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**INFLUENCE OF PHOSPHORUS ON THE MOBILIZATION  
AND ATTENUATION OF IONOGENIC HERBICIDES IN NC PIEDMONT  
SOILS: IMPLICATIONS FOR WATER QUALITY**

By  
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## ABSTRACT

This study examined 2,4-D and alachlor retention dynamics in NC Piedmont Ultisols (Georgeville series) under no-cultivation (forest), agriculture (farm), and turf maintenance (golf course). Research was designed to test the following hypotheses: inorganic phosphate accumulation from soil fertilization and liming to reduce exchangeable aluminum (Al) will influence the nature and extent of carboxylic acid herbicide sorption onto soils and leaching into groundwater. Following extensive characterization of soil properties, single and double solute batch sorption experiments were conducted with 2,4-D/alachlor (0-0.45 mM) and phosphate (0-9.69 mM) and the extent of sorption onto unaltered soil matrices and Na and Al saturated soils was quantified. A suite of soil properties, including mineralogy (particularly soil iron and aluminum (Al) oxide content), exchangeable Al content, and soil phosphate content, influenced the sorption of anionic herbicide, 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 and/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 sorb to soil by a cation bridging mechanism involving an exchangeable Al ion and the carboxylate group of 2,4-D. Sorption of the non-ionic alachlor was unaffected by soil P or phosphate and only influenced by soil organic carbon content. Our results suggest that anionic herbicides may be more easily leached in intensively managed NC Ultisols subject to continued phosphate fertilization and liming.

**(Key words:** phosphate, herbicides, sorption, leaching, competition, fertilization, land use, exchangeable Al, 2,4-D, alachlor, Ultisol, iron oxide, variable charge soils)

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## SUMMARY AND CONCLUSIONS

The influence of land use and management on nutrient and herbicide dynamics, and ultimately their environmental fates, evolves out of a complex web of effects of soil type, method, timing and type of agrochemical application, tillage and cropping practices, land management history, and many other factors. Understanding how land management may impact nutrient and herbicide losses, however, is essential to protect ground and surface water, which are vital resources for a large population in the North Carolina Piedmont. Because it is not possible to study simultaneously the effects of all of the factors associated with land use, we have focused on how two management practices (phosphate fertilization and liming) influence selected soil properties that in turn determine herbicide sorption and leaching. This research compares the sorption of and competition between phosphate and two common herbicides, 2,4-D and alachlor, in A and B horizons of North Carolina Piedmont soils from three land uses of increasing management intensity: Forest, Golf Course (turf) and Farm (no-till continuous corn). In order to specifically probe the role of exchangeable Al, 2,4-D sorption was compared between soils altered by saturation with either Al or Na.

For all land uses investigated, soils were generally typical of North Carolina Piedmont Ultisols of the Georgeville series. Generally, all were fine-textured, high surface area (14.6-44.7 m<sup>2</sup>/g) silt loam to clay soils, with high Fe and Al oxide contents, low organic matter content (0.06-1.5%), pH ranging from 4.05-6.14, and significant AEC despite overall net negative charge. Exchangeable Al, exchangeable Ca, exchangeable K, pH, organic matter content, total phosphorus (P) and extractable phosphate, and ECEC were the soil properties most affected by land use, and (with a few exceptions) all of them generally increased with increasing management intensity (Forest < Golf Course < Farm) for a given horizon, with the notable exception of exchangeable Al, which followed the opposite trend. These trends are congruent with the expected effects of lime and fertilizer inputs. Furthermore, the Forest soil profiles exhibited distinct horizonation, particularly between A and B horizons, whereas disturbance from tillage and golf course construction and operation seemed to have disrupted the horizonation in the Farm and Golf Course profiles.

Single solute sorption studies probed the specific effects of soil properties and land use on sorption of 2,4-D, alachlor and phosphate, and were used to speculate differences in sorption mechanisms between the solutes. Not surprisingly, sorption of 2,4-D (anionic) and alachlor (neutral) correlated to different soil properties. Sorption of 2,4-D was strongly related to exchangeable Al and surface area for all land uses and horizons and, in Forest and Golf Course horizons, was also related to Fe and Al oxide contents. When compared across land use, 2,4-D sorption was greatly suppressed with increasing management intensity (Farm < Golf Course << Forest). Possible causes for the reduced retention capacity for 2,4-D in intensively managed Farm soils could include saturation of sorption sites by residual fertilizer phosphate, blockage of sites by organic matter coatings on soil particles, the loss of exchangeable Al from liming, and changes in soil particle charge due to liming or sorbed phosphate, or increased pH from liming. In comparison of 2,4-D sorption onto Na and Al saturated soils, 2,4-D sorption onto Al saturated soils was 2-2.5 times greater at pH 3.6-4.4 and 3-10 times greater at pH 4.5-4.9 than onto Na saturated soils. This clearly demonstrated that exchangeable Al can play a dominant role in 2,4-D sorption, possibly through a cation bridging mechanism involving the -COO group of 2,4-D.

In contrast, alachlor sorption was greatest in the Farm soils (Farm > Forest > Golf Course), and for Farm and Forest profiles sorption was greatest in the A horizons. Alachlor sorption was most highly correlated with organic carbon and appeared to be unrelated to soil mineralogy. In this case, land management did not seem to enhance leachability of this herbicide.

Phosphate sorption (under our single solute experimental conditions) was strongly correlated to surface area, AEC, Fe and Al oxide content, as well as exchangeable Al. Phosphate sorption increased with depth for all land uses, was similar across land use in the A horizons, but in the B horizons was greatest in the Forest soil (e.g., Forest B1 > Farm B1 > Golf Course B1). Evidence from this study suggested that leaching of phosphate through the subsoil is unlikely at this time, although the current phosphate status of the soils may affect the leachability of other organic (and inorganic) anions.

Sorption studies with phosphate and either 2,4-D or alachlor investigated the ability of phosphate to compete with herbicides for sorption in A horizons. There was no evidence of competition between phosphate and alachlor. Between 2,4-D and phosphate, however, competition was clearly evident across all land uses, with phosphate apparently being the stronger competitor. With few exceptions, increasing phosphate from 0-9.69 mM decreased 2,4-D sorption. When compared to 2,4-D sorption with no phosphate added, 2,4-D sorption at the highest initial phosphate level (9.69 mM) was reduced by up to 80.7% (Forest A) at initial 2,4-D of 0.23 mM, and up to 76.5% (Golf Course A) at initial 2,4-D of 0.45 mM. The effects of phosphate on 2,4-D sorption were most pronounced in the Forest soil. These results corroborate the findings of the single solute studies that residual soil phosphate from fertilization has the potential to significantly limit 2,4-D retention in soils.

Sorption of the two herbicides correlated with distinctly different soil properties: alachlor sorption related to organic carbon content suggesting that partitioning into organic matter may be a dominant mechanism, whereas 2,4-D sorption correlated with properties describing soil mineralogy such as surface area, Fe and Al oxides, AEC, and, most significantly, exchangeable Al. Mechanisms involved in 2,4-D retention are likely to include both electrostatics and coordination with exchangeable Al through a cation bridge. Therefore, liming to reduce soil acidity, a common practice in cultivated soils, may enhance leachability of 2,4-D. Additionally, phosphate competed strongly with 2,4-D for sorption and residual phosphate from fertilizer in Farm and Golf soils appeared to restrict 2,4-D sorption, both results indicating that fertilizer P inputs are likely to alter the leachability of 2,4-D in North Carolina Ultisols. In contrast to 2,4-D, alachlor was more strongly retained in the A horizons of the more intensively managed systems suggesting that fertilizer and lime inputs do not promote losses of alachlor through the soil profile. These findings strongly suggest that accurate prediction of 2,4-D and possibly other anionic herbicides fates should consider land use history and previous management practices, particularly those that influence soil extractable phosphate and exchangeable Al.

## RECOMMENDATIONS

Our results demonstrate that the non-ionic pesticide alachlor and the anionic pesticide 2,4-D interact with Ultisols of the NC Piedmont via distinct sorption mechanisms governed by different soil properties. In NC Ultisols, differences in land management practice, particularly liming and fertilizer inputs, may affect leachability of 2,4-D but not necessarily alachlor. Neither residual phosphate from fertilization, added phosphate nor reduced exchangeable Al content, decreased retention of alachlor in these soils. The diminished sorption of 2,4-D observed in both agricultural and golf course soils compared to an unamended forest soil was likely a combined effect of both liming and P fertilization. We suggest that residual phosphate from continual fertilizer inputs sorbed to soil surfaces reducing available sites for 2,4-D and subsequently elevates leachability of 2,4-D in these soils. Although this study specifically addressed phosphate and 2,4-D retention in Ultisols, sorption of 2,4-D and other anionic herbicides may also be reduced by additional inorganic anions common in fertilizers, such as sulfate. Also, since liming causes a decrease in the exchangeable Al content of the soil, we suggest that liming can translate into a decreased capacity for 2,4-D sorption via cation bridging and increased leaching of 2,4-D.

Soil characteristics commonly used to estimate leaching potential (e.g., texture, organic matter, pH) appear to be suitable for non-ionic alachlor, but were not sufficient to describe anionic 2,4-D sorption. Here, we have presented evidence that 2,4-D sorption is favored in the presence of soil Fe and Al oxides and exchangeable Al ions but hindered by sorbed phosphate and organic matter coatings on the soil surface. It is imperative that predictive models of anionic herbicide leaching potential account for the capacity of soil Fe and Al oxides and exchangeable Al ions to promote anionic herbicide sorption and the inhibitory effect of residual soil phosphate and organic matter coating on sorption.

## 1. INTRODUCTION

Herbicides and phosphate in fertilizers currently receive much attention in North Carolina and globally with regard to their potential to negatively impact soil and groundwater quality (Pierzynski et al., 2000; U.S. Geological Survey, 1999). Both herbicides and phosphate are commonly applied to soils since they are often necessary for plant growth in many different land uses including agriculture and turf management (e.g., for Golf courses), economically important operations for North Carolina. However, little is known about how their simultaneous interactions in soil may affect their respective environmental fates. The few studies that exist on phosphate-herbicide competition with regard to environmental fate have focused on only a few pesticides such as glyphosate (de Jonge et al., 2001) and still fewer have focused on the large constituent of soils of the North Carolina Piedmont called “red clays,” acidic Ultisols with variable charge, high iron-oxide contents, and low activity clays (e.g., kaolinite). Conversely, extensive research has been conducted on the sorption of phosphate and individual herbicides as single solutes in soil systems, as well as on competition between phosphate and other inorganic ions (e.g., sulfate, arsenate), small organic ligands (e.g., oxalate, citrate). Lui et al., 1999 (phosphate, sulfate, and oxalate); Geelhoed et al., 1997 (phosphate and sulfate); Nilsson et al., 1996 (o-phthalate and phosphate); Violante and Gianfreda, 1993 (phosphate and oxalate); Zhao and Stanforth, 2001 (phosphate and arsenate); Geelhoed et al., 1998 (phosphate and citrate)].

As a single solute, phosphate and its fate in soils have been examined in a wide variety of soil systems (Bolland and Allen, 1998; Harris et al., 1996; Indiaty and Sharpley, 1997; Morris et al., 1992; Nanzyo, 1987; Pierzynski et al., 2000; Sanchez and Uehara, 1980. ) and mechanisms of phosphate retention in soils are relatively well understood. Several studies focusing on phosphate dynamics in highly weathered soils, such as Oxisols and Ultisols, similar to North Carolina “red clay” soils, have demonstrated that fine-textured highly weathered variable charge soils have a substantial capacity for phosphate retention (Linguist et al., 1997; Linguist et al., 1997; Owusubenoah et al., 1997; Sharpley et al., 1989). Furthermore, the phosphate retention capacity in these soils is strongly influenced by the presence of soil Al and Fe oxides, Ca carbonates, and 1:1 clay aluminosilicates (such as kaolinite) with the metal oxides possessing a higher sorption capacity than the clay minerals. Studies on molecular interactions of phosphate with pure phase metal oxides and clays have shown that phosphate ions adsorb to Fe/Al oxide surfaces via electrostatic interaction and ligand exchange with surface bound  $\text{OH}^-$  and/or  $\text{OH}_2^+$  groups, and that similar exchange reactions also occur on the edge sites of kaolinite clay minerals (Dimirkou and Theodoropoulou, 1996; Hingston et al., 1967; Nagarajah et al., 1970; Parfitt and Atkinson, 1976; Parfitt et al., 1977; Saha et al., 1998; Tejedor-Tejedor and Anderson, 1990).

Anions such as sulfate, arsenate, selenite, and small organic ligands (such as oxalate, citrate, malate and others) as well as some fractions of dissolved organic matter have been shown to compete with phosphate for sorption onto soil or oxide surfaces (e.g., (Fontes et al., 1991; Kaiser and Zech, 1996; Ohno and Crannell, 1996; Ohno and Erich, 1997; Sibanda and Young, 1986). Studies of organic ligands or dissolved organic matter have shown that such ligands complex Al and Fe oxides by mechanisms similar to those described for phosphate and also effectively compete for sorption sites and decrease the extent of phosphate retention on soil surfaces (Bhatti et al., 1998; Cajuste et al., 1996; Hingston et al., 1971; Kaiser and Zech, 1998; Nagarajah et al., 1970; Ohno and Crannell, 1996; Yang et al., 1994). These studies suggest that perhaps a similar

competition may occur in systems where phosphate is present with anionic herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D), the subject of this study.

In this research, 2,4-D was selected as the herbicide competitor because of its high usage (4<sup>th</sup> highest usage in the U.S.) and because it is among the 21 most detected compounds in streams and groundwater (Barbash et al., 1999). The retention and mineralization of 2,4-D in agricultural and managed turf/Golf course soils have been the subject of several investigations (Ryals et al., 1998; Sannino et al., 1997; Smith and Bridges, 1995; Smith and Tillotson, 1993; Willems et al., 1996), however, our knowledge of the influence of soil phosphorus (P) on 2,4-D sorption is limited. A single study by (Madrid and Diaz-Barrientos, 1991) on the competitive effect of phosphate on the adsorption of 2,4-D at low pH (3.0) onto lepidocrocite, a pure phase Fe oxyhydroxide, showed a decrease in 2,4-D sorption in the presence of adsorbed phosphate. To our knowledge, no additional research exploring this competition in whole soils exists to confirm whether or not a similar interaction may play a role in soils under different management practices with these agrochemicals.

Land management practice may also affect the competition between and environmental fates of phosphate and anionic herbicides. Specific factors involved may include not only the rates of P fertilization and herbicide application but also liming regime. In Ultisols, exchangeable Al often dominates exchange sites and controls soil acidity and buffering capacity (Sposito, 1989), resulting in heavy reliance on liming practices in order to optimize soil acidity/fertility for plant growth. Liming agents (e.g., CaCO<sub>3</sub>, CaO, CaOH, and others) are added to increase soil pH to a range optimal for the intended crop, reduce exchangeable acidity, and remove Al<sup>3+</sup> from solution (Sposito, 1989). Consequently, liming practices significantly alter the exchangeable Al content of the soils.

In a few studies, soil exchangeable acidity, which is largely comprised of exchangeable Al, and/or extractable Al oxides in most soils, has been found to correlate with the extent 2,4-D sorption (Dubus et al., 2001; Johnson and Sims, 1993; Johnson and Sims, 1998) and other herbicides such as glyphosate (Piccolo et al., 1994). Some research on Al-coated clays has shown that Al may also play a significant role in the sorption of 2,4-D (Sannino et al., 1999; Sannino et al., 1997). Recent research in our laboratory established that soil Fe and Al oxides strongly influence the retention of the carboxylic acid herbicides 2,4-D and quinmerac in NC Ultisols (Vasudevan et al., 2002) and suggested the potential influence of exchangeable Al on 2,4-D sorption (Vasudevan and Cooper, 2002). 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, ethylacetate), 2.94-5.32 for dicarboxylates (e.g., malate, phthalate), and 5.32-7.98 for tricarboxylates (e.g., citrate) (Martell, 2001; Nordstrom and May, 1989. ). This raises the possibility that complexation of carboxylic acids to surface bound exchangeable Al may occur. Knowledge of 2,4-D-exchangeable Al interactions will help understand how liming to reduce exchangeable Al could also influence anionic herbicide retention, a relatively unexplored possibility.

## **2. PROJECT HYPOTHESIS AND OBJECTIVES**

Research was designed to test the following hypotheses: 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. The objectives of this study were to understand the (i) competition between herbicide and phosphate sorption in NC 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.

### 3. METHODOLOGY

#### 3.1. Solutes

Three test solutes (Figure 1) were used in this study. 2,4-D (2,4-dichlorophenoxyacetic acid, Aldrich) was used as the test carboxylic acid herbicide; it has a  $pK_a$  of 2.5 (Wauchope et al., 1992) and is therefore predominantly anionic above pH 3.5. Alachlor (2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide, Chemservice) was used as the test non-ionic herbicide; it does not have a carboxylic acid group or other groups capable of interacting with surficial Fe and Al atom. Furthermore, it is non-ionic or neutral and hence an electrostatic interaction with charged surfaces is precluded. Three forms of phosphate,  $H_3PO_4$ ,  $KH_2PO_4$  and equimolar solution of  $KH_2PO_4/K_2HPO_4$  were screened in preliminary sorption experiments for use as inorganic phosphate source. Of the three forms evaluated,  $KH_2PO_4$  had the smallest effect on soil pH (the difference between the pH of a 200-300 g/L slurry containing no phosphate and slurries containing 50 mg P/L as  $KH_2PO_4$  was only  $\pm 0.25$  pH units) and was hence selected as the inorganic phosphate source for subsequent sorption experiments.

#### 3.2. Soils

Three Ultisols of Georgeville series (fine, kaolinitic, Typic Kanhapludults), each representing distinct land uses (Farm, Forest, Golf course) and hence distinct phosphorus (P) fertilization and liming histories were obtained from the NC Piedmont. All soils had no prior history of 2,4-D or alachlor application. Forest soil was obtained from a freshly dug pit located near gate 11 in the Duke Forest at depths of 0-30, 43-69, and 69-94 cm; these soils have no record of N, P, and K fertilization or liming. Farm (agricultural) soil was sampled at depths of 0-30.5, 30.5-50, and 56-80 cm from a field in north Durham, NC, which was under no-till corn/winter wheat rotation and periodically limed and fertilized with N, P, and K. Golf course soil samples, which were under turf management, were taken from a fairway on the Willowdale Golf Course in Durham, NC, at 0-30.5, 30.5-50, and 56-80 cm. The fairway periodically received N, P, and K fertilizer, was routinely mowed and had not been limed in five years. All soil samples were air dried, passed through a 2 mm sieve, stored in sealed plastic containers at room temperature. Subsamples were oven dried at 105° C prior to use for all studies except where indicated. A total of nine "whole" soil samples (3 depth samples from each site) were used in this study; labels assigned to the soil samples are listed in Table 1.

To evaluate the role of exchangeable soil cations on 2,4-D sorption, samples of the lowermost horizons of each soil (Forest-B2, Farm-B2, Golf-B2) were saturated with either Na or Al as follows. 75 g "whole" oven-dried soil was placed in a 250 mL centrifuge bottle, 150 mL of either 3 M NaCl or 1 M AlCl<sub>3</sub> was added, and soils were gently shaken on an end-over-end shaker for 0.5 h. Soils were then centrifuged at 2200 rpm for 20 min and the supernatant was discarded, and the saturation-wash was repeated two more times. Soils were then washed in a likewise manner with DI water until the conductivity of the supernatant reached a final value of  $\sim 30$ -50  $\mu$ mho and did not decrease further. Washed soils were transferred to lyophilization flasks, frozen, and lyophilized to dryness.

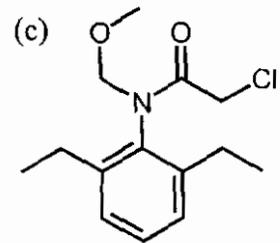
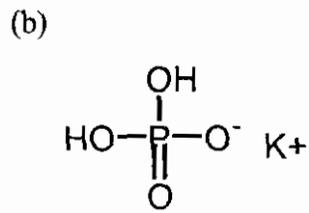
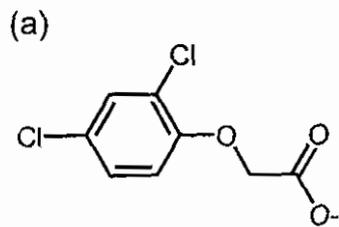


Figure 1. Chemical structures of the test solutes. (a) 2,4-D, (b) Potassium phosphate, (c) Alachlor.

Table 1. Selected soil properties of Farm, Forest and Golf Course soils.

Soil Label	Sample depth	Horizon	Textural Class	Sand	Silt	Clay	Surface Area	pH <sub>w</sub>	P <sub>max</sub>	Electrophoretic Mobility
	---cm---			-----%-----			----m <sup>2</sup> /g---		---mmol/kg-	--(s/μm)/(V/cm)--
Farm-A	0-30	A	Clay	18.3 ± 0.9	40.0 ± 0.6	41.7 ± 0.8	25.2 ± 0.9	5.73	60.5 ± 2.2	-2.38 ± 0.04
Farm-B1	30-56	B	Clay	18.1 ± 1.0	35.9 ± 0.9	46.0 ± 0.3	31.1 ± 1.0	6.14	47.8 ± 1.3	-2.23 ± 0.06
⊙ Farm-B2	56-80	B	Clay	19.0 ± 0.8	38.5 ± 0.9	42.5 ± 0.6	31.1 ± 0.7	4.71	44.6 ± 1.4	-2.21 ± 0.12
Forest-A	0-30	A	Silt loam	15.9 ± 5.1	59.5 ± 5.4	24.6 ± 0.5	14.6 ± 0.2	4.91	23.2 ± 2.0	-2.78 ± 0.18
Forest-B1	43-69	B	Clay	7.0 ± 1.0	39.8 ± 1.7	53.3 ± 0.9	36.2 ± 0.8	5.36	68.9 ± 2.4	-2.62 ± 0.14
Forest-B2	69-94	B	Clay	3.8 ± 1.1	36.3 ± 1.1	59.9 ± 0.3	44.7 ± 1.1	5.30	50.5 ± 1.5	-2.00 ± 0.16
Golf -A	0-30	A	Clay loam	21.8 ± 3.4	41.2 ± 7.8	37.0 ± 4.4	21.4 ± 0.9	5.45	36.9 ± 0.8	-2.03 ± 0.10
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	57.8 ± 1.5	-1.74 ± 0.05
Golf-B2	56-80	B	Silt loam	25.3 ± 0.2	54.5 ± 0.7	20.2 ± 0.8	18.6 ± 1.5	4.05	37.0 ± 1.3	-1.82 ± 0.17

### 3.3. Soil Characterization

Characterization of the nine “whole” soils samples was conducted using standard methods described by Sparks (1996) and Carter (1993). Soil characteristics measured included pH in a 1:1 soil:water slurry ( $\text{pH}_w$ ), electrical conductivity by a saturated paste extract method,  $\text{N}_2\text{BET}$  surface area (Micromeritics Gemini 2360 Surface Area Analyzer), effective cation exchange capacity (ECEC) at the pH of the soil by summation of exchangeable cations (Al, Ca, K, Mg, Mn and Na) compulsively exchanged with 0.1 M  $\text{BaCl}_2$  (individual concentration of exchangeable cations calculated from the same exchange procedure are denoted as  $\text{ExAl}$ ,  $\text{ExCa}$ ,  $\text{ExMg}$ ,  $\text{ExK}$ ), anion exchange capacity (AEC) at soil pH by saturation with 1 M KCl and compulsive exchange with 0.5 M  $\text{NaNO}_3$ , total carbon (C) and nitrogen (N) by combustion (CE Instruments Flash EA 1112 Series CHN/S analyzer), organic carbon by the Walkley-Black method, particle size and related soil texture (%clay, %silt, and %sand) by the pipet method, operationally defined “free” or crystalline Al and Fe oxides by extraction with sodium citrate-dithionite-bicarbonate at  $80^\circ\text{C}$  (DCBAI, DCBFe), operationally defined poorly- or non-crystalline Al and Fe oxides by extraction with acidified ammonium oxalate in the dark (AAOAl, AAOFe). We note a possible overestimation of ECEC values because the summation of charge contributions from the exchanged cations by convention (Sparks, 1996) assumed a +3 charge for all Al species and the presence of other hydrolysis and polymerization species of lower charge was not accounted for. Total P and total S were determined by nitric-perchloric digestion, sorbed sulfate from an extraction with 500 mg P/L as  $\text{KH}_2\text{PO}_4$ , and maximum phosphate sorption capacity ( $\text{P}_{\text{max}}$ ) as determined by fitting phosphate sorption isotherms to the Langmuir equation (Sposito, 1989). For these isotherms, 0.1 g soil was pre-equilibrated for 24 h on an end-over-end shaker with 5 mL of DI water, after which 5 mL of one of eight P stock solutions solutions was added to give final concentrations ranging from 0 to 300 mg P/L and samples were shaken 48 h, filtered through 0.2  $\mu\text{m}$  polycarbonate filter and the supernatant analyzed for phosphate concentration. Additional indices of available soil phosphate included Mehlich III phosphate extracted by 0.2 M  $\text{CH}_3\text{COOH}$ , 0.25 M  $\text{NH}_4\text{NO}_3$ , 0.015 M  $\text{NH}_4\text{F}$ , 0.013 M  $\text{HNO}_3$ , and 0.001 M EDTA, and readily desorbable phosphate (RDP) extracted by 0.01 M  $\text{CaCl}_2$  (Sparks, 1996) We note that  $\text{pH}_w$ ,  $\text{N}_2\text{BET}$  surface area, ECEC, AEC, DCBFe, DCBAI, AAOFe, AAOAl values for the forest soils were measured previously (Vasudevan et al., 2002).

Phosphate concentrations in the RDP, and Mehlich III phosphate extractions and  $\text{P}_{\text{max}}$  experiments were analyzed using a modified molybdate blue method (Murphy and Riley, 1962; Watanabe and Olsen, 1965). 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 x 250 mm column, 8 mM  $\text{NaHCO}_3$ : 1 mM  $\text{Na}_2\text{CO}_3$ ). All other elemental analyses were determined by inductively coupled plasma-mass spectrometry (ICP-OES, Perkin-Elmer model 2000 DV ICP Optical Emission Spectrometer) or direct current plasma-optical emission spectroscopy (Fisons Spectraspan 7)

For the prepared Na and Al saturated soil, exchangeable Na and Al in the soils was extracted with 0.1 M  $\text{BaCl}_2$  as described above and Na or Al in the extract was analyzed by atomic absorption spectroscopy (Perkin Elmer 5100PC). Selected soil properties measured, as described above, included  $\text{pH}_w$ , ECEC, and  $\text{N}_2\text{BET}$  surface area.

### 3.4.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.

*3.4.1.Single Solute Batch Sorption Experiments:* Soil was first pre-equilibrated by shaking end-over-end overnight with deionized (DI) water. Soil:solution loadings were selected to 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, B2), 300 g/L for Forest-A soil. Following pre-equilibration, 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 9.686 mM P as  $\text{KH}_2\text{PO}_4$ ). 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 and samples were filtered through 0.2  $\mu\text{m}$  polycarbonate membranes and solute concentration 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.

2,4-D sorption onto Na and Al saturated B2 horizon soils (Forest-B2, Farm-B2, 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  $\mu\text{L}$  aliquots of 0.1-3 M HCl or 0.1-1 M NaOH and all additions were recorded. Generally, pH adjustments altered ionic strength by  $< 0.006$  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  $\sim 3.6$ - $4.4$  and in the “higher pH” experiments from  $\sim 4.5$ - $4.9$ . 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 solid), which were treated and measured in the same manner as solid-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 solid-containing reactor from the initial (blank) concentration. Compound concentration in the blanks was monitored over the duration of the experiment to evaluate potential test compound loss to reactor walls and degradation; no loss was observed.

*3.4.2.Double Solute Batch Sorption Experiments:* Double-solute batch studies were used to evaluate herbicide-phosphate competition in the A horizons 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 pre-equilibrated in 8 mL of 0, 2.018, or 12.108 mM P (as  $\text{KH}_2\text{PO}_4$ ) for 24 h,

after which a 2 mL aliquot of herbicide stock solution was added to achieve a final 2,4-D concentrations of 0, 0.23 and 0.45 mM or an alachlor concentration of 0 or 0.09 mM, and final phosphate concentration of 0, 1.614 or 9.686 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.

*3.4.3. 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 x 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 for all studies except single-solute batch kinetic studies with Forest soils, which were conducted using a mobile phase of 65% methanol:35% 0.017 M H<sub>3</sub>PO<sub>4</sub> (pH 2.27) and detection at 234 nm. Alachlor was separated on a Zorbax XDBC18 5  $\mu$ m 25 cm x 0.46 cm column 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 colorimetrically by a modified molybdate blue method (as previously described), while for double-solute studies phosphate was analyzed by ion chromatography as described above.

### 3.5. Statistical Analyses

Langmuir isotherm parameters were determined from non-linear fits in JMP IN, Version 3.2.1. Correlation coefficients (r) for selected soil properties and test compound sorption were determined from bivariate linear regression (LR) using JMPIN (Version 3.2.1 for Windows, SAS Institute), all ANOVAs were computed in S-Plus (2000 Professional Edition for Windows, Release 2, Insightful Inc.).

## 4. RESULTS

### 4.1. Characterization of Unaltered Soil Matrices

Farm A and B horizon clays possessed similarly high surface areas (25-31 m<sup>2</sup>/g), whereas Forest A horizon silt loams were coarser (14.6 m<sup>2</sup>/g) in comparison to the B horizon clays (36-45 m<sup>2</sup>/g). For the Golf course soils, the A horizon clay loam, B1 horizon silty clay and the B2 silt loam were generally coarser (18-23 m<sup>2</sup>/g) than all Farm soils and the Forest B horizon soils (Table 1). Forest and Golf soils possessed more acidic pH values (4.05-5.45) than the Farm soils (4.71-6.14) (Table 1). The organic carbon (OC) content in all B horizons was distinctly low (0.06-0.3%), whereas A horizon OC values were higher (0.5-1.5%) with the Farm A horizon possessing the highest OC content (Figure 2a).

The mineralogy of all soils was dominated by iron (Fe) in the crystalline oxide phase (DCBFe) (245-834 mmol/kg), followed by aluminum (Al) in the crystalline oxide phase (DCB Al) (39-147 mmol/kg). Fe and Al present as amorphous oxide phases (AAOFe and AAOAl, respectively) were also important constituents of these soils (8-37 mmol/kg). Notably, DCBFe, DCBAl, AAOFe, and AAOAl values were generally higher in the Farm A horizon as compared with Forest and Golf course A horizons (Figure 2b-e). For the Farm soils, DCBFe and DCBAl values were generally similar through the soil profile (i.e., across A, B1, and B2 horizons) much like surface area, whereas AAOFe and AAOAl values showed a slight decrease with soil depth. In general, the DCBFe, DCBAl, AAOFe, and AAOAl in Golf course soils were lower than values of Farm and Forest soils of comparable horization and showed a slight decrease with soil depth. Forest soils exhibited a distinct increase in DCBFe, DCBAl, AAOAl values with soil depth, a marked difference as compared with Farm and Golf course soils. AAOFe in the Forest soils exhibited only a slight increase with depth.

The ECEC of Farm A horizon (8.4 cmol<sub>c</sub>/kg) was distinctly higher than the ECEC of all other soils (2.1-6.4 cmol<sub>c</sub>/kg) (Figure 3a). Although the ECEC of the Farm soils (5.3-8.4 cmol<sub>c</sub>/kg) was generally higher than the Golf course soils (2.1-3.7 cmol<sub>c</sub>/kg), both soils showed a slight decrease in ECEC with soil depth. In contrast, ECEC values increased with depth in the Forest soils (2.1-5.8 cmol<sub>c</sub>/kg) and the Farm and Forest B horizons possessed comparable ECEC values. ExMg was an important contributor to the ECEC in all Farm (20-31% of total exchangeable ions calculated on a mmol/kg basis), Forest (34-63%), and Golf course (26-45%) soils (Figure 3b). ExCa was also a significant source of ECEC in all the Farm (57-67%) and Golf course soils (35-57%), but not in the Forest soils (6-9%) (Figure 3c). ExK was only important in the A horizons of Farm (22%) and Golf course (27%) and the Golf B2 horizon (17%) (Figure 3d). Notably, ExAl was an important contributor to ECEC only in the Forest soils (21-51%) and was low to negligible in the Farm and Golf soils (0-12%) (Figure 3e). Within all soils profiles, soil AEC values were higher in the B horizons (2.5-3.4 cmol<sub>c</sub>/kg) than in the A horizons (1.1-1.5 cmol<sub>c</sub>/kg). For the Forest soils, AEC values increased with depth much like ECEC values. On the other hand, the increase in AEC values with soil depth observed in Farm and Golf course soils was counter to the ECEC depth trends in these soils (Figure 4a).

Farm soils possessed a higher total P content (14-30 mmol P/kg) than Forest and Golf course soils of comparable depth (5.3-10.6 mmol P/kg) and the Farm A horizon had the highest total P

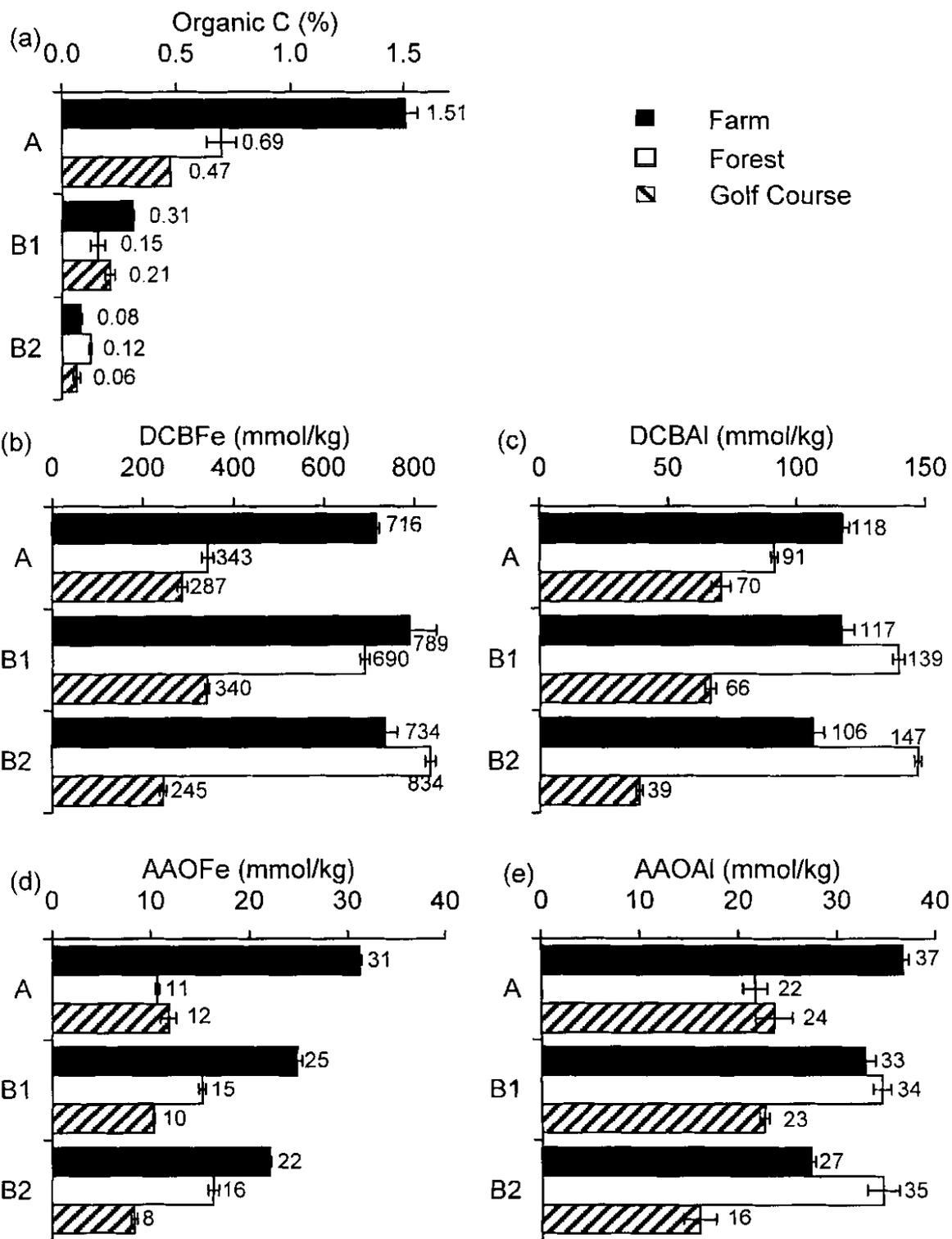


Figure 2. Contents of (a) organic carbon, (b) Fe in crystalline oxides (DCBFe), (c) Al in crystalline oxide (DCBAI), (d) Fe in amorphous oxides (AAOFe) and (e) Al in amorphous oxides (AAOAI) as a function of depth in the Farm, Forest and Golf course soils. Data labels denote x-axis values.

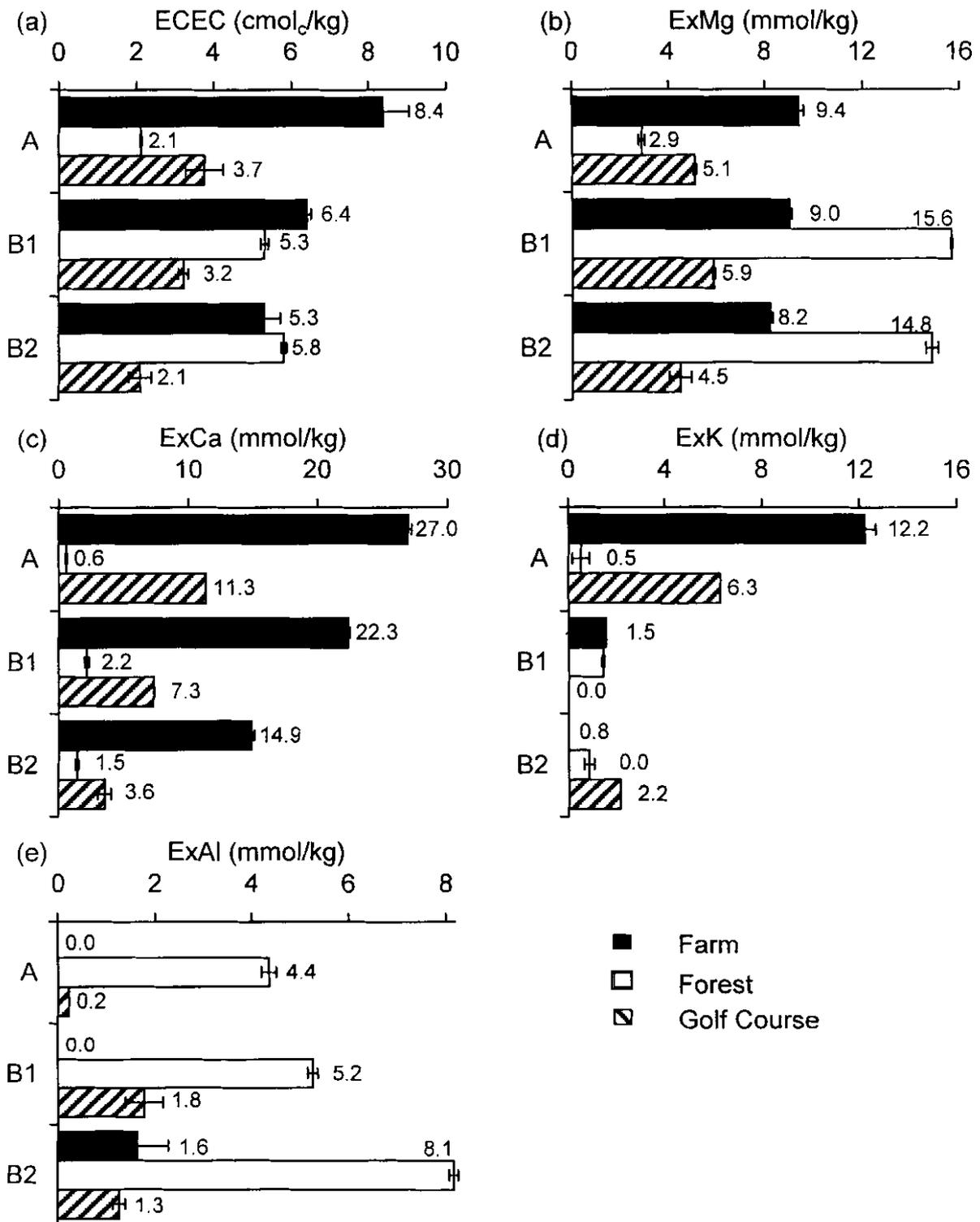


Figure 3. The (a) Effective cation exchange capacity (ECEC), (b) Exchangeable Mg, (c) Exchangeable Ca, (d) Exchangeable K, and (e) Exchangeable Al contents as a function of depth in the Farm, Forest and Golf course soils. Data labels denote x-axis values.

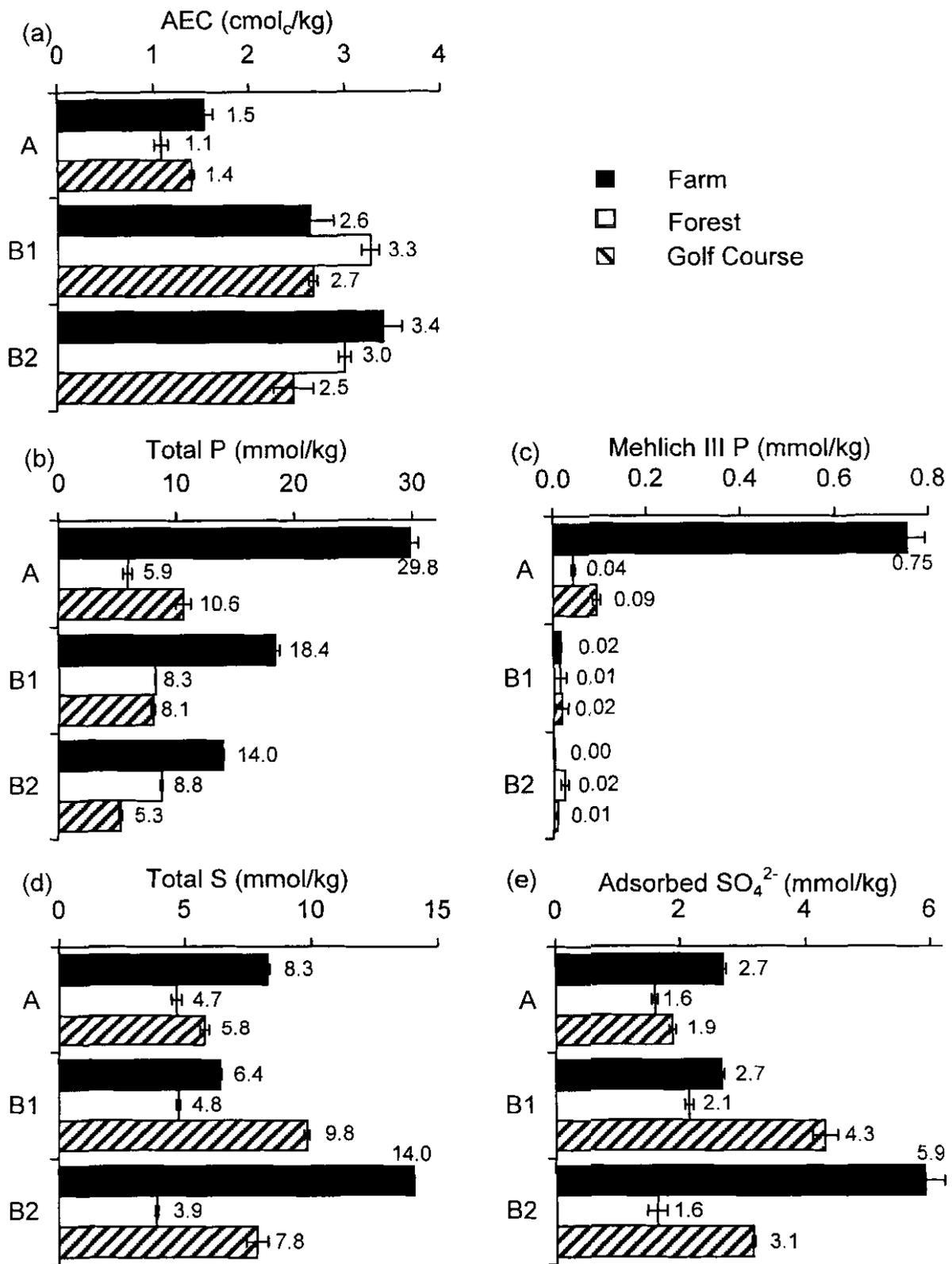


Figure 4. The (a) Anion exchange capacity (AEC), (b) total P, (c) Mehlich III P, (d) total S, and (e) adsorbed sulfate values as a function of depth in Farm, Forest and Golf Course soils. Data labels denote x-axis values.

content (30 mmol P/kg) of all soils (Figure 4b). Mehlich III P values (a measure of plant available phosphate), much like total P content, were the greatest for Farm A horizon (0.75 mmol P/kg), followed by Golf and the Forest A soils; all B horizons had little to no Mehlich III P (Figure 4c). Likewise, readily desorbable phosphate (RDP) was relatively high in the Farm A horizon ( $2.2 \times 10^{-2}$  mmol P/kg) but low to negligible ( $1.1 \times 10^{-3}$ – $3.6 \times 10^{-4}$  mmol P/kg) in all other soils (data not shown). The capacity for phosphate sorption ( $P_{\max}$ ) decreased with depth in Farm soils, whereas in the Forest and Golf course soils  $P_{\max}$  initially increased with depth (A to B1) and then decreased slightly in the B2 horizon (Table 1). Henceforth, measures of Mehlich III phosphate and RDP will be used to operationally denote “residual soil phosphate from P fertilization”.

When compared to the Forest soils, the Farm and Golf course soils possessed higher total S contents (6.4-14 and 5.8-9.8 mmol S/kg, respectively) and showed distinct depth trends, whereas the total S in Forest soils was relatively low and similar in magnitude across the soil profile (3.9-4.8 mmol S/kg). Farm soils exhibited a slight decrease in total S with depth (A to B1) followed by a dramatic increase in B2 horizon. On the contrary, total S in the Golf Course soils peaked in the B1 horizon (Figure 4d). Adsorbed sulfate values, although consistently lower than total S values (33-45% of total S), mimicked the trends exhibited by total S (Figure 4e).

#### 4.2. Characterization of Na and Al saturated soil matrices

Na and Al saturated soil matrices were characterized for specific soil properties in order to discern the extent to which the saturation procedures altered the original soil matrices. The surface areas of the Na and Al saturated soil matrices were relatively similar (within  $\pm 0.19$ -2.5  $\text{m}^2/\text{g}$ ) to those of the original soils from which they were prepared (Table 2). Soil  $\text{pH}_w$  values, however, were significantly altered in comparison to the original soils:  $\text{pH}_w$  values of the Na exchanged soils were generally higher ( $\text{pH}_w$ : 5.3-5.7), whereas the  $\text{pH}_w$  values of the Al exchanged soils were substantially lower ( $\text{pH}_w \sim 3.5$ ) (Table 1-2). The ECEC 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: ECEC values were within  $\pm 0.11$ -0.46  $\text{cmol}_c/\text{kg}$  of each other (Table 2). 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  $\text{pH}_w$  of the soils.

#### 4.3 Single-solute sorption

*4.3.1. Sorption to unaltered soil matrices:* 2,4-D, alachlor and phosphate achieved sorption equilibrium in 24-48 h (data not shown). Comparisons of solute sorption are henceforth based on the extent of sorption measured at 48 h (Figure 5-6). Within the Forest soil profile, the extent of 2,4-D sorption markedly increased with soil 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 5a). Trends across landuse (Farm, Forest, Golf Course) are preserved even when differences in surface area are accounted for (Figure 5b). Although it is well established that 2,4-D sorption to soil decreases with increase in pH (Barriuso et al., 1992; Kavanagh et al., 1980), the observed differences in 2,4-D sorption in our soils could not be attributed to differences in soil pH alone. For example, the pH

Table 2. Selected soil properties of Na and Al saturated B2 horizons of Farm, Forest and Golf Course soils.

Soil Label	Original Soil	pH <sub>w</sub>	N <sub>2</sub> BET	Exchangeable	ECEC
			Surface Area	Cation	
			---m <sup>2</sup> /g---	----mmol/kg----	----cmol <sub>c</sub> /kg----
<b>Na Saturated Soils</b>					
Na-Farm-B2	Farm-B2	5.67	32.12	38.70 ± 0.55	3.87 ± 0.05
Na-Forest-B2	Forest-B2	5.30	44.51	51.24 ± 3.15	5.12 ± 0.31
Na-Golf-B2	Golf-B2	5.66	17.35	38.70 ± 1.48	3.87 ± 0.15
<b>Al Saturated Soils</b>					
Al-Farm-B2	Farm-B2	3.50	33.57	13.57 ± 0.30	4.07 ± 0.09
Al-Forest-B2	Forest-B2	3.47	47.23	15.54 ± 0.48	4.66 ± 0.14
Al-Golf-B2	Golf-B2	3.42	19.22	13.26 ± 1.55	3.98 ± 0.47

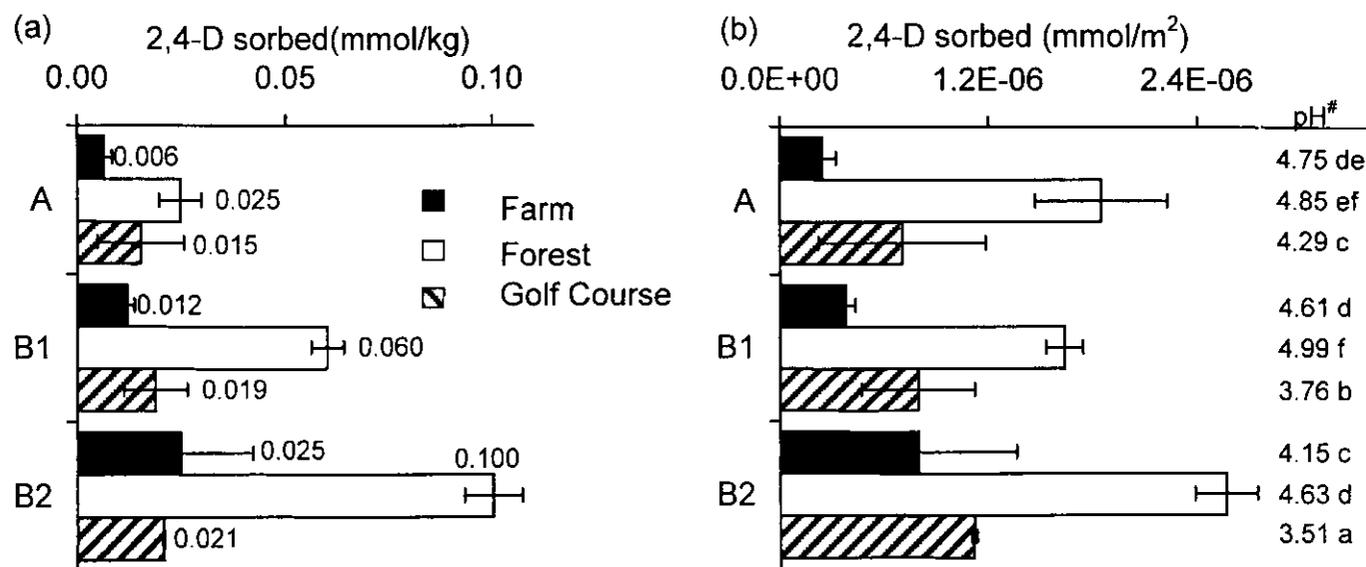


Figure 5. Sorption of 2,4-D as function of depth in Farm, Forest and Golf Course soils in units of (a) mmol/kg and (b) mmol/m<sup>2</sup>. Initial [2,4-D]: 0.045 mM; Soil loading: 100-300 g/L; equilibration time: 48 h. Data labels denote x-axis values.

\*Slurry pH values; values followed by the same letter are not significant at  $\alpha=0.05$  by Fisher LSD test.

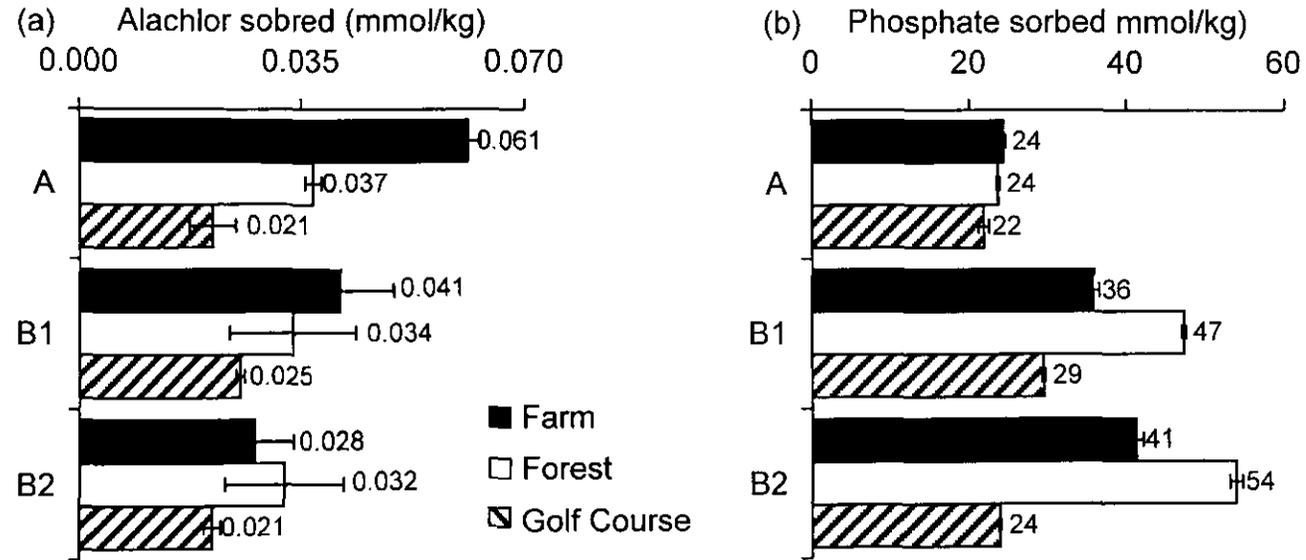


Figure 6. Sorption of (a) alachlor (mmol/kg) and (b) phosphate (mmol/kg) as a function of depth in Farm, Forest and Golf Course soils. Initial [alachlor]: 0.036 mM; Initial [phosphate]: 9.69 mM; Soil loading: 100-300 g/L; equilibration time: 48 h. Data labels denote x-axis values.

of the Forest A- and Forest B1-2,4-D slurries were not significantly different, however 2,4-D sorption in the Forest B1 horizon was greater than in the A horizon. Similarly, 2,4-D sorption in the Forest A horizon was higher than sorption in the Farm A horizon despite the similar pH of the Farm A- and Forest A-2,4-D slurries (see ANOVAs in Figure 5). Distinctly different trends were observed for alachlor sorption within and across the soil profiles: sorption within the Farm soil profile showed a discernable decrease with soil depth, whereas an obvious depth trend was not noted in the Forest and Golf course profiles (Figure 6a). The extent of alachlor sorption (0.02 –0.06 mmol/kg) was significantly lower than that of 2,4-D sorption in all soils.

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 6b). Although the extent of sorption was general 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).

*4.3.2. Sorption to Na and Al saturated soils:* In the “higher” pH (4.5-4.9) experiments 2,4-D sorption in Al saturated Farm, Forest Golf soils was distinctly greater (68-90%) than sorption onto comparable Na saturated soils (Figure 7). The pH values of all six slurries compared were not statistically different ( $\alpha=0.05$ ) (see ANOVAs, Figure 7). As expected, the extent of sorption onto a particular soil in “lower” pH (3.6-4.4) experiments was generally greater in the “higher” pH experiments and the greater sorption onto the Al saturated matrices was again clearly discerned. In the “lower” pH experiments, the pH of the Na saturated matrices was significantly greater than that of the Al saturated soils, therefore, the greater extent of sorption on the Al saturated soils is partly due to the lower pH of these slurries (Figure 7).

#### 4.4. Double solute sorption studies

Herbicide-phosphate competition was examined only on the A horizon unaltered soil matrices because the A horizons directly receive solutes from fertilization and herbicide application. 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, compared to treatments where no phosphate was added (Figure 8a-b). Although a discernable effect of phosphate on 2,4-D sorption was not observed in Golf-A soils at a “low” initial 2,4-D concentration, a significant decrease in sorption (77-80%) with increase in phosphate concentration did occur at “high” initial 2,4-D concentration (0.45mM). In Farm A, the effects of phosphate concentration on 2,4-D sorption were inconclusive: “high” phosphate resulted in a slight but statistically insignificant decrease 2,4-D sorption at “low” 2,4-D, but did not affect 2,4-D sorption at “high” 2,4-D. (Figure 8a-b). In contrast, at both “low” and “high” phosphate, the extent of phosphate sorption was relatively unaltered in all soils when 2,4-D concentrations were increased from 0 to 0.23 to 0.45 mM (Figure 9): differences in phosphate sorption were between 0.3-1.4 mmolP/kg. Also, the effect of phosphate on alachlor sorption is not discerned in Farm, Forest and Golf soils (Figure 8c).

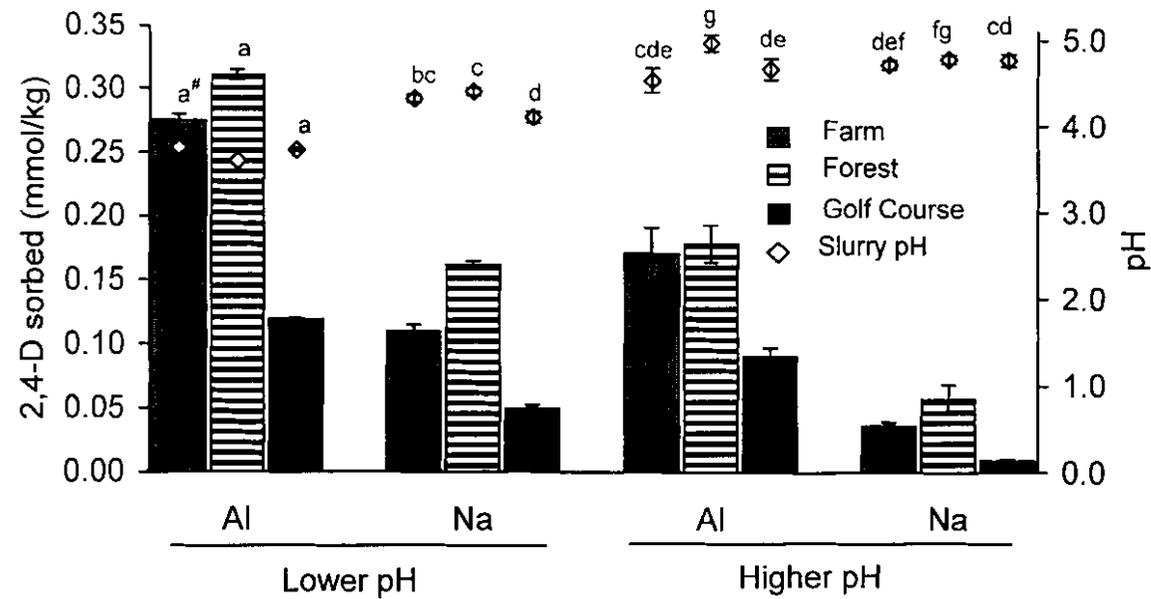


Figure 7. Sorption of 2,4-D in Na and Al saturated B2 horizons of Farm, Forest and Golf Course soils in the "lower" and "higher" pH experiments. Initial [2,4-D]: 0.045 mM; Soil loading: 100-200 g/L.

# Slurry pH points with the same letter are not significant at  $\alpha=0.05$  by Fisher LSD test.

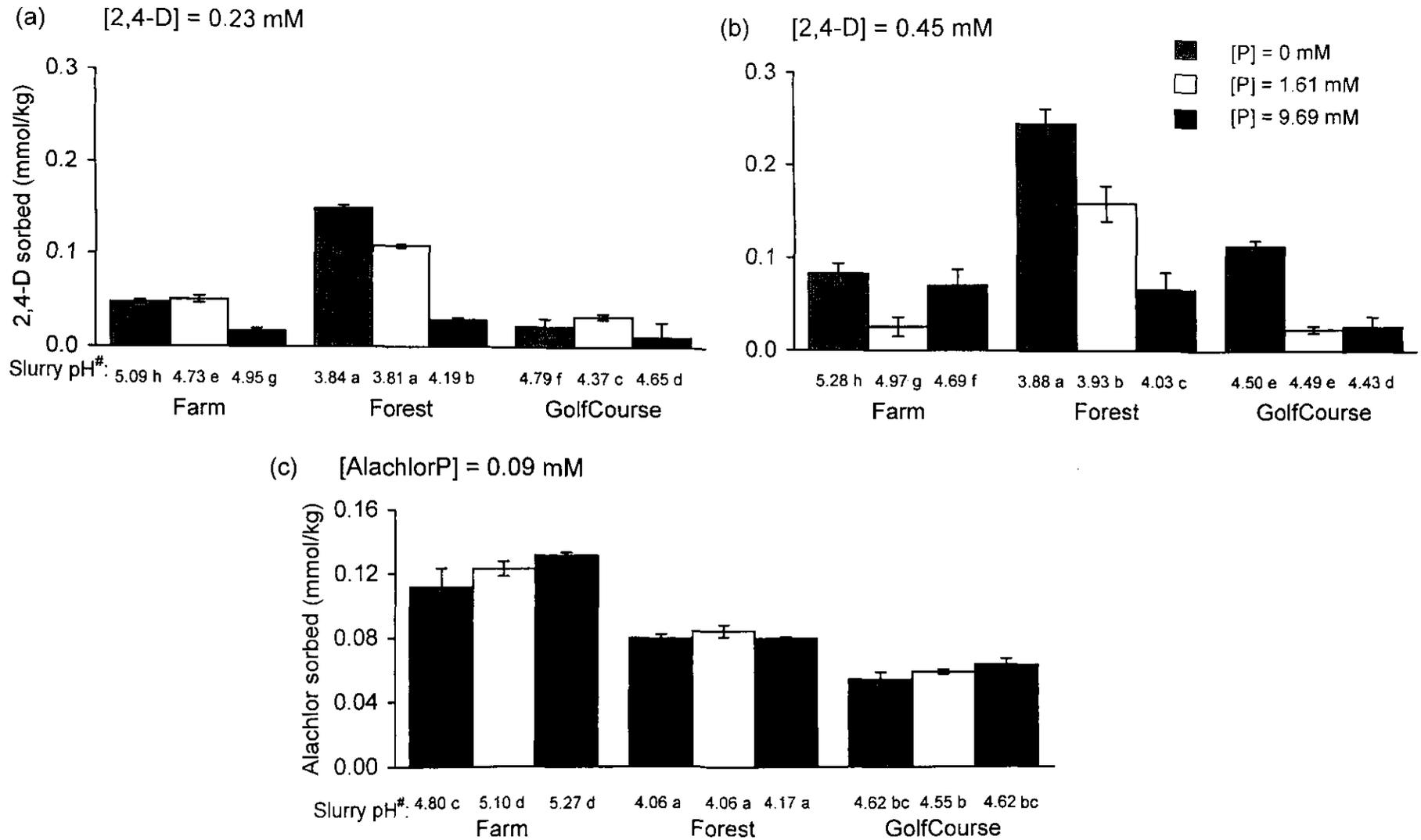


Figure 8. Sorption of (a) 0.23 mM 2,4-D (b) 0.45 mM 2,4-D and (c) 0.09 mM alachlor in the presence of phosphate in Farm, Forest and Golf course A horizons. Soil loading: 100-300 g/L.

\*Values followed by the same letter are not significantly different for a given pesticide at  $\alpha=0.05$  by Fisher LSD test.

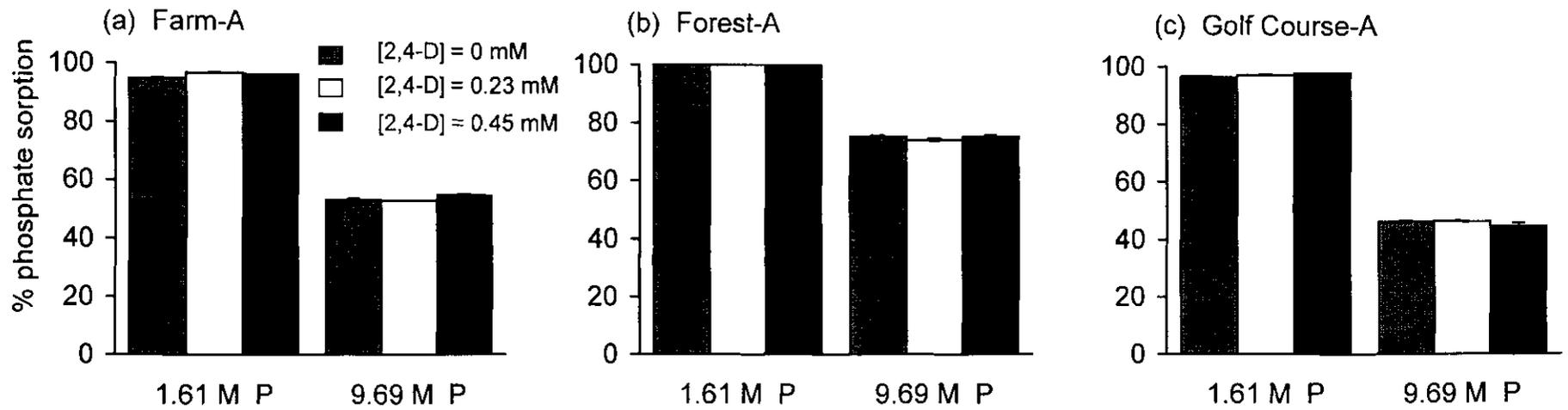


Figure 9. Percent phosphate sorption in the presence of 0, 0.23, and 0.45 mM 2,4-D in (a) Farm, (b) Forest and (c) Golf course A horizons. Soil loading: 100-300 g/L.

## 5. DISCUSSION

### 5.1. Comparison of soil properties of the unaltered soils

The Forest, Farm, and Golf course profiles all exhibited soil properties characteristic of their soil order (Ultisols) and series (Georgeville) (Brady and Weil, 1997; Dunn, 1977). All soil samples were generally acidic, heavy textured soils with high clay and Fe oxide contents. 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 the a typical Georgeville soil and represents a profile that was relatively unaltered as evidenced from the increase in fine texture, surface area, Fe and Al oxide content, ECEC and AEC with depth. Furthermore, the low ExCa, ExK, and P contents 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. In contrast, the Farm and Golf soils possessed profiles that reflect 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 Fe and Al oxide contents were either relatively uniform or showed a slight decrease along the soil profile, suggesting that land management may have disrupted distinction between horizons. The higher ExCa, ExK, and P contents, particularly in A horizons, emphasized repeated fertilization of the Farm and Golf soils. In direct contrast, total S and adsorbed sulfate increased with depth in the Farm and Golf soils. 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.

### 5.2. Influence of soil properties on herbicide sorption

*5.2.1. 2,4-D.* The extent of single solute sorption onto the unaltered soils provided important clues to the influence of soil properties, particularly soil P and exchangeable Al, on the extent of solute sorption. The increase in 2,4-D sorption with depth in the Forest soil profile followed the depth trends for surface area, soil crystalline and amorphous Fe and Al oxide contents, exchangeable Al content and AEC within this profile but was contrary to the decrease in organic carbon content with depth (Figure 2-5). This observation corroborates with our previous finding (Vasudevan et al., 2002) that the reactive mineral component of the soil, particularly Fe and Al oxide contents, strongly influence the extent of carboxylic acid herbicide sorption onto Ultisols with low organic carbon contents (> 0.75%). The lower extent of 2,4-D sorption observed in Golf course soils (as compared with the Forest soils) was keeping with the coarser texture and lower Fe and Al oxide contents of these soils.

2,4-D sorption in the Farm A soil was significantly lower than in all horizons of the forest soil (Figure 5a) despite the facts that (i) Farm A soil had a higher surface area, Fe and Al oxide and organic carbon contents than Forest A soil, and (ii) Farm A soil possessed comparable (or higher) Fe and Al oxide contents to Forest B1 and B2 soils (Figure 2, Table 1). It appears that soil Fe and Al oxide contents alone cannot account for sorption in Farm and Forest soils. 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 P 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.

Four hypothesis are proposed to rationalize the low 2,4-D sorption in the Farm A soils: (i) the high residual soil phosphate from fertilization suppressed 2,4-D sorption because the phosphate anions occupied surface sites that may have otherwise been available for 2,4-D; (ii) the high residual phosphate and OC contents resulted in high soil negative charge which caused repulsion of the 2,4-D anion from the surface; (iii) the high OC content resulted in organic matter coatings on soil oxides that blocked potential sites of 2,4-D sorption; and (iv) low exchangeable Al content resulted in lower 2,4-D sorption.

The first hypothesis regarding the role of soil phosphate was confirmed based on the following rationale. As a single solute, phosphate sorbed to a significantly greater extent than 2,4-D: in A horizons 95-100% phosphate sorption was observed from a 1.61 mM solution (Figure 9), whereas only 3-18% 2,4-D sorption was observed from a 0.45 mM solution (Figure 8b). This confirms a greater phosphate affinity to the Ultisols investigated in this study. In the presence of both solutes, 2,4-D sorption from a 0.45 mM slurry was decreased by ~73-77% in Forest and Golf course soils (which possessed low residual phosphate) as the concentration of phosphate added to the slurry was increased (Figure 8). Phosphate sorption, however, was relatively unaltered by 2,4-D (Figure 9). It appears that phosphate, the stronger sorbate, can suppress 2,4-D by binding to surface sites that may otherwise be accessible to 2,4-D. Also, phosphate sorption can increase surface negative charge and limit 2,4-D anion sorption. The effect of phosphate on 2,4-D sorption was not discerned in the Farm A soil probably because the high residual soil phosphate was already sufficient to suppress 2,4-D sorption, such that the effect of additional phosphate was not easily discerned. Alternatively, sorption may be suppressed by the higher soil negative charge resulting from higher residual phosphate and OC contents.

The second hypothesis regarding the role of soil negative charge in low 2,4-D sorption observed in the Farm A soil was rejected based on the observation that the electrophoretic mobility (particle movement toward a positive electrode) was greater for the clay fraction of the unaltered Forest A soil as compared with the clay fraction of unaltered Farm A soil (Table 1). All else equal, it was concluded that the Farm A soil had lower negative charge than the Forest A soil and therefore electrostatic repulsion did not play an important role in the low 2,4-D sorption. All the same, the possibility that added phosphate, in the double batch experiments, can increase soil negative charge and decrease 2,4D anion sorption cannot be excluded.

Soil OC content does not appear to favor 2,4-D sorption in our test soils. The third hypothesis regarding the role of organic matter coatings could not be conclusively confirmed or rejected based on evidence from this study: the lack of a discernable effect of phosphate on 2,4-D sorption onto Farm A soil, along with the high OC content of this soil suggest that organic matter coatings on mineral surfaces and/or residual soil phosphate can suppress 2,4-D sorption. 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 oxides 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.

Several striking lines of evidence from our studies pointed to a possible role of exchangeable Al in 2,4-D sorption (fourth hypothesis). 2,4-D sorption was significantly higher in the Forest B horizons (B1 and B2) than the comparable Farm B horizons (Figure 5) despite both soils possessing similar Fe and Al oxide contents (Figure 2). Since both soils possessed similarly low residual soil phosphate and OC contents (Figure 2, 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 the absence of exchangeable Al in Farm B horizons limited sorption. We note that adsorbed sulfate, which is greater in Farm B2 than Forest B2 soil could have suppressed 2,4-D sorption by blocking surface sites in these studies. However, a large difference in 2,4-D sorption was observed in Farm B1 and Forest B1 soil despite similar adsorbed sulfate values; lending further support that exchangeable Al plays a role in 2,4-D sorption in these soils.

This assertion is confirmed by the single solute experiments conducted on Na and Al saturated soil matrices: a significantly higher extent of 2,4-D sorption was observed in Al saturated soils as compared with Na saturated soils, particularly at higher pH treatments where differences in pH were not significant. Also, sorption of 2,4-D onto Farm-B2 soil was significantly lower (75%) than sorption onto Forest B2 soil (Figure 5a), whereas 2,4-D sorption onto Al-Farm-B2 (0.17 mmol/kg) and Al-Forest B2 (0.18 mmol/kg) was comparable in the “higher” pH condition and sorption on the Al-Farm B2 was only slightly lower (12%) than onto Al-Forest-B2 in the “lower” pH condition (Figure 7). We offer that 2,4-D coordination to exchangeable Al ions plays an defining role in determining the extent of sorption: sorption was low in Farm B soils despite the high Fe and Al oxide contents because of these horizons’ low exchangeable Al. It appears that 2,4-D sorbs to soils by a cation bridging mechanism involving an exchangeable Al ion and the carboxylate group of 2,4-D. Previous studies (Dubus et al., 2001; Johnson and Sims, 1993; Johnson and Sims, 1998) have noted the possible role of exchangeable acidity in 2,4-D sorption; here we have provided conclusive evidence by employing Al saturated soil matrices. 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 (Sannino et al., 1997; Vasudevan et al., 2002). Here, we have identified that surface bound exchangeable Al ions in soils may constitute an important source of positively charged sites for 2,4-D sorption.

Our results allude to the fact that exchangeable Al content plays a more prominent role than soil Fe and Al oxide content in determining the extent of 2,4-D sorption. This may be likely in net negatively charged soils where surface bound exchangeable Al ions provide an important source of positively charged sites. However, several studies have showed significant 2,4-D sorption onto pure phase Fe and Al oxides (Celis et al., 1999; Kavanagh et al., 1980; Vasudevan et al., 2002); these systems had no source of exchangeable Al. Therefore, the role of soil Fe and Al oxide in determining 2,4-D sorption cannot be excluded.

*5.2.2. Alachlor.* Alachlor sorption within a soil profile appeared to follow the OC content of the soil ( $r = 0.817$ ) and did not seem to be related to soil mineralogy. This was consistent with our expectation that the neutral alachlor likely sorbs to soils via partitioning to organic matter and

was similar to findings of other studies. As would be expected for compounds that primarily partition to organic matter, alachlor sorption did not appear to be influenced by soil phosphate: high residual soil phosphate in Farm A soil did not suppress alachlor sorption and increase in phosphate concentrations in the double solute experiments did not reduce the extent of alachlor sorption. Similarly, it appears that low exchangeable Al content in Farm A soil did not affect alachlor sorption. All of these observations emphasize that 2,4-D and alachlor interact with NC Ultisols by distinct sorption mechanisms.

## 6. CONCLUSIONS

Sorption of 2,4-D and alachlor were influenced by distinctly different soil properties: alachlor sorption related to organic carbon content suggesting that partitioning into organic matter may be a dominant mechanism, whereas 2,4-D sorption correlated with properties describing soil mineralogy such as surface area, Fe and Al oxides, AEC, and, most significantly, exchangeable Al. Mechanisms involved in 2,4-D retention are likely to include both electrostatics and coordination with exchangeable Al through a cation bridge. Therefore, liming to reduce soil acidity, a common practice in cultivated soils, may enhance leachability of 2,4-D. Additionally, phosphate competed strongly with 2,4-D for sorption and residual phosphate from fertilizer in Farm and Golf soils appeared to restrict 2,4-D sorption, both results indicating that fertilizer P inputs are likely to alter the leachability of 2,4-D in North Carolina Ultisols. In contrast to 2,4-D, alachlor was more strongly retained in the A horizons of the more intensively managed systems suggesting that fertilizer and lime inputs do not promote losses of alachlor through the soil profile. These findings strongly suggest that accurate prediction of 2,4-D and possibly other anionic herbicides fates should consider land use history and previous management practices, particularly those that influence extractable phosphate and exchangeable Al content.

Soil characteristics commonly used to estimate leaching potential (e.g., texture, organic matter, pH) appear to be suitable for non-ionic alachlor, but were not sufficient to describe anionic 2,4-D sorption. It is imperative that predictive models of anionic herbicide leaching potential account for the capacity of soil Fe and Al oxides and exchangeable Al ions to promote anionic herbicide sorption and for the inhibitory effect of extractable soil phosphate and organic matter coating on sorption.

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