DATA EVALUATION RECORD

STUDY 3

CHEM 109101 Mepiquat Chloride §162-2

STUDY ID 41889010

Huber, R. INVESTIGATIONS INTO THE ANAEROBIC DEGRADATION OF MEPIQUAT CHLORIDE IN SOIL. Performed by BASF, Limburgerhof, FRG under Registration Document No. BASF 91/10108; Sponsored and Submitted by BASF Corporation, Research Triangle Park, NC; Completed March 1991; Received by EPA 27 May 1991.

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REVIEWED BY: G. Maske
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 557-8245

SIGNATURE: [signature] 7 OCT 1993

Approved by: P. Mastradone
TITLE: Chief, Section 1
ORG: EFGWB/EFED/OPP
TEL: 557-0335

[signature] 7 OCT 1993

CONCLUSIONS:

Anaerobic Soil Metabolism

The anaerobic soil metabolism study is scientifically valid and can be used as supplemental data. However, it cannot be used to fulfill the data requirement. Confirmatory analysis of Radio-TLC data for parent material and degradates during aerobic and anaerobic phases (showing degradation during aerobic phase and stability during anaerobic phase) of the study was not furnished. The initial analysis of TLC data should be supported by other analytical methodology (preferably MS). These data are needed to fully assess the environmental fate of mepiquat chloride under anaerobic conditions.

Mepiquat chloride was reported to be stable when applied to sandy loam soil (USDA classification could not be determined-see COMMENT 2) and exposed to anaerobic conditions for 60 days. However, mepiquat chloride was not reported as stable on soil under aerobic conditions. A half-life of ≈21 days was given for the aerobic portion of the study.

MATERIALS AND METHODS:

Test Material: 1,1-dimethylpiperidinium chloride was used which was reported to have a specific activity of 1.804 mCi/mMol radiochemical purity of >99%. Chemical purity was not furnished.

Test Solution: 1564.5 µg ai/5 mL

Reference Standards: No chemical purity was given for:

1,1-dimethylpiperidinium chloride
1-methyl-piperidine
piperidine

Soil: A sandy loam soil collected in the USA was used which had the following characteristics (See Appendix 3):

pH:	6.0
CEC(meq/100g):	16.4
% Organic matter:	2.5
% Sand:	68
% Silt:	17
% Clay:	15

Sampling: Soil samples were taken at days 0, 2, 6, 14, 21 (0), 35(14), 51(30), and 81(60) days posttreatment. The numbers in the parenthesis reflect the duration of anaerobic conditions.

The samples were immediately analyzed. Aliquots were analyzed in duplicate.

Test System: See Appendix 4.

METHODOLOGY:

Twelve glass Petri-dishes were filled with 146.94 grams of moist soil (prior to initiation of the test the soil was moisten to 75% of its 1/3 bar field capacity). The treat soil, which had a soil density of 1.4 g/mL, was placed at a depth of 7.5 cm. A nominal concentration of 1 mg/kg mepiquat chloride was targeted which if equal distribution was assumed should correspond to 1 kg/ha.

The Petri-dishes were immediately placed after preparation into the soil reactor (See Appendix 4) on a stainless steel rack. The reaction vessel had a cover on top which was sealed with a plastic O-ring. The soda lime tower 2 removed CO_2 from the supplied air to monitor the air emanated through the reactor vessel. The flow rate of air was approximately 0.5 to 1 L/hr.

The exiting air/volatiles were passed through a set of three absorption traps which were filled with 5 mL ethylene glycol, 0.5N H_2SO_4, or 25 mL LSC-cocktail.

At day 21, the supply of air was stopped and the hose connected to pure N_2-supply. The soil reactor was thoroughly flushed with N_2 for about 5 minutes and adjusted back to the flow rate of 0.5 to 1 L/hr. The N_2-supply was maintained throughout the duration of the anaerobic study.

The room where the soil reactors were operated was climatized and kept at 20 ± 2°C. In addition, the test room was dark except for sampling times.

Soil samples were taken at days 0-2hrs, 2, 6, 14, 21 (0), 35 (14), 51(30), and 81 (60). Except for balance values, the samples were normally extracted and analyzed in duplicates immediately after sampling. The samples were analyzed by Radio-TLC or LSC.

The extractable radioactive residues were extracted/partitioned from aqueous solutions into dichloromethane at a pH range 7 to 9 with hexanitrodiphenylamine in dichloromethane. Removal of the solvent, inorganic acids or adsorptive materials like silicagel on TLC-plates predominantly decomposed it to its original components.

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Fractionation of bound residue into fulvic acids, humic acids, and humins was achieved by 0.5N HCl extraction, followed by three 0.5N NaOH extractions. The humic acids then could be precipitated by HCl-acidification. The insoluble humins were then determined by combustion/radioassay.

Radio-TLC was used to detect the radioactive components in the dichloromethane extracts. Aliquots of concentrated extracts were thoroughly streaked onto the TLC-plates. The plates were developed using the following solvent system:

Solvent system I: Methanolic HCl/acetone 85/15 of 80/20 (v/v).

At each soil sampling interval, traps 1 - 3, were drained and the absorption solution replaced. Aliquots of the trapping solutions collected were radio assayed by LSC.

Samples (100-200 mg) usually were combusted in duplicate and the values were averaged. The $^{14}CO_2$-trapping scintillation cocktails were Oxosol and Picofluor 15.

DATA SUMMARY:

Mepiquat chloride had a half-life of ≈21 days when exposed to aerobic conditions. The only radioactive degradate formed was CO_2.

However, when anaerobic conditions were imposed at 21 days the CO_2-evolution rapidly ceased to zero (The course of CO_2-evolution is depicted in Table 3.). Also, the composition of the extracted radioactivity stayed approximately the same. Therefore, a half-life was not calculated for the anaerobic part.

The dissipation course of the initially supplied amount of radioactivity is depicted in Tables 1 and 2. The dichloromethane extracted radioactivity is delineated in Table 2. At day 21 only 22% of the applied was extracted. Again, under anaerobic conditions the composition of these extracted residues remained fairly consistent.

The dichloromethane extracted radioactivity consisted in the ion pair complex formed from mepiquat chloride with dipicrylamine. Upon radio-TLC this complex mostly decomposed to mepiquat chloride. Neither N-methylpiperidine nor piperidine had been formed during the aerobic and anaerobic degradation of mepiquat chloride.

Radioactive residues remaining in the aqueous phases after dichloromethane extractions were mostly at or below 1% of applied. The same was true for the methanol extracts obtained from the dichloromethane/dipicrylamine preextracted soil residues.

In Table 4 balance values are presented. They average 88.5% (range 77.5 to 99.9%) of the applied radioactivity. The study author felt the material balance was adequate considering the tremendous difficulties in achieving adequate balances when a lot of initial CO_2-evolution is involved.

COMMENTS:

1. EFGWB prefers that [^{14}C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, and GC) with solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

In this study, the samples were analyzed using TLC using one solvent systems and Radio-TLC or HPLC or LSC. Radioactive areas on the TLC plates identified only by comparison to the location of known reference standards.

2. The soil fractions for the test soil was reported in a manner that the USDA soil texture of the soils used in the study could not be verified. However, it does appear that soil texture reported as loam would not be a loam soil under USDA classification. For loam soils with clay content of ≤15% the sand content is <55% using USDA classification. See Appendix 3 for details.

Soil Size Reported for Sandy Loam and Loam		USDA Soil Sizes	
0.2-0.02	-sand =68%	2.0-0.05	-sand
0.02-0.002	-silt =17%	0.05-0.002	-silt
<0.002	-clay =15%	<0.002	-clay