

# Release Routes of Incorporated Desmetryn from EVA-Films. An Example for the Behavior of Low Volatility Additives in Polymers Under Outdoor Conditions

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## Synopsis

Release of desmetryn into the gas phase from films of ethylene-vinyl acetate copolymer, in which the herbicide was incorporated for special agricultural applications, was investigated for comparison with release into water and under outdoor conditions. It could be shown that the rate of release of the active chemical into the gas phase was negligible compared with that into water and only slightly dependent on temperature in the range 0–75°C.

## INTRODUCTION

Agriculture today is dependent on the application of a great number of chemicals, many of them toxic, so that the possibility arises of contamination of food and environment. Many efforts are therefore made to find novel methods of achieving better control over the release of these chemicals, so that the desired effects are attained by application of smaller amounts (controlled release technology)<sup>1-3</sup>. One such method was developed for applying pesticides in the film cultivation of early vegetables<sup>4,5</sup> and investigated under practical conditions using the herbicide desmetryn.<sup>6</sup> This method is based on physical incorporation of the active ingredient into thermoplastic polymers, preferably ethylene-vinyl acetate copolymers (EVA), so as to form a homogeneous solution. The release of the active chemical takes place by diffusion-controlled migration to the surface of the film, where it can be dissolved by rain, dew, or condensing water or can evaporate into the atmosphere. However, assessing the efficiency of pesticides thus formulated requires measurement of the relative amounts released by those two routes. Determination of the transfer to the gas phase is of particular interest, because this may represent undesired loss of the active chemical from the upper surface of the films.

To this end a method was developed to quantify the release of desmetryn from EVA films under reproducible conditions. Films of the same batch were used to determine the release of the herbicide into water.

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## MATERIALS AND METHODS

## Chemicals

Ethylene-vinyl acetate copolymer FV2030 VP (10% vinyl acetate), from Hoechst AG, produced by Ruhrchemie, Oberhausen, FRG, had a melt flow index (MFI) 190/2.16 of 0.59 g/10 min and a density of 0.926 g/cm<sup>3</sup>.

Desmetyrn (97.1%) was from Ciba-Geigy AG, Basel, Switzerland; a calibration sample (99%) was obtained from the firm of Dr. S. Ehrenstorfer, Augsburg, FRG.

## Determination of the Transfer to the Gas Phase

Desmetyrn-containing EVA films were cut into strips of about 8 cm × 30 cm (about 70–80 μm thickness). These were loosely fixed on special glass cages as shown in Figure 1 and introduced into a thermostated sample chamber, which was purged with thoroughly dry, oxygen-free nitrogen. After 1 h of initial purging, the outlet of the chamber was connected by a short glass tube to a train of three 20-cm long sections of fused silica gas chromatographic capillary columns (530 μm ID; methylsilicone phase, 2.65 μm thickness, from Hewlett Packard). These capillaries were connected with each other by zero-dead volume fittings. They were enclosed in a silicon-rubber tube (8 mm ID) for protection from mechanical damage and were cooled at ca. -18° in a Dewar flask containing an ice/NaCl mixture. This temperature was found to be low enough to trap desmetyrn quantitatively without causing blocking of the capillaries by freezing out other volatiles, as occurred repeatedly when a dry-ice/propanol-2 mixture was used, despite thorough drying of the purge gas. The nitrogen effluent from the capillary train passed through a 30-cm tube (3 mm ID), which was long enough for temperature equalization. The flow rate was adjusted by a needle valve and a bubble flow meter to 0.7 l/h. Films with desmetyrn at the two highest concentrations were kept in the

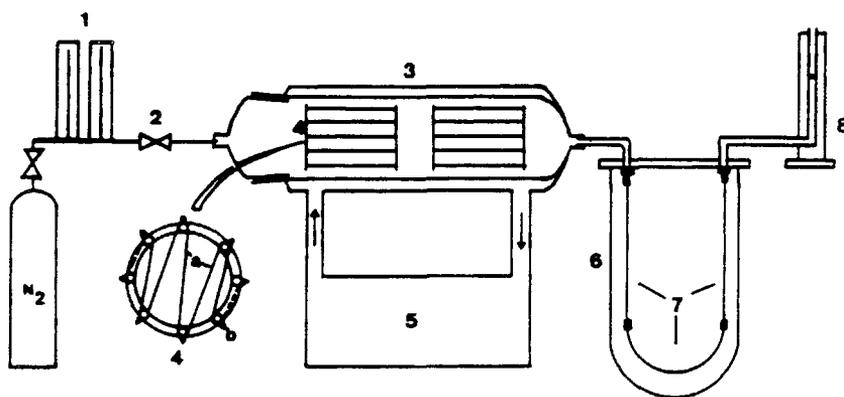


Fig. 1. Scheme of release and trapping apparatus: 1 = drying column and oxygen absorber; 2 = needle valve for gas-flow adjustment; 3 = thermostatable sample chamber; 4 = glass cage for films (a = film, b = spacer burl); 5 = thermostat; 6 = dewar flask with ice/NaCl-mixture (-18°C); 7 = sections of fused silica capillary column (20 cm length, 530 μm ID, methylsilicone phase 2.65 μm thickness); 8 = bubble-flow meter.

TABLE I  
Transfer of Desmetryn from EVA Films and Coated Glass Plates into Dry Nitrogen (flow 0.7 l/h)

Concentration of desmetryn in films (%)	Temperature (°C)	Total surface (cm <sup>2</sup> )	Amount of a.i./unit surface <sup>a</sup> (μg/cm <sup>2</sup> )	Mean concentration in gas phase <sup>b</sup> (ng/L)	Normalized release pg/L · cm <sup>2</sup>	Amount of desmetryn released in 4 days <sup>c</sup> (% of initial value)
0.07	25	1056	2.4	3.1	2.9	0.0083
0.14	0	1118	4.2	9.5	8.5	0.014
	25	1118	4.2	10.2	9.1	0.015
	50	1118	4.2	12.5	11.2	0.018
	75	980	4.1	14.2	14.5	0.024
0.35	25	1244	8.2	16.0	12.9	0.011
0.35 washed	25	1347	7.9	16.2	12.5	0.010
0.62	0	1288	18.7	25.0	19.4	0.0070
	25	1288	18.7	27.0	21.0	0.0075
	50	1288	18.7	32.0	24.8	0.0090
	75	1288	18.7	34.0	26.4	0.0095
Glass Plates						
± 0.07	25	300	2.3	4.0	13.3	0.038
± 0.62	0	50	20.0	10.2	204.0	0.069
	25	50	20.0	11.1	222.2	0.075
	50	50	20.0	16.5	330.0	0.111
	75	50	20.0	19.7	394.0	0.132

<sup>a</sup>Total amount based on weight of film.

<sup>b</sup>Three repetitions, glass plates one measurement.

<sup>c</sup>Extrapolated from two days with 0.35% and 0.62% films.

sample chamber for two days, the results being extrapolated to four days, while measurements with the other concentrations were carried out for the full four-day period.

Transfer of unformulated herbicide into the gas phase was studied with plates of glass (5 cm × 20 cm) coated partially or wholly with the chemical. The coating was prepared by uniformly spreading a dichloromethane solution of desmetryn on the predetermined area and cautiously removing the solvent. The amounts of herbicide were chosen so as to give a surface-to-herbicide ratio similar to that in the corresponding films (see Table I).

### Analysis of Trapping Capillaries

The three fused silica capillary sections used as traps for the volatiles in the purge gas were separated from each other, and each was connected in turn to the desorption unit shown in Figure 2. With a carrier gas ( $N_2$ ) flow of 7 mL/min the capillary was heated by a jacketed miniature resistance heater to 230°C within 0.5 min. This temperature was maintained for 6 minutes. The capillary column (10 m long, 530  $\mu$ m ID, phase methyl phenyl silicone, Hewlett Packard) of the gas chromatograph (Carlo Erba 2300, equipped with a Hewlett Packard capillary injection port, FID) was held at 70°C during the desorption period in order to reconcentrate the low volatiles of the desorbed compounds. The column-oven temperature was then raised at 10°C/min to 230°C and held there for 12 minutes. The peak areas were automatically integrated and compared with those from external standards which could be injected directly onto the capillary column through the septum. The final result for each trapping run was the sum of the values measured for the three capillary sections. A measure of how quantitative this procedure was is given by the fact that usually 90% of the trapped herbicide was in the first capillary of the train, while the third never had more than 5%.

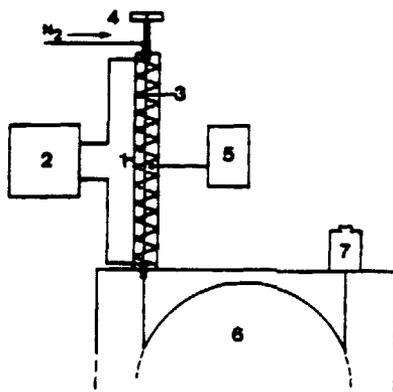


Fig. 2. Scheme of desorption unit: 1 = coppertube with jacketed miniature resistance heater; 2 = potentiometer; 3 = section of fused silica capillary, 20 cm length; 4 = nitrogen inlet and septum injection port; 5 = thermocouple with electronic thermometer; 6 = GC-oven with fused silica capillary column, 530  $\mu$ m ID, 10 m length, methylphenyl-silicone phase; 7 = flame-ionization detector.

### Release into Water

Pieces weighing 0.15 g were taken from each film and cut into 2 cm × 2 cm squares as far as possible. These were mechanically shaken at a moderate rate at room temperature with 50 mL of doubly distilled water in an Erlenmeyer flask until no more desmetryn was released. At regular intervals the water was removed for analysis and replaced by fresh water to avoid saturation and readsorption effects. The herbicide content of the water samples was measured with a photometer at 222 nm and quantified with a calibration curve.

### Release at a High Air Flow Rate

Strips of the herbicide films (80 cm × 9 cm) were hung in a fume hood (air flow ca. 600 m<sup>3</sup>/h). At intervals of several days, sections 10 cm long were cut off, weighed, and analyzed for the active chemical as described below.

### Analysis of Desmetryn in EVA films

Desmetryn was extracted from the EVA films with chloroform (8–12 h). Codissolved polymer was precipitated by stepwise concentration of the solution and addition of methanol. The herbicide in the resulting largely methanolic solutions was analyzed by HPLC with an ultraviolet detector (column 25 cm × 4.6 mm, Hypersil ODS RP18 5 μm; acetonitrile: water 90:10, 0.7 mL/min; 222 nm), the peak areas being compared with those of external desmetryn standards.

## RESULTS AND DISCUSSION

Data on the transfer of desmetryn into the gas phase from EVA films and coated glass plates are given in Table I. The release of the active chemical, normalized with regard to unit area and nitrogen volume, increased as expected with concentration in the films, but in general remained very low. In comparing these values with those from the coated glass plates it should be observed that the desmetryn-releasing surfaces had to be considerably reduced in order to avoid overloading the capillary traps. Thus the volatility indicated by the normalized data is probably too low in this group of experiments. Nevertheless, the present data show clearly that the release of desmetryn is retarded by the polymer matrix.

The release rate from a 0.35% film, that had been washed quickly with a small amount of methanol, was almost identical with that from the untreated sample, indicating that the effect of any herbicide that may have sweated out onto the surface of the film during storage was negligible. This conclusion is presumably valid not only for the films with lower desmetryn concentrations, but also for the 0.62% film, since it was shown in an earlier study that desmetryn is soluble to the extent of 2.1% in the type of EVA used here.<sup>4</sup>

The temperature dependence of the release rates from the 0.14% and 0.62% films was examined, since under outdoor conditions, the temperature may vary as much as several tens of degrees. The temperature-dependent release of the active chemical from one of the coated glass plates is also shown in Table I. While the transfer of desmetryn from both films into the gas phase increased only slightly and almost linearly with temperature, loss from the

TABLE II  
Calculated Vapor Pressures ( $P$ ) and Saturation Concentrations ( $C_S$ ) of Desmetyrn  
at Various Temperatures

Temperature (K)	Vapor pressure (Pa · 10 <sup>4</sup> )	Saturation concentration $C_S$ (ng/L; dried N <sub>2</sub> )
273	0.064	0.6
298	2.7	23.4
323	64.7	514.0
348	978.0	7200.0

glass plate nearly doubled over the temperature range 0–75°C. Possibly, the increase with temperature of the vapor pressure of desmetyrn having migrated to the surface of the film is largely compensated for by a higher solubility in the polymer.

The vapor pressure of desmetyrn (GS 34360 in Ref. 7), as measured in dry nitrogen by Friedrich and Stammach,<sup>7</sup> amounts to  $1.0 \times 10^{-6}$  mmHg at 20°C ( $1.3 \times 10^{-4}$  Pa). On the assumption that this low vapor pressure leads to near-ideal gas behavior, its saturation concentration  $C_S$  can be calculated from the transformed Eq. (1) for the ideal gas law<sup>8</sup>

$$C_S = \frac{W}{V} = \frac{P \cdot M}{R \cdot T \cdot 10^3} \quad (1)$$

where  $W$  = weight of evaporated substance (g);  $P$  = saturation vapor pressure (Pa, Nm<sup>-2</sup>);  $M$  = Molecular weight (g);  $V$  = Volume of nitrogen (dm<sup>3</sup>);  $R$  = gas constant (8.314 Nm mol<sup>-1</sup>K<sup>-1</sup>);  $T$  = absolute temperature (K).

The value calculated for  $C_S$  (20°C) thus is 11.38 ng/liter. The vapor pressures and saturation concentrations of desmetyrn at the temperatures used in this study are listed in Table II. They were calculated by means of the vapor pressure constants of the compound ( $A = 12.101$ ;  $B = 5302^7$ ) and the semiempirical Eq. (2),

$$\lg P = A - \frac{B}{T} \quad (2)$$

where  $P$  = vapor pressure (mmHg) and  $T$  = absolute temperature (K). After transformation of  $P$  values into SI units, saturation concentrations could be derived from Eq. (1).

The concentrations of desmetyrn found in the purge gas from films and glass plates were in general significantly lower than or just in the range of the theoretical values. Only the measurements at 0°C gave concentrations that considerably exceeded the calculated maximum values. Possibly the simplified correlation of vapor pressure and temperature by Eq. (2) is insufficient at this temperature. However, as mentioned above, preliminary experiments with the coated glass plates also indicated a higher volatility of desmetyrn at the other temperatures than was to be expected from the literature. Because the apparatus was not appropriate and the objectives of this work were different, plans to verify the calculated saturation concentrations and vapor pressures were renounced.

TABLE III  
Release of Desmetryn from Films at High Air-Exchange Rate (about 600 m<sup>3</sup>/h)

Time (d)	Concentration of desmetryn in films (%)			
	0.07	0.14	0.35	0.62
	% of initial concentration released			
2.9	10.7	18.4	13.6	22.0
5.9	20.6	30.7	18.6	27.5
22.9	36.7	40.4	33.6	40.2
34.1	45.4	—	57.4	48.7
39.0	51.5	66.0	64.7	51.0
60.9	72.4	80.1	82.4	76.0

In Table III are the results of the experiments in which strips of the films were hung in a fume hood with a high air-exchange rate as a better approximation to open-air conditions, which were undertaken because of the limited flow rates possible with the sample chamber. Release of desmetryn is considerably faster under these conditions, but it is nevertheless extended over the relatively long period of several months.

Release of the herbicide from the films into stirred water was, as shown in Figure 3, very quick in comparison with transfer to the gas phase and almost quantitative within 6 h. Because the water solubility of the chemical is 580 ppm (29 mg/50 mL) and the maximum which could be released was only 0.948 mg, saturation effects could be neglected. It can be assumed that this rapid release was influenced not only by diffusion-controlled migration of the

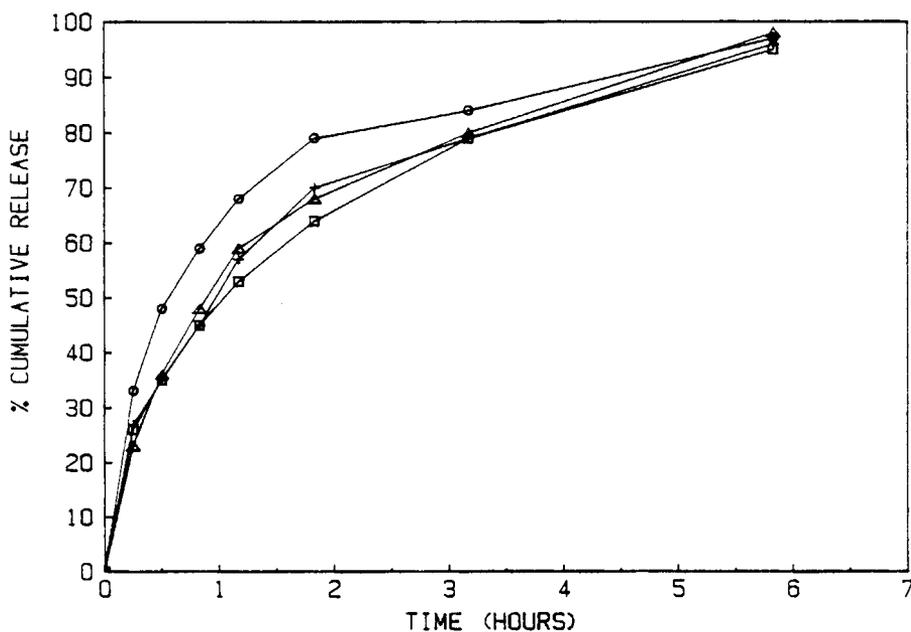


Fig. 3. Release of desmetryn from EVA-films into water: □, 0.07%, △, 0.14%, ○, 0.35%, +, 0.62% incorporated desmetryn.

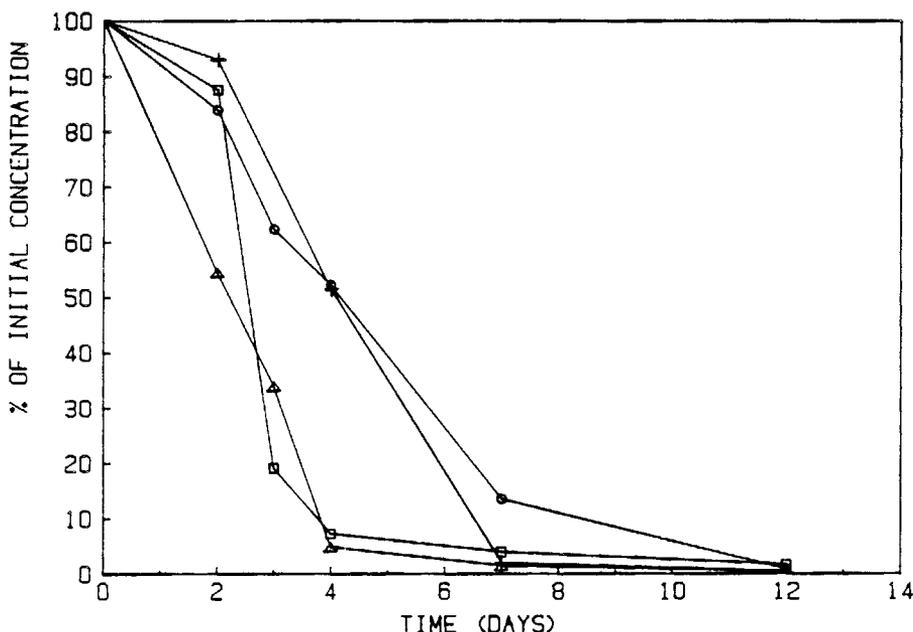


Fig. 4. Decrease of desmetryn concentration from initial value in EVA films during field trial: □, 0.07%, Δ, 0.14%, o, 0.35%, +, 0.62% desmetryn.

chemical to the polymer/water boundary but by leaching as well, because a certain amount of water can penetrate into the outer layers of the EVA polymer.

Herbicidal films from the same batches were exposed in a field trial under practical conditions. The release profiles for the incorporated desmetryn are presented in Figure 4. Some irregularity in the curves is probably due to difficulties in obtaining representative samples, as the films puckered and developed an uneven surface. This may have led to unequal removal of desmetryn, especially during rainfalls, when channels and puddles formed. During the first ten days of outdoor exposure, relatively heavy rainfall was recorded (41.1 mm). From the laboratory experiments it can be concluded that this, in combination with water condensing on the underside of the films, was the major reason for the release of desmetryn from the polymer matrix.

### CONCLUSION

A method has been developed to determine the rate of transfer of incorporated desmetryn from EVA films to the gas phase under defined conditions. The very low release rate and its slight dependence on temperature could be attributed essentially to the release-controlling properties of the polymer matrix. The much faster release observed under natural weathering was still relatively low compared with that into pure water under experimental conditions. Thus, in practical application of the films, the depletion of the active chemical is mainly determined by rain and water of condensation, and no significant losses to the gas phase are to be expected. The method presented

can in principle be adopted to measure the transfer of other relatively non-volatile pesticides from various matrices to the gas phase. Of further interest would be studies of migration and volatilization of polymer additives and impurities with low vapor pressures.

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