

A Model for the Controlled Release of Tri-*n*-Butyltin Fluoride from Polymeric Molluscicides and Mosquito Larvicides

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Synopsis

Tri-*n*-butyltin fluoride (TBTF) is used as a controlled release mosquito larvicide and molluscicide. The Ecopro 1370, which was used in this work, is a commercially available larvicide containing 20% TBTF in low density polyethylene. The larvicide has a theoretical life of 3.7 years. The release mechanism was studied in water and yields a strange type IB release curve with an initial peak after 10 days, a minimum release at 13 days, and steady state release after 24 days. The strange release curve is due to the initial release of TBTF from the surface of the formation. The release is inhibited as water diffuses into the matrix where it reacts with the TBTF to form immobile tri-*n*-butyltin hydroxide. The latter dehydrates to bis(tri-*n*-butyltin) oxide which diffuses into the aqueous layer to yield the steady state system. A model containing three reaction zones can be used to explain these phenomena.

INTRODUCTION

The use of tri-*n*-butyltin fluoride (TBTF) and bis(tri-*n*-butyltin) oxide (TBTO) as a controlled release mosquito larvicide, a molluscicide, and as an antifouling agent has been frequently reported in the literature.¹⁻⁵ Although only two formulations [BioMet-SRM® (registered trademark; M & T Chemicals, Rahway, N.J.) and Ecopro 1370® (registered trademark; Environmental Chemicals, Barrington, Ill.)] are in commercial production, the pesticide potential has been repeatedly demonstrated in the field.^{6,7} The formulations appear to be environmentally safe.

The TBTF hydrolyzes to tri-*n*-butyltin hydroxide [TBT(OH)] with a half-life of about 9 days, the TBT(OH) degrades into bis(tri-*n*-butyltin) oxide (TBTO) with a half-life of about 4 days, and the TBTO degrades into dibutyltin compounds with a half-life of about 15 days.^{3,8} TBTF, TBT(OH), and TBTO possess high bioactivity, whereas the dibutyltin degradation products are either inactive or of low activity. In water TBTF and its degradation products have an active life of less than 30 days; however, when manufactured into a controlled release formulation (CRF), they exhibit toxicity towards the target vectors for more than 3 years.^{3,9} Ecopro 1370, which contains 20% TBTF in low density polyethylene, is a CRF currently being tested as a larvicidal agent.

EXPERIMENTAL

The samples of Ecopro 1370 (approximately 0.150 g) were dispersed in 1.000 L of distilled water. The samples were mixed and allowed to set quiescently at

TABLE I
 Ecopro 1370 (20% TBTF) Release Rate in Distilled Water^a

Days	μg of TBTF in 25.0 mL aliquot	Accumulative % of bioactive material released from the samples	$\sqrt{\text{Days}}$
1	2.10 ± 0.52	$0.28 \pm 0.07\%$	1
3	3.14 ± 0.47	$0.71 \pm 0.16\%$	1.73
7	5.32 ± 0.26	$1.41 \pm 0.20\%$	2.65
10	5.65 ± 0.61	$2.17 \pm 0.27\%$	3.16
13	2.98 ± 0.41	$2.56 \pm 0.32\%$	3.61
17	5.38 ± 0.38	$3.28 \pm 0.37\%$	4.12
24	7.82 ± 0.29	$4.32 \pm 0.40\%$	4.90
38	7.23 ± 0.51	$5.28 \pm 0.46\%$	6.17
61	7.67 ± 0.74	$6.31 \pm 0.56\%$	7.81
93	6.94 ± 0.34	$7.23 \pm 0.60\%$	9.64

^a 0.150 ± 0.005 g Sample in 1.000 L of H₂O.

ambient conditions ($21 \pm 3^\circ$ and 740 ± 15 torr) for 24 h. The solution is mixed, the Ecopro 1370 is allowed to settle, and a 25.0-mL aliquot was transferred to a 250 mL separatory funnel. The remaining solution was withdrawn and discarded. The Ecopro 1370 sample was redispersed in 1.000 L of distilled water and allowed to set at ambient conditions until day 3. The separation was repeated on days 3, 7, 10, 17, 24, 38, 61, and 93 as previously described.¹⁰

The 25.0-mL sample was immediately extracted with three 10.0-mL aliquots

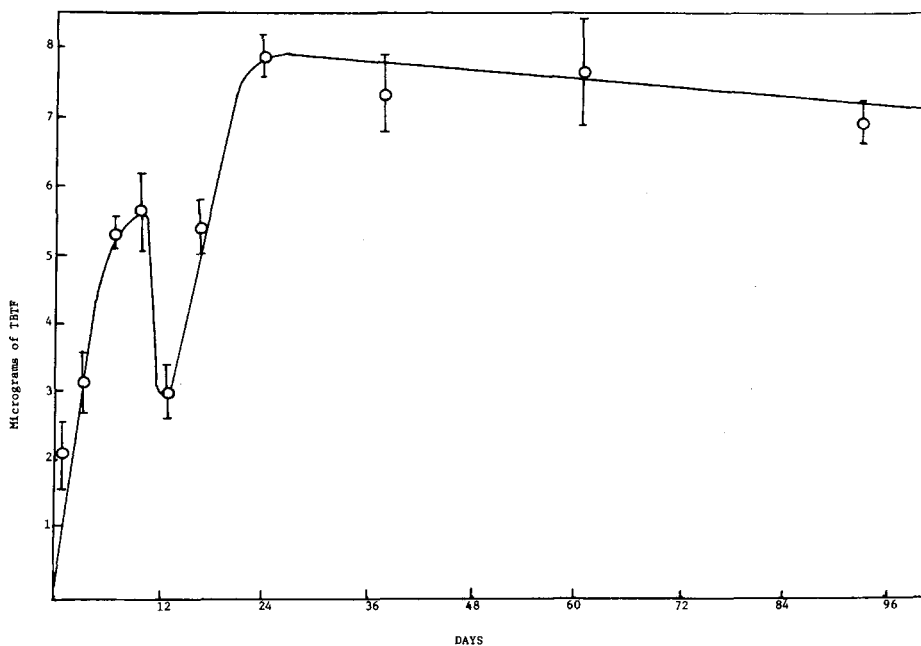


Fig. 1. μg of TBTF emission from 0.1500 g Ecopro 1370 vs. days of exposure to 1.000 L of distilled water. Analysis of 25.00 mL aliquots.

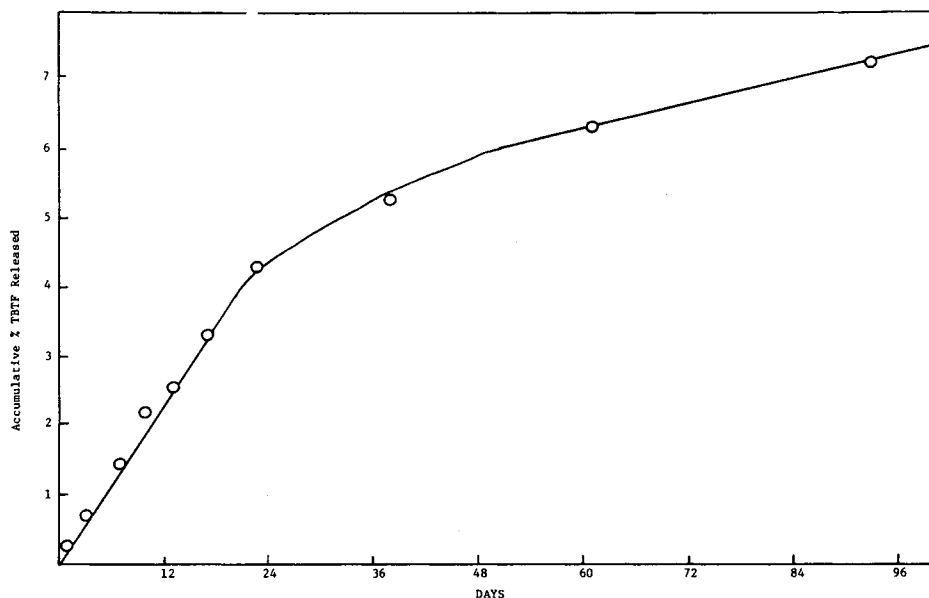


Fig. 2. Accumulative % of TBTF released from 0.1500 g of Ecopro 1370 into 1.000 L of water over 93 days.

of hexane and analyzed for organotins by the phenylfluorone method,^{3,11} using TBTF (38.4% Sn) (C.A. reg # 1983-20-4) for the calibration curve. The quantity of TBTF recovered for each day is given in Table I.

RESULTS

When the quantity of TBTF released from the Ecopro 1370 formulation is plotted vs. days (Fig. 1), a rather strange curve is obtained. The release system is observed with all TBTF formulations prepared with a polyethylene, rubber, or silicone resins matrix. If only the data after day 10 is considered, the data fits into a classical type IA release curve.¹² When a plot of accumulated % vs. days is plotted, a smooth curve is produced (Fig. 2). This does not fit into any of the normal simple release schemes.¹² When a plot of accumulated % vs. $t^{1/2}$ is prepared (Fig. 3), an S-shape curve results, which indicates the emission system is not a classical diffusion controlled release system (type II A).¹² As can be expected, the release data for TBTF cannot be explained by diffusion-controlled equations.¹³ Several attempts have been made to develop mathematical models for tributyltin compounds,^{14,15} but these models exhibit a poor fit when compared to the experimental data because they ignore the contribution of the degradation products to the system.

If the two values at 13 and 17 days are ignored, the emission rate curve for the Ecopro 1370 fits a type IB release system (Fig. 1)¹² with a concentration limitation of about $0.3 \mu\text{g/mL}$ (300 ppb). However, the concentration dip between 10 and 20 days is real and has been observed with all TBTF formulations regardless of the matrix composition. The release mechanism, which is observed with Ecopro

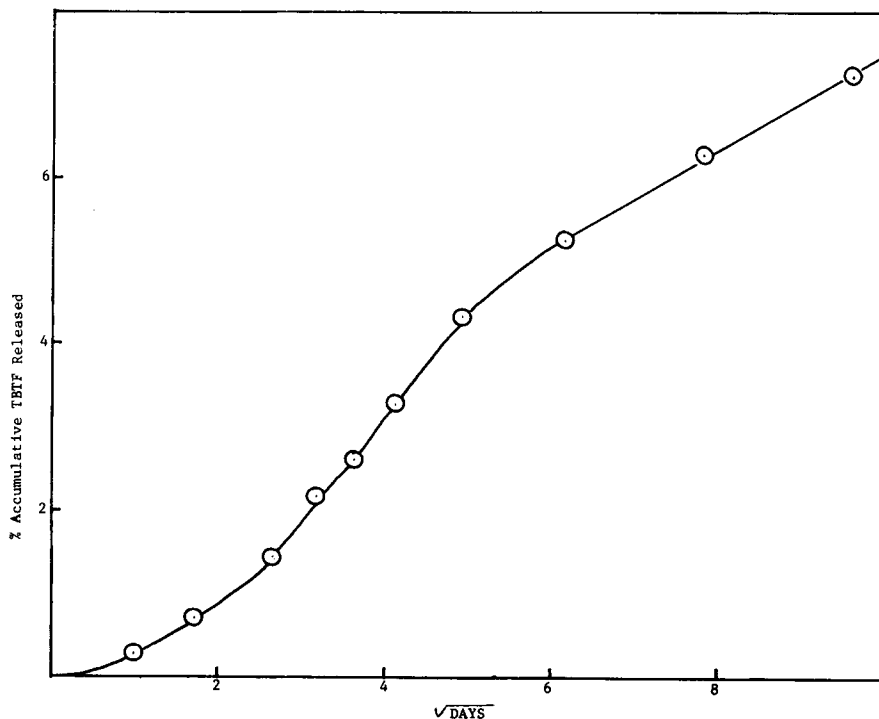


Fig. 3. Accumulative % of TBTF released from Ecopro 1370 vs. $t^{1/2}$.

1370, can be schematically seen when the time scale for the first 25 days is expanded (Fig. 4). Seven points have been selected along the time-concentration axis and designated $t_1, t_2, t_3, \dots, t_7$. These arbitrary points were selected in order to explain the change in chemistry or release mechanism whenever a change appears to be evident. The strange release values observed at time t_4, t_5 , and t_6 indicates either a change in the release mechanism or a change in chemical diffusibility. Since no evidence of bioerodibility, mechanical erodiability, or other release mechanism could be observed, the strange emission curve must be due to a change in the TBTF itself.

Ecopro 1370 appears to exhibit three release systems as illustrated by points at times t_2, t_4 , and t_6 in Figure 4. If this assumption is made, a model can be logically constructed establishing the diffusion zone for the CRF, as represented in Figure 5. The model is presented as dimensional zones for visual simplicity not as an area where the reactions take place. The heterogeneous boundary between the CRF and the solvent is represented by the solid line on the right. Zone I corresponds to the surface and immediate volume behind the surface; the portion of the CRF where classical diffusion processes control the release of the bioactive material. Zone II is portion of the CRF where chemical kinetics of TBTF degradation effect the release of bioactive material. Zone III is the portion of the CRF where the original concentration of TBTF has exhibited little change due to either diffusion into the solvent or degradation to daughter compounds.

Using the model the diffusion of TBTF from zone I into the solvent will account for the organotin concentration observed at times t_1, t_2 , and t_3 and gives

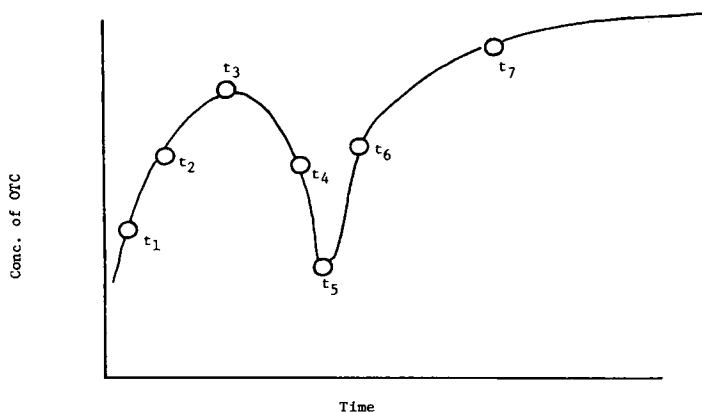


Fig. 4. An expanded scale model for release of TBTF from 0 to 25 days. $t_1 \dots t_7$ are arbitrary times when an apparent change in the release mechanism of the organotin biostine material has occurred.

Time	Bioactive material	Zone
t_1	TBTF	Surface
t_2	TBTF	1
t_3	TBTF; max diffusion	1
t_4	TBTF reacts with water	1
t_5	TBTF totally reacts with water residue in solution	1, 2
t_6	TBTO begins to diffuse into solution	2
t_7	TBTF diffuses into reaction zones	3

rise to the initial TBTF concentration during the early exposure of the formulation to the solvent; as zone I is depleted of TBTF, the concentration of TBTF decreases, as exhibited at times t_4 and t_5 . Throughout this time, water is diffusing into the CRF and reacts with the TBTF in zone II to form TBT(OH),

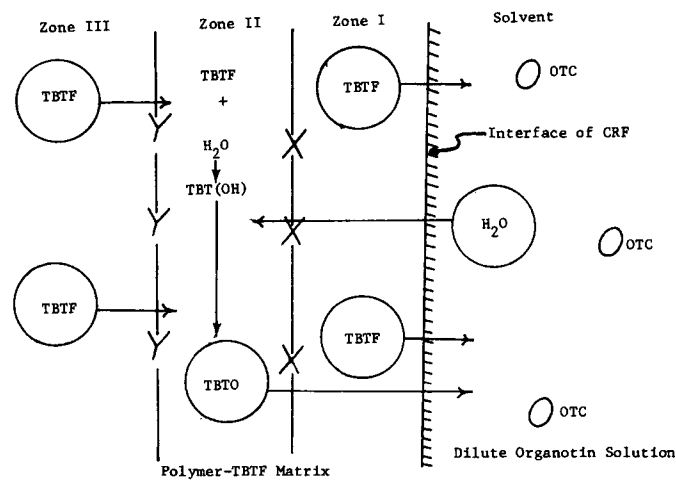


Fig. 5. A reaction zone model to represent the reaction zone and release of the bioactive material from Ecopro 1370.

TABLE II
Mechanisms Controlling the Release of TBTF from ECOPRO 1370

Process		Reaction Time
TBTF	Out	t_1^a
H ₂ O	In	t_2^a
TBTF	TBT (OH)	t_3
TBT (OH)	Out (negligible)	t_4
TBT (OH)	TBTO	t_5
TBTO	Out	t_6^a
TBTF	Reaction zone	t_7

^a Processes which effect the organotin concentration in the solvent.

which is immobile in the matrix.¹ The TBT(OH) dehydrates to TBTO; the latter is soluble in the matrix and diffuses through zone I into the solvent. As the concentration of TBTO increases in the matrix, the rate of release for the organotin increases, as exhibited at times t_6 and t_7 . Zone III depicts the portion of the CRF where the TBTF retains its original composition. The TBTF diffuses from zone III into zone II, where it reacts with water. A steady state system is achieved, and the concentration of organotin compounds in the solvent approaches a limiting value. The resulting graphical plot after 24 days (Fig. 1) appears to be a type 1B release system.¹²

Therefore, if diffusion is assumed to be the only mass transfer mechanism, the four mechanisms controlling emission become:

Mechanism	Reaction zone	
TBTF diffusion into the solvent	zone I reaction	(1)
H ₂ O diffusion into the matrix	zone II reaction	(2)
TBTO diffusion into the solvent	zone I, II reactions	(3)
TBTF diffusion into reaction zone	zone III reaction	(4)

Seven processes are identifiable with the CRF release curve (Fig. 4). Process 1 (time = t_1) is the dissolution of TBTF from the surface of the Ecopro 1370 formulation. As water diffuses into the matrix, a dynamic diffusion system is established in zone I and the TBTF release increases (time = t_2, t_3). At time t_3 sufficient water has diffused into the matrix to react with the TBTF to inhibit its flow to the surface. At time = t_4 and t_5 very little TBTF is being released and the majority of the organotin in zone II has been converted to immobile TBT(OH). However, the TBT(OH) spontaneously dehydrate to TBTO which diffuses through zone I to the surface where it is released into the solvent (time = t_5, t_6). As the quantity of TBTO increases in zone II, the quantity of organotin increases in the solvent. At time = t_7 the CRF has attained a dynamic equilibrium with the system, and the quantity of organotin is dependent upon the diffusion of TBTF from zone III into zone II and the subsequent diffusion of TBTO into the solvent. A summary of the processes is given in Table II.

Fortunately, only process 1, 2, and 6 effect the actual release of organotin compounds from the CRF. The diffusion of TBTF into the solution (t_1) yields the initial rise in TBTF concentration, the diffusion of water into the matrix causes the decrease in TBTF concentration (t_2), and the diffusion of TBTO from the matrix (t_6) yields the steady state conditions.

CONCLUSION

The emission of TBTF from the ECOPRO 1370 formulation is not a simple process and involves many physical chemical parameters, although diffusion is the primary phenomena. Because of the large number of variables and the interdependence of the various release processes, theoretical calculations on the release system were too imprecise to be useful.

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