1 for studies at 100°C. The identities of volatiles (Table 2) were the same as those obtained at lower temperature (Table 1), demonstrating that the increase in temperature did not induce additional reactions or thermal decomposition. Thus, under inert gas atmospheres, components emitted from cotton and plastics originate with thermal desorption of substances that are either residual constituents in or adsorbed compounds on the materials. The rates of emission for components are increased only slightly for both plastic and cotton; however, a significant difference was seen in the relative distribution of peak intensities in chromatograms from Figs. 1 and 2. For example, the chromatogram for a polymer at 150°C (Fig. 2, top frame) shows that peaks at drift times >40 min are present at levels equal to or greater than peaks at drift times <40 min. This shift in intensity contrasts with earlier results at 100°C (Fig. 1, top frame), where later eluting chemicals were not so abundant. These peaks were hydrocarbons from octadecane (C<sub>18</sub>H<sub>38</sub>) to heneicosane (C<sub>21</sub>H<sub>44</sub>), that is, relatively high-

molecular-weight volatile organic compounds with comparatively low vapor pressures. This pattern toward increased levels of compounds of low volatility is consistent with a thermal desorption where vapor abundances are governed by the composition of the material and by the vapor pressures of individual chemicals. As expected from the relationship between temperature and vapor pressure, increases in temperatures elevated the abundances of the low-vapor-pressure compounds. The results showed that decomposition of the polymer did not occur in the temperature increase from 100 to 150°C in inert atmospheres. This result is consistent with literature reports where polymer decomposition in inert atmospheres occurs only above ~300°C.

In summary, volatile organic compounds released into the headspace above cotton and polypropylene at 100 and 150°C were comparatively complex mixtures with distinct chromatographic profiles or chemical compositions. Compounds below C numbers of 10 were not detected in either material, presumably lost to ambient atmospheres

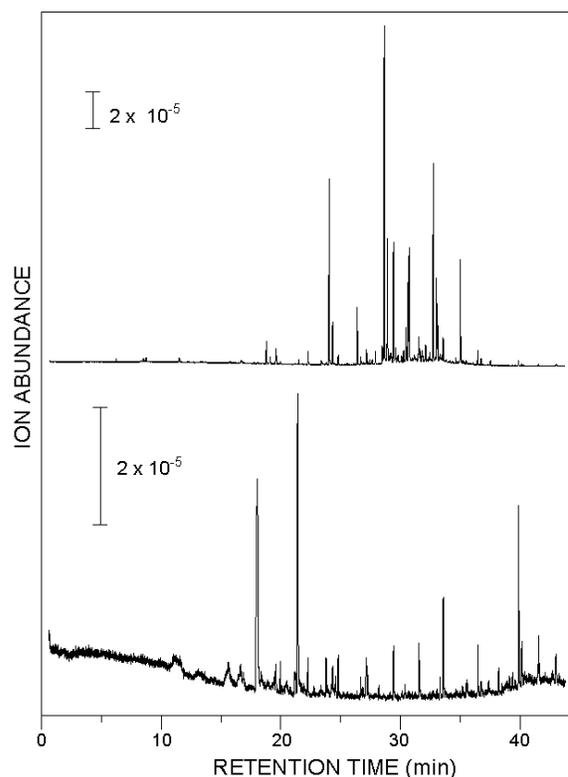


**Fig. 3.** Total ion chromatograms from gas chromatograph-mass spectrometer analysis of vapors from new polypropylene (top frame) and cotton (bottom frame) in air atmosphere at 100°C.

during natural aging of the sample. The emission rates of volatile organic compounds from plastic tarp were easily 10 times those from cotton, and increases in temperature did not appreciably increase the amount of chemical desorbed from the materials suggesting a finite amount of such constituents in the materials. Rather, increases in temperature caused increases in emission rates for compounds of reduced volatility. No thermal decomposition of the plastic tarp or cotton was observed and none was expected at these temperatures with an inert atmosphere. The volatile organic compounds arose here through thermal desorption only. Presumably the substances detected were impurities in the plastics originating with the manufacture of the plastic tarp.

#### Vapor Composition of Polypropylene-based Tarp and Cotton in Air at 100 and 150°C

The contact of synthetic polymers with  $O_2$  from air was anticipated to create thermal decompositions at temperatures  $>200^\circ\text{C}$ ; the effects on volatile



**Fig. 4.** Total ion chromatograms from gas chromatograph-mass spectrometer analysis of vapors from new polypropylene (top frame) and cotton (bottom frame) in air atmosphere at 150°C.

organic compounds from cotton were unknown. Identities and distributions of volatile organic compounds from plastics heated in air (Figs. 3, 4; Tables 3, 4) were comparable to those described above with inert gas atmosphere. For example, the overall distributions of peaks were comparable and components were normal alkanes with C numbers from 14 to 18. Some significant changes could be seen in the abundances of compounds and there seemed to be a suppression of the alkenes under air conditions. Presumably, the alkenes underwent oxidative decomposition or reactions to nonvolatile products. Few, if any, substances were detected under these conditions of time and temperature that did not also appear in the inert atmosphere experiments. The emission rates for individual components were  $0.7$  to  $4 \mu\text{g g}^{-1}$  at  $100^\circ\text{C}$  and  $0.8$  to  $11 \mu\text{g g}^{-1}$  at  $150^\circ\text{C}$ . In summary, volatile organic compounds from polypropylene heated in air for 10 min suggested only a change in the quantitative distribution of components toward chemicals with molecular weights  $>200$  Da (with low vapor

**Table 3. Chemical identity and abundances for major volatile components released from plastic and cotton at 100 °C in air.**

<u>Blue plastic new ( 15 mg)</u>					
Retention time	Base peak	Abundance	MW†	Chemical identity	Emission rate
min		x10 <sup>6</sup>			µg g <sup>-1</sup>
26.24	57	2.0	198	tetradecane, C <sub>14</sub> H <sub>30</sub>	3.9
30.61	57	2.0	226	hexadecane, C <sub>16</sub> H <sub>34</sub>	3.9
31.36	161	1.2	218	oxidized product of BHT	2.4
32.62	57	0.2	240	heptadecane, C <sub>17</sub> H <sub>36</sub>	0.56
34.51	57	0.3	254	octadecane, C <sub>18</sub> H <sub>38</sub>	0.74
<u>Cotton (13.8 mg)</u>					
		x10 <sup>5</sup>			
20.57	77	3.5	106	xylene	0.97
23.76	105	6.0	120	propyl benzene	1.5
38.04	57	9.0	282	eicosane, C <sub>20</sub> H <sub>42</sub>	2.2
41.29	57	2.0	296	heneicosane, C <sub>21</sub> H <sub>44</sub>	0.64
42.88	149	1.7	278	dibutyl phthalate	0.58

† MW is molecular weight in atomic mass units.

**Table 4. Chemical identity and abundances for major volatile components released from plastic and cotton at 150 °C in air.**

<u>Blue plastic new (15.7 mg)</u>					
Retention time	Base peak	Abundance	MW†	Chemical identity	Emission rate
min		x10 <sup>6</sup>			µg g <sup>-1</sup>
22.02	43	0.4	124	branched or unsat alkane	0.95
26.25	57	3.0	198	tetradecane, C <sub>14</sub> H <sub>30</sub>	5.9
28.49		1.0		unidentified hydrocarbon	2.1
30.65	57	6.0	226	hexadecane, C <sub>16</sub> H <sub>34</sub>	12
30.90		2.0		unidentified hydrocarbon	4.0
31.38	161	2.0	218	oxidized product of BHT	4.0
32.62	57	1.9	240	heptadecane, C <sub>17</sub> H <sub>36</sub>	3.8
34.53	57	3.5	254	octadecane, C <sub>18</sub> H <sub>38</sub>	6.9
34.79	55	1.5	252	octadecene, C <sub>18</sub> H <sub>36</sub>	3.0
34.85		0.9		unidentified hydrocarbon	1.9
36.69	43	1.6	270	unidentified hydrocarbon	3.2
38.05	57	0.3	282	eicosane, C <sub>20</sub> H <sub>42</sub>	0.76
<u>Cotton (14.6 mg)</u>					
		x10 <sup>5</sup>			
20.59	77	2.5	106	xylene	0.71
23.78	105	5.5	120	propyl benzene	0.13
24.58	44	3.7	128	unidentified hydrocarbon	0.96
35.32	57	1.5	182	unsaturated alkane	0.51
38.04	57	0.9	282	eicosane, C <sub>20</sub> H <sub>42</sub>	0.38
41.29	57	2.4	296	heneicosane, C <sub>21</sub> H <sub>44</sub>	0.69

† MW is molecular weight in atomic mass units.

pressures). No new organic compounds were evident and no thermal decomposition was suggested from these results.

In contrast to the results with the synthetic polymer, experiments with cotton heated in air at 100 and 150 °C showed a marked increase in the amounts of volatile components emitted into

headspace vapors. The emission rates for individual components were 0.5 to 2 µg g<sup>-1</sup> at 100 °C and 0.4 to 1.3 µg g<sup>-1</sup> at 150 °C and constitute nearly a fivefold increase compared with those for cotton heated in He. There was a decrease in the amount of unresolved organic mass appearing early and late in the chromatogram (Fig. 3 vs. Fig. 1). The addition of

air caused a dramatic increase in the abundance of two peaks, present at very low levels in the volatile organic compounds under inert atmosphere. These were xylenes and propyl benzene ( $C_9H_{12}$ ) and their quantities were pronounced at both 100 and 150°C and seem to have arisen through oxidative decomposition of components in the cotton sample. The origins of these chemicals and pathways to the products have not been determined. Dibutyl phthalate ( $C_{16}H_{22}O_4$ ) was seen sporadically throughout these studies and was deemed a procedural artifact; henicane was not commonly observed with cotton samples and may have been a residual from previous measurements.

### Precision of Determinations

Comparison of the results from gas chromatograph-mass spectrometer determinations in Figs. 1 through 4 and in Tables 1 through 4 is predicated upon the repeatability of the gas chromatograph-mass spectrometer determination. Results from eight replicate determinations on fresh samples of plastic are shown in Table 5 and include both sample and procedural variance. The repeatability, expressed as relative standard deviation, ranged from 11 to 133% with an average value of 36%, roughly three times greater than ordinary syringe-based scanning gas chromatograph-mass spectrometer determinations commonly held to be ~10% without internal standard methods. In view of the errors associated with variability of manufacture of the plastic and the additional experimental variables such as heating and time of heating, this increase was understandable. The findings suggest that the variations seen in Figs. 1 through 4 are not experimental artifacts and reflect actual differences in composition of the vapor emissions into the headspace over the materials which, in turn, should be a measure of residual volatile organic compounds in the materials or of the creation of new substances through thermal decomposition.

Repeatability of the measurements showed a trend apparently related to the retention time of the component. Components with long retention times exhibited increased variability. This pattern can be understood as variance associated with surface adsorption of high-molecular-weight components

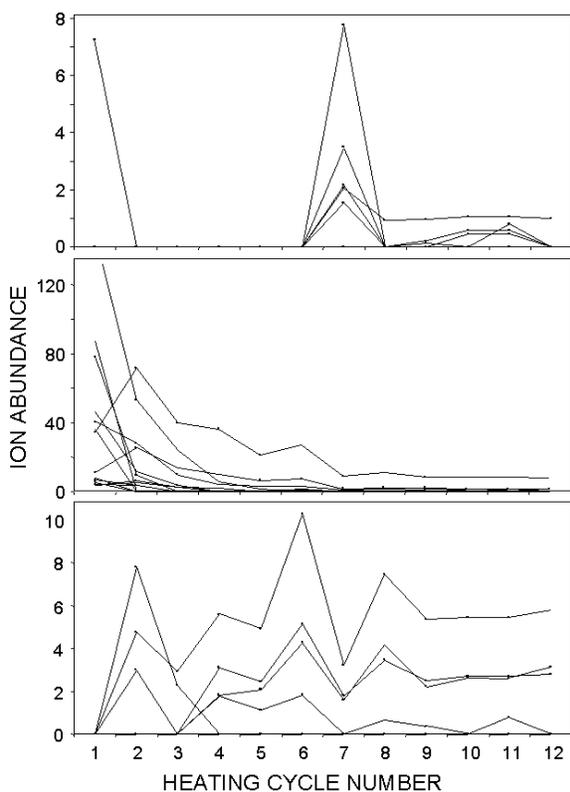
**Table 5. Reproducibility of determinations by thermal desorption gas chromatography-mass spectrometry.**

Retention time	Area	Std deviation	RSD
min	----- N x 10 <sup>6</sup> -----		%
21.24	7.32	0.98	14
26.23	50.99	0.58	11
26.52	11.16	0.12	11
28.47	19.85	4.81	24
29.93	3.72	0.80	21
30.62	195	46.44	24
30.87	47.89	12.31	26
31.07	8.44	1.92	23
31.36	7.61	1.70	22
31.53	5.28	1.49	28
31.73	4.52	1.46	32
32.16	6.55	2.01	31
32.36	61.2	13.2	22
32.5	35.5	10.1	28
33.69	9.26	3.14	34
33.92	14.4	9.51	66
34.51	148	44.4	30
36.3	14.3	15.1	106
38.05	20.70	27.5	133

with decreased vapor pressure and an increased tendency to adsorb on surfaces. Surfaces were available for such depositions in the tubes used in the desorption chamber, the gas-tight switching valve, and the additional length of 1/16-in stainless-steel tubing used to join the chamber with the injection port of the gas chromatograph-mass spectrometer.

### Effect of Time at Elevated Temperatures on Polypropylene-Based Tarp Heated in Helium

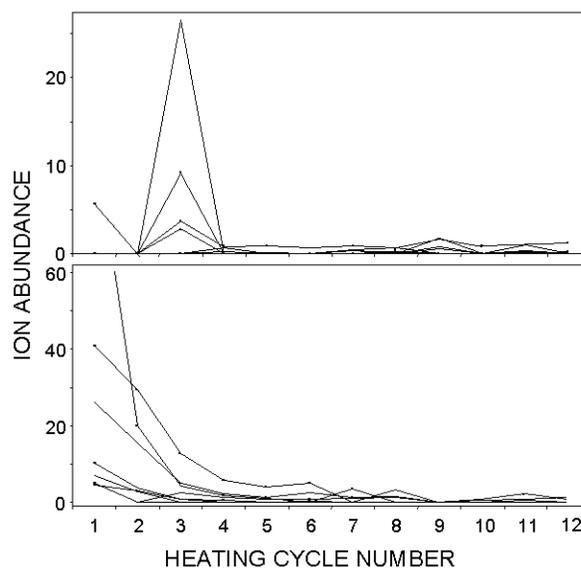
Twelve cycles of heating and cooling for 120 min total exposure of the plastic to 100°C are summarized in Fig. 5, demonstrating the effect of repeatedly heating polypropylene in the chemically inert atmosphere of He. Abundances of individual chemicals are shown in frames that are grouped by vapor pressure (in brackets of retention time): Group I, 0 to 25 min; Group II, 25.01 to 30 min; Group III, 30.01 to 35 min; and Group IV, 35.01 to end of chromatogram. The vapor pressures decreased by Groups (I > II > III > IV) and molecular weights increased (I < II < III < IV). Figure 5 (top frame) shows the Group I compounds from polyethylene which were emitted in low abundance early in the



**Fig. 5.** Plots of abundances of volatile organic compounds released from plastic with repeated heating at 100°C in He for 10 min. Individual constituents were shown to represent patterns from a range of volatilities (retention times) including Group I (top frame), Group III (middle frame), and Group IV (bottom frame). See text for discussion of Groups.

heating cycles. Presumably these emissions are fairly volatile, are not present at high levels initially, and are not removed by ordinary handling during production of the plastic. However, low-molecular-weight volatile organic compounds suddenly appear again after a sum of 60 min exposure (Fig. 5, top frame). This pattern is suggestive of thermal decomposition of the polymer to low-molecular-weight (volatile) fragments.

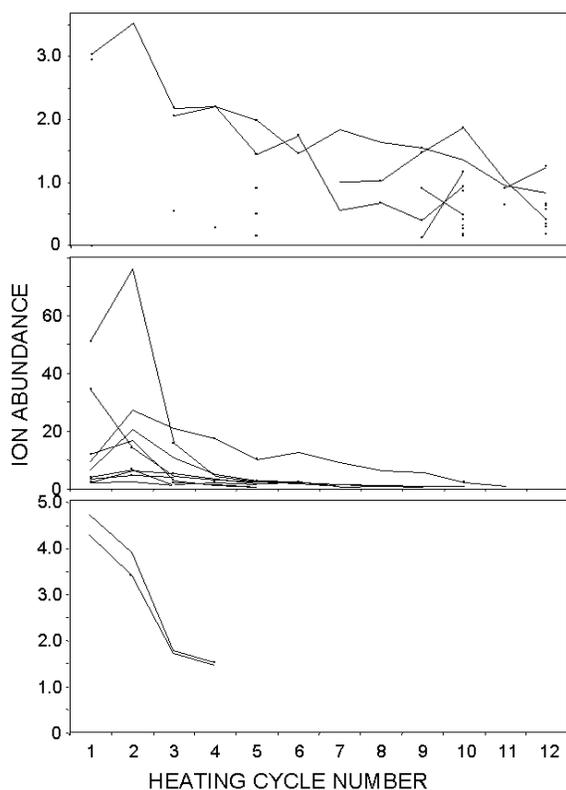
The loss patterns for chemicals of intermediate molecular weight in the Group III chemicals are shown in Fig. 5 (middle frame). Trends in time are characteristic of thermal desorption of residual impurities in the polypropylene-based tarp. Relatively high intensities early in the experiment declined rapidly for most chemicals in the first three treatments. This pattern indicates volatilization or distillation of impurities from the plastic and was also seen with the Group II chemicals, which desorbed completely in fewer cycles than the Group



**Fig. 6.** Plots of abundances of volatile organic compounds released from plastic with repeated heating at 150°C in He for 10 min. Individual constituents were shown to represent patterns from a range of volatilities (retention times) including Group I (top frame) and Group IV (bottom frame).

III compounds. Since the chemicals in Group III have lower volatility than those in Groups I or II, the time to distill the compounds from the plastic is comparatively long. High-molecular-weight compounds (i.e., Group IV) exhibited persistence greater than that for Group III (Fig. 5, bottom frame). The compounds of Group IV, with C numbers of 20 and above, showed a persistence or prolonged presence, even though levels are very low, suggestive of low-vapor-pressure chemicals distilling from the plastic over an extended period.

Although temperature had no significant effect on the quantitative aspects of emission rates for a particular compound, prior discussion suggested that vaporization increased for compounds with high molecular weights as temperature was increased. This idea is supported by the time-resolved emission profiles of Fig. 6. The decomposition to low-molecular-weight compounds, seen in the sixth cycle at 100°C (Fig. 5), is now seen in the third cycle at 150°C. The increase in temperature shortened the time of exposure necessary to induce the decomposition event, suggesting a certain energy is needed to induce the decomposition and that increased temperature accelerates the decomposition (70 min at 100°C and 30 min at 150°C). As with the previous set, volatile organic compounds at low

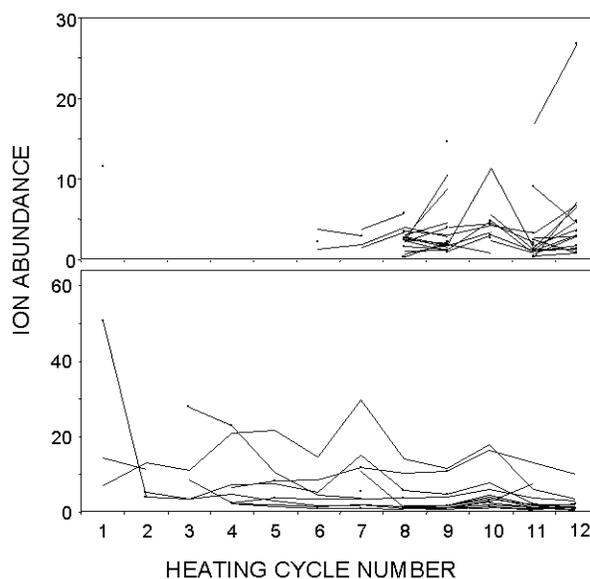


**Fig. 7.** Plots of abundances of volatile organic compounds released from plastic with repeated heating at 100°C in air for 10 min. Individual constituents were shown to represent patterns from a range of volatilities (retention times) including Group I (top frame), Group III (middle frame), and Group IV (bottom frame).

levels of emission were evident throughout the remainder of the exposure. The effect on temperature was also seen dramatically in the bottom frame of Fig. 6 where Group IV chemicals are reduced by more than 80% in vapor levels released from the plastic in the first four exposures (i.e., 40 min), consistent with a distillation or volatilization of high-molecular-weight components from the sample. The Group II and III chemicals exhibited time-resolved profiles of emission rates that were rapid and consistent with desorption of compounds with elevated vapor pressures.

#### Effect of Time at Elevated Temperatures on Polypropylene-based Tarp Heated in Air

The vapor emission profiles from repeated heatings of samples in air showed complex behavior not observed from a single thermal desorption (Fig. 4) nor from repeated thermal desorption of plastics



**Fig. 8.** Plots of abundances of volatile organic compounds released from plastic with repeated heating at 150°C in air for 10 min. Individual constituents were shown to represent patterns from a range of volatilities (retention times) including Group I (top frame) and Group IV (bottom frame).

in He (Figs. 5 and 6). After several exposures at 100°C, volatile compounds became persistently recurring constituents from polypropylene in air (Fig. 7, top frame). Since this pattern was not seen under identical conditions with He, the peaks are believed to be products of oxidative decomposition of the polymer. The increase in mass of these chemicals seems to be offset by the loss in mass of Group IV substances, as shown in Fig. 7 (bottom frame). This result suggests that components in Group IV may arise from thermal decomposition and that they are stable intermediates. An alternative explanation is that the route toward formation of Group IV compounds has been blocked by oxidative reactions. A third possibility is that the patterns are unrelated and the Group IV chemicals are lost through paths not measured in these experiments. Finally, Group IV chemicals may be decomposed to Group III chemicals and the trend is lost in abundances. No further attempt was made to rationalize these paths of desorption or decomposition since the objective of this work was to establish inputs for creating chemical sensors of plastics in cotton. The findings suggest that temperature-time variables may affect the vapor composition presented to a chemical sensor and, consequently, the sensor response.

An increase in temperature to 150°C in air created comparable patterns in the time-resolved emission profiles for these chemicals from polypropylene, but the effects were exaggerated in time and amounts. Vapor levels of Group I chemicals were 10 to 30 times those observed at 100°C and were observed after 60 min of exposure (Fig. 8, top frame). The complexity and increased abundances of these peaks, not seen at lower temperatures, lower exposure times, or in He, were suggestive of substantial oxidative decomposition of the polypropylene. The mass spectra support this analysis. The polymer structure appears to have been affected with a large increase in the less volatile compounds of Group IV (Fig. 8, bottom frame). The large abundance with time cannot be understood as simple thermal desorption and must arise from thermal decomposition. This finding is the first to demonstrate that polypropylene undergoes thermal decomposition at such a low temperature with prolonged exposure to heat in air. Protracted heating may supplement exposure to light in artificial or accelerated aging and weathering of plastics.

### CONCLUSIONS

These findings demonstrate that polypropylene-based tarp, when heated, will release volatile organic compounds that are different in amounts and identity to volatile organic compounds emitted from cotton under identical conditions. The findings are consistent with existing models of plastics in which volatile organic compounds arise through thermal desorption at low temperatures. Unlike prior work, these results show that heating of plastics and cotton in air will create decomposition at temperatures well below those required in an inert atmosphere. Such findings portend variance in the relative distributions of volatiles released from plastics as a function of age and severity of weathering. These findings provide a potential basis for the design of chemical sensors for detecting plastic waste in cotton; however, the volatile organic compounds released from the cotton will be background chemical noise and will necessitate highly selective sensors. Successful detection of plastic in cotton with chemical vapor sensors will be governed by specificity of the sensor toward chemicals characteristic of the synthetic polymers.

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