Leaching characteristics of the bipyridylium herbicide paraquat in soil column

Jeong-Wook Kwon and Jae-Koo Lee[*]

Department of Agricultural Chemistry, Chungbuk National University, 361-763 Cheongju, Korea

Abstract : The leaching behaviour of ^{14}C-paraquat in soil was investigated using soil columns (5 cm I.D. × 30 cm H.) packed with two soils of different physicochemical properties. ^{14}C-Activities leached from the soil A (loam) columns with and without rice plants for 117 days were 0.42 and 0.54% of the originally applied, whereas those from the soil B (sandy loam) were 0.21 and 0.31%, respectively. ^{14}C-Activities absorbed by rice plants from soil A and B were 3.87 and 2.79%, respectively, most of which remained in the root. Irrespective of soil types, more than 96% of the total ^{14}C resided in soil, mostly in the depth of 0~5 cm. The water-extractable ^{14}C in soil was in the range of 6.10~9.01% of the total ^{14}C applied. The rest of ^{14}C, which corresponds to non-extractable soil residues of [^{14}C]paraquat, was distributed in humic substances in the decreasing order of humin>humic acid>fulvic acid. The soil pH of the columns without rice plants increased after the leaching experiment due to the flooded anaerobic condition resulting in the reduction of the H^+ concentration, whereas that of the columns with rice plants did not increase by the offsetting effect of the acidic exudates from the roots. Low mobility of paraquat in soil strongly indicates that no contamination of ground water would be caused by paraquat residues in paddy soils under normal precipitation.(Received May 13, 1999; accepted July 22, 1999)

Key words : leaching, ^{14}C-paraquat, soil column, non-extractable soil residues.

Introduction

Downward mobility of pesticides in soil is of special interest from a health standpoint, because groundwater is the main source of drinking water and, as a result, contamination of groundwater by pesticides could be a serious problem. (Kruger et al., 1996). The possibility of the groundwater contamination is much greater where persistent and mobile pesticides are used in large quantities at locations overlying shallow water tables (Felding, 1992). The extent to which a herbicide leaches is dependent on adsorptive relationships between the herbicide and soil, water solubility of the herbicide, and the amount of water moving downward through a soil profile (Ashton and Monaco, 1991).

Therefore, herbicides with high water solubility and low soil adsorption coefficient (K_d) strongly influence the tendency of a pesticide to leach (Saeed et al., 1996). Methods for investigating the mobility of pesticides include soil thin-layer chromatography (Helling and Turner, 1968; Ambrosi and Helling, 1977; Sánchez-Martín et al., 1994), soil column (Sundaram, 1997; Kyung et al., 1998; Lee et al., 1998a), and lysimeter (Lee et al., 1994; Lee et al., 1996). The problems that plants can not be grown in soil TLC and those related to location, cost, and other limitations in the lysimeter experiment can be solved by using soil column for the elucidation of leaching characteristics of pesticides in soil in the presence of crops grown. Controlled laboratory studies using soil column have provided useful information on the mobility, persistence, and metabolic fate of various chemicals in agricultural soils (Sundaram, 1997).

[*]Corresponding author (Fax : +82-431-271-5921, E-mail : jklee@cbucc.chungbuk.ac.kr)

Paraquat is a non-selective and fast-effective herbicide developed by ICI and has been used all over the world since 1950's. In Korea, it was introduced in 1970 and has been used for weed control in orchard and the non-agricultural area. It is a dicationic chemical which is adsorbed very strongly to negatively charged soil particles, especially to clay minerals. So, it is certain that leaching of the herbicide is confined. Paraquat loosely bound to soil organic matter, however, shows the possibility to be desorbed by tillage and fertilizer application and to be degraded by soil microorganisms (Lee, et al., 1998b).

This investigation was aimed at elucidating vertical movement of the herbicide paraquat in flooded soil with and without rice plants grown, and absorption/ translocation by rice plants, with the aid of soil columns and the ^{14}C-tracer.

Materials and Methods

Chemical and soil

Methyl-^{14}C-paraquat dichloride (specific activity : 469.9 MBq/mmol, Sigma) and non-labelled paraquat (content : 42.5%) were used. Its chemical structure and the labelled positions are shown in Figure 1.

Soils used were collected from rice paddies in Cheongju (soil A) and Cheongwon (soil B), Chungbuk, air-dried, and passed through a 2-mm sieve. The physicochemical properties of the soils are presented in Table 1.

Leaching

To elucidate the leaching behaviour of paraquat, glass columns (5 cm I.D.×34 cm L.) packed with two types of soils were used according to the method of Lee et al. (1998a) and Kyung et al.
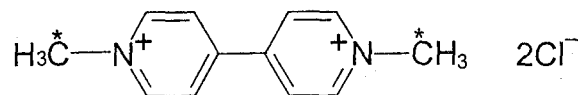

Fig. 1. Structural formula and labelled position(*) of paraquat(1,1'-dimethyl-4,4'-bipyridinium dichloride).
Specific activity : 469.9 MBq/mmol.

(1998). The bottom of the column was plugged with glass wool and the rest was packed with soils by tapping until the soil height reached 29 cm, and saturated with water (soil A, 700 g, 1.22 g/cm³; soil B, 670 g, 1.17 g/cm³). The saturation process was slowly conducted from the bottom to expel the entrapped air in soil and to avoid channeling in the column. The packed columns were then wrapped with moistureproof paper to cut the effect of light and temperature, and stabilized for 2 days. The 35-day-grown rice plant seedlings (Oryza sativa cv. Akibare, Japan) were transplanted onto the soil columns. After 7 days, 20 g of soils (corresponds to 1 cm height of soil columns) treated with ^{14}C-paraquat (8.33 kBq) and non-labelled paraquat which were added to the top of each soil column, and the rice plants were grown for 117 days. The application dose of paraquat corresponded to 1.5 mg /kg soil. Soil columns without rice plants were placed as the control and each treatment was done in triplicate. The volumes of leachates (17.5 mL/day) were calculated on the basis of the average precipitation in the Cheongju area during the period of July and August, '91~'96, and the leachates were collected at regular intervals. As pore volumes of the soil columns were 318.6 and 330.4 mL in soil A and B respectively, the total volume of leachates for 117 days was 6.3 times

Table 1. Physicochemical properties of the soils used

Soil	Texture	Sand	Silt	Clay	pH (H₂O, 1:5)	Organic matter (%)	C.E.C. (mmol(+)/ kg soil)
		(%)					
A	L	50.2	37.1	12.7	5.3	1.3	71
B	SL	66.6	22.2	11.2	5.5	1.5	103

larger than the pore volume of the soil column.

Measurement of radioactivity

The leachate was mixed with Aquasol (Du Pont, NEN Research Products, U.S.A.) and the radioactivity was measured with a liquid scintillation counter (LSC, TRI CARB 1500, Packard). For soil samples, every 5-cm segment from the top was cut, air-dried, and ground in a mortar. Rice plants were divided into shoot, root, ears without grain, and unhulled rice grain, freeze-dried, and pulverized. The soil samples (0.3 g) and rice plant samples (0.2 g) were combusted with the biological oxidizer (R. J. Harvey Instrument Corporation, U.S.A.) and the evolved $^{14}CO_2$ was absorbed in the ^{14}C-cocktail (For Harvey Biological Oxidizer, R. J. Harvey Instrument Corporation, U.S.A.) to measure the radioactivity.

Extractable and non-extractable ^{14}C in soil

Water was used for the extraction of soil samples. Each soil sample (20 g) of 0~5 cm depth was extracted with 50 mL of distilled water for 5 hr and centrifuged (SUPRA 21K, Hanil Science Industrial Co., Ltd.) at 15,540 g for 15 min. The extraction was repeated until the radioactivity of the extract showed the background level.

For bound residues in soil, two grams of the soil samples, which were previously extracted with water, were exhaustively extracted with 0.1 M sodium pyrophosphate. The extract was centrifuged to precipitate humin. To the supernatant was added concentrated HCl to precipitate the humic acid. After the supernatant fulvic acid was separated from humic acid by centrifugation, the humic acid was redissolved with 0.1 N NaOH and the radioactivity was measured. Radioactivity in the humin fraction was measured by combustion.

Soil pH

Each soil sample (10 g) of the 0~5 cm depth was added to 50 mL of distilled water, the soil suspension was stirred from time to time for 1 hr, and the pH was measured by a pH meter (Expandable Ion Analyzer EA.940, ORION).

All measurements were made in triplicate. To examine the effect of the root exudates on soil pH, rice plants grown for 3 days in an incubator were transferred to Petri dishes containing 35 mL of distilled water and sampled after 0, 7, 14, 21 days. Loss of water was replenished with distilled water so that the final volume was 35 mL and the pH was measured.

Results and Discussion

Leaching of paraquat

The amounts of ^{14}C leached from each soil column treated with [^{14}C]paraquat were given in Figure 2. ^{14}C activities leached from unplanted and planted soil A were 0.54% and 0.42% of the originally applied ^{14}C and those of soil B 0.31% and 0.21%, respectively. The leaching of paraquat in soil column was much restricted and not affected by planting or soil types. Cohen et al. (1984) and Cohen (1990) characterized potentially leachable pesticides as those having water solubility of >300 $mgkg^{-1}$; soil/water distribution coefficient (K_d) <5; soil organic carbon/water partition coefficient (K_{oc}) <300~500; Henry's law constant (H) <1 Pa m^3 mol^{-1}; a hydrolysis half-life >25 weeks; photolysis half-life >1 week (for surface deposits); and soil half-life >2~3 weeks. Considering its water solubility (700 g/L, 20°C), paraquat seems to be very leachable. However, its soil/water distribution coefficient and soil half-life are 140~2,990 depending on soil types and about 7 years, respectively (Constenla et al., 1990).

Accordingly, it is evident that leaching of chemicals does not depend on water solubility merely, but is related to many factors.

Paraquat is stable in neutral and acidic media (Tomlin, 1994) and also seems to be stable to chemical degradation in soil (Hance, 1967). Therefore, it has been considered to remain unaltered in soil for a long time. On the contrary, Funderburk and Bozarth (1967), Burn and Audus (1970), Hance et al. (1980), Carr et al. (1985), and Constenla et al. (1990) reported the possibility of microbial degradation of paraquat. When leached

Table 2. Distribution of ^{14}C in each soil layer after the leaching experiment for 117 days

Soil	Rice planting	^{14}C (% of total)						Total (%)
		Soil depth (cm)						
		0~5	5~10	10~15	15~20	20~25	25~30	
A	No	98.68	1.11	0.09	0.02	ND[a]	ND[a]	100.90
	Yes	96.54	0.06	0.02	ND[a]	ND[a]	ND[a]	96.66
B	No	96.50	0.13	ND[a]	ND[a]	ND[a]	ND[a]	96.63
	Yes	96.39	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	96.39

[a]Not detected (below the background level).

^{14}C is expressed as paraquat, the total concentrations of leachates from soil A for 117 days were 0.79±0.12 (unplanted) and 0.54±0.12 (planted) μg/L and those from soil B were 0.43±0.06 (unplanted) and 0.28±0.12 (planted) μg/L.

The pesticide residue standards (Lee et al., 1995) in drinking water in Korea were set for only four organophosphorus insecticides and paraquat was not included in the list. Standards for paraquat, however, have been set in Canada (10 ppb) and Australia (40 ppb). On the basis of the Canadian standard, the concentrations detected in this study are only 2.8~7.9% of it, verifying its very little downward movement in soil.

Changes in paraquat concentration of the leachates are shown in Figure 3. The paraquat concentration is very low during the first 2 weeks, but it increased very rapidly for 2~3 weeks. This
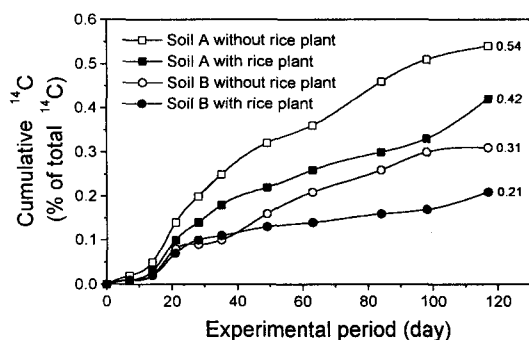
Fig. 2. Cumulative ^{14}C leached from the soil columns treated with [^{14}C]paraquat in the absence and presence of rice plants.
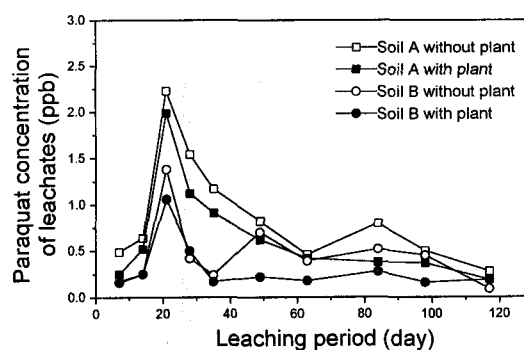
Fig. 3. Changes in the paraquat concentration of leachates from the soil columns with time. Paraquat concentration was calculated on the basis of radioactivity.

would be due to the dead volume occupying the pore volume of each soil. After 3 weeks, the concentration of the leachates decreased gradually.

Radioactivities distributed in each soil layer after the leaching are shown in Table 2. More than 96% of the ^{14}C applied was distributed at the depth of 0~5 cm and the leaching of paraquat in soil was not affected by rice planting.

^{14}C uptake and distribution in rice plants

Radioactivity absorbed by rice plants and its distribution in various parts of rice plant during the leaching period are presented in Table 3. Little difference in absorption and translocation of ^{14}C was recognized among soils, that is, bioavailability of paraquat residues in soil to rice plants was not affected by soil types. Radioactivities translocated into shoots were 21.5~25.8% of those in roots,

indicating that the translocation of ^{14}C absorbed by roots to shoots was very restricted. Paraquat equivalents of the ^{14}C activities in roots and unhulled grains are 1.17~1.78 ppm and 0.03~0.06 ppm, respectively, as calculated on the basis of the specific ^{14}C activities of the paraquat applied (Table 3).

The octanol-water distribution coefficient (K_{ow}) has been mainly used as an index to predict the absorption and distribution of pharmaceuticals within the tissues of living organisms. Lee and Kyung (1995) reported that log K_{ow} of TCAB (3,3',4,4'-tetrachloroazobenzene) was about 4.71 and its high value explained low absorption and translocation of TCAB residues by rice plants.

Considering the water solubility of paraquat, log K_{ow} of paraquat should be very low. Comparing paraquat with TCAB, it can be considered that absorption and translocation of paraquat residues by rice plants are easier than those of TCAB. Uptake of paraquat residues by rice plants, however, showed a similar result to TCAB. It is clear that the low uptake of paraquat residues by

rice plants is due to the formation of the tightly bound residues in soil. Therefore, prediction of the absorption and translocation of chemicals by plants by means of the log K_{ow} value needs to be more careful.

The overall balance of paraquat in soil columns for 117 days is presented in Table 4. The recoveries ranging from 97 to 101% are a good indication that the experiments were performed quite accurately.

Distribution of extractable and non-extractable soil residues

Since paraquat is insoluble in most organic solvents, but highly soluble in water (700 g/L, 20 ℃), water was used for the extraction of soil samples. The results of the soil extraction with water and the distribution of the non-extractable soil-bound residues are given in Table 5. Regardless of the soil types and the presence and absence of rice plants, only 6.1~9.0% of ^{14}C in soil was extracted. The distribution of the non-extractable soil-bound residues of [^{14}C]paraquat and its metabolites was in the order of humin (59.0~77.6)

Table 3. Distribution of radioactivities in rice plants grown for 117 days after planting on the [^{14}C]paraquat-treated soil

Soil	^{14}C (% of total)				Total	Remarks (MRL)
	Shoot	Root	Ears without grain	Unhulled grain		
A	0.77±0.15 (0.27±0.03)[a]	3.09±1.44 (1.78±0.65)	0.00±0.00 (0.05±0.03)	0.00±0.00 (0.06±0.02)	3.87±1.58	Brown rice (0.5 ppm, 1996)
B	0.44±0.22 (0.23±0.05)	2.05±0.64 (1.17±0.30)	0.01±0.00 (0.02±0.00)	0.00±0.00 (0.03±0.01)	2.79±0.87	

[a]Figures in parentheses indicate the paraquat equivalent (mg/kg) calculated on the basis of the specific ^{14}C activity of the paraquat applied.

Table 4. Balance of radioactivity for 117 days after treatment of [^{14}C]paraquat

Soil	Rice planting	Radioactivities (% of total ^{14}C)			Recovery (%)
		Leachate	Soil	Rice plant	
A	No	0.51±0.09	100.90±2.57	-	101.41±2.48
A	Yes	0.44±0.03	96.63±2.03	3.87±1.58	100.93±3.34
B	No	0.30±0.04	96.63±2.58	-	96.93±2.56
B	Yes	0.19±0.09	96.39±0.28	2.79±0.87	99.37±0.96

> humic acid (9.4~26.0) > fulvic acid (5.1~7.9%).

Pesticides of bound type are distributed in fulvic acid early in treatment but the residues are incorporated into humic acid and humin gradually (Ahn et al. 1998).

Therefore, these results showed the normal distribution. The distribution of humic acid in soil B was higher than that in soil A, but that of humin was the opposite.

Soil pH

After leaching, while soil pH in the presence of rice plants did not change, that in their absence increased in the range of 0.8~0.9 unit (Table 6). Generally, under the flooded conditions, the pH of acidic soils increases and that of alkaline soils decreases (Cho et al., 1990). That is, under the flooded anaerobic conditions without rice plants, the H^+ concentration was reduced, leading to an increase in pH. However, in the soil columns with rice plants, the acidic exudates from the roots offset

the effect. As can be seen in Table 1, before the experiment, the pH's of soil A and B were 5.3 and 5.5, respectively. The experiment to elucidate the effect of the exudates from the roots of rice plants on the soil pH shows that the root exudates contain some acidic compounds to lower the pH of the culture solutions (Table 7). This result will be enough to explain the reason why the soil pH's in the presence of rice plants are much lower than those in their absence.

Literature cited

Ahn, K. C., J. K. Lee and K. S. Kyung (1998) Behaviour of the soil residues of the herbicide quinclorac in the micro-ecosystem (pot). The Korean J. Pestic. Sci. 2(3):96~106.

Ambrosi, D. and C. S. Helling (1977) Leaching of oxadiazon and phosalone in soils. J. Agric. Food Chem. 25(1):215~217.

Ashton, F. M. and T. J. Monaco (1991) Weed

Table. 5. Distribution of radioactivity in soils

Soil	Rice planting	% of total ^{14}C				
		Water-extractable	Non-extractable	Fulvic acid	Humic acid	Humin
A	No	9.01	90.99	6.09	9.75	75.15
	Yes	6.81	93.19	6.25	9.35	77.59
B	No	6.10	93.90	5.12	22.74	66.04
	Yes	7.16	92.84	7.87	25.99	58.98

Table 6. Change in soil pH as affected by the cultivation of rice plants

Experiment	Rice planting	Soil A	Soil B
Before		5.3	5.5
After	No	6.1	6.4
	Yes	5.3	5.5

Table 7. Change in the pH of the culture solutions in the absence and presence of rice seedlings

Rice Planting	Days after transplanting			
	0	7	14	21
No	6.04	6.70	6.77	6.66
Yes	6.04	5.75	4.90	4.60

Science-principles and practices, 3rd ed., pp. 18 5~189, A Wiley-Interscience Publication, John Wiley & Sons, Inc. U.S.A.

Burns, R. G. and L. J. Audus (1970) Distribution and breakdown of paraquat in soil. Weed Res. 10:49~58.

Carr, R. J. G., R. F. Bilton and T. Atkinson (1985) Mechanism of biodegradation of paraquat by Lipomyces starkeyi. Appl. Environ. Microbiol. 1290 ~1294.

Cho, S. J., C. S. Park and D. I. Eum (1990) Soil survey and examination. p.256, Sam Jung Soil Science, Hyang Moon Sa.

Cohen, S. Z., S. M. Creegar, R. F. Carsel and C. G. Enfield (1984) Potential for pesticide contamination of ground water from agricultural uses, In Treatment and disposal of pesticide waste, Kruegar, R. F. and Seiber, J. N., Eds., ACS Symp. Ser. 259, American Chemical Society, Washington, DC, 297.

Cohen, S. Z. (1990) Pesticides in ground water: an overview, In Progress in pesticide biochemistry and toxicology, environmental fate of pesticides, Vol.7, Huston, D. H. and Roberts, T. R., Eds., John Wiley & Sons, Chichester, 13.

Constenla, M. A., C. Riley, S. H. Kennedy, C. E. Rojas, L. E. Mora and J. E. B. Stevens (1990) Paraquat behaviour in Costa Rican soils and residues in coffee. J. Agric. Food Chem. 38:198 5~1988.

Felding, G. (1992) Leaching of atrazine into ground water. Pestic. Sci. 35:39~43.

Funderburk, H. H. Jr. and G. A. Bozarth (1967) Review of the metabolism and decomposition of diquat and paraquat. J. Agric. Food Chem. 15:56 3~567.

Hance, R. J. (1967) Decomposition of herbicides in the soil by nonbiological chemical process. J. Sci. Food Agric. 18:544~547.

Hance, R. J., T. H. Byast and P. D. Smith (1980) Apparent decomposition of paraquat in soil. Soil Biol. Biochem. 12:447~448.

Helling, C. S. and B. C. Turner (1968) Pesticide mobility: Determination by soil thin-layer chromatography. Science 162:562~563.

Kruger, E. L., P. J. Rice, J. C. Anhalt, D. A. Anderson and J. R. Coats (1996) Use of undisturbed soil columns under controlled conditions to study the fate of [^{14}C] deethylatrazine, J. Agric. Food Chem. 44:1144~ 1149.

Kyung, K. S., K. S. Oh, K. C. Ahn, J. W. Kwon and J. K. Lee (1998) Leaching behavior of the herbicide bentazon in soil column. The Korean J. Pestic. Sci. 2(1):59~64.

Lee, J. K., F. Führ and K. S. Kyung (1994) Behaviour of carbofuran in a rice plant-grown lysimeter throughout four growing seasons. Chemosphere 29(4):747~758.

Lee, J. K., F. Führ and K. S. Kyung (1996) Fate of the herbicide bentazon in rice plant-grown lysimeters over four consecutive cultivation years. J. Environ. Sci. Health B31(2):179~201.

Lee, J. K. and K. S. Kyung (1995) Uptake of 3,3',4,4'-tetrachloroazobenzene (TCAB) soil residues by rice (Oryza sativa L.). J. Agric. Food Chem. 43(2):519~523.

Lee, J. K., K. S. Kyung, I. S. Jung, K. C. Ahn and J. W. Kwon (1998a) Leaching behaviour of the systemic insecticide carbofuran and the herbicide pretilachlor in soil columns. The Korean J. Pestic. Sci. 2(2):59~67.

Lee, S. L., Y. H. Kim and M. G. Lee (1995) Information resources for the establishment of tolerances on pesticide residues in water quality. Korean J. Environ. Agric. 14(3):351~373.

Lee, S. J., B. H. Kim and J. E. Kim (1998b) Characteristics of adsorption and desorption of herbicide paraquat in soil. The Korean J. Pestic. Sci. 2(1):59~64.

Saeed, I. A. M., J. M. Harkin and D. I. Rouse (1996) Leaching of methyl isothiocyanate in plainfield sand chemigated with metam-sodium. Pestic. Sci. 46:375~380.

Sánchez-Martín, M. J., T. Crisanto, M. Arienzo and M. Sánchez-Camazano (1994) Evaluation of the mobility of ^{14}C-labelled pesticides in soils by thin layer chromatography using a linear analyser. J. Environ. Sci. Health, B29(3):473~484.

Sundaram, K. M. S. (1997) Mobility and metabolic

fate of mexacarbate in soil column containing
sandy and clay loam forest soils. J. Environ. Sci.
Health, B32(2):147~175.

Tomlin, C. (1994) The Pesticide Manual. 10th
Edition, British Crop Protection Council, UK.

토양 column 중 bipyridylium계 제초제 paraquat의 용탈 특성

권정욱 · 이재구*(충북대학교 농과대학 농화학과)

요약 : 물리화학적 성질이 상이한 두 종류의 토양으로 충전된 유리 column (5 cm I.D. × 30 cm H.)을 이용하여 bipyridylium계 제초제 paraquat의 용탈을 조사하였다. 토양 A (양토)의 벼 재배구와 무재배구에서 117일 동안 토양 column으로부터 용탈된 ^{14}C은 각각 총 처리량의 0.42%와 0.54%이었고, 토양 B (사양토)의 경우에는 각각 0.21%와 0.31%이었다. 벼에 흡수된 ^{14}C은 토양 A와 B에서 각각 3.87%와 2.79%이었고 대부분이 뿌리에 분포하였다. 두 토양 모두에서 총 처리량의 96% 이상이 토양중에 남아 있었고, 특히 0~5 cm 부위에 대부분 존재하였다. Paraquat 토양잔류물의 물에 의한 추출율은 6.10~9.10%이었고 추출불가 토양잔류물의 분포 비율은 humin>humic acid>fulvic acid 순이었다. 벼 무재배구의 토양 pH는 담수의 혐기적 조건때문에 용탈 실험 후 증가하였으나 벼 재배구에서의 토양 pH는 벼 뿌리로부터 분비되는 삼출물에 의한 상쇄효과로 증가되지 않았다. 토양중 paraquat의 낮은 이동성은 논에 잔류되어 있는 paraquat에 의한 지하수의 오염가능성이 매우 희박함을 시사해 준다.

---

*연락저자