



A study of Fate herbicide propanil in rice field at AL-Qadisiya covernorate*

I.F.H AL-Jawhary and S.A.W. AL-Rikaby

*Univ. of Al-Qadisiya, Col. of Veterinary Medicine, Div. of Microbiology and
Univ. of Al-Mustansiriya, Col. of Science, Div. of Biology*

Abstract

Persistence of N- (3,4 – dichlorophenyl) propanamide (propanil) 3,4 – dichloroaniline (DCA) has been studied in drainage water canals and soil , following propanil application in rice fields .

Propanil was detected up to 16 weeks after application. However (5) metabolites of propanil were detected in drainage water canal.

* This research is a partial from doctorate thesis

1-Introduction

Propanil (3,4-dichloropropionanilide) is one of the major herbicides used in rice (*Oryza sativa L.*) field due to its selective herbicidal action between rice and certain weeds, especially barnyardgrass (*Echinochloa spp.*). The literature offers much evidences that propanil is cleaved enzymatically in soil by the action of soil microorganisms to dichloroaniline (DCA) during 21day after application of propanil (Bartha and Pramer,1967 ; Bartha, 1968 ; Chisaka and Kearney,1970).

Two molecules of DCA condense and form 3,3,4,4-tetrachloroazobenzene (TCAB) (Bartha and Pramer,1970) . On the chemical formation of DCA and TCAB in dilute aqueous solutions of propanil, by the action of sunlight, has been investigated (Moilanen and Crosby , 1972) . TCAB also results from photolysis of adilute aqueous Solution of DCA(Rosen *et.al.*, 1970; Moilanen and Crosby, 1972; Miller *et.al.*,1980).

Experiments with propanil have been usually conducted, to study herbicide fate , under laboratory conditions. But no attempts were made to examine persistence of propanil and its

degradation products under practical rice-field conditions .

The purpose of the present investigation was to examine Persistence of propanil , DCA, TCAB in rice field soil and in drainage water canals following propanil application in rice field , and to determine whether or not this application causes any toxic to environment.

2- Materials and Methods

Chemicals: Technical propanil , DCA, were supplied by AL-Farouq factory

1- Al-Muthana company . Solvents , reagent were purity and reached to 98.5% to special analytical reference standard.

2-Field application :The field experiment was conducted on a silty clay soil (1.06 % O.M) at the AL-Qadisiya governorate in AL-Shamya , Iraq. A separated field (20 donums or 5 hectares) was seeded with rice (*O.sativa* L."Anbar"-33) July 30,1997. Propanil (Stam F-34) was applied June 24, 1997, when barnyardgrass reached 3-4 leaves stage, at the recommended dose of 2.5L/100L water/do. The field was drained 2 days before application and kept drained 2 days after that. Irrigation / drainage system was then followed continuously . Soil samples were collected from 8-10 lines in rice field after 1.5 hours to application with propanil. Water samples were collected from a definite position in the drainage canal , 200-m far from the field. Sampling was begun on the 4th. Day after application and continued, at regular intervals

, up to the 16th . week and all samples were stored at – 18c° until analyzed.

3-Analysis :A- Extracted from soil samples : The method of analysis followed by Chiska and Kearny (1970) was adopted with some modified .Soil sample was dehydrated in oven with 50c° during 30 minute to reduce moisture, and added to 37.5g anhydrous Na₂SO₄ to 25g from soil with 50 ml acetone and after shaking with orbital shaker incubater, the sample was filtered by filter paper . The residue extracted 3 times with acetone (total 100ml) and filtered sample was added to a chromatographic column to reduce pigments

The filtered sample was evaporated in rotary flask evaporater and redissolved in suitable volume of Benzene (10ml). The latter extract was then subjected to gas and thin-layer chromatographic analysis for propanil ,DCA.

B-Extracted from water sample: The method of analysis followed by Chiska and Kearney (1970) was adopted .Water in 100ml aliquots from the thawed sample was transferred into a 250 ml separatory funnel, acidified with 1-3 drops of HCL and extracted 3 times with benzene (total 50ml). Benzene was evaporated in a rotary flask evaporater , and then residues were dissolved in a suitable volume of n-hexan (1-5ml).The latter extract was then subjected to gas and thin-layer chromatographic analysis for propanil, DCA. Gas chromatographic (gc) analysis were performed on a perkin – Elmer Model 304 gas chromatograph, equipped with a

thermoionic detector (FID), and a $6 \text{ ft} \times \frac{1}{4}$ in o.d. glass column packed with 3% MPS on 80/100 mesh Gas chrom Q. Injection port and detector temperatures were 270 and 285°C respectively. Column temperature were 200 °C for propanil and DCA respectively. Gas flow rates were 40 ml / min for nitrogen.

Under these conditions, retention times obtained for propanil, DCA were similar to those reported by Chisaka and Kearney (1970). Products were quantitated by comparing peak heights with appropriated calibration curves. Recoveries from soil and waters were 90 % for propanil, DCA respectively. Thin layer chromatographic (TLC) analysis were performed on 20x20 cm plates coated with silica Gel GF254 (0.5 mm thickness). Benzene system were tested for developing the compounds. Spots were located under UV light (254 nm). Benzene system was selected to determine sensitivity of the method. n-Hexan extracts remained after gc analyses were concentrated (1ml final volume), these latter extracts were spotted again and separated by benzene system to confirm the presence of propanil, DCA and other compounds.

3- Results and Discussion

Fig (1) indicate to curve of losses of propanil in soil and the concentration of propanil reached to (0.04)ppm after 1 hour from application, but the concentration

reached to (0.03ppm) at the end of the first week, the losses of propanil concentration in comparison with the initial concentration in the field soil occurred by volatilization was due to the physical nature of propanil molecule and the high temperature (43.5°C) (table 2). The concentration of propanil reached to (0.04) ppm during the second week, this result due to that the soil absorbed little amount of the herbicide from field waters slowly after spraying. The decrease of propanil concentration continued gradually by time but trace amounts were detected all over the season. The amount of the absorbed propanil depends upon the texture of the soil and organic matter. The low amount of propanil in amended soil all the season due to anaerobic conditions to decreases activated microorganisms to analyses herbicide, these noticed also revealed by Alexander (1980), when the moist soil decreased the Activation of microorganisms because decreased oxygen and absorbed herbicide by soil, organic matter and cation exchange capacity, all these factors were affected to fate of herbicide in soil.

Gas chromatographic analysis of water sample, collected from the drainage canal, indicated that propanil was persisted up to 16 weeks after application Fig (2). The maximum concentration (0.3 ppm) was reached at the 5th week of application. After the 5th week, concentration of propanil declined continuously and reached 0.02 ppm at the

end of the season Fig(2). However, another 5 metabolites of propanil were detected Fig 3,B . This indicates the long persistence of propanil and its dangerous metabolites like DCA, this means that propanil was not rapidly degraded in soil owing to the poor activity of soil microorganisms, and was continuously leached to drainage canal owing to the nature of the compound and the system of irrigation/drainage. The presence of DCA and 5 metabolites in drainage water from photodecomposition of propanil present in water. The photodecomposition of dilute aqueous solution of propanil by the action of sun light provides the formation of DCA, TCAB (Moilanen and Crosby, 1972).

TCAB results also from photolysis of a dilute aqueous solution of DCA (Rosen *et.al.*, 1970; Moilanen and Crosby, 1972; Miller *et.al.*, 1980).

Thin-layer chromatographic analysis indicate that propanil, DCA, and another compound could be developed by benzene system Fig (4). Sensitivity of the TLC method was determined to be 0.07, 0.47 and 0.66 Rf for propanil, DCA and anon compound

respectively. TLC analysis for benzene extracts of water samples proved the presence of propanil , DCA and anon compound in drainage waters and confirmed gc results .

It has been extensively proved that propanil is biodegradable in soil by the action of soil microorganisms within few week to form DCA and TCAB (Bartha and Pramer, 1967 ; Bartha, 1968 ; Chisaka and Kearny, 1970 ; Bartha, 1971) .So the long persistence of propanil in drainage waters, as observed in the present study , seems to be unexpected . To interprete this case, some facters could be taken in consideration :

1- The soil organic matter content of the field of study was less than 1% .

Biodegradation of propanil is strongly influenced by the organic matter content of soil (Chisaka and Kearny, 1970) .

2- Rice culture in Iraq depend upon continuous irrigation /drainage system.

Propanil is not a soil-bound compound (Bartha, 1971) .

Table (1) Some physical and chemical characteristics to field soil .

Determine degree	Studying characteristic	
11.0 %	Sand	Sand
59 %	Silt	Silt
30 %	Clay	Clay
Silty clay	Texture	Texture
7.88	PH	(Potential of hydrogen ion)
3.45 mmhos/cm	E.C.E	(Electric conductivity xtractable)
25.82 ME _q / 100gm	C.E.C.	(Cation Exchange capacity)
1.06 %	O.M	(Organic Matter)
11.57 %		(Soil moister)

Table (2) Mean of minimum, maximum temperature and relative humidity*

Mean of relative humidity %	Mean of maximum temperature	Mean of minimum temperature	Time
28.8	43.5	26.8	June
29.0	43.5	27.1	July
34.0	41.2	25.2	August
35.5	41.6	23.3	September
49.1	33.6	20.4	October

* Information in this table reveal recorded abstract in AL – Diwaniya city .

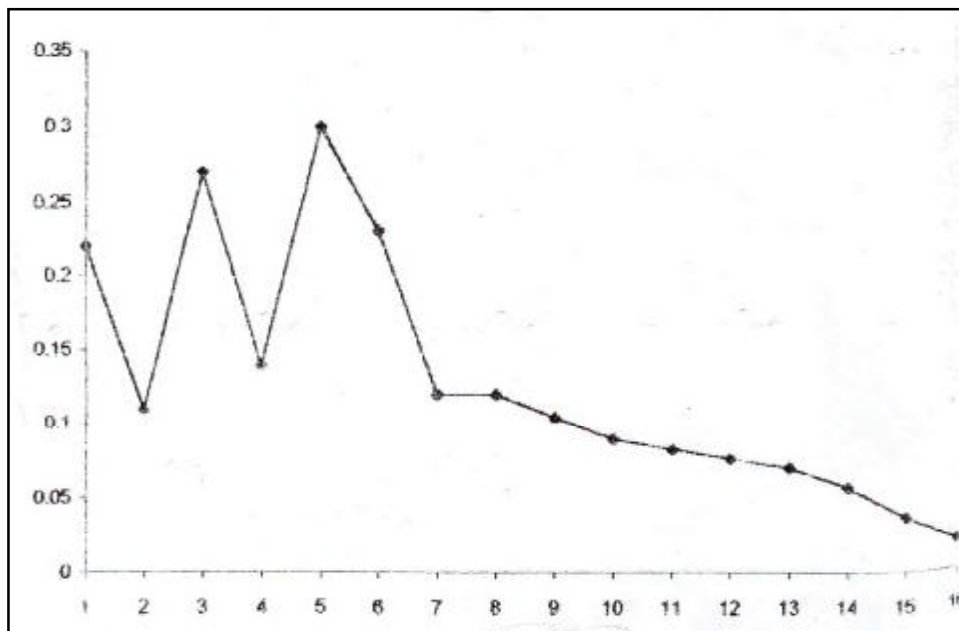
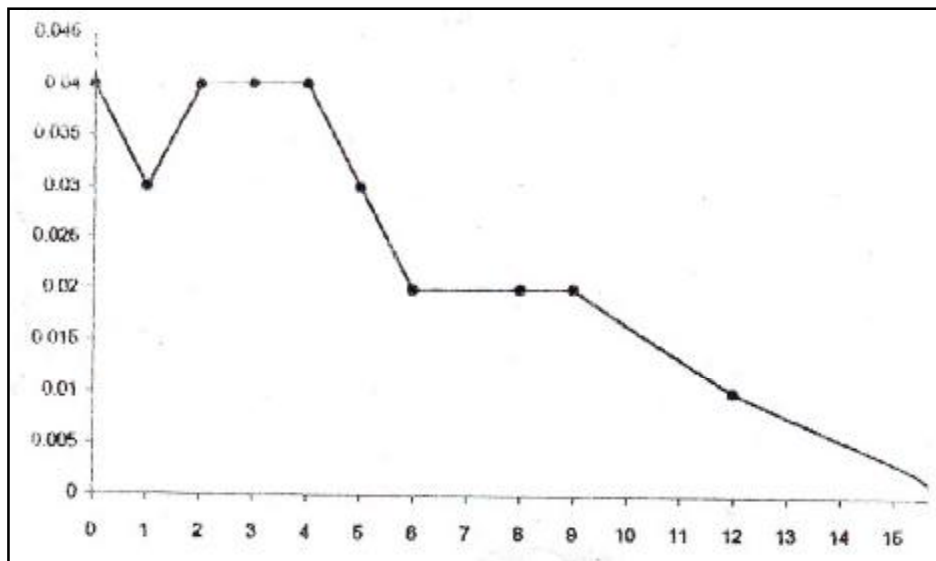


Fig (2) Propanil concentration in drainage waters following propanil application in rice field by gas chromatography .

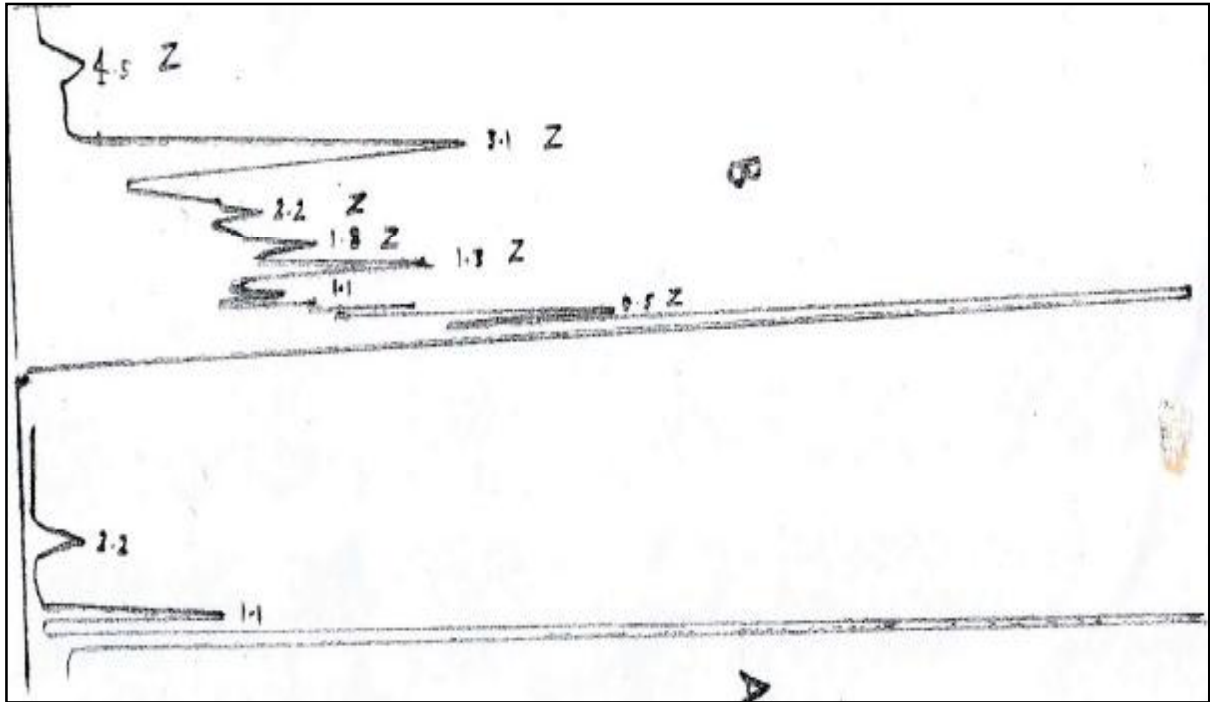


Fig (3) Metabolites of propanil after degradation in drainage waters .

(A) : Standard of propanil 1.1 , DCA 2.2

(B) :Extract of water after application with propanil

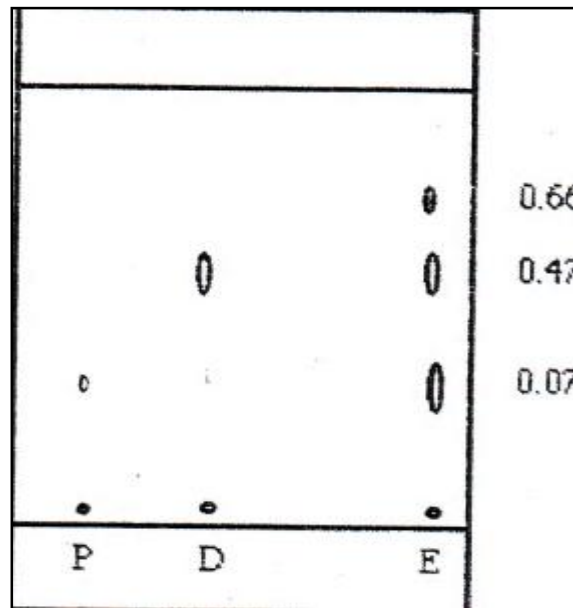


Fig (4) Thin layer chromatography (TLC) contain propanil with metabolites inwaters and soil

P = Propanil (standard). D = 3,4-DCA (standard) E = Soil extract with benzene .

4-References.

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دراسة عن مصير المبيد بروبانيل في حقل رز محافظة القادسية

احسان فليح حسن الجوهري و سجال عبد الوهاب الركابي
جامعة القادسية - كلية الطب البيطري - فرع الاحياء المجهرية
الجامعة المستنصرية - كلية العلوم - قسم علوم الحياة
E-mail: aljowhary@yahoo.com

الملخص

شمل البحث دراسة مدة بقاء مبيد الادغال بروبانيل (N-(3,4-dichlorophenyl) propanamide) وبعض نواتج تحلله الرئيسية (DCA (3,4-dichloroaniline) في التربة وفي مياه الميازل على اثر المعاملة بالمبيد بروبانيل في حقل الرز . ولقد دلت النتائج على وجود المبيد بروبانيل لمدة 16 أسبوعا من تاريخ المعاملة, كما اظهرت الدراسة وجود (5) مركبات كنواتج ايسية للمبيد بروبانيل في مياه الميازل .
