



WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Soil processes impacting groundwater quality in the North Carolina Piedmont: Contamination by organic agrochemicals

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Statement of the Water Problem

Agricultural operations and turf maintenance on golf courses in North Carolina often contribute to the intentional and/or unintentional discharge of organic contaminants at or near land surface areas where ground water systems are replenished (ground water recharge areas). The resulting contamination of soil and groundwater systems is of immediate concern because groundwater is an essential resource for over 50% of North Carolina residents. Previous studies of soil and groundwater contamination in North Carolina have justifiably focused on the coastal plain. Groundwater quality in the coastal plain has an increased susceptibility to deterioration (than the Piedmont and the mountains) as a result of the higher volume of anthropogenic activity (as measured by crop and livestock production and acreage of golf turf), the hydrogeology of the region, 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 much 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. Currently, our ability to evaluate the groundwater contamination potential, by pesticides, in the coastal plain is relatively well advanced. However, our capability to do the same in the Piedmont is limited at the present time.

Generally, evaluations of soil susceptibility to contaminant leaching are based on the following soil properties: organic matter content, texture, and acidity. Several soils systems of the Piedmont are depleted of soil organic matter and are enriched in iron oxides and low activity clays; these soils, also referred to as ultisols, are distinguished by well developed red/yellow clay B horizons. As a result of the extremely small size of clay and iron oxide particles and the reactivity of the electron deficient surface bound iron atoms, these B horizons are the seat of important chemical and physical activity. Due to these unique soil characteristics, the principles and mechanisms governing contaminant fate in NC Piedmont soils are expected to differ from those operative in the sandy soils of the coastal plain. Within ultisols, the eventual disposition of pesticides is governed, in part, by interactions between polar functional groups on the pesticide and the electron deficient metal atoms on soil mineral surfaces. Current understanding of organic contaminant interaction with metal oxides is largely derived from research on small organic ligands and pure phase metal oxides. Extrapolations to predict in situ contaminant fate in ultisols are, therefore, not always successful. The proposed research is aimed at the characterization of abiotic interfacial processes that contribute to 2,4-D, norflurazon, and quinmerac attenuation (sorption and surface assisted transformation) and mobilization (desorption, contaminant assisted surface dissolution, and release of colloidal particles from the immobile solid matrix) in two unique soils of the NC Piedmont (Appling and Georgeville soils). Specifically, the proposed research will evaluate the influence of (1) the physical-chemical characteristics and reactivity of naturally occurring iron oxide surfaces; (2) composition of percolating and interstitial waters; and (3) the molecular structure of the herbicide on test herbicide interaction with the B horizon of two North Carolina Piedmont soils.

Statement of Results, Benefits and Information

The proposed research will identify abiotic interfacial processes that are important to understanding and anticipating ground water contamination by herbicides in the NC Piedmont. By simulating field conditions in well controlled laboratory experiments, the nature of 2,4-D, norflurazon, and quinmerac interaction at the iron oxide/water interface will be examined in relation to the mineralogy, composition, and physical chemical characteristics of two unique soils of the North Carolina Piedmont (Appling and Georgeville series). The research will lend an important perspective to natural attenuation and mobilization of the test herbicides with respect to groundwater contamination in the NC Piedmont. These, in turn, will contribute to improved understanding for the management and regulation of contaminant releases. Understanding the natural herbicide attenuation and mobilization potential of NC Piedmont soils can assist in the protection of groundwater recharge areas, the delineation of well-head protection areas, and the identification of the best placement areas for buffer strips for pollution reduction. Information obtained on the relationship between herbicide structure and the nature of interaction at the oxide water interface can also be applied to the evaluation of the fate of other herbicides of related structure.

The proposed research will contribute to models that evaluate the vulnerability of NC Piedmont area groundwater to pesticide contamination. The pesticide and soil ranking

system for North Carolina developed by McLaughlin, Weber, and Warren (1994) focuses on soils of the coastal plains and provides an excellent guide for estimating groundwater contamination potential. Extrapolations of this ranking system to the Piedmont regions of NC need to be conducted with caution. For example, norflurazon (known to have a moderate leaching potential) was detected twice in groundwater at one of two sites, in Lincoln county (located in the Piedmont), where applications were reported to have occurred within 300 feet of the monitoring wells within five years of sampling. 2,4-D, also of moderate leaching potential, known to be applied yearly in the same region was not detected in the same groundwater (Wade et al., 1997). Given that the wells were located in an iron oxide rich Pacolet soil, it is likely that soil characteristics not accounted for by texture and acidity and competitive interactions from other dissolved constituents played a role in contaminant mobilization. Results from this research will contribute to better characterization of soil leaching potential for red clay soils of the NC Piedmont, especially with respect to the reactivity of the iron-oxide/water interface and composition of percolating waters. Finally, successful implementation of the proposed research will demonstrate to federal funding agencies (such as the EPA, USDA, and NSF) the importance of fundamental mechanistic studies of herbicide interaction at the iron oxide/water interface. These studies will provide important information for the protection of soil and groundwater in red clay regions of NC and the southeastern United States.

Nature, Scope, and Objectives of Research

1. Goals and Objectives

The proposed research is concerned with the fate of herbicides possessing ligand donor groups or polar functional groups (e.g., -COOH, -OH, -NH₂, -SH, and others) in iron-oxide soils representative of the North Carolina Piedmont. The objective is to develop an understanding of abiotic processes that determine herbicide attenuation (sorption and surface assisted transformation) and mobilization (desorption, contaminant assisted surface dissolution, and release of colloidal particles from the immobile solid matrix) through the soil column as function of:

- the physical-chemical characteristics and reactivity of naturally occurring iron oxide surfaces
- composition of percolating and interstitial waters
- the molecular structure of the herbicide. Three herbicides (2,4-D, norflurazon, and quinmerac) and two representative Piedmont soils - Appling and Georgeville series - will be used to achieve the objectives.

2. Relevance to Groundwater Quality in North Carolina

The U.S. EPA's Toxic Release Inventory (TRI) contains several pesticides and herbicides that possess polar functional groups such as metribuzin, acifluorfen and the test herbicides in the proposed 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 and herbicide fate (Wade et al., 1997; USGS, 1995; EPA, 1990; Dietrich et al., 1988).

Activity involving the shipping, distribution, and handling of herbicides, the formulation of herbicide mixtures, and application in agricultural operations, golf turf maintenance, and home lawn care often contributes to the intentional and/or unintentional discharge of herbicides at or near land surface areas where ground water systems are replenished. Persistent herbicides 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 the contaminated soils results in a long term source of groundwater contamination.

Several studies have examined groundwater contamination by pesticides in North Carolina (Wade et al., 1997; Maas et al., 1995; 1992; Jennings, 1993; Jennings et al., 1991; Moreau and Danielson, 1990; Umpstead, 1983). These studies have primarily focused on eastern regions of North Carolina, typically the coastal plain. 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. Only 8 of the close to 100 wells monitored are situated in the Piedmont and mountain regions of North Carolina (GW Branch, NCDEHNR, 1998). As mentioned earlier, this emphasis on the coastal plain is well justified by the fact that groundwater quality has an increased susceptibility to deterioration as a result of the higher volume of agriculture (and consequent agrochemical use), the hydrogeology of the region, and the presence of a larger number of productive aquifer systems.

While aquifers underlying the NC Piedmont are known to be less productive than those in the coastal plain, they are important source of water supply for small cities, farms, and rural homes. Given, that several counties in the Piedmont have a high volume of agricultural activity (e.g., Union county is the second highest producer of soybean), it is imperative that both groundwater recharge areas are protected from pesticide contamination. The detection of pesticides in groundwater monitoring wells in five Piedmont counties underscores the susceptibility for groundwater contamination in the NC Piedmont (Wade et al., 1997).

The composition and physical chemical properties of red clay Piedmont soils are known to be distinct from the sandy soils of the coastal plain (Daniels, 1984). Several soil series in the Piedmont can be categorized as ultisols (Morehead and Drawer, 1990; Daniels 1984), highly weathered acidic soils enriched in iron oxides and translocated low activity clays, such as kaolinite (Brady, 1990). The reactivity of these naturally occurring iron oxide surfaces and the resulting interactions with aqueous phase constituents, pesticide and other constituents of percolating water, has important implications for contaminant fate. An understanding of the interactions between polar functional groups of dissolved

constituents and the electron deficient metal atoms on soil mineral surfaces will lend an important perspective to assessing the groundwater contamination potential by agrochemicals in the ultisols of the North Carolina Piedmont.

3. Relation to current understanding of organic contaminant interaction at the iron-oxide/water interface

Sequioxides (iron and aluminum oxides) are the most important interface next to soil organic matter, with respect to the fate of organic contaminants with polar functional groups (henceforth referred to as OP) (Schwandt et al., 1992). Iron oxides are prevalent in the solid matrix and the colloid phase in several types of soils in the southeastern United States (Brady, 1990). In addition to occurring as pure phase aggregates, crystalline and amorphous iron oxides also occur closely associated with clay silicates and cemented to quartz particles (Schwertmann, 1988). Interstitial and percolating waters are, therefore, exposed to a variety of iron oxide surfaces with distinct mineralogies and surface morphologies.

Within the subsurface, a myriad of physical, chemical, and biological processes serve either to attenuate or to mobilize the contaminant. Of these, sorption and surface assisted transformations are important abiotic interfacial processes that function to attenuate (or diminish) 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; LaKind and Stone, 1987; and others).

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; Chioi et al., 1983, 1979; Means et. al 1982; Karickhoff, 1981,1979; Savage and Wauchope, 1974; Felsot and Dahm, 1970; and others). Research efforts to determine the interactions between neutral hydrophobic organic compounds (NHOCs) and metal oxide surfaces are ongoing (Mader et al., 1997; Perlinger et al., 1993; Schwarzenbach et al., 1993; Backus, 1990; Fowkes, 1964).

Current understanding of OP interaction with metal oxides is largely derived from research conducted using small organic ligands (important substructures of OPs and dissolved natural organic matter) and pure phase oxides (Vasudevan and Stone, 1998; 1996; Ludwig and Schindler, 1996; 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 OPs, particularly herbicides (Schwandt et al., 1992; Watson et al., 1973) and fewer

studies have examined the interaction between OPs and ultisols or minerals coated with iron oxides (Kumar, 1996; Kumar and Fish, 1996; Streck, 1985). Furthermore, our knowledge of competition and displacement effects at the iron oxide/water in multiple solute systems is limited.

A better understanding of the following will help bridge the information gaps and allow for better characterization of in situ contaminant fate in iron oxide rich environments : (1) the relationship between the composition and physical-chemical properties of iron oxide rich soils and the nature and extent of herbicide interaction at the oxide/water interface; (2) the knowledge of competitive reactions and displacement processes in the presence of multiple solutes and the consequent impact on herbicide interaction at the iron oxide/water interface; and (3) the relationship between herbicide structure/properties and the nature and rates of interactions at the oxide/water interface.

4. **Research Hypotheses**

1: Iron oxides are believed to adhere to silica surfaces via coulombic interactions and chemical bonds (Cornell and Schwertmann, 1996; Scheidegger et al., 1993). Surface characteristics of pure phase crystalline iron oxides are, therefore, likely to differ from those of iron oxide coatings on sand grains and clay particles. Differences in surface properties may arise from atoms on the surface of pure phase iron oxides and atoms on the surface of iron oxide coatings residing in distinct environments (Hochella, 1990). Given that the reactivity of iron oxide surfaces is dependent on oxide mineralogy and surface morphology, it is expected that the nature of herbicide interaction at the oxide/water interface and the resulting interfacial processes will be influenced by the "type" of iron-oxide surface encountered (i.e., pure phase hematite vs. hematite coated quartz vs. hematite coated kaolinite).

2: Organic ligands and OPs (ad)sorb reversibly onto metal oxides (Stumm, 1992). In addition, other dissolved organic and inorganic constituents compete with the OP for surface sites on the iron oxide (Watson et al., 1973). Thus, competitive surface reactions and displacement processes, in the presence of multiple solutes, will strongly influence the nature and extent of interfacial phenomena. It is, therefore, proposed that the composition of the percolating water (identity and concentration of organic and inorganic solutes) plays an important role in herbicide attenuation and mobilization in iron oxide rich environments.

3: Studies of small organic ligands have confirmed that organic compound structure/properties influence the nature and extent of adsorption onto oxide surfaces (Vasudevan and Stone, 1998, 1996; and reference cited). The physical-chemical properties of the compound, the identity and position of the ligand donor groups (polar functional groups) and compound hydrophobicity are together expected to determine the nature of the interfacial interactions and the consequent herbicide fate.

Response to potential counter arguments: It is important to point out that arguments have been made to suggest that the impact of iron oxides on the chemical fate of OPs is expected to be minimal. Reasons for these arguments include: (1) iron oxide surfaces are typically coated with natural organic matter (NOM) and, hence, the hydrophobicity of NOM, as opposed to the surface characteristics of iron oxides, determines OP fate; and (2) the molecular structure of OP and their relatively higher solubility makes them particularly susceptible to biotransformation, therefore, abiotic interfacial processes are expected to be inconsequential. With regard to the first argument, the PI submits that the highly weathered B horizons of the ultisols in the southeastern United States have a relatively low organic matter content (Brady, 1990). Additionally, oxides are products of weathering and are constantly being generated by soil processes (Zielke et al., 1989). The role of iron oxide surfaces in contaminant fate is, therefore, worthy of further investigation. Counter to the second argument, several pesticides/herbicides (expected to degrade in the topsoil) have been repeatedly detected in groundwater monitoring wells located in regions of iron oxide rich soils (Wade et al, 1997; Maas et al., 1992). These observations emphasize the need to expand our understanding of the processes that control the fate of herbicides. The proposed research expects to directly contribute to this knowledge.