Evaluation of Polymer Film Enclosures as Protective Barriers for Commodities from Exposure to Structural Fumigants

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Internal concentrations (IC's) of sulfuryl fluoride (SF) or methyl bromide (MB) were quantified by gas chromatography in eight types of sealed polymer film bags that were externally fumigated for 20 h at 22 °C. Of the five closure methods evaluated (knot, twist-tie, tape, Ziploc, heat-seal) for single polyethylene bags, only slight differences in IC values were observed when bags were exposed to SF at 692 mg·h/L. Increases in the ratio of internal air volume to bag surface area resulted in a pronounced nonlinear reduction of IC for SF in single, heat-sealed polyethylene bags exposed to 676 mg·h/L. Optimum protection for each film type occurred in double-bagged enclosures (vs single), and nylon film bags had consistently lower IC's (0.041–484 ppm) than all other film types for the three SF exposures (96.9, 677, 6872 mg·h/L) tested. Exposure of double-bag enclosures to MB at 683 mg·h/L also demonstrated that MB permeation was highly variable between film types. In double-enclosure experiments, polyethylene films afforded the poorest protection against permeation (as low as 64.8 and 93.0%), while nylon polymers gave the best protection (up to 99.98 and 99.997%) for MB and SF, respectively, at comparable exposures.

Sulfuryl fluoride (SF) and methyl bromide (MB) are the only fumigants currently registered in the United States for control of pests in habitable structures. The primary target species for these fumigants are drywood termites (Isoptera: Kalotermitidae), which abound in the southern regions of the United States. In Florida alone, drywood termites accounted for over 40 000 fumigations in 1987 (Scheffrahn et al., 1988). Fumigation requires that the entire exterior of the structure be enclosed in tarpaulins or sealed with plastic film and tape at points where the fumigant might readily escape. All contents within the seal, therefore, are exposed to the fumigant as soon as the gas is dispersed into the building.

Exposure of unprotected commodities to SF may result in (1) adsorption of the parent compound during fumigation followed by initial rapid desorption after fumigation (Scheffrahn et al., 1987a; Osbrink et al., 1988) and/or (2) formation of permanent ionic residues of fluoride, a toxicologically significant product, and sulfate (Scheffrahn et al., 1989a). Currently, the SF label requires that unprotected commodities (i.e., not sealed in highly resistant containers such as glass, metal, or plastic) must be removed from the fumigation site or be sealed in polyethylene bags of at least 4-mil thickness or equivalent (two 2-mil bags). Plastic bags, conceivably, are an effective, practical, and economical means of protecting foodstuffs, medicines, dietary supplements, chemicals, and other reactive or sorptive commodities from exposure to SF during structural fumigation. Transient residues of SF from commodities sealed in two 0.051-mm (2-mil) thick polyethylene bags were reduced to approximately 3% or less of the residues in unprotected commodities after 20-h exposure to SF at 27 °C (Osbrink et al., 1988). Plastic bags, therefore, offer the convenience of storing foods in situ (i.e., kitchen cabinets, counters, refrigerators, freezers, etc.) during a fumigation while keeping SF exposure (and residues) to a minimum. No data are available on the performance of different types of plastic bags in protecting commodities from MB exposure. Currently, one MB manufacturer (Great Lakes Chemical Co.) requires that all unprotected commodities (bagged items included) be removed from a fumigation site. In this case, certain polymer film bags might be well-suited as practical alternative containment barriers.

This study was conducted to evaluate methods of bag closure, determine the effect of trapped air volume on internal SF concentrations, and quantify the performance of eight selected polymer film enclosures (bags) against penetration by SF and MB.

MATERIALS AND METHODS

Note: Sulfuryl fluoride and methyl bromide are colorless and odorless gases at concentrations harmful or lethal to humans and must be handled with extreme caution by certified personnel.

Bag Preparation. Enclosures made from polymer films listed in Table I were procured from retail outlets, distributors, or manufacturers. A silicone/Teflon septum (Supelco 2-3244, 20-mm diameter) was glued silicone side down to the bottom outer surface of each deflated bag with Conbond 985 contact cement (Columbia Cement Co., Freeport, NY). After the cement dried overnight, an 18-mm-diameter plastic vial cap was inserted at the bottom near the septum before the bag was sealed with one of the prescribed closure methods below. The total surface area of each bag was calculated by multiplying the length from the closure zone to the bottom edge by the bag width and then multiplying the resultant area by 2. Bag surface area was measured to calculate the volume needed to attain a predetermined surface area to volume ratio that would be constant for each bag. The bags were filled with air from a 20-gauge syringe needle joined by tubing in series to a micrometering valve (Whitey SS-21RS2), a flow meter (Manostat 36-541-125), and a 275-kPa pressure-regulated air cylinder. Once a predetermined flow rate of air from the needle was established, the bag septum was pierced for a calculated time period to yield the desired volume of air inside the sealed bag.

In double-bag experiments, the inner bag was prepared as above and placed into an identical second bag with the septum in a position corresponding to that of the inner bag. For nontransparent films (E and H), a 25-mm cap was placed in the

0021-8561/90/1438-0904$02.50/0

Table I. List of Selected Film Enclosures Evaluated as Fumigant Barriers

type code	manufacturer	trade name, bag use	$W \times L$, cm	thickness, mm	ply	polymer[a]
A	Dow Chemical Co.	Ziploc, food storage	33 × 38	0.051	1	LDPE
B	First Brands Corp.	Glad-lock, food storage	27 × 28	0.044	1	LDPE
C	Reynolds Metals Co.	Reynolds, oven cooking	36 × 51	0.019	2	NYL 6/NYL 66
D	Soil Chemicals Corp. Products	Fumebags, MB barrier	61 × 93	0.025		(NYL)[b]
E	First Brands Corp.	Glad Handle-Tie, kitchen	61 × 71	0.026	3	LDPE
F	Dow Chemical Co.; Marketing International, Inc.	Saranex 15 Ziploc, tissue sample	29 × 30	0.076	5	LDPE/EVA/Saran/EVA/LDPE
G[c]	Dow Chemical Co.	Nylopac, Dow experimental	33 × 40	0.051	4	HDPE/EAA/NYL/EAA
H	Mobile Chemical Co.	Hefty, trash	76 × 91	0.033	2	LDPE

[a] Key: LDPE = low-density polyethylene (PE); HDPE = high-density PE; NYL = nylon (polyamide/caprolactam); Saran = poly(vinylidene chloride)/poly(vinyl chloride) copolymer; EAA = ethyleneacrylic acid/PE copolymer; EVA = ethylene vinylacetate. [b] Proprietary nylon polymer. [c] Bags of this film were made by folding 35.6 × 80 cm sheets in half and heat-sealing the resultant 40-cm sides.

inner bag to identify it from the outer bag by touch. The outer bag was sealed by the same closure method as the inner bag. The vial caps acted as protective support backings over which the septa and/or outer film layers could be stretched to ensure that the filling, evacuation, or sampling needles would only pierce the film layer adhered to the septum. Air trapped between the two bags was evacuated by piercing the outer bag septum with a syringe needle attached by tubing to the vacuum end of a hand pump. Once the air between the bags was purged, the space was refilled to 0.2 cm^3 of air/cm^2 outer bag surface area. This rate of fill provided only an average 2-mm-wide air gap between layers. Bags for each fumigation were randomly clamped to the rims of four laundry baskets. Nylon monofilament line was strung 4 cm above the bottom of each basket in ca. 9-cm rows to ensure that the bottoms of bags were suspended above the basket floor during fumigation.

Fumigation. The floor of a 4.217-m^3 fumigation chamber (Scheffrahn et al., 1987b) was lined with tissue cover material to protect larger bags from sharp surfaces. The baskets were placed on the chamber floor, and larger bags (D, E, and H, Table I) were draped over the outside of each blanket to ensure that bags would not contact each other and would be freely exposed from all sides by fumigant. All test bags were fumigated under constant air circulation for 20 h at 22 ± 1 °C by the procedure of Scheffrahn et al. (1987b). Fumigation with MB required the following modifications to this procedure: no pressure regulator on the MB delivery cylinder and glass 250-mL gas sampling tubes instead of polypropylene. Chamber atmosphere was sampled in triplicate at ca. 5 min and 19.9 h after fumigant introduction. Chamber air samples (0.5 mL) from gas sample tubes were analyzed for SF or MB concentrations by the gas chromatographic (GC) method below. Both SF (Vikane; Dow Chemical Co.; 99.08%; 4.17 mg/mL) and MB (Meth-O-Gas; Great Lakes Chemical Co.; 100%; 3.874 mg/mL) were of commercial grade.

Postfumigation Analyses of Bag Airspace. Immediately after fumigation, bags were removed from the evacuated chamber and transported to the laboratory. Sample for analysis of terminal SF or MB concentrations inside bags were obtained by piercing the septum (for single bags) or the outer film and inner-bag septum (for double bags) with a 1-mL syringe (Tuberculin, B-D) and removing a 0.5-cm^3 volume for GC injection. For the closure method and fill ratio comparisons, bags were selected in random sequence for GC analysis. For the film evaluations, the bags were analyzed in order starting from the highest to lowest internal concentrations of fumigant for the first fumigation and from lowest to highest for the second fumigation for each combination of external accumulated exposure (ECT; external concentration × time), condition (s, single; d, double), and fumigant.

SF or MB analyses were performed on an HP 5890A GC instrument fitted with two 2.5 m × 2 mm (i.d.) glass columns packed with 80–100-mesh Chromosorb 101 (Alltech Associates, Inc). Low fumigant concentrations were measured with a linearized ^{63}Ni electron capture detector (ECD) with argon–methane (95:5) as carrier gas. Chamber and bag concentrations above ca. 280 ppm were determined with a thermal conductivity detector (TCD) with helium as the carrier. Isothermal oven temperatures of 50 °C for SF and 100 °C for MB at carrier flows of 20 mL/min eluted well-resolved fumigant peaks in ca. 2 or 7 min, respectively. Peaks from atmospheric gases and water vapor were characteristic to all chromatograms. Detector responses were integrated with a Spectra-Physics 4290 computing integrator.

Before each day's analysis, standards were prepared from neat SF or MB by serial dilution with gas syringe into 120-mL serum bottles that were crimp-sealed with the septa (Teflon side down) used on bags. Linear regression of ECD response to five continuous ranges of standards was required to encompass the wide range of concentrations analyzed. Peak areas were quantified by comparison with the appropriate standard response curve selected from integrator memory. SF chamber samples obtained from fumigations where a concentration of 360 mg/L was targeted were diluted 10-fold in serum bottles before analysis.

Closure Method. Single type A bags (Table I), filled with air to 1.0 cm^3/cm^2, were sealed by the following methods: (K) one half-hitch knot; (T) open end of bag twisted thrice to form a neck, bent 180° on itself, and secured with a wire twist-tie; (M) as T, but secured with 15 cm of 2.5-cm-wide masking tape; (Z) Ziploc closure used intact; (H) heat-sealed to form a melted seam with an impulse filament sealer (Clamco Corp., Cleveland, OH). Four bags of each closure type (20 bags total) were exposed to an initial target concentration of 36 mg/L SF during a single fumigation. Terminal internal concentrations (IC's) of SF (ppm, v/v) were statistically analyzed with the general linear models (GLM) procedure (SAS, 1987). Means were separated at $P = 0.05$ by the Student–Newman–Kuels test (SAS, 1987).

Fill (Surface to Volume) Ratio. Single type-A bags were heat-sealed on three sides (1 cm inside manufactured heat-seals) and filled to 0.5, 1.0, 1.5, 2.0, or 3.0 cm^3/cm^2. Four bags of each fill ratio (20 bags total) were exposed to an initial target concentration of 36 mg/L SF during a single fumigation. Data were analyzed by Sigmaplot regression procedure (Jandel Scientific, 1987) to calculate a polynomial equation for the relationship of IC's to fill ratio and to plot data.

Comparison of Single- and Double-Layered Polymer Film Types after SF Exposure. Three enclosures of each film type (Table I) were filled at 1.0 cm^3/cm^2 and exposed to initial target concentrations of either 5.4, 36, or 360 mg/L corresponding respectively, to ca. 1.5, 10, and 100 times the field rate for drywood termite control (Dow, 1988). Bag types A, B, and F were sealed with existing Ziploc-type closures. All other bags were sealed by method T. Fumigations at each target concentration were duplicated for a total of six fumigations. Two intact replicates of each bag type (a third was retained as back-up in case of accidental puncture) were selected for analysis after each fumigation for a total of 16 bags/fumigation. The same procedure was followed in double-bag experiments for an additional six fumigations. IC's of SF (ppm, v/v) were transformed to log (ppm + 1) values and analyzed for significant differences in means by the GLM procedure (SAS, 1987) using an 8 × 3 × 2 factorial design with bags, exposure levels, and single or double condition as the independent variables. Means of transformed data within each variable were separated at $P = 0.05$ by the Student–Newman–Kuels test (SAS, 1987).

Comparison of Double-Layered Polymer Film Types after MB Exposure. Three replicates of each of the eight polymer type enclosures were double-bagged as above and exposed to

Table II. Mean Internal Terminal Concentration (IC) of Sulfuryl Fluoride (ppm ± SD, $n = 4$), Internal Accumulated Exposure (ICT), and Percent Protection of Single 2-Mil-Thick Polyethylene Type A Bags Sealed on One Side by Selected Closure Methods after External Accumulated Exposure (ECT) of 692 mg·h/L (165 954 ppm·h) of SF

closure[a] type	IC,[b] ppm	ICT,[c] ppm·h	% protectn[d]
Ziploc	605 ± 35.4 a	6052	96.4
masking tape	577 ± 26.5 ab	5766	96.5
knot	533 ± 63.0 ab	5334	96.8
heat-seal	513 ± 60.5 b	5132	96.9
twist-tie	504 ± 9.80 b	5035	97.0

[a] Ziploc closure removed from bags before sealing by other methods. [b] Means followed by same letter in columns not significantly different with Student-Newman-Kuels test at $P = 0.05$. [c] Assuming a linear penetration rate, ICT = IC × 10. [d] Percent protection = 1 − [ICT/ECT] × 100%.

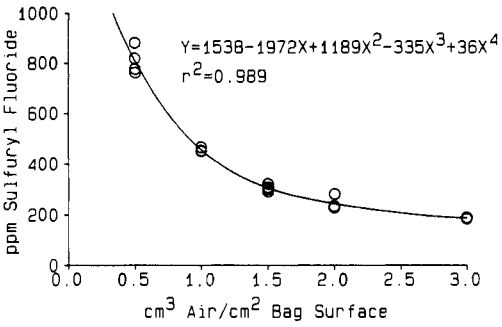

Figure 1. Internal terminal sulfuryl fluoride concentrations (ppm) in single 2-mil-thick polyethylene type A bags versus the ratio of internal air volume to bag surface area (fill ratio) after external accumulated exposure of 676 mg·h/L of sulfuryl fluoride.

an initial target concentration of 36 mg/L of MB. Two intact replicates of each bag type were selected for analysis after each of two fumigations. IC's of MB (ppm, v/v) were transformed to log (ppm + 1) values and analyzed for significant differences in means by the GLM procedure (SAS, 1987), and bag means were separated at $P = 0.05$ by the Student–Newman–Kuels test (SAS, 1987).

RESULTS AND DISCUSSION

Closure Method. Although mean IC's of SF were within 17% of each other for all closure methods tested with the 0.051-mm-thick polyethylene bags, the Ziploc closure allowed significantly more leakage and/or diffusive penetration than the heat-sealed or twist-tied bags (Table II). The mean SF external concentration (EC) during this exposure was 34.6 mg/L, or an external accumulated exposure of 692 mg·h/L (165 954 ppm·h). If the assumption is followed that penetration and/or leakage of SF through the film is constant over the exposure period and that the IC does not exceed EC/2, the mean internal accumulated exposure (ICT; internal concentration × time) would equal [IC (ppm) × time (h)]/2, or ICT = IC × 10 h. From the ICT and ECT values, the time-weighted percent protection afforded by a particular film barrier can be calculated by

$$\% \text{ protection} = 1 - \frac{\text{ICT}}{\text{ECT}} \times 100\%$$

The percent protection values for SF in Table II ranged from 96.4 to 97.0% and are in good agreement with the 96.6% figure calculated from results reported in Osbrink et al. (1988) for 2-mil-thick (=0.051 mm) polyethylene bags filled to 0.67 cm^3/cm^2.

Fill (Surface to Volume) Ratio. As expected, IC's of SF could be substantially reduced by increasing the fill ratio. The relationship, however, is not linear (Figure 1). IC's are reduced rapidly with increased low fill ratios (<1.0) and gradually tail toward zero above 1.5. A fill ratio of 1.0 results in smaller bags such as type A being ca. 25% full, while large bags such as type D are only filled to ca. 10% of capacity. Although large bags have a capacity for holding greater fill ratios than small bags, a constant fill ratio allows comparison of barrier performance of different-sized bags (Table III).

Comparison of Single- and Double-Layered Polymer Film Types after SF Exposure. The IC's of the eight film enclosure types in single or double condition at three ECT levels of SF are given in Table III. Actual ECT values, calculated from initial and final chamber air sample determinations, were 96.9, 677, and 6872 mg·h/L compared to theoretical ECTs of 108, 720, and 7200 mg·h/L [ca. 1.5, 10, and 100 times the field rate for drywood termites (Dow, 1988)]. Chamber sorption and leakage account for the lower measured values.

The four polyethylene films, A, B, E, and H yielded the highest IC values among the enclosures tested (Table III). The pooled (within) bag means of types E (2797), H (2321), and A (1929 ppm) are inversely related to film thickness (Table I). Type B enclosures did not follow this trend. These bags rendered the highest IC's under all conditions due to leakage from minute channels in their lateral heat-seals. The manufactured defects in type B bags were visible at 20× magnification. The Saran poly(vinylidene chloride)-containing film F was a significantly better barrier than polyethylene against SF under all conditions. At 0.076 mm, it was also the thickest film tested in this study.

The nylon (polyamide) and nylon-containing films C, D, and G yielded the lowest IC values of the polymers tested (Table III). Film G produced the highest IC's of this group (287 ppm) and, in some combinations, performed more poorly than film F. The performance of film G may be attributed in part to its stiff, thick texture, making it more difficult to twist and bend, thus potentiating leakage from an unsecured closure. Compared to film G, film C was over 3-fold (88.4 ppm) and film D over 14-fold (20.2 ppm) more resistant to SF penetration. Double films of C and D were the only enclosures in this study providing IC's below 1 ppm at the lowest ECT level (Table III). Both films had pliable textures conducive to tight-seal formation.

Among all 24 comparisons of the single- vs double-bag conditions listed in Table III, IC values of single enclosures were always higher than those of double enclosures. Although the grand IC mean of the single condition for all films was 2.8-fold greater than that of the double condition, single IC to double IC ratios varied considerably within each film type and ECT level. Likewise, comparative IC values for all film type and condition combinations were always greater at greater ECT levels, but these ratios also varied considerably. Overall, ratios between grand IC means (70.3, 479, 6450 ppm) were in reasonable agreement with those of their respective ECT levels (96.9, 677, 6872 mg·h/L).

Comparison of Double-Layered Polymer Film Types after MB Exposure. The IC's of double enclosures exposed to MB at an ECT of 683 mg·h/L are given in Table IV. As with SF exposures, IC's for MB were greatest with the four polyethylene films providing internal protection of between 64.8 and 69.3%. This is a low level of protection compared with the observed values for the same films when exposed to SF at the same ECT

Table III. Mean Terminal Internal Concentrations (IC) of Sulfuryl Fluoride (ppm ± SD, n = 4) inside Single- and Double-Layered (s, d) Polymer Film Bags after Fumigation at Each of Three Mean External Accumulated Exposure (ECT) Levels (mg·h/L ± SD, n = 4) of Sulfuryl Fluoride

	ECT level[a]						within bag mean (n = 24)
	96.9 ± 6.84		677 ± 13.5		6872 ± 92.4		
film type[b]	s[c]	d	s	d	s	d	
A	86.2 ± 6.98 c	32.9 ± 8.82 c	657 ± 133 b	498 ± 221 b	8328 ± 1772 b	1974 ± 370 b	1929 c
B	358 ± 67.5 a	232 ± 46.2 a	2482 ± 151 a	1155 ± 302 a	42957 ± 7239 a	17619 ± 2738 a	10800 a
C	5.24 ± 1.82 e	0.324 ± 0.208 e	26.9 ± 2.06 d	2.18 ± 2.16 e	484 ± 87.1 d	11.6 ± 8.66 d	88.4 f
D	1.39 ± 0.430 f	0.041 ± 0.030 e	7.69 ± 0.847 e	0.512 ± 0.352 f	105 ± 18.0 e	6.42 ± 3.10 d	20.2 g
E	157 ± 16.9 b	52.0 ± 3.59 b	1156 ± 198 b	323 ± 40.5 b	11181 ± 477 b	3915 ± 430 b	2797 b
F	4.07 ± 1.40 e	1.40 ± 0.81 d	130 ± 96.2 c	5.44 ± 4.37 d	2154 ± 2758 c	228 ± 226 c	420 e
G	22.1 ± 12.1 d	1.41 ± 0.53 d	95.9 ± 50.1 c	15.6 ± 6.01 c	1363 ± 888 c	223 ± 133 c	287 d
H	124 ± 11.9 bc	46.5 ± 4.28 b	812 ± 405 b	294 ± 45.9 b	9937 ± 1172 b	2710 ± 315 b	2321 bc
within ECT mean (n = 64)	70.3 A[d]		479 B		6450 C		
within s, d mean (n = 96)	3443 A	1223 B					

[a] Two bags of each type fumigated at similar ECT levels twice for each s and d condition. [b] See Table I for description of film types. Bag types A, B, and F were sealed with existing Ziploc-type closures. All others sealed by method T (see text). [c] Means followed by same lower-case letter in columns not significantly different with Student–Newman–Kuels test at P = 0.05 of log (ppm + 1) transformed data. [d] Means followed by same upper-case letter in rows as in footnote c.

Table IV. Mean Terminal Internal Concentrations (IC) of Methyl Bromide (ppm ± SD, n = 4) inside Double-Layered Polymer Film Bags after Mean External Accumulated Exposure (ECT) of 683 ± 20.5 mg·h/L ± SD (176 303 ppm·h) of Methyl Bromide (MB) and Percent Protection from MB and Sulfuryl Fluoride (SF) Afforded by Each Type of Double-Film Enclosure

film type	IC,[b] ppm MB	% protection[a]	
		MB	SF[c]
A	5412 ± 2197 a	69.3	97.0
B	6218 ± 2517 a	64.8	93.0
C	49.0 ± 26.3 c[d]	99.72	99.987
D	3.85 ± 2.46 d[d]	99.98	99.997
E	5425 ± 2684 a	69.2	98.0
F	37.0 ± 2.09 c	99.79	99.967
G	234 ± 22.2 b	98.7	99.905
H	5432 ± 2298 a	69.2	98.2

[a] Percent protection = 1 − [ICT/ECT] × 100%. [b] Means followed by same letter in columns not significantly different with Student–Newman–Kuels test at P = 0.05 of log (ppm + 1) transformed data. [c] Calculated from IC values in Table III, column 4. [d] An additional, consistent peak eluting ca. 12 min after MB was observed in GC traces of samples taken from these bags.

(Table III). These data suggest that MB has a much greater diffusion coefficient through polyethylene than SF and that this polymer is not well suited for use as an MB barrier. Performance of the Saran-containing film (F) against MB penetration was 1.3-fold greater than film C and over 6-fold greater than film G. All these materials reduced time-weighted MB exposures at substantially higher percentages than polyethylene (Table IV). As with SF, double-layered bags of nylon film D yielded the lowest mean IC values (3.85 ppm) and, therefore, the highest percentage of protection (99.98%) of all film types. An unidentified gaseous compound eluting at ca. 19 min (100 °C) was detected by ECD at a magnitude greater than MB IC's in all C and D film enclosures exposed to MB.

Although polyethylene bags are inexpensive and widely available, this study supports the use of more refractive polymers, such as nylons and Saran, to ensure minimal exposure to structural fumigants, especially MB. A recommendation for the use of double enclosures for field application not only would increase protection significantly over single bags but would ensure reasonable protection of commodities should one of the bags be damaged or poorly sealed. Increased thickness of polymers also reduces penetration, but not to the extent of multiple layers of combined equivalent thickness. For example, Osbrink et al. (1988) found that IC's were only 1.5-fold greater in 2- than 4-mil polyethylene bags. Regardless of the film type, if the bags are not properly sealed or contain a hole, external and internal fumigant concentrations will equilibrate in a matter of minutes or hours, depending on the magnitude of the leak, thereby negating the use of the bag for its intended purpose.

Both fumigants have similar toxicities to motile stages of insect pests (Kenaga, 1957), including drywood termites (Osbrink et al., 1987; Scheffrahn and Su, unpublished results). If commodities were protected in double-nylon or -Saran enclosures (C, D, F) during a typical structural fumigation for drywood termites with either fumigant at ca. 72 mg·h/L and 22 °C, terminal residues inside bags would not likely exceed 5 ppm, the short-term exposure level (STEL) for humans and the level allowed for reoccupation of a structure (Dow, 1988). Under such conditions, protected food items exposed to SF would not yield anionic fluoride residues at detectable levels (Scheffrahn and Hsu, unpublished results; Scheffrahn et al., 1989b). In practice, large double bags filled with commodities would probably be sealed with considerably greater volume to surface areas and would not be exposed directly to circulating fan blast as in our study and, therefore, bag efficiency would be even greater than reported here.

ACKNOWLEDGMENT

We thank T. Center, R. Giblin-Davis, F. W. Howard, and P. Busey for reviewing and improving this manuscript. Florida Agricultural Experiment Stations Journal Series No. R-00062. This research was made possible by a grant from Dow Chemical U.S.A.

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Received for review August 8, 1989. Accepted December 11, 1989.

Kinetic Analysis of Enhanced Biodegradation of Carbofuran

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Mineralization of 0.01, 0.1, 5.0, and 50 mg of carbonyl-^{14}C-labeled 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate (carbofuran) per kilogram of soil was measured in soil that had not been exposed to the pesticide and in soil that had been previously treated with the same concentrations of carbofuran. The stimulation in mineralization rate as a result of previous treatment of the soil with carbofuran was not the result of a substantial increase in the size of the microbial population able to use the compound, as indicated by most probable number counts. Of the Monod (single-substrate) and dual-substrate models of biodegradation kinetics, model I of the dual-substrate models provided the best fit to all curves of mineralization of carbonyl-labeled carbofuran. The fact that model I fit the data supports the hypothesis that the microorganisms mineralizing the carbonyl-labeled molecule do not grow at the expense of the methylcarbamate moiety. This study demonstrates the usefulness of kinetic models for characterizing microbial processes in soil.

The rate of biodegradation of organic compounds in soil is often faster following the second than the first addition of the chemical. Several hypotheses have been proposed to explain this phenomenon of enhanced degradation: growth of the population, induction of enzymes, and selection of new metabolic capabilities produced by genetic change (Spain et al., 1980). Multiplication of the microorganisms carrying out the transformation was responsible for an increase in the rate of degradation of a second application of pentachlorophenol in soil (Watanabe, 1978), 2,4-dichlorophenoxyacetic acid (2,4-D) in soil (Fournier et al., 1981), and *p*-nitrophenol in sediment (Spain et al., 1980). Increased rates of degradation without an increase in the number of organisms able to degrade the test compound were found in soils exposed to 2,4-D (Torstensson et al., 1975) and *S*-ethyl dipropylthiocarbamate (EPTC) (Moorman, 1988). Increased rates of degradation were attributed to the appearance of a new organism, apparently following a mutation, in a mixed microbial population exposed to 2,2-dichloropropionic acid (Senior et al., 1976) and in river water containing aniline (Wyndham, 1986).

Many agricultural soils show enhanced rates of degradation of carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) after repeated applications of the insecticide (Felsot et al., 1981; Hendry and Richardson, 1988), and considerable work has been performed to determine the factors associated with the stimulation. Because of the large number of variables potentially involved in enhanced biodegradation, it is difficult to determine the contribution of a change in an individual factor, such as an increase in the growth rate, to the enhancement.

Kinetics models permit a quantitative determination of the degree of dependence of the rate of biodegradation on each of the parameters controlling the rate; thus, models may provide new insight into the phenomenon of enhanced degradation. A number of theoretical models have been developed to describe the kinetics of biodegradation of organic compounds (Alexander and Scow, 1989). In the Monod family of kinetics models, it is assumed that the rate of biodegradation is controlled only by the substrate concentration and the population density of the microbial population (Simkins and Alex-

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0021-8561/90/1438-0908$02.50/0