■■■■■■■■■■
Note
 ■■■■■■■■■■

Method for Estimating Competitive Adsorption of Herbicides on Soils

Munehiro EBATO* and Koyo YONEBAYASHI†

National Institute of Livestock and Grassland Science, Senbonmatsu
 768, Nishinasuno, Tochigi 329–2793, Japan

† Graduate School of Agriculture, Kyoto Prefectural University,
 1–5 Simogamo, Nakaragi-cyo, Sakyo-ku, Kyoto 606–8522, Japan

(Received January 17, 2005; Accepted April 20, 2005)

The effects of mixed herbicides in soils may differ due to interactions. Since adsorption amounts and ratios change nonlinearly with herbicide concentrations, it is necessary to control the total number of moles of a herbicide in solution to estimate its interactions and competitive adsorption in soils. Under experimental conditions, a method was utilized based on the amount of each herbicide adsorbed when the herbicide's molecular ratio was 100%. When atrazine and linuron were applied to soils, they did not compete in terms of adsorption. © Pesticide Science Society of Japan

Keywords: atrazine, competitive adsorption, estimating method, linuron, soil.

INTRODUCTION

Herbicides differ chemically and thus, adsorb to soils in different ways.¹⁾ To understand the mechanisms of herbicide adsorption on soils, researchers have examined different herbicides.^{2–18)} The major focus of these studies has been adsorption and desorption.^{8–18)}

Mixed herbicides are applied to soils as a method of weed control in fields. However, the effects of the herbicides may differ with their interactions with the soil and with each other. Although a necessary component of modern agricultural systems, herbicides can pollute the environment. Therefore, it is important to understand their behavior in different soils.

We have previously reported methods for predicting the amounts of atrazine and linuron adsorbed in soils.^{19,20)} Competitive adsorption of herbicides is an important problem when considering the usefulness of these methods.

Previous studies have examined the competitive adsorption of herbicides on soils. Using columns of soil, Tan and Singh²¹⁾ showed that the leaching of bromacil and norflurazon decreased when these compounds were sprayed together with other herbi-

cides. McGinley *et al.*²²⁾ estimated breakthrough curves of terachloroethylene and trichlorobenzene after mixing the herbicides in soil columns. When mixed, terachloroethylene and trichlorobenzene adsorption isotherms become looser due to competition for sites of adsorption between the two herbicides. Turin and Bowman²³⁾ studied competitive adsorption among bromacil, napropamide and prometryn, by saturating other herbicides to 50% of their maximum adsorbed amounts. They found that the amounts of bromacil and napropamide adsorbed decreased in the presence of other herbicides, while the adsorption of prometryn was unaffected.

Although previous studies found that some herbicides competed for adsorption, no standard method for estimating competitive adsorption has been established. Also, previous studies could not sufficiently analyze competitive adsorption of herbicides by soils. Adsorption amounts and ratios change nonlinearly with the herbicide concentration. In soil, the molecular amount of herbicide in a solution affects the nonlinear adsorption of the herbicide. To estimate interactions and competitive adsorption of herbicides in soils, it is necessary to control the total number of moles of each herbicide in solution.

The objectives of this study were to investigate competitive adsorption of herbicides on soils using the same number of moles of in solution, and to establish a method for estimating competitive adsorption of herbicides to soils.

MATERIALS AND METHODS

1. Herbicides

Atrazine and linuron were used as adsorbates (Fig. 1). Atrazine is a white powder with a melting point of 171 to 174°C and water solubility of 70 ppm at 25°C.²⁴⁾ Linuron is a white powder with a melting point of 93 to 94°C and water solubility of 75 ppm at 25°C.²⁴⁾ The two high-purity herbicides (98.7 and 99.9%, respectively) were purchased from Wako Pure Chemical Industries, Ltd. (Japan).

Although similar in molecular weight and water solubility, the organic carbon adsorption coefficient (K_{OC}) of linuron is higher than that of atrazine (Fig. 1).

2. Soils

Three Andisols (A-1, A-2, and A-6), 2 Inceptisols (I-6 and I-10), and 3 Entisols (E-1, E-5, and E-7) were used for estimating the competitive adsorption of atrazine and linuron. The soil samples were collected from A or Ap horizons because herbicides are usually scattered on the surface. Andisols and Entisols were cultivated. The physico-chemical characteristics of the soils are listed in Table 1. The quantity and quality of organic matter found in soils affect the adsorption of herbicides. The total carbon content of the soils ranged from 12.0 to 93.7 g kg⁻¹.

The soil samples were air-dried and sieved (2.0 mm). They were analyzed for soil physico-chemical properties and used for adsorption experiments with atrazine and linuron. The physico-

* To whom correspondence should be addressed.

E-mail: evamune@affrc.go.jp

© Pesticide Science Society of Japan

Fig. 1. Chemical structures and characteristics of atrazine (1) and linuron (2).

chemical analyses covered pH (1:5 soil/H₂O, w/v ratio), electrical conductivity (EC, 1:5 soil/H₂O, w/v ratio), total carbon (TC), total nitrogen (TN), particle size distribution, exchangeable cations, and cation exchange capacity (CEC, pH 7.0). Effective CEC (ECEC) was calculated by adding exchangeable sodium, potassium, calcium, magnesium and aluminum.

3. Adsorption Experiments

The adsorbed amount and ratio of herbicide adsorbed on soil differ with the concentrations applied. Different concentrations of prepared herbicide solutions result in different molecular numbers of herbicide in the solution. Therefore, to estimate the interaction or competition between two herbicides, the total molecular number in solution should be the same. For atrazine and linuron, atrazine's molecular number was set at 0, 28, 54, 78, and 100% of the total molecular number in solution (Fig. 2). Three concentrations (50, 100, and 200 $\mu\text{mol l}^{-1}$) of herbicide were used. Ten grams of soil and 20 ml of 0.01 M CaCl₂ solution containing the herbicides (1:2 soil/solution, w/v ratio) were placed in a 50 ml Teflon centrifuge tube, sealed with a Teflon screw cap. Suspensions were shaken at 25±2°C for 24 hr on a reciprocating shaker at 60 rpm and centrifuged at 1500×g for 15 min. Equilibrium concentrations of atrazine and linuron were determined by HPLC with the supernatant. The analytical conditions for HPLC were as follows; Wakopak Wakosil column, 150 mm long×4.6 mm *i.d.*; column packing, C18; flow rate, 1 ml/min; elution system, 60:40 (v:v) acetonitrile–water; UV detection, 254 nm. The amounts of atrazine and linuron adsorbed by the soils were estimated as the difference between the initial and final equilibrium concentrations.

Fig. 2. Molar ratios of atrazine and linuron in the initial solutions. The ratios of the atrazine molecular number were set as 0, 28, 54, 78, and 100% of total molecular number in the solution.

Table 1. Soil characteristics

Soil	Soil type	Horizon	Land use	TC g kg ⁻¹	TN g kg ⁻¹	C/N	Sand g kg ⁻¹	Silt g kg ⁻¹	Clay g kg ⁻¹	Texture	Clay minerals	pH (H ₂ O) μS cm ⁻¹	EC	Exchangeable cations							ECEC ^(a) cmol(+) kg ⁻¹	CEC ^(b) cmol(+) kg ⁻¹	B.S. ^(c) %
														Na	K	Ca	Mg	Al	H				
A-1	Andisol	Ap	upland	33.0	2.6	12.8	697	249	54	SL	Al-Vt,Kt,Q	5.0	69	0.06	0.23	3.69	0.59	1.47	0.45	6.1	10.4	58	
A-2	Andisol	Ap	upland	24.3	2.0	12.0	669	239	92	SL	allophane	5.8	229	0.26	0.55	7.97	1.63	0.16	0.20	10.6	15.2	70	
A-6	Andisol	Ap	upland	65.1	4.7	14.0	584	300	115	L	allophane	5.8	93	0.10	0.21	10.00	0.89	0.14	0.20	11.3	23.8	48	
I-6	Inceptisol	A	forestland	93.7	6.0	15.5	538	208	255	CL	It>Q>Kt>Al-Vt	4.0	68	0.11	0.31	1.14	0.49	9.16	1.73	11.2	20.8	54	
I-10	Inceptisol	B	forestland	57.4	3.1	18.3	262	307	432	HC	Al-Vt>Kt,Q	4.1	56	0.05	0.05	0.10	0.19	11.05	1.21	11.4	29.9	38	
E-1	Entisol	Ap	upland	12.0	1.4	8.6	509	289	202	CL	Sm>>Kt>Q>It	6.7	100	0.07	0.60	7.48	2.91	0.00	0.04	11.1	10.8	102	
E-5	Entisol	Ap	paddy	19.4	2.0	9.8	723	167	110	SL	Kt>Al-Vt>>It,Q	5.7	42	0.10	0.46	3.91	0.69	0.69	0.20	5.8	8.1	73	
E-7	Entisol	Ap	paddy	15.6	1.7	9.0	530	299	171	CL	Sm>>Kt,Q>It	5.3	82	0.09	0.38	5.72	0.96	0.49	0.29	7.6	10.4	74	

^{a)} ECEC: effective cation exchange capacity. ^{b)} CEC: cation exchange capacity. ^{c)} B. S.: base saturation.

Fig. 3. Adsorbed amounts of atrazine and linuron on soils. Y-axes mean total adsorbed amounts of atrazine and linuron, and atrazine molar ratios were serialized on X-axes from 0 to 100% per initial concentration of herbicide solutions.

Fig. 4. Three-dimensional structures of atrazine (1) and linuron (2) molecules. Red and blue dots mean positive and negative polarized, respectively. The points where atrazine and linuron molecules accessed on soils were represented by black circle lines.

Fig. 5. Relationships between sum of extrapolating and measured amounts of adsorbed atrazine and linuron on soils.

RESULTS AND DISCUSSION

1. Amounts of Atrazine and Linuron Adsorbed on Soils

The amounts of atrazine and linuron adsorbed are shown in Fig. 3. The total amount adsorbed increased with the initial concentration of the solution from 50 to 200 $\mu\text{mol l}^{-1}$. When molar ratio of atrazine increased, the amount of atrazine adsorbed increased, and the amount of linuron adsorbed decreased. Therefore, more linuron than atrazine was adsorbed by the soils. The three-dimensional structure, charge density, and dipole moments of atrazine and linuron were calculated with MOPAC97,²⁵⁾ and visualized with Win MOPAC Ver. 2.1.,²⁶⁾ to clarify the difference in adsorption. Although MOPAC97 is a semi-empirical method, it is useful for comparing differences in molecular structures under the same conditions. Atrazine and linuron were polarized as shown in Fig. 4. The soil surface was electronegatively charged, and atrazine and linuron could adsorb on the soil surface at two points and one point, respectively. Since the dipole moment of linuron was larger than that of atrazine, linuron could access the soil surface more

easily. By calculating molecular structures with a computer, it was confirmed that more linuron than atrazine was adsorbed.

2. Method for Estimating Competitive Adsorption of Atrazine and Linuron on Soils

To investigate the competitive adsorption of the herbicides on soils, a method was utilized based on adsorbed amounts of each herbicide when the herbicide molecular ratio was 100%. In the case of atrazine, the equation was as follows; extrapolated value of adsorbed amount of atrazine=(adsorbed amount of atrazine when the atrazine molecular ratio was 100%) $\times$ (ratio of atrazine amount against total herbicide amount in the initial solution). The extrapolated value of the adsorbed amount of linuron was calculated in the same way of atrazine extrapolation. Sums of the atrazine and linuron extrapolations were compared with actual measurements obtained from adsorption experiments (Fig. 5). The dashed lines in Fig. 5 indicate where the extrapolated values overlap the measured values completely. Plots appearing over or under the dashed lines suggest competitive adsorption between

atrazine and linuron. The plots in Fig. 5 were on the dashed lines for all soils, and therefore, atrazine and linuron did not compete for adsorption on soils. This method was easy to understand and useful for estimating competitive adsorption. There are two possible reasons why no competition occurred between atrazine and linuron. Either the number of adsorption sites on the soil surface was much larger than the molecular number of the herbicides, or atrazine and linuron were not adsorbed as monolayers, that is, herbicide molecules might adsorb on the surface which were made after herbicide molecules adsorbed on soil surface.

REFERENCES

- 1) S. U. Khan: "Developments in Soil Science 8 Soil Organic Matter," Elsevier Scientific Publishing, New York, pp. 137–171, 1978.
- 2) R. Calvet: "Interactions between Herbicides and the Soil," Academic Press, New York, pp. 1–30, 1980.
- 3) J. J. Pignatello and L. Q. Huang: *J. Environ. Qual.* **20**, 222–228 (1991).
- 4) L. Cox, M. C. Hermosin and J. Cornejo: *Chemosphere* **27**, 837–849 (1993).
- 5) P. Benoit, E. Barriuso, S. Houot and R. Calvet: *Eur. J. Soil Sci.* **47**, 567–578 (1996).
- 6) G. Sheng, C. T. Johnston, B. J. Teppen and S. A. Boyd: *J. Agric. Food Chem.* **49**, 2899–2907 (2001).
- 7) M. Ebato, K. Matsumura and K. Yonebayashi: *J. Pestic. Sci.* **27**, 337–346 (2002).
- 8) O. P. Bansal: *Soil Sci. Soc. Am. J.* **47**, 877–883 (1983).
- 9) C. A. Bellin, G. A. O'Connor and Y. Jin: *J. Environ. Qual.* **19**, 603–608 (1990).
- 10) A. C. Sharon and C. K. William: *Weed Sci.* **38**, 262–266 (1990).
- 11) J. S. Graham and J. S. Conn: *Weed Sci.* **40**, 155–160 (1992).
- 12) O. Francioso, E. Bak, N. Rossi and P. Sequi: *Sci. Total Environ.* **123/124**, 503–512 (1992).
- 13) L. Gao, T. J. Bicki, A. S. Felsot and T. D. Hinesly: *J. Environ. Qual.* **22**, 186–194 (1993).
- 14) A. Pusino, W. Liu and C. Gessa: *J. Agric. Food Chem.* **42**, 1026–1029 (1994).
- 15) W. O. Werkheiser and S. J. Anderson: *J. Environ. Qual.* **25**, 809–814 (1996).
- 16) E. Barriuso, S. Houot and C. Serra-Wittling: *Pestic. Sci.* **49**, 65–75 (1997).
- 17) R. Celis, J. Cornejo, M. C. Hermosin and W. C. Koskinen: *Soil Sci. Soc. Am. J.* **62**, 165–171 (1998).
- 18) H. Li, G. Sheng, B. J. Teppen, C. T. Johnston and S. A. Boyd: *Soil Sci. Soc. Am. J.* **67**, 122–131 (2003).
- 19) M. Ebato, K. Yonebayashi and T. Kosaki: *Soil Sci. Plant Nutr.* **47**, 221–231 (2001).
- 20) M. Ebato, K. Matsumura and K. Yonebayashi: *Soil Sci. Plant Nutr.* **48**, 601–607 (2002).
- 21) S. Tan and M. Singh: *J. Environ. Qual.* **24**, 970–972 (1995).
- 22) P. M. McGinley, L. E. Katz and W. J. Weber Jr.: *Water Res.* **32**, 3571–3577 (1996).
- 23) H. J. Turin and R. S. Bowman: *J. Environ. Qual.* **26**, 1282–1287 (1997).
- 24) M. Windholz: "The Merck Index Twelfth Edition," Merck & Co., Whitehouse Station, 1996.
- 25) J. J. P. Stewart: MOPAC97, Fujitsu Ltd., Tokyo, 1998.
- 26) Fujitsu Ltd.: WinMOPAC Ver.2.1, Fujitsu Ltd., Tokyo, 1998.