Burgett, C. A., Green, L. E., *J. Chromatogr. Sci.* **12**, 356 (1974).
Damico, J. N., *J. Assoc. Off. Anal. Chem.* **49**, 1027 (1966).
Gunther, F. A., Blinn, R. C., "Analysis of Insecticides and Acaricides", Interscience, New York, N.Y., 1955, pp 135–141.
MacNeil, J. D., Hikichi, M., Banham, F. L., *J. Agric. Food Chem.* **23**, 758 (1975).
Stellar, W. A., Pasarela, N. R., *J. Assoc. Off. Anal. Chem.* **55**, 1280 (1972).

Zwick, R. W., Fields, G. J., Kiigemagi, U., *J. Econ. Entomol.* **68**, 383 (1975).

Dissipation of Molinate in a Rice Field

Charles J. Soderquist, James B. Bowers, and Donald G. Crosby*

The dissipation of the herbicide molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbothioate) in a California rice field was investigated. Laboratory experiments indicated that while dilute aqueous solutions of molinate were stable in sunlight, irradiation in the presence of tryptophan resulted in decomposition primarily to 1-[(ethylsulfinyl)carbonyl]hexahydro-1*H*-azepine, *S*-ethyl hexahydro-2-oxo-1*H*-azepine-1-carbothioate, and hexamethyleneimine. Analysis for molinate and its degradation products at sub-ppm levels in water, soil, and air samples collected from a commercially treated field, together with laboratory studies, showed that volatilization of molinate from water was the primary mode of dissipation, although photodecomposition products were present in field water.

Molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbothioate, I) is the active ingredient in the commercial herbicide Ordram. About one million pounds of molinate were used in California in 1975 (California Department of Food and Agriculture, 1976), essentially all of which was applied in rice culture to control barnyard grass (*Echinochloa* spp.). As part of a study of the effects of chemicals used in rice culture on environmental quality of California's Sacramento Basin (Soderquist and Crosby, 1975), the fate of molinate under typical use conditions was examined.

The objectives of the present investigation were to examine, under controlled laboratory conditions, the processes such as volatilization, hydrolysis, and photolysis responsible for molinate dissipation; to devise analytical methods sensitive to sub-ppm levels for the identification and quantitation of molinate and its degradation products; and to monitor these compounds in the water, soil, and air from an Ordram-treated rice field.

EXPERIMENTAL SECTION

Chemicals. Technical molinate (96.5%) was purified by distillation under vacuum; the highly volatile forerun (about 1% of the molinate) was trapped at –80 °C and identified as diethyl disulfide by gas chromatography–mass spectroscopy (GC–MS). The purified molinate was homogeneous to both thin-layer (TLC) and gas-liquid chromatography (GLC) and was used throughout this study unless otherwise noted. Solvents were distilled twice in glass, and all other commercial chemicals were used as received except as noted. Analysis of a sample of the Ordram 10G to be applied to the field showed 11% molinate but no other products exceeding 20 ppm.

1-[(Ethylsulfinyl)carbonyl]hexahydro-1H-azepine (II). Commercial (5.3%) sodium hypochlorite solution (8.5 mL, 6 mmol of NaOCl) and 1.5 mL of 0.01 M HCl were added with stirring to a solution of I (1.0 g, 5.3 mmol) in 1.5 L of water. After 1 h, the solution was extracted with four

100-mL portions of dichloromethane. The combined extracts were dried briefly over anhydrous sodium sulfate and concentrated under vacuum at less than 40 °C to a clear, viscous liquid. Trituration with hexane at 0 °C followed by drying at room temperature under vacuum yielded white crystals (0.98 g, 90% yield), mp 39–41 °C. The product was free of I and was homogeneous to thin-layer chromatography (TLC), with an R_f (0.21, solvent A) and ninhydrin response similar to that reported by Casida et al. (1975). Spectral data were consistent with structure II: infrared spectrum (IR) 2950, 1690 (CO), 1070 (SO) cm^{-1}; mass spectrum (solid probe) m/e 126 (base, $C_6H_{12}NCO$), 98 ($C_6H_{12}N$), no M$^+$. Published methods (Casida et al., 1975; Tilles and Casida, 1975) utilizing 3-chloroperoxybenzoic acid were less satisfactory.

1-[(Ethylsulfonyl)carbonyl]hexahydro-1H-azepine (III). Hydrogen peroxide (90%) (0.3 mL, 6 mmol) was added to a solution of II (75 mg, 0.37 mmol) in 0.5 mL of formic acid at 20 °C. After 1 h, 50 mL of water was added and the solution extracted with 5 mL of hexane. The hexane was washed with 1 mL of water and then concentrated under nitrogen to yield a white solid (mp 88–90 °C) which was homogeneous to TLC with an R_f (0.61, solvent A) and ninhydrin response similar to that reported by Casida et al. (1975): IR 2940, 1680 (CO), 1310, 1130 (SO$_2$) cm^{-1}; mass spectrum (GC–MS) m/e 126 (base, $C_6H_{12}NCO$), 98 ($C_6H_{12}N$), no M$^+$.

S-Ethyl Hexahydro-2-oxo-1H-azepine-1-carbothioate (IV). Ethyl chlorothiolformate (95% pure) (35.5 g, 0.27 mol) was added dropwise to a vigorously stirred mixture of caprolactam (VI) (31.6 g, 0.28 mol), 200 mL of 1.8 M sodium hydroxide (0.35 mol), and 100 mL of hexane. After stirring for 2 h, the aqueous phase was discarded and the hexane phase washed successively with 50-mL portions of 1.0 M sodium hydroxide, 2.0 M HCl, and water and dried briefly with anhydrous sodium sulfate. The hexane and excess ethyl chlorothiolformate were removed by vacuum distillation (35 °C, 0.1 Torr) and the residue purified by column chromatography on Florisil using hexane–diethyl ether (9:1 v/v). While the yield of IV (a viscous oil) was

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Department of Environmental Toxicology, University of California, Davis, California 95616.

less than spectacular (about 1%), the material was homogeneous to TLC (R_f 0.65, solvent A) and GLC: IR 2950, 1650 (CO), 1700 (CO) cm^{-1}; mass spectrum (GC-MS) m/e 201 (M$^+$), 172 (C$_6$H$_{10}$NOCOS), 140 (base, C$_6$H$_{10}$NOCO), 112 (C$_6$H$_{10}$NO).

S-Ethyl-N-(5-carboxypentyl)thiolcarbamate (*V*). Ethyl chlorothiolformate (95% pure) (104 mg, 0.8 mmol) was added to a solution of 6-aminohexanoic acid (VII) (131 mg, 1 mmol) and sodium carbonate (110 mg, 1 mmol) in a mixture of 10 mL of water and 20 mL of methanol. After stirring for 4 h, 20 mL of water and 5 mL of 12 M HCl were added, and the solution was extracted with three 40-mL portions of dichloromethane. The combined extracts were dried over anhydrous sodium sulfate and concentrated. Recrystallization from hexane–acetone gave a white solid (mp 84.5–85 °C): IR 1640 (CO), 1710 (CO) cm^{-1}; mass spectrum (solid probe) m/e 219 (M$^+$), 158 (M – C$_2$H$_5$S), 140 (base). Treatment with ethereal diazomethane (prepared from Diazald according to Aldrich Chemical Co. instructions) gave the methyl ester: mass spectrum (GC-MS) m/e 172 (M – C$_2$H$_5$S), 140 (base), no M$^+$.

1-Butyl 6-N-Trifluoroacetamidohexanoate (*IX*). 6-Aminohexanoic acid (50 mg, 0.38 mmol) and 1 mL of 2.5 M hydrogen chloride in anhydrous 1-butanol were combined and heated at 110 °C for 30 min in a sealed vial (Zumwalt et al., 1971). After removal of the solvent under nitrogen, 1 mL of dichloromethane and 0.2 mL of trifluoroacetic anhydride (1.5 mmol) were added, and the vial was resealed and heated at 110 °C for 10 min. The mixture was concentrated to a viscous oil which was homogeneous on GLC: mass spectrum (GC-MS) m/e 283 (M$^+$), 210 (base, M – C$_4$H$_9$O).

1-[2',6'-Dinitro-4'-(α,α,α-trifluoromethyl)phenyl]-hexahydro-1H-azepine (*XI*). Hexamethyleneimine (VIII) (1.0 g, 10 mmol) and 4-chloro-3,5-dinitro-α,α,α-trifluorotoluene were combined in 50 mL of acetone. After stirring for 10 min, the mixture was filtered to remove hexamethyleneimine hydrochloride. The product was precipitated by the addition of 150 mL of water, collected by filtration, rinsed with 10 mL of water, and air dried to yield 1.2 g of pale-yellow crystals, mp 95–96 °C (95 °C, Crosby and Bowers, 1968).

Methods. Spectra were obtained under the following conditions: ultraviolet (UV), Cary Model 15, methanol solutions; IR, Perkin-Elmer Model 337, KBr discs or thin films; mass spectra, Finnigan Model 3000 (70 eV ion voltage) via either solid probe or GC-MS with a 1.2 m × 3 mm i.d. column containing 1% OV-1 on 60/80 mesh Chromosorb W, helium flow rate 10 mL/min.

TLC was carried out on precoated 20 × 20 cm, 0.25 mm thick silica gel 60 F-254 plates (Brinkman Co.) developed in acetone–hexane (1:1 v/v, solvent A) or 1-butanol–acetic acid–water (4:1:1 v/v/v, solvent B). Compounds were detected by fluorescence quenching under 254-nm light or by spraying with ninhydrin (1% in ethanol), followed by heating at 110 °C for 15 min.

GLC was performed on a Varian Model 2400 instrument equipped with flame-ionization (FID) and electron-capture (EC) detectors. Various liquid phases coated on 60/80 mesh Gas Chrom Q were employed. Compounds (or their derivatives) I, IV, and X were determined by FID with a 3% OV-17 column; VI by FID with a 1% DEGA column; and IX and XI by EC with a 3% SE-30 column.

Hydrolysis rates of various compounds were determined at pH 5, 7, and 9 in a wide-range (Carmody) boric acid–citric acid–trisodium phosphate buffer system. The compound of interest was added at 1–100 ppm in a sealed flask and held in the dark at 20–22 °C for periods from
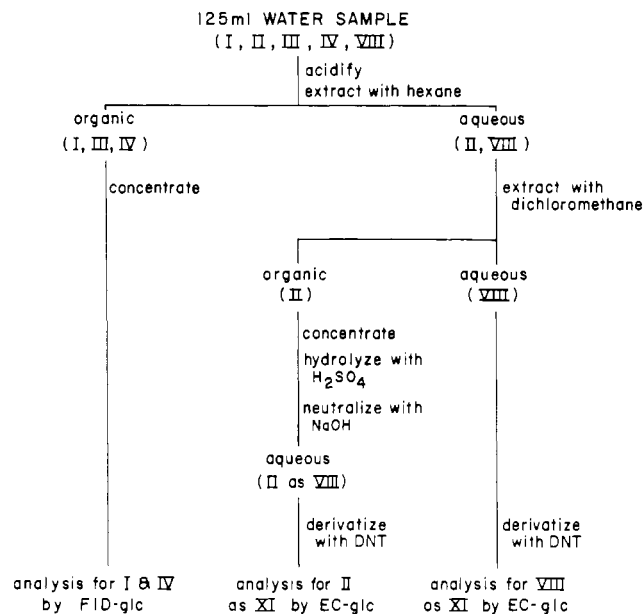

Figure 1. Analytical scheme for molinate and its major degradation products in water.

10 min to 12 days. Samples were withdrawn periodically, extracted according to the appropriate analytical procedure, and the extracts stored at –10 °C until analyzed.

Volatilization rates were determined for the various compounds in dilute aqueous solutions. For example, two beakers (8.5 cm i.d., 12 cm deep) were filled to a depth of 4 cm with 200 mL of water containing I at 10 ppm and placed in a constant temperature bath at 25 °C while open to ambient air. Samples were withdrawn periodically after measuring and then replacing the evaporated water. The samples were combined and stored frozen until analyzed for I by the usual method. The experiment was repeated at 15, 20, and 28 °C.

Field Application. A rice field in Sutter Co., Calif., served to determine the rate of dissipation of molinate under typical use conditions. The 77 ha area (Sacramento clay soil, 10% organic matter) had been in rice cultivation with water from the Sacramento River for 14 years. The field was planted May 12, 1975 and treated with Ordram 10G (3.36 kg of molinate/ha) by aircraft on May 23, 1975. Water, mud, and air samples were collected from the lower rice check, near an outlet to a drainage canal, before treatment and at regular intervals up to 13 days after treatment. Soil samples were collected occasionally up to 1 year later. All samples were returned immediately to storage at –10 °C until analyzed.

Duplicate water samples were collected in polyethylene containers below the water surface without filtering. Water temperature varied from 18 to 35 °C and water depth was held at about 15 cm, without field spillage, for 11 days after application. The water pH averaged 7.3. Air samples were collected before and after treatment with a Bendix high-volume air sampler identical with one described previously (Soderquist et al., 1975) except that an Amberlite XAD-4 macroreticular resin (Rohm and Haas Co.) trapping medium replaced the Chromosorb A. Duplicate soil samples were collected by retrieval of a series of perforated cans (6.1 cm diameter × 12 cm height) previously buried level with the soil surface. Field, preapplication (control), reagent blank, and fortified control samples also were analyzed according to the procedures described below.

Analysis. *Water* (*Figure 1*). The thawed sample (125 mL) was acidified with one drop of 12 M HCl and ex-

tracted with two 25-mL portions of hexane to remove compounds I and IV. The combined hexane extracts were concentrated under a stream of nitrogen below 35 °C to no less than 1 mL and analyzed for I by FID–GLC at 180 °C. After further concentration, the extract was analyzed for IV by FID–GLC at 205 °C.

The remaining aqueous phase was extracted with two 25-mL portions of dichloromethane to remove II. The combined extracts were concentrated under vacuum to about 1 mL, transferred to a 50-mL centrifuge tube, and concentrated under a stream of nitrogen to about 0.5 mL. Concentrated sulfuric acid (0.50 mL) was added, the layers mixed with a vortex stirrer, and the remaining dichloromethane (upper layer) removed completely under a stream of nitrogen. The tube was sealed and heated at 85–90 °C for 30 min. After cooling, about 5 g of ice, 1.8 mL of 9 M sodium hydroxide, and one drop of phenolphthalein indicator solution (1.0% in ethanol) were added, and the mixture (containing VIII from the hydrolysis of II) was vortex stirred. While stirring, additional 9 M sodium hydroxide was added to the phenolphthalein endpoint. After adjustment to a known volume (e.g., 8 mL), the solution was transferred to a 50-mL volumetric flask with a 5 mL benzene rinse and 0.5 mL of derivatizing reagent solution (0.27 mg of 4-chloro-3,5-dinitro-α,α,α-trifluorotoluene per mL of acetone) added. The stoppered flask was heated in a water bath at 50–55 °C for 1 h with occasional shaking to mix the two phases, cooled, and diluted with hexane. Analysis by EC–GLC at 190 °C was standardized against an authentic sample of XI.

After sulfoxide extraction, the aqueous solution was made basic (phenolphthalein) with dilute aqueous sodium hydroxide and a 10.0-mL aliquot transferred to a 50-mL volumetric flask. Benzene (5 mL) and 0.5 mL of derivatizing reagent were added, and the mixture was analyzed for VIII as described above.

Soil. Soil samples were divided to represent the 0–5 cm and 5–12 cm layers, thawed, and a weighed subsample (about 500 g) and 2.5 L of distilled water were placed in a 5-L round-bottom flask equipped for distillation. The collected distillate (400 mL) was acidified with 1 mL of 12 M HCl and extracted with two 30-mL portions of dichloromethane. The combined extracts were concentrated under vacuum and analyzed for I by FID–GLC at 180 °C. Recoveries averaged 85–90%.

Air. Field air samples were analyzed by elution of the Amberlite resin with 100 mL of acetone. The acetone was concentrated and levels of I determined by FID–GLC at 180 °C. Recoveries were about 70% at the ng/m^3 level.

Laboratory Photolysis. Irradiation of aqueous solutions of molinate or related compounds was carried out with a photoreactor which closely simulated the effects of sunlight (Crosby and Tang, 1969). For example, a solution containing 25 mg (10 ppm) of I and 125 mg (50 ppm) of tryptophan in 2.5 L of deionized water was divided into two equal portions; a photoreactor equipped with external cooling coils, an F40/BL light source (General Electric Co.), and an air inlet (to provide oxygen) was filled with one portion of the solution, and an identical reactor lacking only the light source contained the second portion and served as a control. Temperatures were maintained at 21–22 °C in both reactors. Samples (100 mL) were withdrawn at various intervals and stored at –10 °C until analyzed.

Products were identified by cochromatography with authentic standards or authentic derivatives by GLC and, in some cases, confirmed with TLC. I and its photoproducts II, IV, and VIII were quantitated as described

above for field water samples. The presence and concentration of S-ethyl-N-(5-carboxypentyl)thiolcarbamate (V), caprolactam (VI), 6-aminohexanoic acid (VII), and ethanesulfonic acid (X) in photolysis, control, and fortified samples were indicated by the following procedures: *V.* The sample (10 mL) was acidified with 0.5 mL of 12 M HCl and extracted with two 10-mL portions of dichloromethane. The combined extracts were concentrated under a stream of nitrogen to about 0.2 mL, treated with ethereal diazomethane, and analyzed as the methyl ester at 220 °C with FID–GLC.

VI. The sample (40 mL) was extracted with two 25-mL portions of dichloromethane. The combined extracts were concentrated to an appropriate volume and analyzed for VI at 190 °C with FID–GLC.

VII. The sample (1.0 mL) was concentrated to dryness at 80 °C under a stream of nitrogen, derivatized according to the procedure of Zumwalt et al. (1971), and analyzed for the derivative IX by EC–GLC at 185 °C.

X. In a separate experiment, I (100 ppm) was irradiated in the presence of tryptophan for 3 months. An identical solution held in the dark served as a control. After extraction with dichloromethane, the aqueous photolysate was passed through a column of 11 g of Dowex-3 ion-exchange resin (chloride form), the column eluted with 25 mL of 1.0 M ammonium hydroxide, and the eluate concentrated under vacuum just to dryness. The residue was dissolved in about 0.5 mL of methanol, treated with ethereal diazomethane, and analyzed for methyl ethanesulfonate by FID–GLC at 85 °C. The identity of the ester was confirmed by comparing its mass spectrum (m/e 124, 95, 79) and GLC retention time with those of authentic methyl ethanesulfonate. The dark control contained no X. Gas chromatographic analysis of the dichloromethane extract from this experiment also gave small amounts of a material with a retention time close to that of IV; analysis by GC–MS gave a parent and base peak identical with those from IV, indicating an isomer with oxidation at another position on the ring.

RESULTS AND DISCUSSION

Analytical Methods. While a GLC determination of molinate (I) had been described previously (Onley and Yip, 1971), methods for its degradation products II–VIII had not. Only I, IV, and VI responded well to chromatography; the others required formation of derivatives. Water analysis for I (Figure 1) included the determination of II, IV, and VIII which laboratory work had shown to be the major degradation products.

Determination of II was accomplished by hydrolysis to VIII, followed by derivatization to XI. The advantages of this derivative included a longer retention time and more detection sensitivity (Crosby and Bowers, 1968). Since I, II, and III hydrolyzed in a similar fashion, the analytical scheme required separation of II, I + III, and VIII prior to the hydrolysis–derivatization steps. Both the sulfoxide II and the amine VIII are protonated under acidic conditions and do not partition into hexane; molinate and the sulfone III do so readily. Dichloromethane was sufficiently polar to remove II, while VIII again remained in the aqueous phase. Compound III did not respond to chromatography under our conditions and did not interfere with analysis of I in the hexane extracts. Table I summarizes a typical (triplicate) analysis and demonstrates the lack of cross interferences between the compounds analyzed.

Laboratory Photolysis. Since molinate has a UV absorption maximum at 225 nm (ϵ 10^3 in methanol) with no apparent absorption above 290 nm, it would not be

Table I. Analytical Recoveries from Water Samples[a]

Compd	Minimum detectability, ppm	Amount added, ppm	Amount found, ppm[b]			
			I	II	IV	VIII
I	0.010	2.0	2.2 ± 0.1	0.009 ± 0.005	<0.01	<0.005
II	0.0010	0.10		0.082 ± 0.007		
III		0.10		<0.003		
IV	0.010	0.10			0.079 ± 0.002	
VIII	0.0050	0.10		<0.001		0.11 ± 0.02

[a] Water samples (125 mL) were individually fortified with the indicated compound and analyzed according to the water analysis procedure (see Experimental Section). [b] Average and average deviation from three determinations.
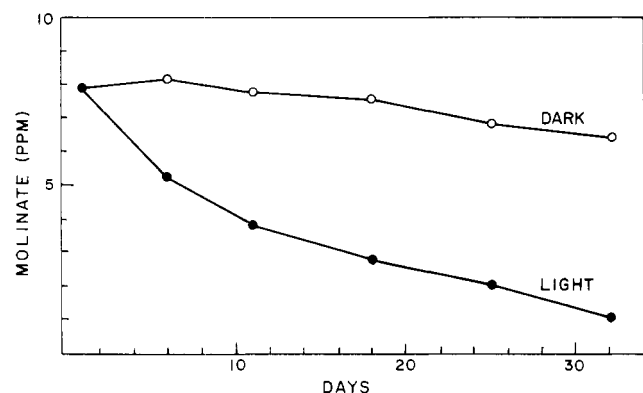
Figure 2. Molinate photodecomposition in aqueous tryptophan.

expected to undergo photolysis in sunlight. Indeed, a 10 ppm solution of molinate in deionized water was unchanged after 7 days of irradiation; Casida et al. (1975) have reported its light stability on a solid surface. However, we found that tryptophan, previously implicated as a naturally occurring photosensitizer in field water (Ross, 1974), promoted the photodecomposition of molinate in water.

Photolysis experiments used an initial concentration of I (8 ppm) near that commonly encountered in field situations (2–3 ppm) but which maximized both the rate and product yields. Tryptophan was added in molar excess as sensitizer, and the solution was not buffered. During the experiments, the pH dropped to about 4.5, presumably due to acidic byproducts of tryptophan decomposition.

A typical photolysis experiment resulted in a molinate half-life of about 10 days (Figure 2). Loss in the control (dark) reactor was due to volatilization; no products were detected in the absence of light. Several photoproducts appeared to be quite stable (Figure 3) and were due primarily to initial oxidation on the sulfur atom and the hexahydroazepine ring, possibly by different tryptophan-induced mechanisms. For example, both II and III were readily produced from I in the dark by oxidants such as 3-chloroperoxybenzoic acid or hypochlorite, while ring oxidation (to IV) apparently required free radical (light) mediation. The exact role of tryptophan in the photooxidation of molinate is under exploration.

Cleavage of the carbonyl–sulfur bond would be expected to lead to either ethanethiol, ethanesulfinic acid, or ethanesulfonic acid, depending upon the extent of oxidation of the precursor. This sulfur pool ($C_2H_5SO_xH$) should ultimately be represented by stable ethanesulfonic acid (X). Repeated attempts to develop a reliable quantitative analytical method for X failed, but its presence as a photolysis product was confirmed by ion-exchange chromatography, methylation, and subsequent GC–MS of the methyl ester.

Examination by GLC and TLC indicated no products other than those shown in Figure 4. Their mass balance at each sampling time averaged 91 ± 14%. The proposed
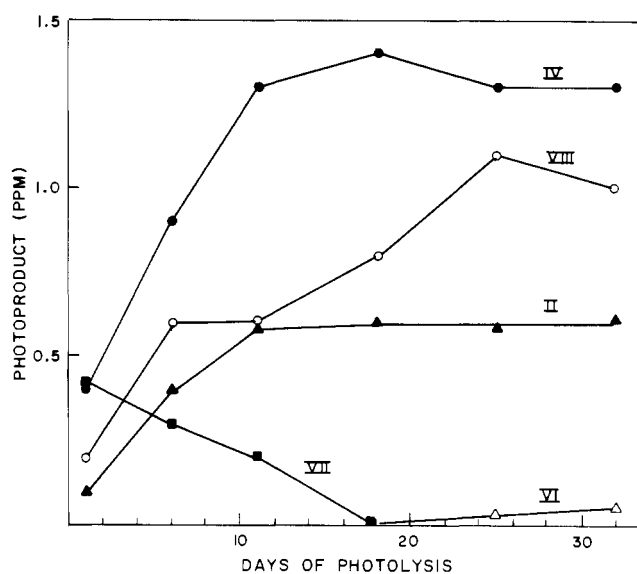

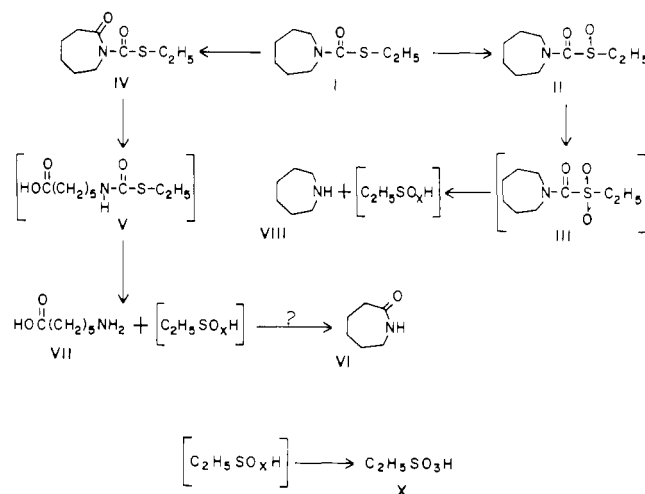Figure 3. Products of the tryptophan-sensitized photolysis of molinate.

Figure 4. Proposed degradation pathway for molinate (I).

Table II. Hydrolysis Rates at 25 °C

Compd	Approx. half-life in water			Max. time sampled
	pH 5.0	pH 7.0	pH 9.0	
I	n[a]	n	n	10 day
II	n	n	28 h	30 h
III	n	10 min	8 min	10 min
IV	n	11 day	2 day	12 day
V	n	n	10 day	6 day
VI	n	n	n	7 day

[a] No measurable loss during sampling period.

degradation pathway for molinate (Figure 4) combines both those products formed by sensitized photolysis and
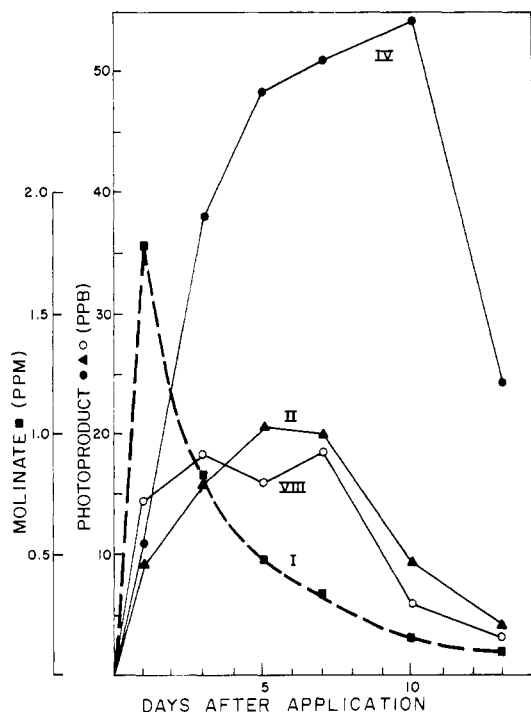
Figure 5. Molinate (■) and photoproduct (●, ▲, ○) concentrations in water from a commercially treated rice field.

Figure 6. Molinate concentration in soil (0–5 cm deep) from a commercially treated rice field.

those resulting from subsequent dark hydrolysis (Table II). Photolysis of a pH 4.8 solution of II (8 ppm initial) for 6 days in the presence of tryptophan resulted in VIII; III and IV were not detected. The absence of IV precludes an intramolecular transfer of oxygen from the sulfur of II as a mechanism of ring oxidation. While we did not establish whether VIII resulted from II directly or through the sulfone (III), the latter seems more likely. III is extremely unstable in water (Table II) and is readily produced from II by oxidation (Casida et al., 1974). VIII was resistant to light under our conditions.

Major photolysis products and molinate were examined for hydrolytic stability at pH 5, 7, and 9 (Table II). Molinate and caprolactam were stable at 25 °C at all three pH values; the other compounds exhibited various degrees of instability. While hydrolysis of the ring-oxidized product IV produced no detectable VI, V formed readily and may be the source of the observed amino acid VII; however, VI was formed during the photolysis experiment, perhaps from VII. The pH will have a major effect on the ultimate fate of molinate in natural and field waters via its affect on the photooxidation products.

Field Dissipation. Analysis of water samples from the Ordram-treated field showed no molinate prior to application but a concentration of 0.6 ppm 1 h after treatment; the maximum concentration was not reached until the following day (Figure 5), in line with laboratory observations which showed that about 18 h was required for complete solution of I from its granular formulation. One day after application, the average content of I was 1.8 ppm in water and 0.44 ppm in mud (0–5 cm depth). Estimating the weight of water and mud to be 1.5 × 10⁵ g/m² and 2.7 × 10⁴ g/m², respectively, leads to a corresponding molinate distribution of 0.27 g/m² and 0.012 g/m² and 83% recovery of the theoretical applied rate (3.4 kg/ha), of which 96% occurred in the water.

The remaining 4% was found in the top 5 cm of submerged soil (Figure 6). The molinate concentration remained almost constant for several months and finally declined to the preapplication level (0.1 ppm) as the field
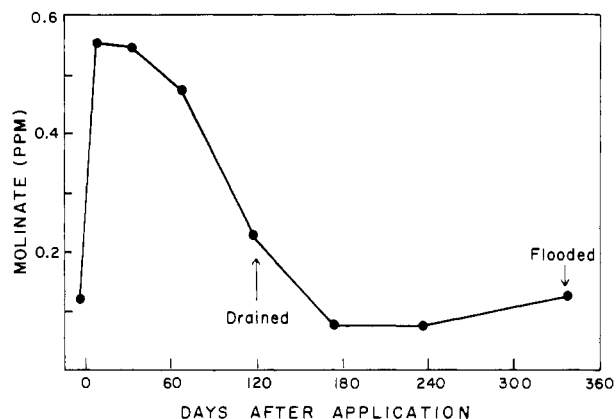
dried out. Residues in soil below 5 cm were initially lower (about 0.1 ppm) but behaved in the same manner. This persistence in anaerobic soils has been described previously (Tanji et al., 1974).

Degradation of I in the field water was primarily photochemical. Hydrolysis and microbial breakdown were demonstrated to be negligible; when field water containing I at 10 ppm was placed in a sealed flask in outdoor sunlight for 8 days, only 44% of the herbicide remained compared with an identical (unchanged) solution covered to exclude sunlight. The striking similarity between the concentration profiles of photoproducts II, IV and VIII in the laboratory experiments (Figure 3) and those in field samples (Figure 5) also supports photodecomposition as the significant force in molinate breakdown. Unlike the results from laboratory experiments, the field experiments indicated that photoproducts disappeared rapidly under practical use conditions. Although Ross and Crosby (1977) have shown the tryptophan and tyrosine found in rice-field water to be responsible for similar photooxidations, no attempt was made to identify the field photosensitizer in this case.

The literature offers few data for quantitative estimate of molinate uptake by biota. However, one calculation yields a plant biomass for a rice field at 15 days of about 60 g/m² (Ishizuka, 1964; Oelke et al., 1967); even an extreme uptake to give a herbicide concentration of 250 ppm in the largely submerged seedlings would account for less than 5% of the molinate present in the 0.15 m deep field. Rough extrapolation of the data of Chen et al. (1968) and Santi and Gozzo (1976) suggests that this value is high.

While the major degradative route for molinate was photochemical, volatilization from field water to the atmosphere was by far the major route of dissipation. The high volatility of thiolcarbamate herbicides has long been recognized (Gray, 1965; Gray and Weierich, 1965; Kauffman, 1967; Koren et al., 1969; Fang et al., 1961; Fang, 1969), although molinate has been reported to be the least volatile. Our experiments indicate that molinate volatilizes readily from dilute aqueous solution (Figure 7), the rate of loss being negligible at 15 °C but very rapid (half-life of 1.6 day) at the typical field temperature of 28 °C; field water temperatures occasionally reached 35 °C during our experiments. Half-life values ($t_{1/2}$), calculated from slopes in Figure 7 and converted into rate constants (k) through the relationship $k = 0.693/t_{1/2}$, yielded 0.11, 0.28, and 0.43 day⁻¹ for 20, 25, and 28 °C, respectively. The volatilization rate depends upon the amount of water lost from the system (Mackay and Wolkoff, 1973); division of the rate constants by the water loss (grams per day) for each temperature gave a constant value (0.11 ± 0.01 mL⁻¹) as
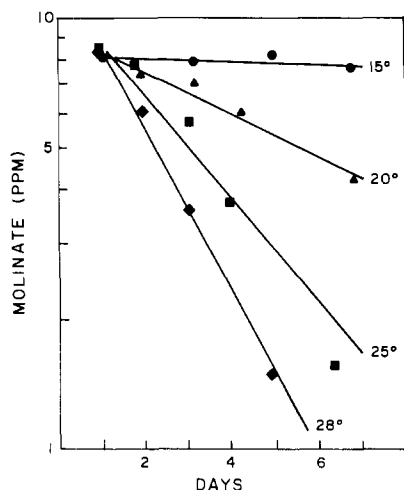
Figure 7. Volatilization of molinate from aqueous solution.

Table III. Loss of Molinate from an Ordram-Treated Field

Process	Estimated loss, %
Soil adsorption and metabolism	<10
Plant uptake and metabolism	<5
Aqueous microbial metabolism	<1
Hydrolysis	<1
Photolysis	5-10
Volatilization to atmosphere	75-85

expected. Comparison of the volatilization rate constants (0.11 to 0.43 day^{-1}) with the rate constant for laboratory photolysis (0.03 day^{-1} at 22 °C) again shows the overriding importance of volatilization. Another calculation, based upon the material (mole) balance in the field water, lends support to this statement. Molinate loss, accounted for as photoproducts, averaged about 4% of the maximum molinate concentration (1.8 ppm) at each sampling time. For example, by day 7 when 17% of the original molinate remained, 5% was accounted for as photoproducts; the bulk of the difference (78%) could only be transported to the atmosphere.

The presence of molinate in the atmosphere above the field was confirmed experimentally by high-volume air sampling. While the herbicide was not detectable beforehand, about 10 μg/m^3 was found at a height of 0.1 m 1 day after application. Air sampling only demonstrated the presence of molinate in the atmosphere above the field; no reliable method exists whereby the total flux of a chemical from an open field to the atmosphere can be measured by air sampling (Mackay and Cohen, 1976), and our estimate of the contribution of this dissipative route is, of necessity, by difference. However, comparison of the other potential routes (Table III) as well as the demonstrated rate of molinate volatilization from aqueous systems strongly supports the predominance of dissipation to the atmosphere.

The dissipation of molinate from the rice field can be summarized as follows (Table III). Of the molinate accounted for on day 1, less than 10% reached the sub-

merged soil; soil residues subsequently declined slowly to an eventual level of 0.1 ppm or less. The remainder of the molinate went into solution in the field water, where plant uptake and microbial metabolism removed only a minor part. Comparison of the rate of molinate photolysis with that of volatilization at 25 °C, as well as estimates based on the material balance in the field, indicate that photochemical breakdown in solution accounted for another 5 to 10%; however, that the molinate was photolyzed at all provides field-scale verification of the importance which photochemically generated oxidants may have in the environmental fate of xenobiotics.

LITERATURE CITED

California Department of Food and Agriculture, "Pesticide Use Report 1975", California Department of Food and Agriculture, Sacramento, Calif., 1976.

Casida, J. E., Gray, R. A., Tilles, H., Science 184, 573 (1974).

Casida, J. E., Kimmel, E. C., Ohkawa, H., Ohkawa, R., Pestic. Biochem. Physiol. 5, 1 (1975).

Chen, T. M., Seaman, D. E., Ashton, F. M., Weed Sci. 16, 28 (1968).

Crosby, D. G., Bowers, J. B., J. Agric. Food Chem. 16, 839 (1968).

Crosby, D. G., Tang, C.-S., J. Agric. Food Chem. 17, 1041 (1969).

Fang, S. C., in "Degradation of Herbicides", Kearney, P. C. and Kaufman, D. D., Ed., Marcel Dekker, New York, N.Y. 1969, p 147.

Fang, S. C., Theisen, P., Freed, V. H., Weeds 9, 569 (1961).

Gray, R. A., Weeds 13, 138 (1965).

Gray, R. A., Weierich, A. J., Weeds 13, 141 (1965).

Ishizuka, Y., in "The Mineral Nutrition of the Rice Plant", International Rice Research Institute Symposium, Johns Hopkins Press, Baltimore, 1964, p 199.

Kauffman, D. D., J. Agric. Food Chem. 15, 582 (1967).

Koren, E., Foy, C. L., Ashton, F. M., Weed Sci. 17, 148 (1969).

Mackay, D., Cohen, Y., Proceedings of the Symposium on Nonbiological Transport of Pollutants on Land and Water, Gaithersburg, Md., May 13, 1976.

Mackay, D., Wolkoff, A. W., Environ. Sci. Technol. 7, 611 (1973).

Oelke, E. A., Morse, M. D., Mikkelsen, D. S., "Rice Stand Establishment", California Agricultural Extension Service, 1967.

Onley, J. H., Yip, G., J. Assoc. Off. Agric. Chem. 54, 1366 (1971).

Ross, R. D., Ph. D. Thesis, University of California, Davis, Calif., 1974.

Ross, R. D., Crosby, D. G., submitted to Photochem. Photobiol., 1977.

Santi, R., Gozzo, F., J. Agric. Food Chem. 24, 1229 (1976).

Soderquist, C. J., Crosby, D. G., Pestic. Sci. 6, 17 (1975).

Soderquist, C. J., Crosby, D. G., Moilanen, K. W., Seiber, J. N., Woodrow, J. E., J. Agric. Food Chem. 23, 304 (1975).

Tanji, K. K., Biggar, J. W., Mehran, M., Cheung, M. W., Henderson, D. W., Calif. Agric. 28(5), 10 (1974).

Tilles, H., Casida, J. E., U. S. Patent 3 896 169, July 22, 1975.

Zumwalt, R. W., Kuo, K., Gehrke, C. W., J. Chromatogr. 57, 193 (1971).