# Controlled Release of 2,4-D (2,4-Dichlorophenoxy Acetic Acid) from the Complex of Rice Husk Lignin and 2,4-D

## IV. Variation of Herbicidal Activity by Soil Environmental Factors

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# 租穀 Lignin과 2,4-D (2,4-Dichlorophenoxy Acetic Acid) 結合體의 放出制御 硏究

## IV. 土壤環境要因에 따른 除草活性의 變異

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## ABSTRACT

Inactivation in soil absorption, translocation of 2,4-D by plants vary depending upon soil environments and herbicide formulations. Experiment was conducted in a glasshouse using rectangular pots(1350cm$^2$) to evaluate the growth responses of barnyardgrass (*Echinochloa crus-galli*) and indian jointvetch (*Aesehynomene indica*) to two formulations of 2,4-D. The formulations used were 40% 2,4-D amin salt (2,4-D/AS) and 19.7% complex of rice husk lignin and 2,4-D (2,4-D/LG) which were applied at 200g ai/ha. Soil environments included fertilizer levels, soil pH, organic matter contents, and soil textures. Each treatment was replicated three times. The herbicidal activity of 2,4-D increased and lasted with increased levels of fertilizer. The activity also increased and lasted with low soil pH and decreased content of organic matter. Generally 2,4-D/LG showed higher and longer herbicidal activity than 2,4-D/AS for both test plants under all conditions applied. However, the herbicidal activity was influenced by the formulations more than by soil textures. It was thought that 2,4-D/AS was released in a short time and inactivated readily while 2,4-D/LG was slowly released and gave an opportunity of absorption by plants for a long period.

## INTRODUCTION

2,4-D is absorbed by leaves or roots according to the forms of formulations. Also, it show strong herbicidal activities at appropriate rates, but at low rates it inhibits rooting and flowering of plants and regulates ripening of plants as a plant growth regulator. The herbicidal activity of 2,4-D can be reduced by change of translocation at high rates(12). In addition, the intensity of 2,4-D action is obviously different among plant species in that 2,4-D shows its phytotoxicity by producing ethylene within plants(10). Therefore, to rationally use 2,4-D by inducing high selectivity between crop and weed the properties of the formulations and a standard form utilization of 2,4-D should be investigated to improve the activity. Especially controlled release formulation of 2,4-D should be investigated on effects of soil location, soil water status, soil microorganisms (6), and of temperature(4) and light intensity(9)

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at time of application.

The authors investigated the release rate(3) in a laboratory and growth responses of plants(6) of 2,4-D lignin complex under the conditions of water itself and flooded soil. Also, they reported herbicidal activity and selectivity of 2,4-D lignin complex beween rice and weeds under paddy rice conditions(5). The release of 2,4-D lignin complex is physicochemically high within 20 hours after application but thereafter its release is constant and lasted(3). This fact was recognized by biological tests with test plants(6). However, there were injuries to rice by excess release right after application although weeds emerged in mid to late-season were susceptible under paddy rice conditions.

The objectives of this research were to evaluate the responses of weeds to the release rate of 2,4-D formulations as affected by organic matter content, soil pH, soil texture, and rate of fertilizer, and to provide basic information for searching the feasibility to use in transplanted rice.

## MATERIALS AND METHODS

This experiment was conducted in a glasshouse using pots(30x45x13cm) in 1989. Paddy soil was air dried and seived to divide into clay and fine sand. The ratio of clay and fine was 75 : 25% for control treatments. Table 1 shows the environmental factors of the soil used in the experiment. The factors included the amount of fertilizer application, soil pH, organic matter content and soil texture. Each factor contained two variables and each formulation of 2,4-D was biologically tested for properties of controlled release. To adjust soil pH, 2000 and 5.000 ppm of 95% $H_2SO_4$ was incorporated into the soil, respectively, and the soil was stored for 2 weeks in a cold room and then was air dried for 1 day.

The test plants were barnyardgrass (*Echinochloa curs-galli* Beauv.) that was sensitive to 2,4-D by the responses of bending growth(5), and indian jointvetch(*Aeschynomene indica* L.) that germinated well in water and showed the responses of bending growth by 2,4-D in the preliminary study. Their seeds were incorporated into top soil (0.5cm deep) at 1 day before herbicide application. The pots were subirrigated and water was kept 1cm in depth. 2,4-D/LG (complex of rice husk lignin and 2,4-D, 19.7%)and 2,4-D/AS (2,4-D amine salt, 40%) were applied to soil surface at 200 g/ha in active ingredients, respectively. Each treatment was replicated three times.

To evaluate growth rosponses of weeds the visual ratings for barnyardgrass were taken at 10, 20, 30, and 45 days after application by four separates persons. The evaluation was scaled from 0 to 9, where 0 represents no inhibition and 9 represents complete death. At 45 days after application, fresh weights were measured for barnyardgrass and indian jointvetch.

**Table 1.** Comparison of soil condition applied in the experiment

| Soil Conditions | Fertilizer ($N-P_2O_5-K_2O$, Kg/Ha) | Organic matter (Kg/Ha) | Soil pH | Soil (ratio) Clay | Fine sand | Code |
|---|---|---|---|---|---|---|
| Check | 0-0-0 | 0 | 5.4 | 75 | 25 | 0/5.4/C |
| Fertilizer(I) | 140-100-100 | 0 | 5.4 | 75 | 25 | /x1 |
| Fertilizer(II) | 280-200-200 | 0 | 5.4 | 75 | 25 | /x2 |
| Soil pH(I) | 0-0-0 | 0 | 3.6 | 75 | 25 | /3.6 |
| Soil pH(II) | 0-0-0 | 0 | 4.1 | 75 | 25 | /4.1 |
| Organic matter(I) | 0-0-0 | 10,000 | 5.4 | 75 | 25 | /10 |
| Organic matter(II) | 0-0-0 | 20,000 | 5.4 | 75 | 25 | /20 |
| Soil type(I) | 0-0-0 | 0 | 5.4 | 50 | 50 | /L |
| Soil type(II) | 0-0-0 | 0 | 5.4 | 25 | 75 | /S |

## RESULTS AND DISCUSSION

### 1. Influence of fertilizers.

The responses of barnyardgrass to two formulations of 2, 4-D as influenced by levels of fertilizer application are shown in Figure 1. Under no fertilization, barnyardgrass was recovered from 2, 4-D damage with time. However, control of barnyardgrass was increased until 20 days after application and after that it tended to be lasted or decreased. Of the formulations, 2, 4-D/LG was higher in herbicidal activity and longer in durability of the activity than 2, 4-D/AS under any level of fertilization.

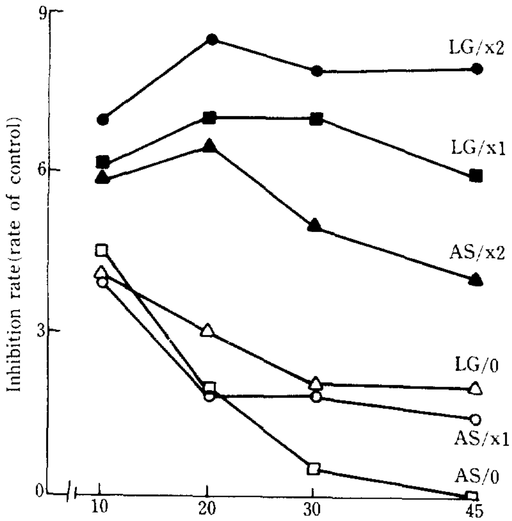


**Fig. 1.** Change in visual rate of growth inhibition (rate of control) of *Echinochloa crus-galli* as affected by different 2, 4-D formulations under different fertilization levels.

In addition, this effect of 2, D-4/LG was reconfirmed by fresh weight determination of barnyardgrass and indian jointvetch at 45 days after application(Table 2). Barnyardgrass growth was increased with fertilizer application but fresh weight of indian jointvetch was decreased with increased levels of fertilizers, when herbicide was not applied. Under all levels of fertilizer application, effect of 2, 4-D/LG was higher than 2, 4-D/AS, especially to indian jointvetch. Also the effects were increased with increased levels of fertilizer. This response is related with vegetative growth of plant kingdoms. Ashton and Crafts(2) states that when young plants grow actively under enough nutrient conditions, ethylene production and inhibition of plant metabolism are increased by 2, 4-D. The difference in response between barnyardgrass and indian jointvetch was probably due to differences of tolerance between them and the difference in response to fertilizer levels was probably due to the rate of metabolism. Growth inhibition by 2, 4-D/LG was greater than that by 2, 4-D/AS because the durability of 2, 4-D/LG release was long by controlled release and because absorption, translocation and accumulation of 2, 4-D within the plants were lasted for a long time(1).

**Table 2.** Fresh matter weight of test plants at 45 days after treatment under different fertilization levels[a].

| Fertilization | Check[b] | 2, 4-D/AS | 2, 4-D/LG |
|---|---|---|---|
| | ........................ | (g/pot) | ........................ |
| | *Echinochloa crus-galli* | | |
| Fertilizer-free | 10.2(0) | 9.6( 5.9b) | 5.1(50.0b) |
| Conventional rate | 48.0(0) | 26.1(45.6a) | 19.0(60.4b) |
| Double rate | 34.0(0) | 17.7(47.9a) | 3.5(89.7a) |
| | *Aeschynomene indica* | | |
| Fertilizer-free | 2.3(0) | 1.3(43.8b) | 0.6(73.9b) |
| Conventional rate | 1.2(0) | 1.1( 8.3c) | 0.2(83.3b) |
| Double rate | 1.0(0) | 0(100.0a) | 0(100.0a) |

[a] Means within a column followed by the same letter are not different at the 5% level of significance by DMRT.

[b] Numbers in the parenthesis indicate the percentage of growth inhibition as compared with the untreated check.

## 2. Influence of soil pH

The overall soil pH in the experiment ranged from 3.6 to 5.5. The herbicidal activity of 2,4-D to barnyardgrass was relatively high under low soil pH(3.6 to 4.1), but when soil pH was increased to 4.1 to 5.4, the activity was dropped rapidly. However, 2,4-D/LG lasted it herbicidal activity longer than 2,4-D/AS in all soil pH ranges(Fig. 2). This was recognized from fresh weight of barnyardgrass at 45 days after application(Table 3). In pots without herbicide application, fresh weight of barnyardgrass was increased as soil pH was decreased. Effect of 2,4-D treatment was decreased with high soil pH and was increaed with low soil pH. Also, overall herbicidal activity was higher with treatments of 2,4-D/LG than with those of 2,4-D/AS. On the other hand, indian jointvetch has shown low adaptibility to low pH in that growth of indian jointvetch was decreased with decreased soil pH even in pots of no herbicide treatment, and was impossible by 2,4-D treatment. Indian jointvetch growth was deadly ingibited more by 2,4-D/LG than by 2,4-D/AS.

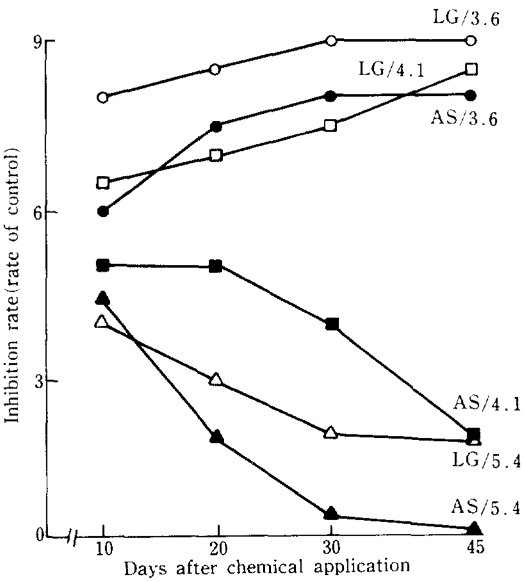


**Fig. 2.** Change in visual rate of growth inhibition (rate of control) of *Echinochloa crus-galli* as affected by different 2,4-D formulations under different soil pHs.

2,4-D is an acid and has a negative charge (-COO) in solution so that 2,4-D is not readily adsorbed to soil even at high soil pH(14). As soil pH is decreased, ionization of 2,4-D is stimulated at and its herbicidal is probably high by stimulated absorption by plants. Also, under extremely low soil pH, microorganisms that degrade 2,4-D may be low in populations or its succession may be occurred, so that its degredation is delayed(13) and its absorption by antsmay be increased. In this experiment, 2,4-D/LG showed higher activity and was more stable by vatiations of soil pH than 2,4-D/AS.

## 3. Influence of organic matter content

The adsorption of herbicides varies with organic matter content, there by the activity of herbicides varies by the degree of herbicide inactivation.

**Table 3.** Fresh matter weight of test plants at 45 days after chemical treatment under different soil pHs[a].

| Soil pH | Check[b] | 2,4-D/AS | 2,4-D/LG |
|---|---|---|---|
| | ......(g/pot)...... | | |
| | *Echinochloa crus-galli* | | |
| 5.4 | 10.2(0) | 9.6( 5.9c) | 5.1( 50.0b) |
| 4.1 | 10.8(0) | 5.6(48.2b) | 0.4( 96.3a) |
| 3.6 | 17.7(0) | 0.5(97.2a) | 0(100.0a) |
| | *Aeschynoment indica* | | |
| 5.4 | 2.3(0) | 1.3(43.5b) | 0.6(73.9b) |
| 4.1 | 1.8(0) | 0.8(55.6b) | 0(100.0a) |
| 3.6 | 0.6(0) | 0(100.0a) | (100.0a) |

[a] Means within a column followed by the same letter are not different at the 5% level of significance by DMRT.

[b] Numbers in the parenthesis indicate the percentage of growth inhibition as compared with the untreated check.

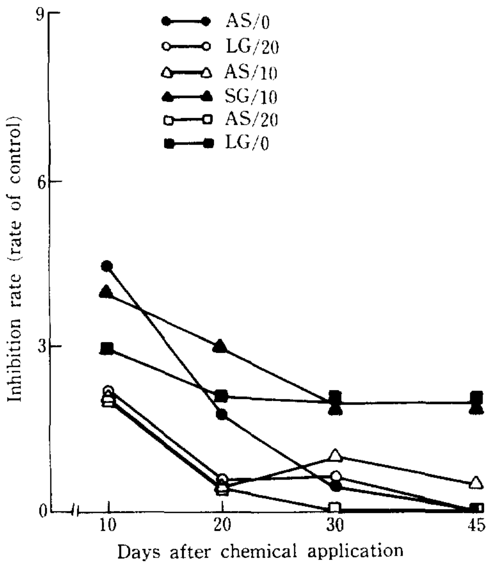


**Fig. 3.** Change in visual rate of growth inhibition (rate of control) of *Echinochloa crus-galli* as affected by different 2,4-D formulations under different organic matter content.

Figure 3 shows the response of growth inhibition of barnyardgrass by two formulations of 2,4-D. The herbicidal activity of 2,4-D in a short period of application was high when no or a little organic matter was added, regardless of the formulation, but activity was decreased with time. When the double rate of organic matter was added, any herbicidal activity was not expected regardless of the formulations.

However, 2,4-D/LG showed relatively high activity as compared with 2,4-D/AS even by adding 10 tons/ha of organic matters. The increase of organic matter stimulates inactivation and degradation of 2,4-D(7,14) which has high water solubility(12), by increasing adsorption materials(11) and by giving favorable conditions for habitation of microorganisms(8). Therefore, despite addition of organic matters, that 2,4-D/LG showed the herbicidal activity longer than 2,4-D/AS was probably due to a slow release of 2,4-D and to increased absorption by plants.

According to fresh weights at 45 days after 2,4-D application(Table 4), indian jointvetch was more susceptible to 2,4-D than barnyardgrass. When organic matter was not added, the herbicidal activity was higher by 2,4-D/LG than by 2,4-D/AS, while the activity difference between two formulations was remarkably reduced by addition of organic matters, especially on indian jointvetch.

#### 4. Influence of soil texture

As shown in Figure 4, the activity difference between two soil textures was remarkable at 10 to 20 days after 2,4-D application, but was reduced with time. Also the overall activity was decreased with time. Generally the herbicidal activity of 2,4-D/LG was higher and lasted longer than that of 2,4-D/AS under all soil texture

**Table 4.** Fresh matter weight of test plants at 45 days after chemical treatment under different organic matter contents[a].

| Compost application | Check[b] | 2,4-D/AS | 2,4-D/LG |
|---|---|---|---|
| | ........ (g/pot) ........ | | |
| | *Echinochloa crus-galli* | | |
| Compost-free | 10.2(0) | 9.6( 5.9a) | 5.1(50.0a) |
| Conventional rate | 9.7(0) | 8.7( 10.3a) | 6.9(28.9b) |
| Double rate | 6.8(0) | 7.5(-10.3b) | 6.7( 1.5c) |
| | *Aeschynomene indica* | | |
| Compost-free | 2.3(0) | 1.3(43.5a) | 0.6(73.9a) |
| Conventional rate | 2.1(0) | 1.1(47.6a) | 0.9(57.1a) |
| Double rate | 1.7(0) | 1.4(17.7b) | 1.4(17.7b) |

[a] Means within a column followed by the same letter are not different at the 5% level of significance by DMRT.

[b] Numbers in the parenthesis indicate the percentage of growth inhibition as compared with the untreated check.

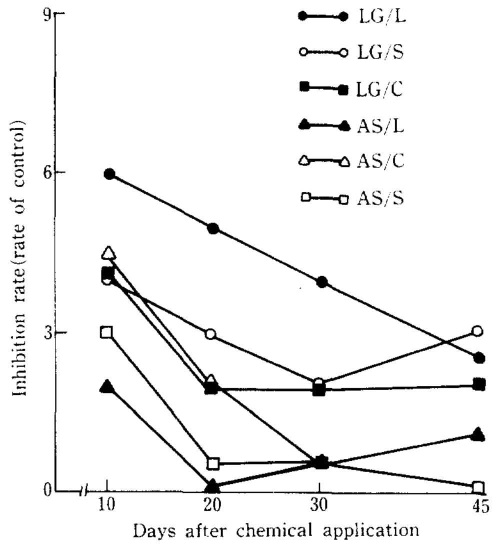


**Fig. 4.** Change in visual rate of growth inhibition (rate of control) of *Echinochloa crus-galli* as affected by different 2,4-D formulations under different soil types. [S, 25 : 75, L, 50 : 50 and C, 75 : 25 in clay and sand ratio, respectively.]

conditions.

Fresh weights of barnyardgrass and indian jointvetch at 45 days after 2,4-D application are given in Table 5. In the pots without 2,4-D application, barnyardgrass growth was extremely inhibited with increased sand content in soils but indian jointvetch was not affected much, suggesting that indian jointvetch adapted well to sandy soils. Also, the herbicidal activity was significantly higher by 2,4-D/LG than by 2,4-D/AS, regardless of plants tested. The variation of herbicidal activity for barnyardgrass was higher by 2,4-D/AS than by 2,4/LG, but for indian jointvetch was similar by both formulations and the activity was decreased with increased sand content. Barnyardgrass growth was not influenced by soil textures while indian jointvetch in the ratio of 25 to 75 for clay to sand, respectively, was inhibited. Generally clay minerals in soils stimulate inactivation of herbicides by adsorption (14). On the other hand, sandy soil stimulates leaching of herbicides that has high water solubility (12, 13). Yang (15) reported that the rate of 50% growth inhibition ($GR_{50}$) for 2,4-D was tremendously changed (11 times) from soil texture to soil texture and that the increase of crop injury and decrease of herbicidal activity by herbicides were readily possible in sandy soils. Thus, that 2,4-D/LG showed higher activity than 2,4-D/AS for a long period is probably due to continuous absorption by plants through controlled release of 2,4-D/LG although there were soil adsorption and leaching during the period. However, the difference in herbicidal activity by 2,4-D between barnyardgrass and indian jointvetch may be due to a difference of tolerance.

**Table 5.** Fresh matter weight of test plants at 45 days after chemical treatment under different soil types[a].

| Soil type (clay : sand) | Check[b] | 2,4-D/AS | 2,4-D/LG |
|---|---|---|---|
| | ········ | (g/pot) | ········ |
| | *Echinochloa crus-galli* | | |
| 75 : 25 | 10.2(0) | 9.6( 5.9b) | 5.1(50.0a) |
| 50 : 50 | 5.6(0) | 4.0(28.6a) | 3.0(46.4a) |
| 25 : 75 | 1.6(0) | 1.0(37.5a) | 0.7(56.3a) |
| | *Aeschynomene indica* | | |
| 75 : 25 | 2.3(0) | 1.3(43.5a) | 0.6(73.9a) |
| 50 : 50 | 3.0(0) | 2.2(26.7ab) | 0.8(73.7a) |
| 25 : 75 | 1.8(0) | 1.5(16.7b) | 1.1(38.9b) |

[a] Means within a column followed by the same letter are not different at the 5% level of significance by DMRT.

[b] Numbers in the parenthesis indicate the percentage of growth inhibition as compared with the untreated check.

## GENERAL DISCUSSION

The herbicidal activity of 2, 4-D/LG and 2, 4-D/AS was evaluated as influenced by soil factors such as fertilizer levels, organic matter contents, soil pHs, and soil textures. As the results, the activity was proportional to fertilizer levels, and was inversely proportional to organic matter contents and clay contents. Also, it was increased in acidic soils. However, one important thing was that 2, 4-D/LG showed higher activity than 2, 4-D/AS even at 45 days after application. 2, 4-D is readily soluble in water and readily leached into the layer of subsoil because it is an acidic compound with negative charges(12, 13). Also, 2, 4-D is so decomposed that $DT_{50}$ (50% disappearance time) is 17 days and $DT_{90}$ is 26 days(14). Nevertheless, 2, 4-D/LG lasted its activity for more than 100 days(3, 6), so that this controlled release of 2, 4-D/LG not only reduced the opportunity of inactivation but also enhanced the opportunity of absorption and translocation for plants. In these experimental conditions it was confirmed that the herbicidal activity of 2, 4-D lasted untill 45 days after application. 2, 4-D/LG at the same rate of 2, 4-D/AS injured rice slightly in the previous report(5). The result from these experiment was similar to that of barnyard rass. Therefore, the rate of 2, 4-D/LG application should be reconfirmed to give better selectivity between crop and weeds.


## 摘 要

2, 4-D의 製劑가 달라짐에 따라 多樣한 土壤環境 속에서 放出된 2, 4-D 有效成分이 不活性化하는 속도와 植物에 吸收, 移行하는 속도간에 차이가 유발될 것임을 예상하고, 이들 차이를 검정식물의 생장반응으로 파악할 목적으로 일련의 시험을 하였다. 시험은 온실내에서 30x45x13cm의 4각폿트에 검정식물로 피(*Echinochloa crus-galli*)와 자귀풀(*Aeschynomene indica*)을 供試하여 수행하였으며, 40% 2, 4-D amine salt【2, 4-D/AS】와 19.7% complex of rice husk lignin/2, 4-Dichloropheoxy acetic acid【2, 4-D/LG】를 200g ai/Ha로 處理하였다. 供試된 土壤環境으로는 施肥量, 土壤酸度, 有機物施用量 및 土性으로서 基準土壤(check soil)을 포함하여 각각 3水準을 두고 3反復으로 遂行되었다. 施肥量이 增大될수록 除草活性은 높고 오래 持續되었으며, 酸性이 强化되거나, 有機物 施肥量이 적을수록 除草活性이 높고 持續性이 커지는 傾向이었다. 또한 전반 조건하에서 두 검정식물 모두 2, 4-D/AS보다도 2, 4-D/LG에 의하여 除草活性이 높고 장기간 持續되는 傾向임을 인정할 수 있었다. 그러나 土性에 따라서는, 製劑間에 일정한 경향없이, 2, 4-D/LG가 2, 4-D/AS보다 높은 除草活性과 긴 持續性을 나타내었다. 이와 같은 結果는 2, 4-D/AS가 短期間에 걸친 多樣放出로 植物吸收보다 토양중에서의 불활성화가 크게 야기되는 반면, 2, 4-D/LG는 장기간에 걸친 소량방출로 土壤中不活性化보다 植物吸收機會가 增大되는데 따른 것으로 해석된다.


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