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Loss of MCPA from Simulated Spray Droplets

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MCPA [(4-chloro-2-methylphenoxy)acetic acid], as its dimethylamine (DMA) salt, dissipated from individual microliter droplets of spray solution suspended in sunlight and moving air in a wind tunnel with a half-life of 3.9 h, compared with 4.6 h for MCPA/DMA deposits on glass surfaces. Photolysis was the major dissipative force in both cases, with MCPA volatilization playing a minor role. Identification and quantitation of six photoproducts revealed very similar composition of both residues, although the principal product, 4-chloro-*o*-cresol, volatilized rapidly from the droplets as shown by analysis of the effluent air. This technique confirms that MCPA loss from small droplets such as spray or rain entails conversion to the chlorocresol and subsequent volatilization; conventional methods provide the same conclusion.

The majority of pesticides are applied as sprays, either by aerial means or by ground-rig, and enter the environment in the form of small droplets. The diameters of these droplets vary from below 10 μm to over 1 mm, depending on the type of application, the formulation viscosity, and numerous other physical factors (Matthews, 1979). The smaller droplets are prone to "drift" from the intended application site, a serious problem with many pesticides including phenoxy herbicides such as MCPA [(4-chloro-2-methylphenoxy)acetic acid] (Crosby et al., 1981).

The environmental movement and transformations of MCPA have been studied in both the laboratory and the field (Soderquist and Crosby, 1975; Loos, 1975; Crosby and Bowers, 1985), but no previous investigation of the breakdown of any pesticide within aqueous spray droplets has been reported. Indeed, very little has been established regarding the chemical influences imposed upon drifting droplets, previous investigations having centered around the physical changes occurring as droplets evaporate.

Whytlaw-Gray and Patterson (1932) studied the evaporation of very small (1- μm radius) droplets of several pure substances and showed that the decrease in surface area was linear with time. For droplets containing a mixture of solutes, however, the rate of surface area decrease slowed toward the end of the evaporation, as the concentration of the less volatile component increased. Ranz and Marshall (1952) and Charlesworth and Marshall (1960) reported similar results for droplets containing dissolved solids in moving air. Langstroth et al. (1950) examined the evaporation of 1-mm-diameter droplets of nine pure substances of various volatilities, supported from a fine thermocouple in still air, and showed that their surface

temperature was lower than their internal temperature. They also noted that convection occurred within the droplets, even in still air.

The chemical microenvironment of an airborne droplet appears to be unique: a maximum surface-to-volume ratio, maximum exposure to oxygen and other gaseous reagents, and full exposure to direct sunlight. The possibility exists that the fate of agricultural chemicals in spray drift, or of any chemical in fog or raindrops, could be markedly different from that observed in bulk solutions or surface coatings. The purpose of this investigation was to determine the fate of MCPA in individual microliter "spray droplets" and compare it with that observed in bulk solutions and solid deposits.

EXPERIMENTAL SECTION

Chemicals. MCPA dimethylamine salt was obtained as a 589 g/L (4 lb of MCPA/gallon) commercial aqueous formulation (Dow Chemical Co.). This solution was diluted 1:40 with water to obtain the recommended field spray concentration of 14.7 mg/mL (0.10 lb of MCPA/gallon). Analysis of the starting material showed it also to contain traces of two contaminants, (2-methylphenoxy)acetic acid and (2,4-dichloro-6-methylphenoxy)acetic acid (Crosby and Bowers, 1985).

Amberlite XAD-4 macroreticular resin was cleaned before use by wetting it with HPLC grade methanol, washing with 1 N NaOH followed by 1 N HCl, and then extracting in a Soxhlet extractor with methanol for 2 h, acetonitrile for 2 h, and finally diethyl ether overnight.

4-Chloro-*o*-cresol (III), 5-chlorosalicylaldehyde (IV), and *o*-cresol (V) (Aldrich Chemical) were used without further purification.

(4-Chloro-2-methylphenoxy)-*N,N*-dimethylacetamide (VII). One gram of MCPA was refluxed for 3 h with 4 mL of thionyl chloride, the mixture evaporated to

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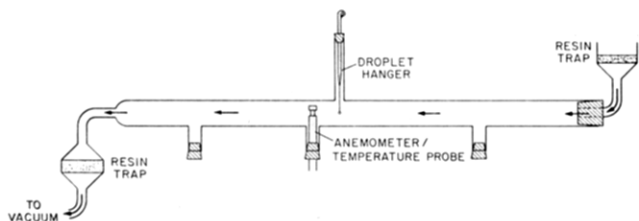


Figure 1. Schematic of droplet wind tunnel, 3-cm o.d. \times 60-cm length.

remove excess thionyl chloride, the residue dissolved in 20 mL of benzene and chilled, and a 4 M excess of dimethylamine (40% solution) added dropwise while stirring. After the mixture was stirred for 2 h in an ice bath and 6 h at room temperature, the benzene was evaporated to give a viscous liquid that provided white crystals from chloroform after drying with Na_2SO_4 : mp 43.5–44.5 $^\circ\text{C}$; mass spectrum m/e 227 (M^+), 192 ($\text{C}_{11}\text{H}_{14}\text{NO}_2$), 155 ($\text{C}_7\text{H}_6\text{ClO}$), 72 ($\text{C}_3\text{H}_6\text{NO}$, base); IR 1660 cm^{-1} (CO).

4-Chloro-2-methylphenyl Formate (II). 4-Chloro-*o*-cresol was treated with an equivalent mixture of acetic anhydride and formic acid containing 1% of sodium formate (Van Es and Stevens, 1965). After the mixture was stirred for 24 h, water was added, the formate extracted into chloroform, and the residue after evaporation crystallized from carbon tetrachloride; it continually was contaminated with III. GC/MS analysis showed a major component: m/e 170 (M^+), 142 ($\text{C}_7\text{H}_7\text{ClO}$ base), 107 ($\text{C}_7\text{H}_7\text{O}$).

4-Chloro-2-methylanisole (VI). A 60% yield of the anisole was obtained by treating 0.02 mol (2.84 g) of 4-chloro-*o*-cresol in methanol with 0.021 mol (3.1 g) of methyl iodide and 3 g of K_2CO_3 . The mixture was allowed to stand 3 days at room temperature with occasional stirring; at the conclusion of the reaction, the mixture was added to 1 L of 0.1 N NaOH and extracted twice with isooctane. Evaporation of the isooctane yielded a clear liquid that formed white needles when placed on dry ice but melted at room temperature. GC/MC analysis showed no 4-chloro-*o*-cresol and a single product: m/e 156 (M^+), 141 ($\text{C}_7\text{H}_6\text{ClO}$), 125 ($\text{C}_7\text{H}_6\text{Cl}$), 121 ($\text{C}_8\text{H}_9\text{O}$), 77 (C_6H_5 , base).

Apparatus. The borosilicate glass wind tunnel (Figure 1) consisted of a 3 \times 60 cm cylindrical chamber containing a 6-mm-diameter portal in the top to admit a glass droplet support and 10-mm-diameter portals in the base for insertion of a hot-wire anemometer and temperature probe (Model 100 VT airflow meter, Datametrics, Inc., Wilmington, MA). A vacuum line was attached to one end of the chamber, and the air velocities up to 2 m/s were controlled by adjusting a stopcock in it. Effluent organic vapors were trapped on macroporous resin (Amberlite XAD-4) contained in a holder that widened to 6 cm diameter to minimize airflow resistance. In sunlight, this trap was shielded to prevent possible photoreactions of adsorbed compounds, and a similar trap was placed at the entrance to the wind tunnel to screen out background organics.

Inside the wind tunnel, droplets were suspended from the tips of glass rods drawn down to diameters in the range of 50–100 μm and melted to form a small bead that facilitated adherence of the droplets. Each fiber was dipped in a water-repellent coating (Dri-Cote, Fisher Scientific Co.) and baked at 120 $^\circ\text{C}$ overnight.

Single microliter droplets of the MCPA spray solution, formed with a 1.0- μL syringe (Scientific Glass Engineering, Ltd., North Melbourne, Australia) whose needle had been blunted and lightly coated with paraffin, were transferred to the tips of the rods or to 200- μm -diameter quartz fibers.

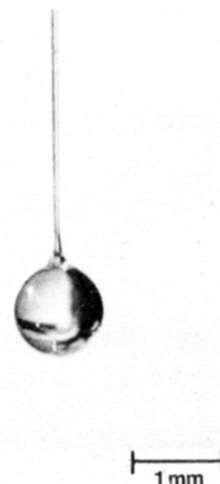


Figure 2. Droplet on its support.

The droplets appeared perfectly spherical (Figure 2) with only 1% of their original surface area in contact with the support. Droplet diameter was measured by high-magnification photography; a 35-mm SLR camera with a 24-mm lens attached to a reversed 135-mm lens provided approximately 25 \times magnification, and droplet diameters were determined photographically by comparison with the known thickness of the droplet support as measured accurately by microscope.

MCPA Loss from Droplets. Residues remained in the chamber for up to 5 days, exposed to outdoor sunlight and constant airflow of 1 m/s. Supports were then rinsed in 50 μL of methanol, and duplicate 20- μL HPLC injections were made for quantitation of remaining MCPA.

Longer term loss (up to several weeks) was studied by placing a single microliter droplet on the tip of each of several 4-cm segments of 200- μm -diameter quartz fiber. After initial evaporation (about 0.5 h), the fibers were positioned vertically and exposed to sunlight or held in a darkened room. At intervals, fibers were removed from the chamber and individually analyzed as previously described.

To determine the nonvolatile droplet residue components, six of the quartz fibers, 30 cm in length, were suspended horizontally in summer sunlight, each fiber having 50 droplets placed by syringe along its length. After 6 days, each was suspended vertically and rinsed four times with 50 μL of ethanol, the combined solutions were divided into two fractions, and one was treated with ethereal diazomethane while the other remained unmethylated. Each fraction was subsequently reduced to 100 μL under N_2 and analyzed for degradation products.

To determine vapor components, three quartz fibers bearing 100 droplets total were placed in the wind tunnel and exposed to sunlight and 1 m/s airflow for 5 days. The downwind resin trap was emptied, the resin extracted overnight with 45 mL of methanol, the solvent evaporated, and half of the residue methylated with ethereal diazomethane.

Surface Irradiation. MCPA spray solution (40 μL containing 480 μg of MCPA) was coated on the inner surface of several 10-mL beakers; the beakers were inverted, placed either in summer sunlight or in the dark, and rinsed at specific intervals with 2 mL of methanol, and the extract was analyzed for MCPA. Alternatively, 20 mL of MCPA solution was placed in each of two 9-cm Petri dishes, the water was allowed to evaporate, and the dishes were exposed to sunlight for 6 days. One dish was rinsed with 20 mL of dichloromethane, the solvent evaporated

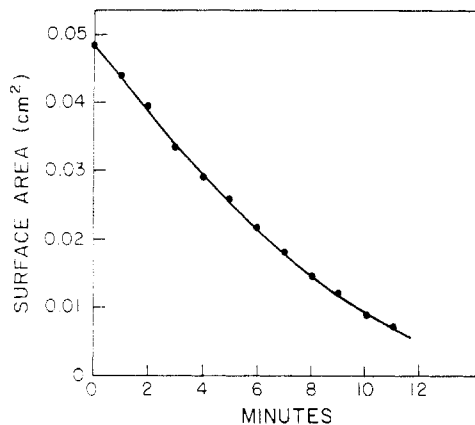


Figure 3. Evaporation rate of MCPA droplets at 25 °C, air velocity 1 m/s.

to 2 mL, and the solution treated with ethereal diazomethane and then analyzed on GLC and GC/MS. The remaining dish was rinsed with 20 mL of methanol, which was reduced to 2 mL under nitrogen and analyzed by HPLC.

Chromatography. HPLC was performed with a Waters Associates Model M-6000A liquid chromatograph, a Whatman Partisil-10 ODS 4.6 × 25 cm column, and a Waters Associates Model 440 UV absorbance detector (254 nm). The solvent was methanol-water (4:6 v/v) adjusted to pH 3.0 with phosphoric acid, flow rate 1 mL/min.

GLC was performed on a Varian Model 1700 gas chromatograph equipped with a flame ionization detector, 150 cm × 3 mm i.d. stainless-steel column packed with 3% OV-17 on 80/120 Gas-chrome Q, column temperature 200 °C, injector and detector temperatures 275 °C, and nitrogen carrier gas flow rate 30 mL/min.

Mass spectrometry was performed on a Finnigan Model 3200 gas chromatograph/mass spectrometer interfaced to an INCOS data system. The chromatograph utilized a 30 m × 250 μm i.d. J&W DW-1 fused-silica column, helium velocity 30 cm/s, and ionization voltage 70 eV. Column temperature was raised from 60 to 300 °C at 10 °C/min.

RESULTS AND DISCUSSION

Physical Changes during Droplet Evaporation. The droplets had an initial diameter of 1240 μm, an accommodation of the smaller size typically seen in MCPA applications—VMD 435 μm with a principal range of 300–500 μm (Yates, 1981)—to the need to have enough MCPA in each drop for quantitation. Although the size of experimental droplets initially lay just outside the range actually present during an application, rapid evaporation of water placed them well within the application size distribution within several minutes.

The evaporation rate was determined by measuring a droplet's diameter microscopically at 1-min intervals in the wind tunnel, in sunlight, with the airflow velocity across the droplet steadily decreased to mimic the decreasing velocity of a falling droplet; based on a spherical shape, the corresponding total surface area then was plotted against time. The average results from the three droplets (Figure 3) showed rapid loss of water, terminating beyond the limits of accurate size determination in about 15 min to leave an oily residue on the tip of the droplet support.

During the evaporation, mixing of droplet contents was evident, as occasional dust particles could be observed swirling within the drops. The droplets remained at the very tip of the drawn glass supports and retained their spherical shape until shortly before evaporation was complete, when they tended to climb the support fiber and

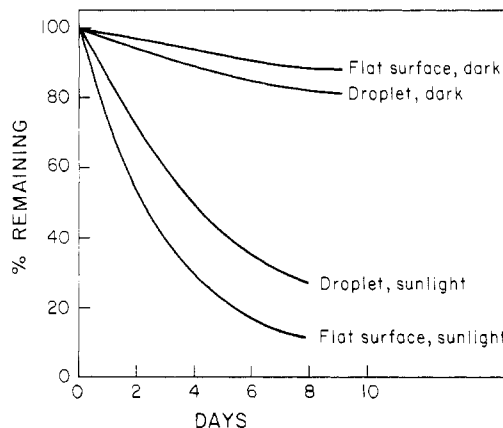


Figure 4. MCPA loss from droplets and glass coatings in sunlight and dark.

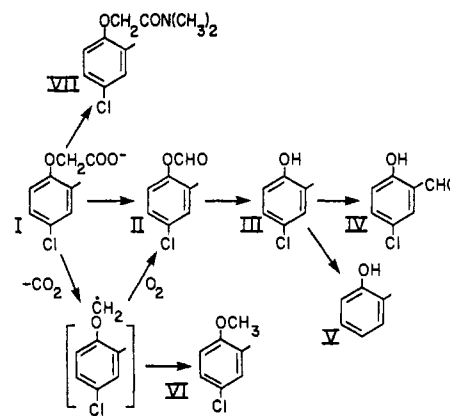


Figure 5. Proposed MCPA degradation pathway.

eventually coat the support's tip. This oily residue then remained visually unchanged for an indefinite time (>5 days) without drying, even though exposed to both sunlight and air currents.

Although the initial decrease of surface area with time was linear, the later part of the evaporation was slowed somewhat, similar to the decreased evaporation observed by Ranz and Marshall (1952). This was not due to decreasing air velocity—zero airflow produced a similar curve with complete evaporation in about 25 min—but probably to decreasing vapor pressure as the MCPA solute concentration increased.

Rates of MCPA Loss. The oily residue remaining after 0.5 h retained all the original MCPA. Half-lives for the loss of MCPA as a thin coating on a glass surface (beakers) were 3.9 days in sunlight and approximately 43 days in the dark; corresponding rates for droplet residues were 4.6 and 36 days, respectively (Figure 4). Photolysis plays a much more important role in MCPA loss than does volatilization; the slight inhibition of photolysis in the droplet compared to the surface coating is considered to be primarily an artifact of the glassware.

Droplet Residue Photoproducts. HPLC and GLC analyses of the residues on the sunlight-exposed Petri dishes detected six photoproducts, five of which were identified by GC/MS as 4-chloro-2-methylphenyl formate (II), 4-chloro-*o*-cresol (III), *o*-cresol (V), 4-chloro-2-methylanisole (VI), and MCPA dimethylamide (VII). A trace product with a retention time equal to that of 5-chlorosalicylaldehyde (IV) was detected by HPLC but could not be confirmed by either GLC or GC/MS, since the aldehyde is not stable to diazomethane. These results are consistent with those of related studies (Crosby and Bowers, 1985; Benoit-Guyod et al., 1985) and support the

Table I. Photoproducts from Bulk-Scale and Droplet Irradiation of MCPA/DMA

	coating residues ^a		droplet residues ^b		droplet vapor ^c	
	wt, mg	%	wt, mg	%	wt, mg	%
MCPA (I)	138	48	1.2	61	0.008	5
4-chloro- <i>o</i> -cresol (III)	140	49	0.70	36	0.144	92
MCPA dimethylamide (VII)	7.1	2	0.04	2	nd ^d	
4-chloro-2-methylanisole (VI)	2.4	0.5	0.02	1	0.004	2
5-chlorosalicylaldehyde (IV)	tr		tr		nd	
<i>o</i> -cresol (V)	tr		tr		nd	
4-chloro-2-methylphenyl formate (II)	tr		nd			
total as MCPA/DMA	81%		68%		21%	

^a40 mL of original solution. ^b300 combined droplet residues. ^cVapor from 100 droplets. ^dNone detected.

photodegradation sequence shown in Figure 5.

Analysis of the sun-exposed droplet residues confirmed the presence of III, V, VI, and VII. Again, a trace of a compound coeluting with 5-chlorosalicylaldehyde (IV) was seen on HPLC but remained unconfirmed by GC/MS. The only photoproduct from bulk irradiation that remained undetectable in the droplet residues was 4-chloro-2-methylphenyl formate (II), known to be a transient intermediate (Crosby and Bowers, 1985).

Relative quantities of the various photoproducts after 6 days of irradiation in the bulk scale and droplet photolyses are listed in Table I. The residues were quite similar, the reduced amount of 4-chloro-*o*-cresol in the droplet residues being due to the enhanced volatilization resulting from the larger surface-to-volume ratio. Analysis of the vapor trap at the end of the wind tunnel confirmed this, the vapor from the sun-exposed droplets consisting almost entirely of 4-chloro-*o*-cresol (Table I) together with small proportions of MCPA and 4-chloro-2-methylanisole, another highly volatile photoproduct. No appreciable degradation products were obtained from dark controls.

Previous work (Crosby and Bowers, 1985) identified (4-chloro-2-methylphenoxy)-*N,N*-dimethylacetamide (VII) as a photoproduct in MCPA bulk-scale photolysis. The levels of VII were monitored over several days in sunlight (Figure 6), and those in the droplet residues closely paralleled that from the bulk photolysis but were lower than those from a surface. In all cases, the concentration of VII peaked at about the fourth day, and none could be detected in the vapor trap.

The volumes and concentrations of the MCPA droplets are considered to be representative of actual spray, although the dissipation results could be biased by the need to physically support each droplet; a method has yet to be developed that would allow irradiation of truly free-floating droplets and their residues for up to several days. Even so, photolysis emerges as the key factor affecting the loss of MCPA. While the relative importance of photolysis and volatilization may differ for other pesticides or even for different formulations of MCPA, significant loss of this herbicide from droplets by photoconversion to 4-chloro-*o*-cresol and subsequent volatilization is supported by field observations (Crosby et al., 1981).

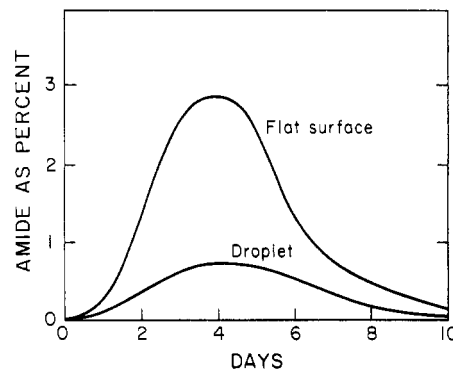


Figure 6. Formation and degradation of MCPA dimethylamide (VII) in droplet residues and surface coatings.

Pesticides and many other chemicals have been recognized as contaminants in fog and raindrops, and the present methods and results would be equally applicable to them. Although we have shown that the degradation of chemicals under such circumstances can be simulated satisfactorily in suspended droplets, the processes involved appear to be modeled quite well by the more convenient bulk-scale experiments utilizing conventional techniques that yield very similar photolysis rates and product ratios.

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