Adsorption of Herbicidally Active Degradate 2-(2,4-Dichloro-3-methylphenoxy)propanoic Acid on an Andosol

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The adsorption of 2-(2,4-dichloro-3-methylphenoxy)propanoic acid (DMPA) on the surface horizon of a humus-rich Andosol was examined. To investigate the mechanisms of adsorption, chemically treated Andosols, such as organic matter removed Andosol, organic matter and active metals removed Andosol, and clay minerals of the Andosol, were prepared. Furthermore, humic acid was extracted from the Andosol. The mechanisms of the DMPA adsorption were identified by using those untreated and chemically treated Andosols and the humic acid. The amount of DMPA adsorbed increased with decreasing equilibrium pH value. Active surface hydroxyl groups were identified as the most important soil functional group in DMPA adsorption. The predominant mechanism of DMPA adsorption on the Andosol is a ligand-exchange reaction, in which an active surface hydroxyl on Al and/or Fe is replaced by a carboxylic group of DMPA. A comparative study revealed that the amount of DMPA adsorbed was slightly greater than that of (2,4-dichlorophenoxy)acetic acid (2,4-D), especially at equilibrium pH values below 5. This is because the octanol–water partition coefficient (log K_{ow}) of DMPA in the equilibrium pH range is higher than that of 2,4-D, and SOM participates in the adsorption process through a hydrophobic interaction.

KEYWORDS: Adsorption; clomeprop; 2-(2,4-dichloro-3-methylphenoxy)propanoic acid; (2,4-dichlorophenoxy)acetic acid (2,4-D); metal−humate complexes

INTRODUCTION

The phenoxyacetic acid herbicide (*R,S*)-2-(2,4-dichloro-3-methylphenoxy)propionanilide (clomeprop, **Figure 1A**) has been used as a soil-applied and selective herbicide to control broad-leafed and Cyperaceous weeds in paddy fields (*1*) in many Asian countries. Clomeprop itself shows no herbicidal activity against plants, but its hydrolyzed product, 2-(2,4-dichloro-3-methylphenoxy)propanoic acid (DMPA, **Figure 1B**), has a strong and auxinic herbicidal activity (*1–5*). The reason for the widespread use of clomeprop is its effectiveness against weeds that are resistant to sulfonylurea herbicides (*6*). Since the 1980s, sulfonylurea herbicides have been widely and continuously used for the control of broad-leafed weeds in cereal fields. As a result, weeds that are resistant to sulfonylurea herbicides have emerged

in many areas (*7, 8*). The amount of clomeprop that is used has increased since 2000. Because the herbicidal activity of clomeprop in soils is caused by DMPA (*9, 10*), it is important to investigate the mechanisms of adsorption of DMPA in soils.

The mechanisms of adsorption of DMPA in soils have not been investigated, although the adsorption of phenoxyacetic acid herbicides, especially (2,4-dichlorophenoxy)acetic acid (2,4-D, **Figure 1C**), in soils has been well studied. The adsorption of phenoxyacetic acid herbicides on soils is controlled by (i) an electrostatic ion-exchange reaction between a positively charged, active surface hydroxyl on metal (hydr)oxides and a negatively charged carboxylate group on the dissociated phenoxyacetic acid herbicide molecule (*11, 12*); (ii) a ligand-exchange reaction between the active surface hydroxyl group on metal (hydr)oxides and the carboxylic group of the phenoxyacetic acid herbicide molecules (*13, 14*); or (iii) hydrophobic interactions between hydrophobic constituents of soils (e.g., humic substances) and hydrophobic portions of the phenoxyacetic acid herbicide molecules (e.g., aromatic and aliphatic moieties) (*15–17*). The adsorption of DMPA on soils may be also controlled by one of these three possible mechanisms.

Andosols, which are derived from volcanic materials, occur in volcanic regions such as the Pacific Rim and have a high

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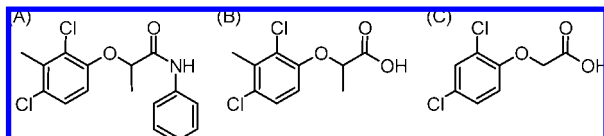Adsorption of DMPA on Andosol

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Figure 1. Chemical structures of (**A**) (*R,S*)-2-(2,4-dichloro-3-methylphe-noxy)propionanilide (clomeprop), (**B**) its metabolite 2-(2,4-dichloro-3-methylphenoxy)propanoic acid (DMPA), and (**C**) (2,4-dichlorophenoxy)-acetic acid (2,4-D).

potential for agricultural production (*18*). Andosols are characterized by a high content of aluminum/iron (hydr)oxides and large contents of soil organic matter (*19, 20*). Hiradate et al. (*14*) studied the adsorption of 2,4-D on an Andosol and suggested that the main mechanism of 2,4-D adsorption is a ligand-exchange reaction on metal (hydr)oxides, although the Andosol contains a large amount of organic matter. Therefore, to clarify the mechanism of adsorption of DMPA on Andosols, it would be useful to perform a comparative study of the adsorption of 2,4-D and DMPA, because these compounds have similar chemical structures.

Our main aim, therefore, was to clarify the detailed mechanism of adsorption of DMPA on a humus-rich Andosol and to compare the adsorption phenomena of DMPA with those of 2,4-D. To identify the major soil components involved in the DMPA adsorption on Andosols, we investigated adsorption mechanisms by using untreated Andosol, chemically treated Andosol (e.g., organic matter removed Andosol, organic matter and active metals removed Andosol, and clay minerals of the Andosol), and soil organic matter (humic acid) extracted from the Andosol.

MATERIALS AND METHODS

Soil Samples. A soil sample, UG5, was collected from the Ap horizon of an upland experimental field of the National Institute for Agro-Environmental Sciences, Tsukuba, Japan [Melanudand; USDA Soil Taxonomy (*21*); Silandic Andosol; WRB (*18*)]. The soil sample was prepared, as described by Hiradate and Uchida (*22*), as follows. The sample was air-dried, ground, and passed through a 0.5 mm sieve (untreated UG5 soil). The untreated UG5 soil was boiled repeatedly with 6% H_2O_2 until the soil organic matter (SOM) was almost completely decomposed. The contents of soil organic carbon were determined with a C/N analyzer (dry combustion method). The sample was then washed once with 20 g L^{-1} aqueous Na_2CO_3 (without pH adjustment) to remove organic molecules adsorbed on the soil particles, three times with 1 M NaCl at pH 5, and three times with deionized water. The treated soil sample was freeze-dried and sieved (<0.5 mm, UG5-SOM).

To remove the active hydroxides, the UG5-SOM was shaken with 0.2 M sodium oxalate−oxalic acid mixed solution (pH 3.0, soil sample/solution = 1:25 mass/volume) at 150 rpm in the dark for 4 h at 30 °C. The treated soil sample was washed sequentially with 20 g L^{-1} Na_2CO_3 (without pH adjustment), 1 M NaCl, and deionized water and then freeze-dried and sieved, as described above (UG5-SOM-AM).

To remove the free metal (hydr)oxides, 10 g of UG5-SOM-AM was suspended in a mixed solution of 100 mL of 0.3 M sodium citrate and 12.5 mL of 1 M sodium bicarbonate at 80 °C, and 1 g of sodium dithionate was added. The mixture was incubated for 15 min with occasional shaking, and the supernatant was removed by centrifugation (∼300*g*). This procedure (DCB treatment) was repeated twice. The treated soil sample was washed, freeze-dried, and sieved as described above (UG5-SOM-FM).

Adsorption of DMPA and 2,4-D. DMPA (400 μM, 100 mg L^{-1}) and 2,4-D (400 μM, 88 mg L^{-1}) stock solutions were prepared by dissolving DMPA (>99% purity; Bayer CropScience K.K., Tokyo, Japan) and 2,4-D (>98% purity; Wako Pure Chemical Industries, Ltd., Osaka, Japan), respectively, in deionized water with the addition of

400 μM NaOH. A 250 mg portion of the soil sample (untreated UG5, UG5-SOM, UG5-SOM-AM, UG5-SOM-FM) was placed in a glass centrifuge tube (12 mL) with a Teflon-lined screw cap. Deionized water (2.25 to 4.7 mL), 1 M $CaCl_2$ (0, 0.05, or 0.5 mL), 1 M H_3PO_4 (0, 0.05, or 0.5 mL), 0.1 M HCl or NaOH (0 to 1.2 mL), and 400 μM DMPA or 2,4-D aqueous solution (0.25 mL) were added to the tube to give a final volume of 5.0 mL; an equilibrium pH value between 4 and 8; a $CaCl_2$ concentration of 0, 0.01, or 0.1 M; a H_3PO_4 concentration of 0, 0.01, or 0.1 M; and an initial DMPA or 2,4-D concentration of 20 μM (5.0 mg L^{-1} for DMPA and 4.4 mg L^{-1} for 2,4-D). The mixture of soil sample and DMPA/2,4-D solution was shaken at 120 reciprocations per minute for 1–32 h at 25 °C in the dark. A clear filtrate was obtained by passing the soil suspension through a filter membrane with a 0.2 μm pore size (DISMIC, Advantec Toyo Kaisha Ltd., Tokyo, Japan). The equilibrium pH of a 2 mL portion of the filtrate was measurement by using a pH-meter (F-21, Horiba Ltd., Kyoto, Japan) with a glass electrode (6378-10D, Horiba Ltd.). A 1 mL portion of the filtrate was analyzed for DMPA/2,4-D by using a high-performance liquid chromatography unit (HPLC pump, L-6200; UV–vis detector, L-4200H; autosampler, AS-2000; column oven, L-5025; chromatogram integrator, D-2500; Hitachi High-Technologies Corp., Tokyo, Japan) equipped with a reversed-phase analytical column (Inertsil ODS-3, 5 μm, 4.6 mm i.d., 250 mm length; GL Sciences Ltd., Tokyo, Japan). In the HPLC analysis, DMPA and 2,4-D were eluted with a mixed solution of 0.05 M phosphoric acid and acetonitrile (3:7 v/v) at a flow rate of 1 mL min^{-1}, a column temperature of 40 °C, and detection at 210 nm. The retention times of DMPA and 2,4-D in the HPLC system were 6.5 and 4.8 min, respectively.

The amount of DMPA/2,4-D adsorbed on the soil sample, Q (mmol kg^{-1}), was calculated by using the equation

$$Q = \frac{(M - CV)}{W}$$

where C (μmol L^{-1}) is the equilibrium concentration of DMPA/2,4-D in the aqueous solution, M (μmol) is the amount of DMPA/2,4-D initially added, V (L) is the volume of aqueous solution (0.005 L), and W (kg, dry weight basis) is the weight of the soil sample. Because the weight of the chemically treated UG5 samples (UG5-SOM, UG-SOM-AM, and UG5-SOM-FM) was decreased as a result of the removal of soil components from the original UG5 soil (*22*), the amount of DMPA/2,4-D adsorbed on these treated soil samples, Q_T (mmol kg^{-1}), was calculated on the basis of untreated UG5 soil

$$Q_T = RQ$$

where R is the weight percentage of the treated soil sample to untreated UG5 soil (oven-dry basis).

Preparation of Soil Humic Acid. A humic acid sample was prepared according to the procedure of Yonebayashi (*23*) and Yonebayashi and Hattori (*24*), as follows. Humic acid was extracted from the untreated UG5 soil with 0.1 M NaOH overnight at 60 °C. The extract was centrifuged (20000*g*), and the supernatant was acidified to pH 1.2 with 4 M HCl, allowed to stand overnight to separate humic acid (precipitate) from fulvic acid (supernatant), and then centrifuged. The precipitated portion (humic acid) was again dissolved by adding NaOH, centrifuged to remove soil minerals, precipitated by adding HCl, and centrifuged once more to remove fulvic acid. This procedure was repeated until the acidified supernatant became light yellowish in color. The purified humic acid fraction was redissolved in a small amount of NaOH solution and centrifuged (20000*g*) for 2 h to remove coarse minerals. After acidification (pH 1.2) of the humic acid fraction, a 0.3 M solution of HF in 0.1 M $HClO_4$ was added, and the mixture was stirred for 5 h at room temperature to dissolve and remove fine minerals. The precipitated (humic acid) fraction was washed with deionized water, redissolved in a small amount of NaOH solution, dialyzed (critical MW 8000) until the electrical conductivity of the equilibrated outer solution reached 10 μS cm^{-1} or less, passed through an Amberlite IR-120 resin (H^+ form) column, and freeze-dried (H^+ humic acid). The major chemical composition of humic acid in soil is not change by this extraction procedure (*25*). The ash content of the humic acid as determined by dry combustion (550 °C) was 0.64% (*26*). The acidity

Table 1. Characteristics of Untreated and Chemically Treated Soil Samples (*22*)

			selective dissolution analyses[d]					
soil sample[a]	wt[b] (%)	C content[c] (g kg^{-1})	Al$_{pyr}$[e] (g kg^{-1})	Fe$_{pyr}$ (g kg^{-1})	Al$_{OX}$ (g kg^{-1})	Fe$_{OX}$ (g kg^{-1})	Si$_{OX}$ (g kg^{-1})	Fe$_{DCB}$ (g kg^{-1})
untreated UG5	100	71.9	10	4	45	12	8	42
UG5-SOM	83	3.5	−	−	38	14	8	29
UG5-SOM-AM	65	1.6	−	−	11	7	3	32
UG5-SOM-FM	53	1.5	−	−	7	1	3	1

[a] UG5-SOM, SOM was removed by H$_2$O$_2$ treatment; UG5-SOM-AM, SOM and active metal hydroxides were removed by H$_2$O$_2$ and acid−oxalate treatments; UG5-SOM-FM, SOM and active and free metal (hydr)oxides were removed by H$_2$O$_2$, acid−oxalate, and dithionite−citrate−bicarbonate treatments. [b] Weight percentage of the soil sample to untreated UG5 soil (oven-dry basis). [c] Oven-dry basis. [d] Values were calculated based on the weight of the untreated UG5 soil (oven-dry basis). [e] Al$_{pyr}$, pyrophosphate-extractable Al; Fe$_{pyr}$, pyrophosphate-extractable Fe; Al$_{OX}$, acid oxalate-extractable Al; Fe$_{OX}$, acid−oxalate-extractable Fe; Si$_{OX}$, acid−oxalate-extractable Si; Fe$_{DCB}$, dithionite−citrate−bicarbonate-extractable Fe; −, not determined.

of the humic acid, which originated primarily from its carboxylic groups, was estimated by neutralization of the humic acid (H$^+$ form) to pH 7 [COOH acidity, 4.07 mol$_c$ kg^{-1} (*26*)]. A solid-state cross-polarization magic-angle-spinning (CPMAS) ^{13}C nuclear magnetic resonance spectrum of the H$^+$ form of the humic acid showed it to be rich in aromatic and carboxylic carbon atoms (*26, 27*).

Adsorption of DMPA by Metal−Humate Complexes. The H$^+$ humic acid was dissolved in a dilute NaOH solution to give a H$^+$ humic acid concentration of 4.0 g L^{-1} and a pH value of 6.0 (stock solution). A 0.5 mL portion of this stock solution, deionized water (1.5−4.2 mL), 1.0 M CaCl$_2$ (0.05 or 0.5 mL), and 0.1 M HCl or NaOH (0−2.30 mL) were mixed in a 12 mL glass centrifuge tube, and the mixture was allowed to stand overnight. A 100 μM aqueous solution of DMPA (1.0 mL) was added to the tube by means of a continuously adjustable air-displacement pipet to give a final volume of 5.0 mL, an amount of H$^+$ humic acid of 2.0 mg, an equilibrium pH value between 4 and 8, a CaCl$_2$ concentration of 0.01 or 0.1 M, and an initial DMPA concentration of 20 μM (5.0 mg L^{-1}). In this solution, the humic acid precipitated with Ca by forming a calcium−humate complex that subsequently reacted with DMPA. The mixture of the calcium−humate complex and DMPA solution was shaken at 120 rpm for 4 h at 25 °C in the dark. A clear filtrate was obtained by passing the calcium−humate complex suspension through a filter membrane with a pore size of 0.2 μm (DISMIC, Advantec Toyo Kaisha Ltd., Tokyo, Japan). The equilibrium pH value and DMPA concentration in the filtrate were determined as described above. The amount of DMPA adsorbed by the calcium−humate complex was calculated as the difference between the amount initially present in the solution and that in the filtrate. To clarify the effects of other metals on DMPA adsorption, similar experiments were conducted in the presence of 0.01 M AlCl$_3$ or 0.01 M FeCl$_3$ instead of CaCl$_2$. The amount of DMPA adsorbed by aluminum hydroxide, prepared by neutralization of 5.0 mL of 0.01 M AlCl$_3$ with 0.1 M NaOH, was also compared with that adsorbed by an aluminum−humate complex, prepared by mixing 5.0 mL of 0.01 M AlCl$_3$ and 2.0 mg of H$^+$ humic acid at equilibrium pH values between 4 and 8.

Octanol–Water Partition Coefficients of DMPA and 2,4-D. 1-Octanol saturated with deionized water and deionized water saturated with 1-octanol were prepared by shaking these two phases at 150 reciprocations per minute for 24 h and separating the upper and lower phases after centrifuging (1200*g*) for 15 min. DMPA (400 μM, 100 mg L^{-1}) and 2,4-D (400 μM, 88 mg L^{-1}) stock solutions were prepared by dissolving DMPA or 2,4-D in 1-octanol-saturated deionized water containing 400 μM NaOH. The water-saturated 1-octanol (30 mL) was placed in a 62 mL glass centrifuge tube with a Teflon-lined screw cap. 1-Octanol-saturated water (26−27 mL), 1-octanol-saturated water saturated with 0.1 M HCl or NaOH (0–1 mL), and 400 μM DMPA or 2,4-D aqueous solution saturated with 1-octanol (3 mL) were added to the tube to give a final aqueous phase volume of 30 mL. The tube was rotated vertically (20 rpm) for 24 h at 25 °C in the dark. The two phases were separated by centrifugation (1200*g*) for 15 min at 25 °C. The concentrations of DMPA and 2,4-D in both phase were determined by HPLC. The analytical conditions for HPLC were as described above. The equilibrium pH value of the aqueous phase was determined by means of a pH-meter as described above.

Statistical Method. Analysis of covariance (ANCOVA) was used to examine the differences in the adsorption of DMPA/2,4-D on soil (*28*), where pH was treated as covariate. Prior to the statistical analysis, logarithmic transformation was performed. The statistical analysis was performed with SAS 9.1.3 (SAS Institute Inc.) (*29*).

RESULTS AND DISCUSSION

Chemical Properties of Soil Samples. The chemical properties of the untreated UG5 soil and chemically treated soil samples (UG5-SOM, UG5-SOM-AM, and UG5-SOM-FM) have been reported by Hiradate and Uchida (*22*). The pH(H$_2$O), pH(KCl), and pH(NaF) values of the untreated UG5 soil are 5.8, 4.5, and 11.2, respectively. The adsorption of P on the untreated UG5 soil was examined by batch equilibrium method. The P retention value of the untreated UG5 soil is 92%, which means 92% of P in aqueous phase was removed by the soil. These results suggest that the untreated UG5 soil has a considerable content of active surface hydroxyl groups. The hydroxyls can act as ion-exchange and ligand-exchange sites. The major clay minerals of the untreated UG5 soil in the <2 μm clay fraction are allophane, imogolite, ferrihydrite, goethite, kaolinite, and hydroxyaluminum−vermiculite complex (*22*). These clay components, together with Al−SOM and Fe−SOM complexes, are the major sources of active surface hydroxyls.

Table 1 shows the organic C contents and the amounts of various forms of Al and Fe in untreated and chemically treated UG5 soil. In the UG5-SOM, almost all SOM was removed from untreated UG5 soil samples. Therefore, Al and Fe complexed with SOM in the untreated UG5 soil were presumably released and precipitated as aluminum and iron hydroxides (*22*). In UG5-SOM-AM, portions of the ferrihydrite, allophane, and imogolite were removed, as shown in the reduced Al$_{OX}$, Fe$_{OX}$, and Si$_{OX}$ values. In UG5-SOM-FM, crystalline iron (hydr)oxides in addition to ferrihydrite, allophane, and imogolite were completely removed, as shown in the very low Al$_{OX}$, Fe$_{OX}$, Si$_{OX}$, and Fe$_{DCB}$ values.

Kinetics of DMPA Adsorption on Untreated UG5 Soil at Various Equilibrium pH Values. In paddy fields, the usual application rate of clomeprop is 0.45−2.2 kg ha^{-1}. The concentration of clomeprop in paddy-flooded water is expected to be 0.90−4.4 mg L^{-1} (2.7 to 13.6 μM), if the flood depth is assumed to be 5 cm. Therefore, the concentration of DMPA was set at 5.0 mg L^{-1} (20 μM) in our adsorption experiment. This concentration has also been recommended in the Organization for Economic Cooperation and Development (OECD) test guidelines for pesticide adsorption/desorption study (*30*).

A study of the adsorption kinetics was conducted to determine the time required to achieve thermodynamic equilibrium, and this value was then used in the studies of the DMPA adsorption mechanisms. When a DMPA aqueous solution was mixed with the untreated air-dried UG5 soil, the DMPA concentration in the solution decreased quickly within several hours (**Figure 2**).
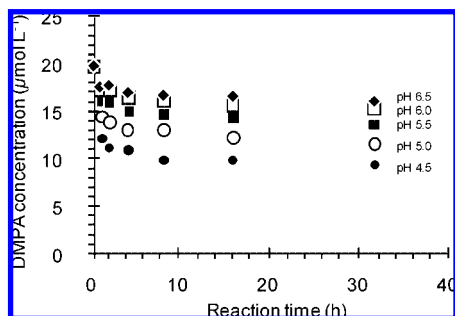
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Figure 2. Kinetics of DMPA concentration changes in aqueous solution in the presence of an Andosol (untreated UG5 soil) at equilibrium pH 4.5, 5.0, 5.5, 6.0, and 6.5: initial DMPA concentration, 20 μM (5.0 mg L^{-1}); amount of soil, 50 g L^{-1} (oven-dry basis); background electrolyte, 0.01 M CaCl$_2$. First, a relationship between DMPA concentration in aqueous solution in the presence of the untreated UG5 soil and equilibrium pH was plotted at each reaction time (10 plots between pH 4 and 8), and then DMPA concentration at equilibrium pH 4.5, 5.0, 5.5, 6.0, and 6.5 at each concentration time was read from the relationship and plotted. The equilibrium pH value increased 0−0.5 unit with reaction time depending on the initial pH value.
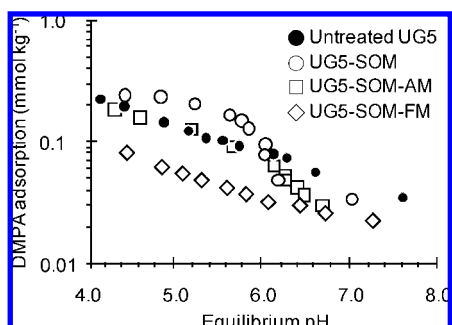

Figure 3. Amount of DMPA adsorbed on untreated UG5 soil (●), UG5-SOM (○), UG5-SOM-AM (■), and UG5-SOM-FM (◇) in the presence of 0.01 M CaCl$_2$ as a function of equilibrium pH: reaction time, 4 h; initial DMPA concentration, 20 μM (5.0 mg L^{-1}); amount of soil, 50 g L^{-1} (oven-dried and untreated UG5 soil basis). Had the soil adsorbed all DMPA in this experiment, the amount of DMPA adsorption would have reached 0.4 mmol kg^{-1}.

The decrease in DMPA concentration was greater at lower equilibrium pH values. DMPA does not degrade in several hours in soil (*9*). During the 8–36 h after the mixing, the concentration remained virtually unchanged. Therefore, the rapid decrease of the DMPA concentration in solution must have been caused by the adsorption of DMPA on the soil. At all equilibrium pH values shown in **Figure 2**, the decreased concentration of DMPA in the solution after 4 h was ∼80% or more of the decreased concentration after 36 h of mixing. Therefore, a contact time of 4 h was used in subsequent experiments when the adsorption mechanisms of DMPA were investigated. These kinetic characteristics for adsorption of DMPA, such as the pH dependency, the rapid decrease in DMPA concentration, and the subsequent constant DMPA concentration, are very similar to the characteristics for 2,4-D in our previous study (*14*). 2,4-D does not degrade in soil in several hours (*31–33*); accordingly, a contact time of 4 h was also used in subsequent experiments of 2,4-D.

Soil Components Adsorbing DMPA. The amount of DMPA adsorption on the untreated and chemically treated UG5 soil samples increased with decreasing equilibrium pH values (**Figure 3**). A similar tendency has been observed for the adsorption of 2,4-D on iron (hydr)oxides (*11, 13, 34*), sandy

Table 2. Results of the Analysis of Covariance for the Amount of DMPA Adsorbed on Untreated UG5 Soil and Chemically Treated UG5 Soil^a

soil sample^b	estimated intercept	standard error
untreated UG5	0.5019	0.1248
UG5-SOM	0.9313	0.0342
UG5-SOM-AM	0.4597	0.0380
UG5-SOM-FM	−0.3635	0.0338

^{a} Prior to performing the ANCOVA, logarithmic transformation was performed. ^{b} UG5-SOM, SOM was removed by H$_2$O$_2$ treatment; UG5-SOM-AM, SOM and active metal hydroxides were removed by H$_2$O$_2$ and acid−oxalate treatments; UG5-SOM-FM, SOM and active and free metal (hydr)oxides were removed by H$_2$O$_2$, acid−oxalate, and dithionite−citrate−bicarbonate treatments.

and loamy soils from Belgium (*35*), and Oxisols (*36*); for the adsorption (*R,S*)-2-(2,4-dichlorophenoxy)propanoic acid (dichlorprop) on silt clay loamy and silt loamy soils from Norway (*37*); for the adsorption of (4-chloro-2-methylphenoxy)acetic acid (MCPA) on iron (hydr)oxides (*11*); for the adsorption of (*R,S*)-2-(4-chloro-2-methylphenoxy)propanoic acid (mecoprop) on iron (hydr)oxides (*34*); and for the adsorption of (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) on iron (hydr)oxides (*11*).

To identify the most important soil constituent for DMPA adsorption on untreated UG5 soil, the adsorption of DMPA on untreated and various chemically treated UG5 soil was conducted (**Figure 3**). **Table 2** shows the estimated intercept by the ANCOVA. The amount of DMPA adsorbed was greater (*p* < 0.001) on UG5-SOM (**Figure 3**, ○) than on untreated UG5 soil (**Figure 3**, ●). Because almost all SOM was removed in UG5-SOM, it could be concluded that SOM is not an important adsorbent for DMPA and that hydrophobic interactions may not be the major adsorption mechanism. On the other hand, after the removal of active and free metal (hydr)oxides, the amounts of DMPA adsorbed were significantly decreased (*p* < 0.001, respectively) in UG5-SOM-AM (**Figure 3**, □) and UG5-SOM-FM (◇) compared with UG5-SOM (○), suggesting that the active surface hydroxyls derived from the active and free metal and metal−SOM complexes could play an important role in the DMPA adsorption process. In UG5-SOM-FM, the major DMPA-adsorbing components are hydroxyaluminum−vermiculite complexes and kaolinite, and these have a limited role in the adsorption of DMPA on untreated UG5 soil.

The characteristics of adsorption of DMPA on untreated UG5 soil and on chemically treated samples were similar to those of 2,4-D (*14*). More 2,4-D is adsorbed by UG5-SOM than by untreated UG5 soil (*14*). This increase could be explained by the presence of newly formed aluminum and iron (hydr)oxides in UG5-SOM. In untreated UG5 soil, a portion of Al and Fe is complexed with SOM, and the surface of aluminum and iron (hydr)oxides is masked by SOM. The Al and Fe occluded by SOM cannot adsorb DMPA or 2,4-D. After the removal of SOM from the untreated UG5 soil, Al and Fe released from SOM may precipitate as newly formed aluminum and iron (hydr)oxides, and the surfaces of aluminum and iron (hydr)oxides that were previously masked by SOM may be exposed to the solution phase. These act as newly revealed surfaces of aluminum and iron (hydr)oxides in UG5-SOM, which adsorb DMPA and 2,4-D.

Mechanisms of DMPA Adsorption Caused by Active Surface Hydroxyls. On the basis of the above results, ion-exchange reactions or ligand-exchange reactions are the dominant mechanism of adsorption of DMPA on active surface hydroxyls. In the ion-exchange reaction, positively charged active surface hydroxyls attract negatively charged carboxyl groups of DMPA through electrostatic interactions. The active
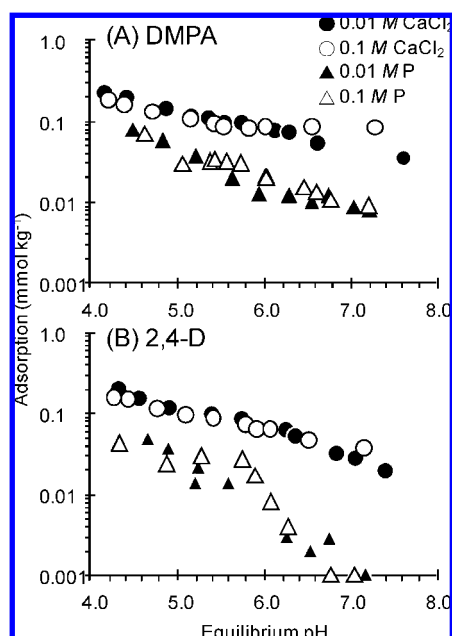
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Figure 4. Effects of CaCl$_2$ (●, 0.01 M; ○, 0.1 M) and P (▲, 0.01 M; △, 0.1 M) concentrations on the amount of (**A**) DMPA and (**B**) 2,4-D adsorption on the untreated UG5 soil as a function of equilibrium pH: reaction time, 4 h; initial DMPA and 2,4-D concentrations, 20 μM (5.0 mg L^{-1}) and 20 μM (4.4 mg L^{-1}), respectively; amount of soil, 50 g L^{-1} (oven-dry basis). Had the soil adsorbed all DMPA and 2,4-D in this experiment, the amount of DMPA and 2,4-D adsorption would have reached 0.4 mmol kg^{-1}, respectively.

Table 3. Results of the Analysis of Covariance (ANCOVA) for the Effects of CaCl$_2$ and Phosphate Concentrations on the Amount of DMPA and 2,4-D Adsorption on the Untreated UG5 Soil as a Function of Equilibrium pH[a]

chemical	estimated intercept	standard error
DMPA	0.1293	0.0672
2,4-D	−0.0763	0.1802

[a] Prior to performing the ANCOVA, logarithmic transformation was performed.

surface hydroxyls are amphoteric, and a net positive charge develops at equilibrium pH values below the point of zero charge. In the ligand-exchange reaction, active surface hydroxyl groups on metal (hydr)oxides or metal−humate complexes may be replaced by carboxyl groups from DMPA, forming a strong coordination bond between the metal and DMPA. It is well-known that active surface hydroxyls can adsorb organic acids and phosphate by means of a ligand-exchange reaction (*38*) and that phosphate considerably inhibits the adsorption of organic acids on the surface of metal (hydr)oxides (*39–41*).

To clarify whether the ion-exchange reaction or the ligand-exchange reaction plays the dominant role in DMPA adsorption, the adsorption of DMPA on untreated UG5 soil was compared with that in the presence of 10 times higher concentration of Cl$^-$ and in the presence of phosphate (**Figure 4**). **Table 3** shows the estimated intercept by the ANCOVA. The adsorption of DMPA in the presence of 0.01 M CaCl$_2$ was essentially the same (influence of concentration: $p = 0.5570$) as that in the presence of 0.1 M CaCl$_2$, but it was markedly decreased ($p < 0.001$) in the presence of 0.01 and 0.1 M phosphate. If the DMPA adsorption was controlled by the ion-exchange reaction, it should be inhibited not only by the presence of phosphate but also by the presence of Cl$^-$. The highly selective adsorption of DMPA compared with Cl$^-$ cannot be explained in terms of
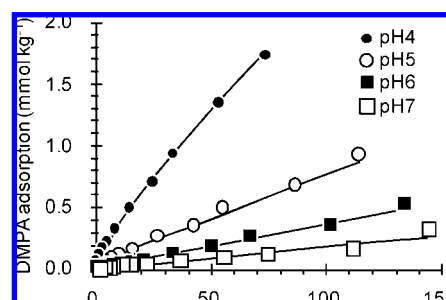

Figure 5. Adsorption isotherms of DMPA on the untreated UG5 soil: amount of soil, 50 g L^{-1} (oven-dry basis); background electrolyte, 0.01 M CaCl$_2$; reaction time, 4 h. To describe the DMPA adsorption isotherm, first, a relationship between DMPA adsorption and equilibrium pH was drawn at each initial DMPA concentration (six to seven plots between pH 3.5 and 7.5), and then DMPA adsorption at pH 4.0 (●), 5.0 (○), 6.0 (■), and 7.0 (□) at each initial DMPA concentration was read from the relationship and plotted.
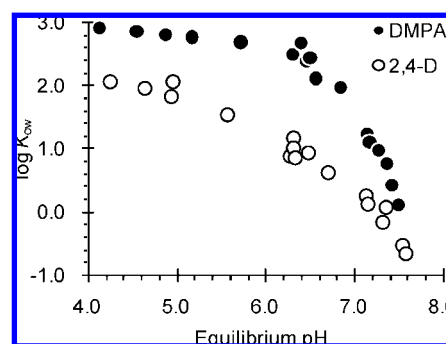

Figure 6. log K_{ow} of DMPA (●) and 2,4-D (○) as a function of equilibrium pH of the aqueous phase: reaction time, 24 h; volume of 1-octanol phase and water phase, 30 and 30 mL, respectively; amount of DMPA and 2,4-D, 20 μM (5.0 mg L^{-1}) and 20 μM (4.4 mg L^{-1}), respectively.

the ion-exchange reaction, but it can be explained in terms of the ligand-exchange reaction. These adsorption phenomena of DMPA were almost the same as those of 2,4-D, in which its adsorption reaction has been reported to be controlled by a ligand-exchange reaction.

The amount of DMPA adsorbed on untreated UG5 soil (**Figure 5**) was similar in magunitude to that of 2,4-D (*14*). On the other hand, the amount of phosphate adsorbed (*22*) was 100 times that of DMPA or 2,4-D. Therefore, the adsorption of DMPA and 2,4-D may be decreased by the presence of phosphate as a result of competition between phosphate and the phenoxyacetic acid herbicides for adsorption sites of the surface of the metal (hydr)oxides. From these results described above, we conclude that the ligand-exchange reaction on metal (hydr)oxides is the dominant mechanism for the adsorption of DMPA and 2,4-D on untreated UG5 soil.

Figure 4 shows that, even in the presence of excess phosphate, small amounts of DMPA and 2,4-D are still adsorbed, particularly at equilibrium pH values below 5. This phenomenon could be partly explained in terms of the hydrophobic interactions. The values of the octanol–water partition coefficient (log K_{ow}) of DMPA as a function of the equilibrium pH increased with decreasing equilibrium pH value, and they were greater than the corresponding values for of 2,4-D (**Figure 6**). This hydrophobic phenomenon provides an explanation for the adsorption of DMPA and 2,4-D in the presence of P. The amount of DMPA adsorbed (**Figure 4A**, ▲ and △) was greater ($p < 0.001$) than that of 2,4-D (**Figure 4B**, ▲ and △), particularly in the range of low equilibrium pH values. This
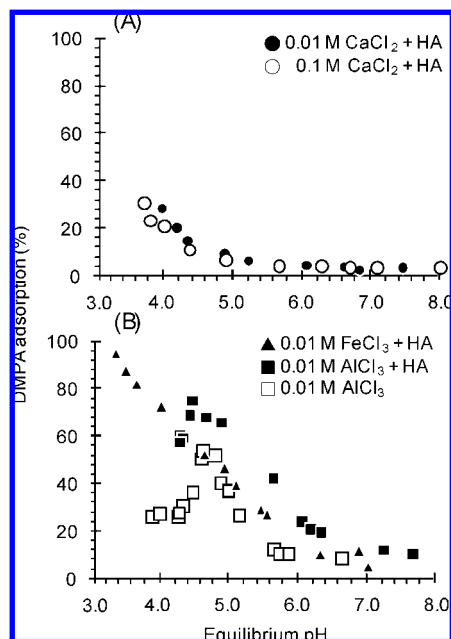
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Figure 7. Comparison of DMPA adsorption ability among metal−humate complexes: (**A**) humic acid was complexed in the presence of 0.01 M CaCl$_2$ (●) and 0.1 M CaCl$_2$ (○); (**B**) humic acid was complexed in the presence of 0.01 M FeCl$_3$ (▲) and 0.01 M AlCl$_3$ (■), and aluminum hydroxide (0.01 M AlCl$_3$) was precipitated by adding NaOH in the absence of HA (□). Reaction time was 4 h; initial DMPA concentration was 20 μM (5.0 mg L^{-1}); humic acid added was 2.0 mg; Al or Fe added was 50 μmol; and Ca added was 50 or 500 μmol.

suggests that the hydrophobic interactions between these herbicides and the untreated UG5 soil play a minor role in the adsorption reactions of herbicides, particularly at low equilibrium pH values.

Role of Soil Organic Matter in DMPA Adsorption. As described above, the active surface hydroxyl group was identified as the dominant site for DMPA adsorption in untreated UG5 soil. However, it has been reported that SOM enhances the adsorption of phenoxyacetic acid herbicides (*17, 35, 37, 42, 43*). We therefore conducted additional experiments on the adsorption of DMPA on purified H$^+$ humic acid prepared from the untreated UG5 soil. In general, Japanese Andosols accumulate large amounts of SOM in their thick surface horizons [usually up to 50 g of C kg^{-1} and 150 g of C kg^{-1} in extreme cases (*19, 20*)]. These accumulations are in the form of Al− and Fe−SOM complexes, and more than half of the SOM is typically composed of humic acid (*19*). We therefore assumed that the prepared H$^+$ humic acid was representative of the SOM of the untreated UG5 soil. The ash content of the H$^+$ humic acid was 0.64% (*26*), suggesting that the amounts of Al and Fe in the humic acid were very low. The H$^+$ humic acid was soluble in water under weakly acidic conditions and required the presence of polycations (e.g., Ca^{2+}, Al^{3+}, or Fe^{3+}) for it to separate as a precipitate (metal−humate complex). Thus, interactions between the humic acid and DMPA were investigated in the presence of excess polycations, so that the negative charge on the carboxylic group of SOM would be canceled by the polycations, and the humic acid could be separated as precipitates.

The adsorption of DMPA on calcium−humate complexes (**Figure 7A**, ● and ○) was very limited at equilibrium pH values between 5 and 8, suggesting that the purified humic acid did not contain forms of Al and Fe that were active for DMPA adsorption and that hydrophobic interactions between the

calcium−humate complexes and DMPA were very weak in this equilibrium pH range. At equilibrium pH values below 5, more DMPA adsorption was observed on calcium−humate complexes. This would be caused by the hydrophobic interactions as described earlier.

On the other hand, a significant amount of DMPA was adsorbed on the iron−humate (**Figure 7B**, ▲) and aluminum−humate complexes (**Figure 7B**, ■). This observation revealed the importance of active surface hydroxyl groups on Al and Fe complexed with humic acid in DMPA adsorption. In this experimental system, 8.14 μmol of COOH groups on the humic acid and 50 μmol of Al or Fe were present. Therefore, part of the Al and Fe could not react with the humic acid, and precipitates of aluminum and rion hydroxides were formed. However, the adsorption of DMPA on 50 μmol of Al in the form of aluminum hydroxide was significantly increased by the addition of the humic acid (**Figure 7B**, ■ and □). This may be because the humic acid inhibited the polymerization of Al (and Fe) by a complexation reaction, and adsorption sites on Al (and Fe) could be kept available for the adsorption of DMPA. Similar effects of SOM on the adsorption of phosphate have been reported (*22, 44*).

In the case of the aluminum−humate complexes, the maximum level of DMPA adsorption occurred at an equilibrium pH value of about 4.3. At equilibrium pH of 4.3, Al could be present as an aluminum−humate complex and as aluminum hydroxide, and the active surface hydroxyls on Al could act as exchangeable ligands for DMPA adsorption. Below an equilibrium pH of 4.3, the aluminum−humate complex and aluminum hydroxides would be dissolved, releasing Al as ions and resulting in a decrease in DMPA adsorption. In the case of the iron−humate complex, the adsorption of DMPA increased with a decrease in equilibrium pH. We hypothesize that little Fe^{3+} was released from the iron−humate complex and that because of the high stability of the complex, dissolution of iron hydroxide did not occur in this equilibrium pH range.

As described above, DMPA molecules were adsorbed on the UG5 Andosol by the ligand-exchange reaction in which active surface hydroxyls associated with metal (hydr)oxides were replaced by the carboxyl group of DMPA. Under the conditions of our experiments, the amounts of DMPA on SOM and humic acid were both small. We hypothesized that, in the presence of iron or aluminum hydroxides, humic acid increased DMPA adsorption by preventing polymerization of the metal hydroxides and thus preserving more active surface hydroxyl groups capable of adsorbing DMPA through a complexation reaction.

The adsorption phenomenon and mechanism of adsorption of DMPA on metal−humate complexes are similar to those of 2,4-D (*14*). However, the amount of DMPA adsorbed was higher than that of 2,4-D, especially on the calcium−humate complex at equilibrium pH values below 5. This difference could be caused by the higher log K_{ow} value of DMPA compared with 2,4-D. The adsorption of DMPA on calcium−humate complex/ SOM at equilibrium pH values below 5 would then be partly due to hydrophobic interactions between the hydrophobic moieties of DMPA and the hydrophobic moieties of calcium− humate complex/SOM, although the principal mechanism of adsorption of DMPA on untreated UG5 Andosol remains the ligand-exchange reaction.

Conclusions. The mechanisms for adsorption of DMPA on an Andosol were studied. Although the SOM content of the Andosol was very high (71.9 g kg^{-1}), the major mechanism of adsorption of DMPA on the Andosol was the ligand-exchange reaction between the carboxylic group of DMPA and active

surface hydroxyls on metal (hydr)oxides, as in the case of 2,4-D. The mechanisms of adsorption of DMPA were the same as those for 2,4-D. At lower equilibrium pH values below 5, hydrophobic interactions between the hydrophobic moieties of DMPA and the hydrophobic constituents of the Andosol contribute to the adsorption of DMPA, although the major adsorption mechanism remains the ligand-exchange reaction. Because the octanol–water partition coefficient (log K_{ow}) of DMPA is greater than that of 2,4-D, the adsorption resulting from hydrophobic interactions would be greater in DMPA than in 2,4-D because DMPA has a higher hydrophobicity of DMPA than 2,4-D.

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