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**SOIL PROCESSES IMPACTING GROUNDWATER QUALITY IN THE NORTH
CAROLINA PIEDMONT: CONTAMINATION BY ORGANIC AGROCHEMICALS**

by

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ABSTRACT

This research explores the potential for *sorption, desorption, and transformation* of three herbicides, 2,4-D, norflurazon, and quinmerac, in two representative iron-oxide rich soil profiles of the North Carolina Piedmont, Appling and Georgeville series. Following extensive characterization of the soils, we used batch and continuous flow stirred tank reactors (CFSTRs) to examine the *above mentioned processes* as a function of soil sample depth, composition, and physical-chemical properties and herbicide molecular structure and physical-chemical properties. Loss of the two ionogenic herbicides, 2,4-D and quinmerac, from soil solution was primarily due to sorption; the loss was strongly correlated with soil surface area, total Al and Fe, and crystalline iron oxide and amorphous aluminum oxide content. Loss of the neutral herbicide, norflurazon, however, was only correlated to total soil carbon. Under the experimental conditions of our CFSTR, we observed that deionized water could either completely or partially desorb the sorbed herbicide and that desorption was initially more rapid than sorption. We hypothesize that the mass of 2,4-D and quinmerac involved in reversible sorption is associated with soil iron oxides via favorable electrostatic interactions and/or weak surface complexation, while desorbing norflurazon fraction is associated with soil organic matter. The irreversibly retained herbicide mass is most likely involved in strong surface complexation or is entrapped within the soil matrix. Our results suggest that along with traditionally used soil properties, total Fe and Al and/or crystalline iron oxide content may be important in determining the fate and transport of ionogenic herbicides in NC ultisols.

(Key words: sorption, desorption, ultisols, iron oxides, herbicides, pesticides, 2,4-D, quinmerac, norflurazon, stirred-flow)

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SUMMARY AND CONCLUSIONS

The NC Piedmont is dominated by heavy-textured ultisols (“red clay soils”), acidic soils that have low organic matter, high iron (Fe), and high content of low-activity clays (e.g., kaolinite), particularly in the subsoil horizons. These and other attributes, including the soil’s potential for possessing variable charge, make Piedmont red clay soils physically and chemically distinct from many of the soils of the Coastal Plain. As a result of the extremely small size of clay and Fe oxide particles and the reactivity of the electron-deficient surface-bound Fe atoms, subsurface horizons of the red clay soils are the seat of important physical-chemical activity. Systems and guidelines for evaluating pesticide/herbicide fate developed from information based on the more commonly studied temperate soils have been successful for the Coastal Plain, however, additional research on other soil types will help determine how we can best adapt these and other systems for the evaluation of pesticide/herbicide fate in the NC Piedmont.

This research explores abiotic interfacial (surfacial) processes that contribute to the attenuation and mobilization of three polar/ionogenic herbicides in two common soils of the NC Piedmont. More specifically, we have examined the potential for sorption, desorption, and surface assisted transformation of 2,4-dichlorophenoxyacetic acid (2,4-D), norflurazon, and quinmerac in Appling and Georgeville soils as a function of (1) the mineralogy, composition, and physical-chemical properties of the soil, and (2) the molecular structure and physical-chemical properties of the herbicide. Samples of Appling and Georgeville soils were obtained from sites in the Duke forest at gates 12 and 11, respectively. Samples were taken at five depths between 0-200 cm to represent all prominent soil horizons as determined by visual and physical changes in the soil profile. Each soil sample was characterized for several parameters including total elemental composition, texture, pH, effective cation exchange capacity, saturated paste conductivity, N₂BET surface area, extractable aluminum (Al) and iron (Fe) oxide content, and maximum capacity for phosphate sorption. Well-controlled laboratory batch and continuous flow stirred tank reactors (CFSTR) were used to evaluate the nature and extent of herbicide sorption, desorption, and transformation at soil pH in the various soil samples. Statistical tools including linear regressions and principal component analysis (PCA) were used to evaluate the relatedness of soil properties and influence of soil properties on herbicide-soil interactions.

Soil Composition and Physical-Chemical Properties

The upper horizons (0-70cm) of the Appling soils can be categorized as sandy loams and the lower horizons evaluated (70-170cm) as clay soils. In the case of the Georgeville soils, the uppermost (0-30cm) and the lowermost (150-200cm) horizons evaluated are silt loams and the intermediate horizons (40-150cm) are clay soils. Both soils are relatively acidic, with a pH values between 4.5-5.4. Trends with respect to surface area, total and extractable Al and Fe content, and phosphate sorption capacity as a function of soil depth are closely related to soil texture, with the clay soils possessing higher values of these measured parameters than the sandy and silt loams. Total carbon is highest in the uppermost horizons of the two soils, and the nitrogen and phosphorus content is low in all soil horizons.

Batch studies of herbicide-soil interactions

We find that the extent of loss from soil solution of the two *ionic* herbicides, 2,4-D and quinmerac, as a function of soil depth differs considerably from the neutral norflurazon. In all

cases, loss from solution is believed to be primarily due to sorption onto the soil matrix. Additionally, the behavior and extent of loss from solution for all herbicides differs between Appling and Georgeville soils and appears to be related to differences in soil properties. Correlations between the extent of herbicide loss and soil properties reveal that 2,4-D and quinmerac loss are strongly correlated with surface area, clay content, total aluminum, total iron, and free (or crystalline) iron oxide content, while norflurazon loss can only be correlated to total soil carbon. Batch studies with pure phase minerals, hematite, goethite, γ -aluminum oxide, and kaolinite, confirmed that iron and aluminum oxides are important sorptive surfaces for 2,4-D and quinmerac. These minerals, however, do not have a capacity for norflurazon sorption.

Soil iron and aluminum oxides are expected to have a net positive charge at the measured soil pH (4.5-5.4). Hence, we speculate that the high retention of 2,4-D (negatively charged at soil pH) and quinmerac (neutral to negatively charged) in iron-rich mineral horizons is due to favorable electrostatic interactions with the soil surface. In addition, simultaneous complexation of the carboxylic acid groups with surface-bound electron deficient iron centers, via ligand exchange with surface bound $-\text{OH}$ and H_2O , is also likely. In the absence of an ionizable group such as the carboxylic group, as is the case for norflurazon, interaction with soil minerals is less likely and hydrophobic interactions with soil bound organic matter is the dominant process for herbicide retention.

CFSTR studies of sorption-desorption phenomena

Evidence of partial or complete desorption using deionized water in the CFSTR experiments confirms that the observed loss from soil solution in the batch studies is primarily due to sorption. Furthermore, for 2,4-D and quinmerac, desorption is initially more rapid than sorption; this indicates that H_2O and/or OH^- can competitively desorb 2,4-D, and quinmerac. It also provides additional evidence that the herbicide mass involved in reversible sorption is bound to the soil surface via favorable electrostatic interactions. Irreversible retention of 2,4-D and quinmerac likely results from strong complexation or entrapment within soil aggregates or particle micropores. For norflurazon, sorption and desorption appear to occur at the same rate; this provides further evidence that nature of norflurazon-soil interactions are distinct from 2,4-D- and quinmerac interactions with Appling and Georgeville soils. These findings demonstrate that CFSTR studies conducted in conjunction with batch studies allow for improved evaluation of sorption/desorption phenomena at the soil-water interface.

Statistical Analyses

Our findings based on batch and CFSTR laboratory experiments are substantiated by principle component analysis conducted to establish the inter-relatedness of soil parameters and the influence of soil parameters on the nature and extent of herbicide retention. The analysis confirms that crystalline iron oxide content, non-crystalline aluminum oxide content, total iron and aluminum content, and surface area play the most important role in the retention of ionogenic herbicides (2,4-D and quinmerac) and that these soil properties are more influential than pH and organic matter content. The analysis also shows the expected dependence of norflurazon retention on soil carbon.

Conclusions

Our study clearly demonstrates that in ultisols (or red clay soils) of NC Piedmont, herbicide properties other than hydrophobicity, and soil properties other than organic matter, texture, and acidity should be considered when evaluating ionogenic herbicide fate and transport. Polar ionogenic compounds possessing ligand donor groups (such as $-\text{COOH}$) can be retained in the mineral horizons of the ultisols via favorable electrostatic interactions and surface complexation with soil Al and Fe oxides. For neutral herbicides, partitioning to organic matter is expected to dominate.

For the soil types examined, it appears that in the absence of rapid microbial degradation 2,4-D and quinmerac are less likely to be retained in the uppermost soil horizon as compared with the lower horizons, while the opposite may be expected for norflurazon. Our results also suggest that norflurazon that migrates below the uppermost soil horizon is less likely to be attenuated in the subsoil and is hence more susceptible to leaching and groundwater transport. Furthermore, the nature of the herbicide-soil interaction is relatively weak for a significant mass of the herbicide attenuated by the soil matrix (sorbed on the soil), hence, precipitation or irrigation can easily transport (or leach) the “reversibly” retained fraction through the soil profile and potentially into groundwater. However, the mass that is entrapped within the soil matrix will likely prove more recalcitrant with respect to the susceptibility for leaching into groundwater. Additionally, herbicides that are transported to lower soil horizons where microbial activity is typically low may persist in the environment longer than expected. Therefore, a significant fraction of herbicide mass remaining in the uppermost soil horizon has a high susceptibility to leach into groundwater under intensive rainfall and irrigation.

RECOMMENDATIONS

Our results suggest that the leaching of non-ionic herbicides and pesticides in NC ultisols can be estimated by traditionally used soil parameters including soil organic matter content, acidity and texture. However, these same properties are insufficient to evaluate the leaching potential of ionogenic herbicides and pesticides in NC ultisols. For these herbicides, evaluation of extractable iron and aluminum oxide content may be necessary in order to accurately predict the fate and transport. Furthermore, both the ionic and neutral herbicides examined desorb relatively easily from the soil matrix of red clay soils, and thus have a high potential for leaching and persisting below the microbially active horizons and contaminating groundwater sources. In soil systems in which microbial degradation of the herbicide is not expected to be rapid, care should be taken in herbicide application (for agricultural operations, forestry, golf courses, and lawn and ornamental care) to vulnerable areas where groundwater quality is directly threatened by the quality of infiltrating water.

1. INTRODUCTION

1.1 Statement of the Issue

Agricultural operations and golf courses in North Carolina often apply organic agrochemicals (pesticides and herbicides) at or near land surface areas where ground water systems are replenished (ground water recharge areas). The resulting impact on the groundwater system is of immediate concern because groundwater is an essential resource for over 50% of North Carolina residents.

In North Carolina, understanding and evaluating pesticide fate has focused on the Coastal Plain with less attention directed at the Piedmont and mountain regions (Wade et al., 1997; Maas et al., 1995; 1992; Jennings, 1993; Jennings et al., 1991; Moreau and Danielson, 1990). In addition, most of the currently active monitoring wells maintained by NCDEHNR and North Carolina district of the United States Geological Survey (through the USGS-NCDEHNR Cooperative Agreement) are located in the Coastal Plain and relatively few wells are situated in the Piedmont and mountain regions of North Carolina (GW Branch, NCDEHNR, 1998). This attention to groundwater quality in the Coastal Plain is well justified because the groundwater has an increased susceptibility for deterioration due to the higher volume of anthropogenic activity (as measured by crop and livestock production and acreage of golf turf), the region's hydrogeology, and the presence of a larger number of aquifer systems.

Select counties in southern and central NC Piedmont (e.g., Union and Iredell) also have a large volume of anthropogenic activity and serve as important groundwater recharge areas. Although aquifers underlying the Piedmont (the surficial aquifer and the fractured bedrock aquifer) are less productive than those in the Coastal Plain, groundwater is an important source of water supply for small cities and industries and the primary source of water for farms and rural homes. Hence, it is important that groundwater quality is protected in the NC Piedmont. The detection of certain pesticides in regions of shallow groundwater in Iredell, Lincoln, and Rowan counties by Wade et al., (1997) emphasizes the vulnerability of Piedmont groundwater to contamination.

Systems and guidelines for evaluating pesticide fate developed from information based on commonly studied temperate soils have been successful for the Coastal Plain (McLaughlin et al., 1994). Generally, evaluations of soil susceptibility to contaminant leaching are based on the following soil properties: organic matter content, texture, and acidity. The NC Piedmont is dominated by heavy textured ultisols ("red clay soils"), acidic soils that have low organic matter, high iron, and high content of low activity clays (e.g., kaolinite), particularly in the subsoil horizons. The extremely small size of the clay and iron oxide particles, the reactivity of the electron deficient surface bound iron atoms, and the soil's potential for possessing variable charge make Piedmont red clay soils physically and chemically distinct from many of the soils of the coastal plain.

Different pesticide classes (e.g., hydrophobic organochlorines vs polar phenoxyacetic acids) will likely have distinct leaching potentials in these ultisols. It is our hypothesis that the leaching of hydrophobic compounds is likely to be governed by similar soil properties (soil organic matter content and texture) in red clay and other soils, while the leaching of polar/ionogenic compounds will potentially be influenced by soil iron and aluminum oxides, which are dominant in red clay

soils. Investigation of pesticide interactions in Piedmont soils should yield information necessary to adapt current successful models and guides for evaluating polar/ionogenic pesticide leaching and fate in NC red clay soils.

This research explores abiotic surface processes that contribute to the attenuation and mobilization of three polar/ionogenic herbicides, a widely-used group of agrochemicals in NC, in two common soils of the NC Piedmont, Georgeville and Appling soils. Currently, our knowledge of the chemical interactions of these compounds in whole red clay soils is limited. However, research on small organic ligands, similar in structure to commonly used herbicides and pesticides, and pure phase iron oxides (e.g., hematite, goethite, and other oxides typically found in red clay soils) has demonstrated the importance of sorption and transformation of polar/ionogenic organic compounds at the metal oxide-water interface (Biber and Stumm, 1994; Evanko and Dzombak, 1998; Torrents and Stone, 1991; Vasudevan and Stone, 1996; 1998). This lends support that similar interactions may occur with polar/ionogenic herbicides and red clay soils, and consequently may indicate that soil components other than organic matter, clay content, and acidity are important in assessments of pesticide fate.

1.2 Goals and Objectives

The goal of this research is to develop an understanding of abiotic interfacial processes that determine polar/ionogenic herbicide attenuation (via sorption and surface-assisted transformation) and mobilization (via desorption) through the soil profile in NC Piedmont ultisols. The objectives are to:

- (1) conduct laboratory experiments to examine the potential for sorption, desorption, and transformation of three herbicides, 2,4-dichlorophenoxyacetic acid (2,4-D), quinmerac, and norflurazon, (Figure 1) in two representative NC Piedmont ultisols, Georgeville and Appling soils, as a function of
 - ❖ soil depth, composition, and physical and chemical properties, and
 - ❖ herbicide molecular structure and physical-chemical properties.
- (2) evaluate the implications of the laboratory results for the prediction of polar/ionogenic pesticide fate in NC Piedmont soils.

1.3 Relevance

The U.S. EPA's Toxic Release Inventory (TRI) contains several pesticides that possess polar functional groups such as metribuzin, acifluorfen and the test herbicides that are the subject of this study. Repeated detection of these and other compounds in surface and ground waters, in the North Carolina Piedmont and nationwide, and knowledge of their potential toxicity, carcinogenicity, and/or endocrine disrupting capacity, emphasizes the urgency for an improved understanding of pesticide fate (Wade et al., 1997; USGS, 1995; EPA, 1990; Dietrich et al., 1988).

Persistent pesticides can reach groundwater as a result of direct transport or contaminate the soil by association with the solid matrix. The leaching of pesticides (and associated transformation products) from soils may result in a long-term source of groundwater contamination. It is

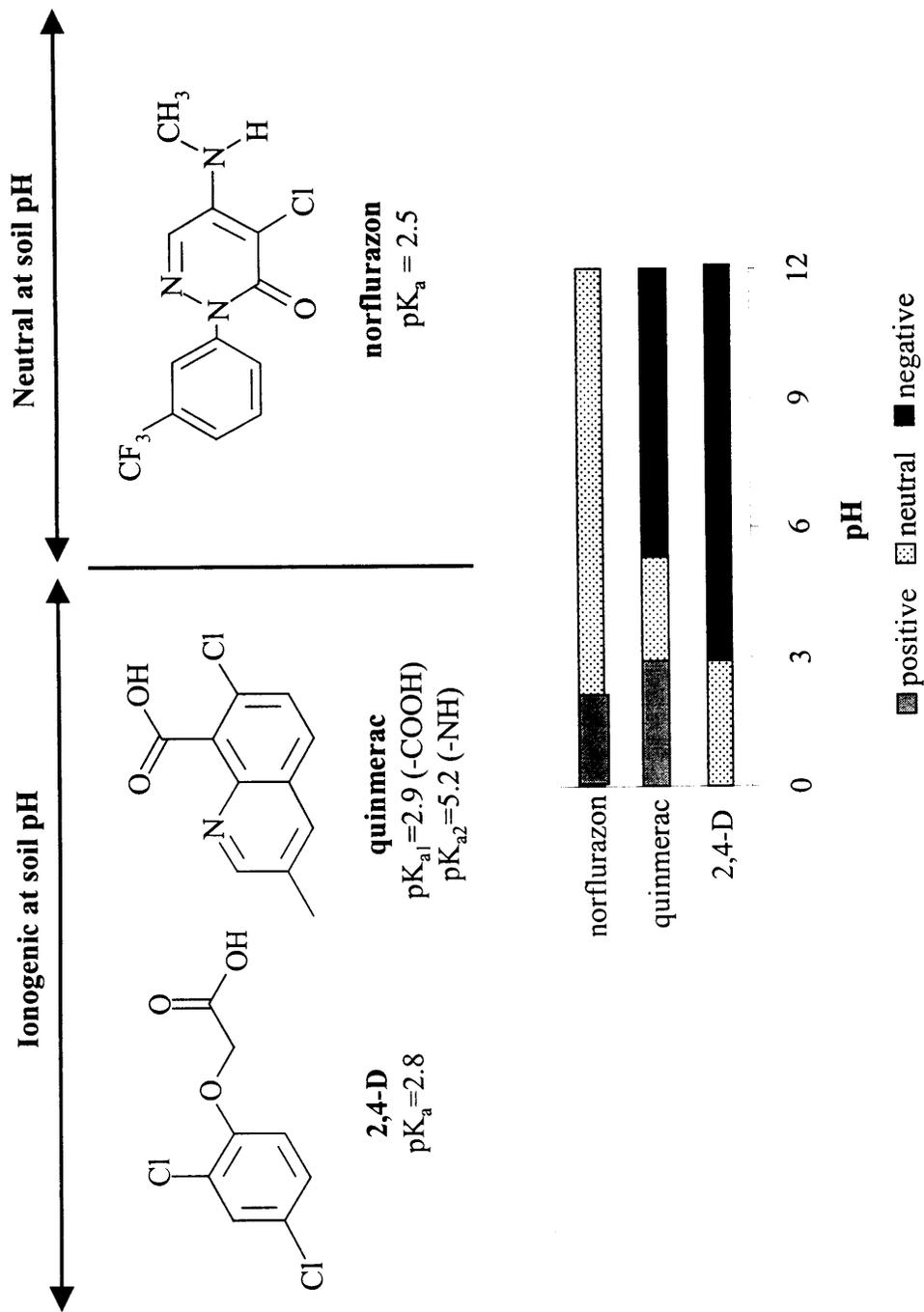


Figure 1. Molecular structures and the charging behavior of 2,4-D, quinmerac, and norflurazon.

therefore important to understand the role of surface processes in contaminant attenuation and mobilization. An understanding of these processes will contribute to better characterization of soil leaching potential for red clay soils of the NC Piedmont and improved management and regulation of pesticide use. It will also assist in the protection of groundwater recharge areas, the delineation of wellhead protection areas, and the identification of placement areas for buffer strips for pollution reduction.

1.4 Background

1.4.1 Composition and reactivity of soil iron oxides

The North Carolina Piedmont has a large array of iron oxide rich soils. Key soils in the felsic and mafic crystalline terrains include ultisols (Appling, Cecil, and Davidson soils) and alfisols (Enon, Mecklenburg, and Coronaca soils). In the Slate Belt, Herndon and Georgeville are the key soils, and in the Triassic Basin the key soils are Mayodan, Creedmoor, and White Store (Daniels, 1984).

Iron oxides (collective terms for oxides, hydroxides and oxyhydroxides) in the subsurface occur as discrete crystals, as coatings on clay silicates and humic substances, and as mixed gels (Sparks, 1995). With the exception of ferrihydrite ($\text{Fe}_{10}\text{O}_5 \cdot 9\text{H}_2\text{O}$), which is semi-crystalline, iron oxides commonly occur in distinct crystalline forms (Cornell and Schwertmann, 1996). The mineralogy, the degree of structural order, and the crystal size of the oxides found within a given soil setting depend on the moisture content, the temperature, the organic matter content, and the pH. Goethite ($\alpha\text{-FeOOH}$) has a high thermodynamic stability and is, therefore, the most frequently occurring form of iron oxide. Soils containing goethite occur ubiquitously and predominate in cool-to-temperate, humid climates. Hematite ($\alpha\text{-Fe}_2\text{O}_3$), the second most common oxide, is restricted to soils of warmer, subtropical and tropical, climates. Other forms, lepidocrocite ($\gamma\text{-FeOOH}$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and ferrihydrite, are less common. While the mineralogy of pure phase oxides is relatively simple, soil iron oxides are significantly heterogeneous with respect to mineralogy and purity (Barrow, 1987). In the United States, iron oxide rich soils (ultisols or "red clay" soils) are dominant in the southeast; in this region, hematite is often found in close association with kaolinite (Brady, 1990).

The structure and reactivity of the iron oxide surface determines the nature of interactions with the aqueous and solid phase subsurface components (Schwertmann and Taylor, 1982). In the presence of water, iron atoms at the surface complete their coordination shell of nearest neighbors by complexation with hydroxyl groups or water molecules. The protonation/deprotonation of these hydroxyl groups results in the development of surface charge and surface acid/base character. Depending on the pH and the ionic strength of the aqueous medium, the surface can develop a positive or negative charge and a corresponding surface potential, hence these oxide rich soils are commonly referred to as variable charge soils. This charging behavior has implications with respect to surface reactivity and the interaction of iron oxides with solutes and other solid components (Stumm, 1992).

The stable aggregation of oxidic soils is often attributed to the close association between iron oxides and clay silicates (Schwertmann and Taylor, 1982). Iron oxides are believed to interact with kaolinite and other silicates by coulombic and non-coulombic interactions (Schwertmann, 1988; Jepson, 1988). The association of iron oxides with clay silicates has been confirmed, by

electron micrographs, in both natural soils and in synthetically created oxide coatings (Cornell and Schwertmann, 1996). Coulombic associations occur as a result of interactions between the permanent negative charge on the clay silicates and the pH dependent positive charge on the iron oxides. These associations are, therefore, reversible with changes in pH. On the basis of X-ray photoelectron spectroscopy, it has been speculated that a chemical Fe-O-Si bond is responsible for the more stable coatings formed (Scheidegger et al., 1993).

It has been proposed that iron oxide coated sands are somewhat more heterogeneous in their adsorption properties than pure phase oxides (Kumar, 1996). The reactivity of the oxide/water interface is, therefore, dependent on the mineralogy of the iron oxide and the surface morphology and characteristics of the exposed surface. Due to the fact that iron oxides do not exclusively exist in the pure phase, it is important to understand the surface characteristics and reactivity of soil iron oxides as found in ultisols and other oxide rich soils.

1.4.2 Soil processes impacting contaminant attenuation and mobilization: Role of soil oxides.

Within the subsurface, a myriad of physical, chemical, and biological processes serve either to attenuate or to mobilize any contaminant. Of these, sorption and surface assisted transformations are important abiotic interfacial processes that function to *attenuate* (or diminish) organic contaminant movement through the soil column. Alternately, desorption, contaminant assisted surface dissolution, and contaminant assisted release of colloidal particles (from the immobile solid matrix) serve to *mobilize* (enhance) contaminant movement. It is important to note that sorption is often a precursor to surface dissolution, contaminant transformation, and colloid release; thus, it is central to understanding attenuation and mobilization (Herring, 1995; Torrents and Stone, 1991; Laha and Luthy, 1990; and LaKind and Stone, 1987).

Previous research has significantly advanced our understanding of how organic matter and clay fractions of the subsurface influence contaminant fate (Leboeuf and Weber, 1997; Xing and Pignatello, 1997; Johnston, 1996; Weber and Huang, 1996; Weber and Miller, 1989; Chou et al., 1979; Means et. al 1982; Karickhoff, 1981; Karickhoff et al., 1979; Savage and Wauchope, 1974; and Felsot and Dahm, 1979). Research efforts to determine the interactions between neutral hydrophobic organic compounds (NHOCs) and metal oxide surfaces is also advancing (Mader et al., 1997; Perlinger et al., 1993; Schwarzenbach et al., 1993; Backus, 1990; Fowkes, 1964).

Current understanding of polar/ionogenic organic compound (P/IOC) interaction with metal oxides is largely derived from research conducted using small organic ligands (important substructures of P/IOCs and dissolved natural organic matter) and pure phase oxides (Vasudevan and Stone, 1998; 1996; Ludwig and Schindler, 1995; Biber and Stumm, 1994; Stone et al., 1993; McBride and Kung, 1991; Stumm et al., 1980; Kummert and Stumm, 1980; Rubio and Matijevic, 1979; Davis and Leckie, 1978; Parfitt et al., 1977a;1977b). A few studies have been conducted using the larger P/IOCs, particularly herbicides (Schwandt et al., 1992; Watson et al., 1973) and fewer studies have examined the interaction between P/IOCs and ultisols or minerals coated with iron oxides (Kumar, 1996; Kumar and Fish, 1996; Streck, 1985). A detailed discussion of soil processes of relevance to contaminant fate in iron oxide rich soils is provided below.

(Ad)sorption is, often, a required first step to subsequent interfacial processes such as surface dissolution and sorbate transformations. The physical-chemical characteristics and high surface area of soil oxides and clay silicates make them effective sinks for anions, cations, and other organic ligands (sorbates). With respect to the oxide surface, the surface bound oxygen atom of the hydroxyl group (-OH) can interact with protons and other metal ions in aqueous solution. The underlying surface metal ion can act as a Lewis acid and exchange the surface bound OH group for other organic and inorganic ligands in solution. Studies of adsorption onto pure-phase oxides have followed three main themes: (1) measurement of the extent of adsorption of inorganic and organic compounds (including natural organic matter, NOM) as a function of surface and aqueous medium characteristics (Cornell and Schwertmann, 1996; Tipping, 1981; and references cited); (2) determination of the structure of the surface complex using spectroscopic techniques (review by Brown, 1990); and (3) the development of surface complexation models (SCMs) for modeling and predicting adsorption at the oxide/water interface (Filius et al., 1997; Kumar, 1996; Dzombak and Morel, 1990).

The adsorption of inorganic anions and cations onto soil oxide surfaces has been widely examined (Cornell and Schwertmann, 1996 and cited references). With respect to the adsorption of organic compounds, several studies have examined the interaction of organic acids, amines, sugars, fatty acids, phenols, chelating agents, pesticides, humic substances, and neutral hydrophobic organic compounds with metal oxides (Mader et al., 1997; Vasudevan, 1996; Cornell and Schwertmann, 1996; Murphy et al., 1990; Schwant et al., 1992; Backhus, 1990; Tipping, 1981; Watson et al., 1973). These studies have helped ascertain that both physical and chemical forces are involved in adsorption. Physical forces include van der Waals and electrostatic forces, while chemical forces include covalent- and hydrogen- bonding. Additionally, these studies have helped identify the physical-chemical properties of the surface, the sorbate, and the aqueous medium that affect sorption phenomena. Interaction between a non-polar organic compound and soil organic matter results from van der Waal's forces, while attraction between a cation and a negatively charged soil surface results from favorable electrostatic forces. The complexation of phosphate to the soil-bound iron is an example of surface complexation via covalent bonding. Soil pH, charge, organic matter content, and presence of accessible iron and aluminum atoms are examples of some soil properties that play an important role in solute sorption to soils.

Most of the studies cited above have been conducted in batch systems using single sorbate-pure phase oxide systems and have significantly advanced our understanding of fundamental processes at the oxide/water interface. Fewer studies have, however, examined sorption behavior organic ligands on minerals with oxide coatings or whole soils (Kookana and Naidu, 1998; Roden and Zachara, 1996; Szecsody et al., 1994; Zachara et al., 1989; Streck, 1985) and explored competition and displacement effects in multiple solute systems (Ali and Dzombak, 1996; Gu et al., 1996; Vasudevan and Stone, 1996; Balistrieri and Murray, 1987). These topics, although more complex than the simple systems commonly studied, are more closely related to actual soil systems.

In addition to sorption, desorption and associated sorption/desorption kinetics is important from the perspective of contaminant fate and mobility. Short contact times (resulting from storm-related resuspensions, soil erosion, and fast groundwater infiltration rates) may not always

expose the solid matrix to the contaminant for periods of time sufficient to attain sorption/desorption equilibrium (Roberts et al., 1986; Ball and Roberts, 1991). The comparative rates of sorption and desorption determine the extent of contaminant attenuation or mobilization through the soil column.

Traditionally, the dissolution of oxide surfaces has been examined from the perspective of the buffering of acidic deposition, soil formation, iron cycling, and the removal of corrosion products (Kraemer and Herring, 1997; Cornell and Schwertmann, 1996 and references cited). Solution pH and the presence of organic ligands strongly influence the potential for and kinetics of mineral dissolution (Furrer and Stumm, 1986). From the standpoint of contaminant fate, dissolution of the soil matrix results in the release of both the surface metal ion and the adsorbed compound into solution; thus, contaminant speciation is altered and consequently so are the contaminant physical-chemical properties that govern its behavior in soil systems. Although sorption of a compound portends attenuation, subsequent dissolution can release the compound into solution.

Organic compounds are, in general, susceptible to chemical and biological transformations. The molecular structure of polar/ionogenic organic compounds, in particular, enhances this susceptibility. P/IOCs in aqueous solution can be transformed by the following abiotic reactions to yield products of increased or decreased toxicity: hydrolysis, oxidation-reduction, isomerization, and photochemical reactions. Oxide surfaces are known to promote many of these reactions (McBride, 1994; Larson and Webber, 1994; Torrents and Stone, 1994, 1991; Schwarzenbach et al., 1993). Thus, knowledge of the rate of compound disappearance and product identification is crucial to understanding contaminant fate.

2. APPROACH

The potential for the sorption, desorption, and transformation of the three test herbicides within the soil column of Appling and Georgeville soils was explored in well-controlled laboratory experiments. The experimental work followed three phases. In Phase I, soils samples with no exposure to the test herbicides were obtained and soil composition and physical-chemical properties were ascertained as a function of soil depth (0-200cm). In Phase II, batch studies were employed to identify the potential for herbicide sorption and transformation as a function of soil depth. The extents of these processes were then evaluated as a function of soil composition and physical-chemical properties in order to understand the nature of herbicide-soil interactions and identify herbicide structural criteria and soil properties influencing these interactions. In Phase III, continuous stirred flow tank reactor (CFSTR) studies were employed to confirm the processes observed in batch studies and examine sorption and desorption phenomena under non-equilibrium scenarios. Statistical analyses were conducted at each stage to evaluate the implications of our laboratory results for the prediction of herbicide fate in NC Piedmont soils.

3. SOIL COLLECTION AND CHARACTERIZATION

As mentioned earlier, iron-oxide rich red clay soils are the subject of this research. A detailed discussion of the composition and reactivity of soil iron oxides is found in section 1.4.1.

3.1 Methods

Samples of two common soil series of the North Carolina Piedmont, Georgeville and Appling, were obtained from Duke Forest at gates 11 and 12, respectively. These soils were located under hardwood (Georgeville) and coniferous (Appling) tree stands and had received none of the test herbicides prior to the study. Each soil series was sampled from a freshly dug pit at five depths, from 0 to 200 cm for Georgeville and 0 to 170 cm for Appling, to represent all horizons as differentiated by visual and/or textural variations in the soil profile. After collection, the soils were air dried, ground to pass a 2 mm sieve, stored in sealed plastic containers at room temperature, and oven dried at 105°C prior to use for all studies except where indicated. Table 1 lists the soil properties measured, the method used, and rationale for evaluating each parameter. Detailed description of the methodology is provided below.

General mineralogical characterization of clay minerals from selected soils (G2-5, A2 and A5) was conducted by x-ray diffraction (XRD) analysis (Phillips Electronic Instruments XRC-3000) of soil clay fractions (particles < 2 µm diameter) that had been cleaned of organic matter and Fe and Al oxides and saturated with Mg following the procedure described in the Methods of Soil Analysis (Klute, 1986). Additional general soil characterization was conducted primarily by standard methods described in the Methods of Soil Analysis (Sparks, 1996) and Soil Sampling and Methods of Analysis (Carter, 1993), and included pH in 1:1 soil:water slurry (pH_w) and in 1:1 soil:0.01 M CaCl₂ slurry (pH_s), electrical conductivity by saturated paste extract method, N₂BET surface area (Quantichrome Monosorb), effective cation exchange capacity at the pH of the soil (ECEC) by summation of exchangeable bases (Al, Ca, K, Mg, Mn and Na) compulsively exchanged with 0.1 M BaCl₂, available NH₄-N and NO₃-N by 2 M KCl extraction of fresh soil and automated colorimetric analysis (Traacs 800), total carbon (C) and nitrogen (N) by combustion (PerkinElmer 2400 Series II CHNS/O analyzer), particle size by the pipet method, total elemental analysis by HF digestion, “free” (operationally defined as crystalline) Al, Fe and Mn oxides by extraction with sodium citrate-dithionite-bicarbonate at 80°C (DCBAI, DCBFe, DCBMn), “amorphous” (operationally defined as poorly- or non-crystalline) Al, Fe and Mn by extraction with acidified ammonium oxalate in the dark (AAOAl, AAOFe, AAOMn). Unless otherwise indicated, all elemental analyses for the above-mentioned tests were conducted by inductively coupled or directly coupled plasma-mass spectrometry (I/DCP-MS) by Duke University Earth and Ocean Sciences.

Additionally, water extractable phosphorus (P) was determined by equilibrating 4 g soil with 40 ml deionized water on a reciprocating shaker for 24 h, extraction through 0.2 µm polycarbonate membrane, and analysis by ICP-MS. Orthophosphate sorption capacity (P_{max}) was determined by fitting the sorption isotherms to the Langmuir equation (Sposito, 1989). For the isotherms, 0.5 g soil was equilibrated 24 h on an end-over-end shaker with 10 ml of one of eight solutions ranging from 0 to 200 mg P/l, filtered through 0.2 µm polycarbonate filter, and analyzed for final orthophosphate concentration using a modified molybdate blue method (Murphy and Riley, 1962; Watanabe and Olsen, 1965).

Table 1. Soil characterization parameters and their roles in studying herbicide-soil interactions.

Parameter	Method	Potential role
pH	1:1 soil:water slurry	affects herbicide speciation and soil mineral surface charge
Effective cation exchange capacity	compulsive cation exchange with 0.1M BaCl ₂	yields types and amounts of exchangeable cations
Electrical conductivity	saturated paste extraction	describes soil salinity and soil solution ionic strength, which influences sorption processes
Surface area	N ₂ BET Surface Area analyzer	gives overall area of mineral surfaces available for herbicide sorption
Soil texture (% sand, silt and clay)	pipet method with chemical dispersion	gives proportion of soil mineral particle sizes, of which clay is most reactive in sorption/transformation processes
Total carbon (C)	combustion	total carbon is most likely to be present as organic matter, which is considered a primary sink for hydrophobic compounds
Total nitrogen (N)	combustion	nitrogen content describes soil nutrient status, and along with total carbon provides insight into the type and degradation potential of soil organic matter
Available N (NH ₄ -N and NO ₃ -N)	2M KCl extraction of fresh soil	describes soil nutrient status, which affects soil biological activity and in turn the degradation of organic matter and herbicides
Available phosphorus (P)	water extraction	
Total elemental composition	HF digestion with DCP/ICP analysis	broadly describes soil mineralogy; soil minerals have varying influences on the type and rate of herbicide retention
"Free" iron (Fe), aluminum (Al) and manganese (Mn) oxides	extraction with sodium citrate, bicarbonate, and dithionite	characterizes type and composition of crystalline and non-crystalline Fe, Al and Mn oxides, which are considered key soil components involved in herbicide retention
"Amorphous" iron (Fe), aluminum (Al) and manganese (Mn) oxides	extraction with acidified ammonium oxalate in the dark	
Maximum orthophosphate sorption capacity	determined from Langmuir fitting of a sorption isotherm using 24h equilibration	quantifies the potential number of sites available on soil surfaces for PO ₄ ⁻ or compounds of similar structure

3.2 Results and Discussion

Soil composition and physical-chemical properties of our Appling and Georgeville soils as a function of soil depth are found in Tables 2 and 3 and Figures 2-5. Appling soils have a yellow B horizon, while the Georgeville soils have a distinctly red B horizon. The visual characteristics indicate differences between the type of iron oxides present in the two soils. The yellow color is usually indicative of the presence of goethite, while the red color is characteristic of hematitic soils.

3.2.1 Soil Texture, Surface Area and Mineralogy

In the Appling (A) soils the sand content decreased with depth, the silt content remained relatively constant, and the clay content increased with depth. Based on the percentage of sand, silt, and clay, the upper two horizons (0-70cm) were classified as sandy loams and the lower horizons as clay soils (Table 2, Figure 2). The Georgeville (G) soils decreased in sand and increased in clay content up to a depth of 152cm; the uppermost horizon was classified as a silt loam and subsequent horizons (G2-G4) as clay soils. The lowest horizon evaluated (G1, 152-203cm), showed an increase in sand and silt content and a decrease in clay content and was classified as a silt loam (Figure 2). We believe that the observed texture for G1 is not an experimental artifact of particle cementation because we also observed a dramatic decrease in the total Al content (Table 3) which is consistent with a decrease in the soil clay content. Additionally, this soil is closest to the underlying C horizon, where weathering of parent material may be less extensive than in the upper horizons. For both the A and G soil profiles, the trend observed with respect to N₂BET surface area (a general increase in surface area with soil depth) was consistent with the measured soil textures (Figure 2); soils with higher clay content possessed higher surface areas. XRD analyses of the soils revealed that both A and G soils had a dominant kaolinite content at soil depths between 40-200cm.

3.2.2 Soil composition and physical-chemical properties

Soil moisture increased with depth up to 127cm for A and 152cm for the G soils and then decreased (Table 2). Total carbon (C) was low in all soils with the highest content observed in the uppermost horizons (Figure 4). Total N, organic N, NH₄-N, and NO₃-N was generally low in all soils, as was total P and water extractable P in all soils with the exception of A5 (Table 2-3). Soil pH_w was between 4.9 and 5.4 for the A soils and between 4.5-5.4 for the G soils. Soil ECEC generally increased with depth for both soils. P_{max} generally increased with soil depth and decreased in the lowest horizons evaluated, A1 and G1.

Both A and G soils have a high iron and aluminum content (Table 3). The total iron (Fe) and aluminum (Al) generally increased as a function of depth for the A and G soils, and decreased in the lower most Georgeville horizon, G1 (Figure 3). Visually, the observed trends mirror those observed for surface area and clay content, as expected (Figure 2).

3.2.3 Extractable Soil Oxides

“Free” or crystalline iron oxides may be operationally defined as DCB extractable iron oxides, while “active” or poorly crystalline iron oxides may be quantified using AAO extraction. Likewise, DCB extractable aluminum oxides represent the poorly ordered high surface area crystalline phases, while the AAO extractable oxides may be defined as the non-crystalline phase. We found that the extractable Fe and Al oxides content as a function of depth closely

Table 2. Selected physical and chemical properties of Georgeville and Appling soils.

Soil (horizon)	Depth	Moisture content	pH		Texture			Textural Class	ECEC	N ₂ BET		Organic C	Organic N	NH ₄ -N	NO ₃ -N	Water extractable P
			in water	in 0.01 M CaCl ₂	Sand	Silt	Clay			Surface Area	Organic C					
	-----cm-----	----%---							-cmol/kg-	-m ² /g--	-----%-----			-----mg/kg-----		
Georgeville Series																
G1 (BC)	152 - 203	35.54	4.51	3.98	8.65	68.39	22.97	Silt loam	6.88	28.20	0.12	0.008	0.76	1.54	0.03	
G2 (B)	94 - 152	39.68	5.19	3.94	3.34	38.04	58.62	Clay	7.22	41.90	0.17	0.013	2.00	0.46	0.04	
G3 (B)	69 - 94	37.69	5.30	4.20	3.80	36.33	59.87	Clay	5.80	39.11	0.19	0.018	0.37	nd ^H	0.01	
G4 (B)	43 - 69	28.02	5.36	4.25	6.95	39.78	53.27	Clay	5.30	36.71	0.26	0.024	0.31	nd	0.04	
G5 (A)	0 - 30	14.64	4.91	3.97	18.75	56.55	24.70	Silt loam	2.10	13.26	0.70	0.040	0.64	0.40	0.03	
Appling Series																
A1 (B)	127 - 173	24.29	4.93	3.80	32.17	24.25	43.58	Clay	6.55	30.43	0.09	0.011	0.19	0.44	0.04	
A2 (B)	89 - 127	28.69	5.04	3.88	27.34	24.07	48.59	Clay	6.50	37.48	0.12	0.013	0.17	nd	0.07	
A3 (B)	69 - 89	20.14	5.16	4.09	35.14	18.78	46.07	Clay	5.19	32.69	0.13	0.012	0.23	nd	0.07	
A4 (E)	38 - 69	8.60	5.38	4.36	61.45	23.50	15.05	Sandy loam	1.01	6.79	0.10	0.008	0.19	nd	0.06	
A5 (A)	3 - 13	7.62	5.25	4.26	73.60	21.03	5.37	Sandy loam	0.48	1.57	0.15	0.008	0.38	nd	10.92	

^Hnd=not detected.

Table 3. Total elemental analysis by HF digestion of Georgeville and Appling soils.

Soil	Al	Ba	Ca	Cr	Cs	Cu	Fe	K
-----mg/kg-----								
G1	106864	179	310	98	1.37	69.66	64686	5009
G2	141911	100	330	128	2.30	67.81	84826	2991
G3	130499	129	389	105	2.91	64.51	75173	3894
G4	125743	224	490	109	3.41	60.36	70236	8303
G5	63437	201	955	79	3.16	30.40	33895	5876
A1	126973	338	252	30	4.35	9.56	40459	11972
A2	118171	200	308	32	4.03	9.46	39110	7122
A3	99892	220	493	37	4.82	9.33	36384	7703
A4	29532	112	511	23	2.25	4.76	10137	2841
A5	11487	66	478	12	1.00	4.09	3295	1711
<hr/>								
	Mg	Mn	Na	Ni	P	Pb	Ti	Zn
-----mg/kg-----								
G1	4107	1115	184	37.94	466.09	7.07	9604	59.27
G2	2793	987	151	47.91	414.44	9.37	11084	66.42
G3	2679	1051	211	37.91	301.95	9.51	11563	60.80
G4	2887	1262	330	40.92	319.33	9.96	12903	67.98
G5	1843	3621	1047	20.96	260.77	9.90	13041	51.14
A1	2390	787	171	4.37	136.58	12.57	5476	46.30
A2	1776	929	148	5.54	112.41	11.72	5716	46.19
A3	1813	838	168	7.33	102.72	10.97	6647	48.62
A4	592	1263	149	nd*	86.02	8.38	6606	36.60
A5	169	1258	124	nd*	91.09	7.99	4378	22.12

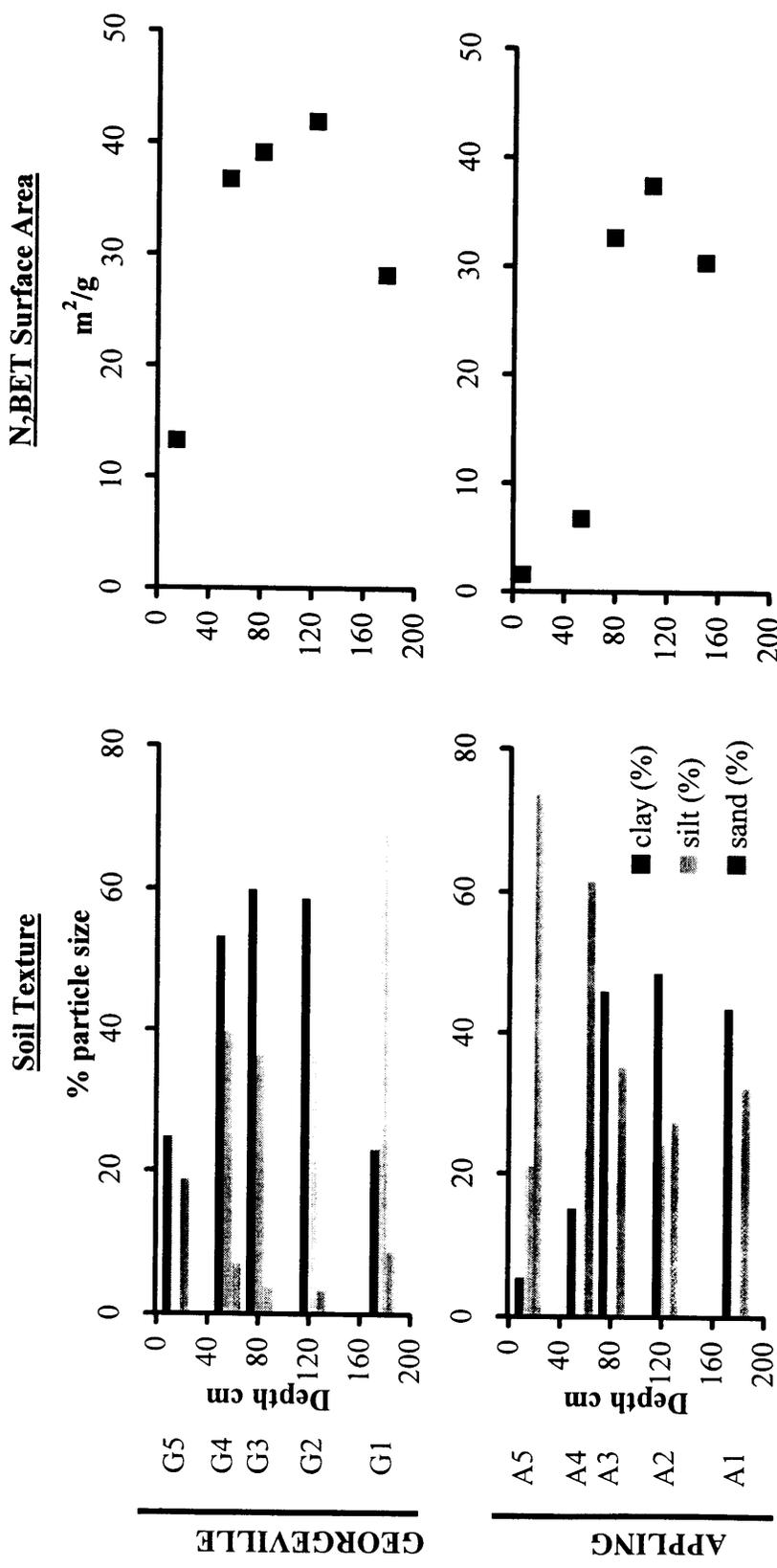


Figure 2. Soil texture (% sand, silt and clay) and N₂BET surface area of Georgeville and Appling soils.

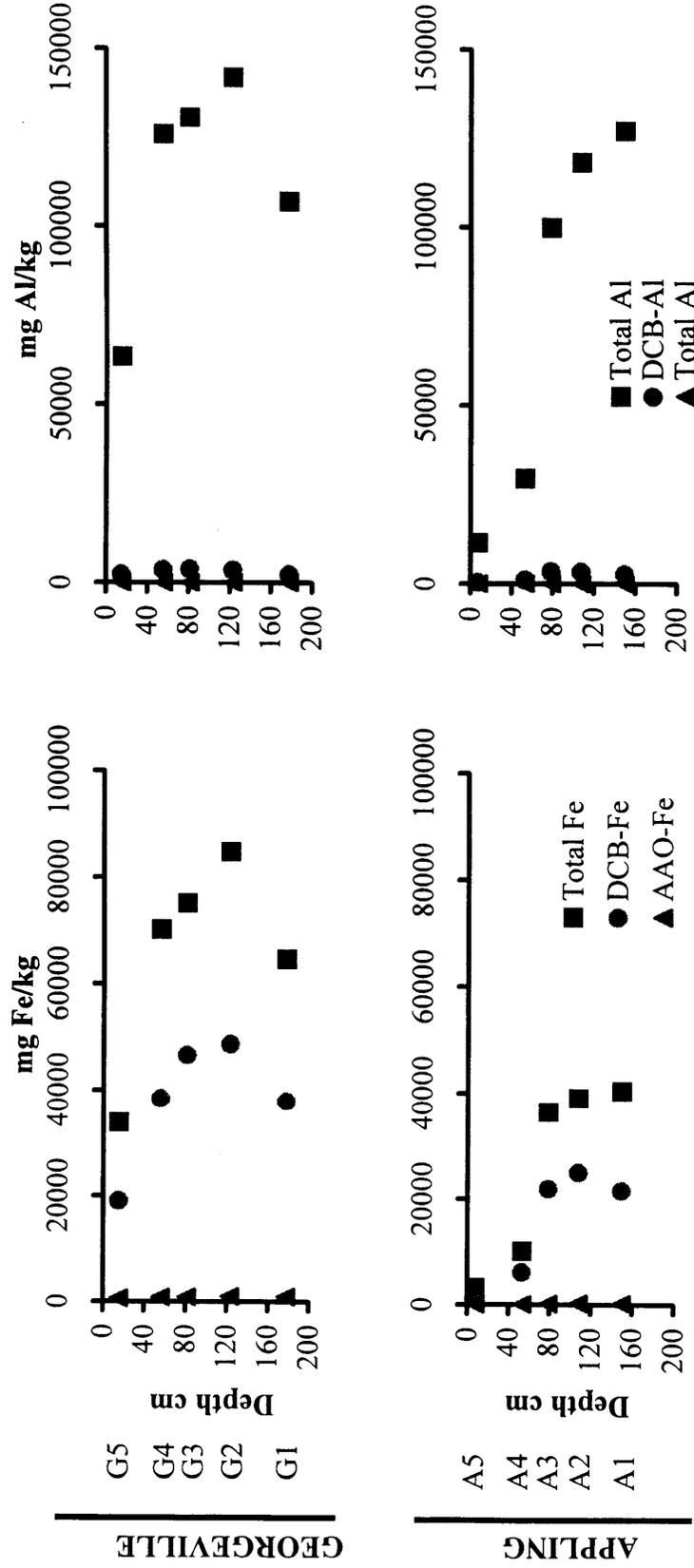


Figure 3. Total and extractable Fe and Al in Georgeville and Appling soils.

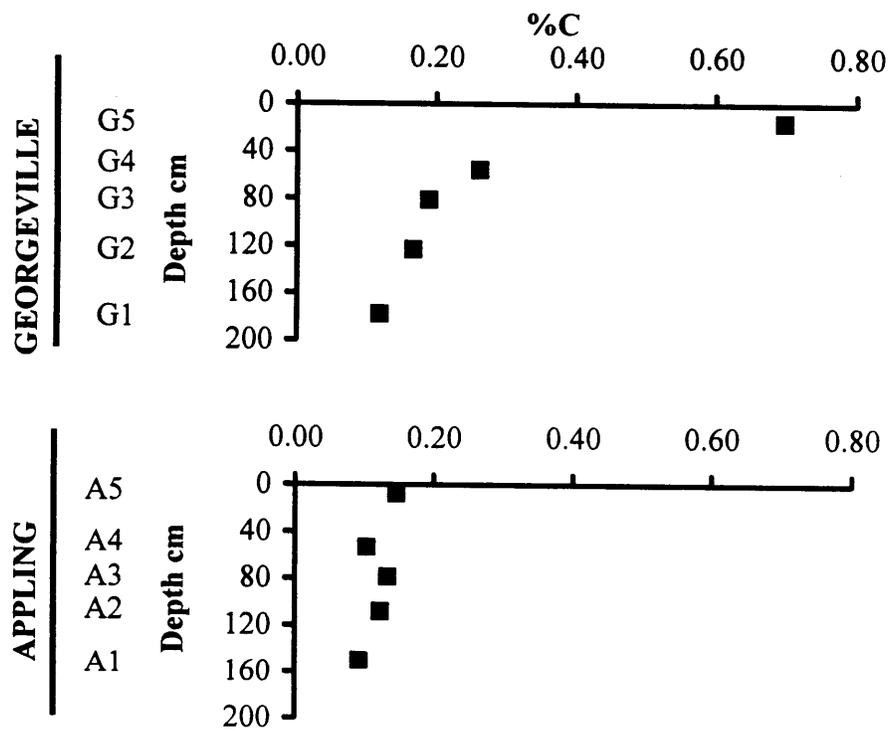


Figure 4. Total carbon (C) in Georgeville and Appling soils.

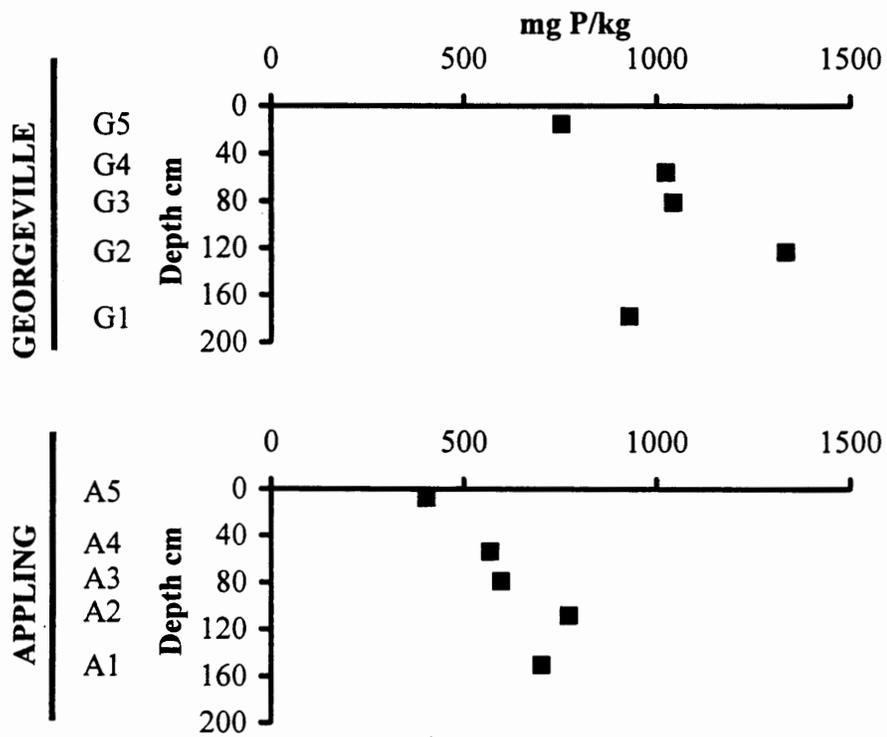


Figure 5. Phosphate sorption capacity (P_{max}) for Georgeville and Appling soils.

follows the same trend as the total Fe and Al content (Figure 3, Table 4). DCB extractable oxides constitute 50-60% of total Fe and 2-4% of total Al, while AAO extractable oxides constitute 0-6% total Fe and 0-3% total Al (Figure 3). These findings suggest that “free” or crystalline iron oxides dominate both A and G soils.

DCB-Mn showed a distinctly different trend; there was a general decrease in concentration with depth, consistent with a decrease in total Mn with depth (Tables 3-4). One difference discerned between A and G soils is that while DCB-Mn in G soils was between 6-8% of total Mn, DCB-Mn in A soils was only between 0.5-2.5% of total Mn. AAO-Mn was below the detection limit in most soils (Table 4). Unlike the extractions Al and Fe oxides, DCB- and AAO- extractions are not used to differentiate the “type” of manganese oxide.

Table 4. Extractable Al, Fe and Mn in Georgeville and Appling soils.

Soil	Al				Fe				Mn			
	DCB		AAO		DCB		AAO		DCB	AAO		
-----mg/kg [†] -----												
Georgeville												
G1	2485	(2.3)	843	(0.79)	38008	(59)	985	(1.5)	58	(5.2)	4	(0.34)
G2	3660	(2.6)	1110	(0.78)	48709	(57)	1031	(1.2)	59	(6.0)	bd [‡]	
G3	3954	(3.0)	933	(0.71)	46624	(62)	914	(1.2)	64	(6.1)	bd	
G4	3754	(3.0)	931	(0.74)	38542	(55)	851	(1.2)	74	(5.9)	12	(0.95)
G5	2456	(3.9)	585	(0.92)	19162	(57)	597	(1.8)	320	(8.8)	229	(6.3)
Appling												
A1	2770	(2.2)	795	(0.63)	21646	(54)	215	(0.53)	6	(0.78)	bd	
A2	3504	(3.0)	880	(0.74)	25085	(64)	277	(0.71)	6	(0.65)	bd	
A3	3571	(3.6)	725	(0.73)	21942	(60)	181	(0.50)	4	(0.53)	bd	
A4	1161	(3.9)	216	(0.73)	6188	(61)	53	(0.53)	15	(1.2)	7	(0.56)
A5	512	(4.5)	307	(2.7)	1360	(41)	80	(2.4)	31	(2.5)	39	(3.1)

[†]Numbers in parentheses are percentages of total Al, Fe, or Mn by HF digestion.

[‡]bd=below detection.

4. BATCH STUDIES OF HERBICIDE-SOIL INTERACTION

4.1 Methods

Sorption studies for 2,4-D, quinmerac, and norflurazon were conducted from 0 to 144 h using batch equilibration with 15 ml polystyrene centrifuge tubes as batch reactors. In each reactor, oven-dried soil was pre-equilibrated overnight with deionized (DI) water, after which an aliquot of herbicide was added to give a final volume of 10 ml and herbicide concentration of 10 mg/l. Soil:solution loadings were selected to normalize all soils approximately on the basis of surface area: 100 g/l for G1-G4 and A1-A3, 300 g/l for G5, and 500g/l for A4 and A5. The batch reactors were continuously shaken for the duration of the experiment. All experiments were conducted at soil pH.

Preliminary experiments for determining the appropriate sampling technique evaluated the change in soil:solution ratio with consecutive slurry sampling, and revealed that a significant change in soil:solution occurred with continued sampling of a reactor. Based on these preliminary investigations, kinetic batch sorption studies were designed so that for each herbicide-soil combination, three replicate batch reactors were sacrificed for each time point including 0, 1, 6, 24, 48, and 144h. For 2,4-D batch studies with soils, additional time points were also included: 0.5, 2, 4, 12, 72, 96, and 120 h. To probe the role of individual soil minerals in herbicide retention, similar sorption studies were conducted using 10g/l of pure phase oxides hematite (J.T. Baker), goethite (Bayer #940 goethite), (γ -aluminum oxide C (Degussa), and cleaned Na-saturated kaolinite (KGa-1b, Source Clay Minerals Repository, MO).

At the predetermined time point, sample pH was measured and samples were filtered through a 0.2 μm polycarbonate membrane and analyzed by HPLC with DAD detection (Hewlett Packard Series 1100) at 1 ml/min flow rate on a Zorbax SBC8 5 μm 15 cm x 0.46 cm column with matching guard column. Mobile phases and other conditions varied for each herbicide: (2,4-D) 65% MeOH:35% 0.017 M H_3PO_4 (pH 2.27), 25 μl injection, 234 nm detection; (quinmerac) 65% ACN:35% 0.017 M H_3PO_4 (pH 2.27), 10 μl injection, 236 nm detection; (norflurazon) 65% ACN:35% DI H_2O , 15 μl injection, 238 nm detection.

4.2 Results and Discussion

Results from the batch experiments are shown in Figures 6 and 7. In all cases, the herbicide was stable in blank solution up to 144 h, hence, herbicide loss to reactor walls or degradation was excluded. In the presence of soil, we observed a rapid loss of 2,4-D and quinmerac from soil solution; the extent of loss reached an apparent plateau at 24-48 h in all layers with the exception of the uppermost layer. For norflurazon, little herbicide loss was observed in all but the uppermost horizons, A5 and G5 (Figure 6-7). We concluded that loss from solution was surface facilitated. The observed plateau likely indicates that microbial degradation does not contribute significantly to the loss from solution. We believe that the loss was primarily due to sorption because we observed desorption in the CFSTR studies (see section 5). Furthermore, we were unable to detect any UV active degradation products in soil solution. While this study focuses on abiotic surface processes, biotic processes were not intentionally inhibited by γ -irradiating or autoclaving the soils. This approach was based on a decision to preserve soil mineralogy and composition. Our results suggest that biotic contribution to herbicide loss in most horizons was small or negligible; however, some biological degradation of the test herbicide was possible in the uppermost horizons at long equilibration periods.

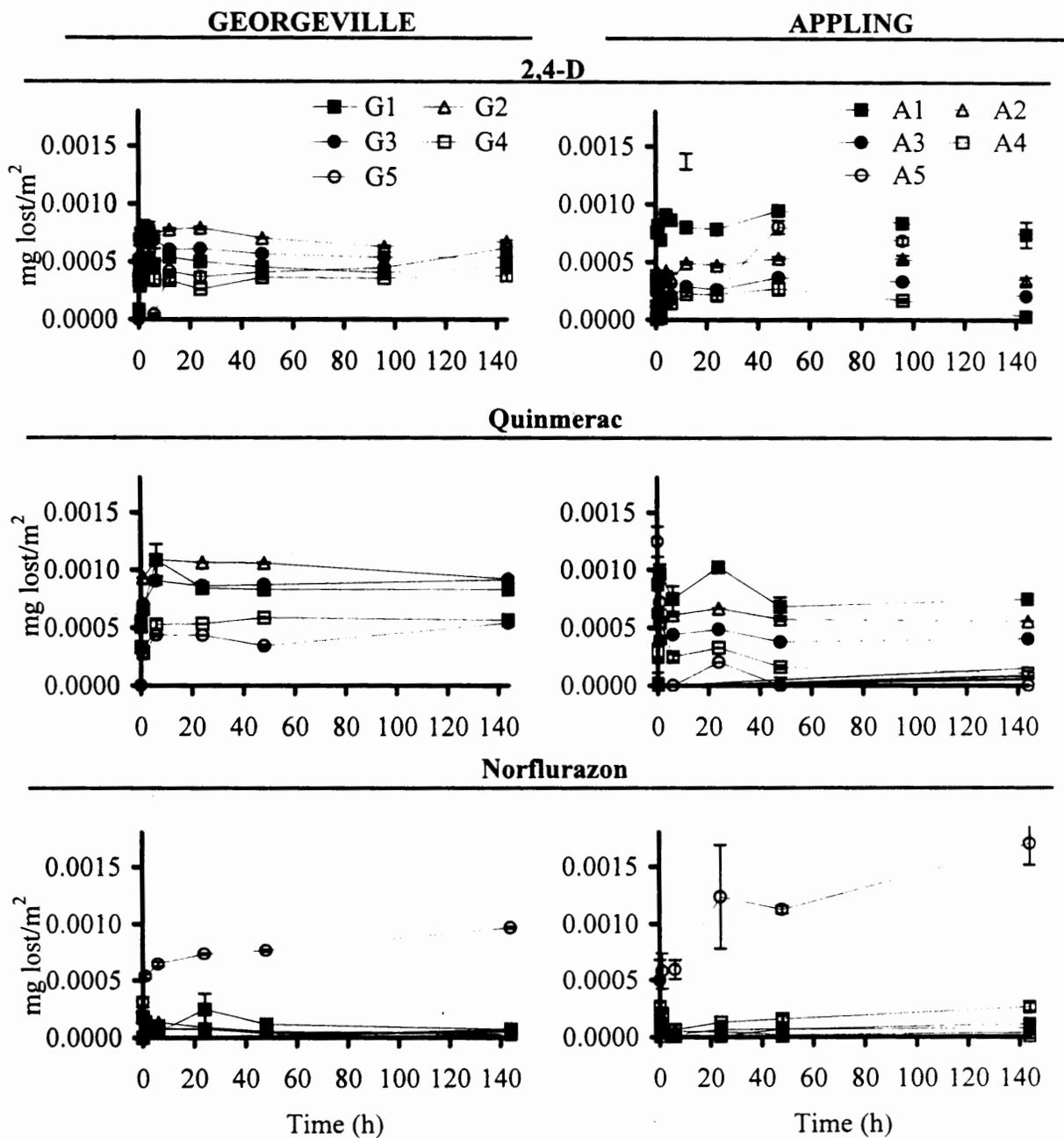


Figure 6. Loss of 2,4-D, quinmerac, and norflurazon (10 mg/l) from soil solution as a function of time in various depth samples of Georgeville and Appling soils. Loss was examined in batch reactors at soil pH and the following soil: solution loadings- 100g/L for G1-G4 and A1-A3; 300g/L for G5; 500g/L for A4 and A5. The extent of sorption expressed as mg lost/m² accounts for differences in surface areas of the soil samples.

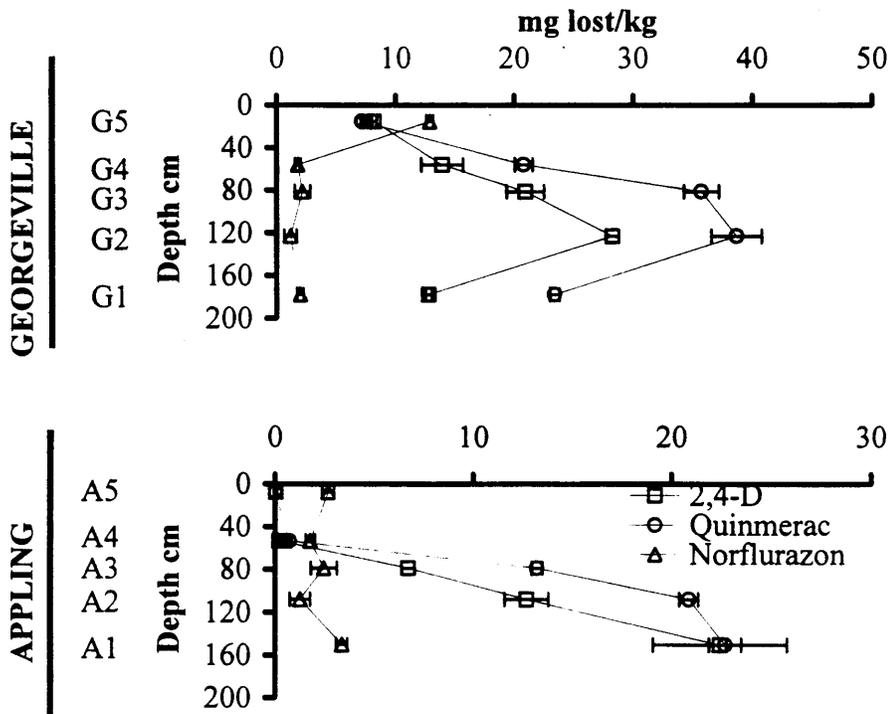


Figure 7. Loss of 2,4-D, quinmerac, and norflurazon (after 144 h equilibration) from the soil solution of Georgeville and Appling soils as a function of soil depth. Loss was measured in batch reactors at soil pH. Loss is expressed in mg/kg to facilitate comparison with other soil parameters expressed with the same units.

Extent of herbicide sorption at 144 h as a function of soil depth is depicted in Figure 7. Quinmerac showed the greatest sorption in the low organic matter-containing layers of both soil profiles, followed by 2,4-D. Norflurazon sorption in both A and G soils was significant only in the uppermost organic-matter containing soil horizon. For 2,4-D and quinmerac, the extent of sorption as a function of depth followed trends similar to total and DCB extractable Fe and Al (Figure 3); for the A soils sorption increased as a function of depth and for G soils sorption increased up to G2 and then decreased in G1. This trend was also consistent with that observed for P_{\max} (Figure 5). Correlations between individual soil properties and between herbicide sorption and soil properties were evaluated using a series of simple linear regressions (Table 5 and Section 6). These correlations indicate that clay content, surface area, total Fe and Al content, crystalline iron oxide (DCB-Fe) and non-crystalline aluminum oxide content (AAO-Al), and P_{\max} most strongly influenced the extent of 2,4-D and quinmerac sorption. Norflurazon sorption was influenced by total soil carbon. *Details of the statistical analyses are found in Section 6.*

4.2.1 Speculated herbicide-soil interactions

2,4-D and quinmerac are ionogenic compounds that show a distinct charging behavior as a function of pH (Figure 1). Additionally, they possess ligand donor groups (-COOH and heterocyclic N) capable of interacting with metal ions. Given that 2,4-D and quinmerac sorption was strongly related to extractable Fe and Al oxide content and that soil Al and Fe oxides were expected to carry a net positive charge at the measured soil pH, we infer that sorption occurred primarily via favorable specific and nonspecific electrostatic interactions between the herbicide anions and the positively charged surface sites. Furthermore, surface complexation involving the -COOH group and the surface metal ions, Al and Fe likely occurs to a lesser extent (Figure 8). Phosphate sorption to soils is known to occur via complexation to surface metal ions, Al and Fe (Sposito, 1989). Similarities in phosphate and herbicide sorption trends (Figure 5, Table 6) also provide indirect evidence for importance of soil oxides in herbicide retention in these soils.

Norflurazon does not possess ligand donor groups capable of interacting with metal ions (metal complexation). Furthermore, it is a neutral compound, hence, electrostatic interactions with the charged soil surfaces may be excluded. Sorption of this compound is only significant in the presence of soil organic matter (G5), therefore, it is likely that sorption occurs via hydrophobic exclusion from solution onto soil organic matter (Figure 8).

We found that the extent of herbicide sorption is higher in G soils than in A soils, even after accounting for differences in surface area. The higher total and extractable iron content of the G soils most likely accounts for the greater extent of sorption. 2,4-D and quinmerac sorption onto G soils as a function of depth appears to follow trends observed for total and extractable Fe and Al, and P_{\max} . A similarly distinct trend is not observed for A soils, suggesting that Fe and Al oxide content alone cannot explain the herbicide sorption in the lower layer of the A soils. Instead, other properties including oxide mineralogy, microstructure, and the nature of the oxide-clay associations are likely to be important.

Table 5. Correlation coefficients (r) of soil properties and herbicide sorption to soils (from batch studies).

	pH _w	ECEC	Silt	Clay	Surface Area	Total C	DCB Fe	DCB Al	DCB Mn	AAO Fe	AAO Al	Total Al
pH _w	1											
ECEC	0.2581	1										
Silt	-0.6552	0.2206	1									
Clay	0.1991	0.7803	-0.0737	1								
Surface Area	-0.0624	0.9297	0.0919	0.9442	1							
Tot C	-0.1223	-0.3191	0.4953	-0.1100	-0.2241	1						
DCB Fe	-0.0589	0.8108	0.3939	0.8291	0.8644	-0.0191	1					
DCB Al	0.0053	0.81	0.1259	0.9539	0.9507	0.0237	0.8333	1				
DCB Mn	-0.2300	0.6516	-0.4780	-0.1520	-0.2320	0.9830	0.0320	-0.0110	1			
AAO Fe	-0.2399	0.5671	0.7425	0.4964	0.5862	0.2261	0.8751	0.5717	0.3180	1		
AAO Al	-0.2056	0.9234	0.2991	0.8729	0.9528	-0.0630	0.9111	0.8971	-0.0450	0.7390	1	
Total Al	-0.1764	0.9519	0.1935	0.9121	0.9748	-0.1577	0.8763	0.9189	-0.1470	0.6268	0.9639	1
Total Ca	0.0918	-0.6377	0.2584	-0.3654	-0.5159	0.8893	-0.3399	-0.2438	0.8470	-0.0911	-0.4357	-0.5008
Total Fe	-0.1339	0.8055	0.4781	0.7860	0.8538	0.0002	0.9866	0.8127	0.0560	0.9117	0.9222	0.8759
Total K	-0.3188	0.4693	-0.0366	0.4486	0.4792	0.0303	0.1807	0.5040	-0.0340	-0.0285	0.4509	0.5661
Total Na	-0.2107	-0.3026	0.5114	-0.1448	-0.2417	0.9858	-0.0688	0.0055	0.9740	0.1696	-0.0953	-0.1567
Total Ti	-0.0138	0.213	0.6961	0.3983	0.3531	0.6335	0.6622	0.5013	0.6690	0.8276	0.4811	0.3969
Total Mg	-0.5184	0.8209	0.6961	0.4880	0.6730	-0.0460	0.7773	0.6083	0.0550	0.8082	0.7376	0.7491
Total Mn	0.0445	-0.478	0.2867	-0.5133	-0.6336	0.7165	-0.4215	-0.4375	0.7270	-0.1464	-0.5777	-0.5831
Total P	-0.4010	0.5244	0.8330	0.3169	0.4615	0.1957	0.7688	0.4135	0.3150	0.9655	0.6430	0.5260
P _{max}	-0.1703	0.6682	0.4548	0.7727	0.8342	0.0780	0.9182	0.8024	0.1340	0.8365	0.8965	0.8442
2,4-D sorbed [†]	-0.1450	0.8216	0.2050	0.7963	0.8129	-0.0988	0.8600	0.7187	-0.0500	0.6524	0.8781	0.8881
Norflurazon sorbed [†]	-0.2776	-0.3897	0.4065	-0.2853	-0.3832	0.9293	-0.2288	-0.1541	0.9230	-0.0122	-0.2379	-0.2829
Quinmerac sorbed [†]	-0.1203	0.8779	0.2518	0.8395	0.8957	-0.1972	0.9517	0.7995	-0.1410	0.7530	0.9291	0.9152

Table 5. Continued.

	Total Ca	Total Fe	Total K	Total Na	Total Ti	Total Mg	Total Mn	Total P	P _{max}	2,4-D sorbed [†]	Norflurazon sorbed [†]	Quinmerac sorbed [†]
pH _w												
ECEC												
Silt												
Clay												
Surface Area												
Tot C												
DCB Fe												
DCB Al												
DCB Mn												
AAO Fe												
AAO Al												
Total Al												
Total Ca	1											
Total Fe	-0.3329	1										
Total K	-0.1824	0.2133	1									
Total Na	0.8806	-0.0437	0.1137	1								
Total Ti	0.4150	0.6909	-0.0120	0.5871	1							
Total Mg	-0.3337	0.8370	0.3196	-0.0088	0.5712	1						
Total Mn	0.8545	-0.4097	-0.3578	0.7467	0.3048	-0.2809	1					
Total P	-0.0988	0.8308	-0.0634	0.1584	0.7533	0.8370	-0.1016	1				
P _{max}	-0.2661	0.9246	0.1350	0.0407	0.6431	0.7494	-0.2613	0.7541	1			
2,4-D sorbed [†]	-0.4815	0.8401	0.3794	-0.1190	0.3918	0.6411	-0.4818	0.5752	0.8297	1		
Norflurazon sorbed [†]	0.8596	-0.2210	0.1149	0.9584	0.3813	-0.1483	0.7365	0.0059	-0.1338	-0.1887	1	
Quinmerac sorbed [†]	-0.5462	0.9261	0.2419	-0.2354	0.4335	0.7189	-0.5722	0.6556	0.8976	0.9393	-0.3436	1

[†]From batch sorption studies at 144 h

* this constitutes the working data set.

** All soils G1-G5 and A1-A5 are included in the analysis.

Table 6. Maximum phosphate and herbicide sorption in batch studies at 144 h, and cumulative sorption and desorption in CFSTR studies for Georgeville and Appling soils.

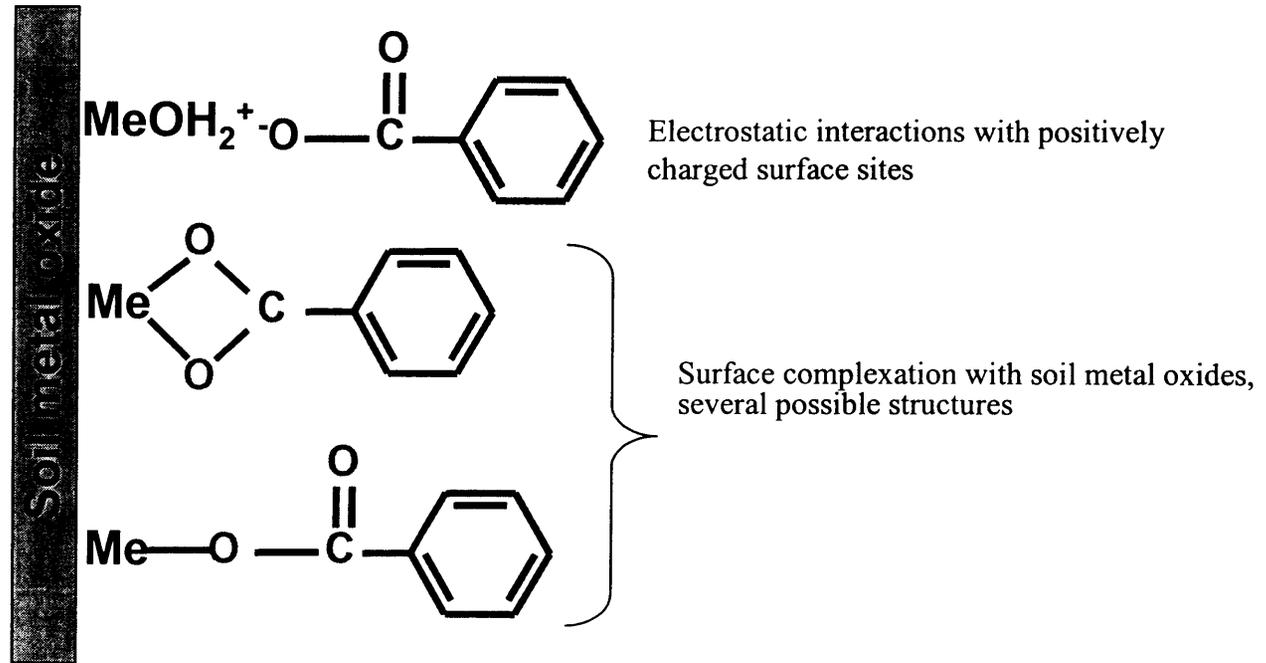
Soil	P_{\max}^{ads}	Batch: mass sorbed		CFSTR: mass sorbed		CFSTR: mass desorbed (% desorbed)	
		2,4-D	Quinmerac	2,4-D	Quinmerac	2,4-D	Quinmerac
-----mg/kg (%)-----							
G5	753	8.19	7.19	107	42.0	86.1 (80.1)	38.7 (92.1)
G4	1025	13.9	20.8	171	138	169 (98.7)	136 (98.6)
G3	1044	20.9	35.7	284	162	199 (69.9)	154 (95.2)
G2	1334	28.2	38.7	215	198	215 (99.7)	138 (69.8)
G1	929	12.8	23.4	139	135	106 (76.1)	123 (91.0)

A5	403	0.04	0.00	n/a	n/a	n/a	n/a
A4	569	0.20	0.72	n/a	n/a	n/a	n/a
A3	598	6.70	13.2	133	104	86.9 (65.3)	106 (102)
A2	773	12.7	20.9	133	109	136 (102.40)	111 (101.73)
A1	703	22.4	22.7	313	141	309 (98.8)	138 (97.9)

norflurazon							
-----mg/kg (%)-----							
G5		12.9		263		118 (45.1)	

A5		2.66		157		159 (101.27)	

2,4-D and Quinmerac



Norflurazon

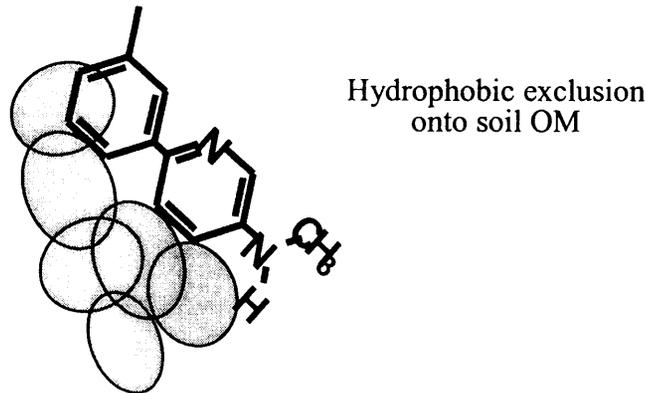


Figure 8. Speculated herbicide-soil interactions.

The role of soil mineral surfaces, particularly Al and Fe oxides, can be confirmed using at least two different approaches, each with its own shortcomings: by removing Al and Fe oxides from the soils and examining herbicide sorption on the altered matrices, or by examining sorption onto cleaned pure-phase iron and aluminum oxides and kaolinite. We used the later approach in this study in order to avoid changes to composition and mineralogy of non-Al and Fe minerals that were likely to result from harsh extractions. As shown in Figure 9, we observed significant sorption of 2,4-D and quinmerac onto aluminum oxide, hematite and goethite and no sorption onto kaolinite. Additionally, norflurazon did not show significant sorption onto any of these soil minerals. These results re-emphasize findings from our batch studies that Fe and Al oxides are important sorptive surfaces for 2,4-D and quinmerac.

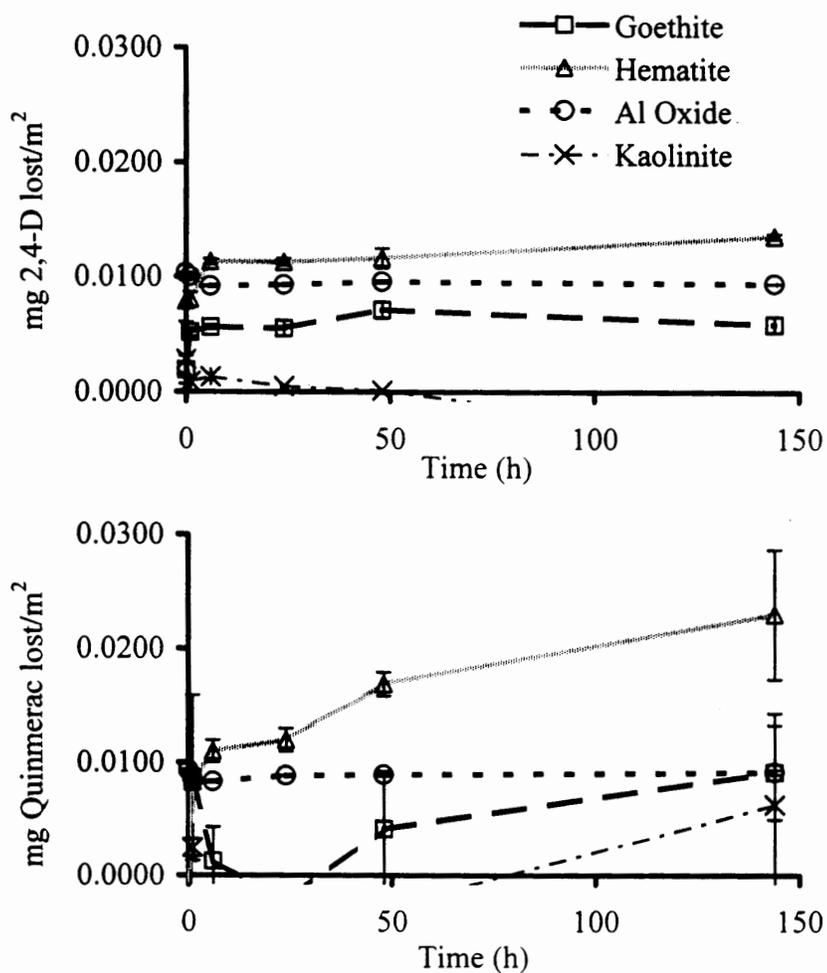


Figure 9. Sorption of 2,4-D and quinmerac (10 mg/l) on goethite, hematite, aluminum oxide and kaolinite (0.1 g/l) from 0 to 144 h in batch reactors. pH of the systems: goethite 3.7; hematite 4.5; Al oxide 4.1; kaolinite 5.7. Sorption is expressed in mg/m² to account for differences in surface area.

5. CFSTR STUDIES OF SORPTION-DESORPTION PHENOMENA

Batch reactors are commonly used to evaluate interfacial processes that govern chemical fate. These systems are advantageous due to their ease of operation, short experimental time scales, and low cost. With respect to simulating “*field relevant*” phenomena, there are several disadvantages to extrapolating from batch systems alone: (1) products accumulate and compositional changes can occur; (2) a new reactor is required to evaluate small changes in aqueous composition (e.g., pH) in a manner that does not alter particle loading and chemical concentrations; (3) investigations of simultaneous reactions, competition between different solutes (desorption), and displacement of sorbed constituents is difficult; (4) transport limitation of phenomena cannot be assessed; (5) colloidal particles may be generated due to mechanical agitation (shaking and stirring); and (6) high solids-to-solution ratios, characteristic of natural systems, are difficult to employ. Currently, there is no ideal experimental technique that avoids all the above mentioned disadvantages.

We have used the “modified” continuous flow stirred tank reactor (CFSTR, Figure 10), to overcome some of the above disadvantages (1-3 above). Our reactor is capable of maintaining a constant particle loading. The exit wall serves as a filtration unit and filters of select pore size prevent particles from leaving the reactor. Since herbicide leaching as a result of infiltration or precipitation is often in dynamic non-equilibrium, CFSTRs afford an important technique for evaluating leaching in a “*field relevant*” manner. Column reactors are also appropriate techniques for evaluating interfacial processes in the context of percolation/infiltration scenarios. However, they are difficult to employ in the study of NC “red clay soils” because these iron oxide rich kaolinitic soils possess low hydraulic conductivities that make flow through columns impracticably slow for our experimental purposes.

5.1 Methods and principles

To compliment the batch sorption studies and to confirm that loss of herbicide from soil solution was attributable to sorption processes, kinetic studies were conducted with CFSTRs. For each sorption-desorption CFSTR experiment, 0.36 g oven-dried soil was placed in a 36 ml reactor with approximately 30 ml DI water and a Teflon-coated stirbar and pre-equilibrated overnight on an end-over-end shaker. After pre-equilibration, the CFSTR was placed on a stir plate and connected to an Ismatec peristaltic pump and a 750 μ l quartz flow cell (Hellma) in a Shimadzu BioSpec-1601 UV-vis spectrophotometer using primarily FEP (chemically inert) tubing with minimal amounts of Tygon RG3603 tubing. A solution of either 10 mg/l herbicide (for sorption studies) or deionized water (for desorption studies) was pumped at 2 ml/min into the reactor. Effluent exited the reactor through a 0.2 μ m membrane filter into the flow cell in the spectrophotometer where herbicide concentration was monitored at 229 nm (2,4-D), 238.8 nm (quinmerac), or 236 nm (norflurazon) at 0.2 min readings for at least 150 min. In addition to the UV measurements, effluent pH was monitored. To confirm that recorded UV absorbance was due only to the herbicide, samples of effluent were periodically collected, filtered through a 0.2 μ m polycarbonate membrane and analyzed by HPLC with DAD detection (Hewlett Packard Series 1100) at 1 ml/min flow rate on a Zorbax SBC8 5 μ m 15 cm x 0.46 cm column with matching guard column. Mobile phases and other conditions were similar to those used in the batch studies (*Section 4.1*). Preliminary investigations of UV absorbance as a function of pH for each test herbicide were used to determine the appropriate detection wavelength for the pH range of each experiment. The sorption and desorption phases were each evaluated for close to 2.5 h.

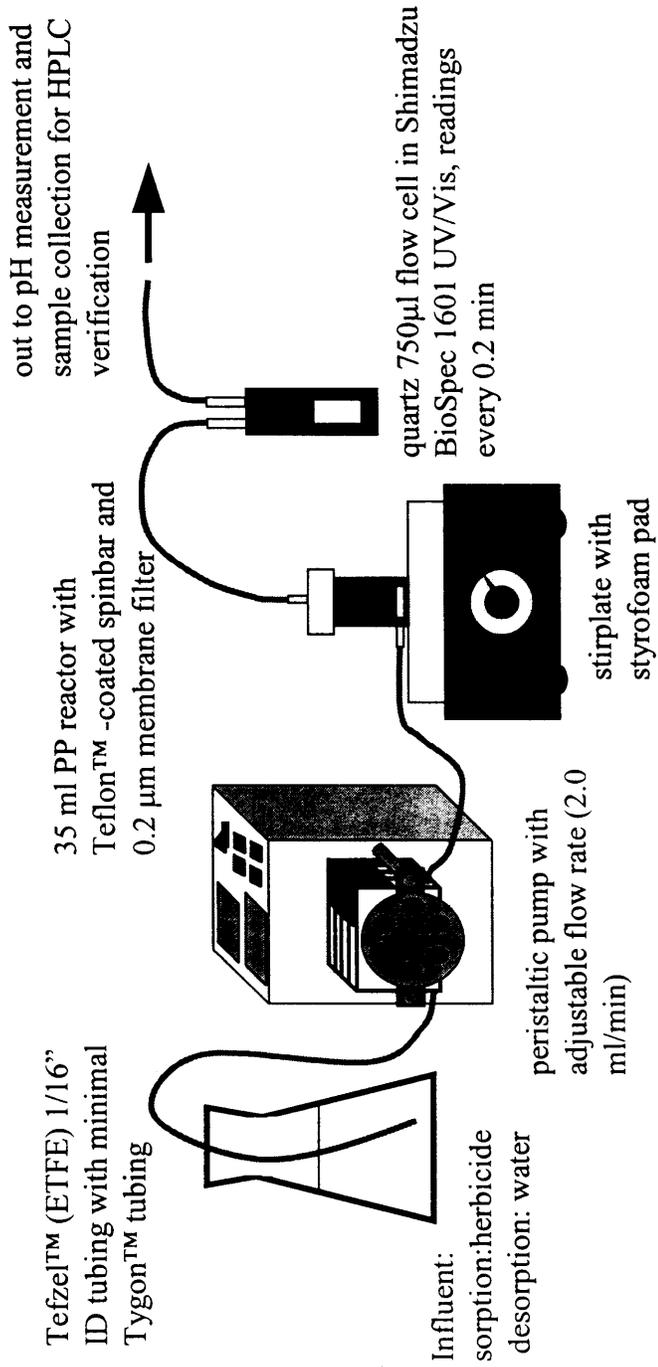


Figure 10. Schematic of CFSTR setup. Herbicide concentration was 10 mg/l, soil loading was 10 g/l, flow rate was 2.0 ml/min.

We chose this time scale to avoid loss due to potential microbial degradation and to minimize stirring and hence avoid particle shearing.

The reactor size, stirring rates, and particle loading were optimized to ensure that particle accumulation at the filter was minimized. Using the lowest depth samples, A1 and G1, a range of soil loadings was screened to evaluate the optimal loading for our experiments. We found that in order to prevent filter clogging, CFSTR experiments had to be conducted at a soil:solution loading 10 times lower than that used in the batch studies for all soils but G5, where a soil:solution of 10 g/l (50 times lower than that used in batch studies) was necessary to keep filters unclogged.

For 2,4-D and quinmerac, the sorption and desorption were evaluated for all five depth samples of the Georgville soils, and the three lowest depths of the Appling soils, A1-A3. CFSTR experiments were not conducted with A5 and A4 soils because the batch studies indicated a negligible amount of sorption. For the same reasons, CFSTR experiments involving norflurazon were conducted only with A5 and G5 soils.

The amount of herbicide sorbed or desorbed during the CFSTR experiment was obtained by comparing the concentration of herbicide inside the reactor containing soil to that inside an identical reactor containing no soil (Figure 11). In the absence of a solid phase, herbicide concentration in the reactor can be described by Equation 1. Herbicide concentrations inside the reactor during sorption or desorption are theoretically described by Equation 2 (Seyfried et al., 1989):

$$(C_i - C_e)J = V_c \frac{dC}{dt} \quad \text{Eqn 1.}$$

$$(C_i - C_e)J = V_c \frac{dC}{dt} + M \frac{dS}{dt} \quad \text{Eqn 2.}$$

where:

C_i = influent concentration (mg/l)

C_e = concentration of effluent (mg/l)

C = concentration inside reactor (mg/l)

J = flow rate (ml/min)

V_c = volume of reactor (l)

t = time (min)

M = mass of soil in reactor (kg)

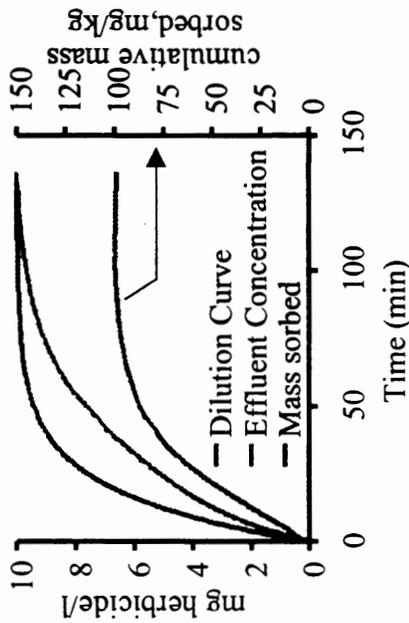
S = amount herbicide sorbed (mg)

Integration of Equation 1 for $C_i = 10$ mg herbicide/l (sorption blank, Eqn. 3) and for $C_i = 0$ mg/l (desorption blank, Eqn. 4) yields herbicide concentrations inside the reactor as a function of time in the absence of a solid phase (dilution curves, Figure 11) (Seyfried et al., 1989):

$$C = C_i [1 - \exp(-Jt / V_c)] \quad \text{Eqn 3.}$$

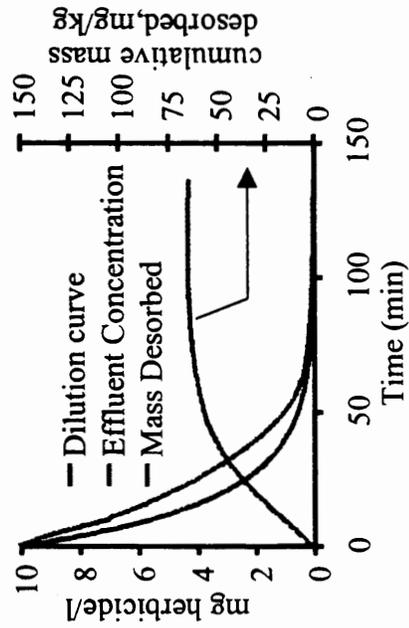
$$C = C_i [C_i^* (1 - \exp(-Jt / V_c))] \quad \text{Eqn 4.}$$

SORPTION



$C_{in} = 10$ g/L, herbicide
Initial $C \sim 0$ g/L

DESORPTION



$C_{in} = 0$ g/L, deionized water
Initial $C \sim 10$ g/L

Dilution curve, no solid in the reactor:

$$\frac{dC}{dt} = \frac{J}{V} [C_{in} - C]$$

Effluent concentration, constant soil loading:

$$\frac{dC}{dt} = \frac{J}{V} [C_{in} - C] - \frac{m}{V} \frac{dS}{dt}$$

- C/C' : concentration in the reactor (mg/L) t : time (min)
- C_{in} : influent concentration (mg/L) J : flow rate (L/min)
- S : concentration sorbed (mg/kg) V : reactor volume (L)
- $C = C_{effluent}$: effluent concentration (mg/L) m : mass solid (kg)

Figure 11. Principles of CFSTR operation.

The cumulative amount of herbicide sorbed or desorbed over time was then determined mathematically by the method of Eick et al. (1990):

$$q(t_i) = \frac{[(c(t_i)_{ns} - c(t_i)_s)V_c] + \sum[(C_{ns} - C_s)J\Delta t]}{M} \quad \text{Eqn. 5}$$

where:

- $q(t_i)$ = quantity of herbicide sorbed at time t_i (mg/kg)
- C_{ns} = concentration of herbicide in effluent when no soil is present (mg/l)
- C_s = concentration of herbicide in effluent when soil is present (mg/l)
- J = flow rate (mg/l)
- t = time (min)
- $c(t)_{ns}$ = concentration of herbicide in the reactor at time t_i when no soil is present (mg/l)
- $c(t)_n$ = concentration of herbicide in the reactor at time t_i when soil is present (mg/l)
- V_c = volume of reactor (l)
- M = mass of soil in reactor (kg)

5.2 Results and Discussion

Results from the CFSTR studies are shown in Figures 12-15 and Table 6. The extent of 2,4-D sorption and desorption in lowest depth samples, A1 and G1, was evaluated as a function of the soil loading in the reactor (Figure 12). A higher extent of sorption was observed at lower soil loadings. Additionally, irreversible retention was observed only at lower soil loadings. This observation suggests that soil aggregates were better dispersed at lower loadings and sorption sites were more accessible and that maximum solute sorption can be achieved only at lower loadings within the time scale of our experiments (2 hours). Furthermore, it is likely that there existed two types of retention sites or mechanisms. At lower soil loadings, the concentration of each type of site was low enough that one type of site was saturated and hence solute-soil interactions at both types of sites were discerned. Based on these studies we employed a significantly lower loading than in our batch studies; details of the loadings used are found in the methods section 5.1.

We found that the trends with respect to the extent of herbicide sorption as a function of soil depth generally follow the trends observed in batch studies (Table 6). For 2,4-D and quinmerac, initially desorption appeared to be more rapid than sorption, and the desorption plateau was reached earlier than the sorption plateau (Figure 13-14). For 2,4-D sorption, close to complete mass recovery via desorption with DI water was observed in A1, A2, G2, and G4 soils, while 28-34% of the mass was not recovered during the desorption phase from soils A3, G1, G3, and G5 (Table 6). Quinmerac was completely recovered during the desorption phase in all soils except G2; where, 30% of the mass was not recovered. For norflurazon, the rate of sorption and desorption appear to be similar in both Appling and Georgeville soils (Figure 15). The difference in the sorption-desorption behavior between norflurazon and 2,4-D/quinmerac provides further evidence that the nature of norflurazon-soil interactions are distinct from 2,4-D- and quinmerac-soil interactions. Complete recovery of norflurazon was observed in A5 soil while about 55% of the mass was not recovered in G5 soil. Henceforth, we will refer to the mass not recovered by desorption with deionized water as the “strongly sorbed” fraction.

Evidence of desorption in the CFSTR experiments confirmed that loss from soil solution in the batch studies was primarily due to sorption. Furthermore, the rapid initial desorption with

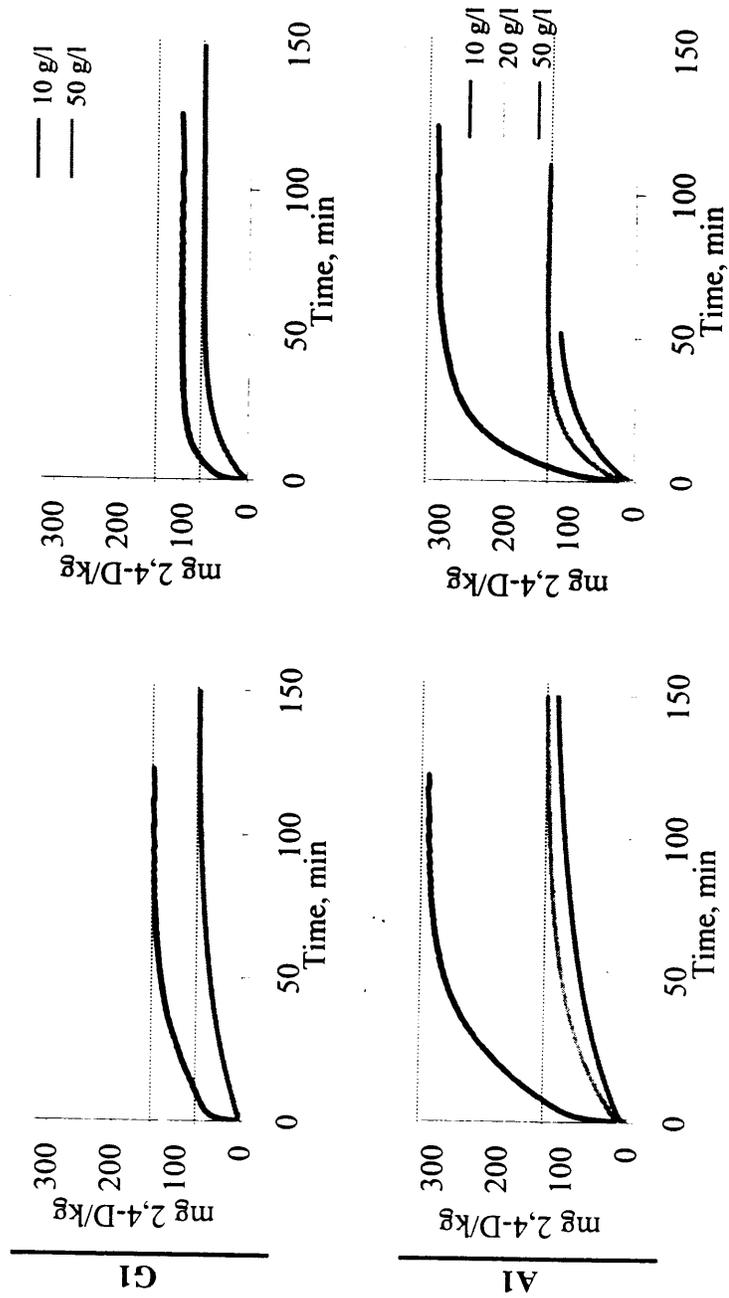


Figure 12. Effect of soil loading (10-50 g/l) on sorption and desorption of 2,4-D (10 mg/l) in G1 and A1 soils as measured in CFSTRs.

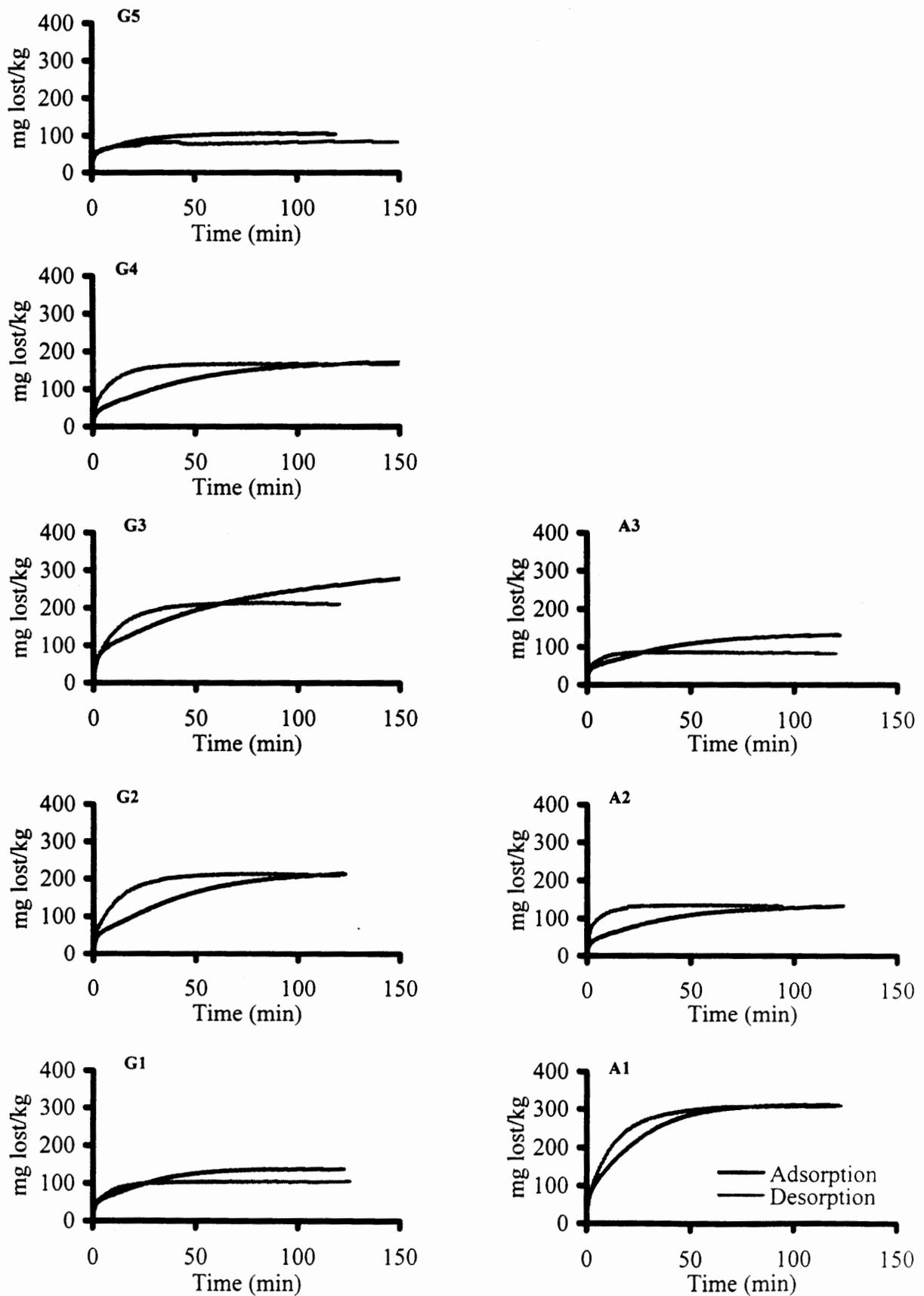


Figure 13. Sorption and desorption of 2,4-D (10 mg/l) in Georgeville and Appling soils. Soil loadings were 10 g/l for all soils. Soils A4 and A5 were not included because batch sorption studies indicated that sorption of 2,4-D was minimal.

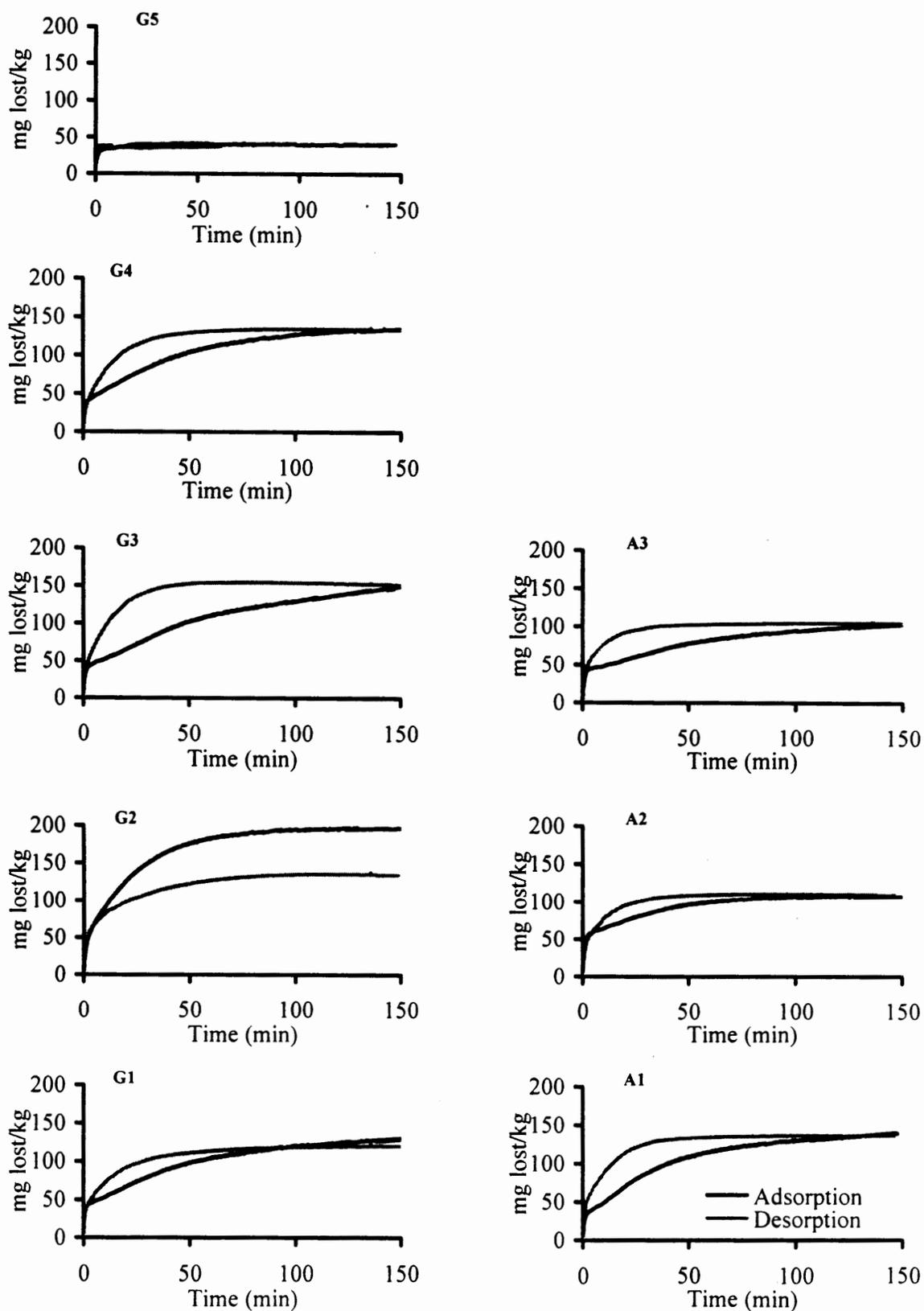


Figure 14. Sorption and desorption of quinmerac (10 mg/l) in Georgeville and Appling soils. Soil loadings were 10 g/l for all soils. Soils A4 and A5 were not included because batch sorption studies indicated that sorption of quinmerac was minimal.

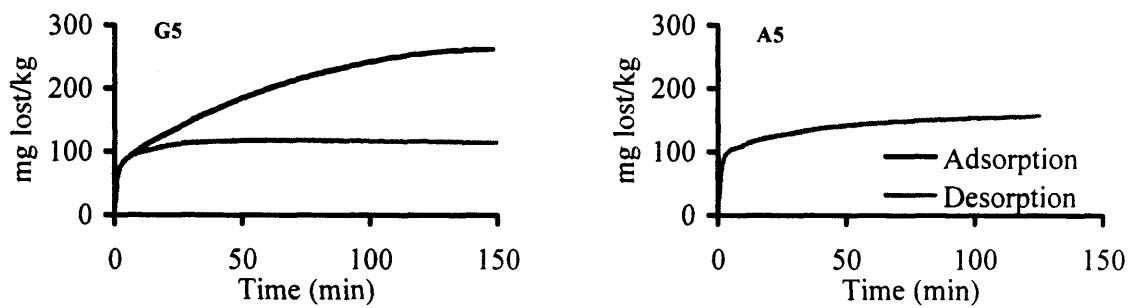


Figure 15. Sorption and desorption of norflurazon (10 mg/l) on Georgeville and Appling soils. Soil loadings were 10 g/l for all soils. Only soils A5 and G5 were included in these studies because batch sorption experiments indicated minimal sorption of norflurazon on G1-G4 and A1-A4. For A5, the sorption and desorption line overlie each other and hence only the desorption line is discerned.

deionized water indicated that H_2O and OH^- can desorb 2,4-D and quinmerac. It also provides additional evidence that the herbicide mass involved in reversible sorption was weakly bound to the soil surface via favorable electrostatic interactions and/or weak complexation. Irreversible retention of all test herbicides likely resulted from strong complexation or entrapment within soil aggregates or particle micropores. For nometuron, a strongly sorbed fraction is observed on G5 but not on A5. It is possible that these differences are most likely attributable to differences in the amount and type of organic matter present; G5 is located under a hardwood, while A5 is under a pine forest managed with prescribed burning.

While the batch studies were useful in determining the sorption behavior of the test herbicides and the nature and extent of sorption as a function of soil depth, the CFSTR studies provide insight into desorption phenomena which in turn provides important perspective on the leaching potential of these herbicides. The CFSTR studies have served to demonstrate that the nature of herbicide-soil interaction is relatively weak for a significant mass of the herbicide retained on the soil matrix; all the test herbicides were partially or completely desorbed by water. This suggests that heavy precipitation or irrigation can easily leach the “reversibly” retained herbicide fraction below microbially active soil horizons and potentially into groundwater.

6. STATISTICAL ANALYSES

Based on our soil characterization, batch, and CFSTR studies we have identified herbicide structural criteria and soil properties that likely play a role in herbicide attenuation and mobilization in NC Piedmont soils. Here, we describe the statistical analyses conducted to strengthen our inferences and hypotheses.

6.1 Methods: Linear Regressions and Principal Component Analysis

Correlation coefficients (r) obtained from bivariate linear regressions (LR) [JMP IN (Version 3.2.1, SAS Institute)] were used to evaluate the correlation between soil properties and herbicide sorption. Principal component analysis (PCA) was conducted using PC_ORD (Version 4.04, MjM software) to evaluate the inter-relatedness of measured soil properties in the various depth samples and to identify soil properties that influence herbicide retention.

Principal Component Analysis (PCA) is an ordination technique based on a basic eigenvalue analysis. The goal of PCA is to achieve an effective data reduction, expressing many-dimensional relationships in a small number of dimensions. The first Principal Component (PC) is the direction of the linear combination of variables in n -dimensional space that exhibits the maximum variance (with respect to that PC). Every following PC is defined as the axis (linear combination of the variables) that maximizes the remaining variance and is perpendicular to previous PCs. Usually only a few PC's are needed to explain most of the variance present in the data. This technique merely rotates the data in such a way the maximum variance is captured in the first few axes. The PCA (Figures 16-20) is shown as Gabriel biplots that depict the projected directions of the variables in relation to the principal components.

We measured nearly 36 parameters describing soil properties and composition on 10 soil samples (A1-A5 and G1-G5). In statistical terms, we have three times as many responses as we have samples and, therefore, we chose to limit the number of soil parameters. First, we preserved all the parameters required to test hypotheses and findings based on laboratory data, including total C, surface area, and total and extractable Al and Fe content. Secondly, we reduced the number of parameters further by eliminating redundant parameters (e.g., pH_w and $\text{pH}_{\text{CaCl}_2}$); dependent variables that could be mathematically derived from two or more variables (e.g., sand, silt, clay content); parameters for which several of the measured values were below the analytical detection limit (e.g., $\text{NO}_3\text{-N}$, Ni); soil properties with limited correlation with other soil properties (e.g., saturated paste conductivity); and trace elemental composition that most likely reflective of bulk soil composition and not surface composition (e.g., Zn, Cr, Cu). We thus arrived at 21 soil parameters (henceforth referred to as the working data set, Table 5) that we used in LRs and PCA described in the results section. Preliminary PCA conducted with all 36 measured parameters confirms our choices; the parameters eliminated did not significantly contribute to principal component 1, 2, or 3 and hence do not play an important role in explaining the similarities and differences in soil properties. Although the working data set contains P_{max} , we conducted PCA both while including and excluding P_{max} in order to systematically evaluate the similarities and differences in soil composition.

6.2 Results and Discussion

As shown in Table 5, surface area, total and DCB- and AAO- extractable Fe and Al, P_{\max} , and clay content showed strong positive correlations with each other. This is consistent with the fact that soil oxides occur in the clay fractions, which have the highest surface area. Total C was correlated to Na, Mn, DCB-Mn, and Ca content, a likely result of high concentrations of these elements in the uppermost horizons. Surface area, total Fe and Al content, crystalline iron oxide (DCB-Fe) and non-crystalline aluminum oxide content (AAO-Al), and P_{\max} were the criteria most strongly related to the extent of 2,4-D and quinmerac sorption. Total soil carbon and other soil parameters that showed a strong correlation with total C influenced norflurazon sorption.

PCA of the *working data set* of soil properties (excluding P_{\max}) is shown in Figure 16-17. The first three principal components explained up to 86% of the variance in the data; principal component (PC) 1 explained 46.3%, while the PC 2 added 29.3%. The most important contributors to PC 1, in order of significance, were DCB-Fe, total Fe, AAO-Al, total Al, surface area, DCB-Al, and total Mg. Total Mg may be a reflection of clay content, because it is often an important constituent of soil clays. Total C, Na, and DCB-Mn contributed significantly to PC 2. pH_w and ECEC were important for PC 3. Including P_{\max} in the analysis resulted in P_{\max} contributing significantly to PC 1, with little or no change to the other axes in the PCA plot.

Scores (weighted linear combinations of soil parameters used in the analysis) for each soil sample with respect to PC 1 and 2 are shown on Figure 16. The clear separation of A and G soils in the plot suggests that the two soils series were distinct with respect to the soil properties examined. This follows visual indications of differing mineralogy between the two soils as well as their differing capacities for herbicide retention. Furthermore, total Ti content was distinctly different in A and G soils as described by the axis of Ti being orthogonal to the imaginary lines connecting all A samples and G samples. This suggests that soil Ti content, often related to the extent of weathering, may be used as a tool to separate A and G soils.

Based on the scores (location) of the soil samples in Figure 16, the soils can be grouped into four categories, each with relatively similar properties: (1) A1, A2, A3; (2) A4, A5; (3) G1-G4; and (4) G5. It is notable that G5 was significantly different from all the other soil samples. Our data alone cannot explain why G5 was chemically and/or physically distinct from the remainder of the G soils, further investigation of other Georgeville profiles is needed to determine if the characteristics that set G5 apart from G1-G4 are typical of Georgeville top soils. The separation of the upper A soils (A5-A4) from the lower A soils (A1-A3) may indicate significant differences in physical and/or mineralogical characteristics with soil depth. The lack of a similarly distinct separation in G soils suggested more consistent mineralogy as a function of depth. Hence, evaluations of herbicide fate in A soils may require careful consideration of mineralogical variability. This is consistent with earlier findings from our batch experiments: the sorption of ionogenic herbicides as a function of depth in A soils could not be explained by surface area and total and extractable Fe and Al content alone, instead mineralogy and other soil properties would also need to be considered.

PCA with the working data set of soil properties (this time including P_{\max}) and the extent of sorption of each herbicide at 144 h (observed in batch studies) is shown in Figures 18-20. 2,4-D and quinmerac contributed significantly to PC1 with little or no significant change in the other

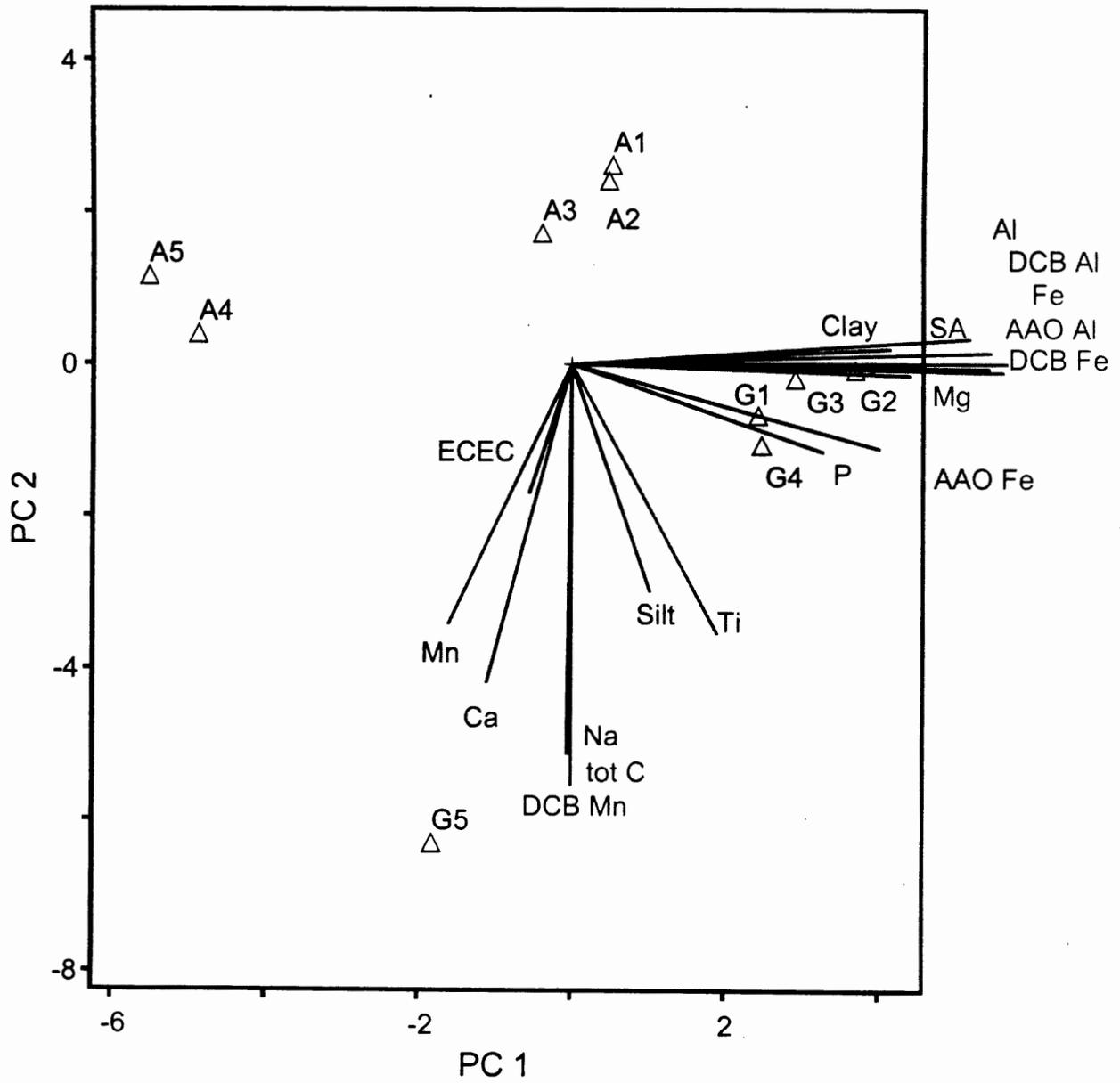


Figure 16. Principal component analysis plot of soil properties (P_{max} excluded): PC 1 vs. PC 2.

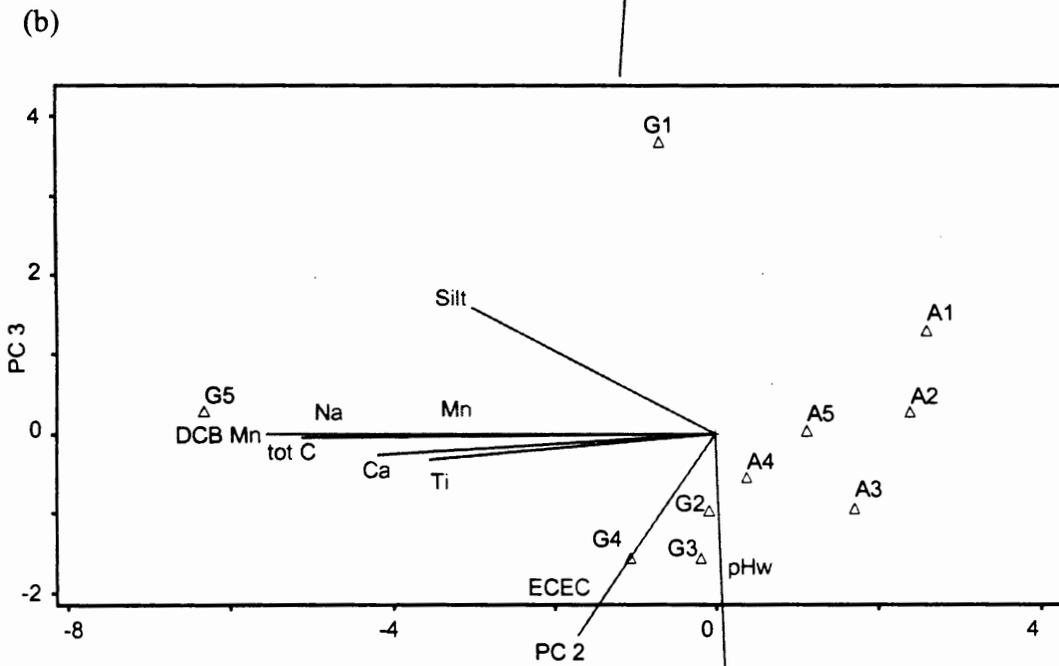
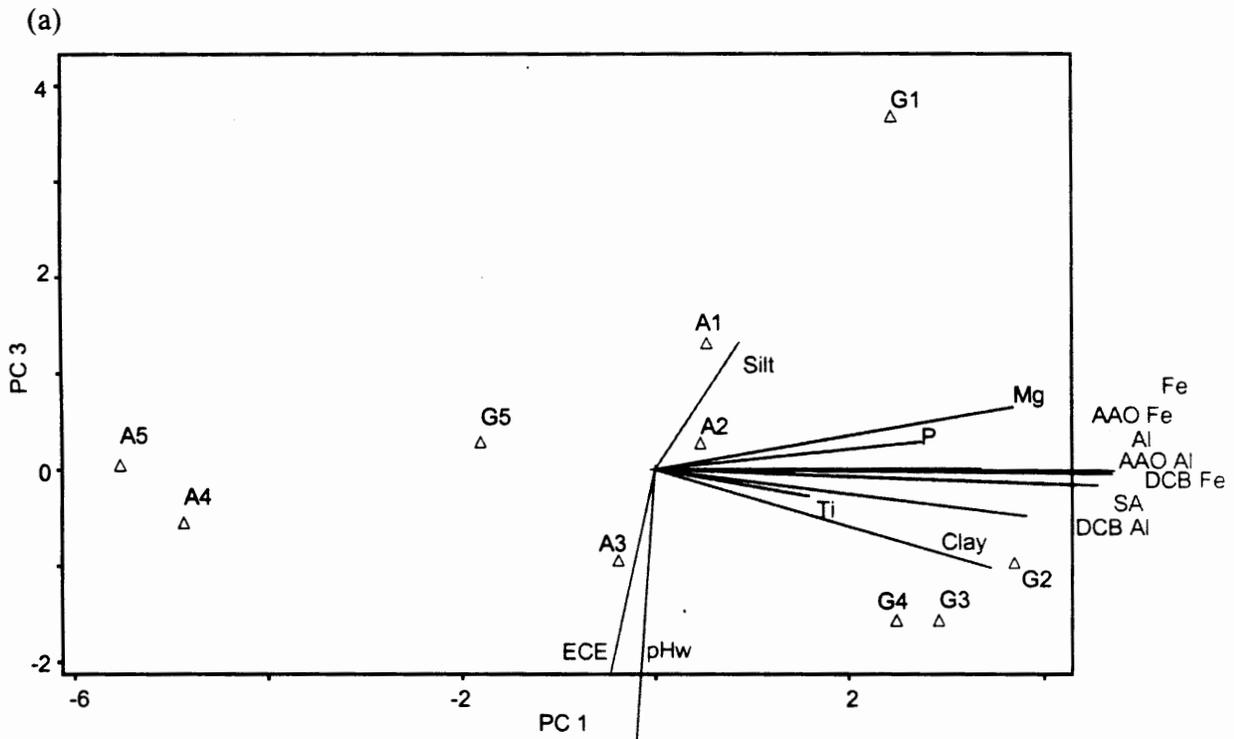


Figure 17. Principal component analysis plot of soil properties (P_{max} excluded) : (a) PC 1 vs PC 3, (b) PC 2 vs. PC 3.

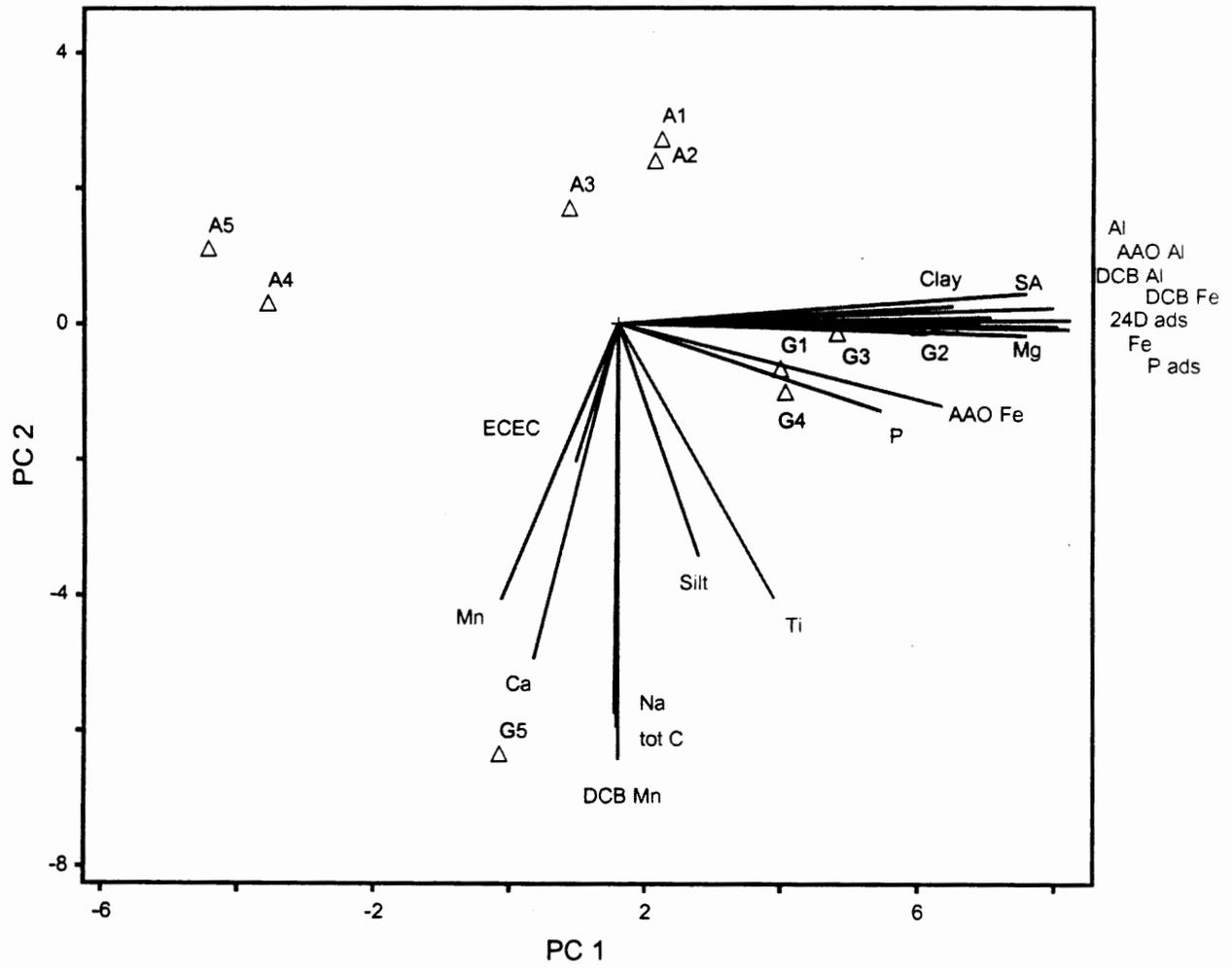


Figure 18. Principal component analysis plot of soil properties and 2,4-D sorption: PC 1 vs. PC 2.

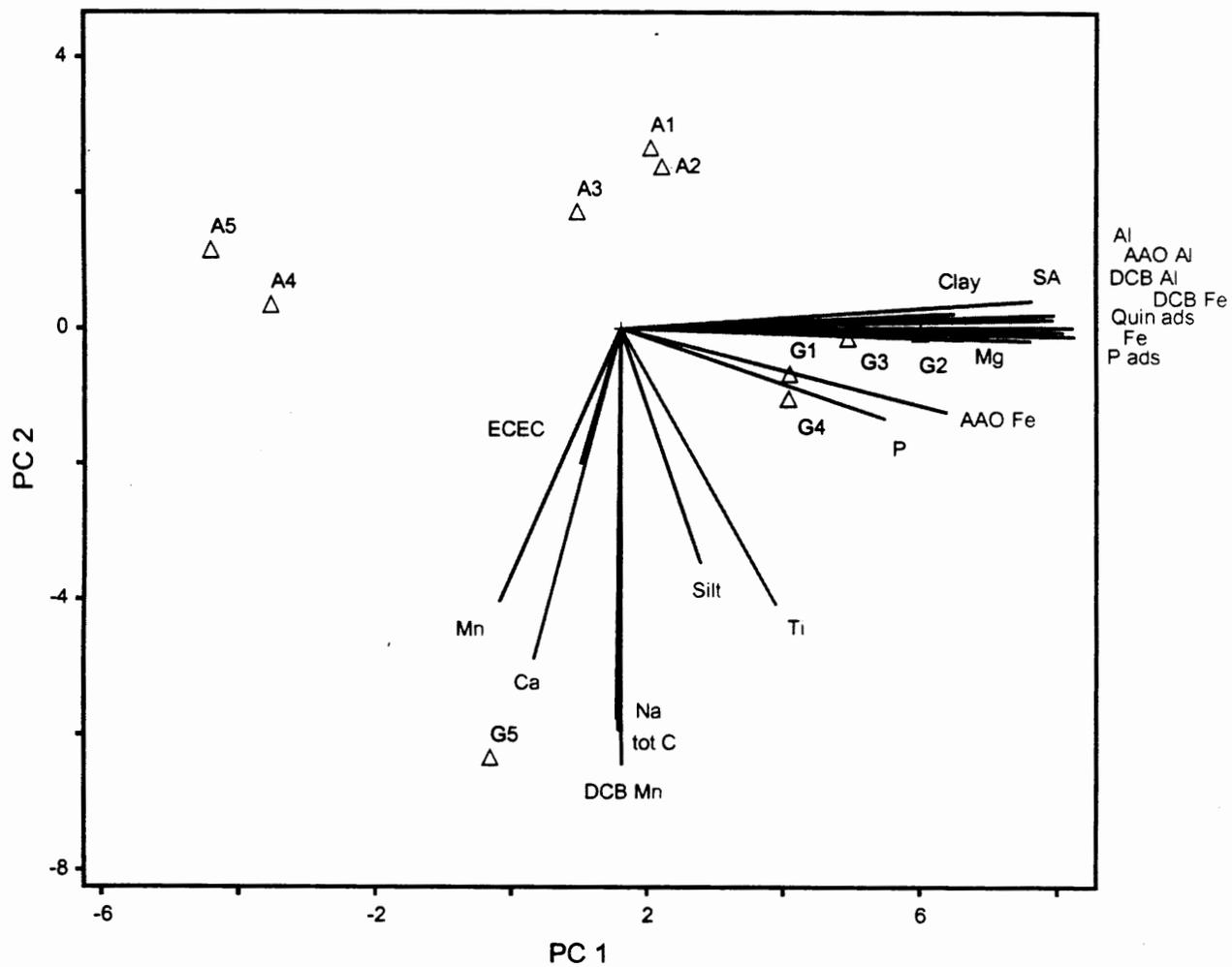


Figure 19. Principal component analysis plot of soil properties and quinmerac sorption: PC 1 vs. PC 2.

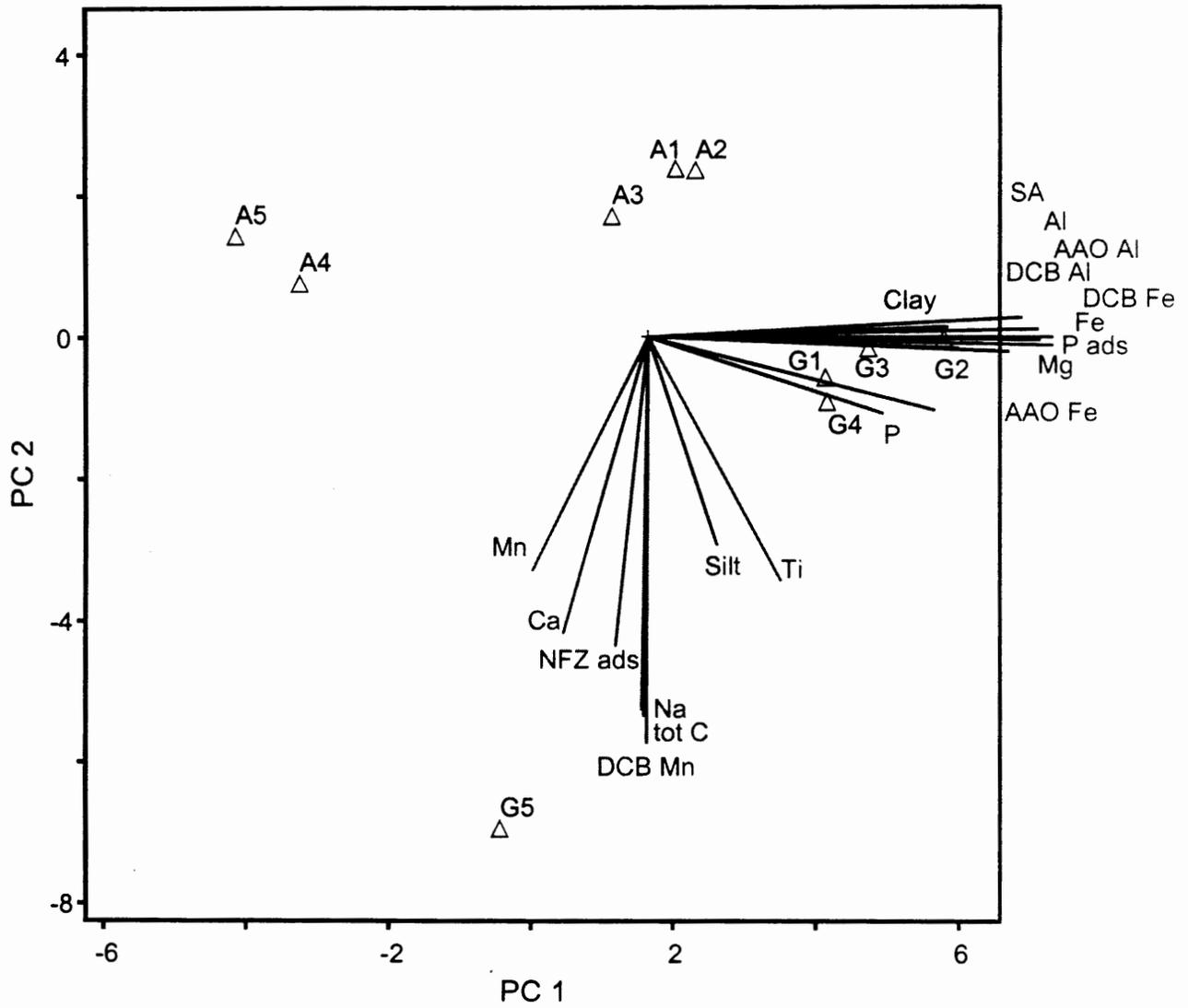


Figure 20. Principal component analysis plot of soil properties and norflurazon sorption: PC 1 vs. PC 2.

parameters. Hence, parameters included in PC 1 (total Fe, DCB-Fe, total Al, AAO-Al, DCB-Al, P_{max} and surface area) were the best predictors of 2,4-D and quinmerac sorption. Alternatively, norflurazon sorption significantly contributed to PC 2; hence, parameters included in PC 2 (total C, DCB-Mn, and Ca) were important predictors of norflurazon sorption. These observations were consistent with the finding from our batch and CFSTR studies. The results of this analysis serve to provide additional evidence for the following laboratory-based findings: 2,4-D and quinmerac interact with soils via a distinct mechanism as compared with norflurazon; properties of A and G soils and their capacity for herbicide retention are different; soil oxides and surface area are important in evaluating the retention of ionogenic herbicides; and neutral herbicides may be evaluated using traditional soil parameters such as organic matter content.

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