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# Hydrolysis of MCPA Esters and the Persistence of MCPA in Saskatchewan Soils

Allan E. Smith and Brian J. Hayden
*Agriculture Canada, Research Station, Box 440 Regina, Saskatchewan Canada S4P 3A2*

The herbicide MCPA (4-chloro-2-methylphenoxyacetic acid) is widely used for the control of broad-leaved weeds in a variety of crops. Its use in Western Canada is increasing and during 1978 approximately 1.5 x $10^6$ kg ester and salt formulations were applied to crops.

Although sprayed on weeds as a post-emergence treatment, a part of the MCPA application does come into contact with the soil where such residues are degraded by microbiological processes (AUDUS 1964, LOOS 1975).

The soil persistence of MCPA has been studied using bioassay procedures (DEROSE and NEWMAN 1947, AUDUS 1951, BURGER et al. 1962, FRYER and KIRKLAND 1970), or using radioactively labelled MCPA (FOSTER and MCKERCHER 1973). Very few such studies have been conducted using gas chromatographic analytical procedures (SODERQUIST and CROSBY 1975, VIRTANEN et al. 1979).

It has been established that esters of the closely related dichlorophenoxyalkanoic herbicides undergo rapid hydrolysis in moist soils to their respective acids (BURCAR et al. 1967, SMITH 1972, MCKONE and HANCE 1972, SMITH 1976), however, the fate of the herbicidal esters of MCPA under such conditions has received no attention.

In the studies to be described, the fate of the iso-butyl, n-butyl, and iso-octyl esters of MCPA was investigated at 20°C in three Saskatchewan soils at 50% and 15% of their field capacity moistures. The degradation of MCPA, as the free acid, was also studied at 20°C in the same soils at 85% and 15% of their field capacity moistures. Gas chromatographic procedures were used to monitor the various MCPA derivatives.

## MATERIALS AND METHODS

Soils. Samples of the clay loam (CL), heavy clay (HvC), and sandy loam (SL) used in these studies were collected in an air-dried state from the 0-5 cm soil horizon, sieved through a 2 mm screen, and stored in the laboratory for 8 weeks before use. The composition and physical characteristics of these soils have al-

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ready been reported (SMITH 1978).

Chemicals. MCPA was purchased from Anachemia Chemicals Ltd., Toronto, Ontario, while the iso-butyl, n-butyl, and iso-octyl esters of MCPA were obtained from Niagara Chemical Co., Regina, Saskatchewan. Individual stock solutions of the acid and esters were prepared in acetone containing 2.0 mg/mL.

Hydrolysis studies. To 20-g samples of clay loam, heavy clay, and sandy loam at 50% (wilting point) and 15% (air-dried) of their respective field capacity moisture levels in 70-ml capacity screw-capped bottles, was added 40 µL of the appropriate ester solution. This rate was equivalent to 4.0 µg/g of moist soil. After thorough mixing to distribute the chemicals, the bottles were capped and incubated in the dark at 20±1°C. Duplicate samples of the iso-butyl and n-butyl ester treated soils were extracted and analysed after 24 hours while the iso-octyl treated soils at the higher moisture level were analysed after 24 and 48 hours. The soils (duplicate samples) at the lower moisture regime and fortified with the iso-octyl ester of MCPA were analysed only after 48 hours.

Ester extraction and analysis. The soil from each bottle was placed in a 125-mL glass-stoppered flask and shaken on a wrist-action shaker for 1 hour with 50 mL of 10% aqueous acetonitrile. Following centrifugation at 3000 rpm for 4 minutes, 25 mL of the acetonitrile extract (corresponding to 10 g soil) were shaken, in a 250-mL separatory funnel, with 100 mL of 5% aqueous sodium sulphate solution and 20 mL n-hexane. The hexane layer was run into a 50-mL glass-stoppered flask, dried over sodium sulphate, and 5 µL portions examined gas chromatographically for ester remaining.

Persistence studies. Fifty-gram samples of all three soil types at 85% or 15% (air-dried) of their respective field capacity levels, were weighed into 175-mL Styrofoam cartons which were then capped with plastic lids and incubated in the dark for 7 days at 20±1°C to allow equilibration. Distilled water was added every second day with mixing, to maintain the moisture content. Following equilibration, 50 µL of the MCPA solution (containing 100 µg of the herbicide) was added to the soils to give a herbicide concentration of 2 µg/g based on moist soil. This rate is approximately equivalent to a field rate of 1 kg/ha assuming incorporation to a depth of 5 cm. The soils were stirred to distribute the MCPA and the re-capped cartons re-incubated in the dark at 20±1°C. Water was added, with stirring, every second day to maintain the moisture.

Duplicate samples from each treatment at the 85% moisture level were analysed for MCPA remaining after 7 and 14 days, whilst duplicate samples at the 15% moisture content were extracted and analysed only at the completion of the degradation study.

Extraction and analysis. The soil from each carton was transferred to a 250-mL glass-stoppered flask and shaken on a wrist-action shaker for 1 hour with sufficient 20% aqueous acetonitrile containing 2% of glacial acetic acid, so that the combined volume of extractant, together with the water present in the soils was 100 mL. After centrifugation at 3000 rpm for 4 minutes, 25 mL of the supernatant were worked up using the exact procedure described for the extraction and analysis of 2,4-D and other dichlorophenoxyalkanoic acid herbicides (SMITH 1978). Following treatment with diazomethane, the evaporated methylated extracts were taken up in 10 mL n-hexane and 5 µL aliquots examined gas chromatographically.

Mean recoveries from air-dried soils fortified with MCPA at the 2.0 µg/g and 0.2 µg/g levels, and equilibrated for 48 hours prior to extraction and gas chromatographic analysis, were reproducible and ranged from 90-95%. Thus, no recovery factors were applied to the MCPA persistence data.

Gas chromatographic analysis. The gas chromatograph used was a Tracor 560, equipped with a Model 700A Hall electrolytic conductivity detector operated in the chloride mode. The glass column (2 m x 2 mm i.d.) was packed with 100-120 mesh Ultrabond 20M, and the carrier gas was helium at a flow rate of 30 mL/min. Flow rate of hydrogen through the detector was maintained at 50 mL/min. The injector, detector base, and detector furnace temperatures were 220°C, 250°C, and 800°C respectively. With a column temperature of 180°C, the retention times for the methyl, iso-butyl, and n-butyl esters of MCPA were 2.5, 3.4, and 4.3 minutes. At a column temperature of 200°C the iso-octyl ester of MCPA had a retention time of 4.1 minutes.

Individual gas chromatographic standards of the four MCPA esters were prepared containing 2 Ng/µL of n-hexane. The concentrations of the various esters present in the samples were calculated by comparing the sample peak heights with those derived from a standard curve, constructed from the appropriate ester. Seperate studies confirmed there to be no interfering substances extracted from any untreated soils.

## RESULTS AND DISCUSSION

The recoveries of the iso-butyl, n-butyl, and iso-octyl esters of MCPA from the soils after various time intervals are summarised in Table 1. In the soils at 50% of field capacity, the recoveries of the esters were very much lower than from the air-dried soils at 15% of their field capacity moistures. After 24 hours no detectable amounts of the iso-butyl or n-butyl esters were observed in the former, whereas, over 90% of both esters were recovered from all treated air-dried soils. A similar situation with the iso-octyl fortified soils was noted after 48 hours. In view of the high ester recoveries from the air-dried

TABLE 1

Recovery of MCPA esters from moist soils (4 µg/g) at 20°C

| Ester | % FC | % Ester recovered[1] | | | | | |
|---|---|---|---|---|---|---|---|
| | | CL | | HvC | | SL | |
| | | 24 hr | 48 hr | 24 hr | 48 hr | 24 hr | 48 hr |
| Iso-Butyl | 50 | <5 | -[2] | <5 | - | <5 | - |
| | 15 | 90 | - | 94 | - | 98 | - |
| N-butyl | 50 | <5 | - | <5 | - | <5 | - |
| | 15 | 92 | - | 96 | - | 100 | - |
| Iso-octyl | 50 | 30 | <5 | 15 | <5 | 17 | <5 |
| | 15 | - | 96 | - | 92 | - | 95 |

[1] Average of 2 replicates. [2] Not determined.

TABLE 2

Recovery of MCPA from moist soils (2 µg/g) at 20°C with time

| Moisture % FC | % MCPA remaining[1] | | | | |
|---|---|---|---|---|---|
| | CL | | HvC | | SL |
| | 7 days | 14 days | 7 days | 14 days | 7 days |
| 85 | 68 | 32 | 54 | 24 | 18 |
| 15 | -[2] | 87 | - | 90 | 80 |

[1] Average of 2 replicates. [2] Not determined.

soils (Table 1), it was assumed that the lower ester recoveries from the soils at the wilting point (50% of field capacity) moistures after 24 or 48 hours, were due to almost complete hydrolysis of the MCPA esters to the free acid. Such a rapid hydrolysis of esters of 2,4-D, 2,4-DB, 2,4-DP, and 2,4,5-T, considered to result from a soil catalysed mechanism on moist soils, but not on air-dried, has already been reported (SMITH

1972, SMITH 1976). The slower hydrolysis of the iso-octyl ester of MCPA, compared to the two butyl esters can probably be attributed to steric effects, a fact already noted to explain the similar slower hydrolysis of the iso-octyl esters of 2,4-D 2,4-DP, and 2,4,5-T (SMITH 1972, SMITH 1976).

The loss of MCPA from all soils at 85% of field capacity moisture was rapid (Table 2). Losses from the air-dried soils was minimal with over 80% of the applied MCPA being recovered after time intervals when the recoveries from the moist soils were less than 32% (Table 2). This lack of breakdown was taken as evidence that the herbicide losses in the moister soils were due to biological mechanisms, rather than chemical processes or inadequate extraction techniques.

Results of the present study indicate that under field conditions, the hydrolysis of MCPA esters to the free acid should occur within a few days providing the soil moisture levels are in excess of the wilting point. The work also confirms the findings of other researchers (FRYER and KIRKLAND 1970, FOSTER and MCKERCHER 1973, SODERQUIST and CROSBY 1975, VIRTANEN et al. 1979) that MCPA acid is rapidly degraded in moist non-sterile soils.

## REFERENCES


AUDUS, L.J.: Plant and Soil 3, 170 (1951).

AUDUS, L.J.: The Physiology and Biochemistry of Herbicides. L.J. Audus, ed. pp. 163-206. London: Academic Press 1964.

BURCAR, P.J., R.J. WERSHAW, M.C. GOLDBERG and L. KAHN: Analysis Instrumentation 4, 215 (1967).

BURGER, K., I.C. MACRAE and M. ALEXANDER: Soil Sci. Soc. Amer. Proc. 26, 243 (1962).

DEROSE, H.R. and A.S. NEWMAN: Soil Sci. Soc. Amer. Proc. 12. 222 (1947).

FOSTER, R.K. and R.B. MCKERCHER: Soil Biol. Biochem. 5, 333 (1973).

FRYER, J.D. and K. KIRKLAND: Weed Res. 10, 133 (1970).

LOOS, M.A.: Herbicides. P.C. Kearney and D.D. Kaufman, eds. pp. 1-28. New York: Marcel Dekker 1975.

MCKONE, C.E. and R.J. HANCE: J. Chromatogr. 69, 204 (1972).

SMITH, A.E.: Weed Res. 12, 364 (1972).

SMITH, A.E.: Weed Res. 16, 19 (1976).

SMITH, A.E.: Weed Res. 18, 275 (1978).

SODERQUIST, C.J. and D.G. CROSBY: Pestic. Sci. 6, 17 (1975).

VIRTANEN, M., M.L. HATTULA and A.U. ARSTILA: Chemosphere 8, 431 (1979).