

Release Kinetics of a Synthetic Tsetse Allomone Derived from Waterbuck Odour from a Tygon Silicon Dispenser under Laboratory and Semi Field Conditions

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Abstract: The tsetse allomone consisted of pentanoic, hexanoic and heptanoic acids, guaiacol, geranylacetone, 2-undecanone and δ -octalactone. These compounds were dispensed singly or as a blend from dispensers with 6.028 cm² diffusion area under laboratory conditions in a two-choice wind tunnel in which the wind speed was maintained constant at 20 cm/sec and the room temperature and relative humidity kept at 24 \pm 1°C and 65 \pm 5%, respectively. The loss in mass of individual compounds was assessed gravimetrically. Zero-, first- and second-order rate models were tested to determine the release kinetics of the individual compounds and the blend. Comparison of the models using correlation index (R^2) indicated that the release of individual compounds followed first-order kinetics while release of the blend followed zero-order kinetics. In the semi field trials, the individual compounds dispensed singly followed first-order release kinetics while their blends followed zero-order release kinetics. It was however, interesting to note that the release kinetics of the individual components of the blend followed zero-order kinetics under semi-field conditions in contrast with the behavior exhibited by the individual components dispensed singly. The compounds placed in dispensers exposed to direct sunlight exhibited higher rate constants than those in the dispensers placed under shade. The rate of release was found to be slightly higher during the first 24 hours and then became steady, obeying Fick's law of diffusion. The release rates were observed to depend on the surface area of the tygon tubing and generally increased with temperature. Rate constants established under laboratory conditions were slightly lower than those obtained under semi field conditions. The results indicate that temperature could be the major environmental determinant of release rates with other variables like relative humidity having little or no effect. However, the magnitude of the effect of temperature on the release rates was not easily demonstrated with the field data. It is thus evident that the release of the compounds was not a simple function of temperature; with the release rates at higher temperatures being lower than would be expected. The zero-order rate equation best described the release of the blend, which was found to be diffusion-controlled.

Key words: Release kinetics • Synthetic tsetse allomone • Waterbuck odor • Tygon silicon dispenser

INTRODUCTION

Several methods have been used for the control of tsetse flies and trypanosomiasis to varying degrees of successes. Among these methods include the use of semiochemicals (repellents and attractants) for the direct control of insect pests and vectors. The devices for use with the semiochemicals have however, been known to

pose serious challenges as they need to meet quite stringent requirements for their successful vector management. Ideally, an efficient dispenser should be designed such that the minimum required dose of the chemical of interest is released at a steady rate over the intended period. However, many dispensers available for practical application do not release the chemicals of interest at a constant rate [1]. Such devices are known

to be prone to progressive decline in release rate with time; a possible consequence of a complex mix of factors associated with aging [2]. Consequently, much of the research conducted on controlled-release devices has been devoted to this aspect of variable release rates.

The dispenser-release rates are known to be influenced instantaneously by environmental factors such as temperature and wind which cause fluctuations in actual release rates [3, 4]. In this study, we report the development of an affordable dispenser for potential use by the rural poor communities in tsetse prone areas who derive their livelihood on livestock. We have endeavored to determine the release kinetics of an allomonal blend for the Savanna group of tsetse flies previously isolated from waterbuck sebum and volatiles by Gikonyo and co-workers [5-7]. It is anticipated that the corresponding release rates will be useful in subsequent dose-response investigations and for interpreting results from the field as well as defining appropriate doses for practical use.

The adoption of the allomonal blend for the Savanna group of tsetse flies in this study was informed by results of work by Gikonyo and co-workers [5, 6, 7]. Gikonyo and co-workers [5] studied the behavior of caged individual teneral *G.m. morsitans* on waterbuck (a non-host) and Ox (a preferred host) and on feeding membranes with and without smears of different doses of waterbuck sebum. In their study, they reported that flies that contacted the body of the waterbuck or areas of the membrane treated with different doses of sebum showed significant reluctance to feed; manifested by high proportions of flies departing, changing probing sites and general delays in the initiation of feeding compared to the ox and untreated zone of the membrane. Their results suggested presence of volatile and non-volatile allomones on waterbuck. The odor composition of the preferred and non-preferred hosts revealed that waterbuck odor consisted of aldehydes, 2-methoxyphenol (guaiacol), 3-isopropyl-6-methylphenol (carvacrol), 3-n-propylphenol, δ -octalactone, straight chain fatty acids (C_5 - C_9) and a series of methylketones (C_8 - C_{13}) which were either not detected or present in trace amounts in the two preferred hosts (buffalo and ox). The preferred host odor comprised medium-chain, saturated or unsaturated aldehydes and phenols [5, 8]. The 2-methoxyphenol was previously reported to be moderately repellent to tsetse flies [9, 10].

In field studies, several C_6 and C_7 methylketones reduced tsetse fly catches although some of the lower homologues (C_3 - C_4) were attractive [11]. Straight chain fatty acids reduced tsetse fly trap catches in the field

[9, 11]. Thus Gikonyo and co-workers [6], concluded that the 2-methylketones, guaiacol, carvacrol and δ -octalactone, in waterbuck odor acting additively or synergistically, could potentially constitute a long range allomonal barrier. The synergistic activity was further demonstrated by Gikonyo and co-workers [7] in a wind tunnel experimental setup. Singularly, δ -octalactone was shown to be repellent to tsetse flies in a wind tunnel experiment [12]. Preliminary testing of the repellent blend in the field indicated that it reduces the number of tsetse flies attracted to the cattle and those that engorge. Hence, the basis of work reported in this manuscript: need to develop an efficient method of dispensing the blend of repellent compounds from the waterbuck in the field.

MATERIALS AND METHODS

Allomonal Blend: The allomonal blend was prepared from synthetic chemicals purchased from Sigma Aldrich, UK and this included; carboxylic acids (i.e., pentanoic, hexanoic and heptanoic acids), ketones (i.e., geranylacetone and 2-undecanone), 2-methoxyphenol (guaiacol) and δ -octalactone. 2-Methoxy-4-methyl phenol used in the preliminary semi-field trials was purchased from EMELT S.R.L, Italy.

Dispenser: The dispenser (Figure 1) consisted of a repellent reservoir and a diffusion area, which made up the dispensing unit whose top, could be unscrewed for refilling. The upper part was a reservoir tube made of aluminum (or polypropylene) of 10 mm diameter and 10 cm length, through which no diffusion of the compounds could take place. The diffusion area was made from tygon silicon tubing (Cole-Palmer Co., Illinois) having an internal diameter 6.4 mm, outer diameter 9.6 mm, thickness 3.2 mm and variable lengths of either 2.0 or 4.0 cm. The dispensing unit was closed with screw caps made of polypropylene on both ends.

Loading of Dispensers: Two sets of dispensers with a tygon silicon tubing of length 4 cm and 2 cm were used. The dispensers were filled in triplicate with the individual repellent compounds leaving a 2 cm vapor space above the repellents in the reservoir. The dispensers were then tightly closed with polypropylene plugs and their masses taken before being placed in the wind tunnel or exposed to the semi-field conditions. For the blend, equal amounts of freshly prepared blend of the seven repellent compounds were introduced into another set of dispensers according to the procedure followed for

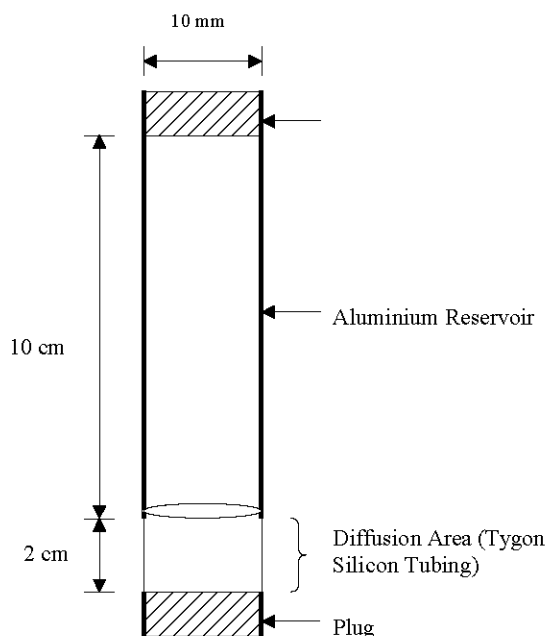


Fig. 1: Schematic diagram of the repellent dispenser unit

the individual compounds. They were then wrapped in aluminum foil, placed in a closed container awaiting transportation to the wind tunnel and the semi field at the *International Center of Insect Physiology and Ecology (ICIPE)*, Nairobi.

Determination of Release Kinetics under Laboratory

Conditions: The kinetics of release of the individual compounds was investigated under controlled conditions in a wind tunnel in the laboratory. The data collected was tested against the zero-, first- and second-order kinetic models.

Laboratory experiments were conducted in a two-choice cylindrical Plexiglas wind tunnel (180 cm long, 24 cm internal diameter) as described by Gikonyo and co-workers [7]. A duct (20 cm diameter) in the middle of the tunnel was connected via a polyvinylchloride (PVC) pipe through which an air-extracting fan was mounted. Air flowed into the tunnel from either arm on switching the fan on, thereby making the middle of the tunnel downwind. The middle duct divided the tunnel into two equal arms with a 20 cm wide middle zone where air from either arm mixed. The upwind of the tunnel was closed with white PVC gauze, while the downwind end was closed with a metallic mesh cover. The two upwind ends of the tunnel were connected to activated charcoal (4-14 mesh, Sigma) air filters made of PVC. Two windows, one on either arm (15 cm x 10 cm) of the wind tunnel were used for introducing sample dispensers. The wind speed

in the tunnel was maintained at 20 cm/sec while the room was maintained at $24 \pm 1^\circ\text{C}$ and $65 \pm 5\%$ relative humidity. The laboratory conditions were determined using a Solomat MPM 500e Electronic Anemometer (Devon, UK).

The dispensers were each placed in the wind tunnel through the window on the upper side of either arm of the tunnel onto a metallic rack positioned 15 cm from the upwind end such that they were mid-height of the wind tunnel and dispensing area facing downwind. The dispensers were carefully removed every 24 hours and their masses taken before being returned to the wind tunnel.

Determination of Release Kinetics Under Semi-Field

Conditions: The dispensers containing the individual repellent compounds and blend (in triplicate) were placed 2.0 m above the ground in the sun and under tree shade using thin metallic wires with the dispensing unit facing downwards. Masses of the dispensers containing the individual repellents and the blend were taken every 24 hours. Using the gravimetric method, release rates were determined for the individual compounds. Continuous daily monitoring of temperature and relative humidity was carried out using a thermohygrometer (Wil. Lambrecht GmbH, Gottingen). The weather data was collected on an hourly basis and the corresponding averages determined.

Statistical Analysis:

The loss in mass data in the dispensers was analyzed for significance in difference in the release rates by ANOVA and ANCOVA [13]. The release data were fitted to the standard Zero-order ($A_t - A_0 = -k_0t$); First-order ($\ln A_t - \ln A_0 = -k_1t$); and Second-order ($1/A_t - 1/A_0 = k_2t$) rate equations in order to determine the appropriate release kinetics of the repellents from the dispensers, where A_0 , A_t , k_0 , k_1 and k_2 and t , take their usual meaning of the initial amount of repellent present in the dispenser, the amount of repellent present in the dispenser at any time t , zero-, first- and second-order rate constants, respectively.

RESULTS AND DISCUSSION

Release Kinetics of 2-methoxy-4-methyl Phenol under

Semi-Field Conditions: Preliminary trial was conducted using the synthetic repellent, 2-methoxy-4-methyl phenol in order to determine the optimum length of the silicon tubing to be used in subsequent kinetics studies involving the waterbuck odor-based repellent blend. The diffusion area was varied by using tygon silicon

Table 1a: Correlation index (R^2) values and the release rate constants for the Zero- and First- Order kinetic models tested to describe the release of the standard repellent, 2-methoxy-4-methyl phenol ($n = 3$)

Length of Tubing /cm	Zero-Order Rate Model				First-Order Rate Model			
	Sun		Shade		Sun		Shade	
	$k_0/g \text{ day}^{-1}$	R^2	$k_0/g \text{ day}^{-1}$	R^2	k_1/day^{-1}	R^2	k_1/day^{-1}	R^2
4	0.276	0.9187	0.215	0.9884	0.060	0.9084	0.040	0.9880
3	0.148	0.9991	0.156	0.9995	0.052	0.9980	0.053	0.9978
2	0.096	0.9979	0.011	0.9990	0.020	0.9972	0.020	0.9980

Table 1b: Correlation index (R^2) values and the second-order release rate constant ($\text{g}^{-1} \text{ day}^{-1}$) for the second-order kinetic model tested to describe the release of the standard repellent, 2-methoxy-4-methyl phenol ($n = 3$)

Length of Tubing /cm	Second-Order Rate Model			
	Sun		Shade	
	$k_2/\text{g}^{-1} \text{ day}^{-1}$	R^2	$k_2/\text{g}^{-1} \text{ day}^{-1}$	R^2
4	0.0110	0.8951	0.0080	0.9856
3	0.0187	0.9911	0.0180	0.9890
2	0.0040	0.9967	0.0039	0.9963

Table 2: Average mass loss (\pm SD) and the corresponding zero-order rate constants of 2-methoxy-4-methyl phenol using different lengths of tygon silicon tubing ($n= 3$)

Length of Tubing /cm	Calculated Diffusion Area / cm^2	Sun		Shade	
		Average Mass Loss /g	Release Rate Constant/ g day^{-1}	Average Mass Loss /g	Release Rate Constant/ g day^{-1}
4	12.056	0.2033 ± 0.0081	0.276	0.1714 ± 0.0099	0.215
3	9.042	0.1642 ± 0.0078	0.148	0.1463 ± 0.0066	0.156
2	6.028	0.1098 ± 0.0042	0.096	0.0991 ± 0.0048	0.011

tubing of different lengths (i.e., 4, 3 and 2 cm) and the corresponding release rates compared under semi-field conditions. The three kinetic models (i.e., Zero-, First- and Second-order) were used to evaluate the release kinetics of 2-methoxy-4-methyl phenol. The experimental data obtained was fitted to the various kinetic models to establish the most appropriate model for the data. The criterion used to determine the best model was the index of correlation (R^2) values (Table 1).

From Tables 1a and 1b, three important observations can be made: First, it is clear that the overall best fit (i.e., highest R^2) is evident with the Zero-order rate expression for all the dispenser lengths employed and therefore we can conclude that the release rate follows Zero-order kinetics. Second, that under every kinetic model tested, the corresponding rate constants reduce with decreasing dispenser tubing length. This implies that the release rate of the compound is influenced by the surface area of the tygon silicon tubing (i.e., that the longer the tubing, the greater the rate of release of the compound). Third, that for the Zero-order model, the rate constants obtained under the sun are, generally larger than the corresponding values obtained under shade.

Table 2 shows the average loss in mass of 2-methoxy-4-methyl phenol determined over the entire period of the trials and the corresponding calculated average zero-order rate constants for the different lengths of the tygon tubing used. It shows the effect of surface area (assumed to be proportional to the length of tubing) on the average loss in mass and Zero-order release rate constant. From the table, it is evident that the longer the silicon tubing, the greater the loss in mass. A compromise 2.0 cm was adopted as the length of choice for subsequent laboratory and semi-field experiments.

Careful scrutiny of the loss in mass data alongside daily temperature recordings, seems to suggest a general tendency for the average mass loss to increase with average daily temperature (Figure 2a). These results do corroborate earlier assertions that the zero-order release rate constants (or mass loss) obtained under the sun are indeed larger than those determined under shade. It is therefore plausible to conclude that any apparent deviations in the loss in mass data recordings could be attributable to the wide variations in temperature within any given day as depicted in Figure 2b.

Table 3: Correlation index (R^2) and rate constant (k_i) values for the various kinetic models tested to describe the release of the individual repellent compounds and the blend under laboratory conditions in the wind tunnel using 2.0 cm silicon tubing.

Compound	Zero-order Rate Model		First-order Rate Model		Second-order Rate Model	
	$k_0/g \text{ day}^{-1}$	R^2	k_1/day^{-1}	R^2	$k_2/g^{-1} \text{ day}^{-1}$	R^2
Pentanoic acid	0.2829	0.9569	0.0808	0.9864	0.0225	0.9835
Hexanoic acid	0.0877	0.9669	0.0197	0.9788	0.0043	0.9750
Heptanoic acid	0.0462	0.9467	0.0082	0.9502	0.0017	0.9233
δ - Octalactone	0.0341	0.9063	0.0121	0.9217	0.0043	0.9190
2-Undecanone	0.1321	0.9147	0.0283	0.9620	0.006	0.9437
Geranylacetone	0.0366	0.9622	0.0069	0.9719	0.0013	0.9666
Guaiacol	0.1580	0.9914	0.0339	0.9978	0.0069	0.9965
Blend	0.0997	0.9992	0.0407	0.9969	0.0166	0.9921

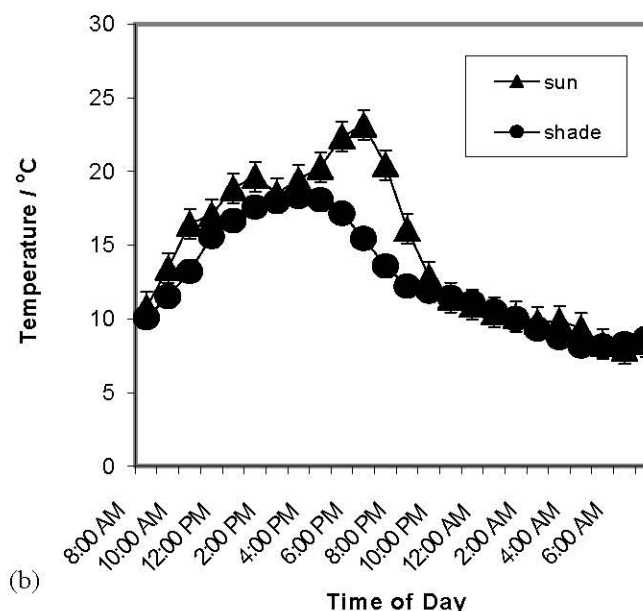
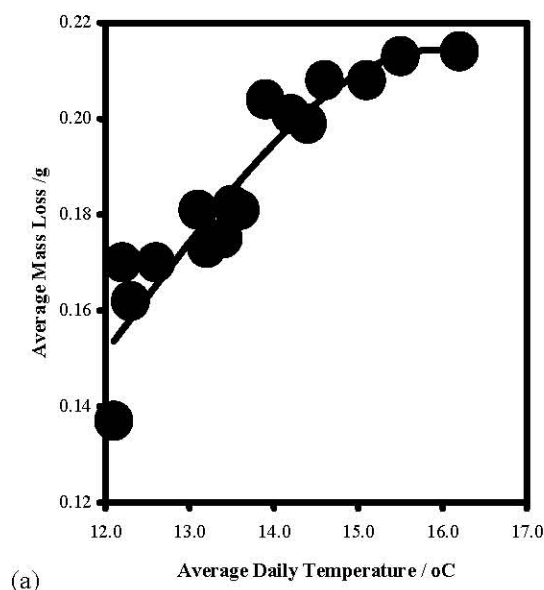


Fig. 2a: Average mass loss of 2-methoxy-4-methyl phenol as a function of average daily temperature obtained with a 4.0 cm tygon silicon tubing

Fig. 2b: Average daily temperature measurements in the sun and under shade.

Kinetics of Release of Individual and Blend Repellent Compounds in the Wind Tunnel:

The kinetics of release of the individual and blended compounds was investigated in a wind tunnel in the laboratory under controlled experimental conditions. The loss in mass data collected was tested against zero-, first- and second-order kinetic models. The release of the individual compounds was found to follow first-order kinetics as evidenced by the higher correlation index values (R^2) of the plots of the experimental data fitted to the first-order model compared to the other two models (Table 3). The first-order release rate constants for the individual compounds were determined graphically from the corresponding straight-line plots using the first-order

model. Pentanoic acid, guaiacol, 2-undecanone and hexanoic acid had the highest first-order release rate constants of 0.081, 0.034, 0.03 and 0.02 day^{-1} , respectively, while δ -octalactone, heptanoic acid and geranylacetone had lower rate constants of 0.012, 0.008 and 0.007 day^{-1} , respectively. The mass loss data indicated that greater mass losses (equivalent to higher release rates) were registered during the first two days of the experiments, followed by a gradual decrease in release rate. These results are consistent with the Fickian diffusion model [14] since the concentration of the compounds within the diffusion volume (the dispenser chamber) changes with time and thus obeying the Fick's law of diffusion [15].

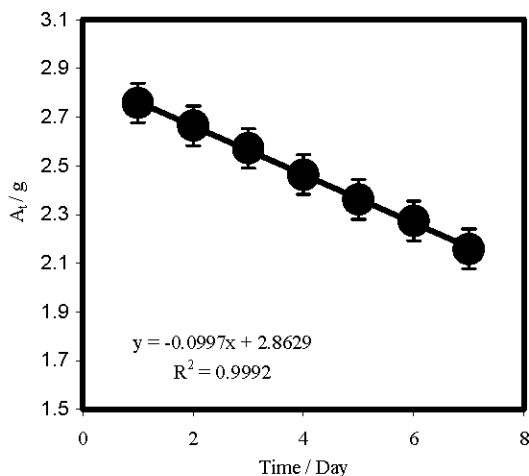


Fig. 3: Release kinetics of the blend under laboratory conditions as described by the zero-order rate equation

It is significant to note that under laboratory conditions, the individual compounds follow first-order release kinetics whereas a uniform blend of the same compounds follow zero-order release kinetics. This is clearly evident from the results of Table 3. This table contains a summary of the results obtained with the blend as well as the rest of the individual compounds fitted to the various kinetic models. It is clear from the table that the R^2 values for all the individual compounds are highest for the first-order model compared to the corresponding R^2 values for the other two kinetic models. Thus the individual compounds follow first-order release kinetics. You will however, notice that the blend has registered a very high R^2 value of 0.9992 for Zero-order kinetics compared to 0.9969 and 0.9921 for first- and second-order kinetic models, respectively. The blend therefore follows zero-order release kinetics, which implies that the release rate for the blend is independent of the amount of blend left in the dispenser at any time.

Figure 3 shows the excellent fit obtained for the experimental data of the uniform blend fitted to the zero-order kinetic model.

The explanation for this difference in the release kinetics between the blend and the single repellent compounds could most probably lie in the differences in the chemical dynamics of the two systems since the environmental conditions in the wind tunnel were held constant. Such dynamics are best described by Raoult's law. According to Raoult's law, the vapor pressure of a substance in equilibrium with a solution containing the substance is equal to the product of the mole fraction of

the substance in the solution and the vapor pressure of the pure substance at the temperature of the solution [16]. It follows that the vapor pressure of the mixed liquids will be dependent on the vapor pressures of the individual compounds and the molar fraction of each compound present [3]. However, in practice, introducing other factors like meniscus curvature, surface tension and diffusion coefficient, which are not precisely known at any one particular instance, introduces complications as some researchers have previously reported [17- 21]. Thus, the observed decline in the release rates of the individual compounds with time can be attributed to the vapor pressure in the dispensers becoming diminished as the amount of the chemical compound decreases. This causes a reduction in the vapor pressure deficit between that inside the dispenser and the external atmosphere (wind tunnel environment), thus affecting the diffusion of the individual compounds [4].

Table 4 shows the average mass loss of the individual compounds and the blend in the wind tunnel.

Another interesting feature following close scrutiny of separate first-order model plots corresponding to all the individual compounds (omitted herein for reasons of brevity, except for pentanoic acid shown in Figure 4a) indicates that the data point corresponding to day 1 in all the plots appear to be consistently higher or above the regression lines drawn. This appears to create the illusion of an upward curvature around this point.

This apparent initial deviation from the linear trend exhibited by the rest of the data points has also been previously observed and reported by other workers [22] who attributed it to non-equilibrium status of the system during day 1 of the experiments. Incidentally, when this data point corresponding to day 1 is omitted, a much higher R^2 value of 0.9987 is obtained as shown in the near-perfect linear profile of Figure 4b and all the plots still show consistency with first-order release kinetics. From these findings, it can be concluded that the release of these compounds individually from the Tygon tubing follows first-order kinetics which is consistent with a Fickian diffusion model [14]. This is because the concentration within the diffusion volume (the dispenser) changes with respect to time, thus obeying Fick's law of diffusion [15].

Release Kinetics Studies of Individual Repellent Compounds under Semi-Field Conditions: The experimental mass loss data for individual compounds exposed to direct sunlight and under the shade was fitted to the zero-, first- and second-order kinetic

Table 4: Average mass loss (\pm SD) of the individual compounds and the blend in the wind tunnel using 2.0cm tygon silicon tubing (n = 3)

Compound	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Pentanoic acid	0.277 \pm 0.077	0.249 \pm 0.037	0.272 \pm 0.041	0.266 \pm 0.012	0.237 \pm 0.045	0.253 \pm 0.075	0.201 \pm 0.009
Hexanoic acid	0.114 \pm 0.007	0.112 \pm 0.035	0.088 \pm 0.027	0.056 \pm 0.012	0.067 \pm 0.020	0.076 \pm 0.018	0.063 \pm 0.012
Heptanoic acid	0.092 \pm 0.008	0.086 \pm 0.019	0.071 \pm 0.024	0.051 \pm 0.016	0.050 \pm 0.032	0.044 \pm 0.009	0.042 \pm 0.008
2-Undecanone	0.161 \pm 0.029	0.160 \pm 0.034	0.137 \pm 0.018	0.090 \pm 0.058	0.076 \pm 0.031	0.062 \pm 0.009	0.076 \pm 0.021
Geranyl-acetone	0.043 \pm 0.024	0.031 \pm 0.005	0.035 \pm 0.019	0.034 \pm 0.007	0.033 \pm 0.006	0.032 \pm 0.017	0.033 \pm 0.004
δ - Octalactone	0.174 \pm 0.079	0.081 \pm 0.022	0.056 \pm 0.016	0.025 \pm 0.007	0.019 \pm 0.004	0.035 \pm 0.012	0.028 \pm 0.021
Guaiacol	0.233 \pm 0.089	0.206 \pm 0.008	0.161 \pm 0.019	0.151 \pm 0.004	0.149 \pm 0.012	0.143 \pm 0.009	0.142 \pm 0.009
Blend	0.097 \pm 0.014	0.070 \pm 0.001	0.072 \pm 0.006	0.072 \pm 0.005	0.085 \pm 0.016	0.064 \pm 0.012	0.073 \pm 0.007

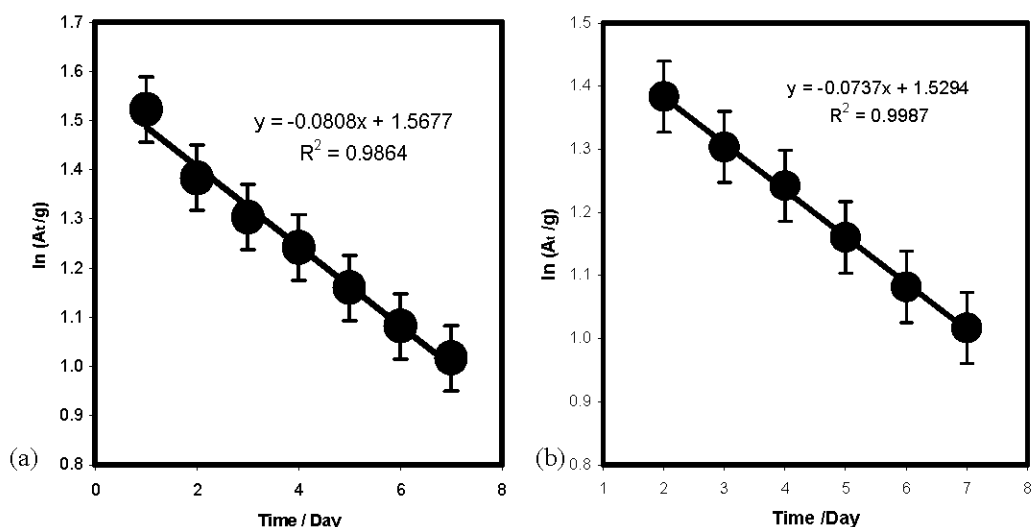


Fig. 4a: Release kinetics of pentanoic acid under laboratory conditions as described by the first-order rate equation

Fig. 4b: Release kinetics of pentanoic acid under laboratory conditions as described by the first-order rate equation but with Day 1 data omitted

models and the release kinetics of the compounds determined. The results are summarized in Table 5. Pentanoic, hexanoic and heptanoic acids, δ -octalactone, 2-undecanone and geranylacetone were found to follow zero-order kinetics under both the sun and the shade. The carboxylic acids (i.e., pentanoic, hexanoic and heptanoic acid) registered the highest zero-order rate constants compared to the ketones (i.e., δ -octalactone and geranylacetone) with pentanoic acid showing the highest rate constants of 0.8841 and 0.6554 g day⁻¹ under the sun and shade, respectively; followed by hexanoic acid with 0.3985 and 0.269 g day⁻¹ under the sun and shade, respectively; and heptanoic acid with 0.1726 and 0.1625g day⁻¹ under the sun and shade, respectively.

Geranylacetone yielded rate constants of 0.156 and 0.0775 g day⁻¹ under the sun and shade, respectively while δ -octalactone had 0.0795 and 0.0528 g day⁻¹ under the sun and shade, respectively. 2-Undecanone registered higher zero-order rate constants of 0.697 and 0.4172 g day⁻¹ under the sun and shade, respectively

compared to hexanoic and heptanoic acids, δ -octalactone and geranylacetone. Guaiacol however, behaved differently from the rest of the repellents and appears to follow first-order release kinetics in the semi field conditions.

Further scrutiny of the results also reveals that the zero-order release rate constants for the carboxylic acids seemed to decrease with increasing boiling points of the respective acids. For instance, whereas the boiling points of the carboxylic acids increase from pentanoic acid through hexanoic acid to heptanoic acid, the zero-order release rate constants determined under the sun appear to decrease from pentanoic acid (0.8441 g day⁻¹) through hexanoic acid (0.3958 g day⁻¹) to heptanoic acid (0.1726 g day⁻¹). This trend however, is not surprising considering the fact that vapor pressure is known to be inversely proportional to boiling point. The same argument however, does not seem to apply among the non-homologous compounds. For instance, whereas 2-undecanone and guaiacol have boiling points of

Table 5a: Correlation index values (R^2) and rate constants for Zero- and First-Order kinetic models used to describe the release of the individual repellent compounds under semi-field conditions using 4 cm length tygon silicon tubing

Compound	Zero-order Rate Model				First-order Rate Model			
	Sun		Shade		Sun		Shade	
	$k_0/\text{g day}^{-1}$	R^2	$k_0/\text{g day}^{-1}$	R^2	k_1/day^{-1}	R^2	k_1/day^{-1}	R^2
Pentanoic acid	0.8441	0.9925	0.6554	0.9982	0.3905	0.9782	0.2043	0.9907
Hexanoic acid	0.3958	0.9983	0.2690	0.9973	0.1003	0.9936	0.6110	0.9956
Heptanoic acid	0.1726	0.9990	0.1625	0.9986	0.0492	0.9986	0.0454	0.9965
δ - octalactone	0.0795	0.9945	0.0528	0.9960	0.0259	0.9936	0.0168	0.9957
Geranylacetone	0.1560	0.9982	0.0775	0.9981	0.0314	0.9978	0.0145	0.9976
2-undecanone	0.6970	0.9963	0.4172	0.9945	0.3117	0.9656	0.1518	0.9807
Guaiacol	0.2539	0.9952	0.2535	0.9956	0.0422	0.9995	0.0401	0.9981
Blend	0.1490	0.9997	0.2019	0.9996	0.0466	0.9976	0.0696	0.9951

Table 5b: Correlation index values (R^2) and rate constant for Second-Order kinetic model used to describe the release of the individual repellent compounds under semi-field conditions using 4 cm length tygon silicon tubing

Compound	Second-order Rate Model			
	Sun		Shade	
	$k_2/\text{g}^{-1} \text{day}^{-1}$	R^2	$k_2/\text{g}^{-1} \text{day}^{-1}$	R^2
Pentanoic acid	0.2150	0.8767	0.0688	0.9572
Hexanoic acid	0.0257	0.9820	0.0139	0.9914
Heptanoic acid	0.0140	0.9948	0.0132	0.9982
δ - octalactone	0.0080	0.9921	0.0050	0.9952
Geranylacetone	0.0060	0.9967	0.0027	0.9970
2-undecanone	0.2651	0.8254	0.0567	0.9530
Guaiacol	0.0061	0.9992	0.0064	0.9944
Blend	0.0147	0.9921	0.0240	0.9840

232°C and 205°C, respectively, their corresponding zero-order release rate constants are 0.697 and 0.254 g day⁻¹, respectively: A trend that is the reverse of that observed with the carboxylic acids.

It is significant to point out that, whereas in the laboratory experiments, data were collected under controlled conditions of temperature, relative humidity and wind speed, these parameters are however, expected to vary significantly under semi-field or field conditions and should therefore influence the release kinetics of the repellent chemicals. In fact, evidence of potential dependence of release rates on temperature can be seen from variations in the release rate constants obtained for the experiments conducted in the sun and under the shade (Table 5). It is clearly evident from the results of Table 5 that for all the compounds, the zero-order release rate constants determined under the shade are lower than the corresponding zero-order release rate constants for the same compounds in the sun. From the aforementioned, it became necessary to take the daily temperature recordings over the entire duration of the experiments conducted under semi-field or field conditions. The daily temperature recordings however,

showed huge variations, especially in the sun and the shade while variations in relative humidity were quite small.

In view of the large variations in daily temperature recordings, it is plausible that ambient air temperature would have a profound effect on mass loss of the repellents from the dispensers and should therefore be expected to cause significant changes in the measured mass loss values. This would therefore be expected to be reflected in the determined release rate constants. It is however, significant to note that even though the release rates are expected to be affected by the ambient temperature, the magnitude of the change is however more difficult to demonstrate with field data as has been previously reported by Holsten and co-workers [4]. In their study, Holsten and co-workers reported that release rates from two separate sites were not significantly different from each other, even though the average temperatures were significantly different. These workers attributed this to a compensatory phenomenon whereby partially compensating effects occur throughout the day [3].

Table 6: Average mass loss (\pm SD) of the blend in sun and shade under semi-field conditions using 2.0 and 4.0 cm lengths of tygon silicon tubing (n = 3)

Day	mass loss /g			
	4 cm Tygon Silicon Tubing		2 cm Tygon Silicon Tubing	
	Sun	Shade	Sun	Shade
1	0.107 \pm 0.001	0.095 \pm 0.009	0.073 \pm 0.006	0.058 \pm 0.006
2	0.136 \pm 0.009	0.101 \pm 0.009	0.065 \pm 0.009	0.052 \pm 0.009
3	0.129 \pm 0.006	0.097 \pm 0.012	0.061 \pm 0.006	0.051 \pm 0.003
4	0.139 \pm 0.009	0.104 \pm 0.006	0.061 \pm 0.009	0.050 \pm 0.003
5	0.131 \pm 0.009	0.105 \pm 0.006	0.056 \pm 0.009	0.045 \pm 0.003
6	0.118 \pm 0.003	0.111 \pm 0.036	0.051 \pm 0.003	0.046 \pm 0.009
7	0.142 \pm 0.003	0.090 \pm 0.006	0.049 \pm 0.006	0.0456 \pm 0.002

Determination of Release Kinetics of the Blend under Semi-field Conditions:

Release kinetics of the blend was determined under semi-field conditions using dispensers fitted with 4 cm and 2 cm tygon silicon tubing. The zero-order rate model best described the release kinetics of the blend as evidenced by the higher R^2 values compared to those obtained with first- and second-order rate models. In all cases examined, the determined zero-order release rate constants are found to be higher for the dispensers exposed to direct sunlight than those placed under the shade. This suggests that temperature is an important determinant in the release kinetics of the blend from the dispensers. This observation is true for both the 4.0 and the 2.0 cm length tygon tubings employed. It is also significant to note from Table 6 that the mass loss data associated with the 4.0cm tygon silicon tubing are nearly twice the values obtained with the 2.0cm tygon silicon tubing. This illustrates the importance of surface area of the dispenser unit on release rates as earlier demonstrated with the standard repellent, 2-methoxy-4-methyl phenol (Table 2).

For the 4 cm tygon tubing, the mass losses under the sun on days 4 and 7 are relatively larger compared to the losses recorded on the other days, even though the average daily temperature for the two days were not very different at $13.8 \pm 1.1^\circ\text{C}$ and $15.2 \pm 1.2^\circ\text{C}$, respectively (see Figures 5a and 5b): both lower than the highest average temperature which was recorded on day 5 at $16.6 \pm 1.1^\circ\text{C}$ (with a lower mass loss). As much as this may seem anomalous, similar findings have been reported previously. Holsten [4] reported that with field data, the magnitude of the effect of temperature on the release rates was more difficult to demonstrate, and they attributed this in part to non-uniform chemical release behavior under actual environmental conditions due to deterioration of the release device. Another possible reason could be due to systematic errors associated with the standard method

of determining the chemical load remaining in the dispensers by weighing the dispensers between periods of field exposures. The errors may occur when dust particles stick to the dispenser surface or due to mass differences caused by changes in relative humidity and rainfall. Still, since the release rate depends on factors like temperature and wind, this procedure inseparably measures the effects of these and other weather effects.

Nevertheless, it is expected that the vapor pressure and thus the mole percentage of the compounds in the vapor state would increase during daytime and more so under the sun than in the shade due to the effects of temperature. Thus, the observed differences in the release rates determined the sun and under shade conditions are therefore to be expected. Moreover, a compensatory effect has previously been reported [3] where a reverse effect that reduces the rate of release (e.g. lower temperature) occurs to counter an effect, which would otherwise increase the release rate due to higher temperatures. Under the semi-field conditions, temperatures varied as shown in Figures 5a and 5b whereas temperature was maintained constant under laboratory conditions. Byers [3] noted that variation in temperature could probably have effects of up to 100 % on the vapor pressures over the daily temperature range. Thus the difference in the release rates in the semi field or the field can be explained by temperature differences [4]. Olsson and co-workers [23] have also suggested that the longer the chain length of the compound, the greater the dependence of the release of a compound (from a release device) on temperature. However, results of the mass analysis and by extension the release rates indicates that the mass losses between the days are not significant, but the mass differences between the dispensers are significant. Mass losses with the dispensers fitted with 4 cm of the tubing are nearly twice those fitted with 2 cm tubing.

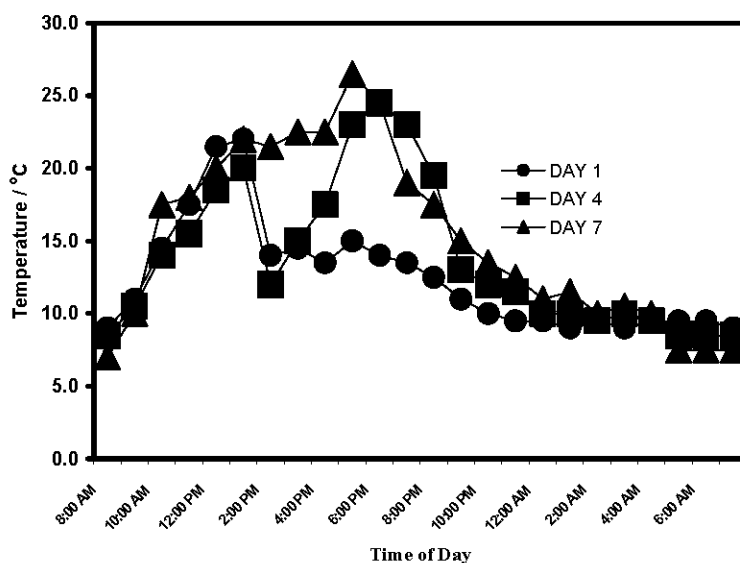


Fig. 5a: Temperature profiles for days 1, 4 and 7 under the sun

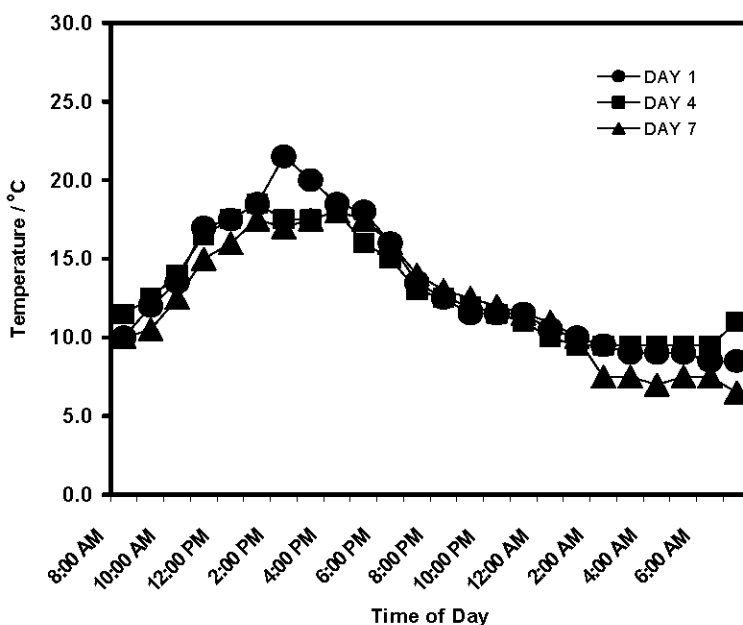


Fig. 5b: Temperature profiles for days 1, 4 and 7 under the shade

CONCLUSION

Under laboratory conditions, the release of the individual compounds followed first-order kinetics while that of the blend followed zero-order kinetics. In the semi field, the individual compounds dispensed singly also followed first-order release kinetics while the blend of the compounds followed zero-order release kinetics. The release of the individual components of the blend-mixture followed zero-order kinetics under semi-field conditions contrary to the behavior exhibited by the individual

components dispensed singly. The zero-order rate constants follow a trend (either increasing or decreasing) among homologous compounds (i.e. carboxylic acids and ketones), an observation that was not made among non-homologous compounds. The results indicate that temperature is a major determinant in the release rates since it affects the rate at which the compounds volatilize, thereby affecting their rates of diffusion. However, it is evident that the release rates, more so in the field, were not a simple function of temperature since the release rates at higher temperatures were consistently less than

was expected. It is plausible to conclude that the compounds in the blend interact with each other to affect the rate at which they volatilize and diffuse from the tygon tubing. Based on the results obtained in this study, the aluminum/silicon tubing dispenser can be used to dispense the tsetse allomone blend at zero-order kinetics in the field.

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