PARAQUAT RESIDUES IN LOWLAND RICE FIELDS

J.M.R.S.BANDARA and P.C. KEARNEY

Department of Agric. Biology, University of Peradeniya Peradeniya, Sri Lanka.
and
Pesticide Degradation Laboratory, BARC West, USDA Maryland, USA.

SUMMARY

Residue levels of paraquat in lowland rice field soil were estimated over a period of 8 weeks after application. Paraquat residue in soils declined significantly from 0.310 to 0.042 ppm in eight weeks. Paraquat in standing and run off water reached very low level within 12 hours. Degradation of paraquat applied to soil was found to be lesser in aerobic soil in comparison to anaerobic soil, in glass house experiments. Natural soil amended with organic matter enhanced degradation of paraquat.

INTRODUCTION

Paraquat (1,1' -dimethyl- 4,4'-bipyridylium dichloride) is a non selective pesticide commonly used in pre ploughing spraying and in zero tillage culture in lowland rice (paddy) fields in Sri Lanka. One of the objectives of the practice of zero tillage using Paraquat is to reduce time period needed for preparation of land which allows minimum of two crops a year.

Bipyridyls are inactivated rapidly in clay soils owing to their strong adsorption properties and interaction with ionic substances (Khan, 1974). Paraquat residues in paddy fields and water may cause direct toxicological hazards.

MATERIALS AND METHODS

Commercial paraquat containing 200g a.i./l (*Gramoxone*) was obtained from Chemical Industries Colombo (CIC).

Field application

Field application were done at the South-end experimental rice fields of Faculty of Agriculture, University of Peradeniya. Test area of 45 sq.m (5m x 9m) was demarcated into three blocks each of 3 x 5 sq.m. Paraquat was applied at the rate of 1.12 kg/ha in 450 l of water using a knapsack lever operated sprayer on to the harvested rice fields covered with weeds and rice stubble. Amount of Paraquat applied for all three blocks of paddy fields was 5.04 g in 2.02 litres of water. Each block was supplied with pesticide free irrigation water through a separate inlet, and drain off water from each block was taken out to the main drain-off channel separately.

Sample collection

Irrigation inlets to the plots were kept closed at the time of spraying. Ten samples of standing water of 25ml each were taken from 10 random locations in each block prior to spraying, soon after spraying, 1h, 2, 4, 8, 12, 24 and 48 hours after spraying.

Similarly three samples of water were taken at the drain off outlets of each block (A, B and C).

Five soil samples were collected at a depth of 15cm from random locations using one inch soil augur before spraying, soon after spraying 1,2,4, and 8 weeks after spraying., Samples collected were stored at -20C until analysis were done. Some of the characters of the soil from the test field are clay 32.15%, organic matter 2.4%. C.E.C. 18 meg/100 g, pH = 5.2, N% = 0.414, C% = 0.52 and Water Holding Capacity is 18.05.

Glass House Experiments

Degradation of paraquat applied to flooded soil and aerobic soil was studied over a period of 12 weeks in the glass house. Large cement pots (37 x 37 x 45) cm filled with sieved soil collected from an uncultivated virgin site were used for this study. Set of ten pots were maintained as flooded-anaerobic soil with 3cm of standing water where as ten others were prepared as pots containing well drained aerobic soil. Pots were regularly watered and kept in the glass house for six weeks prior to the commencement of the experiment.

Twenty five ml of 1000 ppm paraquat was added to each pot. Paraquat residues were analyzed before, soon after, 1,2,4,8, and 12 weeks after the application of paraquat in reduced flooded soil. Similarly in aerated soil, samples were taken for estimation of paraquat residue, before, soon after, 1h,2h,3h,8h,24h, 1w,2w, and 8 weeks after the application of paraquat.

Five soil samples were collected per pot by inserting No. 1 cork borer up to a depth of 8 cm from the surface. Five samples collected from each pot was then mixed together to obtain a homogeneous composite sample for the estimation of paraquat residue.

Effect of organic matter and microorganisms

Effect of organic matter and soil sterilization on degradation of paraquat was assessed under controlled conditions in a laboratory experiment. Paraquat (1000ppm, 25 ml) was added to sterilized soil (750 g) and non sterilized soil kept in nitrogen environment in wide mouthed 1.5 l brown pyrex bottles continuously flushed with nitrogen gas. Paraquat residues in soil were estimated after one and seven month period after addition of paraquat.

Effect of paraquat residues on rice seedlings

Effect of paraquat retained in rice soils on the growth of rice seedlings were also assessed. Rice soils collected from the North End Field were taken in *Eusaco-polyshine* paper cups (340g of soil/cup). Soils in cups were then treated with one ml of 400, 1000 and 4000 ppm paraquat solution. Equal volume of sterile distilled water was added to untreated pots. Each treatment was replicated 20 times. Ten of the cups were seeded with rice cv. BG 3438 seeds on the 21st day after paraquat treatment other ten were seeded 40 days after paraquat treatment. Seedling height on the 22nd day after germination was recorded.

Residue analysis

Residue analysis of paraquat was done as described by Calderbank and Yuen (1965). Ten grams of soil sample was refluxed in 100 ml of 18N sulphuric acid for three hours and vacuum filtered through a acid resistant filter paper. Filtrate was diluted to 1800 ml with distilled water.

Paraquat extract was then passed through a column containing Amberlite IR-120 resin in water at a flow rate of 8 ml/min. Column was then rinsed successively with 25 ml of water, 50 ml of 2N HCl, 50 ml of distilled water and 25 ml of saturated ammonium chloride solution. Final elution of paraquat with a ammonium chloride was done at a flow rate of 8 ml per minute and 25 ml of eluate was collected.

Determination of Paraquat

Ten ml of well shaken effluent was removed with a pipette into a 15 ml glass stopered test tube and mixed with at 2.0 ml of 1% sodium dithionite solution. Optical densities of the solution at 392, 296, 400 and 401 nm using a spectronic 710 spectrophotometer. Optical density of the samples at 396 nm (*E396*) was estimated using the procedure recommended by Calderbank & Yuen (1965).

RESULTS AND DISCUSSION

Paraquat residues detected in standing water and in run off water from sprayed fields are summarized in table 1. Amount of paraquat present in run off water about 10 minutes after spraying was relatively higher (12.56 ppm).

The run off water channels were directed to river Mahaweli in almost all the paddy fields in the area. Use of paraquat in the Mahaweli catchment area is a very common practice especially in the tea plantations in the upper Mahaweli water sheds. In view of this some preliminary studies were also conducted in order to determine the presence of paraquat in several samples of mahaweli river water and samples of silt collected at Polgolla reservoir along the Mahaweli river. None of the samples showed any positive results.

Table 1. Paraquat residues (ppm) in standing water and run off water in sprayed rice fields.

Hours after spraying	Standing water PPM	SD	Run off water PPM	SD
0	2.57	2.36	12.56	8.6
1	0.731	0.70	0.284	0.20
2	0.262	0.43	0.308	0.16
4	0.054	0.07	0.092	0.14
12	0.015	0.03	0.038	0.07
24	0	0	0	0

Depth of standing water in the field was about 5cm.
SD = Standard deviation for ten samples.

Paraquat residues in run off water decline significantly from 12.56 ppm to 0.284 ppm in one hour after spraying. No paraquat were detected in run off water collected after 24 hours from spraying.

Although the amount of paraquat detected in standing water was significantly lower (2.57 ppm) than that of run off water the quantities remained high even after one hour from application and reached very low levels in 12 hours.

This is probably due to the degradation action of UV from sunlight received *ad lib.* during the harvesting season.

Similar reduction of paraquat residue in soils were detected with time (Fig 1.). Paraquat ion is known to remain undisturbed for years in the cation exchange complex in clay. However in this study it was observed that paraquat residue in field soil declined significantly from 0.31 to 0.0425 ppm in 8 weeks (Fig.1. Dunnet LSD = 0.0833 where zero week is used as control test; Fishers LSD = 0.0755).

Green house study conducted with reduced soil under anaerobic environment reveals that paraquat degrade faster under reduced conditions in comparison to paraquat residues in aerobic soil. Paraquat adsorbed in to the clay fraction in upland soil remain almost at a constant level (3 mg/kg of soil) for the test period of 12 weeks (Fig. 2).

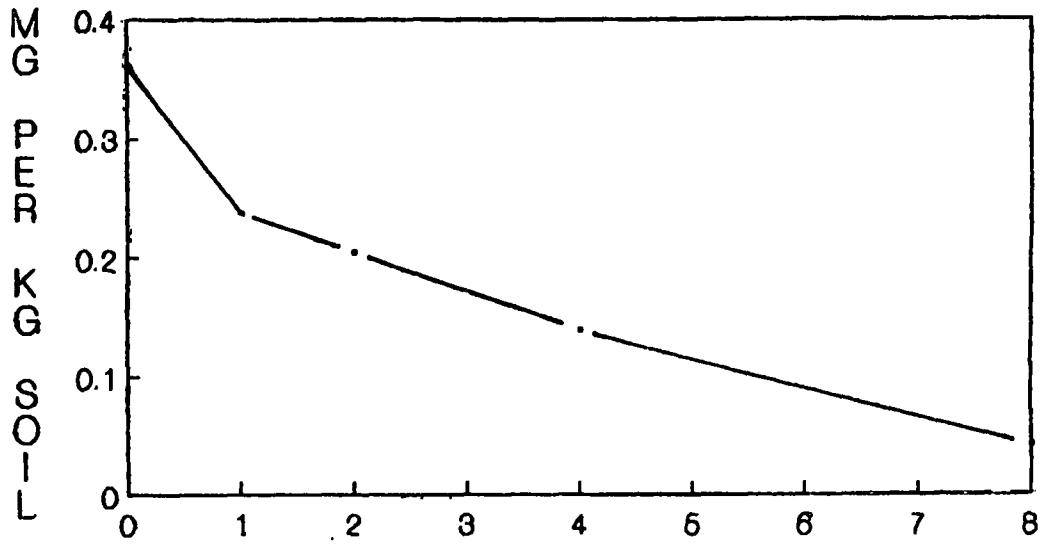

Fig. 1 Paraquat Residues in prayed Lowland Rice Fields

Paraquat is reported to be metabolized completely by *Lipomyces stakeyi,* a yeast (Anderson & Drew, 1972). Similar activity was observed with some unidentified anaerobes and a strain of *Clostridium pasteurianum* (Baldwin *et al.,* 1966).

However, paraquat penetrates the clay lattice in soil and form a absorption complex (Calderbank & Tomlinson, 1968) and as such not readily available for microbial attack (Weber and Coble, 1968). It was observed that significant reduction in paraquat content occurred in reduced paddy soils (Fig. 1 & 2). Laboratory experiments with reduced rice soils maintained in N_2 saturated environment revealed that degradation occurred faster in natural soil containing organic matter. It is evident from the results in this study that presence of organic matter is of more significance in the degradation of paraquat in reduced soils (Fig. 3). The percentage paraquat residue remained at 82–85% even after seven months from application in both natural and sterilized soils when not amended with organic matter. However higher degradation occurred in both natural and sterilized soils containing organic matter. In natural soil containing organic matter paraquat applied degraded faster resulting in a residue level of 40% after period of seven months compared to less than 20% in sterile soil.

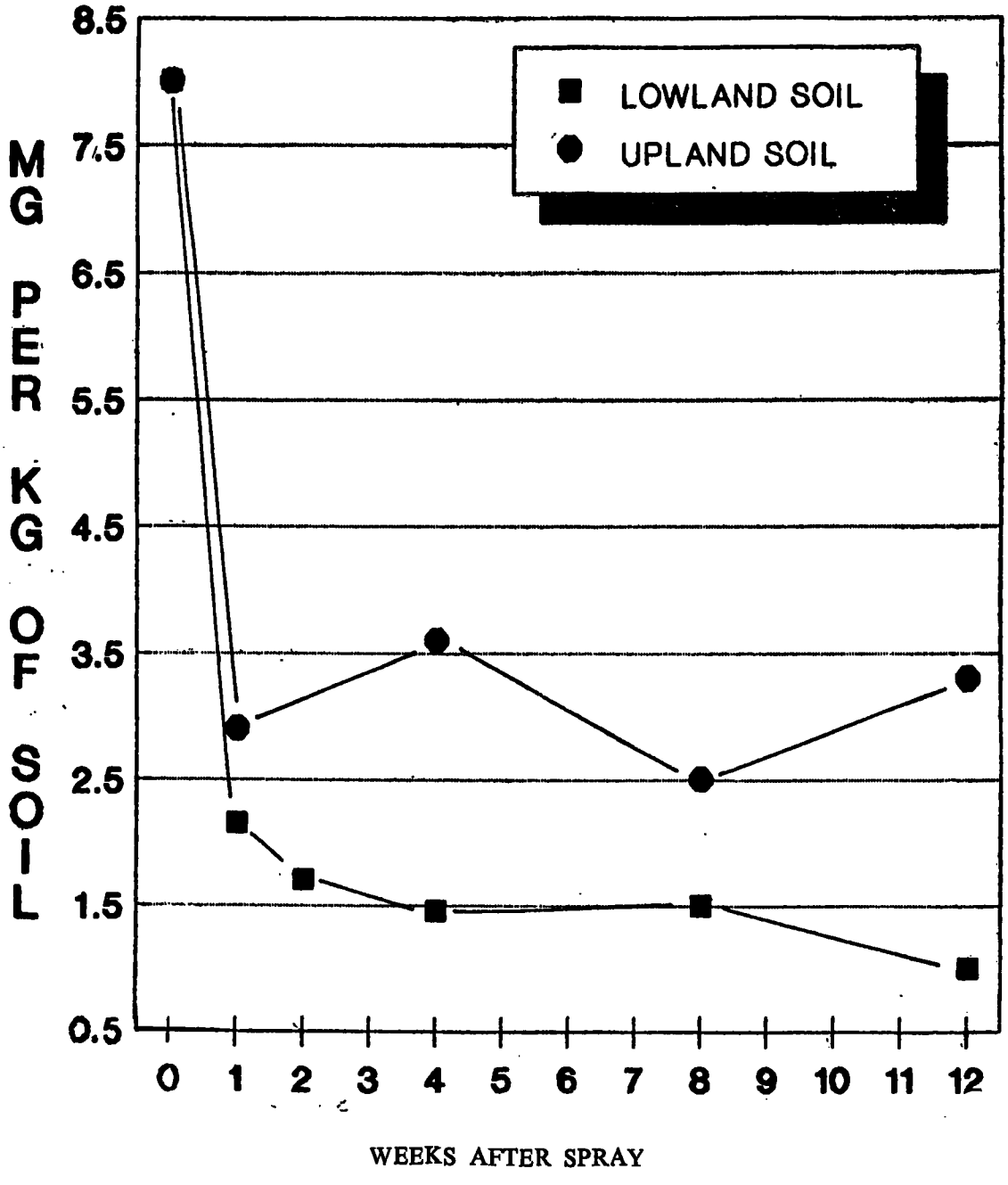

Fig. 2 Paraquat Residues in Upland and Lowland Soil

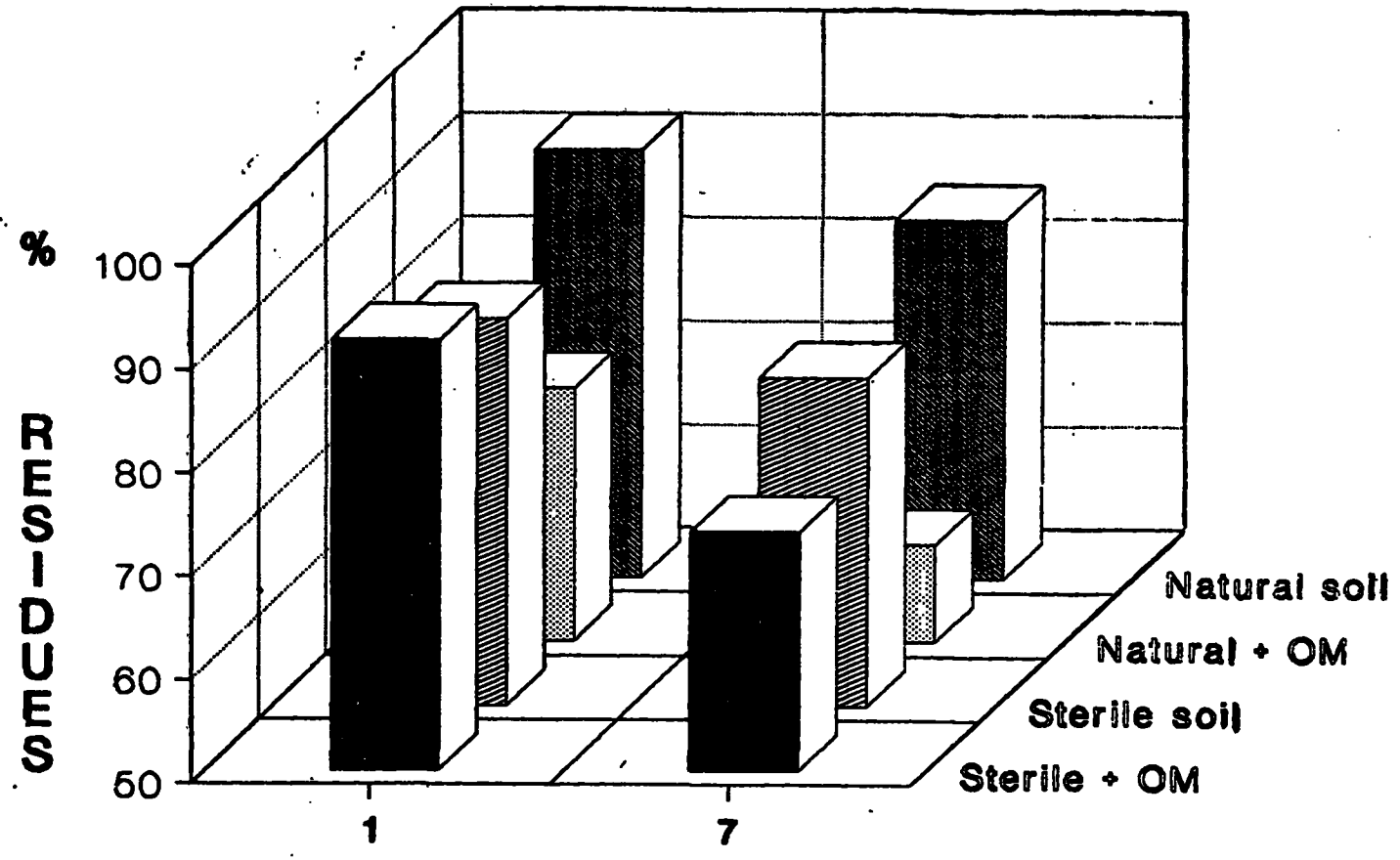

Fig. 3 Percent Paraquat Residues

It is suggested that the presence of organic matter enhanced and facilitate microbial degradation of paraquat under anaerobic conditions. This could be attributed to greater absorption of paraquat to organic matter in soil than penetration into clay lattice of rice soils thus enabling greater microbial degradation. Therefore paraquat used in zero tillage as a total weed killer if applied prior to final ploughing would avoid hazardous accumulation of paraquat in rice soils.

Table 2. Mean plant height of three weeks old rice seedlings grown in paraquat treated lowland rice soils.

Concentration of paraquat (ppm)	Sowing time after Paraquat treatment			
	TWENTY DAYS		FOURTY DAYS	
	Plant height		Plant height	
	in cm	% of control	in cm	% of control
0	19.30 a	100	23.05 a	100
400	19.28 a	100	23.30 a	100
1000	17.14 b	88.8	22.72 a	97.5
4000	9.56 c	49.5	20.22 b	86.78

Values followed by the same letter in each column are not significantly different at $P = 0.05$.

It was also observed that only very high concentration of paraquat (4000 ppm in soil had significant toxic effect on the growth of rice plant under reduced soil conditions (Table 2). Under lowland rice field conditions regular application of paraquat as a total weed killer therefore may not be a potential hazard to rice plants. It is also suggested that lowland clay trap may be used for filtering paraquat in run off water from fields where paraquat is regularly applied to avoid contamination of water ways.

ACKNOWLEDGEMENT

We are grateful to Miss. S. J. M. Srimathie, Mr. Sarath Dissanayake and Mr. D.M.G. Abeysinghe for technical assistance and University of Peradeniya for financial assistance.

REFERENCES

Anderson, J.R. and Drew E.A. 1972. Growth characterististics of a species of *Lipomyces* and its degradation of paraquat. *J. Gen. Microbiol.* 70. 43–58.

Baldwin, B.C., Bray, M.F. and Geoghegan, M.J. 1966. The microbial decomposition of paraquat. *Biochem. J.* 101, 15.

Calderbank. A. and Tomlinson, T.E. 1968. The fate of paraquat in soils. *Outlook on Agriculture* 5, 252–257.

Calderbank, A and Yuen, S.H. 1965. An ion exchange method for determining paraquat residues in food crops. *Analyst* 90, 99–105.

Khan, S.U. 1974. Humic substances reactions involving bipyridylium herbicides in soi and aquatic environments. *Residue Rev.* 52, 1–26.

Weber, J.B. and Coble, H.D. 1968. Microbial decomposition of diquat adsorbed on montmorillonite and kaolinite clays. *J. Agric. Fd. Chem.* 16, 475–478.