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DEVELOPMENT OF A SYNTHETIC MATERIALS MIMIC FOR VULTURE OLFACTION RESEARCH

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Abstract: Since the early 1990's, an increase in damage associated with the activities of black (*Coragyps atratus*) and turkey (*Cathartes aura*) vultures has been observed. These activities include extensive damage to real and personal property. Vultures display an affinity for objects made of synthetic materials such as vinyl or plastic, and frequently damage items such as seat cushions, roof shingles, and caulking sealant. To explore whether this behavior in vultures is olfactorily driven, volatile compounds emitted by 21 vulture-damaged objects were collected and analyzed using purge-and-trap gas chromatography/mass spectrometry. Results from these analyses were tabulated and the 27 most commonly occurring compounds were identified. Six of the vulture-damaged samples contained at least 23 of the 27 identified compounds, and hexanal, octanal, undecane, and nonanal were found in all 21 vulture-damaged samples. Using these data, a water-based emulsion containing the 27 most frequently observed compounds in the vulture-damaged samples was formulated to serve as a synthetic materials mimic (SMM). A sustained volatile release delivery system utilizing cellulose sponges was also developed, and used to deliver the SMM for bioassay trials examining the response of captive vultures to the SMM.

Key Words: black vulture, *Cathartes aura*, *Coragyps atratus*, damage, delivery system, mimic, olfactory, synthetic materials, turkey vulture, volatiles

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INTRODUCTION

Populations of both black vultures (*Coragyps atratus*) and turkey vultures (*Cathartes aura*) are increasing annually in the eastern and southern United States (Sauer et al. 2001). This increase has coincided with the continual expansion of human-related development, resulting in a

wide variety of escalating human-vulture conflicts (Tillman et al. 2002). In addition to increasing problems with aircraft collisions and depredation of livestock, a large increase in vulture-caused damage to residential and non-residential buildings and a wide array of personal property such as

vehicles (boats and cars), construction materials, and household items has been observed (Lowney 1999, Tillman et al. 2002). Vultures of both species display a marked attraction to objects made of synthetic materials such as rubber, plastic, and vinyl, and do substantial damage primarily by ripping and tearing such items.

While the reason for this behavior is unknown, synthetic products may share volatile chemical compounds found in carrion which stimulate the pecking and tearing behavior. Alternatively, plastics are frequently found in association with human foodstuffs (through wrapping and packaging), and plastic odors may be directly associated with edible contents. To explore the hypothesis that the vulture's

behavior is olfactorily driven, samples of 21 vulture-damaged objects (Table 1) were collected in northern and central Florida and sent to the Analytical Chemistry Section of the USDA's National Wildlife Research Center (NWRC) in Fort Collins, Colorado for analysis and characterization of the volatile compounds. One sample (Boat Cushion #1) was divided into two components; the outer black covering and the foam cushion, yielding a total of 22 samples. Each vulture-damaged sample was analyzed separately. The compounds most commonly found were then obtained and combined to produce a liquid synthetic materials mimic (SMM) formulation for use in further vulture olfaction research.

Table 1. Vulture-damaged objects and associated collection locales.

<u>Object</u>	<u>Collection Locale</u>
Blue plastic pipe	Gainesville
Red rubber ball ¹	Gainesville
Pink plastic	Gainesville
Black rubber snake	Orlando
Black gasket ¹	Orlando
Blue seat cushion ¹	Dade City
Clear plastic bag	Orlando
Black roof shingle	Kissimee
Black boat cushion #1	Orlando
Black boat cushion #2	Orlando
Green caulking ¹	Gainesville
Black armrest	Dade City
Sandbag	Orlando
Blue plastic toy	Gainesville
Black seat cushion ¹	Dade City
Green rubber ball ¹	Gainesville
White caulking	Jacksonville
Black foam insulation	Jacksonville
White rubber roofing	Sarasota
Black mesh screen	Orlando
Black vinyl ground cover	Interlocken

¹ Samples chosen as representative for the synthetic materials mimic formulation.

METHODS

Sample Preparation and Analysis

Each item was finely chopped using a razor blade and a one gram portion (if available) was placed in a 25-mL glass test

tube. The tube was fitted to a purge-and-trap concentrator (Model 3000; Tekmar, Cincinnati, OH) and attached to an HP 5890 gas chromatograph (Agilent Co., Sunnyvale,

CA) equipped with an HP 5972 mass selective detector (GC-MSD). The sample was heated to 55° C for one hr and the volatile compounds released by the sample were captured on a Purge Trap “K” (Vocarb 3000; Supelco; Bellefonte, PA). The trap was then heated to 250° C to release the trapped compounds onto the GC-MSD for separation and subsequent identification. The GC analytical conditions were: Analytical column: J&W DB 5.625; Oven temp: 0° C (cryo) for 8 min, 7° C/min to 70° C, then 20° C/min to 300° C; Flow: He, 4.8 psi constant at 0° C, then constant flow at 35.2 cm/sec; Splitless mode; Inlet temp: 200° C; Transfer line temp: 280° C; Run time: 30 min.

Analysis of each sample yielded a chromatogram similar to the one produced by the red rubber ball (Figure 1), with each peak corresponding to a particular compound (e.g., 2-ethyl-1-hexanol) contained by the sample. Each sample contained an average of over 100 compounds to be identified, yielding a total of over 2000 potential compound identifications for all samples. Mass spectra were collected for all peaks. Peaks were either identified by spectral match or classified by retention time for comparison with the mass spectra of peaks at the same retention time in other samples.

Table 2. Compounds identified in vulture-damaged samples.

<u>Compound & Source</u>	<u>Frequency</u>	<u>% Original (n=6)</u>	<u>% of Mimic</u>
hexanal ¹	22	2.67	7.2
octanal ¹	22	4.43	11.9
undecane ¹	22	1.84	4.96
nonanal ¹	22	5.67	15.3
p-xylene ¹	18	0.226	0.61
heptanal ¹	18	2.27	6.13
naphthalene ¹	18	0.362	0.976
octamethylcyclotetrasiloxane ¹	17	0.719	1.94
6-methyl-5-hepten-2-one ¹	17	1.11	2.99
1,3,5-trimethylbenzene	17	0.484	0.484
decane ¹	17	0.421	1.14
3,7-dimethyldecane*	17	2.46*	12.0*
decamethylcyclopentasiloxane ¹	17	1.15	3.10
3,6-dimethyldecane*	16	1.98*	_*
dodecane ¹	15	0.304	0.820
decanal ¹	14	0.873	2.35
p-cymene ¹	13	0.332	0.895
1,2,4-trimethylbenzene ¹	12	0.863	2.33
1,2,3-trimethylbenzene ¹	11	0.181	1.31
limonene ¹	11	0.437	1.18
hexamethylcyclotrisiloxane ¹	10	0.271	0.734
2-ethyl-1-hexanol ¹	10	6.13	16.5
benzaldehyde ¹	10	0.391	1.06
2-ethyl-p-xylene ²	9	0.275	0.742
acetic acid, butyl ester ⁴	9	0.458	1.24
1,2,4,5-tetramethylbenzene ¹	8	0.323	0.871
toluene ⁴	8	0.447	1.21

* 3,6-dmd and 3,7-dmd not available commercially, combined as 2,6-dimethyldecane³

¹Aldrich, Milwaukee, WI ²TCI, Portland, OR ³Chemsampco, Trenton, NJ ⁴Burdick and Jackson, Muskegon, MI.

Analysis of all samples yielded several hundred identifiable compounds. Twenty seven compounds (Table 2) were selected due to the frequency of their occurrence across samples. Four compounds (hexanal, octanal, nonanal, and undecane) were present in all samples. The other 23 compounds were found in 8 or more of the samples.

Formulation

The six samples (Table 1) which contained the greatest number of common compounds provided the basis for the formulation. The chromatographic response of each compound was calculated as a percent of total (including zero) for each sample, then averaged across all six samples. This average percentage was then normalized so that a mixture of all 26 compounds would yield 100% of a total mixture. This served as the formula for the production of a synthetic materials mimic (SMM).

High purity standards of each selected compound were obtained in order to produce the liquid SMM (see Table 2 for chemical sources). Two compounds, 3,6-dimethyldecane and 3,7-dimethyldecane, were not commercially available. Their percentages in the mimic were combined and 2,6-dimethyldecane was used to replace both, leaving 26 compounds in the SMM. Since all compounds were moderately to very non-polar, a suitable solvent or suspending agent(s) had to be found in which all compounds would be soluble, which would permit free volatilization of all compounds, but which would not add to the volatile profile of the mixture. Both mineral oil and 70% glycerol were evaluated, but neither permitted free volatilization of all compounds. Mineral oil retarded free volatilization of late eluting (high boiling point) compounds, while 70% glycerol impeded volatilization of early eluting (low

boiling point) compounds. However, a mixture of two surfactants, Tween 80 (polyoxyethylene sorbitan monoleate) and Span 80 (sorbitan monoleate) (Sigma, St. Louis, MO) formed a stable milky emulsion in water from which all mimic components were suspended homogeneously and could freely volatilize. Repeated shaking and sonication interspersed with chilling and warming was found to be important for the production of a stable, homogeneous emulsion.

Response Factor

To duplicate the chromatographic responses of the selected compounds in the original vulture-damaged samples, it was necessary to determine the chromatographic response factor for each compound as part of the total SMM formulation. This was done by placing 0.100 mL aliquots (or 100 mg aliquots of the three solid compounds: naphthalene, 1,2,4,5-tetramethylbenzene, and hexamethyl cyclotrisiloxane) plus 0.2 mL each of Tween 80 and Span 80 into 50 mL water and mixing thoroughly. Three pairs of the selected compounds (octamethyl cyclotetrasiloxane:6-methyl-5-hepten-2-one, 2-ethyl-1-hexanol:limonene, and 2,6-dimethyl decane:1,2,4,5-tetramethyl benzene) coeluted chromatographically. To obtain accurate response factors for the coeluting compounds, a second formulation was prepared containing one compound from each pair. This resulted in two formulations, one with 23 compounds and the second with the remaining three. This pattern of dual formulations was maintained throughout the development of the SMM. For analysis, the highly concentrated SMM was diluted 1:20,000 in water, and a 3-mL aliquot placed on a 2 cm x 4 cm x 1 cm piece of cellulose sponge placed in a glass sampling vessel. The sample was then analyzed using the method described previously.

For chromatographic response factor determination, 1-ethyl-2-hexanol (the principal component in the SMM, Figure 1) was used as the “reference peak.” The ratio of the peak area of each selected compound divided by the 1-ethyl-2-hexanol peak area yielded that compound’s response factor. This number was then used to correct the volume (or mass) of each compound necessary to achieve the desired percentage in the final SMM formulation (Table 2). The percentages were then treated as volume (or mass) for each compound and multiplied by 50 to yield quantities which could be delivered or weighed.

A series of formulations were prepared to adjust the individual components of the SMM formula to match the target formula values as closely as possible.

Delivery System

The delivery system had to meet two criteria: 1) SMM components had to volatilize continuously over a 48 hr period, and 2) SMM components had to volatilize with a profile qualitatively similar to the average of the six samples containing all selected components. Cellulose sponges (11.9 cm x 7.9 cm x 1.6 cm; Spontex, Columbia, TN) were chosen as a reservoir for the SMM formulation due to their consistency, availability, and lack of additional volatile compounds. The entire sponge was used to provide a reservoir of sufficient volume to allow 50 mL of the SMM to yield volatiles for 48 hrs.

A series of volatility duration experiments were performed in an environmental chamber programmed to mimic conditions at the vulture test site (NWRC, Gainesville, FL). Uncovered sponges exhausted quickly and had to be wrapped to reduce the formulation loss rate. The wrapping could not be made from a synthetic material or contain compounds

which would add to the chemical profile of the SMM formulation. Aluminum foil was chosen, but further experiments showed that compounds in the formulation caused surface oxidation of the aluminum and loss of formulation components. Using a commercially available teflon-coated aluminum foil eliminated this problem and allowed sealing by simple repeated folding of the aluminum, eliminating the need for synthetic adhesives.

Placement and size of holes were then evaluated to optimize longevity and repeatability of SMM volatilization.

RESULTS AND DISCUSSION

The average value of each component from the final two SMM formulation preparations was very similar to the corresponding target formulation value (Table 3), and a chromatogram of the SMM is provided (Figure 2). Production of the SMM was somewhat variable, due primarily to technician-to-technician differences in the preparation of the final emulsion. The SMM was a very complex mixture of compounds with widely varying chemical properties, and the use of the Tween80/Span80 combination was critical for the creation of a water-based emulsion. Using water as the primary solvent prevented the introduction of undesirable and potentially repellent compounds into the SMM. Once production of the SMM emulsion was complete, refrigeration was found to increase the chemical stability of the preparation.

Environmental chamber experiments demonstrated that 1 to 2 large (~13 mm) holes in the aluminum wrapping allowed the SMM to exhaust almost as quickly as unwrapped sponges. Varying the number and location of small (~1 mm) holes through the aluminum allowed control of the loss rate. A series of 4 holes along each of the long sides of the wrapped sponge allowed the sponge to release SMM volatiles for the

full 48 hr period. The 1:20,000 dilution provided a volatilization profile that was qualitatively similar to a generalized profile obtained from the original vulture-damaged plastics. The intensity of SMM presentation can be varied by increasing the number of holes in the aluminum wrapping (or removing the wrapping altogether) or by decreasing (or increasing) the dilution of the original SMM. The SMM and delivery system described in this report are currently being evaluated in vulture bioassay trials to examine the response of captive vultures to the SMM.

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Table 3. Comparison of average (n = 2) Synthetic materials mimic (SMM) formulation to the target formulation.

<u>Compound</u>	<u>Target % in SMM</u>	<u>Actual % in SMM</u>
toluene	1.21	0.872
hexanal	7.20	6.74
acetic acid, butyl ester	1.24	1.03
hexamethylcyclotrisiloxane	0.734	0.74
p-xylene	0.610	0.51
heptanal	6.13	6.79
benzaldehyde	1.06	1.03
1,3,5-trimethylbenzene	0.488	0.45
6-methyl-5-hepten-2-one	2.99	4.01 ¹
octamethylcyclotetrasiloxane	1.939	
1,2,4-trimethylbenzene	2.33	1.78
decane	1.14	0.94
octanal	11.9	11.1
1,2,3-trimethylbenzene	1.30	1.02
p-cymene	0.895	0.72
limonene	1.18	23.0 ²
2-ethyl-1-hexanol	16.5	
2-ethyl-p-xylene	0.742	0.63
undecane	4.96	4.13
nonanal	15.3	14.4
2,6-dimethyldecane	12.0	11.5 ³
1,2,4,5-tetramethylbenzene	0.871	
decamethylcyclopentasiloxane	3.10	2.47
naphthalene	0.976	0.93
dodecane	0.820	0.68
decanal	2.35	2.18

¹combined % of 6-methyl-5-hepten-2-one & octamethylcyclotetrasiloxane

²combined % of limonene & 2-ethyl-1-hexanol

³combined % of 1,2,4,5-tetramethylbenzene & 2,6-dimethyldecane

Figure 1. Chromatogram of red rubber ball volatiles.

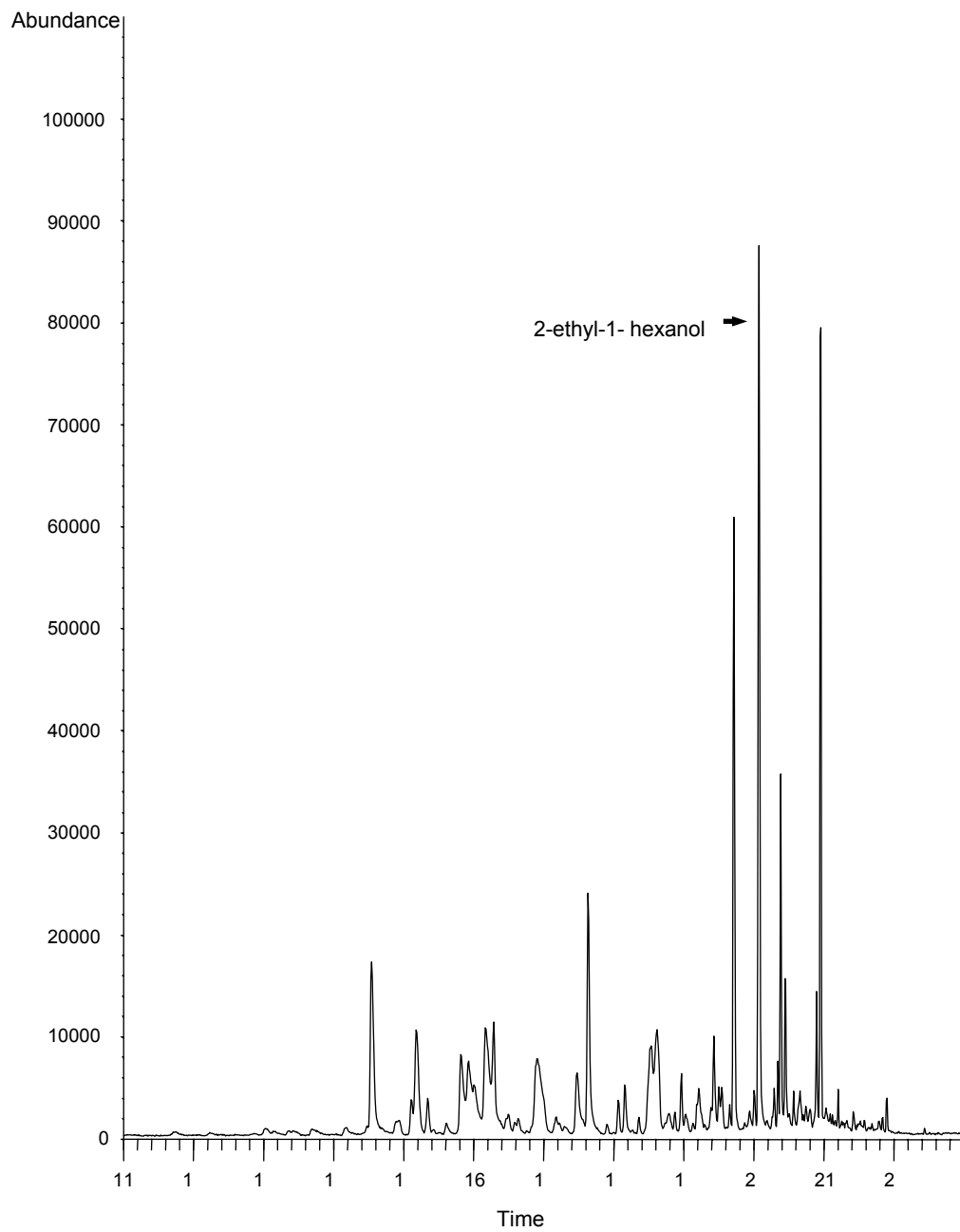


Figure 2. Chromatogram of synthetic materials mimic formulation.

Peak	Compound	Peak	Compound
A	toluene	N	1,2,3-trimethylbenzene
B	hexanal	O	p-cymene
C	acetic acid, butyl ester	P	limonene
D	hexamethylcyclotrisiloxane	Q	2-ethyl-1-hexanol
E	p-xylene	R	2-ethyl-p-xylene
F	heptanal	S	undecane
G	benzaldehyde	T	nonanal
H	1,3,5-trimethylbenzene	U	2,6-dimethyldecane
I	6-methyl-5-hepten-2-one	V	1,2,4,5-tetramethylbenzene
J	octamethylcyclotrisiloxane	W	decamethylcyclopentasiloxane
K	1,2,4-trimethylbenzene	X	naphthalene
L	decane	Y	dodecane
M	octanal	Z	decanal

