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# 2,4-D Sorption in Iron Oxide-Rich Soils: Role of Soil Phosphate and Exchangeable Al

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This study examined herbicide retention in iron oxide-rich variable charge soils (Ultisols) under no cultivation (forest), agriculture (farm), and turf maintenance (golf course) to explore the following hypothesis: inorganic phosphate accumulation from soil fertilization and liming to decrease exchangeable aluminum (Al) content will influence carboxylic acid herbicide sorption onto soils and leaching into groundwater. A suite of soil properties, including mineralogy (particularly soil iron and aluminum oxide content), exchangeable Al content, and soil phosphate content, influenced sorption of the anionic, 2,4-D. In general, 2,4-D sorption was lower in the presence of phosphate, possibly due to competition between phosphate and 2,4-D for surface sites or increase in surface negative charge resulting from phosphate sorption. Additionally, 2,4-D sorption was greater in the presence of exchangeable Al. It appears that 2,4-D may form surface complexes with or be electrostatically attracted to exchangeable aluminum in the soil. Our results suggest that carboxylic acid herbicides may be more easily leached in intensively managed Ultisols subject to continued phosphate fertilization and liming.

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## Introduction

Herbicides and phosphate (in fertilizers) currently receive much attention globally with regard to their potential to negatively impact soil and groundwater quality (*1*, *2*). Both herbicides and phosphate are commonly applied to soils since they are often necessary to optimize crop growth in many different land uses including agriculture and turf management. However, little is known about how their simultaneous interaction with soil may affect their respective environmental fates. The few studies that exist on phosphate−herbicide competition with regard to environmental fate have focused on a small number of herbicides such as glyphosate (*3*) and still fewer have focused on Ultisols, a prominent soil order of the tropics, subtropics, and the southeastern United States characterized as acidic variable charge soils with high contents of iron oxides and low activity clays (e.g., kaolinite).

Several studies focusing on phosphate dynamics in highly weathered soils such as Oxisols and Ultisols have demonstrated that these fine-textured highly weathered variable charge soils have a substantial capacity for phosphate retention (*4*−*6*). Furthermore, the phosphate retention capacity in these soils is strongly influenced by the presence of soil aluminum and iron oxides, calcium carbonates, and 1:1 clay aluminosilicates (such as kaolinite) with the metal oxides affording a higher sorption capacity than the clay minerals. Studies of organic ligands or dissolved organic matter have shown that such ligands complex aluminum and iron oxides by mechanisms similar to those described for phosphate, effectively compete for sorption sites, and decrease the extent of phosphate retention on soil surfaces (*7*−*11*). On the basis of these studies, we propose that perhaps a similar competition may occur in systems where phosphate is present with carboxylic acid herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D), the subject of this study.

2,4-D sorption is known to be pH-dependent and to occur via specific and nonspecific electrostatic attraction of the 2,4-D anion to positively charged surface sites; in addition, complexation to surficial Fe and Al via the carboxylate group has also been suggested (*12*−*14*). Nevertheless, available knowledge of the influence of soil phosphorus on 2,4-D sorption is limited. A few studies have shown that 2,4-D sorption onto lepidocrocite and goethite is decreased in the presence of adsorbed phosphate (*15*). Additional systematic research exploring this competition in whole soils, particularly with respect to soils under different management practices, is warranted.

Beyond phosphate application, other land management practices, particularly the liming regime, may also affect the environmental fates of carboxylic acid herbicides. In Ultisols, exchangeable Al often dominates exchange sites and controls soil acidity and buffering capacity (*16*), resulting in heavy reliance on liming practices to optimize soil acidity/fertility for plant growth. Liming agents (e.g., $CaCO_3$, CaO, CaOH, and others) are added to increase soil pH to a range optimal for the intended crop, to reduce exchangeable acidity, and to remove $Al^{3+}$ from solution (*16*). In a few studies, soil exchangeable acidity, which is largely comprised of exchangeable Al and/or extractable aluminum oxides, has been found to correlate with the extent of 2,4-D sorption (*17*−*20*) and the sorption of other anionic herbicides such as glyphosate (*21*). Some research on Al-coated clays has shown that Al may also play a significant role in the sorption of 2,4-D (*12*). The nature of the role of exchangeable Al in 2,4-D sorption was not specifically elucidated in any of the above studies. Also, Al and carboxylic acids form stable complexes in solution: stability constants are in the general ranges of 1.1−2.38 for monocarboxylates (e.g., acetate, ethyl acetate), 2.94−5.32 for dicarboxylates (e.g., malate, phthalate), and 5.32−7.98 for tricarboxylates (e.g., citrate) (*22*, *23*). This raises the possibility that complexation of carboxylic acids to surface-bound exchangeable Al may also occur. Knowledge of 2,4-D−exchangeable Al interactions will help in understanding how liming to reduce exchangeable Al could also influence carboxylic acid herbicide retention, a relatively unexplored possibility.

Here, we test the hypothesis that inorganic phosphate accumulation from soil fertilization and liming to reduce exchangeable aluminum will influence the nature and extent of carboxylic acid herbicide sorption onto soils and leaching into groundwater, whereas nonionic herbicides such as alachlor (also the subject of this study) will be unaffected by soil phosphate and exchangeable Al. This study specifically addresses (i) the nature of and competition between herbicide and phosphate sorption in Ultisols as a function of soil composition, mineralogy, and P content and (ii) the role of exchangeable Al on the extent of carboxylic herbicide sorption.

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**TABLE 1. Selected Soil Properties of Farm, Forest and Golf Course Soils**

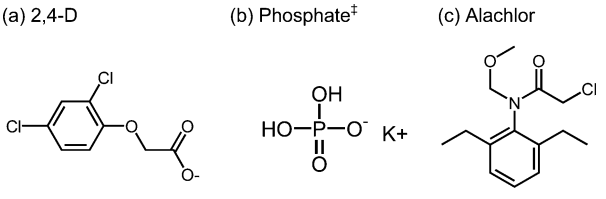
| soil label | sample depth (cm) | horizon | textural class | sand (%) | silt (%) | clay (%) | surface area ($m^2$/g) | $pH_w$ |
|---|---|---|---|---|---|---|---|---|
| farm[a] A | 0−30 | A | clay | 18.3 ± 0.9 | 40.0 ± 0.6 | 41.7 ± 0.8 | 25.2 ± 0.9 | 5.73 ± 0.04 f[d] |
| farm B1 | 30−56 | B | clay | 18.1 ± 1.0 | 35.9 ± 0.9 | 46.0 ± 0.3 | 31.1 ± 1.0 | 6.14 ± 0.16 g |
| farm B2 | 56−80 | B | clay | 19.0 ± 0.8 | 38.5 ± 0.9 | 42.5 ± 0.6 | 31.1 ± 0.7 | 4.71 ± 0.02 c |
| forest[b] A | 0−30 | A | silty loam | 15.9 ± 5.1 | 59.5 ± 5.4 | 24.6 ± 0.5 | 14.6 ± 0.2 | 4.77 ± 0.03 c |
| forest B1 | 43−69 | B | clay | 7.0 ± 1.0 | 39.8 ± 1.7 | 53.3 ± 0.9 | 36.2 ± 0.8 | 5.13 ± 0.01 d |
| forest B2 | 69−94 | B | clay | 3.8 ± 1.1 | 36.3 ± 1.1 | 59.9 ± 0.3 | 44.7 ± 1.1 | 5.04 ± 0.06 d |
| golf[c] A | 0−30 | A | clay loam | 21.8 ± 3.4 | 41.2 ± 7.8 | 37.0 ± 4.4 | 21.4 ± 0.9 | 5.45 ± 0.04 e |
| golf B1 | 30−56 | B | silty clay | 15.9 ± 0.7 | 43.2 ± 1.0 | 40.9 ± 0.3 | 23.4 ± 0.5 | 4.48 ± 0.07 b |
| golf B2 | 56−80 | B | silty loam | 25.3 ± 0.2 | 54.5 ± 0.7 | 20.2 ± 0.8 | 18.6 ± 1.5 | 4.05 ± 0.01 a |

[a] From a field in North Durham, NC; no-till corn/winter wheat rotation; periodically limed and fertilized with N, P, and K. [b] From Gate 11, Duke Forest, NC; no record of N, P, and K fertilization or liming. [c] From fairway of Willodale Golf Course in Durham, NC; routinely mowed; periodic N and K fertilization; has not been limed or P fertilized in 5 yr; liming and P history prior to 5 yr is unknown. [d] Values followed by the same letter are not significantly different at $\alpha = 0.05$ by Fisher test.

**TABLE 2. Selected Soil Properties of Na- and Al-Saturated B2 Horizons of Farm, Forest, and Golf Course Soils**

| soil label | original soil | $pH_w$ | surface area ($m^2$/g) | exchangeable cation (mmol/kg) | ECEC ($cmol_c$/kg) | DCBFe (mmol/kg) | DCBAl (mmol/kg) | AAOFe (mmol/kg) | AAOAl (mmol/kg) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **Na-Saturated Soils** | | | | | |
| Na farm B2 | farm B2 | 5.67 | 32.12 | 38.70 ± 0.55 | 3.87 ± 0.05 | 732 ± 9 | 122 ± 3 | 20.1 ± 0.6 | 28.9 ± 1.0 |
| Na forest B2 | forest B2[a] | 5.30 | 44.51 | 51.24 ± 3.15 | 5.12 ± 0.31 | 984 ± 6 | 186 ± 0 | 27.0 ± 0.3 | 49.9 ± 0.6 |
| Na golf B2 | golf B2 | 5.66 | 17.35 | 38.70 ± 1.48 | 3.87 ± 0.15 | 202 ± 14 | 37 ± 1 | 6.5 ± 0.3 | 15.2 ± 0.3 |
| | | | | **Al-Saturated Soils** | | | | | |
| Al farm B2 | farm B2 | 3.50 | 33.57 | 13.57 ± 0.30 | 4.07 ± 0.09 | 713 ± 10 | 115 ± 3 | 19.2 ± 0.4 | 30.6 ± 0.3 |
| Al forest B2 | forest B2[a] | 3.47 | 47.23 | 15.54 ± 0.48 | 4.66 ± 0.14 | 960 ± 12 | 177 ± 2 | 25.6 ± 1.8 | 50.3 ± 5.1 |
| Al golf B2 | golf B2 | 3.42 | 19.22 | 13.26 ± 1.55 | 3.98 ± 0.47 | 212 ± 8 | 37 ± 3 | 6.5 ± 0.3 | 17.7 ± 1.5 |

[a] DCBAl, DCBFe, AAOAl, and AAOFe values for the Na- and Al-saturated forest soils alone were higher than the values for the originial forest soils. We attribute this to the use of a different ICP-MS for the Fe/Al analyses of the original forest soils.




‡Three forms of phosphate, $H_3PO_4$, $KH_2PO_4$ and equimolar solution of $KH_2PO_4/K_2HPO_4$, were screened for use as the inorganic phosphate source. Under our experimental conditions, $KH_2PO_4$ had the smallest effect on soil pH (+/- 0.25 pH units) and was hence selected as the inorganic phosphate source for subsequent sorption experiments.

**FIGURE 1. Chemical structures of the test solutes.**

## Methodology

**Solutes and Soils.** 2,4-D (2,4-dichlorophenoxyacetic acid; Aldrich), the test carboxylic acid herbicide, has a $pK_a$ of 2.5−2.7 (*24*) and is predominantly anionic above pH 3.5 (Figure 1). Alachlor (2-chloro-2′,6′-diethyl-*N*-(methoxymethyl)acetanilide; Chemservice), the test nonionic (neutral) herbicide, does not have a carboxylate functionality or other groups capable of interacting with surficial Fe and Al atoms. Additionally, the absence of charge in alachlor precludes its electrostatic interaction with charged surfaces.

Three Ultisols of the Georgeville series (fine, kaolinitic, and Typic Kanhapludults), each representing distinct land uses (farm, forest, and golf course) and hence distinct P fertilization and liming histories, were obtained from the North Carolina Piedmont in the United States. All soils had no prior history of 2,4-D or alachlor application. A total of nine unaltered soil samples (3 depth samples from each site) were used in this study; labels assigned to the soil samples, sampling depth, and fertilization/use histories are listed in Table 1. All soil samples were air-dried, passed through a 2-mm sieve, and stored in sealed plastic containers at room temperature. Subsamples were oven dried at 105 °C prior to use for all studies except where indicated.

To evaluate the role of exchangeable soil cations on 2,4-D sorption, samples of the lowermost horizons from each land use (forest B2, farm B2, golf B2) were saturated with either Na or Al as follows: 75 g of oven-dried soil was placed in a 250-mL centrifuge bottle, 150 mL of either 3 M NaCl or 1 M $AlCl_3$ was added, and soils were gently shaken on an end-over-end shaker for 0.5 h. The low pH of both the 1 M $AlCl_3$ solution (pH ∼1.7) and the 1 M $AlCl_3$−soil slurries (pH 1.8−2.0) precluded the precipitation of additional aluminum oxide phases. Significant surface dissolution is not expected because of the short contact times. Furthermore, solution speciation calculations (MINEQL+, Version 4.5) for a 1 M $AlCl_3$ solution at pH 2 denoted $Al^{3+}$ as the dominant species and the absence of aluminum oxide precipitates. Soils were then centrifuged at 2200 rpm for 20 min, the supernatant was discarded, and the saturation-wash was repeated two more times. Soils were then washed in a likewise manner with deionized (DI) water until the conductivity of the supernatant reached a final value of ∼30−50 $\mu$S/cm (0.0003−0.0005 dS $cm^{-1}$) and did not decrease further. Washed soils were transferred to lyophilization flasks, frozen, and lyophilized to dryness. Labels assigned to the Na- and Al-saturated soils are listed in Table 2.

**Soil Characterization.** Characterization of the nine unaltered soil samples was conducted using standard methods described by Sparks (*25*) and Carter (*26*). Soil characteristics measured included $pH_w$, $N_2$BET surface area (Micromeretics Gemini 2360 surface area analyzer), anion-exchange capacity (AEC), organic carbon (OC), soil texture, operationally defined "free" or crystalline aluminum and iron oxides (DCBAl, DCBFe), operationally defined poorly or noncrystalline (or amorphous) aluminum and iron oxides (AAOAl, AAOFe), and maximum orthophosphate sorption

capacity ($P_{max}$). Methods for the above analyses have been previously described (*13*).

Effective cation-exchange capacity (ECEC) at the pH of the soil was determined by summation of exchangeable cations (Al, Ca, K, Mg, Mn, and Na) compulsively exchanged with 0.1 M $BaCl_2$; individual concentration of exchangeable cations calculated from the same exchange procedure are denoted as ExAl, ExCa, ExMg, and ExK. We note a possible overestimation of ECEC values because the summation of charge contributions from the exchanged cations by convention (*25*) assumed a +3 charge for all Al species, and the presence of other hydrolysis and polymerization species of lower charge was not accounted for. DCBAl and AAOAl values have been corrected to exclude ExAl, which is expected to be extracted under both methods. We note that $pH_w$, $N_2$BET surface area, ECEC, AEC, DCBFe, DCBAl, AAOFe, and AAOAl values were measured previously (*13*) for the forest soils alone.

Total P and total S were determined by nitric−perchloric digestion, sorbed sulfate from an extraction with 500 mg of P $L^{-1}$ as $KH_2PO_4$. Additional indices of available soil phosphate included Mehlich III phosphate extracted by 0.2 M $CH_3COOH$, 0.25 M $NH_4NO_3$, 0.015 M $NH_4F$, 0.013 M $HNO_3$, and 0.001 M EDTA and readily desorbable phosphate (RDP) extracted by 0.01 M $CaCl_2$ (*25*). Henceforth, measures of Mehlich III phosphate and RDP will be used to operationally denote "extractable soil phosphate" and to loosely serve as an indicator of the intensity of P fertilization over years of cultivation.

Phosphate concentrations in the RDP and Mehlich III phosphate extractions and $P_{max}$ experiments were analyzed using a modified molybdate blue method (*27*, *28*). Total P was determined by automated molybdate blue method (Lachat QuikChem 8000). Sulfate concentrations were determined using ion chromatography (Dionex DX-120 IC, AS14A 4.6 × 250 mm column, 8 mM $NaHCO_3$:1 mM $Na_2CO_3$). All other elemental analyses conducted in this study were determined by inductively coupled plasma-mass spectrometry (Perkin-Elmer model 2000 DV ICP optical emission spectrometer).

For the prepared Na- and Al-saturated soil, exchangeable Na and Al in the soils was extracted with 0.1 M $BaCl_2$ as described above, and Na or Al concentration in the extract was determined by atomic absorption spectroscopy (Perkin-Elmer 5100PC). Selected soil properties measured, as described above, included AAOAl, AAOFe, DCBAl, DCBFe, $pH_w$, ECEC, and $N_2$BET surface area.

**Sorption Experiments.** All experiments used 15-mL polypropylene centrifuge tubes as batch reactors, which were determined through preliminary experiments to have negligible effects on test compound concentrations. For this research, biotic processes were not intentionally inhibited by sterilization in order to preserve soil mineralogy and surface properties.

*Single-Solute Batch Sorption Experiments.* Soil was first preequilibrated by shaking end-over-end overnight with DI water. Soil−solution loadings were selected to facilitate analytical detection of loss from solution and approximately normalize all slurries on the basis of surface area (i.e., lower loadings were used for soils with higher surface area: 100 g/L for forest B1, forest B2, farm B1, farm B2; 200 g/L for farm A and all golf soils (A, B1, and B2); and 300 g/L for forest A soil). Following preequilibration, an aliquot of the test compound was added to achieve a final volume of 10 mL and the desired test compound concentration (0.045 mM for 2,4-D, 0.037 mM for alachlor and 9.69 mM P as $KH_2PO_4$). The reactors were shaken end-over-end for the desired time (0, 1, 6, 24, 48, and 144 h) after which slurry pH was measured, samples were filtered through 0.2-$\mu$m polycarbonate membranes, and solute concentrations in the filtrate were determined as described below (see Determination of Solute Concentration). Separate reactors were used for each time point because preliminary experiments showed that continued sampling from the same reactor resulted in a considerable change in soil−solution ratio. Soil pH was not altered in these experiments.

A separate experiment was conducted on forest A, farm A, and golf course A soils to evaluate the effect of initial and final slurry pH on the extent of 2,4-D sorption. Soil was preequilibrated with 9 mL of DI water overnight, after which the slurry was adjusted to desired pH (∼4, 5, or 6) by microliter additions of HCl or NaOH and equilibrated 3 h. The pH adjustment−3-h equilibration was repeated followed by a final pH adjustment and 15-min equilibration. At this point, the slurry pH was recorded as the "initial" experimental pH. 2,4-D stock solution was then added to the reactor to achieve an initial concentration of 0.045 mM and equilibrated for 48 h after which the "final" slurry pH was measured. The soil slurry was filtered as described above, and 2,4-D concentration in the filtrate was analyzed.

2,4-D sorption onto Na- and Al-saturated B2 horizon soils (forest B2, farm B2, and golf B2) was evaluated at two initial pH values (3.5 and 4.5) using the same general methodology described above with a few modifications. Adjustments to pH were achieved with microliter aliquots of 0.1−3 M HCl or 0.1−1 M NaOH, and all additions were recorded. Where necessary, the pH of the Al-saturated soils was modified only slightly with HCl in the lower pH experiments targeted at pH 3.5; NaOH was not added. Generally, pH adjustments altered ionic strength by <0.0006 M. Preliminary sorption experiments comparing 2,4-D sorption in a background matrix of either water or 0.001 M NaCl showed that ionic strength differences in this range minimally influenced sorption (data not shown). The target initial pH values were not precisely achieved due to the buffering capacity of the soil; final pH values in the "lower" pH experiments ranged from ∼3.6 to 4.4, and those in the "higher" pH experiments from ∼4.5 to 4.9. Here, 2,4-D sorption was measured at a single time point after 48 h of equilibration.

Every sorption experiment was replicated three times and included triplicate blanks (reactors containing no soil), which were treated and measured in the same manner as soil-containing reactors. The compound concentration in the blank solution served as the initial concentration. The concentration sorbed to soil was calculated from mass balance by subtracting the concentration recovered in the supernatant of a soil-containing reactor from the initial (blank) concentration.

*Double-Solute Batch Sorption Experiments.* Double-solute batch studies were used to evaluate herbicide−phosphate competition in the A horizon soils (forest A, farm A, and golf A). Soil−solution loading and reactor volume were the same as for the single-solute batch studies. Soils were preequilibrated in 8 mL of 0, 2.02, or 12.11 mM P (as $KH_2PO_4$) for 24 h, after which a 2-mL aliquot of herbicide stock solution was added to achieve final 2,4-D concentrations of 0.23 and 0.45 mM; an alachlor concentration of 0.09 mM; or final phosphate concentration of 0, 1.62, or 9.69 mM. Samples were shaken for 48 h after which pH was measured and samples were filtered and analyzed as described below for 2,4-D, alachlor, and phosphate.

*Determination of Solute Concentration.* Herbicides were analyzed by HPLC with diode array detection (DAD) (Hewlett-Packard series 1100) at 1 mL/min flow rate. 2,4-D was separated on a Zorbax SBC8 5 $\mu$m 15 cm × 0.46 cm column with matching guard column using a 65% methanol:35% 0.006 M phosphate buffer at pH 2.2 and detected at 236 nm. Alachlor was separated on a Zorbax XDBC18 5 $\mu$m column (25 cm × 0.46 cm) with matching guard column using a mobile phase of 77% acetonitrile:23% DI water and detected at 205 nm. For single-solute experiments, phosphate was analyzed

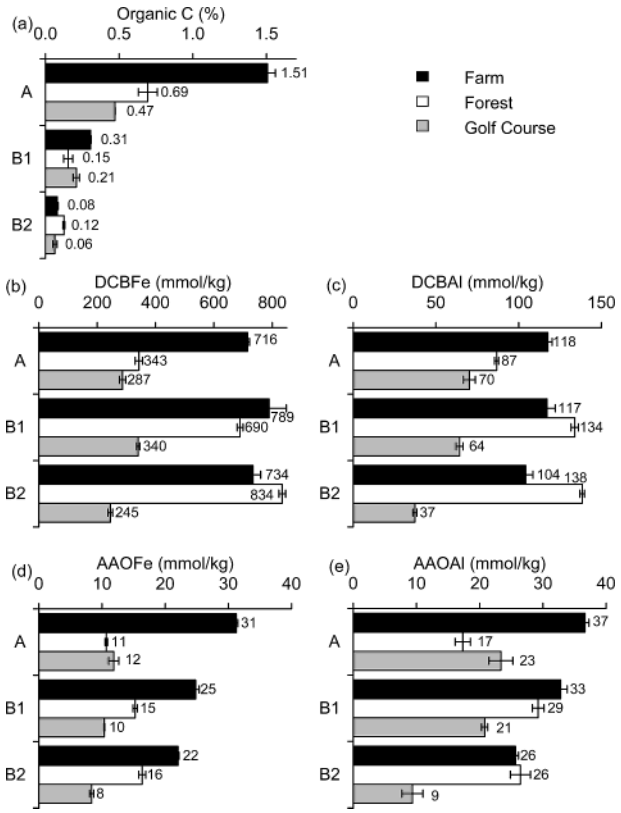



**FIGURE 2. (a) Organic carbon, (b) Fe in crystalline oxides (DCBFe), (c) Al in crystalline oxides (DCBAl), (d) Fe in amorphous oxides (AAOFe), and (e) Al in amorphous oxides (AAOAl) as a function of depth in the farm, forest, and golf course soils.**

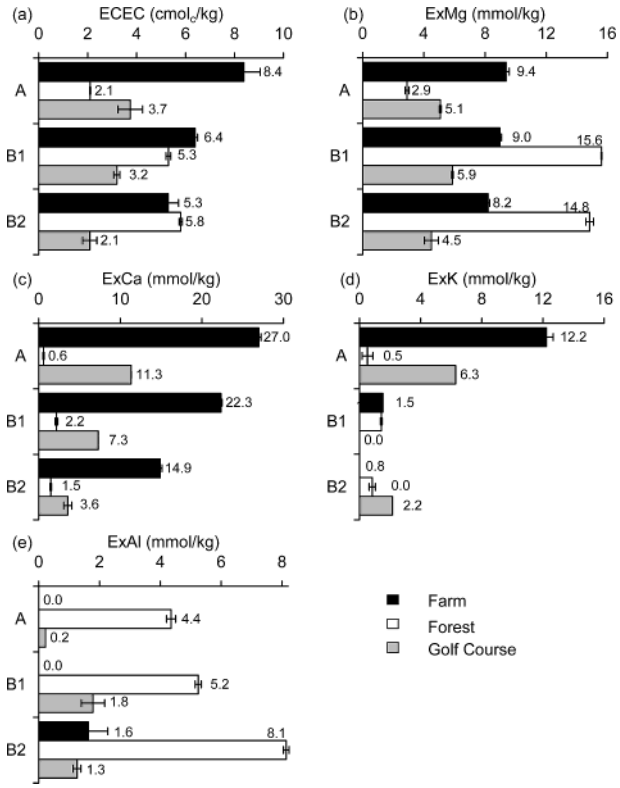



**FIGURE 3. (a) Effective cation-exchange capacity (ECEC), (b) exchangeable Mg, (c) exchangeable Ca, (d) exchangeable K, and (e) exchangeable Al contents as a function of depth in the farm, forest, and golf course soils.**

colorimetrically by a modified molybdate blue method (as previously described), while for double-solute studies phosphate was analyzed by ion chromatography as described above.

## Results

**Comparison of Soil Properties of Unaltered Soils.** The forest, farm, and golf course profiles all exhibited soil properties characteristic of their soil order (Ultisols) and series (Georgeville) (*29*, *30*). All soil samples were generally acidic, heavy textured soils with high clay and iron oxide contents (Table 1, Figure 2). Fe in the crystalline oxide phase (DCBFe) dominated the mineralogy of all soils (245−834 mmol/kg), followed by Al in the crystalline oxide phase (DCB Al) (37−138 mmol/kg) (Figure 2b,c). Fe and Al present as amorphous oxide phases (AAOFe and AAOAl, respectively) were also important constituents of these soils (8−37 mmol/kg) (Figure 2d,e).

As detailed below, differences in soil composition and properties across the three land uses (farm, forest, and golf course) and within each soil profile (A and B horizons) were likely related to the distinct land management histories. Forest soil closely matches a typical Georgeville description and represents a profile that was relatively undisturbed as evidenced from the increase in fine texture, surface area, iron and aluminum oxide content, ECEC, and AEC with depth (Table 1, Figures 2 and 3). Furthermore, the low ExCa, ExK, P, and phosphate contents and high ExAl content throughout the soil profile were typical of a vegetated, unfertilized soil system in which most of the nutrients have either been taken up by biota or leached from the upper horizons (Figures 3 and 4).

In contrast, the farm and golf soils profiles reflected disturbance from tillage and golf course construction and operation, respectively. Surface area and texture were relatively uniform through the farm and golf soil profiles and soil iron and aluminum oxide contents were either relatively uniform or showed a slight decrease along the profile, suggesting that land management may have disrupted distinction between horizons (Table 1, Figure 2). The higher ExCa, ExK, P, and phosphate contents and the lower ExAl contents, particularly in A horizons, emphasized repeated fertilization and liming of the farm and golf soils (Figures 3 and 4). In direct contrast, total S and adsorbed sulfate increased with depth in the farm and golf soils (Figure 4). This may have been a result of phosphate application causing mobilization of soil sulfate from the upper A horizons and an accumulation in the lower B horizons, another signature of continued fertilization.

The characteristics of the farm soils, particularly the farm A horizon, were notably different from the other soils examined and reflected agricultural management. The farm A horizon possessed the highest OC, ECEC, and total P of all soil horizons in this study (Figures 2a, 3a, and 4b). Specifically, farm soils possessed higher total P than forest and golf course soils of comparable depth (Figure 4b). Much like total P content, extractable soil phosphate (Mehlich III phosphate and RDP) was the greatest for farm A horizon followed by golf and forest A soils, whereas all B horizons had little to no extractable soil phosphate.

**Properties of Na- and Al-Saturated Soil Matrixes.** Analysis of the properties of Na- and Al-saturated soil matrixes helps discern the extent to which the saturation procedures altered the original soil matrixes. The surface areas of the Na- and Al-saturated soil matrixes were relatively similar (within $\pm 0.19-2.5$ m$^2$/g) to those of the original soils from which they were prepared (Tables 1 and 2), suggesting that high surface area oxides were not formed or lost in the preparation of the saturated soils. Likewise, the ECEC, AAOAl, AAOFe,

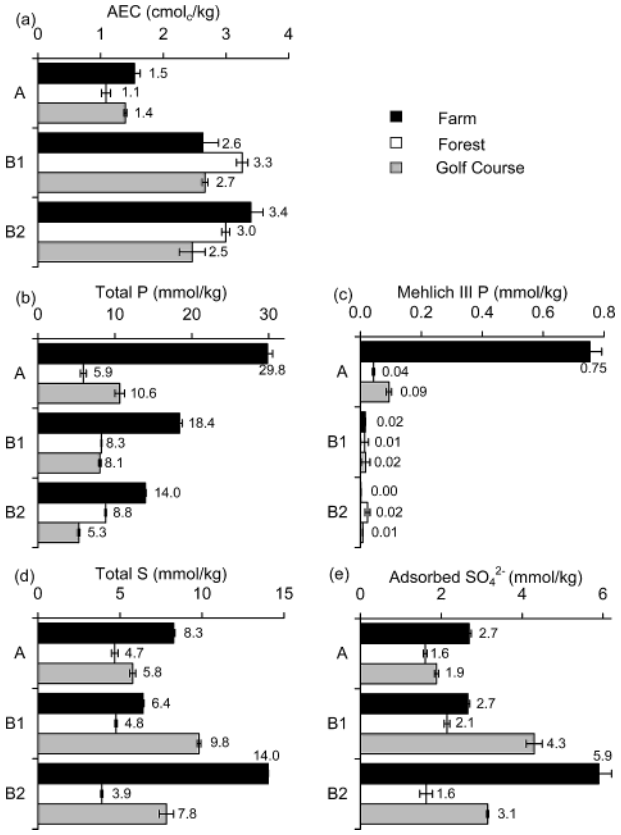
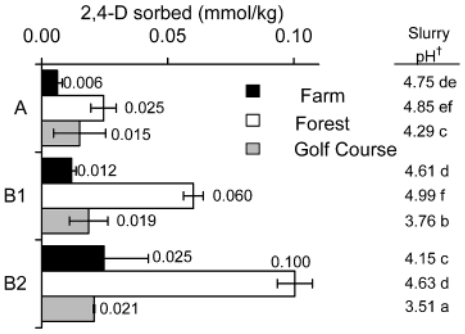



**FIGURE 4. (a) Anion-exchange capacity (AEC), (b) total P, (c) Mehlich III phosphate, (d) total S, and (e) adsorbed sulfate values as a function of depth in farm, forest, and golf course soils.**

DCBAl, and DCBFe values of the Na- and Al-saturated soil derived from the same unaltered soil (e.g., Na farm B2 and Al farm B2) were relatively similar to each other. Furthermore, the exchangeable Na content of a Na-saturated soil was approximately three times the exchangeable Al content of the comparable Al-saturated soil, in keeping with the +1 charge of Na, the +3 charge of Al, and the $pH_w$ of the soils (Table 2).

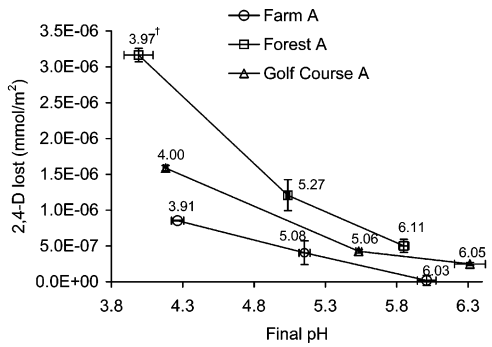
Soil $pH_w$ values, however, were significantly altered in comparison to the original soils: $pH_w$ values of the Na-exchanged soils were generally higher ($pH_w$: 5.3−5.7), whereas the $pH_w$ values of the Al-exchanged soils were substantially lower ($pH_w$ ~3.5) (Tables 1 and 2). We acknowledge that the saturation procedures may result in the creation of soils with significantly different properties than the original soils from which they were prepared. Nevertheless, the above characterization shows the similarity in the reactive mineral component of the Na- and Al-saturated matrixes and thus justifies comparison of sorption behavior within the two altered soils.

**Single-Solute Sorption.** *Sorption to Unaltered Soil Matrixes.* Analysis of 2,4-D, alachlor, and phosphate concentrations as a function of time did not reveal a significant change in the extent of sorption following 24−48 h of equilibration (data not shown). Comparisons of solute sorption are henceforth based on the "extent of sorption measured at 48 h at soil pH" (Figures 5 and 6). This index for comparing test compound sorption was selected because our previous work (*13*) on Georgeville soils conducted under similar experimental conditions has shown that sorption at an initial 2,4-D concentration of 0.045 mM (used in this study) falls well within the linear range of the sorption isotherm. This index is employed for comparisons within and across soils but is not intended to serve as an indicator of sorption capacity or a sorption constant.




†Measured following 48 h equilibration with 2,4-D; Values followed by the same letter are not significantly different at α=0.05 by Fisher test.

**FIGURE 5. Sorption of 0.045 mM 2,4-D as a function of depth in farm, forest, and golf course soils.**




† Labels indicate initial pH values; average difference between initial and final pH is ± 0.21 pH units.

**FIGURE 6. Sorption of 0.045 mM 2,4-D as a function of pH in farm, forest, and golf course A horizons.**

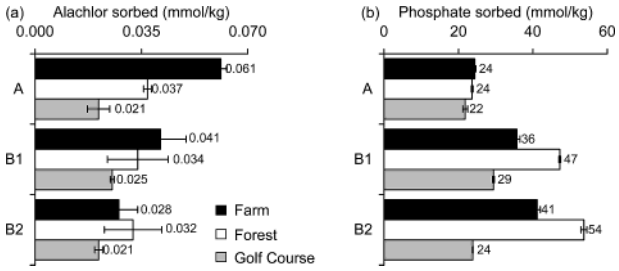
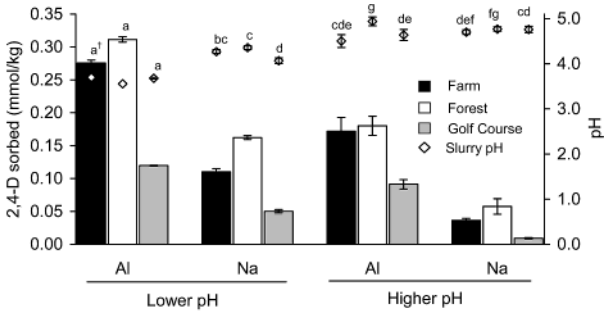



**FIGURE 7. Sorption of (a) 0.036 mM alachlor and (b) 9.69 mM phosphate as a function of depth in farm, forest, and golf course soils.**

Within the forest soil profile, the extent of 2,4-D sorption at soil pH markedly increased with depth from 0.025 mmol/kg in A horizon to 0.1 mmol/kg in B2 horizon. In all horizons of the farm and golf soils, 2,4-D sorption was low to negligible, and a sorption depth trend was not discerned (Figure 5). These same trends were preserved even when differences in surface area were accounted for (data not shown). For forest, farm, and golf A horizon soils, 2,4-D sorption decreased with increase in pH (initial or final) (Figure 6); however, differences in 2,4-D sorption across soils was preserved: forest A > golf course A > farm A. Hence, differences in 2,4-D sorption across land use observed at soil pH (Figure 5) may not be attributed to differences in soil pH alone.

Distinctly different trends were observed for alachlor sorption within and across the soil profiles: sorption within the farm soil profile showed a discernible decrease with soil depth, whereas an obvious depth trend was not noted in the forest and golf course profiles (Figure 7a). The extent of alachlor sorption (0.02−0.06 mmol/kg) was significantly lower than 2,4-D sorption in all soils.




†For pH, points followed by the same letter are not significantly different at α=0.05 by Fisher test.

**FIGURE 8. Sorption of 0.045 mM 2,4-D in Na- and Al-saturated B2 horizons of farm, forest, and golf course soils in the "lower" and "higher" pH experiments.**

Phosphate sorption increased with soil depth within the farm and forest soil profiles, and sorption did not appear to vary significantly with depth in the golf soils (Figure 7b). Although the extent of sorption was generally similar in the three A horizons (22−24 mmol/kg), sorption in the farm and forest B horizons (36−45 mmol/kg) was greater than in the golf B horizons (24−29 mmol/kg).

*Sorption to Na- and Al-Saturated Soils.* As expected, the extent of 2,4-D sorption onto a particular soil at lower pH (3.6−4.4) was generally greater than at higher pH (4.5−4.9) (Figure 8). In both pH ranges, 2,4-D sorption onto Al-saturated farm, forest, and golf soils was distinctly greater than sorption onto the Na-saturated counterparts. This result (increase sorption in Al-saturated soils) is unambiguous in the higher pH range because the pH values of all six slurries were not statistically different (see ANOVA results, Figure 8). In the lower pH range, the pH values of the Na-saturated matrixes were slightly higher than those of the Al-saturated soils; therefore, the greater extent of sorption on the Al-saturated soils may be partly due to the lower pH of these slurries (Figure 8).

**Double-Solute Sorption Studies.** Herbicide−phosphate competition was examined only on the A horizon unaltered soil matrixes because the A horizons directly receive solutes from fertilization and herbicide application. The addition of phosphate clearly decreased 2,4-D sorption in the forest and golf soils (Figure 9a). At a low initial 2,4-D concentration (0.23 mM), increasing initial phosphate to 1.61 mM (low phosphate) and 9.69 mM (high phosphate) significantly reduced 2,4-D sorption in forest A by 28% and 81%, respectively, as compared to treatments where no phosphate was added (Figure 9a,b). A similar effect was also observed at high initial 2,4-D (0.45 mM). Likewise, in the golf A soils, a significant decrease in sorption (by 77−80%) did occur with increase in phosphate concentration at high initial 2,4-D concentration (0.45 mM) where 2,4-D sorption in absence of phosphate was significant (Figure 9b). In systems with negligible 2,4-D sorption (less than 5% loss from solution) in the absence of phosphate (such as golf A soil at low initial 2,4-D concentration and farm A at both low and high initial 2,4-D), the effect of additional phosphate could not be reliably detected. Apparently, the effect of phosphate addition is less evident in the farm A soil under our experimental conditions.

An effect of phosphate on alachlor sorption is not discerned in any of the soils (data not shown). Furthermore, under all experimental conditions the extent of phosphate sorption was relatively unchanged in the presence of 2,4-D (data not shown).

## Discussion

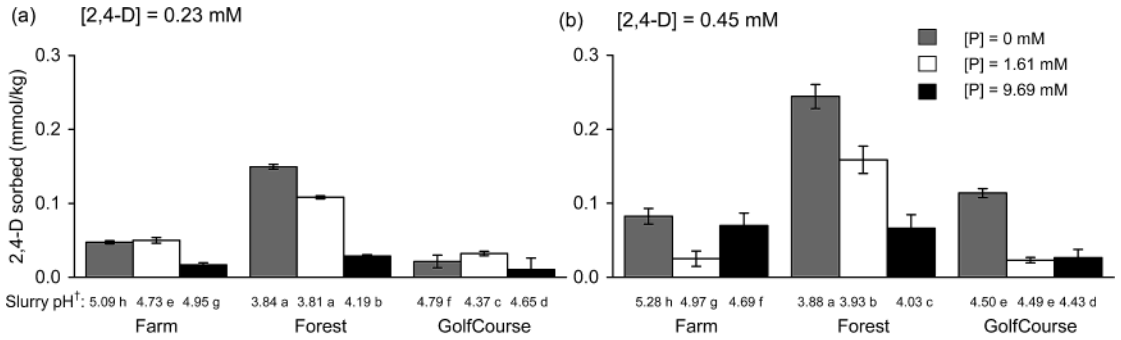
Characteristics describing the reactive mineral component of soil, particularly iron and aluminum oxide contents, are known to strongly influence the extent of carboxylic acid herbicide sorption onto forest Ultisols with low organic carbon contents (<0.75%) and no known history of previous liming or fertilization with phosphate (*13*). In line with these findings, the observed increase in 2,4-D sorption with depth in the forest soil profile followed the depth trends for surface area, soil crystalline and amorphous iron and aluminum oxide contents, exchangeable Al content, and AEC within this profile (Table 1, Figures 2 and 3).

In contrast, but consistent with the distinctly unique properties of the farm soil profile, 2,4-D sorption onto farm soils was not in line with the above-mentioned trends. Sorption onto the farm A soil was significantly lower than onto forest A soil (Figures 5 and 6) despite the farm A soil possessing a higher surface area, iron and aluminum oxide, and organic carbon contents. Also farm A, forest B1, and forest B2 soils possessed relatively similar iron and aluminum oxide, soil P, and OC contents (Figure 2, Table 1); however, the farm A soil showed significantly lower 2,4-D sorption. Notably, the observed differences in 2,4-D sorption in the three A soils at soil pH (Figure 5) is maintained in studies conducted across a range of pH values (Figure 6); therefore, we can exclude the possibility that differences discerned at soil pH are simply due to differences system pH. Farm A soil, the most intensively managed of all soils investigated, received the greatest agrochemical input (phosphate fertilizer and lime) and had the greatest OC content, possibly a result of crop residues. Also ECEC, ExCa, ExK, total P, RDP, and Mehlich III phosphate were highest in farm A soil, and exchangeable Al was notably the lowest. None of these soil characteristics appear to favor 2,4-D sorption.

Three hypotheses are proposed to rationalize the differences in 2,4-D sorption across the soils: (i) high extractable soil phosphate suppressed 2,4-D sorption; (ii) high exchangeable Al content resulted in greater sorption of 2,4-D; and (iii) organic matter coatings on soil surfaces blocked potential sites of 2,4-D sorption and caused repulsion of the anionic 2,4-D.

The role of soil OC in 2,4-D sorption onto our test soils was unclear whereas the role of OC in alachlor sorption was evident since the greatest sorption occurred in farm A with the highest OC content (Figure 7). Noticeably, 2,4-D and alachlor interacted with Ultisols by distinct sorption mechanisms. The low 2,4-D sorption onto farm A soil could be attributed to either high phosphate, low ExAl, higher OC content, or a combination of all three factors. We are able to test the influence of soil phosphate and ExAl content (below); however, the operational manner in which many soil characteristics must be measured does not permit us to determine the nature of organic matter coatings on soil surfaces and the likely influence on sorption phenomena. Furthermore, the low OC content (<0.7%) of the forest and golf A soils precluded us from garnering additional evidence regarding the role of organic matter. Therefore, the third hypothesis regarding the role of organic matter coatings could not be conclusively confirmed or rejected based on evidence from this study.

The first hypothesis regarding the role of soil phosphate was confirmed based on the results of the double solute experiments. In the presence of both 2,4-D and phosphate, forest and golf course soils (characterized by lower extractable phosphate than farm soils) showed a dramatic decrease in 2,4-D sorption (by 73−77%) as the concentration of phosphate added to the slurry was increased from 0 to 9.69 mM P (Figure 9). We propose that the effect of added phosphate on 2,4-D sorption was not discerned in the farm A soil possibly because the high extractable soil phosphate was already sufficient to suppress 2,4-D sorption (yielding less 5% loss from solution) and therefore obscured the effect of additional phosphate. Indeed, this suggestion is in line with added




†Slurry pH values: values followed by the same letter are not significantly different at $\alpha$=0.05 by Fisher test.

**FIGURE 9. Sorption of (a) 0.23 mM 2,4-D and (b) 0.45 mM 2,4-D in the presence of phosphate in farm, forest, and golf course A horizons.**

phosphate inhibiting 2,4-D sorption in the forest and golf soils, which possessed low to negligible extractable phosphate contents.

Unlike 2,4-D, alachlor sorption did not appear to be influenced by soil phosphate: high soil phosphate in farm A soil did not suppress alachlor sorption, and increasing added phosphate concentrations in the double-solute experiments did not reduce the extent of sorption. Since both phosphate and carboxylate anions bind surficial Fe and Al atoms and are electrostatically attracted to positively charged sites, phosphate can suppress 2,4-D by binding to surface sites that may otherwise be accessible to 2,4-D and by modifying surface characteristics (e.g., increase surface negative charge) such that 2,4-D sorption is inhibited. Alachlor, which does not possess a carboxylate moiety or negative charge, is unaffected by phosphate.

Several lines of evidence point to the possible role of exchangeable Al in 2,4-D sorption, our second hypothesis. 2,4-D sorption was significantly higher in the forest B horizons (B1 and B2) than the farm B horizons (Figure 5) despite both subsoils possessing similar iron and aluminum oxide contents (Figure 2). Since subsoils from both B horizons possessed similarly low total P, extractable phosphate, and OC contents (Figures 2 and 4), the role of phosphate or organic matter in suppressing 2,4-D sorption can be excluded. We propose that the higher exchangeable Al in forest B horizons (Figure 3) facilitated 2,4-D sorption and that the absence of exchangeable Al in Farm B horizons limited sorption. Seemingly, adsorbed sulfate could have also suppressed 2,4-D sorption by blocking surface sites; however, the large difference in 2,4-D sorption in soils with similar adsorbed sulfate values (farm and forest B1 soils) refutes this possibility.

Single-solute experiments conducted on Na- and Al-saturated soil matrixes provide additional support: a significantly higher extent of 2,4-D sorption was observed in Al-saturated soils as compared with Na-saturated soils. Also, sorption of 2,4-D onto unaltered farm B2 soil was significantly lower (by 75%) than sorption onto unaltered forest B2 soil (Figure 5), whereas 2,4-D sorption onto Al-farm B2 (0.17 mmol/kg) and Al-forest B2 (0.18 mmol/kg) were comparable in the higher pH condition and sorption on the Al-farm B2 was only slightly lower (by 12%) than onto Al-forest B2 in the lower pH condition (Figure 8). We offer that 2,4-D interaction with exchangeable Al ions may play an defining role in determining the extent of sorption: sorption was low in farm B soils despite the high iron and aluminum oxide contents because of these horizons' low exchangeable Al. We hypothesize that 2,4-D may form surface complexes with exchangeable Al ions (possibly via a cation bridging mechanism involving an exchangeable Al ion and the carboxylate group of 2,4-D) or be electrostatically attracted to the positively charged exchangeable Al ion. Spectroscopic evidence is required to propose a mechanism of interaction. Several studies have shown significant 2,4-D sorption onto pure phase iron and aluminum oxides (*13*, *31*, *32*) in systems without exchangeable Al. Additionally, previous studies (*17*−*19*) have noted the possible role of exchangeable acidity in 2,4-D sorption, and several studies have emphasized the importance of specific electrostatic attraction of 2,4-D to positively charged surface sites in soils and pure phase minerals (*12*, *13*). Here, we have employed Al-saturated soil matrixes and identified that surface-bound exchangeable Al ions in soils may constitute an important source of sites for 2,4-D sorption. Therefore, our results suggest that exchangeable Al content plays a similarly prominent role as soil iron and aluminum oxide content in determining the extent of 2,4-D sorption in acidic Ultisols or other soils that have net negative charge and where surface-bound exchangeable Al ions provide an important source of positively charged sites.

Previous work in anion sorption (*4*−*11*) has clearly shown that multiple soil properties, including surface area, aluminum and iron oxide content, OC content, and pH define the nature and extent of sorption. Here, we offer that soil phosphate and exchangeable Al content are additional properties that play a significant role in the sorption of carboxylic acid herbicides. Our findings indicate that liming to reduce soil acidity and fertilizer P inputs are likely to enhance the leachability of 2,4-D in Ultisols. Therefore, accurate prediction of the fates of 2,4-D and possibly other carboxylic acid herbicides should consider land-use history and previous management practices, particularly those that influence extractable phosphate and exchangeable Al content. Studies on other soil types will be needed to extrapolate our finding to other soil orders and soil management practices.

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