Occurrence of Trifluralin and Its Photoproducts in Air

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Trifluralin vapor photodecomposed to a number of products in a laboratory vapor-phase reactor which simulated sunlight conditions. For analysis, an air sampling method utilizing a coated solid adsorbent as a vapor trap was developed which trapped these materials at air flow rates greater than 1 m^3/min and with a limit of detectability of less than 1 ng/m^3. Trifluralin and several photoproducts were detected in the air above both surface treated and soil incorporated fields. These photoproducts probably arise primarily from photolysis of trifluralin on the soil surface followed by volatilization; however, the contribution of vapor-phase photolysis of trifluralin undoubtedly increases with increasing air residence time.

Photodecomposition is often one of the primary modes of environmental dissipation of chemicals, and the breakdown of many pesticides under sunlight conditions has been demonstrated both on solid surfaces and in water. Recently, attention has been given to photolysis in another environmental compartment—the atmosphere. For example, the vapor-phase photolyses of aldrin and dieldrin (Crosby and Moilanen, 1974) and DDT (Moilanen and Crosby, 1973) in a laboratory photoreactor were recently reported. The present study was undertaken to investigate the possible occurrence of this process under actual field conditions.

Trifluralin (2,6-dinitro-*N,N*-dipropyl-α,α,α-trifluoro-*p*-toluidine) (I), a widely used preemergence herbicide, was selected as a study model. The manufacturer generally recommends immediate soil incorporation since three to four times as much trifluralin is needed for equal efficacy when applied as a surface spray. This led to early speculation that trifluralin may undergo volatilization and/or photodecomposition in the field. In fact, both of these processes occur: Wright and Warren (1965) showed that trifluralin decomposed in sunlight on glass plates or soil surfaces, and Crosby and Leitis (1973) identified a number of photoproducts formed during irradiation at sunlight wavelengths in water. The relatively high vapor pressure (2.42×10^{-4} Torr at 30°; Spencer *et al.*, 1973) is manifested by significant vapor loss from soil, the rate being a function of soil moisture content among other factors (Bardsley *et al.*, 1968; Ketchersid *et al.*, 1969; Parochetti and Hein, 1973; Spencer *et al.*, 1973).

In the present study, the vapor-phase photolysis of trifluralin in a laboratory reactor was examined; a novel method utilizing a coated solid adsorbent was developed to trap trifluralin and its photoproducts from air; and, finally, field tests were conducted to assess the extent to which these photoproducts occur in the atmosphere above treated soil.

EXPERIMENTAL SECTION

Chemicals. Technical trifluralin (95%) (Eli Lilly and Co., Indianapolis, Ind.) was recrystallized from absolute ethanol to a mp of 48° (48.5–49°, Probst *et al.*, 1967). 2,6-Dinitro-*N*-propyl-α,α,α-trifluoro-*p*-toluidine (II), 2,6-dinitro-α,α,α-trifluro-*p*-toluidine (III), 2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole (IV), and 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole (V) were synthesized according to the procedures of Leitis and Crosby (1974). All solvents were distilled twice in glass prior to use.

Vapor-Phase Photolysis. The vapor-phase photoreactor and light source were described previously (Crosby and Moilanen, 1974). Trifluralin (5 mg) was dissolved in 2–3 ml of hexane, the solution placed on a 48-cm watch glass, and the solvent evaporated in a current of air to leave a thin solid film. The dry watch glass was placed at the bottom of the reactor chamber and warmed to 35° to enhance volatilization.

After several hours, during which the trifluralin vaporized in the chamber, irradiation was commenced. Photolysis proceeded for up to 12 days at 25–30°, after which the reactor was dismantled and rinsed with four 500-ml portions of hexane and two 500-ml portions of acetone. The combined rinses were concentrated to a small volume and subjected to thin-layer chromatography (tlc) (0.5-mm silica gel G containing 1% zinc orthosilicate phosphor, developed in hexane–acetone, 3:1). The resulting bands were detected by fluorescence quenching with 254-nm light and visual observation, scraped off, eluted with warm acetone, and quantitated by gas chromatography–mass spectrometry (gc–ms). A Finnegan Model 3000 peak identifier equipped with a 1.5 m × 3 mm (i.d.) glass column containing 2% OV-1 on 60–80 mesh Chromosorb G was employed. The column temperature was programmed from 150 to 270° at 10°/min; injector and detector temperatures were both 240°, and the carrier gas (helium) flow rate was 16 ml/min. As each compound eluted, its mass spectrum was recorded and identified by comparison with that of an authentic specimen.

A simultaneous experiment was conducted in an identical reactor except that the light trap was replaced with a spherical reflector (Crosby and Moilanen, 1974); a dark control was included in yet another flask. All experiments were analyzed in an identical manner.

Photolysis of Trifluralin on Coated Dust. Light from an RS sunlamp (Crosby and Moilanen, 1974) was directed horizontally through a 5-l. round-bottomed flask attached with a 24/40 ground-glass joint to a rotary evaporator motor (Calab Co., Oakland, Calif.). Standardized Air Cleaner Test Dust, Fine (Air Filter Testing Labs, Inc., Louisville, Ky.) was coated to 20 ppm by the addition of I in a small volume of diethyl ether followed by drying at ambient temperature, and 0.25 g placed inside the flask. The standard dust was mainly (91 ± 3%) in the 0–40 μ range and contained 1.3% organic matter and 1.0% moisture. Rotation of the flask about the horizontal axis effectively suspended a portion of the coated dust in the light beam. After irradiation for 1–15 hr, the dust and flask were rinsed with two 10-ml portions of acetone. Trifluralin was quantitated by electron-capture gas chromatography as described later. An identical experiment conducted in the absence of light served as a dark control.

Air Sampling Equipment. Air sampling for trifluralin vapors above treated fields was conducted with two types of apparatus. A commercial Hivolume Sampler (Figure 1; Natural Environmental Instruments, Inc., Fall River, Mass.), fitted with an 8 in. × 10 in. glass fiber filter (Reeve Angel Co., Clifton, N.J.) and charged with 30 g of

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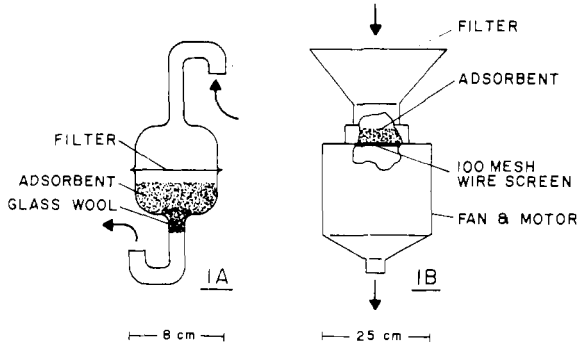

Figure 1. Schematic representations of the Lovol (A) and Hivol (B) Samplers. Scale indicates approximate size.

adsorbent, processed about one cubic meter of air per minute. Low-volume sampling was carried out using an Air Sampling Assembly (Microchemical Specialties Co., Berkeley, Calif.) modified as follows. The filter cup was charged with 30 g of adsorbent held in place with glass wool at the bottom and a glass fiber filter at top (Figure 1A), covered with aluminum foil, mounted on a 5 cm diameter × 4 m vertical pipe, and connected to the pump assembly with vacuum tubing. It processed about 0.03 m^3 of air per min. The liquid impingers were not used. These traps are referred to as the Hivol and Lovol Samplers in the subsequent discussion.

The adsorbent was 20–30 mesh Chromosorb A (Applied Science Labs, Inglewood, Calif.) purified by Soxhlet extraction with acetone overnight and then coated to 5% (w/w) with paraffin oil previously purified by extraction in succession with concentrated sulfuric acid, water, and acetonitrile.

Analytical Methods. *Chromatography.* Gas–liquid chromatography (glc) was carried out with a Varian Model 2100 gas chromatograph equipped with a 1.8 m × 2 mm (i.d.) glass column containing 5% OV-17 on 60–80 mesh Chromosorb G and a tritium electron capture detector. Column, injector, and detector temperatures were 160, 225, and 215°, respectively; carrier gas (nitrogen) flow rate was 25 ml/min. Thin-layer chromatography (tlc) was carried out on 20 cm × 20 cm, 0.25 mm thick Anasil GF silica gel plates (Analabs Inc.) developed with hexane.

Air Samples. A sealed 250-ml erlenmeyer flask containing the adsorbent from a sampler and 100 ml of acetone was agitated with rotary shaking for 1 hr. The acetone was decanted and filtered through Whatman No. 1 paper. Additional acetone (50 ml) was swirled with the adsorbent, decanted, and filtered. The combined filtrates were adjusted to 100 ml, and a 50-ml aliquot was concentrated to 2 ml and analyzed for trifluralin by glc.

Another aliquot (25 ml) was concentrated in a 15-ml centrifuge tube until only paraffin oil remained; the residue was chilled in ice and twice extracted with 1 ml of cold acetone by vortex stirring followed by centrifugation. The combined acetone extracts were concentrated and the acetone extraction repeated, if necessary, until a volume convenient for spotting on a tlc plate (0.1–0.2 ml) was attained. Samples were run alongside enough trifluralin standard for visual confirmation of its R_f value. After development in hexane, the silica gel between the origin and the R_f of trifluralin was scraped off and eluted with acetone. The acetone was concentrated to about 0.1 ml and analyzed for photoproducts II–V by glc.

The Hivol glass fiber filters were placed in a 250-ml erlenmeyer flask with 100 ml of acetone and agitated on a rotary shaker for 1 hr. The acetone was decanted, filtered through Whatman No. 1 paper, concentrated to an appropriate volume, and analyzed for I by glc.

Soil Samples. Composite soil samples were mixed thoroughly without adjustment of the moisture content and analyzed by a modification of the procedure of Smith (1972): a 20-g sample was weighed into a 125-ml erlenmeyer flask, 50 ml of benzene and 25 ml of 2-propanol were added, the flask was sealed, and the mixture was agitated for 30 min on a rotary shaker. After settling, two 25-ml aliquots were each rinsed twice with 15-ml portions of 3% aqueous sodium chloride to remove the 2-propanol. The benzene was dried briefly with anhydrous sodium sulfate, analyzed for I, and then subjected to tlc as described above for analysis of II–V. Acetone was used to extract soil samples too wet to be extracted with benzene–2-propanol with equivalent results. Limits of detectability for I–V were about 0.01 ppm. Soil moisture content was determined by overnight drying (110°) of an accurately weighed 1–2-g sample followed by cooling and reweighing.

Field Experiments. In one experiment, a 15 m × 15 m bare soil plot at the University of California, Davis, was disced to a depth of 0.15 m and surface treated (1.7 kg/ha of I) with Treflan emulsifiable concentrate (Elanco Products Co., Indianapolis, Ind.) without soil incorporation in June, 1973. The field was sprinkler irrigated with water to a depth of 3 cm 2.8 days after application to enhance the volatilization of trifluralin. Lovol Samplers were mounted on a pipe tower in the center of the plot at 0.5 and 1.8 m above ground, a Hivol Sampler was placed 0.5 m above ground, and a portable weather station which monitored temperature, relative humidity, and wind conditions was located adjacent to the plot.

Air samples were collected immediately after, and for 7 days following, trifluralin application. Each Lovol Sampler was run during daylight for about 10 hr (about 18 m^3 of air sampled) and the Hivol Sampler for about 3 hr (about 180 m^3 of air sampled). Adsorbent was removed on the following morning into foil covered flasks and returned to the lab, 100 ml of acetone was added, and the mixture was stored at −10° until processed. Soil core samples (2.5 cm × 7.5 cm deep) were collected daily from 20 random locations within the plot, composited, and stored at −10° in foil-lined bags.

A second experiment was performed whereby Treflan was soil incorporated to a depth of 15 cm. A 61-ha field in Sutter County, Calif., was disced repeatedly, treated with Treflan (0.9 kg/ha of I), disced twice again, and planted in safflower in April 1974. The Hivol Sampler was run daily for 4 hr during midafternoon near the center of the field. Air and soil samples were processed as described above, except that emphasis was given to the determination of I and II.

These two experiments will be referred to as the surface treatment and soil incorporation experiments in subsequent discussion.

RESULTS AND DISCUSSION

Laboratory Photolysis. The photoreactor was designed so that a light beam shining through the substrate vapor would not intercept the walls, except at the end of the flask where a small window allowed light to exit into a light trap. Alternatively, wall irradiation, and hence surface-induced photoreactions, could be promoted by replacing the light trap with a spherical reflector (Crosby and Moilanen, 1974). Irradiation of trifluralin in the reactor under normal conditions (*i.e.*, with the light trap) resulted in conversion to a number of products, and reflection of light onto the reactor wall produced no discernible change in the amount or nature of photoproducts. Trifluralin vapor was stable in the dark.

The dinitrotoluidines II and III, benzimidazoles IV and V, and benzimidazole precursors VI, VII, VIII, and IX reported by Leitis and Crosby (1974) were detected (Figure 2). Short term irradiation produced primarily II while longer irradiation (12 days) resulted mainly in IV and V

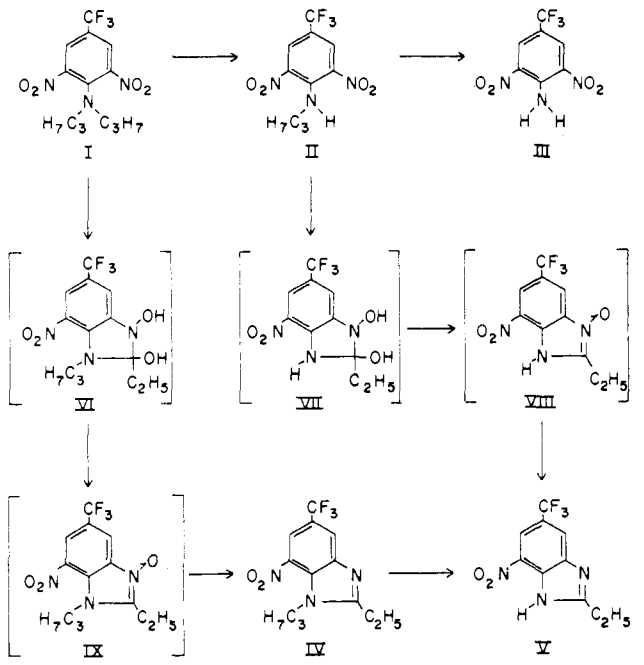

Figure 2. Proposed vapor-phase photolysis pathway of trifluralin (I).

Table I. Vapor-Phase Photoproducts of Trifluralin

Compound	R_f value[b]	Amount, mg[a]
I	0.60	0.7
II	0.52	0.3
III	0.40	0.1
IV	0.39	2.1
V	0.23	1.7

[a] Amount found after irradiation of 5 mg of I for 12 days. [b] Silica gel G (0.5 mm) developed in hexane–acetone (3:1).

(Table I). Irradiation of IV resulted in its facile conversion to V which was resistant to further photolysis. All of the volatile photoproducts were identified by comparing their R_f values, retention times, and mass spectra with those of authentic standards. In addition to the volatile products, a highly colored (orange-brown) band remained at the origin of the tlc plate. Characterization of this band following elution with warm methanol employed a thermal degradation method (Leitis and Crosby, 1974) in which the eluted material was subjected to glc analysis. The resulting pattern of three peaks indicated the presence of the benzimidazole precursors reported by Leitis and Crosby (1974) (Figure 2): 2,3-dihydroxy-2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazoline (VI); 2,3-dihydroxy-2-ethyl-7-nitro-5-trifluoromethylbenzimidazoline (VII); 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole-3-oxide (VIII); and 2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole 3-oxide (IX).

The vapor-phase photolysis of trifluralin involves both oxidative dealkylation and cyclization. Photochemical N-dealkylation of amines appears to be a free-radical oxidation by atmospheric oxygen (Sharkey and Mochel, 1959). Benzimidazole formation, reported by Crosby and Moilanen (1972) and Crosby and Leitis (1973), has been confirmed for similar dinitroaniline herbicides (Newsom and Woods, 1973; Plimmer and Klingebiel, 1974; Niles and Zabik, 1974). These cyclization reactions may be accounted for (Leitis and Crosby, 1974) by a modification of the free-radical mechanism proposed by Doepp (1971) to explain the photochemical formation of indole *N*-oxides

Table II. Trapping Efficiencies for Trifluralin and Its Photoproducts from Air[a]

Compd	Recovery,[b] % 1.0 μg[c]	25 μg[c]
I	40 ± 7	48 ± 4
II	36 ± 4	61 ± 10
III	49 ± 8	67 ± 11
IV	85 ± 10	91 ± 10
V	84 ± 5	101 ± 5

[a] Air at 30° (125 m^3) processed with Hivol Sampler. [b] Average and standard deviation of three determinations. [c] Amount introduced onto the filter.

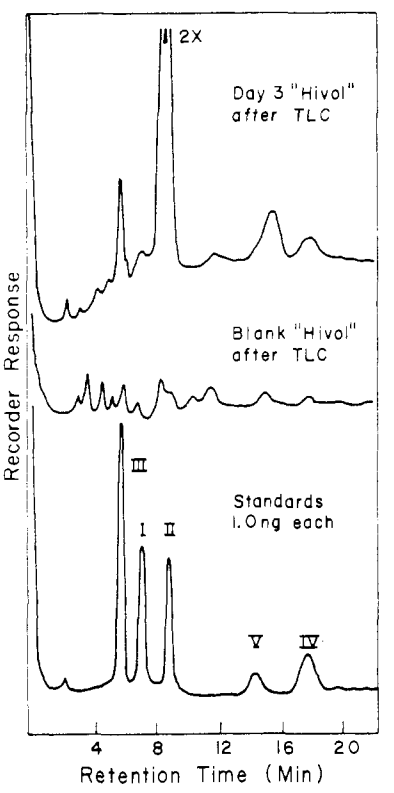

Figure 3. Typical chromatograms of a sample, blank, and standard compounds I–V.

from nitroaralkanes. The proposed mechanism is consistent with vapor-phase conditions, since it represents light-induced polarization of the nitro group and subsequent intramolecular rearrangements which do not require external reagent. Photolysis in I in the absence of oxygen produced exclusively IV.

Photolysis of trifluralin films, solutions, and coated soils was also carried out. For example, the irradiation of suspended dust coated with I gave results essentially identical (half-life of 2.5 hr at 20 ppm on standard test dust) with those obtained by irradiation of I on soil in a Petri dish (half-life of 2.2 hr at 50 ppm on Dinuba fine sandy loam soil). In general, it appears that I decomposes faster in solution, as a thin film on glass, and when adsorbed to soil or suspended dust than as a vapor, although difficulties inherent in measuring the rate of vapor-phase photolysis have precluded confirmation of this view.

Trifluralin and photoproducts II–IV are all photolabile; V, however, appears to resist further photolysis. For example, irradiation of V at 20 ppm on suspended standard test dust for 3 hr resulted in its quantitative recovery. Prolonged irradiation (200 hr) of V in the vapor-phase

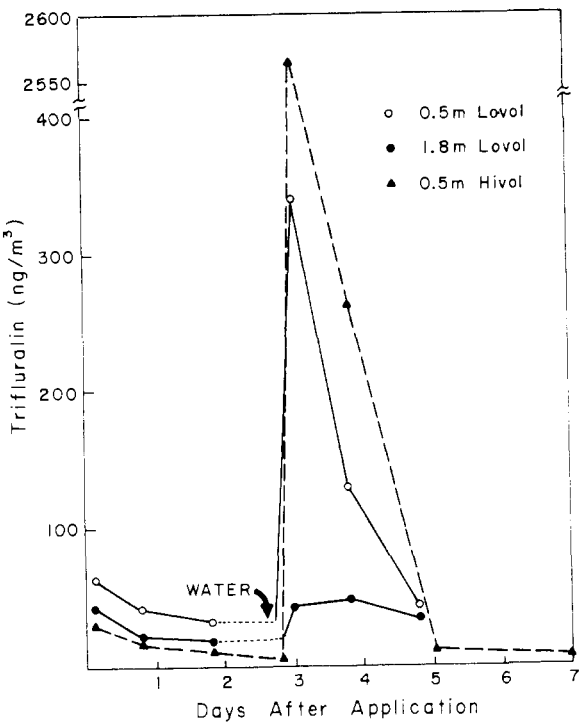

Figure 4. Trifluralin concentrations in air over a surface treatment plot.

photoreactor confirmed that V should be considered a photochemically stable product.

Air Sampling Techniques. Air sampling techniques for pesticides usually consist of drawing air through a solvent-filled bubbler or impinger (Miles *et al.*, 1970). Drawbacks to this method include a restricted sampling rate (0.03 m^3/min) which necessitates long sampling periods, and expensive and fragile glassware often inconvenient for portable use. Solid trapping agents offer an alternative to liquid absorption methods (Seiber and Woodrow, 1974). The system adopted for the trifluralin studies utilized a filter bed consisting of Chromosorb A coated to 5% with paraffin oil, although several other solid trapping agents were effective. Trapping efficiencies for vapors of trifluralin and its photoproducts (determined by spiking the Hivol filter with known amounts of I–V and measuring the per cent of the vaporized material trapped on the solid after 2 hr of sampling) were adequate and reproducible (Table II). Furthermore, extraction recoveries of I–V (2 μg) from the adsorbent exceeded 85%. For analysis of photoproducts II–V, the large excess of I was conveniently removed from air sample extracts by preparative tlc. The chromatograms of Figure 3 illustrate typical results. From the glc response of standards relative to air blanks, the usual detection limits of I–V were calculated to be 0.5–1.0 ng/m^3.

Surface Treatment Plot. Following the completion of the laboratory photolyses and method development, several experiments were carried out to check for the presence of I and its breakdown products in the field. In one experiment, I was applied to the surface of bare soil with no incorporation. Although this condition does not reflect application practice recommended by the manufacturer, it afforded enhanced volatilization for the quantitation of I–V in the air. Volatilization was further enhanced by overhead irrigation 2.8 days after application. Samplers placed in the center of the plot indicated concentrations of I of less than 61 ng/m^3 for the initial 2.8 days before the dramatic effect of soil moisture on the volatilization rate of I occurred (Figure 4). The concentration of I measured by the Hivol Sampler on day 3 exceeded that of the Lovol Samplers (Figure 4) since the Lovol values are an average of 10 hr of sampling, the latter portion of which probably contained much less trifluralin than immediately after water application. The Hivol sample on the other hand is an average of only the first 2 hr after water application when trifluralin volatilization was at its maximum. Trifluralin was still vaporizing after 7 days, but at a lower rate than for the 0–2.8 day period.

Table III. Photoproducts in Air (Surface Treatment, Hivol, Day 3)

Compd	Amt, ng/m^3
I	2570
II	12.4
III	0.73
IV	≤0.50
V	≤0.50

Table IV. Soil Residues from Surface Treatment

Days after application	Soil residue, ppm[a] I	II	III	IV	V
1	2.03	0.060	0.005	0.048	0.027
2.7	1.18	0.095	0.014	0.037	0.050
7	0.45	0.057	0.010	0.020	0.028

[a] Averages of three determinations with relative deviations of 14%.

Analysis of the day 3 Hivol sample for photoproducts (Table III) showed the unmistakable presence of II, and III, while the benzimidazoles IV and V were tentatively identified at levels near their detection limit. These results conform to the laboratory model in which II was the initial product, while prolonged irradiation (12 days) yielded primarily IV and V. Since the atmospheric residence time of I before reaching the sampler undoubtedly was quite brief, little localized formation of V was expected or found. The possibility that II–V originated from impurities in the herbicide formulation was precluded by careful analysis of a sample taken directly from the spray tank. Possible degradation of I to II–V on the adsorbent surface was ruled out by their absence from a sample of Chromosorb A spiked with I and used to sample clean air for 2 hr.

Analysis of soil samples showed that residues of I declined from 2.03 to 0.45 ppm in 7 days (Table IV). Photoproducts appeared in the first sample (0.1 day), increased slightly at day 2.7, and declined by day 7. The existence of "polar products" (Probst *et al.*, 1967) and the tentative identification of polar azoxy derivatives (Leitis, 1973) argue for the existence of other breakdown pathways in addition to photolysis; microbial action probably played a minor role, since I was not incorporated and the soil was extremely dry except during and just after irrigation. Probst *et al.* (1967) concluded that while microorganisms may contribute to the eventual destruction of trifluralin, this cannot be considered a major pathway of degradation.

Soil Incorporation Plot. While the surface treatment experiment was successful in proving the existence of I and some of its photoproducts in air, a similar evaluation under more realistic conditions was clearly desirable. Thus, in a second field experiment, I was soil incorporated into a larger area (61 ha).

This time, concentrations of I in the air measured by Hivol Sampler (Figure 5) declined from 12 ng/m^3 to less than 1 ng/m^3 within 3 days. A heavy rain (0.37 in.) on

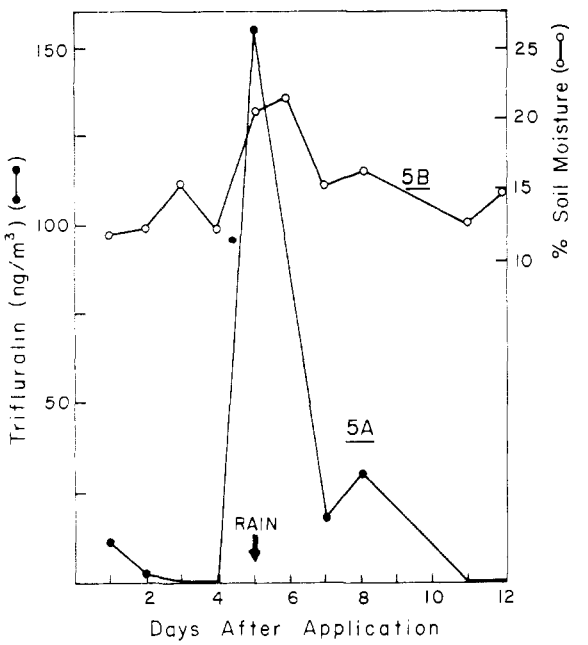

Figure 5. Trifluralin concentrations in air (A) and per cent soil moisture (B) for a soil incorporated field.

day 5, and again between days 7 and 8, increased air levels as in the previous experiment. While the overall appearance of Figure 5A matches Figure 4, the maximum values are significantly less in the former, indicating the less drastic effect of water on soil incorporated I. Comparison of concentrations of I to the soil moisture plot (Figure 5B) reemphasizes the correlation between the volatilization rate of I and soil moisture content. A summary of the results of the second experiment is presented in Table V; the presence of II in the air was confirmed by gc–ms analysis of pooled samples 5, 6, and 8, the mass spectrum and retention time being identical with those of II. The fact that I was incorporated to a depth of 15 cm while the soil was sampled to a depth of only 7.5 cm, coupled with the movement of I to the soil surface by moisture, accounts for the trend of increasing concentrations of I in soil with time (Table V).

Source of Photoproducts. While some trifluralin photoproducts (*e.g.*, II) unquestionably were present in the air after both surface treatment and soil incorporation of I, their origin is not as clear. Three potential routes of photoproduct formation must be considered: (1) *via* photolysis of I vapors in the atmosphere; (2) *via* photolysis of I on the soil surface followed by volatilization; and (3) *via* photolysis of I on air-suspended dust. The importance of these routes depends not only on the relative photolysis rates at the appropriate sites, but on transport to the sites as well. For example, the volatilization rate of I from soil into the atmosphere may limit the importance of route 1 more than the rate of vapor-phase photolysis. Since route 3 would significantly contribute to the disappearance of I only in cases of very dry soil and appreciable wind, attention will be focused on the other possibilities with specific reference to the formation of II.

Evidence to support the formation of II on soil surfaces (route 2) derives from the laboratory photolysis of I on soil (and on suspended dust) and detection of II in the soil immediately after both surface and soil incorporated application of I in the field. If this route were to predominate, the ratios of II to I in air and soil would be identical after correction for their relative volatilities. If route 1 was significant, the ratio of II to I in the air should exceed that in soil; however, the ratios of II to I in soil and air (soil incorporation experiment, Table V) were essentially identical. The soil ratio ideally should be determined on a sample taken from the top few millimeters of soil where II would be formed; however, the fact that soil was sampled to a depth of 7.5 cm further decreases the significance of route 1 in these experiments.

Nevertheless, vapor-phase photolysis remains undeniable. To confirm the laboratory results, I (5 g) was vaporized directly into a field atmosphere from an electrically heated glass tube (5 cm o.d. × 20 cm) by means of a blower within 25 m of a Hivol Sampler placed 1 m above ground. The sampler was run for 15 min while I was being vaporized; analysis indicated 0.55% breakdown of I to II (0.52 μg of II and 94 μg of I trapped) while the unvaporized solid remaining in the tube contained undetectable (less than 0.1%) II as an impurity.

The above field-test data indicate that route 2—photolysis of I at the soil surface followed by volatilization—must predominate. However, while the direct-vaporization experiment shows vapor-phase photolysis to occur at an appreciable rate, the air samples were collected so close to the ground that I vapor would have had only brief residence in the atmosphere. As a major proportion of the trifluralin lost from the soil moves as vapor (Parochetti and Hein, 1973; Savage and Barrentine, 1969), the atmosphere must provide a significant repository in which trifluralin eventually is degraded until only photochemically stable products remain.

Table V. Summary of the Soil Incorporation Experiment

Days after application	Weather conditions; wind[a] & air temp, °C	Air samples[b]				Soil samples		
		I, ng/m³	II, ng/m³	II/I, %	I on filter, μg	I,[c] ppm	II,[b] ppm	II/I, %
1	Light; 23	11.7	0.42	3.6	0.45	0.48	0.017	3.5
2	Heavy; 25	2.7			1.10	0.42	0.014	
3	None; 27	<1			0.23	0.52	0.024	
4	Heavy; 24	<1			0.22	0.65	0.021	
5	Heavy; (rain)	155	4.9	3.1	0.28	0.65	0.030	4.6
6	Heavy; 15	91.4	2,4	2.6	0.18	0.52	0.027	5.2
7	Light; 20	17.4	0.44	2.5	0.32	0.88	0.021	2.4
8	Light; 15	31.3	1.0	3.2	0.40	0.71	0.017	2.4
11	Heavy; 31	<1			0.35	0.70	0.026	
12	Moderate; 28	<1				0.45	0.024	
				Av 3.0%				Av 3.6%

[a] Light = 0–5 mph; moderate = 5–10 mph; heavy = >10 mph. [b] Single determinations. [c] Averages of three determinations with relative deviations of 13%.

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LITERATURE CITED

Bardsley, C. E., Savage, K. E., Walker, J. C., *Agron. J.* **60**, 89 (1968).
Crosby, D. G., Leitis, E., *Bull. Environ. Contam. Toxicol.* **10**, 237 (1973).
Crosby, D. G., Moilanen, K. W., *Arch. Environ. Contam. Toxicol.* **2**, 62 (1974).
Crosby, D. G., Moilanen, K. W., 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, Abstract PEST-27.
Doepp, D., *Chem. Ber.* **104**, 1043 (1971).
Ketchersid, M. L., Bovey, R. W., Merkle, M. G., *Weeds* **17**, 484 (1969).
Leitis, E., Ph.D. Thesis, University of California, Davis, 1973.
Leitis, E., Crosby, D. G., *J. Agr. Food Chem.* **22**, 842 (1974).
Miles, J. W., Fetzer, L. E., Pearace, G. W., *Environ. Sci. Technol.* **4**, 420 (1970).
Moilanen, K. W., Crosby, D. G., 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973, Abstract PEST-21.
Newsom, H. C., Woods, W. G., *J. Agr. Food Chem.* **21**, 598 (1973).
Niles, G. P., Zabik, M. J., *J. Agr. Food Chem.* **22**, 684 (1974).
Parochetti, J. V., Hein, E. R., *Weed Sci.* **21**, 469 (1973).
Plimmer, J. R., Klingebiel, V. I., *J. Agr. Food Chem.* **22**, 689 (1974).
Probst, G. W., Golab, T., Herberg, R. J., Holzer, F. J., Parka, S. J., Van der Schans, C., Tepe, J. B., *J. Agr. Food Chem.* **15**, 592 (1967).
Savage, K. E., Barrentine, W. L., *Weed Sci.* **17**, 349 (1969).
Seiber, J. N., Woodrow, J. E., 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, Abstract PEST-3.
Sharkey, W. H., Mochel, W. E., *J. Amer. Chem. Soc.* **81**, 3000 (1959).
Smith, A. E., *J. Agr. Food Chem.* **20**, 829 (1972).
Spencer, W. F., Farmer, W. J., Claith, M. M., *Residue Rev.* **49**, 1 (1973).
Wright, W. L., Warren, G. F., *Weeds* **13**, 329 (1965).

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Fate of Pyrazon in a Model Ecosystem

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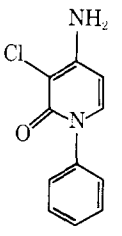
Pyridazinone ring-^{14}C-labeled pyrazon [5-amino-4-chloro-2-phenyl-3(2*H*)-pyridazinone] was slowly degraded in water. Thirty-two days after application of the compound to a model ecosystem, about 66% of the radioactivity in the water was found to be the parent compound. Very small amounts of 2-dephenylpyrazon [5-amino-4-chloro-3(2*H*)-pyridazinone] and five other unknown spots (combined total 1%) were detected only after acid hydrolysis. The remainder of the radioactivity was present as unextractable water-soluble products (33%). Combined parent compound and metabolites in organisms living in the ecosystem ranged from 0.06 ppm in fish to 0.6 ppm in crab. Analysis of the crab extracts revealed that no 2-dephenylpyrazon was present and that the parent pyrazon constituted about 76% of the total radioactivity in that organism. There was no evidence to indicate that pyrazon and its degradation products were magnified through the food chain.

Pyrazon, 5-amino-4-chloro-2-phenyl-3(2*H*)-pyridazinone (I), is a selective herbicide used in red beet and sugar beet production (Fischer, 1962). Metabolism of this compound in plants and soil has been investigated (Frank and Switzer, 1969a,b; Ries *et al.*, 1968; Smith and Meggitt, 1970a,b; Stephenson and Ries, 1967, 1969). However, the fate of pyrazon in a food chain is not known. Recently, Metcalf *et al.* (1971) developed a model ecosystem to facilitate the study of the biodegradability and accumulation of pesticides in the environment. Several pesticides have been examined in this system (Yu *et al.*, 1974; Sanborn and Yu, 1973; Booth *et al.*, 1973). This study, which is part of a continuous effort to examine the fate and effects of pesticides in the environment, considers the fate of pyrazon in a model ecosystem.



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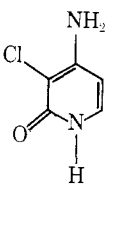

II

MATERIALS AND METHODS

Labeled Compound. Pyridazinone ring-^{14}C-labeled pyrazon (sp act., 4.7 mCi/mmol; radiochemical purity 98% by tlc and radioautography) was obtained from BASF Corporation.

Model Ecosystem. The procedures described by Metcalf *et al.* (1971) with some modifications (Yu *et al.*, 1974) were followed and the experiment with pyrazon was replicated two times simultaneously. Ring-^{14}C-labeled pyrazon (2.36 mg, 50 μCi) in 0.5 ml of acetone was applied to the base of the 7-day-old sorghum plants.

Sample Preparation. The work-up procedures were described previously (Yu *et al.*, 1974).

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