

토양 중 Trifluralin의 용탈

김정호*

Leaching of Trifluralin in the Commerce Clay Loam Soil

Jung-Ho Kim*

Abstract

Trifluralin was selected to study the leaching potentials related to the pollution on Commerce silty clay loam soil near Baton Rouge, Louisiana, USA. The batch equilibrium of trifluralin resulted in the Koc value of 875. When the soil columns(5.4 cm i.d. × 26 cm length) were leached with three pore volumes of water, the distributions of trifluralin in soil and leachate were 99.993% and 0.007% of the total recoveries, respectively. When applied at the rate of 1,683 g/ha in the field, the amount of trifluralin within the 0~10 cm soil depth was 96.9% of that within the 0~60cm soil depth 31 days after application. The concentrations of trifluralin detected in 1- and 2m- depth wells during 62 days after application ranged from 0.04 ng/mL to 0.08 ng/mL, which were lower than 2.0 ng/mL of the U.S. EPA advisory levels for drinking water. Trifluralin was strongly adsorbed on soil and hardly reached ground water. The leaching properties of trifluralin in the fields were predicted and concurred with those in the columns.

Key words : Trifluralin, Adsorption, Leaching, Soil.

Introduction

The pesticides are biocides applied mainly to agroecosystems. Recently the fate of pesticides in the environment has been attracted more atten-

tion because of its pollution on the surrounding environment. The translocation of agrochemicals from target to nontarget sites seems difficult to be controlled. The areas for fate of pesticides were separated the atmosphere, the lithosphere,

*Dept. of Environmental Science, Kyungsan University, Kyungsan, Kyungpook, 712-240 Korea

the hydrosphere, and the biosphere, but, which were mixed¹⁾.

When applying pesticides, most of the chemicals will directly or indirectly reach the soil. On reaching the soil, losses for most pesticides occur through volatilization soon after application. The remaining pesticides are more or less strongly adsorbed in the organic and mineral soil fractions. The persistence and fate of pesticides is dependent on the nature of the chemical itself and a multitude of environmental factors, such as soil types, temperature, light, moisture, microorganism, etc¹⁾.

Trifluralin (2,6 - dinitro - N, N - dipropyl - 4 - (trifluoromethyl) benzenamine) is the selective herbicide for the preemergence control of annual grasses and broadleaf weeds in soybean, corn, cotton, and peanut production in Louisiana²⁾. Water solubilities of Trifluralin were 0.3mg/L²⁾. The U.S Environmental Protection Agency advisory levels of trifluralin for drinking water was 2.0ng/mL³⁾.

Evaluation of pesticide losses by the runoff process has received considerable attention⁴⁾. Pesticides on the soil surface are lost with surface runoff water and also subjected to downward movement into the soil profile by leaching with water. Transport by leaching might cause contamination of groundwater⁵⁾. The extent of losses with runoff water and downward leaching of pesticides in soil is generally dependent on the soil and pesticides properties, soil management, timing of leaching event and the amount of leached water⁶⁾.

In intensive farming areas, such as the warm and humid climate area in the Lower Mississippi Valley, large quantities of fertilizers and pesticides were used in crop production. Baton Rouge, Louisiana, is an excellent site to conduct a groundwater pollution experiment. Results from the warm,

humid climate and clay soils with high watertables could be put into practice readily throughout the Lower Mississippi Valley and perhaps extended into other areas of the Southeastern United States⁷⁾.

The objective of this study was to identify adsorption and leaching properties of trifluralin in the lab. scale, to compare with the fields in Louisiana USA and to evaluate groundwater quality with U.S EPA advisory levels for the drinking water.

Materials and Methods

Materials

The soil used was classified as a Commerce clay loam⁷⁾. Selected characteristics of the soil include : sand of 48%, silt of 21%, clay of 31%, pH of 6.1, bulk density of 1.41 Mg/m³, soil porosity of 47%, and organic C content of 1.14%⁸⁾.

Trifluralin (Salute 4EC, Mobay Chemical Co.) was dissolved in water for the adsorption experiment and field experiment. Trifluralin, (99.0% each, Crescent Chemical Co.) dissolved in acetone was used for the leaching experiment.

Adsorption experiment

Adsorption isotherm was determined by placing 4 g of air-dried soil and 40 mL of trifluralin solution into 50mL sealed centrifuge tubes. The samples were shaken (135 strokes per minute) for 24 hr, the period that preliminary studies had shown was sufficient to attain equilibrium. Samples were then centrifuged at 3000 rpm for 30 min and the supernatant was used for trifluralin analysis. Difference between the added amounts of trifluralin

and the remaining amounts in the supernatant was considered to be the amounts adsorbed. Desorption was determined on the same samples used for adsorption.

Leaching Experiment

The columns(i.d. 5.4cm) were uniformly packed to a depth of 23 cm (bulk density 1.23 Mg/m³, soil porosity of 41.1%) with untreated soil and saturated with distilled water prior to applying the trifluralin^{9,10}. It was then covered with a depth of 3 cm (84.92 g) of soil treated 4521mg of trifluralin. Amount of trifluralin added to column was 1683g/ha of trifluralin, the same rate of trifluralin applied in cotten field studies in Louisiana, USA¹¹.

The soil column was leached with either 245 mL of distilled water (one pore volume) or 735 mL distilled water (three pore volumes). The 224 ± 6.76 mL of leachate from one pore volume of water was collected during 33.0 ± 8.8 hr (rate of 7.41 ± 1.98 mL/hr). The soil samples were divided into 0-5, 5-8, 8-11, 11-14, 14-20 and 20-26 cm after leaching.

Fields Experiment

The research farm was located on the Mississippi River alluvial flood plain with a 0.1% slope at the Louisiana Agricultural Experiment Station's Ben Hur Farms about 6 km south of Baton Rouge, Louisiana, USA.

Drain plots(3.72ha) were surface drain and had subsurface drain tubing installed one meter below the soil surface. Nondrain plot (3.56ha) had only surface drainage. To quantify a ground water pollution, two monitoring wells were installed in the

center of each field to depth of 1m and 2m¹². The 1m well was placed in the C soil horizon. The 2m well was placed to determine the concentration of trifluralin percolating into the C horizon.

A 48.04% emulsifiable concentrate (Elanco products company) of trifluralin was applied to give 1683g/ha at drain plot on June 4 and at Nondrain plot on June 30, 1991. Soybean was planted on the fields in July.

Sampling in the Fields

Soil samples were collected with 8.3cm diameter soil auger. Soil was collected from the top 0-60 cm of the soil profile, air-dried at room temperature, lightly crushed, and passed through a 2 mm sieve. The initial concentrations of trifluralin in this soil were below detection limits.

The groundwater on 1m and 2m was sampled by suction sampler. Groundwater samples were transported immediately after collection to USDA laboratory at Baton Rouge, LA, where they were stored frozen until analysis.

Analysis

Trifluralin extraction of water was accomplished by mixing water with 100 mL hexane in a magnetic stirrer for 2 hr. Trifluralin extractions of soil were accomplished by soxhlet extracting 30 g air-dried soil for 3 hr with 200 mL n-hexane : acetone (41 : 59, v/v)¹³.

Trifluralin concentrations in the extracts were analyzed using a Tracor 540 GC equipped with ⁶³Ni electron capture detectors. A Megabore column (15 m long × 0.53 mm i.d.) of DB210 was used.

Results and Discussion

Adsorption

Graphs of experimental data fitted to linear forms of Freundlich equation were presented in Fig. 1. Model parameters for adsorption and desorption of trifluralin were shown in Table 1.

Table 1. Freundlich equation parameters for the adsorption and desorption of trifluralin in soil.

	Kd ¹⁾	Koc ²⁾	1/n ¹⁾
Adsorption	9.97	875	0.97
Desorption	644	56540	1.01

¹⁾log A=log Kd+(1/n) log C.

where A : amount adsorbed (ng/g), C : equilibrium concentration (ng/mL).

²⁾Koc=Kd/Foc

where : Foc is the fraction by weight of organic carbon in the soil (0.0114).

The Kd value for adsorption was 9.97. The large value of Kd indicated strong adsorption on the soil and a low leaching potential. Koc is a soil water partitioning constant based on the organic C fraction (0.0114) of a soil. The Koc value for adsorption was 875. A large value of 1/n may be attributed mainly to the adsorption of trifluralin on clay minerals. Values of 1/n for organic matter rich soils are less than unity. Low organic matter content soils show values greater than unity¹⁴⁾.

The desorption isotherms did not overlap the adsorption isotherms(Fig. 1). Noncoincidence of adsorption and desorption isotherms is called hysteresis¹⁵⁾. The desorption datum was also described by the Freundlich equation parameters(Table 1). The Kd desorption/adsorption ratio was 65 for trifluralin. The higher ratio for trifluralin is fur-

ther evidence of its stronger adsorption tendency.

The leaching indices (LI) of the pesticides were calculated using equation from Laskowski¹⁶⁾ :

$$LI=(S) (t 1/2)/(Vp)(Koc) \\ = (0.3) (42.6)/(1.0 \times 106)(875)$$

where S is water solubility (mg/L at 25°C, t 1/2 is half life of pesticide in soil (day), Vp is vapor pressure (mm Hg) at 25°C and Koc is an organic C partition coefficient. With literature values for S and Vp²⁾ and t 1/2¹⁷⁾ and Koc values from the present study, LI values was calculated in 1.4 × 10⁴, which shows a low leaching potential.

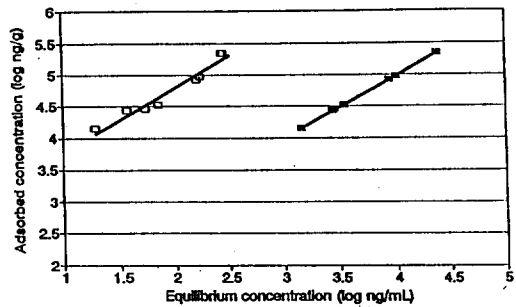


Fig. 1. Batch adsorption and desorption of trifluralin in a Commerce silty clay loam. (■ : Adsorption, □ : Desorption)

Leaching in soil columns

Distribution of trifluralin in soil columns and leachate water is given in Fig. 2. Total recoveries (soil+leachate) after leaching with control (no leaching), one, and three pore volumes were 74.6 %, 73.2%, and 70.0% of applied amount for trifluralin, respectively.

After leaching with one pore volume, 68.74% of applied amount was in the 5-cm depth (3 cm of treated zone plus 2 cm of untreated zone), while the trifluralin amounts in the untreated zone (below the 5cm depth) were 4.53% of the applied

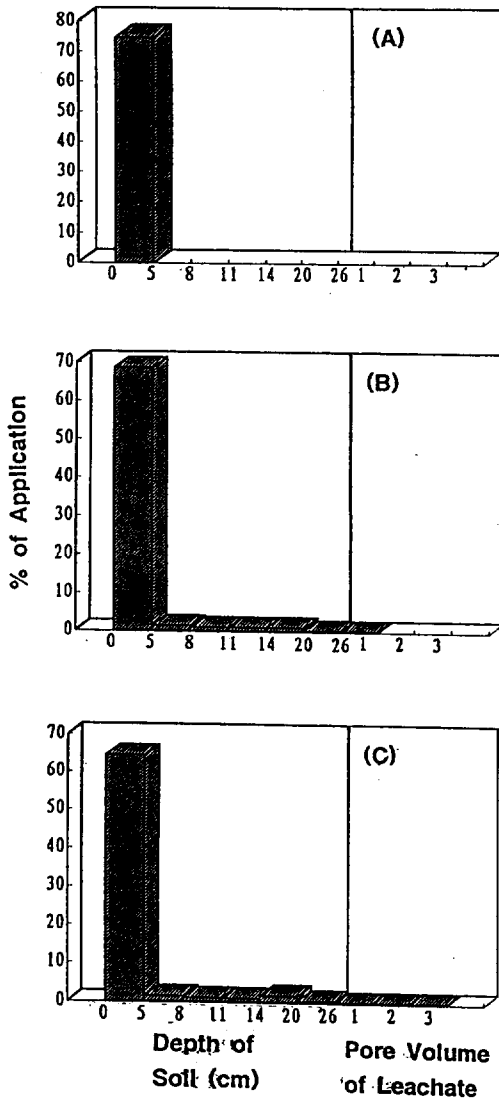


Fig. 2. Distribution of trifluralin in soil column and leachate after leaching with (A) no leaching (B) one pore volume and (C) three pore volume of water.

amount. With three pore volumes of leachate, 64.50%, 5.83%, and 0.005% of applied trifluralin were appeared in the treated zone soil, the untreated zone soil and leachate water, respectively (Fig. 2). This result was concurred with Smith

and Willis's report, which trifluralin in the leachate was 0.003 % of that applied by three pore volumes⁹⁾. The low mobility of trifluralin in the soil column was resulted from undoubtedly strong adsorption to the soil ($K_d=9.97$) and low water solubility(0.3 mg/L).

Leaching in field soil

Trifluralin of distribution of soil depth is given in Fig. 3 at drained plot and Fig. 4 at nondrained plot. Trifluralin on the soil surface was subjected

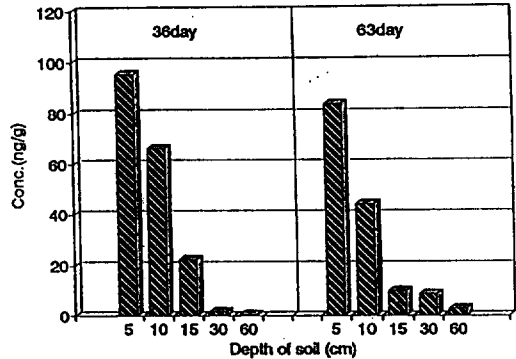


Fig. 3. Distribution of trifluralin in the soil within 0-60cm depth in drained plot applied 1683g/ha in Louisiana.

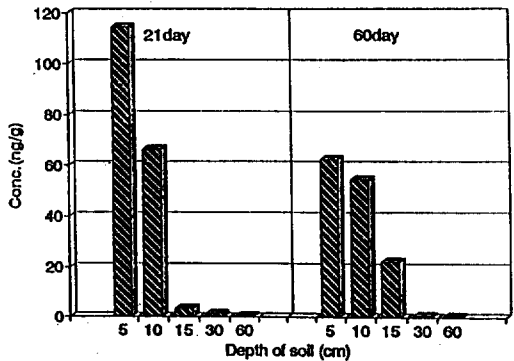


Fig. 4. Distribution of trifluralin in the soil within 0-60cm depth in nondrained plot applied 1683g/ha in Louisiana.

to downward movement into the soil profile by leaching with water. Leaching of trifluralin within the 0 to 10 cm depth was 96.9% of amount within the 0 to 60cm soil depth on 31 days after application. Trifluralin was found mainly in the surface 10cm of soil. Trifluralin strongly adsorbed on soil has a low potential for leaching.

Leaching in groundwater

High watertables were often caused by excessive precipitation. A portion of this excessive water was infiltrated into the soil and was caused

the watertables to rise near the surface. The concentration of trifluralin in groundwater in the above C layer (1m well) and in the below C layer (2m well) was shown in Fig. 5 at drained plot and Fig. 6 at nondrained plot.

The concentration of trifluralin showed the range from 0.04 ng/mL to 0.08 ng/mL in 1m and 2m well at drained plot and nondrained plot during 62 days after application. U.S EPA advisory levels of trifluralin was 2.0 ng/mL¹⁸⁾. The concentrations of trifluralin in the 1m and 2m wells were lower than that of the U.S. EPA advisory.

This result was similar to Goodrich's report¹⁸⁾ that the concentration of trifluralin in ground water was reported to be 2.20 ng/mL for maximum contaminant level and 0.40 ng/mL for median contaminant level. Leaching properties of trifluralin in the fields were predicted and concurred with those in the columns.

요 약

Commerce silty clay loam 토양에서 제초제 trifluralin의 용탈을 조사하였다. Trifluralin의 Koc값은 875이었다. 토양 컬럼(5.4 cm i.d. × 26 cm length)을 이용한 용탈실험에서, 3배의 pore부피에 해당하는 물로 trifluralin을 침출 할 경우, 토양 층에는 99.993%이었고, 0.007%의 미량만 침출수로 침출 되었다. 야외포장 실험에서는 미국 Louisiana Baton Rouge에 있는 포장에 trifluralin을 1683g/ha 살포하였다. 처리 31일 후, 0-60cm 토양 층에 있는 trifluralin 전체 량의 96.9%가 0-10cm 토양 층에 분포되었다. 또한, 62일 후 1m 및 2m 지하수에서 trifluralin의 농도는 0.04-0.08ng/mL이었다. 이는 미국 EPA의 음용수 중 trifluralin의 허용농도인 2.0ng/mL보다 낮았다. Trifluralin은 토양에 강하게 흡착되었기 때문에 토양 column 및 야외 포장에서의 침출량은 매우 적었으며, 토양 column 및 야외 포

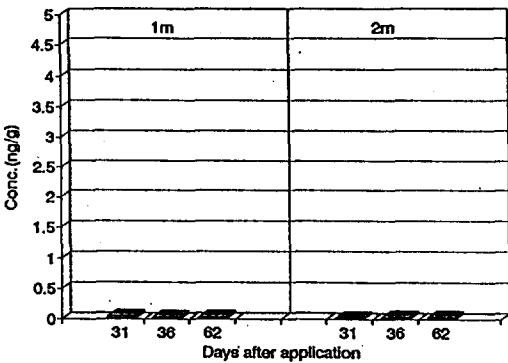


Fig. 5. Concentration of trifluralin in 1m and 2m well in drained plot applied 1683 g/ha in Louisiana.

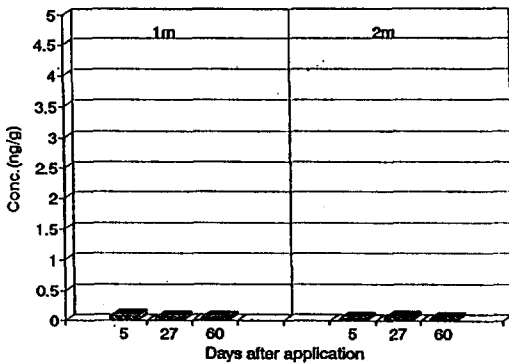


Fig. 6. Concentration in 1m and 2m well of trifluralin in nondrained plot applied 1683g/ha in Louisiana.

장에서의 결과는 일치하였다.

Acknowledgments

This research was a contribution from USDA-ARS, Louisiana and supported by Louisiana State University Agricultural Center, Louisiana Agricultural Experiment Station in USA and Korea Science & Engineering Foundation in Korea in 1991-1992.

References

1. Green, R.E. and S.W. Karickhoff, (1989), Sorption estimates for modeling, *In* H.H. Cheng. Pesticide in the soil environment : Processes, Impacts, and Soil Modeling. Soil Science, Society of America, Inc. Wisconsin. p. 79~101.
2. Humbrug, N.E., (1989), Herbicide Handbook of the Weed Science Society of America, Weed Science Society of America, Champaign, Illinois, p. 180~183 and 252~256.
3. Goodrich, J.A. , W.L. Jr. Benjamin, and M.C. Eobert, (1991), Drinking water from agriculturally contaminated groundwater, *J. Environ. Qual.*, **20** : 707~717.
4. Wauchope, R.D., (1978), The pesticide content of surface water draining from agricultural fields - a review, *J. Environ. Qual.*, **7** : 459~472.
5. Hall, J.K. , M.R. Murray, and N.L. Hartwing, (1989), Herbicide leaching and distribution in tilled and untilled soil, *J. Environ. Qual.*, **18** : 439~445.
6. Starr, J.L., and D.E. Glotfelty, (1990), Atrazine and bromide movement through a silt loam soil, *J. Environ. Qual.*, **19** : 552~558.
7. Camp, C.R., (1976), Determination of hydraulic conductivity for a Louisiana alluvial soil, Proceedings of the Third National Drainage Symposium, ASAE, St. Joseph, Mi 49085. p. 104~108.
8. Bleyerveld, S. and C.P. Kim, (1989), Application of the creams model on the alluvial soils in Southern Louisiana, Dept. of Agricultural Engineering, Louisiana State University, Baton Rouge, Louisiana.
9. Smith, S. and G.H. Willis, (1985), Movement of pesticides in soils, columns as affected by anhydrous ammonia, *Environ. Toxic. Chem.*, **4** : 425~434.
10. Feagley, S.E. and J-H. Kim, (1995), Adsorption and leaching of cis and trans-permethrin in the soil, *J. Korean Environ. Sciences*, **4(4)** : 379~386.
11. Southwick, L.M., J.P. Clower, D.F. Clower, J.B. Graves and G.H. Willis, (1983), Effect of ultra low volume and emulsifiable concentrate formulations on permethrin coverage and persistence on cotton leaves, *J. of Economic Entomology*, **76** : 1442~1447.
12. Isensee, A.R., R.G. Nash, and C.S. Helling, (1990), Effect of conventional vs. no-Tillage on pesticide leaching to shallow groundwater, *J. Environ. Qual.*, **19** : 434~440.
13. Southwick, L.M., G.H. Willis, R.L. Bengtson and T.J. Lormand, (1990), Effect of subsurface drainage on runoff losses of atrazine and metolachlor in southern Louisiana, *Bull. Environ. Contam. Toxicol.*, **45** : 113~119.
14. Hata, Y. and T. Nunoshige, (1982), Adsorption and desorption of piperophos by soil, *J. Pest. Sci.*, **7** : 155~160.
15. Allan, F. and P.A. Dahm, (1979), Sorption of organophosphorus and carbamate insecticides by soil, *J. Agric. Food Chem.*, **27** : 557~563.

16. Laskowski, D. A., (1982), Terrestrial environmental, environmental risk analysis for chemicals. R.A. Conway, ed., Van Nostrand Reinhold co. New York, N.Y., p. 198-240.
17. Kim J.-H., S.E. Feagley, L.M. Southwick, W.H. Willis and R. L. Bengtson, (1992), Movement of trifluralin, metolachlor and metribuzin in the soil environment-Runoff and leaching from fields in Louisiana, In 84th Annual meeting of ASA, CSSA, SSSA. Nov. 1-6, 1992. Minneapolis, MN. p. 126.
18. Goodrich, J. A. , W.L. Jr. Benjamin, and M.C. Robert, (1991), Drinking water from agriculturally contaminated groundwater, J. Environ. Qual., **20** : 707~717.