Development of a Pheromone Elution Rate Physical Model

M. E. Teske, H. W. Thistle, B. L. Strom, H. Zhu

ABSTRACT. *A first principle modeling approach has been applied to available data describing the elution of semiochemicals from pheromone dispensers. These data included field data for 27 products developed by several manufacturers, including homemade devices, as well as environmental chamber data collected on three semiochemical products. The goal of this effort was to understand the underlying mechanisms controlling the elution process and to provide guidance to forest managers responsible for positioning these devices to avert insect infestation of valuable timberlands in the U.S.*

Keywords. *Dispenser, Elution rate, Model pheromone, Semiochemical.*

The term "semiochemical" was introduced in 1971 from the Greek word *semeion* (a mark or signal) to describe chemicals that mediate interactions between organisms (Law and Regnier, 1971). The term "pheromone" was introduced in 1959, based on the Greek words *pherein* (to transport) and *hormone* (to stimulate), to describe chemical signals that generate desirable innate behavior, especially in insects (Karlson and Lüscher, 1959). The USDA and the USDA Forest Service currently use semiochemicals in detection, surveying, monitoring, and insect control programs (Leonhardt and Moreno, 1982).

The discovery of a bark beetle (Coleoptera: Curculionidae) pheromone in 1966 (Silverstein et al., 1966), along with subsequent identifications and syntheses of many insect semiochemicals, generated significant excitement and led to field deployment by pest managers seeking advantage against pest insects via their chemical ecology. Semiochemicals have since become important staples for species detection and population monitoring in forestry but have met with more limited success as resource protectants (Ross et al., 2002; Progar, 2005; Billings and Upton, 2010; Strom and Clarke, 2011). There is still much to learn regarding the chemical ecology and behavioral manipulation of forest insects, but management failures are often attributed to faulty elution devices and typically result from release rates being unpredictable and thereby leaving the resource unprotected (Holsten et al., 2002, 2003; Strom and Clarke, 2011).

Semiochemicals deployed for forest insect management are nearly always released passively, with devices being classified as first-order emitters (Holsten et al., 2003). Semiochemical delivery is through a dispenser that ideally releases material at a sustained rate over an extended period of time (Doane, 1999). These dispensers have evolved from typ-

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ically handmade devices with a fluid reservoir and passive evaporation or elution (we use "elution" as a synonym for emission or release) via a wick or septum, to commercially available devices that most often elute semiochemical through a plastic membrane (Hayes et al., 1994; Ross et al., 2002; USDA, 2010). Commercial devices in forestry are severely constrained by cost and the various problems associated with field use (such as weathering, fouling, and UV degradation); consequently, these devices are only designed for the most economically important pest systems and are usually quite rudimentary. The cost of the semiochemicals and the labor to deploy and monitor the devices are significant obstacles, as are labeling for appropriate biologically active application rates (Clarke et al., 1999; Strom and Clarke, 2011). Deployment patterns are instead based on predicting the average longevity of deployed devices *in situ* (usually an extrapolation from data gathered in the laboratory), which is then considered along with the cost of labor and materials. The active concentrations and plume structures necessary for eliciting target behaviors are unknown, so the use of semiochemical devices is achieved through an estimate of field longevity, whenever and wherever these devices are deployed. Improving upon this essentially qualitative strategy (i.e., when to replace a group of devices), along with attempts to stabilize elution rates, are areas of emphasis for researchers that begin with an improved understanding of the process of elution from a device.

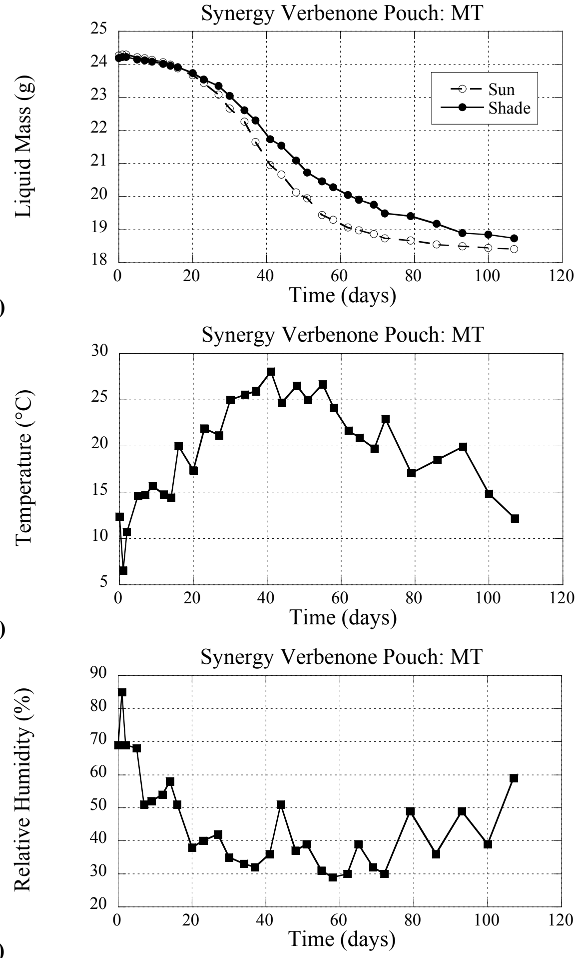
On-going engineering and biological efforts have been directed toward designing and implementing dispensers that elute at a known rate, on an insect-by-insect basis (Wall, 1989, 1990). While measurement of elution rates is not typically performed in the field, a lack of standardization among studies that have been conducted to date makes comparisons and inferences difficult.

In this study, a first principle modeling approach was applied to available data to describe the elution of semiochemicals from dispensers. The goal of the overall effort was to understand the underlying mechanisms controlling the elution process and provide guidance to practitioners who are responsible for deploying these devices to manage forest insects. Standardizing protocols and collecting meteorological data, in conjunction with elution data, are seen as being integral to explaining release rates and improving their predictability. Over the years, databases have been collected to quantify the behavior of various dispensers developed (and refined) to achieve a desired end result. One such database has been assembled by the USDA Forest Service (USDA, 2010), and this database was examined to determine whether the measured data (loss of semiochemical mass over time and ambient meteorology) could be explained, in an effort to aid in the understanding of the behavior of the selected pheromone dispensers for their intended field applications.

Model Development

The time history behavior of the mass remaining in the device, along with temperature and relative humidity readings, as shown in figure 1 by example, suggests that a simple diffusion model might capture most of the physics of the elution process. From Fick's first law, based on an analogy to Fourier's law of heat conduction (Fick, 1855), diffusion from a volume through a membrane can be represented by the equation:

$$\frac{\partial M}{\partial t} = -SD\frac{\partial C}{\partial x} \tag{1}$$



(a)

(b)

(c)

Figure 1. Time histories of data collected at Missoula, Montana, for dispensers positioned in the sun (open symbols) and shade (closed symbols): (a) average mass remaining in ten Synergy Verbenone Pouches, (b) average ambient temperature, and (c) ambient relative humidity (day 0 is 5 April 2007).

where $M = CV$ is the enclosed mass (g) with concentration C (g cm^{-3}) and volume V (cm^3), S is the surface area (cm^2) across which diffusion occurs, D is the diffusion coefficient (cm^2 d^{-1}), t is time (days), and x is the thickness (cm) of the porous membrane. Once mass passes through the membrane, its further behavior can be represented by a simple diffusion rule, which gives:

$$C = C_S \exp\left[-\frac{x}{\lambda}\right] \tag{2}$$

where C_S is the concentration on the outer surface of the membrane and λ is a decay length (cm). Differentiation of equation 2 and substitution into equation 1 (recognizing that an increase in material on the outside of the membrane C_S reflects a decrease in material on the inside of the dispenser C) results in the equation:

$$\frac{dM}{dt} = -\frac{SDC}{\lambda} \tag{3}$$

By defining a variable α as:

$$\alpha = \frac{SD}{\lambda V} \tag{4}$$

which combines the surface area, diffusivity, decay length, and dispenser volume into one parameter (with units of d^{-1}), equation 3 can be rewritten:

$$\frac{dM}{dt} = -\alpha M \tag{5}$$

While the surface area is constant for each device, and dispenser volume has fallen out of the equation, the diffusivity and decay length may be functions of temperature, relative humidity, and other environmental factors, as well as membrane wall thickness and other parameters not modeled here. A first step in the analysis would be to assume the simple behavior:

$$\alpha = a\left[\frac{273.15 + T}{300.0}\right]^b \left[\frac{RH}{100.0}\right]^c \tag{6}$$

for temperature T (°C) and relative humidity RH (%), where the correlation parameters a, b, and c are determined from the data. If ambient conditions are constant (as in an environmental chamber), equation 5 can be integrated to give:

$$M = M_{initial} \exp[-\alpha t] \tag{7}$$

where $M_{initial}$ is the initial mass in the dispenser.When temperature and relative humidity vary with time during the elution process (as they do in the field), it seems appropriate to use the difference form of equation 5:

$$\frac{1}{M_{initial}} \frac{\Delta M}{\Delta t} = -\alpha \frac{M}{M_{initial}} \tag{8}$$

Model Validation

Field Experiments

Available pheromone elution data are provided in spreadsheet format (USDA, 2010) for tests conducted in Missoula, Montana (MT); Pineville, Louisiana (LA); and Susanville, California (CA). The 27 datasets are summarized in table 1. Initial sun and shade masses are averaged across five dispensers each. Two sites were duplicated (for Synergy Sirex UHR Pouch and Synergy Frontalin Pouch), and two datasets recorded only shade conditions (Homemade Ethanol Releaser Bottle (100 mL) and Synergy High-Release Heptanol Pouch). The data include the running measurement day (day 0 began between 6 April and 12 September 2007), the mass of liquid remaining in the device, ambient

Table 1. Summary of elution datasets collected in 2007 (from USDA, 2010).

Product	Test Site	Initial Sun Mass (g)	Initial Shade Mass (g)
Synergy Verbenone Pouch	MT	24.27	24.39
Synergy Verbenone Pouch	LA	21.61	21.90
Phero Tech Verbenone Pouch	MT	9.49	9.46
Phero Tech Verbenone Pouch	LA	9.21	9.22
Synergy UHR Ethanol Sleeve	MT	79.0	79.0
Synergy UHR Ethanol Sleeve	LA	89.82	89.85
Synergy UHR Ethanol Sleeve	CA	75.0	75.0
Phero Tech UHR Ethanol Sleeve	MT	120.0	120.0
Phero Tech UHR Ethanol Sleeve	LA	125.05	124.26
Phero Tech UHR Ethanol Sleeve	CA	120.0	120.0
Homemade Ethanol Releaser Bottle (100 mL)	LA	-	110.47
Homemade Ethanol Releaser Bottle (250 mL)	LA	237.21	245.89
Synergy Green Leaf Volatiles Pouch	MT	26.35	26.33
Synergy Green Leaf Volatiles Pouch	LA	23.80	23.98
Synergy UHR Alpha-Pinene Sleeve	CA	170.0	170.0
Phero Tech UHR Alpha-Pinene Sleeve	CA	170.0	170.0
Synergy Sirex SPB UHR Pouch	LA	100.55	100.79
Synergy Sirex UHR Pouch	LA	90.78	95.02
Synergy Sirex UHR Pouch (second test site)	LA	81.39	81.12
Synergy Frontalin Pouch	LA	2.37	2.29
Synergy Frontalin Pouch (second test site)	LA	1.37	1.38
Synergy High-Release Heptanol Pouch	LA	-	26.51
APTIV Jeffrey Pine Beetle Lure	LA	9.05	9.82
Homemade Turpentine Releaser Bottle (250 mL)	LA	254.51	251.56
Synergy Terpinolene	LA	17.99	18.39
Synergy MCH Bubble Cap	LA	1.26	1.27
Synergy Myrcene	LA	17.77	17.84

temperature, ambient relative humidity, and wind speed. Temperature appears to play a critical role in the elution process, while wind speed effects (ventilation) were not included in the present analysis. Wind speeds were collected at a single location during each test; the high stall speed of the cup anemometers (around 1 m s^{-1}) was problematic in those data (the average wind speed was 1.2 m s^{-1}). Any airflow past the dispensers would tend to increase the elution rate by enhancing the removal of semiochemical from the membrane surface. This effect confounds the field data but is not present in the environmental chamber measurements.

These data were examined to remove data points where the mass of the device was not measured, or where the data were judged to be erroneous (as identified in the Excel spreadsheets for each device). The data were designated as measured in the “sun” and “shade” (data from ten dispensers, five in the sun and five in the shade, were recorded during each test, except when dispensers were inoperative). Six of the 27 datasets were digitized from PDF data sheets to complete data input. Multiple measurements made during the same day (separated into sun and shade) were averaged. Temperatures were almost always measured in the shade, or at least aspirated, and are considered more reliable when applied to shade data. Sun data showed more variability than shade data (as shown in the Model Accuracy section). As a consequence, sun data may be associated with temperatures that are lower than they should be, and do not reflect temperatures at or near the membrane surfaces.

Environmental Chamber Experiments

The elution of three semiochemicals from dispensers was also measured at five constant air temperatures (20°C, 25°C, 30°C, 35°C, and 40°C) and three relative humidity

Table 2. Summary of elution datasets collected in 2013 (Zhu et al., 2015).

Product				Test Site
Synergy Sirex UHR Pouch				OH
Synergy Terpinolene				OH
ChemTica MCH Bubble Cap				OH
Temperature (°C)	Relative Humidity (%)	Initial Sirex Mass (g)	Initial Terpinolene Mass (g)	Initial MCH Mass (g)
20.0	50.0	69.61	19.10	1.62
25.0	50.0	90.72	18.44	1.47
30.0	30.0	94.75	15.01	1.53
30.0	50.0	91.26	18.44	1.56
30.0	50.0	83.59	13.94	1.51
30.0	50.0	90.43	15.22	1.56
30.0	80.0	88.98	15.42	1.19
35.0	50.0	88.05	19.77	1.50
40.0	50.0	85.13	18.39	1.45

levels (30%, 50%, and 80%) in an environmentally controlled chamber at the USDA-ARS Application Technology Research Unit in Wooster, Ohio (OH) (Zhu et al., 2015). These datasets are summarized in table 2. The semiochemicals tested were Synergy Sirex UHR Pouch, Synergy Terpinolene, and ChemTica MCH Bubble Cap. The test system was able to control air temperature to within ±1.0°C and relative humidity to within ±2.0% independently, and measured the semiochemical weight to a resolution of 0.1 mg.

Model Accuracy Analysis

Comparisons between data and model predictions were quantified by computing the average error between model predictions of mass remaining ($M_{prediction}$) and data (M_{data}):

$$\text{Percent error} = \frac{100}{N} \sum \left| \frac{M_{prediction} - M_{data}}{M_{data}} \right| \tag{9}$$

where the summation is performed each day for N days for each dataset.

Results

Field Data

The correlation parameters a, b, and c (defined in eq. 6) were determined by a least-squares algorithm (Kahaner et al., 1988) for the field datasets, based on the solution of equation 8, and are compiled in table 3. The six digitized datasets do not include measurements of relative humidity. Comparison plots are shown in figure 2. The following comments apply to the data comparisons in figure 2:

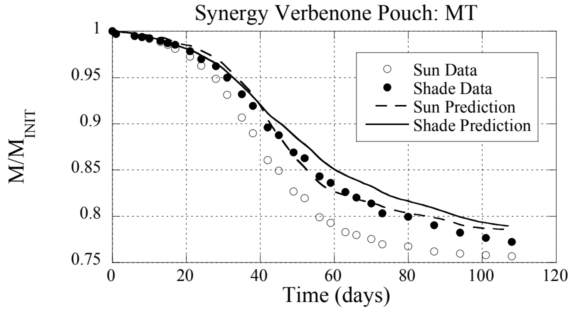
- Figure 2a: Shade predictions followed the data more closely in all four plots than sun predictions and suggest that the inclusion of accurate wind speed and sun temperature measurements would improve model predictions.
- Figure 2b: The model accurately predicted the behavior of the Synergy Ethanol Sleeve elution, while the predicted slopes of the Phero Tech Ethanol Sleeve data are incorrect. Relative humidity data were available for the Synergy data in Pineville only. Inclusion of relative humidity measurements might improve the Phero Tech prediction.

Table 3a. Summary of correlation parameters from the elution datasets (sun).

Product and Test Site	Sun *a* (d^{-1})	Sun *b*	Sun *c*
Synergy Verbenone Pouch: MT	0.02276	72.78	1.21
Synergy Verbenone Pouch: LA	0.00489	-14.80	3.09
Phero Tech Verbenone Pouch: MT	0.10042	51.40	1.55
Phero Tech Verbenone Pouch: LA	0.00731	46.31	-3.75
Synergy UHR Ethanol Sleeve: MT	0.00197	28.83	-
Synergy UHR Ethanol Sleeve: LA	0.01027	26.19	-0.16
Synergy UHR Ethanol Sleeve: CA	0.00185	48.18	-
Phero Tech UHR Ethanol Sleeve: MT	0.00100	-31.51	-
Phero Tech UHR Ethanol Sleeve: LA	0.07143	99.60	4.42
Phero Tech UHR Ethanol Sleeve: CA	0.00170	-3.61	-
Homemade Ethanol Releaser Bottle (100 mL): LA	-	-	-
Homemade Ethanol Releaser Bottle (250 mL): LA	0.00637	-5.45	-3.02
Synergy Green Leaf Volatiles Pouch: MT	0.00718	48.82	-0.31
Synergy Green Leaf Volatiles Pouch: LA	0.00438	29.33	-0.47
Synergy UHR Alpha-Pinene Sleeve: CA	0.00620	31.25	-
Phero Tech UHR Alpha-Pinene Sleeve: CA	0.00666	31.91	-
Synergy Sirex SPB UHR Pouch: LA	0.01479	19.95	-2.84
Synergy Sirex UHR Pouch: LA	0.01830	18.92	-2.09
Synergy Sirex UHR Pouch (second test site): LA	0.23142	7.01	9.86
Synergy Frontalin Pouch: LA	0.00361	-47.29	5.05
Synergy Frontalin Pouch (second test site): LA	0.00033	9.13	-8.12
Synergy High-Release Heptanol Pouch: LA	-	-	-
APTIV Jeffrey Pine Beetle Lure: LA	0.22919	95.52	7.97
Homemade Turpentine Releaser Bottle (250 mL): LA	0.00330	-82.26	2.98
Synergy Terpinolene: LA	0.00303	-26.58	-4.13
Synergy MCH Bubble Cap: LA	0.00161	-8.71	-4.84
Synergy Myrcene: LA	0.00695	-7.99	-2.58

Table 3b. Summary of correlation parameters from the elution datasets (shade).

Product and Test Site	Shade *a* (d^{-1})	Shade *b*	Shade *c*
Synergy Verbenone Pouch: MT	0.00335	38.82	-0.31
Synergy Verbenone Pouch: LA	0.00209	73.22	-1.77
Phero Tech Verbenone Pouch: MT	0.32883	80.49	2.11
Phero Tech Verbenone Pouch: LA	0.03796	53.82	2.34
Synergy UHR Ethanol Sleeve: MT	0.00248	41.50	-
Synergy UHR Ethanol Sleeve: LA	0.00841	8.47	-1.44
Synergy UHR Ethanol Sleeve: CA	0.00147	29.53	-
Phero Tech UHR Ethanol Sleeve: MT	0.00123	-14.86	-
Phero Tech UHR Ethanol Sleeve: LA	0.00841	20.09	-0.43
Phero Tech UHR Ethanol Sleeve: CA	0.00084	-15.53	-
Homemade Ethanol Releaser Bottle (100 mL): LA	0.01044	8.15	1.24
Homemade Ethanol Releaser Bottle (250 mL): LA	0.00437	-89.12	-5.76
Synergy Green Leaf Volatiles Pouch: MT	0.00665	39.13	-0.09
Synergy Green Leaf Volatiles Pouch: LA	0.00275	106.62	-2.32
Synergy UHR Alpha-Pinene Sleeve: CA	0.00536	36.78	-
Phero Tech UHR Alpha-Pinene Sleeve: CA	0.00701	37.52	-
Synergy Sirex SPB UHR Pouch: LA	0.03269	15.61	-0.96
Synergy Sirex UHR Pouch: LA	0.03270	16.17	-0.69
Synergy Sirex UHR Pouch (second test site): LA	0.06500	22.59	5.34
Synergy Frontalin Pouch: LA	0.00100	-53.13	4.57
Synergy Frontalin Pouch (second test site): LA	0.00099	-0.57	-2.63
Synergy High-Release Heptanol Pouch: LA	0.01249	-19.37	13.86
APTIV Jeffrey Pine Beetle Lure: LA	0.19939	102.80	8.66
Homemade Turpentine Releaser Bottle (250 mL): LA	0.00326	-80.01	3.40
Synergy Terpinolene: LA	0.00110	-81.46	-8.68
Synergy MCH Bubble Cap: LA	0.00146	4.78	-7.05
Synergy Myrcene: LA	0.00370	10.62	-9.45



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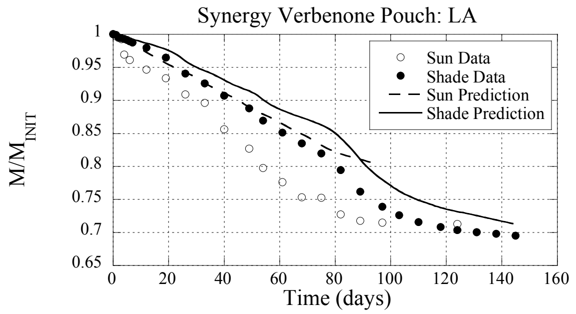

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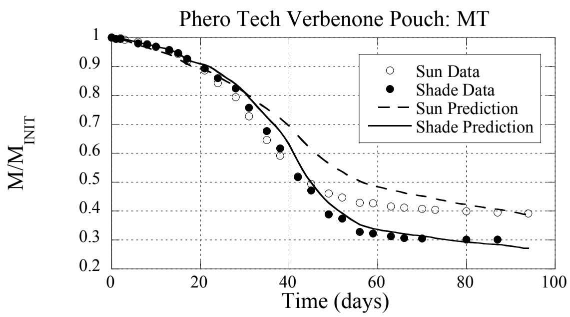

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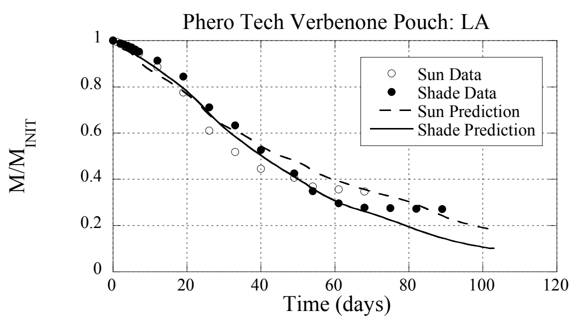
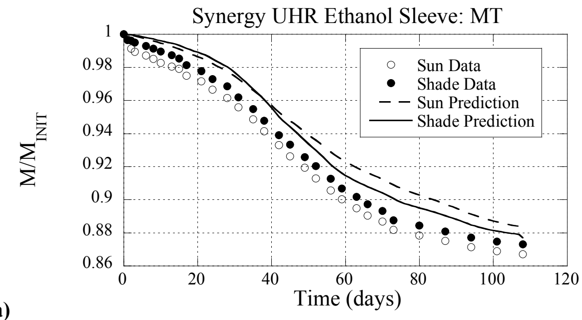


(d)

Figure 2a. Model sun/shade predictions (dashed/solid curves) compared with sun/shade data (open/closed circles) for Synergy Verbenone Pouch collected at (a) Missoula, Montana (day 0 is 5 June 2007) and (b) Pineville, Louisiana (19 May 2007) and for Phero Tech Verbenone Pouch collected at (c) Missoula, Montana (5 June 2007) and (d) Pineville, Louisiana (19 May 2007).



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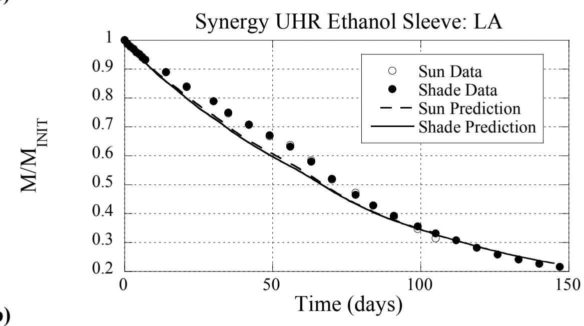

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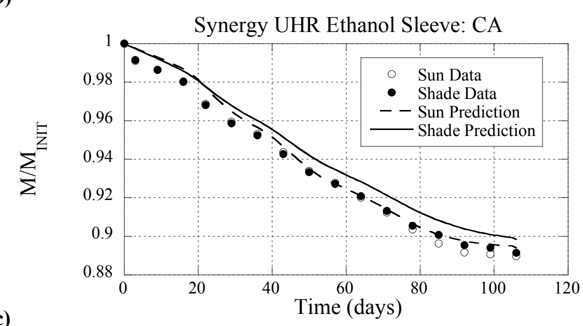

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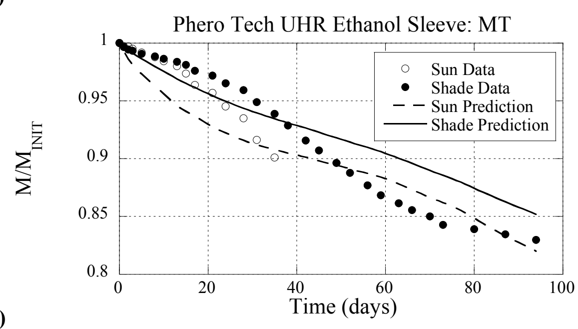


(d)

Figure 2b. Model sun/shade predictions (dashed/solid curves) compared with sun/shade data (open/closed circles) for Synergy UHR Ethanol Sleeve collected at (a) Missoula, Montana (day 0 is 5 June 2007), (b) Pineville, Louisiana (7 June 2007), and (c) Susanville, California (17 June 2007) and (d) for Phero Tech UHR Ethanol Sleeve collected at Missoula, Montana (5 June 2007).

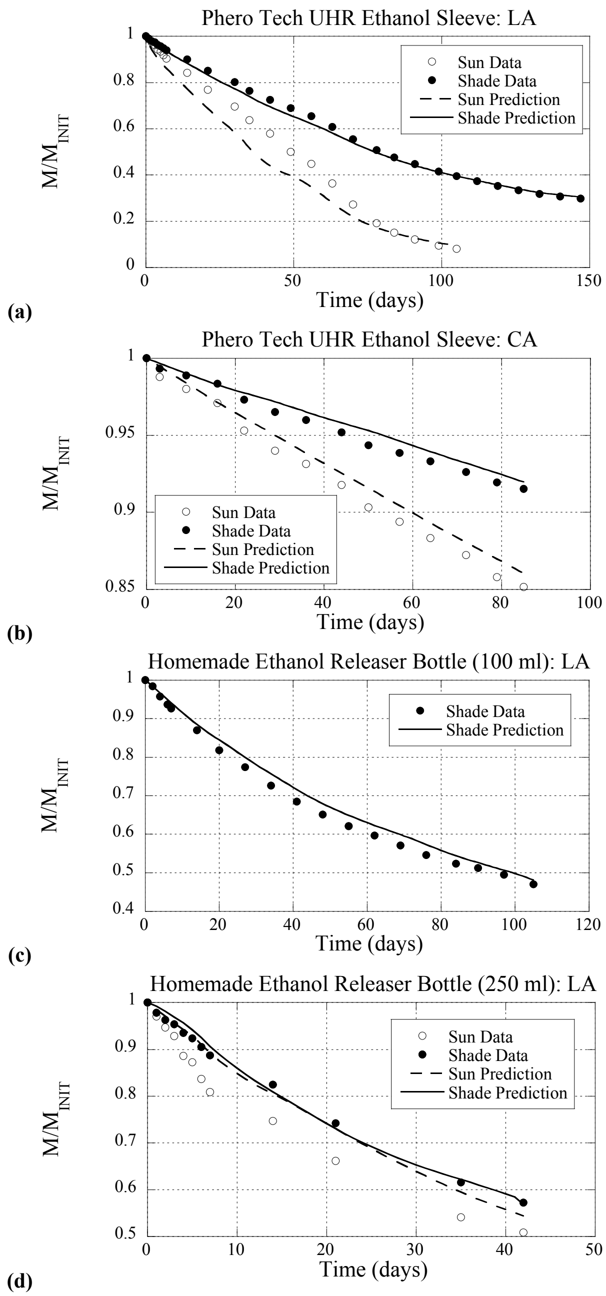
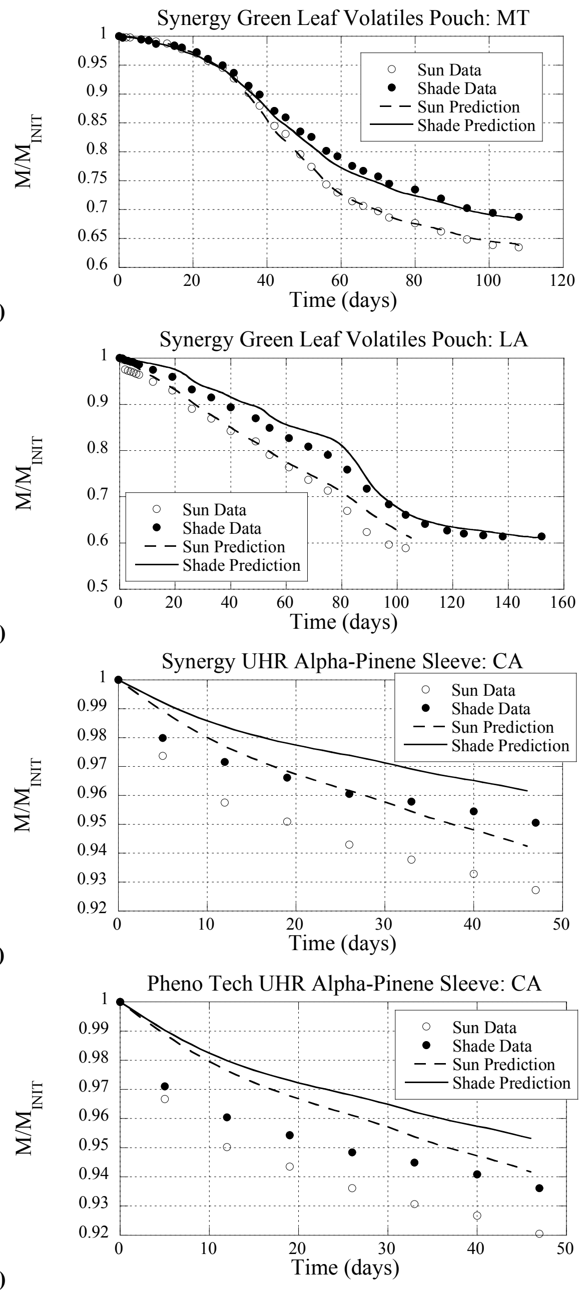


Figure 2c. Model sun/shade predictions (dashed/solid curves) compared with sun/shade data (open/closed circles) for Phero Tech UHR Ethanol Sleeve collected at (a) Pineville, Louisiana (day 0 is 7 June 2007) and (b) Susanville, California (5 June 2007), (c) for Homemade Ethanol Releaser Bottle (100 mL) collected at Pineville, Louisiana (31 August 2007), and (d) for Homemade Ethanol Releaser Bottle (250 mL) collected at Pineville, Louisiana (7 June 2007).



(a) (b) (c) (d)

Figure 2d. Model sun/shade predictions (dashed/solid curves) compared with sun/shade data (open/closed circles) for Synergy Green Leaf Volatiles Pouch collected at (a) Missoula, Montana (day 0 is 5 June 2007) and (b) Pineville, Louisiana (19 May 2007), (c) for Synergy UHR Alpha-Pinene Sleeve collected at Susanville, California (12 September 2007), and (d) for Phero Tech UHR Alpha-Pinene Sleeve collected at Susanville, California (12 September 2007).

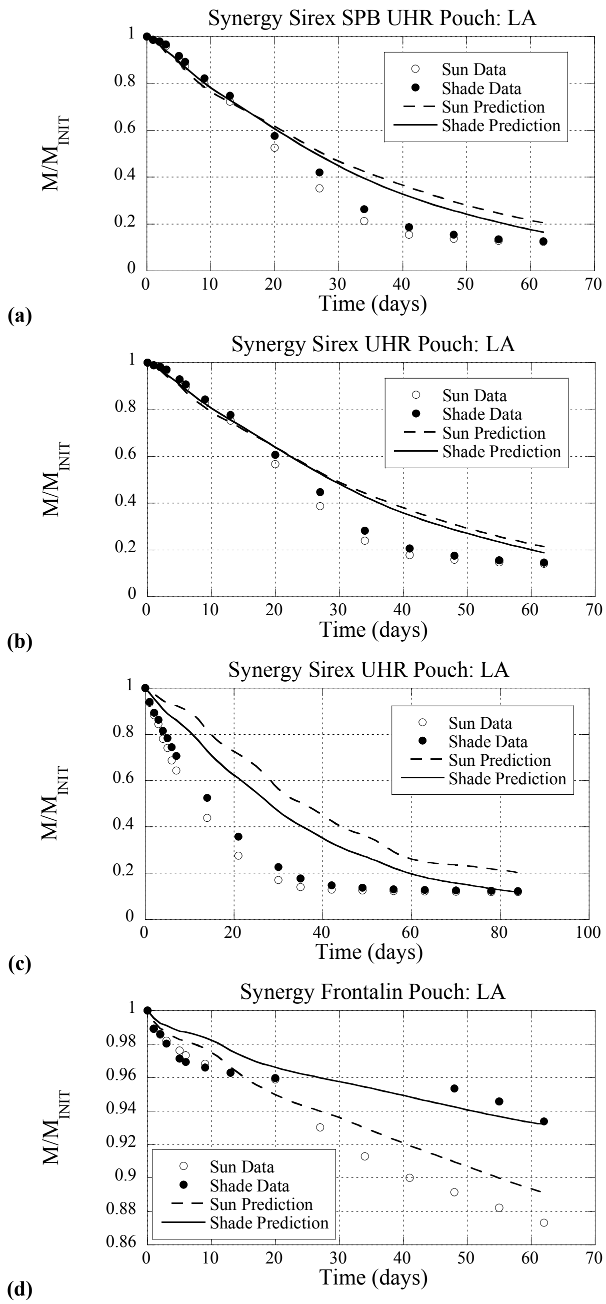
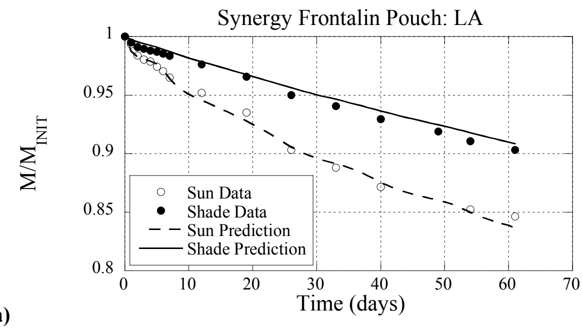


Figure 2e. Model sun/shade predictions (dashed/solid curves) compared with sun/shade data (open/closed circles) (a) for Synergy Sirex SPB UHR Pouch collected at Pineville, Louisiana (day 0 is 6 April 2007), for Synergy Sirex UHR Pouch collected at Pineville, Louisiana (b) 6 April 2007 and (c) 7 June 2007 (second test site), and (d) for Synergy Frontalin Pouch collected at Pineville, Louisiana (6 April 2007).



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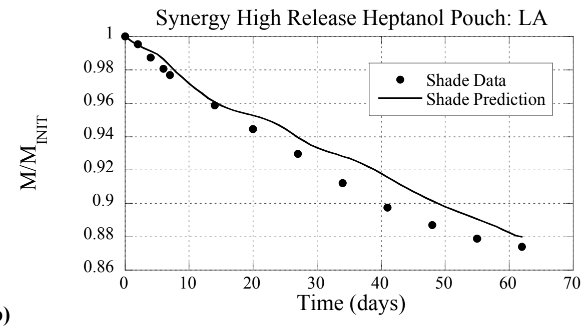

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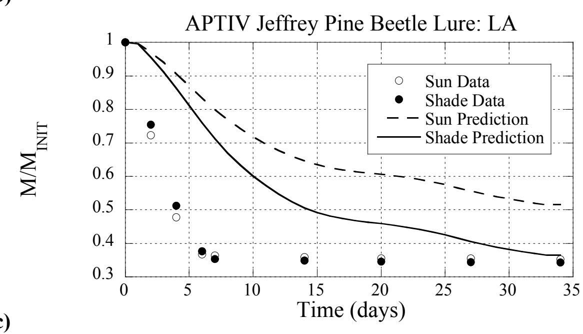

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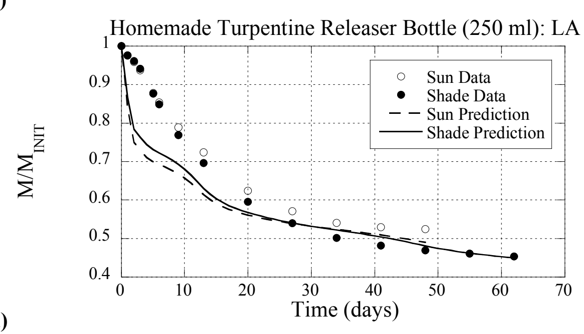

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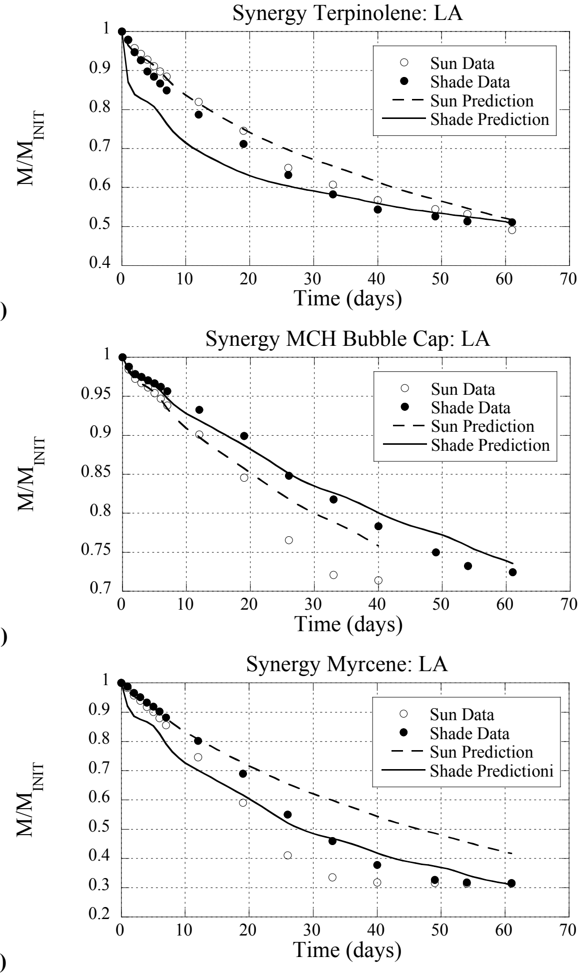
Figure 2f. Model sun/shade predictions (dashed/solid curves) compared with sun/shade data (open/closed circles) for (a) Synergy Frontalin Pouch collected at Pineville, Louisiana (day 0 is 19 May 2007, second test site), (b) Synergy High-Release Heptanol Pouch collected at Pineville, Louisiana (31 August 2007), (c) APTIV Jeffrey Pine Beetle Lure collected at Pineville, Louisiana (31 August 2007), and (d) Homemade Turpentine Releaser Bottle (250 mL) collected at Pineville, Louisiana (6 April 2007).



(a) **(b)** **(c)**

Figure 2g. Model sun/shade predictions (dashed/solid curves) compared with sun/shade data (open/closed circles) for (a) Synergy Terpinolene collected at Pineville, Louisiana (day 0 is 19 May 2007), (b) Synergy MCH Bubble Cap collected at Pineville, Louisiana (19 May 2007), and (c) Synergy Myrcene collected at Pineville, Louisiana (19 May 2007).

- Figure 2c: Curiously, the other Phero Tech Ethanol model predictions were quite good, even though the Susanville data did not include relative humidity measurements. Shade model predictions were quite good for the Homemade Ethanol bottles (only shade data were available for 100 mL).
- Figure 2d: The model accurately predicted the Synergy Missoula data, with some slope influence in the shade prediction in Pineville. The Alpha-Pinene data were underpredicted; relative humidity measurements were not available for either dataset.
- Figure 2e: Model agreement with the data appeared reasonable, except for the Synergy Sirex UHR Pouch.

- Figure 2f: The Frontalin data were accurately predicted by the model, as were the Heptanol Pouch data (only shade data were available). The prediction for APTIV Jeffrey Pine Beetle Lure was poor when compared with the data. It appeared that the model could not track the rapid decrease in mass as well as it should.
- Figure 2g: Myrcene model predictions underpredicted elution. All results in shade appeared reasonable.

Correlation parameters (shown in table 3) for the same elution devices (Synergy and Phero Tech Verbenone Pouch, Synergy and Phero Tech UHR Ethanol Sleeve, Synergy Green Leaf Volatiles Pouch, Synergy and Phero Tech UHR Alpha-Pinene Sleeve, Synergy Sirex UHR Pouch, and Synergy Frontalin Pouch) showed variations that indicated that different manufacturers and different application locations gave different results. Environmental conditions (such as temperature and relative humidity), as well as variations in the physical parameters that constitute the α parameter (eq. 4), may be responsible for this apparent lack of consistency.

Environmental Chamber Data

The least-squares analysis results, based on equation 7, for the correlation parameters a, b, and c are summarized in table 4, with comparison plots shown in figure 3. Since one elution material was used for each of nine tests for each product, it was assumed that the nine datasets for each product would have the same correlation parameters. The comparisons with data showed how closely the assumed behavior matched the data, represented here by their daily values.

It may be seen from the environmental chamber data shown here that most of the tests were terminated well before the semiochemicals were completely eluted. Note also from the several tables that comparisons of correlation parameters for similar materials tested in the environmental chamber and in the field showed little similarity between comparable datasets.

Model Accuracy

Model prediction errors for the field data and environmental chamber measurements are shown in tables 5 and 6, respectively. The environmental chamber data predictions were particularly accurate, with an average error of 1.04%. The average error of the field data predictions was 11.1% and was within 10% of the data in 41 of the 52 datasets (counting sun and shade data separately), or 79% of the datasets. The average ratio of the sun error to the shade error was 1.80, supporting the observation that the shade data (temperature) more accurately reflected the temperatures at the shaded devices.

Five field results gave larger than anticipated errors: Synergy Sirex SPB UHR Pouch, Synergy Sirex UHR Pouch, Synergy Sirex UHR Pouch (second test site), APTIV Jeffrey Pine Beetle Lure, and Synergy Myrcene.

Table 4. Summary of correlation parameters from the environmental chamber datasets.

Product and Test Site	a (d^{-1})	b	c
Synergy Sirex UHR Pouch: OH	0.04549	22.53	0.12
Synergy Terpinolene: OH	0.02452	21.26	0.09
ChemTica MCH Bubble Cap: OH	0.00465	31.69	-0.26

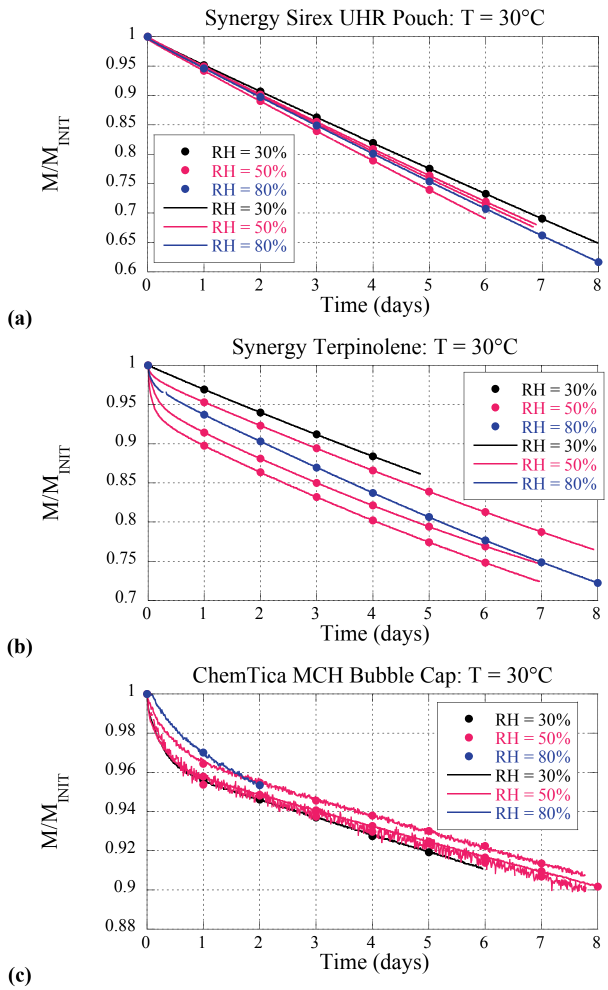


Figure 3a. Model comparison with data collected in an environmental chamber at a fixed temperature of 30°C for (a) Synergy Sirex UHR Pouch, (b) Synergy Terpinolene, and (c) ChemTica MCH Bubble Cap. The curves are model predictions, and the symbols are daily data. Note that three sets of data were taken at a relative humidity of 50% (red curves and symbols), as summarized in table 2.

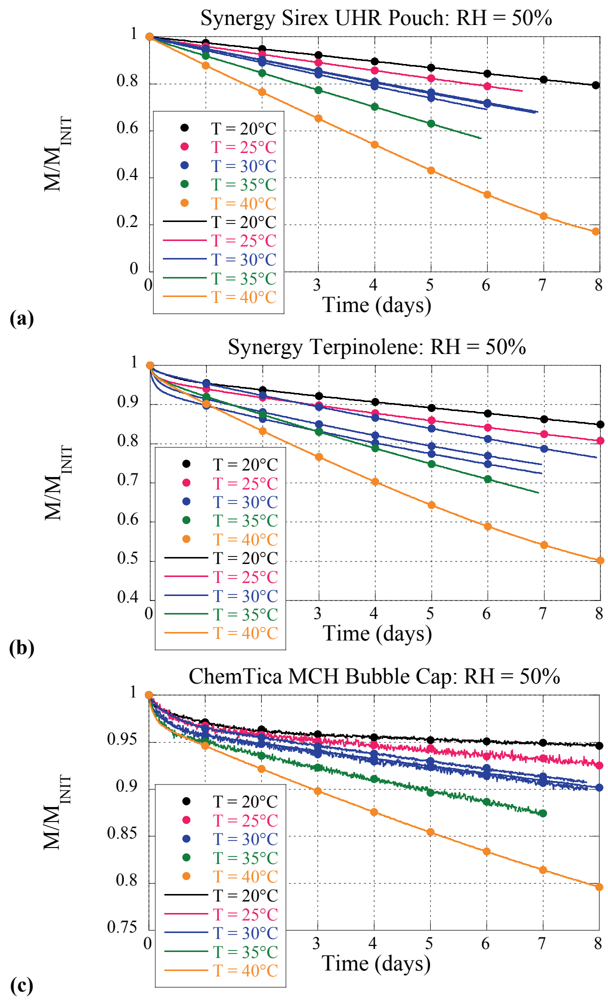


Figure 3b. Model comparison with data collected in an environmental chamber at a fixed relative humidity of 50% for (a) Synergy Sirex UHR Pouch, (b) Synergy Terpinolene, and (c) ChemTica MCH Bubble Cap. The curves are model predictions, and the symbols are daily data. Note that three sets of data were taken at a temperature of 30°C (blue curves and symbols), as summarized in table 2.

Table 5. Accuracy of the field data predictions.

Product and Test Site	Sun Error (%)	Shade Error (%)
Synergy Verbenone Pouch: MT	3.20	1.27
Synergy Verbenone Pouch: LA	5.99	2.85
Phero Tech Verbenone Pouch: MT	9.14	3.79
Phero Tech Verbenone Pouch: LA	7.50	8.14
Synergy UHR Ethanol Sleeve: MT	1.91	0.96
Synergy UHR Ethanol Sleeve: LA	4.05	4.25
Synergy UHR Ethanol Sleeve: CA	0.45	0.82
Phero Tech UHR Ethanol Sleeve: MT	2.03	2.13
Phero Tech UHR Ethanol Sleeve: LA	11.08	1.79
Phero Tech UHR Ethanol Sleeve: CA	0.90	0.55
Homemade Ethanol Releaser Bottle (100 mL): LA	-	3.09
Homemade Ethanol Releaser Bottle (250 mL): LA	6.73	1.69
Synergy Green Leaf Volatiles Pouch: MT	0.33	0.93
Synergy Green Leaf Volatiles Pouch: LA	2.15	1.85
Synergy UHR Alpha-Pinene Sleeve: CA	1.71	1.16
Phero Tech UHR Alpha-Pinene Sleeve: CA	2.39	1.84
Synergy Sirex SPB UHR Pouch: LA	40.88	22.09
Synergy Sirex UHR Pouch: LA	33.88	21.41
Synergy Sirex UHR Pouch (second test site): LA	100.47	44.76
Synergy Frontalin Pouch: LA	1.17	1.10
Synergy Frontalin Pouch (second test site): LA	0.37	0.48
Synergy High-Release Heptanol Pouch: LA	-	0.93
APTIV Jeffrey Pine Beetle Lure: LA	78.07	50.13
Homemade Turpentine Releaser Bottle (250 mL): LA	13.05	8.33
Synergy Terpinolene: LA	2.77	6.96
Synergy MCH Bubble Cap: LA	2.12	1.18
Synergy Myrcene: LA	25.40	8.12

Table 6. Accuracy of the environmental chamber data predictions.

Product and Test Site	Error (%)
Synergy Sirex UHR Pouch: OH	1.91
Synergy Terpinolene: OH	1.02
ChemTica MCH Bubble Cap: OH	0.24

Discussion

In addition to the comments made above regarding the data and their least-squares curve fits, the following observations may be made:

- For the most part, the assumption of a simple diffusion process accounted for the mass release trends observed in both field and environmental chamber data.
- Temperature was the dominant physical parameter controlling mass release from the pheromone dispensers. This effect was most easily seen by separating temperature effects into sun and shade conditions. Relative humidity played a smaller, but still important, role in the elution process. Wind speed effects will require a more accurate measurement technique.
- The definitions of "sun" and "shade" conditions should be better quantified, as there are numerous datasets shown here where sun exposure retained more material in the dispenser than shade exposure, contrary to what might be expected. It is thought that the sun samples had more exposure to the wind than the shade samples, which were often tucked away in the shade. Their field positioning might explain some of the counterintuitive results with the sun data.
- Results from the environmental chamber data clearly showed that, after an initial

settling period, the three dispensers released material at a constant rate for as long as the tests were conducted. Unfortunately, environmental chamber results cannot be replicated in the field because ambient temperature and relative humidity do not remain constant there.

Some issues remain:

1. Different manufacturers of the same type of dispenser appeared to give different behavior and different results. Overall, a field test may be needed for each type of dispenser, to recover the representative correlation parameters discussed here.
2. Site location for the dispensers appeared to be important, a conclusion that may not lend itself to generalization of the results presented here, further suggesting that a field test would be needed for each dispenser application.
3. This study did not address the variability in the parameters that make up the parameter α, namely the surface area S, dispenser volume V, diffusion coefficient D, and decay length λ (defined in eq. 5). Variations in these parameters (including membrane thickness) may account for the observed differences between dispenser behavior from different manufacturers, and there may be substantial variability in component material properties between batches from a given manufacturer. The assumption of a constant diffusion coefficient may need further study.

Overall, it should be possible to develop a computer program (app) that would, on a daily basis, access transmitted temperature and relative humidity readings from the field and then apply the model to refine its correlation parameter predictions estimating the decrease in mass in any number of pheromone dispensers as a function of atmospheric conditions, and thereby indicate when a dispenser should be replaced. As more data are collected on the devices, over time, the app would improve its prediction of mass remaining in the dispensers.

Conclusions

A simple diffusion model was applied to field and environmental chamber data detailing the elution of semiochemicals from pheromone dispensers. These data included detailed measurements of three products (in an environmental chamber) and daily measurements for 27 products (in the field). The data appeared to correlate well with regard to changes in ambient temperature, relative humidity, and remaining mass, suggesting that the model summarized here is a good first step toward understanding and quantifying the behavior of these dispensers.

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