

Table II. Bound Residues in Soil and Humic Materials

compound	ppm <sup>a</sup>			
	soil	humic acid	fulvic acid	humic
atrazine	0.11	0.30	ND	ND
deethylatrazine	T	T	ND	ND
deisopropylatrazine	T	0.12	ND	ND
hydroxyatrazine	0.10	0.30	T	0.11
deethylhydroxyatrazine	0.13	0.20	T	T
deisopropylhydroxyatrazine	0.07	0.20	ND	T

<sup>a</sup>ND = nondetectable; <0.01 ppm. T = trace amount; <0.05 ppm.

Our previous studies have shown a long-term persistence of atrazine and its metabolites in soil under field conditions (Capriel and Haisch, 1983a). Furthermore, it was demonstrated that these residues could be absorbed by oat plants (Capriel and Haisch, 1983b). Data presented in this study indicate that about 50% of the initially applied radioactivity was present in soil in the bound (nonextractable) form even after 9 years of the herbicide application and this bound radioactivity still contains the parent herbicide in addition to other metabolites. This raises the question whether analysis of the extractable residues alone is a valid criteria to determine the persistence of the herbicide under the outdoor conditions described in this study. The observations that soil bound residues are absorbed by plants (Khan, 1982b) and the data presented in this paper should prompt further research to determine whether the long-term accumulation of bound residues

could affect sensitive crops grown in rotation or contribute to the contamination of the environment.

Registry No. Atrazine, 1912-24-9.

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## Composition and Photochemical Reactions of a Dimethylamine Salt Formulation of (4-Chloro-2-methylphenoxy)acetic Acid (MCPA)

Donald G. Crosby\* and James B. Bowers

A commercial formulation of MCPA ((4-chloro-2-methylphenoxy)acetic acid, dimethylamine salt) was found to be over 95% pure, with (2-methylphenoxy)acetic acid as the principal impurity. Sunlight irradiation of a spray mixture and the semisolid residue remaining after its evaporation on a glass surface resulted in >80% loss of MCPA within 6 days and formation of 4-chloro-*o*-cresol and 13 other identified products as well as an unresolved mixture of polycarboxylic acid salts. Unexpected products included (4-chloro-2-methylphenoxy)-*N,N*-dimethylacetamide and 4-chloro-2-methylanisole; amine salts of other phenoxy herbicides also were converted photochemically to corresponding amides. After 31 days of outdoor exposure, only 10% of the original MCPA remained. MCPA would be expected to undergo chemical degradation as long as it remained airborne as spray drift.

MCPA ((4-chloro-2-methylphenoxy)acetic acid) has been applied for weed control in California rice fields since 1951. In 1979, 80% of the state's half-million acres of rice were sprayed with the herbicide, primarily as the dimethylamine (DMA) salt, and in 1982, 200 000 kg of the herbicide was used (CDFA, 1983). Earlier work (Soderquist and Crosby, 1975) indicated that a significant proportion of the aerially applied spray did not reach its intended target, and concern over the environmental fate of possible spray drift prompted the present project.

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

The objectives of our work were (1) to determine the chemical composition and physical characteristics of MCPA/DMA concentrate and spray and (2) to investigate changes in the spray composition due to evaporation, photodegradation, and other environmental factors as they might affect airborne droplets.

## MATERIALS AND METHODS

**Materials.** "MCP Amine" herbicide (Dow Chemical Co.) was the commercial product used in California rice fields. The label correctly stated that it contained 4 lb/gal of MCPA acid equivalent as the dimethylamine salt (52.1%, or 589 g/L, of the salt). Spray mixtures were prepared, according to common practice, by dilution of this

aqueous concentrate with 40 volumes of water (final concentration 14.7 g/L, 0.06 M).

Reagents were purified commercial products and solvents were residue grade. Pure MCPA was prepared by acidification of diluted DMA formulation and repeated recrystallization of the precipitated acid from benzene, mp 119–120 °C. Other phenoxyacetic acid standards were purchased or were prepared from the corresponding pure phenols by reaction with ethyl bromoacetate and subsequent hydrolysis (Synerholm and Zimmerman, 1945). Ethereal diazomethane (CAUTION: EXPLOSIVE) was prepared by the standard procedure (de Boer and Backer, 1963).

**Dimethylamine (DMA) salts** were first prepared by bubbling excess gaseous dimethylamine into a benzene solution of the appropriate acid at room temperature and subsequent evaporation of solvent. The MCPA salt (I) was difficult to crystallize, mp 60–61 °C, and CHN analysis indicated it was impure. Preparation from acid and amine in ether provided purer material, mp 94–95 °C. The salts were soluble in chloroform, dichloromethane, acetonitrile, or alcohols but insoluble in ether, benzene, or acetone.

**(4-Methoxy-2-methylphenoxy)acetic acid (VI)** was prepared by diazotization of 4-methoxy-2-methylaniline (Aldrich Chemical Co.) and hydrolysis of the resulting diazonium salt with hot dilute sulfuric acid (Adams et al., 1972) to 4-methoxy-2-methylphenol. The phenol was converted without further purification to the desired product by reaction with ethyl bromoacetate and subsequent hydrolysis (Synerholm and Zimmerman, 1945). Recrystallization from benzene gave white crystals: mp 118.9–119.4 °C; mass spectrum,  $m/e$  196 ( $M^+$ ), methyl ester  $m/e$  210 ( $M^+$ ); NMR spectrum  $\delta$  2.28 ( $\text{PhCH}_3$ ), 3.76 ( $\text{OCH}_3$ ), 6.7–6.8 (PhH).

**(4-Chloro-2-methylphenoxy)-*N,N*-dimethylacetamide (IX)** was prepared by refluxing MCPA with excess thionyl chloride, evaporation, and reaction of the resulting acid chloride with excess dimethylamine in benzene. The product was recrystallized from isooctane: mp 43.5–44.5 °C; mass spectrum,  $m/e$  227 ( $M^+$ ), 192 ( $M - \text{Cl}$ ), 115 ( $M - \text{CONMe}_2$ ), 72 ( $\text{CONMe}_2$  base); IR spectrum 6.20  $\mu\text{m}$  (amide C=O).

**4-Chloro-2-methylphenyl formate (III)** was prepared by treating the phenol with a mixture of acetic anhydride and formic acid (1:1 v/v) containing a trace of sodium formate as a catalyst (van Es and Stevens, 1965). The material was recrystallized from carbon tetrachloride but decomposed upon heating for a melting point determination.

Mass spectrum,  $m/e$  170 ( $M^+$ ), 142 ( $M - \text{CO}$ ), 107 ( $M - \text{COCl}$ , base). The formate was not stable and decomposed to its phenol within several days at room temperature.

**Formulation Analysis.** Formulation samples were made strongly acidic and extracted with chloroform or dichloromethane, and the extractives remaining after evaporation of the organic solvent were methylated with ethereal diazomethane. Neutral constituents were isolated from the original, alkaline formulation by continuous extraction and benzene. The products were analyzed separately by gas chromatography (GLC) on a Varian Model 1740 instrument fitted with a flame ionization detector and either a 150  $\times$  0.21 cm column of 5% OV-17 on Chromosorb G or a 300  $\times$  0.21 cm column of 10% DC-200 on Gas Chrom Q. Nitrogen carrier gas was used at 30 mL/min with the shorter column and 20 mL/min with the longer one. GLC with a mass spectrometric detector (GCMS) was conducted with a Finnigan Model 3000 Peak Identifier

equipped with a 120  $\times$  0.3 cm glass column containing 2% OV-1 on 60/80 mesh Chromosorb G or a Finnigan Model 3200 GCMS with a 30 m  $\times$  0.25 mm capillary coated with SP-2250 methylphenylsilicone.

Alternatively, formulations and degradation products were analyzed by high-pressure liquid chromatography (HPLC) on a Waters Associates instrument fitted with a Model 440, 254-nm ultraviolet (UV) detector, and a Partisil ODS 10 reverse-phase  $\text{C}_{18}$  column. The preferred solvent system for photoproducts was 50% aqueous methanol, 15% aqueous acetonitrile containing phosphate buffer (pH 2.83) permitted direct injection of the formulation, and 1:1 methanol–0.6% aqueous acetic acid was used to quantitate MCPA.

**Photodegradation.** Thin films (0.025 mm) or 10- $\mu\text{L}$  droplets of MCPA/DMA spray were placed by syringe on the bottom of 20  $\times$  20 cm borosilicate glass dishes and exposed to summer sunlight in Davis, CA, or held in the dark as controls. Temperatures reached about 30 °C. Alternatively, aqueous spray solution was irradiated with an F40BL fluorescent UV lamp in a laboratory photoreactor (Crosby and Tang, 1969) or as thin films on glass under F40BL lamps. Irradiated films were dissolved in methanol, or the irradiated aqueous solutions were extracted with ether, and the organic extracts were analyzed by GLC and GCMS before and after diazomethane methylation. Wherever possible, identities were confirmed by comparison with known standards.

Trapping of volatile photolysis products was accomplished by irradiating a thin film of spray on the walls of a borosilicate glass flask through which a slow stream of purified air was flowing. Volatile products were removed from the exit air by passing it through 0.1 M aqueous sodium hydroxide solution protected from light; at predetermined times, the alkaline solution was removed, acidified, and extracted with dichloromethane, and the extractives analyzed by GLC (usually after methylation). Alternatively, the trap contained ethylene glycol so that photoproducts were not exposed to aqueous base. Volatilization of dimethylamine was measured by bubbling purified air through spray solutions, trapping any evolved amine in dilute acid, and weighing the solid trap residues remaining after evaporation.

**Field Applications.** MCPA/DMA concentrate was diluted with 40 volumes of water and applied as spray from fixed-wing aircraft to two commercial rice fields in Butte Co., CA (Crosby et al., 1981). Air temperature was approximately 25 °C and wind speed 1–8 mph (0.5–3.7 m/s) at the time of application. Field A was calculated to receive 12 oz/acre (840 g/ha) of MCPA acid equivalent, and Field B 14 oz/acre (980 g/ha), from an altitude of approximately 3 m.

Glass dishes were set out, 15 m apart, in each field for 300 m across the path of application. During a period of several hours after spraying, the dishes were collected, rinsed, and the amount of deposited MCPA determined by GLC analysis after methylation.

## RESULTS AND DISCUSSION

**MCPA Formulation.** MCPA/DMA formulations were light to dark brown, almost odorless, homogeneous solutions with a pH of 8.0–8.1. Droplets (10  $\mu\text{L}$ ) of 40:1 aqueous spray on an inert (glass) surface evaporated to sticky, viscous spots rather than to crystalline deposits, and although a thin layer (0.025 mm) of spray largely evaporated within the first hour, loss of water was never complete.

At least 18 impurities have been reported to occur simultaneously in technical MCPA (Sjöberg, 1950; Freeman

Table I. Typical Analysis of MCPA Amine Formulation

constituent	amount, %	method
phenoxyacetate salts		
4-chloro-2-methyl- 2-methyl-	>95	GLC, HPLC, GCMS
6-chloro-2-methyl-	1	HPLC, GCMS
4,6-dichloro-2-methyl-	0.5	GCMS
other dichloro-2-methyl-	0.5	GCMS
phenols		
4-chloro-2-methyl-	0.3	GLC
4,6-dichloro-2-methyl-	trace	GCMS
neutrals		
(4-chloro-2-methylphenoxy)- <i>N,N</i> -dimethylacetamide	0.03	GLC

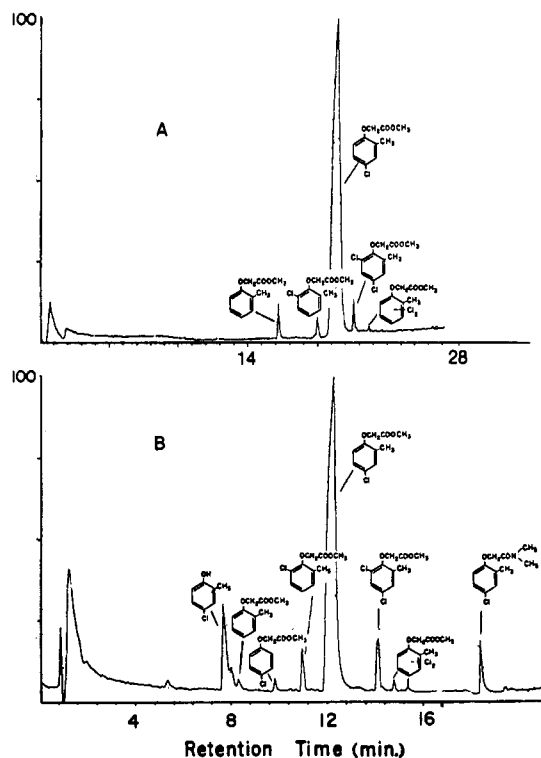


Figure 1. GCMS analysis of methylated acids and neutrals (A) before and (B) after 6 days exposure of MCPA/DMA formulation to summer sunlight. Note that time scales differ.

and Gardner, 1953; Haddock et al., 1959; Gardner and Overton, 1960; Stevens and Grorud, 1979) due principally to the impure *o*-cresol and 4-chloro-*o*-cresol used in earlier periods of manufacture. As confirmed by GLC, HPLC, and GCMS, the MCPA applied to California rice in 1979 was of much higher purity (Table I, Figure 1 part A), perhaps indicating a change in manufacturing process. (2-Methylphenoxy)acetic acid was the principal impurity (1.0%), together with smaller amounts of (6-chloro- and (4,6-dichloro-2-methylphenoxy)acetic acid and traces of other substances.

Neutral extractives were not found at levels above a few ppm except for the amide, IX, discussed later. Huston (1973) reported three bis(dichlorophenoxy)methanes as the principal neutral contaminants of production grade 2,4-D ((2,4-dichlorophenoxy)acetic acid); if the corresponding 4-chloro-2-methylphenyl derivatives were present in the MCPA formulation, they were below the present levels of detection, and other neutrals such as chlorodioxins also remained undetected.

**Photochemical Degradation.** Previous work (Soderquist and Crosby, 1975) indicated that MCPA was photochemically degraded with a half-life of about 18 days in a highly dilute (1.0 mg/L,  $5 \times 10^{-6}$  M) aqueous solution

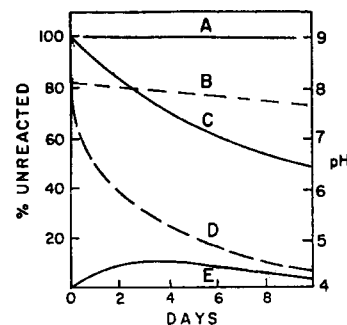


Figure 2. Photodegradation rate of MCPA/DMA spray solution in the photoreactor. Initial concentration 200 mg/L, A = dark control, B = dark control pH, C = MCPA in light, D = in light pH, E = 4-chloro-*o*-cresol.

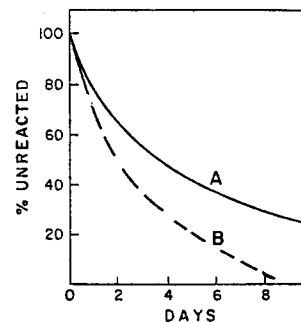


Figure 3. Photodegradation of 4-chloro-*o*-cresol in sunlight. Initial concentrations 100 mg/L, A = chlorocresol, B = MCPA/DMA for comparison.

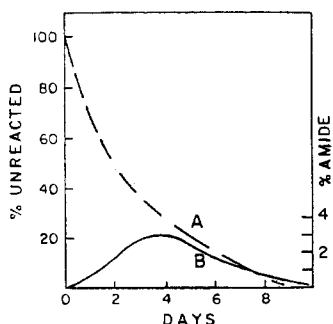
at pH 8.3. However, when droplets of MCPA/DMA spray (14.7 g/L, 0.06 M) were allowed to evaporate on a glass surface exposed to outdoor sunlight, 30% of the MCPA disappeared within one day (about 8 h of irradiation), and less than 20% remained after 6 days (Figure 4); dark controls at the same temperature remained unchanged in composition. MCPA spray solution (0.06 M), irradiated in a photoreactor with no evaporation showed a half-life of about 8 days (Figure 2).

Analysis of the residues by GLC or GCMS revealed several changes (Figure 1 part B): a large increase in the proportion of 4-chloro-2-methylphenol (4-chloro-*o*-cresol, IV), a decline in the level of (2-methylphenoxy)acetic acid (II), and the presence of (4-chlorophenoxy)acetic acid (VII) and two unknowns, A (*m/e* 227) and B (*m/e* 152), not observed in the dark control (Figure 1 part A). The amount of unknown B was very small; the mass spectrum showed it to contain one Cl, and the only reasonable formula appeared to be  $C_9H_5OCl$  (Beynon and Williams, 1963) corresponding to a monochlorobenzofuran possibly derived by self-condensation of (4-chloro-2-formylphenoxy)acetic acid and decarboxylation of the resulting coumarilic acid or by cyclodehydration of III.

Within several minutes after the onset of irradiation of droplets in open dishes, the odor of 4-chloro-*o*-cresol (IV) became noticeable. Analysis of acidic volatiles trapped quantitatively in base during photolysis experiments showed IV to be the principal constituent, along with smaller amounts of *o*-cresol and *p*-chlorophenol presumably derived from II and VII, respectively (Crosby and Wong, 1973). When the trapping medium was neutral ethylene glycol, GLC of the dichloromethane extract provided a substance, *m/e* 170, whose properties were identical with those of synthesized 4-chloro-2-methylphenyl formate (III), the expected intermediate derived from side chain oxidation in phenoxyacetic acid photolysis (Crosby and Wong, 1973). Sunlight irradiation of appropriately dilute (100 mg/L, 0.7 mM) aqueous IV in a flask

**Table II. Photochemical Generation of Dimethylamides in Solid Deposits**

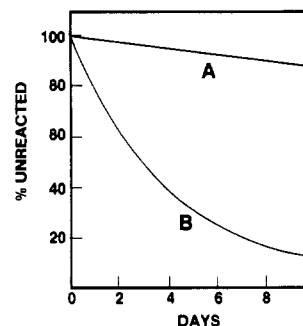
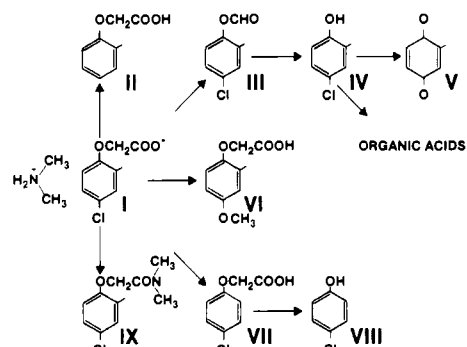
source	<i>N,N</i> -dimethylamide, μg/g	
	dark	light (5 days)
MCPA formulation	391	1375
pure MCPA/DMA	0	350
2,4-D formulation	317	14000
pure 2,4-D/DMA	0	300
pure 2,4,5-T/DMA	0	250

**Figure 4.** Generation of IX by sunlight irradiation of MCPA/DMA. A = MCPA, B = IX (right hand scale).

sealed to prevent volatilization resulted in a photolysis rate almost equal to that of MCPA/DMA at a similar concentration and a photolytic half-life of 2.5 days (Figure 3). HPLC analysis of the irradiated solution of IV showed the presence of many photolysis products, including one coinciding with 2-methyl-*p*-benzoquinone (V), and a highly polar polycarboxylic acid fraction at short retention time. The generation of these acids is reflected in the steady decline in pH which paralleled the photolysis of both MCPA and IV (Figure 2). Individual acids were not identified.

Our previous work with (4-chlorophenoxy)acetic acid (Crosby and Wong, 1973) led us to expect photonucleophilic displacement of the MCPA ring chlorine by hydroxyl and GLC detection of the resulting (4-hydroxy-2-methylphenoxy)acetic acid (VI, R = H) as its methylated derivative. A standard of the acid was synthesized, but repeated attempts to detect it (after methylation) in photolysis mixtures were unsuccessful. However, the detection of the *p*-benzoquinone from photolysis of IV strongly suggests that loss of the acetic acid side chain occurred much more rapidly than chlorine replacement.

The *m/e* 227 of unknown A corresponded to a formula of  $C_{11}H_{14}ClNO_2$ , and the compound proved identical chromatographically and spectrometrically with a synthesized standard of (4-chloro-2-methylphenoxy)-*N,N*-dimethylacetamide (IX). Upon reexamination, other commercial MCPA/DMA herbicides were found to contain up to 300 mg/L of IX, and a commercial formulation of 2,4-D/DMA likewise contained its corresponding amide (Table II). However, sunlight exposure of either the formulations or pure salts as deposits also resulted in amide formation (Table II, Figure 4), the amide in one case representing 6% of the initial MCPA. Although the formation of amides from amine salts in aqueous solution has been described and explained (Morawitz and Otaki, 1963), and the thermal reaction is well-known (Que Hee and Sutherland, 1974), the photochemical conversion has not been described previously. Exposed to sunlight as solid deposits, IX itself decomposed with a half-life of 3.5 days (Figure 5), but the photoproducts were not identified; dark control levels also diminished slowly. The ratio of amide to MCPA was quite variable but IX predominated after about 5 days.

**Figure 5.** Photodegradation of a IX deposit in sunlight, A = dark, B = light.**Figure 6.** Proposed pathway of MCPA/DMA degradation in irradiated spray.**Table III. MCPA/DMA Terminal Residues<sup>a</sup>**

	% original MCPA/DMA	mass spectrum ( <i>m/e</i> )	
		M <sup>+</sup>	base
acids (methylated)			
MCPA	10.0	214	141
4-chloro- <i>o</i> -cresol <sup>b</sup>	1.3	156	77
MCPA isomer (6-chloro?) <sup>b</sup>	c	214	141
(2-methylphenoxy)acetic acid <sup>b</sup>	c	180	57
dichloro-MCPA (2 isomers) <sup>b</sup>	c	248	175
(4-chlorophenoxy)acetic acid	c	200	168
5-chlorosalicylic acid	c	186	154
acids (unmethylated)			
4-chloro- <i>o</i> -cresol	1.1	142	77
neutrals			
4-chloro-2-methylanisole	1.6	156	77
MCPA dimethylamide <sup>b</sup>	1.0	227	72
MCPA monomethylamide	0.5	213	58
MCPA dimethylamide isomer	c	227	72
(2-methylphenoxy)acetic acid dimethylamide	c	193	72
dichloro-2-methylanisole	c	190	175
MCPA methyl ester	c	214	141
other phenoxyacetic esters			
unknown, C <sub>8</sub> H <sub>7</sub> ClO <sub>3</sub>	c	186	107
unknown, C <sub>10</sub> H <sub>12</sub> ClO <sub>2</sub> N	c	213	198

<sup>a</sup> After 31 days outdoor exposure. <sup>b</sup> Also present as a trace in the original MCPA/DMA formulation. <sup>c</sup> Trace amount.

The observed MCPA/DMA photodegradation products are rationalized as shown in Figure 6, as verified by identification of subsequent photoproducts from irradiation of each intermediate. The intermediate in MCPA demethylation to VII and the oxidation of the aromatic ring to aliphatic acids remains unknown.

**Terminal Residues.** To determine the identity of the most stable and persistent MCPA residues, the formulation, diluted with an equal volume of water, was spread evenly over the bottom of borosilicate glass trays and exposed to outdoor summer sunlight for 31 days; few clouds and no rain interfered. The composition of the residue, as

determined by HPLC (for MCPA) and GLC and confirmed by GCMS, is shown in Table III. Less than 10% of the original MCPA could be accounted for as parent or products, the remainder presumably being lost by volatilization as photoproducts or remaining as nonvolatile salts. 5-Chlorosalicylic acid, 4-chloro-2-methylanisole, and (4-chloro-2-methylphenoxy)-*N*-methylacetamide were among the degradation products identified.

**Volatilization.** When air was passed over the formulation during irradiation, the chlorocresol IV was removed by volatilization as it formed. Likewise, the other phenols and the formate ester (III) volatilized readily. MCPA/DMA has been reported to have an extremely low volatility from its formulation (Grover, 1976); in fact, it is likely that the salt is essentially nonvolatile and that the detected MCPA resulted from its hydrolysis. Air stripping of spray solution into acid produced dimethylamine, identified as its 2,4-dinitrophenyl derivative. Neither MCPA nor the amide IX were apparent.

**Fate of Airborne MCPA/DMA.** Analysis of the dishes collected after MCPA/DMA spray application indicated that in field A, treated with 12 oz/acre (0.84 kg/ha) as MCPA, only 0.36 kg/ha (43%) could be accounted for; in field B, receiving 14 oz/acre (0.98 kg/ha), only 0.24 kg/ha (24%) was found. Although such sampling is open to a number of errors—for example, photodegradation in dishes awaiting collection—the results suggest that a significant proportion of small droplets may indeed remain airborne for considerable periods of time.

To investigate the chemical fate of such particles, experiments were conducted with bulk spray or with films and droplets on an inert (glass) surface; simulation of the fate of leaf or soil surfaces was not intended, although many of the results may apply. Subsequent laboratory degradation studies with actual droplets (Freiberg and Crosby, 1985) confirm the present results and allow at least a qualitative picture of the atmospheric fate of MCPA/DMA. Spray droplets evaporate rapidly to give sticky, highly concentrated particles which continue to undergo photochemical degradation with loss of volatile products such as III, IV, VIII, and *o*-cresol. Other volatile photoproducts, such as the dimethylamide IX and *p*-benzoquinone (V), also might be released but at much slower rates due to their slower formation and their own degradation. Within a week, should the particles drift that long, the atmospheric degradation would be largely complete, and the terminal residue from MCPA/DMA application would consist primarily of nonvolatile organic acids and their dimethylamine salts. Clearly, photochemical reactions play a very significant part in the environmental fate of airborne MCPA.

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**Registry No.** I, 2039-46-5; II, 1878-49-5; III, 30114-33-1; IV, 1570-64-5; VI, 13522-81-1; VII, 122-88-3; IX, 36984-10-8; (6-chloro-2-methylphenoxy)acetic acid, 19094-75-8; (4,6-dichloro-2-methylphenoxy)acetic acid, 96259-14-2; 4-chloro-2-methylanisole, 3260-85-3; (4-chloro-2-methylphenoxy)-*N*-methylacetamide, 65195-46-2; 5-chlorosalicylic acid, 321-14-2.

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