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Confounding factors and tertiary-phase control by a surfactive agent on smectite sorption of atrazine

by

Mark Albert Chappell

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Soil Science (Soil Chemistry)

Program of Study Committee:
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Iowa State University
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For the Major Program
Dedication

This work is dedicated to my wife, Pornsawan, and children, Erik, Cameron, Mya, Morgan, and Alex, whose endless patience, love, support, and understanding made the completion of this dissertation possible.
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Abstract

Atrazine is a widely used commercial pesticide applied to soil for the control of broadleaf weeds in agriculture. Frequent detection of atrazine in surface and subsurface waters and the potential for adverse effects on toxicity to aquatic and terrestrial life have generated numerous investigations into the mechanisms governing atrazine sorption by soils. This dissertation seeks to add to that body of knowledge by elucidating basic mechanisms and processes that influence sorption of atrazine on clays in the presence and absence of surfactants commonly used in commercial formulations. Clay-sized (<2 μm) suspensions of the reference smectite, Panther Creek (PC) bentonite, were saturated with Ca or K using a dialysis technique. During this process, sub-samples of the clay suspensions were air-dried, ground, and then resuspended to test the effect of sample handling on atrazine sorption. Sorption studies showed that air-dried (AD), resuspended K⁺-saturated PC (KPC) exhibited a significantly enhanced sorption affinity for atrazine over KPC that was never-dried (ND). Atrazine sorption by AD Ca²⁺-saturated PC (CaPC) was negligibly different from atrazine sorption on ND CaPC. X-ray diffraction (XRD) analysis revealed that air-drying had irreversibly collapsed the basal spacing of KPC. It was hypothesized that the atrazine sorption was enhanced in the collapsed KPC because it provided a less hydrated environment where atrazine’s alkylamino sidechains could simultaneously interact with hydrophobic nanosites on both of the opposing basal surfaces.

Furthermore, this work explored the potential of a nonionic surfactant, Brij 35, which is similar to the surfactant used in commercial atrazine formulations, to modify the sorption chemistry of atrazine. Experiments revealed that lower concentrations of Brij 35 inhibited atrazine sorption while higher concentrations enhanced sorption; an opposite trend from what was expected. At low Brij 35 concentrations, XRD evidence indicated that Brij 35 was intercalated and progressively filled the clay interlayer. At low concentrations, Brij 35 apparently competed with atrazine for sorption sites in the clay interlayer. At high
concentration, interlayer sites were completely filled with Brij 35 and excess surfactant formed micelles on the external surfaces of the smectite quasicrystals. Atrazine sorption was enhanced by partitioning to these surface micelles. Effects of co-solvents on surface micelle formation are discussed.
CHAPTER 1. GENERAL INTRODUCTION: REVIEW OF SOILS (AND REPRESENTATIVE SOIL COMPONENTS), SURFACTANTS, AND ATRAZINE SORPTION

Literature Review

Atrazine (2-chloro-4-ethylamino-6-isopropyl – 1,3,5-triazine, Figure 1-1) is one of the most widely used herbicides in the United States. An estimated 64 to 76 million pounds of atrazine are applied each year, treating 75% of all field corn, 59% of all sorghum, and 76% of all sugarcane grown in the United States (USEPA, 2004). Usually applied to soil as a pre-emergent herbicide, atrazine is apoplastically translocated with water and nutrients to the leaves of growing weeds (Ross and Lembi, 1985). Atrazine acts as a photosynthetic inhibitor in broadleaf weeds and some annual grasses. Its mode of action arises from the binding of a particular protein (Qb) in the light reaction pathway and preventing electron transport from Photosystem II to Photosystem I (Devine et al., 1993; Ross and Lembi, 1985).

The widespread use of atrazine has given rise to its frequent detection in lakes, rivers, and groundwater systems of the Midwestern U.S. Atrazine is often found in these systems at concentrations exceeding the federal water drinking standard of 3 µg L\(^{-1}\) (Scribner et al., 2000; Shelton, 1989). Atrazine contaminates rivers through tile drainage flows (David et al., 2003; Rebich et al., 2004) while atrazine in groundwater may be linked to landfill leachates (Schultz and Kjeldsen, 1986). Atrazine contamination of surface and subsurface waters has heightened public concern over its environmental impact. Atrazine is an endocrine disruptor in mammals (Islam et al., 2002) and aquatic life (Christin et al., 2004; Le Pennec and Le Pennec, 2001; Moore and Lower, 2001). Also, atrazine alters the effectiveness of insecticides such as chloropyrifos (Belden and Lydy, 2001). Atrazine was officially classified by the US Environmental Protection Agency as a restricted-use pesticide (USEPA, 2002).
Soils and Representative Soil Components

Predicting the environmental fate of atrazine requires an understanding of the molecule's interaction with soil. Soil is a heterogeneous mixture of inorganic minerals, organic material, liquid water, and soil atmospheric gases. The proportion of these components in soil varies with soil type (e.g., organic soil vs. mineral soil) and impacts bulk physical characteristics. Description of atrazine sorption in soils usually involves quantifying sorption on representative soil components: namely, the inorganic clay fraction and the organic matter fraction.

Phyllosilicate clay minerals are the dominant reactive inorganic fraction in most soils. Each layer of a 2:1 phyllosilicate contains two sheets of Si-O tetrahedral sheets (Si$^{4+}$ cations tetrahedrally coordinated with four oxygen atoms) and one Al-O octahedral sheet (Al$^{3+}$ cations octahedrally coordinated with six oxygens or hydroxyl ions). By contrast, the 1:1 phyllosilicates (e.g., kaolinite) consist of one tetrahedral ($T_d$) sheet bound to one octahedral ($O_b$) sheet (Figure 1-2). Iowa soils are dominated by smectites, which are 2:1 phyllosilicates. Layer charge of phyllosilicates is determined by the extent to which Si$^{4+}$ in the $T_d$ sheets is substituted by Al$^{3+}$, and the Al$^{3+}$ in the $O_b$ sheets are substituted by Mg$^{2+}$ and/or Fe$^{2+}$, a process known as isomorphous substitution (ISS). These charge deficits,
which are expressed at the layer surface, give rise to a mineral’s cation exchange capacity (CEC). Smectites possess lower layer charge (-0.2 to -0.6 charge per formula unit), and thus, lower cation exchange capacities than vermiculites which are higher charged 2:1 clays (-0.6 to -0.9 charge per formula unit).

Stacked smectitic layers are separated by a water-filled interlayer region. Some of the physical properties of smectites (such as shrink/swell behavior at the crystalline scale) are largely influenced by processes occurring in the interlayer. Adjacent layers are held in proximity through electrostatic attractions with exchangeable cations in the interlayer. The distance between layers depends in large part on the extent of ISS, the sheet in which ISS occurred (Td or Oh), the type of exchangeable cation, and the activity of water in an equilibrating solution at one atmosphere. Smectite layer charge is sufficiently low to allow
the opposing clay layers to separate up to 2 nm apart (expansion of the vermiculite interlayer is typically limited to a $d$-spacing of 1.4 nm).

The activity of smectite clay depends largely on the hydration status of the interlayer; whether the interlayer is in an expanded or collapsed state. Crystalline swelling theory states that the interlayer may swell to one of four stable but discrete phases in which 0, 1, 2, or 3 layers of interlayer water are present in association with interlayer cations (Laird, 1996). Differences in the properties of a collapsed interlayer phase, when compared to the properties of an expanded interlayer phase, arise from the loss or gain of water and cations. Some smectite phases are more stable than others, for example when cations with low hydration energy (such as K) or Al hydroxide satisfy the layer charge. This suggests that the activation energy barriers stabilizing each interlayer phase are not equal, and that certain interlayer phase transitions may be thermodynamically irreversible. Irreversible collapse of a smectite interlayer leads to hysteresis in cation exchange reactions (Laird and Shang, 1997).

Soil organic matter (SOM) represents the dead and decayed materials deposited in soil by plants, animals, or microorganisms. These materials are subject to physical, chemical, and microbiological breakdown, the products of which are called humus. Humic materials, the dominant portion of soil organic matter (Stevenson, 1994), are a heterogeneous mixture of aromatic and aliphatic compounds. Humic substances are also polyelectrolytic, possessing a variety of O-, N-, and S-containing functional groups. The amphilicity of humic substances gives rise to a secondary structure resulting from the spontaneous separation of hydrophobic groups from hydrophilic groups and water (Engebretson et al., 1996; Ferreira et al., 2001; Varga et al., 2000). Humic substances are divided into three main fractions: humic acids, fulvic acids, and humin (Stevenson, 1994). Humic acids are distinguished from fulvic acids (Figure 1-3) by their black color, higher molecular weight, and lower levels of oxygen-bearing functional groups (Aiken et al., 1985).
Figure 1-3. Proposed comparison of humic and fulvic acid structures (from Schnitzer and Khan, 1972; Stevenson, 1982)
Atrazine Sorption on Soils

The sorption of atrazine and other nonpolar compounds on soil is strongly influenced by the soil’s organic matter content (Beck and Jones, 1996; Li and Felbeck, 1972; Rochette and Koskinen, 1996; Socias-Viciana et al., 1999). Sorption of atrazine and other nonpolar compounds is positively correlated with aromatics and low ratios of carbon to oxygen-bearing groups in SOM (Cox et al., 2000; Huang and Weber, 1997). Atrazine sorption in soil is less affected by clay content than by organic matter content of the soil (Laird et al., 1994). Yet, in the absence of SOM, atrazine readily sorbs to soil smectites. The extent of atrazine sorption on smectites varies with pH (Bailey et al., 1968; Weber, 1970), type of exchangeable cation (Celis et al., 1997; Prima et al., 2002; Sannino et al., 1999; Sawhney and Singh, 1997; Sheng et al., 2001), and clay layer charge (Barriuso et al., 1994; Laird et al., 1992).

Atrazine can interact with surfaces via several sorption mechanisms (Figure 1-4). These mechanisms reflect the inherent complexity of the atrazine molecule. Atrazine’s ethyl and isopropyl chains may associate with hydrophobic domains; the triazine ring acts as a Lewis base that may form H-bonds with surface-coordinated water; protons on ethyl- or isopropyl-amino groups may H-bond with the Lewis base sites on the surface (Laird and Koskinen, 2004). The relative importance of the different bonding mechanisms varies from system to system. However, hydrophobic bonding appears to be the dominant mechanism driving atrazine sorption in soils (at circumneutral pH).

Atrazine Formulations

Atrazine is poorly soluble in water and impossible to concentrate in aqueous solution without co-solubilizing agents. Commercially available atrazine formulations contain a variety of adjuvants to overcome this limitation, as well as to promote its distribution and stability in the environment. The basic components of most pesticide formulations include emulsifiers, solvents and co-solvents, wetting, dispersing, anti-freezing agents, and inert support materials (Knowles, 1995). Formulation types can vary depending on the
composition and proportion of these components. Currently, atrazine formulations are available as flowable concentrates, water-dispersible granules (dry flowables), a ready-to-use product (aqueous concentrate), and in granular form (USEPA, 2004).

Commercial pesticide formulations are designed to enhance the efficacy of the bioactive ingredient, while facilitating the simple and safe handling and application of the pesticide. For this reason, solutions of formulated atrazine are expected to behave differently in soils than are simple aqueous atrazine solutions. For example, Evangelou and Wang
(1993) learned from Ciba-Geigy researchers (manufacturers of atrazine formulations) that commercially formulated atrazine is much less soluble in water than reagent grade atrazine. Investigators typically employ "neat" solutions of reagent-grade chloro-atrazine in sorption experiments. Modeling the sorption behavior of atrazine using neat pesticide solutions may inadequately describe its environmental fate. Thus, improved predictions of atrazine's environmental fate may arise from appropriately considering the effects of the formulation components.

Quantifying the sorption behavior of individual formulation components may improve understanding of the sorption behavior of formulated atrazine. Next to solvents, nonionic surfactants make up the largest group of adjuvants in pesticide formulations (Krogh et al., 2003, and references therein). Yet, the choice of surfactant mainly determines the properties of the formulation (e.g., bioactive species maximum concentration, particle or droplet size, long-term stability) (Knowles, 1995). Nonionic polyoxyethylene oxide (PEO) alcohols are commonly used in s-triazine formulations (Edwards, 1998). Therefore, improved predictions of the environmental fate of formulated atrazine may be linked to the solution properties and sorption behavior of PEO surfactants.

**Solution Properties and Sorption Behavior of PEO Surfactants**

PEOs are amphiphilic, nonionic surfactants possessing a linear alkyl chain (the hydrophobic moiety) spatially separated from a hydrophilic polar ethylene oxide (EO) chain (where EO = OCH₂CH₂). A typical example of a PEO surfactant is Brij 35 (C₁₂EO₂₃; Figure 1-5). Like all surfactants, these molecules condense to form stable micelles in solution at characteristic polymer concentrations, called the critical micelle concentration or CMC. The free energy for micelle formation arises from the transfer of the alkyl chain group to the hydrophobic core of the micelle. In general, the CMC (an empirical index of a surfactant's aggregation number, or the number of surfactant molecules needed for micellization) of PEOs increases with increasing EO number because a higher concentration of surfactant is
needed to overcome steric hindrances caused by larger polar chains. Also, steric interactions reduce the size of the hydrophobic core (with increasing EO), and thus prevent formation of large micelles that occur with small-EO polymers (Bohmer et al., 1992).

PEO alcohols are often classified according to hydrophile-lipophile balance scores or HLB. The HLB is an empirical index of a PEO’s relative hydrophobicity and hydrophilicity. The HLB of PEO alcohols can be estimated by the formula \(E/5\), where \(E\) is the weight percent of ethylene oxide content in a surfactant molecule (Edwards, 1998). In general, PEOs with lower HLB values (shorter EO chain) are relatively hydrophobic compared to higher HLB PEOs (longer EO chain), which are more hydrophilic. Relationships of EO size and HLB score with PEO applications are summarized in Table 1-1.

The amphilicity of PEO molecules allows the surfactant to adsorb to a wide variety of surfaces. PEO surfactants undergo high affinity sorption on both hydrophilic solids, e.g., silica; (Kibbey and Hayes, 1997; Kibbey and Hayes, 2000; Koltalo-Portet et al., 2003; Levitz et al., 1984) and hydrophobic solids, e.g., polystyrene; (Geffroy et al., 2000). The extent of PEO adsorption mainly depends on the EO homolog size and the properties of the sorbent. In general, the sorption maximum of shorter EO surfactants (Figure 1-6) is greater than the
sorption maximum of longer EO surfactants on hydrophilic surfaces. This trend is mostly attributed to the smaller surface coverage of each shorter EO polymer. But, as shown in Figure 1-6, surfaces adsorb longer EO surfactants over a broad concentration range, suggesting that the surfaces may be selective for longer polymers. On a hydrophilic surface, where adsorption occurs via the EO portion of the polymer, the PEO with the longer, EO chain is preferred over the surfactant with the shorter EO chain. Thus, one way to characterize a surface is to determine the preferred EO size of a surfactant.

The low-cost commercial method for producing PEO alcohols employs a base-catalyzed (KOH) reaction of a long-chained alcohol (e.g., dodecanol) with $n$ moles of ethylene oxide (Edwards, 1998). This method gives rise to a mixture of PEO oligomers with broad EO size distributions. Thus, the nature of a surface may also be characterized by determining the EO homolog distribution during sorption (Figure 1-7). In theory, hydrophilic surfaces will preferentially adsorb longer, high HLB homologs. Hydrophobic surfaces will prefer the shorter homologs.

During adsorption, PEO surfactants modify the properties of the solid-liquid interface. This ability is a product of the molecule’s amphilicity and varies with EO chain length. For example, silica saturated with short EO polymers (Figure 1-8), becomes hydrophobic (Somasundaran et al., 1997). This occurs, as modeling studies predict, because the surfactant tail is pushed away from the surface following sorption so that it “sticks out”.

<table>
<thead>
<tr>
<th>HLB</th>
<th>EO content (wt%)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 - 6</td>
<td>20 - 30</td>
<td>Water in oil emulsion</td>
</tr>
<tr>
<td>7 - 15</td>
<td>35 - 75</td>
<td>Wetting agent</td>
</tr>
<tr>
<td>8 - 18</td>
<td>40 - 90</td>
<td>Oil in water emulsion</td>
</tr>
<tr>
<td>10 - 15</td>
<td>50 - 75</td>
<td>Detergent</td>
</tr>
<tr>
<td>10 - 18</td>
<td>50 - 90</td>
<td>Solubulizer</td>
</tr>
</tbody>
</table>
Figure 1-6. Sorption isotherms of two PEO surfactants with different EO chain sizes on silica (Redrawn from Somasundaran et al., 1997)
Figure 1-7. Distribution of EO homologs compared with PEO sorption (adapted from Cowell et al., 2000; Kibbey and Hayes, 1997). The solid line serves as both the sorption plot of the surfactant (for both surfaces) and the plot representing the average EO number for PEO adsorbed to a hydrophilic surface.
Figure 1-8. Change in hydrophobicity of silica as affected by sorption of two PEO surfactants with differing EO size (Redrawn from Somasundaran et al., 1997).
Figure 1-9. Drawing showing the shape and orientation of a “pinched” micelle formed on surfaces at high concentrations of long EO surfactant polymers, as predicted by self-consistent field (SCF) theory. The model predicts the hydrophobic core to be slightly raised off the surface and exposed to the bulk solution (drawn from description by Bohmer et al., 1992).

toward the bulk solution (Bohmer et al., 1992). Further adsorption of short EO polymers leads to the formation of a surface bilayer, which endows the silica with hydrophobic character. In contrast, silica remains hydrophilic following high surface coverages of long EO polymers. Instead of forming bilayers, long EO polymers are believed to form a type of “pinched” micelle (Figure 1-9) on the surface, with a hydrophobic core that is slightly raised off the surface (Bohmer et al., 1992; Toerne et al., 2001).

**Pesticide – Surfactant Interactions during Sorption**

Formulations are specifically designed to promote the distribution of pesticides on soil. Thus, surfactants are expected to modify the inherent sorption behavior of pesticides. Most of the work investigating nonpolar solute – surfactant interactions involves organically modified smectites. In this work, nonpolar organic compounds (NOC) are adsorbed onto smectite clays that have been saturated with cationic alkylammonium surfactants. The surfactants differ in the size of their hydrophobic moieties. For example, trimethylammonium (TMA) surfactants have short alkyl chains and hexadecyltrimethylammonium (HDTMA) surfactants possess long alkyl chains. For the
HDTMA-modified clays, enhanced NOC sorption was positively correlated with the degree of HDTMA saturation of the clay (Jaynes and Boyd, 1991b). On the other hand, enhanced NOC sorption was negatively correlated TMA saturation (Jaynes and Boyd, 1991a). In the former case, high-charge smectites adsorbed sufficient quantities of HDTMA to form a paraffin-like matrix in the clay interlayer that promoted partitioning of the nonpolar solutes. In the latter case, TMA was thought to “shield” the charged smectite sites, in effect, enhancing the influence of noncharged interlayer sites.

The effect of nonionic surfactants on the sorption behavior of NOCs (including atrazine) is less understood. Evidence for both enhanced and suppressed NOC sorption in the presence of nonionic surfactants is available (Lee et al., 2000; Sun et al., 1995). Sun et al. (1995) hypothesized that NOC sorption was inhibited when a sufficient concentration of surfactant remained in the equilibrium solution to form micelles. Solution micelles should compete with the surface for NOCs. However, this hypothesis does not explain how nonionic surfactants can enhance NOC sorption. Abu-Zrieg et al (1999) and Iglesias-Jiminez (1996) observed enhanced sorption of atrazine by soil when simultaneously adding high concentrations of the nonionic surfactants Rexonic, Rexol, or Tween 80 into solution. This information suggests some form of cooperative interaction between atrazine and the surfactants. On the other hand, nonionic surfactants can enhance atrazine mobility in soils and clays (Huggenberger et al., 1973; Prima et al., 2002; Sanchez-Camazano et al., 1995), suggesting that nonionic surfactants inhibit atrazine sorption.

**Hypotheses and Objectives**

The main hypotheses of this dissertation are as follows:

- Exchangeable cation type and sample handling (e.g., air-drying) irreversibly alter the hydration status of smectite interlayer, affecting atrazine sorption affinity.
Atrazine sorption is significantly impacted by the presence of the nonionic surfactant Brij 35.

The main objectives of this dissertation are:

- To elucidate the effects of exchangeable cation type and sample handling on the interlayer space of a reference smectite and to correlate these changes with sorption affinities of atrazine.
- To elucidate the effect of the surfactant Brij 35 on sorption of atrazine by soils and clay.

**Dissertation Organization**

This dissertation is organized into 6 chapters and 4 appendices. Chapter 1 contains a general introduction of the dissertation, reviewing critical aspects of soils (and their representative components), surfactants, and atrazine sorption. Chapter 2 deals with relationships among the type of exchangeable cation, sample handling of a reference smectite, and atrazine sorption affinity. Chapter 3 investigates sorption and surface-induced degradation of the nonionic surfactant, Brij 35. Chapter 4 presents the influence of Brij 35 on the sorption of atrazine on a reference smectite. Chapter 5 investigates the influence of Brij 35 on the sorption of atrazine on soils. Chapter 5 also presents data on the sorption behavior of the commercial atrazine formulation, Aatrex 4L. Chapter 6 contains the general conclusions of the dissertation. Appendices containing supplementary data are numbered 1 – 4, corresponding to Chapters 2 through 5. The bibliography containing the references listed makes up the last section of this dissertation.
CHAPTER 2. SAMPLE HANDLING EFFECTS ON SORPTION AFFINITY OF ATRAZINE BY SMECTITIC SOILS AND REPRESENTATIVE SOIL COMPONENTS

A paper to be submitted to Environmental Science and Technology

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Abstract

Sorption studies are important both for investigations of interaction mechanisms between organic molecules and soil surfaces and to parameterize models that predict the fate of organic contaminants in soils. Experiments showed that air-drying caused an irreversible decrease in the basal spacing of K-saturated Panther Creek smectite (PC), while basal spacings of never-dried and air-dried-rehydrated Ca-PC were similar. The affinity of atrazine sorption was twice as high for the never-dried K-PC as the never-dried Ca-PC. Air-drying K-PC increased its sorption affinity by one order of magnitude, while no significant effect of the air-drying treatment was observed for Ca-PC. Air-drying resulted in no significant difference in the affinity of Ca-humic acid (Aldrich humic acid) samples for atrazine. Choice of background solution (20 mM KCl versus 10 mM CaCl2) and air-drying treatments significantly affected atrazine sorption affinities for the three-smectitic soils,

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however the trends were not consistent with those observed for the reference smectite. Further, extending the initial rehydration time from 24 to 240 h (prior to adding atrazine) significantly decreased the soil’s sorption affinity for atrazine. We conclude that the hydration status of smectites has a large influence on the affinity of atrazine sorption, and air-drying treatments have the potential to modify the sorption affinity of smectitic soils for organic molecules such as atrazine.

Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is one of the most widely used selective herbicides in commercial agricultural operations throughout the world. Because of its widespread use, atrazine is frequently found as a pollutant in lakes, rivers, and groundwater, often in concentrations exceeding the 3 µg L⁻¹ federal drinking water standard (Scribner et al., 2000; Shelton, 1989). The recently recognized ability of atrazine to behave as an endocrine disrupter in mammals (Islam et al., 2002) and aquatic life (Le Pennec and Le Pennec, 2001; Moore and Lower, 2001) emphasizes the need to understand the fate of atrazine in the environment.

Atrazine is a weak base (pKa = 1.68) and has a relatively low solubility (33 mg L⁻¹) in water. Because of its relatively hydrophobic nature, atrazine was assumed for many years to be primarily adsorbed by soils through partitioning of the atrazine into soil organic matter (Chiou et al., 1979; Chiou et al., 1983; Karickhoff, 1981). In the early 1990’s, however, new understanding about the nature of clay mineral surfaces raised awareness of the fact that soil clays can also play a prominent role in determining the fate of atrazine and other weakly polar organic molecules in soil environments. Lee et al. (1990) demonstrated an inverse relationship between sorption of aromatic compounds from aqueous systems and the layer charge of organic-modified smectites (saturated with tetramethyl ammonium ions). The authors suggested that the aromatic molecules were interacting directly with the siloxane surfaces between charge sites. These results prompted Jaynes and Boyd (1991b) to use various aromatic compounds to further probe the nature of the siloxane surfaces of organic-
modified smectites and to conclude that the siloxane surfaces of the smectites must have some hydrophobic character. Shortly thereafter, Laird et al. (1992) demonstrated that Ca-smectites could adsorb from zero to 100% of added atrazine from mildly acidic (pH = 4.8 to 6.5) aqueous solutions. In this study, an inverse relationship was observed between the affinity of atrazine sorption and layer charge of the smectites. Because the pH of the systems was well above the pKa of atrazine, the authors argued that atrazine was sorbed as a neutral species through hydrophobic interactions with molecular scale uncharged regions on the siloxane surfaces. Later Laird and Fleming (1999) probed the nature of smectite surfaces with 3-butylpyridine and found clear evidence for sorption of the ionic species at pH's below the pKa and sorption of molecular species for pHs above the pKa of the 3-butylpyridine. Adsorption of the molecular species was attributed to a combination of hydrophobic interactions involving uncharged nanosites on the siloxane surfaces and polar interactions involving the ring N and water molecules solvating the interlayer cations. Other workers have found that smectites have substantial potential for sorption of a wide range of weakly polar and nonpolar organic compounds (Sheng et al., 1996).

The type of exchangeable cations on the clay surfaces influences the affinity of smectites for atrazine. For example, less atrazine was retained by a Ca-smectite than a mixed ion (9:1 Na:Ca) smectite (Prima et al., 2002). Potassium-saturated smectite exhibited a higher sorption affinity (Kf) for atrazine than Ca-smectite (Sheng et al., 2001). Fe-saturated Wyoming bentonite had nearly 100x greater affinity for atrazine than its Ca-saturated counterpart (Celis et al., 1997). Similarly, smectite saturated with Al^{3+} had a much higher affinity for atrazine than Ca-smectite (Sawney and Singh, 1997). Conversely, introduction of charged Al_{x}(OH)_{x} polymers decreased the affinity of atrazine sorption by montmorillonite (Sannino et al., 1999).

Smectites can exist in multiple hydration phases, variously having 0, 1, 2, 3, or 4 discrete layers of interlayer water molecules. The process whereby a smectite transitions between two or more of these hydration phases is known as crystalline swelling. The extent of crystalline swelling for a smectite is influenced by properties of the smectite (e.g., total
layer charge and percentages of tetrahedral charge), nature of the saturating cations (e.g., valence and hydration energy), and the activity of water in the equilibrating solution or atmosphere. Activation energy barriers stabilize each hydration phase, causing hysteresis in crystalline swelling (Kittrick, 1969; Laird et al., 1995). Hysteresis in crystalline swelling is believed to be the primary cause of hysteresis in cation exchange reactions (Laird and Shang, 1997; Verberg and Baveye, 1994).

Most soils collected from the field are routinely air-dried before use in sorption experiments. We hypothesized that air drying of smectitic soils may cause an irreversible change in the hydration status of the soil smectites which, in turn, may affect the affinity of the soil for atrazine. Several studies have evaluated the effect of rehydration time on atrazine sorption. Rewetting of an air-dried soil typically occurs as a bimodal process: rapid rehydration followed by a prolonged rehydration stage (Thouvenin et al., 2002), indicative of intraparticle diffusion of water. These stages of rewetting are often reflected in the rates of pesticide uptake (Belleveau et al., 2000; Gamble, 2000). Both atrazine sorption (K_f) and sorption-desorption hysteresis were shown to increase for soils rehydrated for longer periods of time (Borisover et al., 2001; Lesan and Bhandari, 2003). The potential influence of hysteresis in crystalline swelling of soil smectites on sorption of organic molecules by soils has not been previous considered.

The specific objectives of this study were: 1) to determine whether the extent of crystalline swelling influences sorption of atrazine by a reference smectite, 2) to determine whether sample handling (e.g., air-drying which may impact crystalline swelling) influences sorption of atrazine by a reference smectite and humic acid samples, and 3) to assess whether sample handling (e.g., air-drying) has the potential to adversely affect the accuracy of sorption studies involving smectitic soils.
**Materials and Methods**

**Reagents**

Atrazine (99% purity) was obtained from Chem Service (West Chester, Pennsylvania, USA) and used as received. A.C.S-certified dimethyl sulfoxide (DMSO), methanol (MeOH), acetonitrile, and potassium phosphate were obtained from Fisher Scientific (Madison, Wisconsin, USA). Methanol and acetonitrile were HPLC quality.

**Sample Preparation**

Panther Creek (PC) bentonite was obtained from the A.D. Scott mineral collection at Iowa State University. The PC is a low-charge beidellite (surface charge density = 1.42 μmol_c m^-2, 52 % tetrahedral charge, (Laird et al., 1992). For the study, the raw PC ore was first washed with 0.5 M NaCl, and then the clay-size fraction (<2.0 μm e.s.d) was collected by sedimentation. Suspensions of <2.0 μm Na-PC were transferred to Spectra/Por membrane tubing (MWCO 4-6,000) and initially dialyzed against 100 mM CaCl_2 or 200 mM KCl. When the Na concentrations in the equilibrating solution decreased to approximately 1 mg L^-1, the samples were equilibrated with dilute CaCl_2 (5 mM) or KCl (10 mM) to prepare the final Ca-PC and K-PC suspensions. Portions of the Ca-PC and K-PC suspensions were stored at 4°C (referenced as the “never-dried sample” or “ND treatment”). Another portion of each suspension was air-dried under filtered (0.45 μm) air; crushed in an agate mortar, then the air-dried clays were resuspended in, and dialyzed against the dilute CaCl_2 or KCl solutions (referenced as the “air-dried, resuspended sample” or the “AD treatment”). The treated clays were stored as suspensions for approximately two months at 4°C before their use in the atrazine sorption experiments.

Sodium-saturated Aldrich humic acid (HA) was suspended in 0.5 M CaCl_2, and titrated to pH 1 with 5 M HCl. The HA precipitate was collected by centrifugation (13,182 x g for 10 min), and after decanting the supernatant, was resuspended in 0.5 M CaCl_2. The HA precipitate was then titrated to pH 6.0 with saturated Ca(OH)_2, and dialyzed against dilute CaCl_2. As described for the PC clays, one portion of the Ca-HA sample was stored as a
never-dried suspension and another sample was air-dried and then resuspended in dilute CaCl₂ dialyzed to equilibrium.

Three smectitic soils from the Midwestern U.S. were also studied. After field collection, one portion of each sample was sealed in airtight plastic bags and stored at 4 °C (referenced as “never-dried”). Another portion of each sample was air-dried, crushed in an agate mortar, and passed through a 2-mm sieve prior to use (referenced as “air-dried”).

**XRD Analysis**

A special liquid sample cell was constructed to measure the basal spacings of clay minerals in suspensions. The cell was similar to that described by Shang et al. (1994) except that the cell was designed for operation in reflection mode rather than transmission mode. X-ray diffraction analysis of the clay suspensions (20 mg clay ml⁻¹ water) was conducted with a Siemens D5000 x-ray diffractometer using CuKα radiation, with a step size of 0.05 degrees and dwell time of 108 to 120 sec per step (the analysis took approximately 4 hours per sample). The cell was tested by analyzing a suspension of a reference glauconite that gave the anticipated 10 Å peak. All of the studied clays remained dispersed throughout the entire analysis period except the air-dried, resuspended Ca-PC, which tended to settle out after about one hour. For this sample, the analysis was halted every 30 min to re-disperse the sample by shaking.

**Atrazine Sorption Experiments**

Cation-saturated PC clay suspensions were added to 30-ml Nalgene Teflon tubes at a solid-solution ratio of 12.5 mg mL⁻¹ (or 250 mg of solids), containing dilute CaCl₂ (10 mM) or KCl (20mM) background electrolyte. Atrazine, originating from a stock solution of 30 mg L⁻¹ atrazine in 96% water + 4% methanol (v/v), was added and the systems were equilibrated on a rotary shaker (70 rpm) for 24 hrs. The clay suspensions were centrifuged (6722 x g for 10 min) and the clear supernatant was analyzed for atrazine. The amount of atrazine sorbed was calculated by subtraction. For quality-control purposes, the sorbed atrazine was also extracted from the clay samples and analyzed separately. The extractant was a 60:40 mixture
of dimethyl sulfoxide (DMSO) and 10 mM CaCl₂ (adjusted to pH 9.5 using saturated Ca(OH)₂). The clay samples were resuspended in the extractant by vortexing for 30 sec and then equilibrating for 1 h on a rotary shaker. After centrifugation (6722 x g for 10 min), the supernatant was decanted and analyzed for atrazine and hydroxyatrazine by HPLC. The extraction procedure was repeated three or four times for each sample. Total recovery of the sorbed atrazine averaged 98% (ranging from 78 to 114% recovery). No hydroxyatrazine was detected in either the supernatant for the adsorption experiment or extracted solutions.

Sorption of atrazine on the air-dried and never-dried Ca-saturated humic acid (Ca-HA) samples was also determined. The air-dried Ca-HA sample was rehydrated using Teflon tubes for 24 h in dilute CaCl₂ (10 mM) before adding atrazine. Handling and analysis of the air-dried and never-dried Ca-HA suspensions (solid-to-solution ratio = 12.5 mg ml⁻¹) were similar to that described above for the PC clay suspensions. We attempted to run a similar analysis for K-saturated humic acid (K-HA) but were unsuccessful due to our inability to separate K-HA from solution by centrifugation. Also, we did not attempt to extract sorbed atrazine from the Ca-HA samples, because the extractant would have solubulized substantial amounts of the humic material.

Both air-dried and never-dried soil samples (4 g) were suspended in dilute CaCl₂ (10 mM) or KCl (20 mM), and equilibrated on a rotary shaker for 24 h prior to the addition of atrazine. Otherwise the procedure used to investigate atrazine sorption by was similar to that described above. Again, it was not possible to extract sorbed atrazine from the soils because significant quantities of humic materials would have been solubulized by the extractant. Selected chemical and physical properties of the soils used in this study are presented in Table 2-1. The effect of soil rehydration time on atrazine sorption was tested by suspending air-dried Sparta soil in the dilute (20 mM) CaCl₂, and allowing the suspensions to equilibrate from 24 to 240 h on a side-to-side shaker. Afterwards, atrazine was added and the soil suspensions were equilibrated for an additional 24 hours. Sorbed atrazine was calculated as described above.

All atrazine sorption experiments for PC, HA, and soils were conducted in triplicate.
Table 2-1. Selected physical and chemical characteristics of three smectitic soils.

<table>
<thead>
<tr>
<th>soil</th>
<th>clay/silt/sand</th>
<th>Org. C</th>
<th>pH$^1$</th>
<th>Sum of Exchangeable Cations$^1$ cmol kg$^{-1}$</th>
<th>Exchangeable Cations$^2$ cmol kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>g kg$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sparta</td>
<td>15 32 53</td>
<td>1600</td>
<td>6.2</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>Sperry</td>
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<td>2100</td>
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<td>15.7</td>
<td></td>
</tr>
<tr>
<td>Zook</td>
<td>43 42 15</td>
<td>2100</td>
<td>5.9</td>
<td>29.8</td>
<td></td>
</tr>
</tbody>
</table>

$^1$: 1:1 water:soil.

$^2$: Obtained by adding 30 ml of 0.2 M NH$_4$Cl to a 50 ml polypropylene centrifuge tube containing 4 g of air-dried soil. The tubes were shaken for 1 hr on a side-to-side shaker, and then centrifuged for 10 min at 9000 rpm. Clear supernatant was collected, and then the soil was rewashed with NH$_4$Cl solution for a total of three times. Supernatant from the three consecutive washes was analyzed by inductively coupled plasma (ICP).
Atrazine Analysis

Atrazine analysis was conducted by reverse phase-high pressure liquid chromatography (RP-HPLC). Chromatographic separations were carried out using a Hewlett-Packard 1050 series HPLC with UV-detection (223 nm) and an Alltech (Alltech Associates, Inc., Deerfield, Illinois) Platinum EPS C18 column (250-mm length, 4.6-mm i.d., 100 Å pore size, 5-µm particle size). The mobile phase consisted of a mixture of (A) 10 mM KH$_2$PO$_4$ (adjusted to pH 3 with concentrated o-phosphoric acid) and (B) acetonitrile. The gradient elution was initially 80:20 (A to B) and graded linearly to 60:40 (A to B) over an 8-min run. The elution rate was 1 ml min$^{-1}$. The method was calibrated with reagent grade atrazine over the range of 0.6 to 10.5 mg L$^{-1}$ ($R^2 = 0.9998$).

Data Analysis

A weighted nonlinear regression was used to fit the measured sorption data to the modified Freundlich equation (Carmo et al., 2000);

$$C_s = K_F' C_r^n,$$

where $C_s$ is the amount of atrazine sorbed at equilibrium (µmol kg$^{-1}$), $C_r$ is the unitless ratio of the equilibrium solution atrazine concentration (µmol L$^{-1}$) to the molar solubility of atrazine (µmol L$^{-1}$), $K_F'$ is the modified Freundlich sorption affinity constant (µmol kg$^{-1}$), and $n$ the coefficient of linearity (unitless). Tests for significance differences among $K_F'$ values were evaluated using a pooled t-test. All statistical analyses and nonlinear fitting were done using SAS (SAS institute, Cary, NC, USA).

Results and Discussion

Panther Creek Smectite

X-ray diffraction analysis of never-dried Ca-PC aqueous suspensions revealed a very broad $d_{001}$ peak centered on 2.1 nm (Fig. 2-1a). The 2.1-nm basal spacing indicates that the never-dried Ca-PC was dominated by domains with four layers of interlayer water molecules.
The very broad nature of the XRD peak was caused both by the random orientation of clay quasicrystals in the suspensions and by disorder in the layer stacking sequence. Previous XRD analysis of Ca-PC prepared as air-dried oriented films showed a basal spacing of 1.5 nm (Laird et al., 1992), which indicates only two layers of interlayer water molecules. Thus in an aqueous suspension, Ca-PC interlayers are much more expanded and more fully hydrated than in the air-dry state, typically analyzed by XRD. This distinction is important, because during an adsorption experiment the solute “sees” the more fully hydrated clay and must compete with water molecules for adsorption into the expanded interlayers.

The air-drying treatment undoubtedly causes the AD Ca-PC to collapse to 1.5 nm, but it is evident from Figure 2-1a that the Ca-PC re-expanded to 2.0 nm when resuspended. The XRD peak for the AD Ca-PC suspension is shifted slightly to the right (2.0 versus 2.1 nm) and is slightly less broad than the XRD peak for the ND Ca-PC suspension. These differences indicate that the coherently diffracting domains in the AD Ca-PC suspensions were larger and more ordered than the domains in the ND Ca-PC suspensions. But it is clear that both the AD and the ND Ca-PC samples are dominated by interlayers with four layers of interlayer water molecules.

X-ray diffraction patterns for the AD and ND K-PC clay suspensions are presented in Figure 2-1b. The XRD peaks (shoulders) for the K-PC suspensions are even broader and more diffuse than the peaks observed for the Ca-PC suspensions. The XRD peak for the ND K-PC suspension is centered on approximately 1.7 nm, which is close to the anticipated peak position for a smectite dominated by three layers of interlayer water molecules (1.75 nm). By contrast, the XRD peak for the AD K-PC suspension is centered at approximately 1.38 nm, which is about halfway between the anticipated peak positions for a two layer hydrate (1.50 nm) and a one layer hydrate (1.25 nm). The results indicate random interstratification of layers with one and two layers of interlayer water molecules in the AD K-PC suspension.

Greater atrazine sorption occurred on K-PC than Ca-PC (Figure 2-2). The air-drying treatment did not significantly affect the sorption affinity of the Ca-PC for atrazine (Tables 2-2 and 2-3), however, the air-dried K-PC had almost an order of magnitude greater affinity
Figure 2-1. X-ray diffractograms of (A) CaPC and (B) KPC clay suspension.
Figure 2-2. Atrazine sorption isotherms for (A) Ca-PC and (B) K-PC clay suspensions.
Table 2-2. Regression coefficients calculated from the nonlinear fit of the modified Freundlich equation to the atrazine sorption data.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cation</th>
<th>Handling</th>
<th>$K_F'$</th>
<th>$K_F'$ st. error</th>
<th>$n$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
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<td>ND</td>
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<td>108</td>
<td>0.66</td>
<td>0.99</td>
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<tr>
<td></td>
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<td>2248</td>
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<td>0.99</td>
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<td>HA</td>
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<td>ND</td>
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<td>1.13</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AD</td>
<td>11098</td>
<td>2150</td>
<td>1.23</td>
<td>0.99</td>
</tr>
<tr>
<td>Sparta</td>
<td>Ca</td>
<td>ND</td>
<td>114</td>
<td>5</td>
<td>0.67</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AD</td>
<td>249</td>
<td>22</td>
<td>0.91</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>ND</td>
<td>160</td>
<td>14</td>
<td>0.83</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AD</td>
<td>283</td>
<td>4</td>
<td>0.87</td>
<td>1.00</td>
</tr>
<tr>
<td>Sperry</td>
<td>Ca</td>
<td>ND</td>
<td>462</td>
<td>10</td>
<td>1.25</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AD</td>
<td>265</td>
<td>26</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>ND</td>
<td>247</td>
<td>10</td>
<td>0.87</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AD</td>
<td>247</td>
<td>1</td>
<td>0.94</td>
<td>1.00</td>
</tr>
<tr>
<td>Zook</td>
<td>Ca</td>
<td>ND</td>
<td>277</td>
<td>39</td>
<td>0.83</td>
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<tr>
<td></td>
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<td>AD</td>
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<tr>
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<td>K</td>
<td>ND</td>
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<tr>
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<td></td>
<td>AD</td>
<td>374</td>
<td>3</td>
<td>0.85</td>
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</tr>
</tbody>
</table>


Table 2-3. Test for statistical differences (pooled t-test) in $K_F'$ between the different treatments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Treatment</th>
<th>Statistical test</th>
<th>df (pooled)</th>
<th>t-statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>Ca</td>
<td>ND vs. AD</td>
<td>10</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>ND vs. AD</td>
<td>10</td>
<td>-16.80*</td>
</tr>
<tr>
<td></td>
<td>ND†</td>
<td>Ca vs. K</td>
<td>10</td>
<td>-8.46*</td>
</tr>
<tr>
<td></td>
<td>AD‡</td>
<td>Ca vs. K</td>
<td>10</td>
<td>-20.61*</td>
</tr>
<tr>
<td>HA</td>
<td>Ca</td>
<td>ND vs. AD</td>
<td>10</td>
<td>-1.18</td>
</tr>
<tr>
<td>Sparta</td>
<td>Ca</td>
<td>ND vs. AD</td>
<td>6</td>
<td>-11.78*</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>ND vs. AD</td>
<td>6</td>
<td>-17.03*</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>Ca vs. K</td>
<td>6</td>
<td>-6.18*</td>
</tr>
<tr>
<td></td>
<td>AD</td>
<td>Ca vs. K</td>
<td>6</td>
<td>-3.06*</td>
</tr>
<tr>
<td>Sperry</td>
<td>Ca</td>
<td>ND vs. AD</td>
<td>6</td>
<td>13.95*</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>ND vs. AD</td>
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<tr>
<td></td>
<td>ND</td>
<td>Ca vs. K</td>
<td>6</td>
<td>31.34*</td>
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<tr>
<td></td>
<td>AD</td>
<td>Ca vs. K</td>
<td>6</td>
<td>1.39</td>
</tr>
<tr>
<td>Zook</td>
<td>Ca</td>
<td>ND vs. AD</td>
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<td>-7.95*</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>ND vs. AD</td>
<td>6</td>
<td>1.06</td>
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<td></td>
<td>ND</td>
<td>Ca vs. K</td>
<td>6</td>
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<tr>
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<td>AD</td>
<td>Ca vs. K</td>
<td>6</td>
<td>6.66*</td>
</tr>
</tbody>
</table>

† Never-dried
‡ Air-dried, resuspended

*Significant at the 0.025 probability level
for atrazine relative to the never-dried K-PC (Figure 2-2a, Table 2-2). The results indicate that hydration status of smectite interlayers has a larger influence on affinity of smectites for atrazine than does the nature of the saturating cation, and that hysteresis in crystalline swelling, caused by different sample handling procedures, can greatly influence pesticide sorption.

Atrazine is adsorbed into the interlayers of smectites and may interact with smectite surfaces through a variety of bonding mechanisms (Laird and Sawhney, 2002). The lone pair electrons of the ring N atoms may form hydrogen bonds with water molecules, especially those solvating the exchangeable interlayer cations. At the same time the alkyl tails of the atrazine molecule may interact with hydrophobic nanosites on the smectite basal surfaces, i.e., valence-satisfied basal oxygens located between charge sites. For a smectite with only one or two layers of interlayer water, the isopropylamino and ethylamino side chains can readily interact simultaneously with hydrophobic nanosites on the opposing basal surfaces. For a more expanded smectite with three or four layers of interlayer water molecules the alkyl side chains will only be able to interact with one basal surface at a time. This difference is believed to account for the dramatic effect of crystalline swelling on the affinity of smectites for atrazine (Figures 2-1 and 2-2).

**Aldrich Humic acid**

The molecular scale conformation of humic materials may be influenced by sample handling. In aqueous systems, hydrophilic moieties of humic substances tend to point outward, while hydrophobic moieties tend to be confined within humic colloids (Mingelgrin, 2001). Air drying treatments have the potential to invert this conformation. Therefore, we evaluated the effect of air-drying treatments on the affinity of Ca-HA for atrazine. The isotherms for sorption of atrazine on Ca-HA were slightly convex (Fig. 2-3) with $n$ values $> 1.0$ (Table 2-2), however, the $K_p'$ values for AD and ND Ca-HA were not significantly different ($P>0.025$, Table 2-3). Total atrazine sorbed by AD and ND Ca-HA was comparable to quantities sorbed by ND K-PC and much less than sorbed by AD K-PC.
Figure 2-3. Effect of sample handling on atrazine sorption isotherms for Ca-HA.

Figure 2-4. An example of the atrazine sorption isotherm obtained for the smectitic soils (Sparta in 10 mM CaCl₂).
Humic acids are extraordinarily complex materials with a vast array of organic functional groups arranged in an almost infinite number of structures (Stevenson, 1994). Any physical or chemical perturbations of a HA sample are likely to alter the molecular scale conformation of potential solute-binding sites within the sample. And change in the conformation of a binding site could alter the binding energy of an organic molecule sorbed to that site. In the studied sample of Ca-HA, we saw no net change in the macroscopic sorption affinity for atrazine due to the air-drying treatment. This result, however, does not mean that the Ca-HA was unaffected by the air-drying treatment nor does it imply that the sorption affinity of other HA samples or the humic materials in soils will be necessarily unaffected by air-drying or other sample handling treatments.

Smectitic Soils

Results for the Panther Creek smectite raise concerns that the reliability of atrazine sorption data for smectitic soils may be adversely affected by sample handling. Therefore, three smectitic soils were analyzed using air-dry and never-dry pretreatments. Although the
Table 2-4. Regression coefficients calculated from the nonlinear fit of the modified Freundlich equation to the atrazine sorption data and test for statistical significance for the air-dried, resuspended Sparta soil in 10 mM CaCl₂.

<table>
<thead>
<tr>
<th>Rehydration time (hr)</th>
<th>Kₚ(t)</th>
<th>Kₚ(t) st. error</th>
<th>n(t)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>395</td>
<td>10</td>
<td>1.03</td>
<td>1.00</td>
</tr>
<tr>
<td>109</td>
<td>278</td>
<td>6</td>
<td>0.95</td>
<td>1.00</td>
</tr>
<tr>
<td>240</td>
<td>221</td>
<td>10</td>
<td>0.86</td>
<td>0.99</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Statistical test</th>
<th>df</th>
<th>t-statistic (pooled)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hr vs. 109 hr</td>
<td>6</td>
<td>-2.22</td>
</tr>
<tr>
<td>109 hr vs. 240 hr</td>
<td>6</td>
<td>-1.77</td>
</tr>
<tr>
<td>24 hr vs. 240 hr</td>
<td>6</td>
<td>-2.97*</td>
</tr>
</tbody>
</table>

*Significant at the 0.025 probability level

soil samples were not saturated with Ca or K prior to the adsorption analysis, we did conduct the sorption experiments using both CaCl₂ and KCl background solutions. Clay content, the most important difference among the soil samples, ranged from 15% in the Sparta to 43% in the Zook (Table 2-1). Organic C levels were similar in the Sperry and Zook and slightly lower in the Sparta. Calcium was the dominant cation on the exchange complex of all three soils (from 71 to 83% of CEC), followed by Mg (14 to 21% of CEC), and K (1.2 to 5.4% of CEC).

An example of the atrazine sorption isotherms obtained in these experiments is shown in Figure 2-4. The trends in the data were variable. Significantly (P<0.025) higher Kₚ' values were obtained for sorption of atrazine on the AD Sparta and AD Zook rehydrated in CaCl₂ relative to the ND Sparta and ND Zook (Tables 2-2 and 2-3). In contrast, ND Sperry rehydrated in CaCl₂ had a significantly higher Kₚ' than AD Sperry rehydrated in CaCl₂.
Also, the $n$ value for ND Sperry rehydrated in CaCl$_2$ was greater than 1.0. In dilute KCl, the AD Sparta exhibited a significantly higher $K_F'$ value than ND Sparta, but the $K_F'$ values for the AD Sperry and AD Zook soils were not significantly different from the $K_F'$ values for the ND Sperry and ND Zook soils. These results indicate that air-drying treatments and choice of background electrolyte can significantly impact atrazine sorption for smectitic soils. The results, however, were not entirely consistent with the trends observed using the Panther Creek smectite.

The effect of soil rehydration time (prior to atrazine addition) on atrazine sorption was studied using the AD Sparta soil suspended in CaCl$_2$ (Fig. 2-5). These data show that the $K_F'(t)$ values decreased significantly by the end of the 240 h rehydration period (Table 2-4). The $n(t)$ values also decreased with rehydration time. Enhanced sorption of atrazine on previously air-dried soil has been shown to occur when a solute moves with a wetting front (Belleveau et al., 2000; Borisover and Graber, 2002). Our data show that the legacy of an air-drying treatment may influence atrazine sorption long after a sample has been rehydrated. In practical terms, the data demonstrate that sample handling can have a substantial impact on sorption of atrazine and probably many other organic compounds by soils and clays and therefore should be carefully considered in both mechanistic studies of sorption phenomena and efforts to model the environmental fate of contaminants in soils and sediments.

**Conclusions**

The affinity of smectites for atrazine is influenced by the hydration status of the interlayer, which is related to the extent of crystalline swelling and the nature of the saturating cations. Hysteresis in crystalline swelling of smectites caused by differences in sample handling (e.g., air-dried versus never-dried) can cause substantial variation in the affinity of smectites for atrazine. Sample handling was not found to affect the affinity of humic acid for atrazine. On the other hand, sample handling does affect the affinity of soils for atrazine, but not necessarily with the same trend as observed for the smectite. The presence in soils of multiple mineral and organic phases as well as interactions between soil...
minerals and organic matter are believed to affect the impact of sample handling on atrazine sorption affinity. Results of this study indicate that sample handling can have a substantial effect on atrazine sorption coefficients.

**Acknowledgments**

Thanks to Scott Schlorholtz of the Material Analysis and Research Laboratory for assistance in designing the XRD liquid sample cell. Partial support for this work from CSREES Regional Committee W82, Iowa State Agriculture and Home Economics Experiment Station, and USDA-National Research Initiative Competitive Grant No. 2003-35107-12899.
CHAPTER 3. LAURYL PEO SORPTION BEHAVIOR ON PANTHER CREEK BENTONITE AS INFLUENCED BY SATURATING CATION AND SAMPLE HANDLING.

A paper to be submitted to Clays and Clay Minerals

Mark A. Chappell¹, Michael L. Thompson¹, and David A. Laird²

Abstract

The widespread industrial use of nonionic polyoxyethylene surfactants has raised important questions about their environmental fate in soil. In this study, we investigated the sorption of a nonionic polyoxyethylene oxide alcohol, Brij 35, by the reference smectite Panther Creek bentonite (PC). This smectite was chosen to represent the clay fraction of many Midwestern U.S. soils. Brij 35 sorption isotherms were constructed using a batch equilibrium technique. The effects of cation saturation and sample handling (e.g., air-drying) on Brij 35 sorption were studied. Brij 35 was strongly adsorbed on PC clays of all treatments, yet slightly higher adsorption occurred by air-dried clay. PC exhibited a higher affinity for longer EO homologs than for shorter EO homologs. XRD analysis linked the high-affinity adsorption of Brij 35 to intercalation in the clay interlayer. Settling studies revealed that adsorbed Brij 35 induced flocculation in Ca-saturated PC (CaPC) suspensions. Effective micelle concentrations (EMC, representing the CMC of residual Brij 35 polymers in solution after sorption) were determined using an iodine assay. The EMC of Brij 35 was approximately 123 mg L⁻¹ higher than its CMC in water, suggesting the surfactant was transformed during sorption. Investigations into mechanisms responsible for EMC > CMC

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revealed that Brij 35 was abiotically degraded by adsorption to PC. Evidence of carbonyl-containing groups, including carboxyl acids, on residual Brij 35 was obtained. Degradation occurred only when Brij 35 was adsorbed below saturation.

Introduction

PEO alcohols are linear, polydisperse amphiphiles. A linear alkyl chain makes up the hydrophobic moiety while the surfactant's hydrophilic moiety contains noncharged ethylene oxide (OCH₂CH₂) chains. PEO alcohols assemble into micelles at critical micelle concentrations (CMC) much lower than ionic surfactants which are regulated by Debye lengths. The CMC of any PEO surfactant varies with differences in EO and alkyl chain sizes. Alkyl and EO chain sizes are also used to classify PEO surfactants by their HLB (hydrophilic-lipophilic balance) scores. The HLB is an empirical system that rates a surfactant's relative hydrophobicity and hydrophilicity. In general, surfactants with high HLB values contain long EO chains and are more hydrophilic than those with lower HLB surfactants, which contain short EO chains and are more hydrophobic.

The unique properties of polyoxyethylene oxide (PEO) alcohols make them desirable in a number of industrial processes and applications. In agriculture, PEO alcohols are used as solubilizing and wetting agents in pesticide formulations, such as commercial s-triazine formulations (Edwards, 1998; Knowles, 1995). The popular use of PEO alcohol surfactants in agriculture and other industries has sparked interest in understanding the fate of the polymers in the environment. For example, several investigators have detected PEO alcohols in wastewater effluents and in lakes, rivers, and ocean waters (Castillo et al., 1999; Crescenzi et al., 1997; Dunphy et al., 2001; Petrovic and Barcelo, 2000; Szymanski et al., 2001). PEO surfactants are considered low-risk contaminants in the environment, demonstrating low toxicities to aquatic and terrestrial life and high biodegradability (Krogh et al., 2003, and references therein). However, little is known about the interaction of PEO alcohols in the soil environment.
PEO alcohols can adsorb to a wide variety of sorbents. PEO alcohols are strongly adsorbed on both hydrophilic solids [e.g., silica (Kibbey and Hayes, 1997; Kibbey and Hayes, 2000; Koltalo-Portet et al., 2003; Levitz et al., 1984)], and hydrophobic solids [e.g., polystyrene (Geffroy et al., 2000)]. Hydrophilic surfaces selectively adsorb longer EO surfactants over shorter ones, while hydrophobic surfaces prefer the shorter, lower HLB surfactants (Cowell et al., 2000; Kibbey and Hayes, 1997). The adsorption of PEO alcohols can also modify the interfacial properties of solids. On a hydrophilic surface, the polar EO groups of a shorter PEO alcohol (EO < 6) will associate with the surface but the nonpolar tail group will point out toward the solution (Bohmer et al., 1992). This behavior gives the surface greater hydrophobic character (Somasundaran et al., 1991). Hydrophilic surfaces typically remain hydrophobic after adsorption of longer PEOs (>EO10) (Somasundaran et al., 1991).

The purpose of this study was to investigate the sorption of PEO alcohols on the reference smectite Panther Creek (PC) bentonite. PC was used as a model sorbent, representative of the smectitic minerals common to many soils in the Midwestern U.S. We used the PEO Brij 35 (C12EO23), a polydisperse surfactant with EO homologs ranging from 4 to 40 EO groups, with an average 23 EO groups. Brij 35 is similar to the type of surfactant used in commercial pesticide formulations. For this work, we tested the influence of cation saturation and air-drying of PC on Brij 35 sorption. In Chapter 2, K-saturation and air-drying of PC were shown to enhance sorption of the weakly polar atrazine molecule. We hypothesized that such treatments may influence Brij 35 sorption as well.

Materials and Methods

Reagents

Brij 35 was obtained from Sigma Chemical Co (St. Louis, Missouri, USA) and was used as received. After opening, Brij 35 was stored at 4 degrees C until used. Iodine, KI, dichloroethane, and HPLC-grade methanol (MeOH) and acetonitrile were all obtained from
Fisher Scientific (Madison, Wisconsin, USA) and used as received without further processing.

**Clay Preparation**

A detailed description of the preparation of Panther Creek (PC) samples is given in Chapter 2. To summarize, the clay sized fraction (< 2 μm) of a Na-saturated PC suspension was dialyzed against 100 mM CaCl₂ or 200 mM KCl until the clays were cation saturated. Then, the suspensions were dialyzed against 5 mM CaCl₂ or 10 mM KCl to remove excess salt. A portion of this “never-dried” ND sample was air-dried, crushed, and then resuspended and dialyzed against the 10 mM KCl or 5 mM CaCl₂ solutions. This represents the “air-dried” or AD treatments. Both preparations were stored and used as suspensions.

**Brij 35 Adsorption Experiments**

Aliquots of cation-saturated ND or AD clay suspension were added to triplicate 30 ml Nalgene Teflon tubes (at a solid-solution ratio of 12.5 mg ml⁻¹) containing 5 mM CaCl₂ or 10 mM KCl solution. A 2% (w/v) Brij stock solution was prepared, and stored at 4 °C when not in use. Aliquots of the stock solution were added to the Teflon tubes to give initial Brij concentrations of 500 to 6000 mg L⁻¹ in 20 ml of solution. Tubes were capped and equilibrated on a rotary shaker at 70 rpm for 24 hr. Afterwards, the tubes were centrifuged at 10,000 rpm (6486 x g) for 10 min. Aliquots of supernatant were used for dissolved carbon analysis and determination of effective micelle concentration (EMC). The EMC represents the CMC of the residual Brij 35 polymers in the supernatant after sorption. C in solution was measured from HCl-acidified samples (to remove inorganic C derived from CO₂ in air) using a Shidmazu TOC 5050 dissolved carbon analyzer (Shidmazu Scientific Instruments, Inc, Tokyo, Japan) at 690°C under TOC-quality air. Samples were not sparged during analysis to prevent the surfactant from foaming and spilling into the sample chamber. EMC was determined using an iodine (I-I) assay (Ross and Olivier, 1959). EMC was measured by adding 50 μL of a 15.2 mM iodine – 28.6 mM KI stock solution to 3 ml of supernatant in disposable polypropylene test tubes. Tubes were capped, vortexed, and allowed to stand.
undisturbed for 45 min for color development (Brown and Jaffe, 2001). Absorbance was measured at 351 nm on a Carey 50 Bio UV-Visible spectrometer (Varian Instruments, Walnut Creek, California, USA) using disposable, two-sided, methylacrylate cuvettes. Readings were averaged over a 3-s integration time and performed in triplicate for each sample.

**XRD Analysis**

Samples of CaPC-Bj suspensions were filtered onto a ceramic tile and oven-dried for 2 hr at 105 °C. Afterwards, the clay-bearing tiles were allowed to cool in a dessicator, and then they were analyzed by XRD under a stream of dehydrated air. In separate XRD analysis, non-centrifuged, PC-Bj suspension samples were injected into the well of a Plexiglas disc covered with x-ray-quality mylar (bonded to the Plexiglas with dichloroethane) and plugged with a miniseptum (see Appendix 2). The suspensions were analyzed by XRD in reflection mode. All XRD analyses were conducted using CuKα radiation from a Siemens D5000 X-ray diffractometer equipped with a solid-state Si (Li) detector. The scanning speed was 200 s step⁻¹.

**FT-IR Analysis of Adsorbed Brij 35**

A 3-ml aliquot of CaPC-Bj suspension was injected into a 25-mm Nucleopore Swinlock filter holder containing Fisherbrand 25-mm nitrocellulose filter paper (0.45 μm). The filter paper was removed from the holder, turned upside down, pressed onto a silicon rectangle (38.9 x 19.5 x 4 mm, Spectra Tech, Inc, Stanford, Connecticut, USA), and air-dried to an undetermined water content. The film was analyzed using a Nicolet Magna 45 infrared spectrometer (Nicolet Analytical Instruments, Madison, Wisconsin, USA) in transmission mode with 300 scans at 4 cm⁻¹ resolution. In addition, Bj was extracted from a separate aqueous solution using dichloroethane as described by (Yuan and Jafvert, 1997). Drops of the Bj-containing dichloroethane were applied to the silicon rectangle, allowed to evaporate under a gentle stream of dry nitrogen, and analyzed by the FT-IR.
**Settling Studies**

The previously described PC-Bj clay suspensions were diluted with 20 mM KCl or 10 mM CaCl₂ solution to a solid-solution ratio of 1 mg clay ml⁻¹. The new suspensions were allowed to stand for 24 h. Afterwards, the suspensions were dispersed with a vortex mixer at high speed for 1 min and then 3 ml of suspension were immediately transferred into a disposable methylacrylate cuvette. Absorbance of the suspension was measured at 600 nm every 2 min using the UV-visible spectrophotometer. Settling data was normalized by dividing the absorbance (A) at time \( t \) by the absorbance at \( t = 0 \) (Ao) or A/Ao. Concentration of dispersed sediment was calculated from a one-point calibration using the absorbance value at the beginning of each run (t = 0), where A/Ao = 1.0. Analysis of settling times were made by calculating the change in sediment concentration at time \( t \) for A/Ao = 0.4. Only one run per sample was conducted with no replication of experiments.

**Concentrating the Equilibrium Solution from Brij 35 Sorption Experiments**

The equilibrium solutions from selected Brij 35 sorption experiments were concentrated onto Alltech Maxi-Clean (900 mg) C18 cartridges (Alltech Associates, Inc., Deerfield, Illinois, USA) that had been previously rinsed with deionized water. Bj was eluted off the cartridge with 5 ml of methanol and then with 25 ml of dichloroethane. Eluant was collected in a 50-ml Teflon centrifuge tube and dried under a stream of nitrogen. Dried Bj was then resuspended in distilled, deionized water and stored at 4°C until needed.

**Chromatographic Separation of Brij 35 Sorption Concentrates**

The EO distribution of the Bj 35 concentrates was analyzed by HPLC, based on the method of Kibbey et al. (1996), which employs a reverse-phase elution on a normal phase column. Separation was carried out using a Hewlett-Packard (HP) 1050 series pump operated by HP ChemStation software. The stationary phase consisted of two columns: an Alltech C18 guard column (10 mm x 4.6 mm i.d., 5 μm particle size) followed by a Supelco Si column (150 mm length, 4.6 i.d., 5 μm particle size). Solutes were detected using an HP
diode array detector (monitored at 220 nm with 600-nm reference wavelength) connected in series with an Alltech 2000 evaporative light-scattering detector (ELSD). The ELSD was operated at 65°C and 1.0 L min\(^{-1}\) argon as carrier gas with the impactor in the off position. An HP 35900E dual-channel interface box was used to import the analog ELSD signal back into the ChemStation software.

Initial preparation for the separation involved "shocking" the Si column with 0.25 % aqueous acetic acid, which was pumped through the column at 0.7 ml min\(^{-1}\) for 1 h. This step was only performed once and never repeated. Samples were manually injected into the column using a 50-μl sample loop. The mobile phase consisted of acetonitrile (A) and 0.25% acetic acid in distilled, deionized water (B). Upon sample injection, the mobile phase consisted of 100% A at a flow rate of 0.3 ml min\(^{-1}\) for 1 min. After 1 minute, the elution proceeded along both linear flow and composition gradients, going from 0 to 31.5% B and 0.3 to 0.845 ml min\(^{-1}\) at 54 min. A monodisperse (99.5%) lauryl EO₈, obtained from Sigma Chemical Co., was used to match to identify the lauryl EO₈ peak in Bj. Other peaks were identified by their position relative to the known lauryl EO₈ peak.

Integration of the peaks was conducted by HP ChemStation software. Past efforts to integrate the separated peaks of Brij 35 have been hampered by a rise in the baseline for homologs of EO = 23 and higher (T.C.G. Kibbey, personal communication). This rise in baseline is apparently linked to the presence of C\(_{14}\)EO\(_{X}\), C\(_{16}\)EO\(_{X}\), and PEG heterologs (Okada, 1992) found in Bj, which separate out on the column at slightly shorter retention times than their C\(_{12}\)EO\(_{X}\) analogs. We attempted to account for this rise in baseline by manually drawing baselines that stretched from peak valley to peak valley. EO fraction was calculated by dividing the peak area by the total area of all of the eluted peaks. Mean EO distribution was calculated as described by Yuan and Jafvert (1997, see Appendix 2).
EMC Determination of Brij 35 Sorption Concentrates

Brij 35 sorption concentrates were diluted to concentrations ranging from 5 – 130 mg L\(^{-1}\) Brij 35 in Teflon test tubes containing 10 ml of distilled, deionized water. EMC was determined by I-I assay as previously described.

Titration of Brij 35 Concentrates

Brij 35 sorption concentrates were diluted to 50 mg L\(^{-1}\) Brij in 20 mM NaCl. The solutions were titrated with 5 mM HCl using a Radiometer TitraLab Tim 900 titration manager (Radiometer Analytical S.A., Lyons, France), equipped with a Radiometer ABU901 autoburette and a Radiometer pHC2401-8 combined Red Rod pH electrode, all controlled with TimTalk 9 software. A 20 mM NaCl solution served as a blank. Titration of a Brij 35 standard solution that was concentrated as previously described served as a reference sample. All samples were gently bubbled with nitrogen for 15 min before each titration.

Results and Discussion

Brij 35 Adsorption

Brij 35 was strongly adsorbed on all PC samples. The Bj isotherm exhibited a distinctive H-type shape (Giles et al., 1960) with some unusual features. For example, Bj was strongly adsorbed on KPC (Figure 3-1a) with high-affinity sites adsorbing over 150,000 mg kg\(^{-1}\) of Bj (region I). As high-affinity sites on ND KPC became saturated with Bj, the sorption isotherm approached its first adsorption maximum at approximately 210,000 mg kg\(^{-1}\) adsorbed Bj (region II). A second adsorption maximum is evident at approximately 258,000 mg kg\(^{-1}\) adsorbed Bj (region III).

For the ND clays, region I adsorption of Bj was slightly higher (approximately 26,000 mg kg\(^{-1}\)) with CaPC (Figure 3-1b) than KPC. More Bj was adsorbed on AD than ND clays. Air-dried, CaPC adsorbed >30% more Bj than the other clays. Chromatographic analysis of the Bj sorption concentrates (Figure 3-2), obtained from regions II and III of the Bj sorption
Figure 3-1. Brij 35 sorption isotherms on (A) KPC and (B) CaPC.
Figure 3-2. EO distribution profiles of Regions II and IV concentrates following sorption of 3000 and 6000 mg L\(^{-1}\) Brij 35, respectively, on ND KPC. Standard solution of Brij 35 in water is included for reference.
isotherm on KPC (Figure 3-1a), demonstrated the potential for PC to selectively adsorb Bj homologs. In region II of the Bj sorption isotherms, the equilibrium solution was enriched with shorter EO homologs, which had an average homolog size of 15.7 EO units. In samples from region III of the Bj sorption isotherms, average EO size (20.3) was similar to the average EO size of Bj (21.6) before sorption. These data suggest that the larger EO homologs were selectively adsorbed by PC in region II of the Bj sorption isotherm. For region III, no such selectivity was apparent.

X-ray diffraction analysis of oven-dried ND CaPC (Figure 3-3a) showed that d_{001} spacings increased from 1.06 to 1.73 nm following Bj sorption. These data offered direct evidence that Bj was intercalated in the clay interlayer, at concentrations corresponding to region I of the Brij 35 sorption isotherm. Also, the breadth of the x-ray peaks diminished with increasing Bj adsorption. This suggests that Bj homogenized the clays by uniformly increasing the basal spacings of the clay’s coherently scattering domains. In suspension (when the clay interlayer is fully hydrated), however, a different pattern emerges (Figure 3-3b). A collapse in d-spacing is indicative of Bj intercalation. For example, the basal spacings of the KPC collapsed by 0.5 nm upon the adsorption of 53,000 mg kg\(^{-1}\) Bj (region I) and displacement of hydration water from the interlayer region (Figure 3-3b). At 257,000 mg kg\(^{-1}\) of adsorbed Bj, a slight increase in d-spacing was observed. Similar results were obtained for AD KPC (See Chapter 4). However, Bj sorption induced only minor shifts in d-spacing (<0.1 nm, see Chapter 4) of ND CaPC. Thus, the interlayer of the CaPC suspension resisted collapse with Bj intercalation, most likely due to the presence of highly hydrated Ca\(^{2+}\) cations.

Brij 35 adsorption and subsequent homogenization of the clay affected the stability of the PC dispersions. Settling rates of ND CaPC increased as the clay became saturated with Bj (Figure 3-4). This suggests that high additions of Bj flocculated ND CaPC. In contrast, smaller quantities of sorbed Bj (<50,000 mg kg\(^{-1}\)) induced flocculation of the AD CaPC suspension. The AD CaPC system was dispersed following adsorption of 150,000 mg kg\(^{-1}\) Bj only to be re-flocculated at 260,000 mg kg\(^{-1}\) Bj. Combined with the XRD data, Figure 3-4
Figure 3-3. X-ray diffraction pattern (top) of oven-dried ND CaPC clay film after sorption of (a) 0, (b) 160,000, (c) 270,000 mg Brij 35 kg⁻¹ clay and (bottom) of ND KPC clay suspension (12.5 mg ml⁻¹) after sorption of (a) 0, (b) 53,000 (c) 257,000 mg Brij 35 kg⁻¹ clay.
Figure 3-4. Effect of Brij 35 sorption on settling rate of AD and ND CaPC suspensions (data were not replicated).
shows the effect of Bj sorption and intercalation on the stability of the clay dispersion. Typically, increase in settling rates suggests an increase in quasicrystal size. Increased settling rates (at B concentrations below saturation of the clay, i.e., regions I and II) could also suggest an increase in quasicrystal density due to the displacement of interlayer water. However, this can be ruled out because ND CaPC resisted collapse following Bj sorption (the same can be assumed for AD CaPC although we did not collect XRD data for this treatment). Bj sorption might increase the quasicrystal density of KPC, but analysis of the settling behavior of the KPC suspensions in the presence of the surfactant was inconclusive (see Appendix 2). Thus, in the case of CaPC, Bj effectively behaves as a flocculant in clays.

**Sorption-Induced Degradation of Brij 35**

The EMC of the residual Bj after sorption on ND KPC (see Figure 3-1a) was 186 mg L\(^{-1}\), or 123 mg L\(^{-1}\) higher than the CMC of Bj in water (63 mg L\(^{-1}\), Figure 3-5a). Other studies have reported similarly higher EMC values. Somasundaran et al. (1991) and Zheng and Obbard (2002) attributed EMC > CMC to the loss of surfactant through sorption. Yet Sun et al. (1995) found that EMC remained higher than CMC even after correcting for surfactant losses by sorption. The authors speculated that the dissolved components in the soil solution interfered with their EMC measurements. To account for possible interferences by dissolved components in the clay suspension, EMC was determined on the Bj sorption concentrates that had been resuspended in distilled, deionized water. EMC values for regions II and III Bj sorption concentrates were 87 and 67 mg L\(^{-1}\), respectively (Figure 3-5b).

If EMC had equaled CMC, then the characteristics of Bj would not have been affected by adsorption to PC. However, EMC > CMC, suggesting that the residual Bj polymers were transformed by adsorption, so that the surfactant no longer possessed its original functionality. To investigate the effect of adsorption on the surfactant, a PC clay film containing adsorbed Bj was analyzed by FT-IR spectroscopy (Figure 3-6). The spectra showed an approximate 20 cm\(^{-1}\) shift in the O-H bending vibration of water (from 1625 –
Figure 3-5. (a) Comparison between CMC determination of Brij 35 in water to EMC determination of residual Brij 35 in equilibrium solutions after sorption on ND KPC. (b) EMC determinations using distilled-water dilutions of Region II and Region III Brij 35 sorption concentrates following sorption of 3000 and 6000 mg L\(^{-1}\) Brij 35 on ND KPC. Error bars represent standard deviation for triplicate samples.
Figure 3-6. FTIR spectra (transmission mode) of (a) AD CaPC, no Brij 35, (b) AD CaPC adsorbed with 145,000 mg kg\textsuperscript{-1} Brij 35 (Region I on the Bj sorption isotherm) dried as a clay film on silicon crystal, and (c) aqueous Brij 35 (extracted with dichloroethane).
1643 cm$^{-1}$) of AD CaPC after adsorption of approx. 140,000 mg kg$^{-1}$ of Bj. Most likely, this band represented interlayer water that remained in the film after preparing the sample for FT-IR analysis, as well as a diagnostic band indicative of. The data suggest that intercalated Bj modified the interlayer environment by restricting the movement of interlayer water, or in essence, modifies the interlayer environment. However, the large size of this band suggests that overlapping bands for the asymmetric C-O stretch for carboxylate anions. Note the broad band around 1470 cm$^{-1}$ which corresponds to both a diagnostic ether band for EO, as well as the symmetric C-O stretch for carboxylate. A broad shoulder centered on 1720 cm$^{-1}$ suggests the formation of carbonyl groups on the adsorbed Bj, including the presence of carboxylic acids. The Brij 35 standard shows an undetermined 1760-1747 doublet, yet lacks any corresponding bands to indicate carboxylate formation and Bj degradation during storage.

Brij 35 sorption concentrates were titrated with HCl to determine if Bj developed charged groups following sorption. CMC values of ionic surfactants are typically higher than PEO surfactants. Micelle formation is inhibited by electrostatic repulsions of similarly charged ionic headgroups at lower concentrations. The formation of ionic groups on Bj would be responsible for EMC > CMC. Potentiometric titrations showed that the region II sorption concentrates were highly buffered between pH 4 – 5, indicative of carboxylic acid groups (Figure 3-7). Region III concentrates titrated similarly to the reference Bj standard, however, the high dilution required to make the 50 mg L$^{-1}$ solution from the Region III concentrate may have diluted the COOH groups sufficiently to obscure their titration. In fact, this high dilution may be the reason that EMC is close to CMC for the Region III sorption concentrate as well.

These data suggest that PC catalyzed abiotic degradation of adsorbed Bj. PEO surfactants readily autoxidize on contact with oxygen through the formation of oxy-radicals (Donbrow, 1987). Both EO groups and alkyl groups on the hydrophobic moiety may be excised. In general, loss of EO groups decreases the CMC while removal of methylene groups in the hydrophobic tail increases the CMC. Thus, the EMC data alone suggests that
Figure 3-7. Titration data for residual Brij 35 after sorption experiment of regions II and III concentrates following sorption of 3000 and 6000 mg L$^{-1}$ Brij 35 on ND KPC.

CH$_2$ groups may have been excised during interaction of Bj with the clay. However, IR and titration data indicate that carboxylic acid groups were formed in Bj. The negatively charged carboxylates would repel one another and make it more difficult for micelles to form. Therefore, EMC > CMC because some of the EO groups had become anionic in character.

A closer look at the data, however, introduces the possibility that PC selectively adsorbed nonionic homologs over homologs that degraded during storage. In this case, the equilibrium solution following sorption would be enriched with anionic homologs, particularly in Region I of the sorption isotherm. No controls were performed to test this hypothesis, however, information in the scientific literature suggests that clay surfaces may adsorb very high quantities of anionic surfactants, in quantities comparable to or greater than
nonionic surfactants, in spite of the potential repulsive interactions arising from negatively charged surface and surfactant (Abu-Zrieg et al., 1999; Koltalo-Portet et al., 2003).

Although oxygen is responsible for abiotic degradation of PEO surfactants, the kinetics of autoxidation are extremely slow in aqueous solution (Donbrow, 1987). However, autoxidation can be catalyzed by the presence of dissolved metals, noble gases, and multiple phases, such as liquid crystals (Andersson et al., 2002; Currie et al., 2004). For example, autoxidation may give a false impression about a surface’s selectivity for PEO alcohols, based on differences in EO homolog sizes. Studies tracking EO distributions of PEO surfactants during sorption have reported results similar to those in Figure 3-2, i.e., that hydrophilic surfaces exhibit preference for longer EO homologs over shorter ones (Kibbey and Hayes, 1997). However, it is also known that longer EO homologs autoxidize faster than smaller homologs (Donbrow et al., 1975). It is unclear whether the data in Figure 3-2 represents selective sorption of longer EO homologs, selective autoxidation of longer EO homologs, or both.

Finally, the products of surface-catalyzed PEO degradation may impact the environment differently than the original PEO surfactants. The broad shoulder around 1720 cm\(^{-1}\) on the IR spectra of adsorbed Bj (Figure 3-6) suggests the formation of a range of carbonyl-containing polymers, from carboxylic acids to possibly aldehydes and ketones. Recent research demonstrated that autoxidized C\(_{12}\)EO\(_{5}\) – aldehydes can behave as allergenic skin-sensitizers to humans (Bodin et al., 2003). The impact of these substances to lower animals is not known. Thus, more work is needed to determine the range of oxidized PEO species produced during sorption, so that the environmental impact of PEOs can be further evaluated.

**Conclusions**

PC was shown to adsorb large quantities of Bj from solution, regardless of cation saturating type and sample handling. However, AD treatment resulted in higher Bj
adsorption than the ND treatment. Sorption of Bj destabilized the PC suspension and induced flocculation. FT-IR and titration evidence for the sorption-induced abiotic degradation of Bj during its interaction with PC suggested that EO groups were converted to anionic carboxyl groups, and possibly other carbonyl-containing compounds. Evidence for abiotic degradation was observed only for Bj adsorbed at sub-saturation, yet, possible selective sorption for nonionic homologs over anionic Bj (degraded during storage) could not be ruled out.

**Acknowledgment**

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CHAPTER 4. CO-SORPTION OF ATRAZINE AND THE NONIONIC SURFACTANT BRIJ 35 ON SMECTITE

A paper to be submitted to Environmental Science and Technology

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Abstract

Commercial atrazine formulations commonly contain nonionic surfactants that serve as solubilizing and wetting agents for enhancing the efficacy of the weakly polar pesticide. Numerous sorption studies have investigated the fate of atrazine in soil, yet most of these studies utilized “neat” atrazine solutions without considering the effect of formulation components. In this study, we investigated the influence of the nonionic surfactant, Brij 35, on the sorption of atrazine. Atrazine sorption isotherms were constructed by adding atrazine-Brij 35 emulsions to suspensions of Panther Creek (PC) bentonite and equilibrating for 24 hr. In general, atrazine sorption was inhibited by Brij 35 additions from 50 to 2100 mg L\textsuperscript{-1}. However, atrazine sorption was enhanced as Brij 35 concentration increased from 2100 to 6300 mg L\textsuperscript{-1}. For concentrations at or below 2100 mg L\textsuperscript{-1}, Bj was apparently filling the clay interlayers and competing with atrazine for sorption sites. By contrast, at 6300 mg L\textsuperscript{-1}, the interlayers were completely filled with Bj and excess Bj accumulated on the external surfaces of the clay as surface micelles. The surface micelles provided an ideal environment for

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retaining atrazine. The potential for MeOH, a co-solvent in this system, to enhance Bj-
surface micellization and promote atrazine partitioning is discussed.

**Introduction**

Pesticide formulations contain adjuvants, a heterogeneous collection of substances
that promote the distribution and bioactivity of the toxicant. Depending on the type of
formulation, adjuvants can include emulsifiers, solvents and co-solvents, wetting, dispersing,
and anti-freezing agents, and inert support materials (Knowles, 1995). Next to the solvents,
nonionic surfactants make up the largest group of adjuvants in pesticide formulations (Krogh
et al., 2003, and references therein).

Surfactants and other adjuvants may influence the sorption of pesticides. A number
of studies published over the last decade, demonstrated the impact of surfactants on sorption
of nonpolar organic compounds (NOC) on clays. Jaynes and Boyd (1991a), Jaynes and Boyd
(1991b), and Sheng et al. (1996) showed enhanced NOC sorption on smectites loaded with
cationic, alkylammonium surfactants. NOC sorption on these organically modified smectites
was related to the extent of surface coverage by the surfactant as well as the orientation of the
surfactant on the surface. In contrast, the influence of nonionic surfactants on the sorption of
NOCs is less predictable. Evidence showing that nonionic surfactants both enhanced and
suppressed NOC sorption is reported in the literature (Lee et al., 2000; Sun et al., 1995).
NOC sorption might be inhibited by competition from nonionic surfactant micelles in
solution if the quantity of surfactant in solution exceeds its critical micelle concentration or
CMC (Sun et al., 1995). Experimental evidence and mechanistic explanations documenting
conditions under which nonionic surfactants alternatively enhance and suppress NOC
sorption is lacking. If weakly polar pesticides such as atrazine exhibit similar interactions
with nonionic surfactants, then the components of the pesticide formulation should influence
the fate of pesticides in soil.

Atrazine (2-chloro-4-ethylamino-6-isopropyl-1,3,5-triazine) is applied to soils for
pre-emergent control of weeds in corn and sorghum production. The world-wide use of
atrazine has prompted a substantial amount of research on its sorption by clays and soils (see a comprehensive review by Laird and Sawhney, 2002). However, most of this research is limited to "neat" atrazine solutions or aqueous solutions with co-solvents (such as ethanol) without considering the effects of the nonionic surfactants found in herbicide formulations. Furthermore, the limited research on the effects of formulation components on sorption is inconsistent. For example, Abu-Zrieg et al (1999) and Iglesias-Jiminez (1996) reported enhanced atrazine sorption on soil in the presence of nonionic surfactants Rexonic, Rexol, or Tween 80. However, other studies showed that nonionic surfactants enhanced atrazine's mobility in soils and clays (Huggenberger et al., 1973; Prima et al., 2002; Sanchez-Camazano et al., 1995) suggesting that the surfactant inhibited sorption. In part, these discrepancies may arise from the sequence of atrazine and surfactant addition (Sanchez-Camazano et al., 1995). Clearly, there is a need for greater understanding of how nonionic surfactants influence the fate of atrazine in soils.

The purpose of this paper is to elucidate the mechanisms by which a nonionic surfactant influences atrazine sorption on Panther Creek bentonite. The nonionic surfactant was a polydisperse, lauryl polyoxyethylene (PEO) nonionic surfactant known as Brij 35 (Bj). Bj has a hydrophobic aliphatic group (-CH₂-)ₙ and a hydrophilic linear chain containing an average of 23 ethylene oxide (EO, where EO = OCH₂CH₂) groups. Due to the amphiphilic nature of the surfactant, Bj readily forms micelle in solutions at approximately 92.3 mg L⁻¹ (see Appendix 4). Bj was selected because it is similar to the nonionic surfactants used in commercial pesticide formulations (Edwards, 1998).

**Materials and Methods**

**Reagents**

Atrazine (99% purity) was obtained from Chem Service (West Chester, Pennsylvania, USA). Brij 35 (specific gravity = 1.02 g cm⁻³) was obtained from Sigma Chemical Co. (St. Louis, Missouri, USA). Both chemicals were used as received. A.C.S.-certified dimethyl
sulfoxide (DMSO), methanol (MeOH), and acetonitrile were obtained from Fisher Scientific (Madison, Wisconsin, USA). MeOH and acetonitrile were HPLC quality.

**Clay Preparation**

The PC clay was prepared to test the effects of saturating cation and air-drying treatments on atrazine sorption. Detailed descriptions of clay preparation procedures are given in Chapter 2. To summarize, the clay sized fraction (< 2 μm) of a Na-saturated PC suspension was dialyzed against 100 mM CaCl₂ or 200 mM KCl to saturate clay samples with Ca²⁺ or K⁺. Then, the suspensions were dialyzed against 5 mM CaCl₂ and 10 mM KCl to remove excess salt. One portion of each prepared clay sample was stored as a suspension at 4°C until used; these samples are referred to as the “never-dried” (ND) samples. Another portion of each prepared clay sample was air-dried, crushed, resuspended, dialyzed against the dilute KCl or CaCl₂ solutions, and then stored at 4°C until used. These samples are referred to as the “air-dried” (AD) samples.

**Brij 35 Adsorption Experiments**

Aliquots of cation-saturated ND or AD clay suspension were added to triplicate 30 ml Nalgene Teflon tubes (at a solid-solution ratio of 12.5 mg mL⁻¹) containing 10 mM CaCl₂ or 20 mM KCl solution. A 2% (w/v) Bj stock solution was prepared, and stored at 4 °C when not in use. Aliquots of the stock solution were added to the Teflon tubes to give initial Bj concentrations of 500 to 6000 mg L⁻¹ in 20 ml. Tubes were then capped and equilibrated on a rotary shaker at 70 rpm for 24 hr. Afterwards, the tubes were centrifuged at 10,000 rpm (6486 x g) for 10 min. Aliquots of supernatant were used for dissolved carbon analysis. Carbon in solution was measured from HCl-acidified samples using a Shidmazu TOC 5050 dissolved C analyzer (Shidmazu Scientific Instruments, Inc, Tokyo, Japan) operated at 690 °C with high quality, carbon-free air. Samples were not sparged during analysis to prevent the surfactant from foaming and spilling into the sample chamber. Mass of Bj in solution was calculated from the mole ratio of carbon in the surfactant. Sorbed Brij 35 was calculated
by difference. Brij 35 sorption coefficients were calculated by nonlinear fit of the sorption data to the Langmuir equation.

**XRD Analysis**

Aqueous suspensions of Bj-treated PC were analyzed by XRD as described in Chapter 2. Total surface area was calculated using its structural formula (Gast, 1977) and elemental concentrations given by Laird et al. (1992). The structural formula of PC was determined as:

\[
\text{Ca}^{2+}_{0.41}\text{K}^{+}_{0.34}(\text{Si}^{4+}_{7.64}\text{Al}^{3+}_{0.36})(\text{Al}^{3+}_{2.99}\text{Fe}^{3+}_{1.19}\text{Mg}^{2+}_{0.41})\text{O}_{20}(\text{OH})_{4}
\]

The interlayer volume of the various PC samples was calculated by multiplying surface area by the measured \(d\)-spacing less the unit layer thickness and dividing by 2. The volume of sorbed Bj was calculated by multiplying the quantity of sorbed Bj (mg kg\(^{-1}\)) by the specific gravity of Bj (1.02 g cm\(^{-3}\)). Percent interlayer volume filled was determined from the ratio of the interlayer volume to the volume occupied by the sorbed Bj.

**Influence of Brij 35 on Atrazine Sorption**

Aqueous atrazine-Brij 35 emulsions were prepared as follows: 3 mg of solid atrazine was dissolved in 4 ml of MeOH. The dissolved atrazine-MeOH solution was then added to a 100 ml volumetric flask containing an aqueous Brij 35 solution, and diluted to volume. The atrazine–Brij emulsion was prepared at least 2 hr before use. Atrazine sorption experiments were carried out as described in Chapter 2 in the presence of 0, 50, 200, 2100, and 6300 mg Brij 35 L\(^{-1}\). Atrazine concentrations ranged from 2.1 to 10.5 mg L\(^{-1}\). To test for degradation of atrazine, the treated clay samples were extracted with a DMSO – 10 mM CaCl\(_2\) (adjusted to pH 9.5 with saturated Ca(OH)\(_2\)) solution. Extracts were analyzed for atrazine and other degraded atrazine products by RP-HPLC, as previously described. Total recovery of the sorbed atrazine by DMSO-CaCl\(_2\) extraction averaged 77.2% (ranging from 26.8 to 147.9% recovered). No hydroxyatrazine or other atrazine degradation products were detected in the equilibrium or extracted solutions.
Atrazine-Brij 35 Co-Sorption Experiments

A combined solution containing 3500 to 6500 mg Brij L\(^{-1}\) and 5.1 mg L\(^{-1}\) atrazine (plus 4 % v/v MeOH) was equilibrated in Teflon tubes for 24 hr on a rotary shaking (70 rpm). Aliquots of the PC clay suspension were added and the tubes were shaken for another 24 hr. The tubes were centrifuged at 6722 x g and the supernatant analyzed for atrazine (by RP-HPLC). Afterwards, the supernatants were leached through Alltech Extract Clean C18 (100 mg) columns to remove atrazine and Brij 35. The eluent was then analyzed for dissolved C to estimate MeOH in the supernatant. Sorbed atrazine and Brij were calculated from the difference between the amount added and the amount found in solution after the equilibrations.

Results and Discussion

Brij 35 substantially impacted atrazine sorption by PC clay (Figure 4-1). In general, atrazine sorption decreased as Brij concentration increased from 50 to 2100 mg L\(^{-1}\). However, atrazine sorption increased when Brij was increased from 2100 to 6300 mg L\(^{-1}\). This pattern was most evident in the AD KPC. In Chapter 2, atrazine sorption on PC was found to be much larger for the K-saturated AD samples relative to the Ca-saturated samples and the K-saturated ND sample. This effect was attributed to irreversible collapse of the clay interlayer caused by the AD treatment. In the present study, the impact of Brij on atrazine sorption was much larger for the AD K-PC sample. Freundlich analysis of the sorption data (Table 4-1) revealed that \(n\) values were substantially less than one for all but one of the isotherms. The \(n\) parameter describes the curvature of the isotherm. The higher concavity of the sorption data (as depicted by the lower \(n\) values) suggests that Brij limited the number of sites available to atrazine for sorption.

In order to understand the mechanisms for interaction between atrazine and Brij, we investigated the sorption of Brij on PC in the absence of atrazine (Figure 4-2). Brij was very strongly sorbed on all four PC clays. At 2100 mg L\(^{-1}\), over 99 % of added Brij was adsorbed,
Figure 4-1. Atrazine sorption on air dried (AD) or never dried (ND) Ca-saturated (CaPC) and K-saturated (KPC) PC as affected by different additions of Brij 35.
Table 4-1. Regression coefficients calculated from the nonlinear fit of the Freundlich equation to the atrazine sorption data.

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Figure 4-2. Brij 35 sorption isotherms on KPC and CaPC. Brij 35 concentrations ranged from 500 – 6000 mg L\(^{-1}\). Arrows indicate portion of the sorption isotherms representing the initial concentrations of 2100 and 6300 mg L\(^{-1}\) Brij 35. Prediction lines were generated by fitting the sorption data to the Langmuir equation by nonlinear regression.
Figure 4-3. Basal spacings for KPC and CaPC as affected by Brij 35 additions. XRD was conducted on PC samples while the clays were in suspension.
Table 4-2. Regression coefficients for nonlinear fit of Brij 35 (Fig. 4-2) sorption data to the Langmuir\(^\dagger\) equation.

<table>
<thead>
<tr>
<th>Clay Handling</th>
<th>Sample</th>
<th>(S_{\text{max}}) (\pm)</th>
<th>(K_L) (\pm)</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KPC ND</td>
<td>238.8 ± 0.6</td>
<td>1.9 ± 0.2</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>KPC AD</td>
<td>263.5 ± 3.7</td>
<td>3.2 ± 0.5</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>CaPC ND</td>
<td>262.6 ± 3.6</td>
<td>3.6 ± 0.4</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>CaPC AD</td>
<td>347.6 ± 4.7</td>
<td>2.0 ± 0.4</td>
<td>0.87</td>
<td></td>
</tr>
</tbody>
</table>

\(^\dagger\) \(S = \frac{1}{K_L} \frac{C S_{\text{max}}}{1 + 1/K_L C}\), where \(S\) = sorbed Bj, \(C\) = Bj in solution, \(S_{\text{max}}\) = Bj sorption maximum, and \(K_L\) = Langmuir affinity constant.

Table 4-3. Calculations to determine the percent volume of interlayer filled by Brij 35 sorption.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Handling</th>
<th>Brij 35 Added</th>
<th>(d)-Spacing (\text{nm})</th>
<th>Interlayer Volume (\text{m}^3 \text{g}^{-1} \times 10^7)</th>
<th>Brij 35 Adsorbed (\text{mg kg}^{-1} \times 10^3)</th>
<th>Volume of Adsorbed Brij 35 (\text{m}^3 \text{g}^{-1} \times 10^7)</th>
<th>% Interlayer Filled</th>
<th>Prediction Equation(^\dagger)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaPC ND</td>
<td>0</td>
<td>19.4</td>
<td>3.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(y = 0.28x + 0.43)</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>19.2</td>
<td>3.7</td>
<td>61.5</td>
<td>0.6</td>
<td>15.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>19.6</td>
<td>3.9</td>
<td>278.2</td>
<td>2.7</td>
<td>72.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KPC ND</td>
<td>0</td>
<td>18.8</td>
<td>3.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(y = 0.54x + 2.3)</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>13.5</td>
<td>1.5</td>
<td>53.7</td>
<td>0.5</td>
<td>35.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>14.2</td>
<td>1.8</td>
<td>257.6</td>
<td>2.5</td>
<td>142.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KPC AD</td>
<td>0</td>
<td>16.5</td>
<td>2.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(y = 0.45x)</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>2100</td>
<td>15.2</td>
<td>2.2</td>
<td>132</td>
<td>1.3</td>
<td>59.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6300</td>
<td>15.2</td>
<td>2.2</td>
<td>258</td>
<td>2.5</td>
<td>117.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^\dagger\) Equations obtained from linear regression of Figure A 3-3.
leaving < 5 mg L\(^{-1}\) of surfactant in solution (well below CMC). Therefore, an insufficient quantity of Bj remained in solution for any micelles to form and compete with the surface by solubulizing atrazine. At the 6300 mg L\(^{-1}\) level, however, approximately 1400 mg L\(^{-1}\) Bj was left in solution, a quantity well above CMC. At these large solution concentrations of surfactant, it was expected that micelles would form to inhibit atrazine sorption, but instead adsorption was enhanced. Hence, the patterns in atrazine sorption cannot be explained by micelle competition.

Earlier XRD work provided direct evidence that Bj adsorbed in the PC interlayer (see Chapter 3). The \(d\)-spacing of oven-dried ND CaPC expanded from 1.06 to 1.44 nm with the addition of 2100 mg L\(^{-1}\) Bj, and then expanded further to 1.73 nm with the addition of 6300 mg L\(^{-1}\) Bj in solution. In this study, XRD analysis of ND K-PC suspensions showed that the \(d\)-spacing decreased from about 1.9 nm to about 1.4 nm when Bj was added to the suspension (Figure 4-3). The \(d\)-spacing of AD K-PC also decreased with addition of Bj but to a lesser extent. No change in \(d\)-spacing was observed after Bj sorption on ND Ca-PC. The decrease in \(d\)-spacing for the K-PC samples indicates that as Bj enters the interlayers it displaces significant amounts of hydration water. Apparently, interlayer Ca\(^{2+}\) cations retained enough hydration water to keep the interlayer propped open.

The amount of Bj adsorbed by PC in the 2100 mg L\(^{-1}\) Bj systems was substantial. Based on the measured \(d\)-spacings, the unit layer thickness, and the surface area of PC, we calculated the total interlayer volume of each sample (Table 4-3). From the mass of Bj adsorbed and the specific density of Bj (1.02 g cm\(^{-3}\)), we estimated that sorbed Bj occupied 41, 74, and 68 % of the available interlayer volume of ND CaPC, ND KPC, and AD KPC, respectively, for the systems with 2100 mg L\(^{-1}\) of added surfactant. These data suggest that competition between Bj and atrazine for sorption sites on the clay are responsible for suppressing atrazine sorption for the 50-2100 mg L\(^{-1}\) Bj systems.

Other research (Jaynes and Boyd, 1991b; Sheng et al., 1996) has shown that sorption of cationic, alkylammonium surfactants on smectites enhances the sorption of weakly polar and nonpolar organic compounds (NOC). Sorption of NOC was shown to occur by
partitioning into hydrophobic regions created by the long alkyl tails of the adsorbed surfactant. Nevertheless, our data show that Bj has the opposite effect on atrazine. Bj has a large EO chain that makes the molecule very hydrophilic and strongly adsorbed by the clay. Apparently, the presence of these long hydrophilic groups not only masked hydrophobic nanosites on the clay but also made the interlayer more hydrophilic, and consequently, a less favorable environment for atrazine.

At 6300 mg L\(^{-1}\) of added Bj, the clay-Bj-atrazine systems behaved very differently. This concentration of Bj exceeded the sorption capacity of PC; hence, a large amount of Bj (exceeding the CMC) was present in the aqueous phase (Figure 4-2). While lower concentrations of Bj suppressed atrazine sorption by the PC, addition of 6300 mg L\(^{-1}\) of added Bj actually increased atrazine sorption by the PC relative to systems treated with 2100 mg L\(^{-1}\) of added Bj (Figure 4-1). An opposite trend would be expected if micelle competition were controlling atrazine sorption.

The enhanced affinity of the clay-Bj systems for atrazine at 6300 mg L\(^{-1}\) of added Bj was probably caused by the formation of surface micelles. From the interlayer volume calculations and volume of sorbed Bj (Table 4-3), it is apparent that the amount of Bj sorbed on KPC treated with 6300 mg L\(^{-1}\) Bj exceeded the interlayer volume. Hence, the excess Bj must have accumulated on the external surfaces. At saturation, the large Bj molecules are expected to form “pancake”-like surface micelles with slightly raised hydrophobic centers (Bohmer et al., 1992; Toerne et al., 2001, see Chapter 1). These structures are anticipated to have a high affinity for atrazine. Figure 4-4 shows the sorption of Bj on KPC in the presence and absence of atrazine. Nearly 50% more Bj was adsorbed by ND KPC from the emulsified atrazine system than in the absence of atrazine. In addition to atrazine, this system also contained 0.5 to 2.5 % (v/v) MeOH, a co-solvent used for solubilizing atrazine. Therefore, it is not clear whether the enhanced Bj sorption was caused by the presence of atrazine, MeOH, or both. According to the available literature, co-solvents can affect the sorption of atrazine on soil. For example, Miller et al. (1988) showed that 6.7% and higher concentrations of MeOH reduced atrazine sorption by enhancing solubility of atrazine in the aqueous phase.
Co-solvents also affect the behavior of surfactants in solution. For example, Becher and Trifiletti (1973) demonstrated that MeOH increased the CMC of PEO surfactants in solution by disrupting micellization. Co-solvents may also impact the formation of micelles on the clay surface. Brinck et al (1999) suggested that long-chained alcohols (dodecanol) enhanced PEO sorption by enlarging the size of the sorbed aggregates, a process known as co-micellization. Dissolved C analysis (Table 4-4) of the equilibrium supernatants from the atrazine sorption experiments (Figure 4-1) demonstrated a substantial increase in dissolved C in the equilibrium solution of the 2100 mg L\(^{-1}\) system. Although the source of C was not positively identified, it was assumed to be primarily MeOH, because the supernatant samples were passed through a C18 cartridge to remove soluble Bj and atrazine before the analysis. This evidence suggests that MeOH sorption in the clay interlayers up to 2100 mg L\(^{-1}\) of added Bj was inhibited due to the clay’s selective sorption of Bj. However, at 6300 mg L\(^{-1}\) of added Bj, the surface "pancake" Bj micelles may have been enlarged by sorption of MeOH, and the enlarged surface micelles may have enhanced atrazine sorption.

**Conclusions**

This work demonstrated the ability of a nonionic surfactant to strongly influence atrazine sorption. There is no evidence that micelle competition inhibited atrazine sorption, indeed the sorption trend is opposite of that which would be expected were micelle competition significant. At lower concentrations, Bj inhibited atrazine sorption by blocking interlayer sorption sites. Once the interlayer filled with Bj, the surfactant enhanced atrazine sorption apparently through the formation of surface micelles. MeOH was present in the systems as a co-solvent and may have affected the results especially at higher atrazine concentrations. These results demonstrate that the effect of formulation components must be considered to reliably predict the fate of pesticides in soil systems.
Figure 4-4. Sorption of Brij 35 (additions ranging from 3500 – 6500 mg L\(^{-1}\)) in the absence and presence of atrazine (added at a constant addition of 5.1 mg L\(^{-1}\)) on ND KPC. Prediction lines were generated by fitting the sorption isotherms to the Langmuir equation by nonlinear regression.
Table 4-4. Dissolved carbon concentrations measured from the equilibrium solution of the atrazine sorption isotherms with 50, 200, and 2100 mg L\(^{-1}\) Brij.

<table>
<thead>
<tr>
<th>Atrazine added (mg L(^{-1}))</th>
<th>Brij 35 added (mg L(^{-1}))</th>
<th>50</th>
<th>200</th>
<th>2100</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td></td>
<td>10.65</td>
<td>14.50</td>
<td>50.27</td>
</tr>
<tr>
<td>4.2</td>
<td></td>
<td>31.12</td>
<td>25.15</td>
<td>78.57</td>
</tr>
<tr>
<td>5.1</td>
<td></td>
<td>37.15</td>
<td>31.30</td>
<td>189.03</td>
</tr>
<tr>
<td>8.4</td>
<td></td>
<td>63.40</td>
<td>53.61</td>
<td>176.29</td>
</tr>
<tr>
<td>10.5</td>
<td></td>
<td>68.13</td>
<td>64.55</td>
<td>167.16</td>
</tr>
</tbody>
</table>

**Acknowledgments**

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CHAPTER 5. SORPTION OF FORMULATED ATRAZINE ON SOILS

A paper to be submitted to Soil Science Society Journal of America

Mark A. Chappell\textsuperscript{1}, Michael L. Thompson\textsuperscript{1}, and David A. Laird\textsuperscript{2},

Abstract

The herbicide atrazine is commercially available in a number of different formulations. One of the main components in these formulations is nonionic polyoxyethylene oxide (PEO) alcohols (C\textsubscript{n}EO\textsubscript{m}, where EO = OCH\textsubscript{2}CH\textsubscript{2}, n = number of linear alkyl groups, and m = number of EO groups). PEO surfactants serve as solubilizing agents for concentrating the atrazine, and as wetting agents to promote the pesticide's distribution when applied to soil. This study investigates the influence of the PEO surfactant Brij 35 (C\textsubscript{12} EO\textsubscript{23}) on atrazine sorption by soil. Effects of air-drying soils and type of cation in the background solution were also studied. Samples of seven air-dried soils, containing varying mineralogy, organic C, and clay content, were rehydrated in either 10 mM CaCl\textsubscript{2} or 20 mM KCl for 24 h. Aliquots of pre-prepared atrazine – Brij 35 emulsions were added and the suspensions were equilibrated for another 24 h. Atrazine sorption was evaluated in the presence of 0, 50, 200, and 2100 mg L\textsuperscript{-1} Brij 35. In general, the surfactant inhibited atrazine sorption, but in some cases, high additions of Brij 35 (2100 mg L\textsuperscript{-1}) enhanced atrazine sorption. Effects of sample handling and the type of cation in the background solution on atrazine sorption were less apparent. In separate experiments, sorption of atrazine originating

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from the commercial formulation, Aatrex 4L, was tested. Some of the sorption isotherms appeared convex, suggesting cooperative atrazine sorption. Using HPLC with evaporative light-scattering detection, we identified the nonionic surfactant in Aatrex 4L as Brij 30 (C\textsubscript{12}EO\textsubscript{4}), a smaller, less hydrophilic polymer than Brij 35. We speculated that favorable interactions between atrazine and Brij 30 might have promoted cooperative atrazine sorption.

**Introduction**

Environmental monitoring studies have demonstrated the potential for agrochemicals applied to soils to make their way into rivers or lakes via surface runoff or subsurface flow, after moving though the soil profile. Transport of one important agricultural pesticide, atrazine, is frequently a subject of such studies. An estimated 64 to 76 million pounds of atrazine are applied annually in the United States (USEPA, 2004). As a result, atrazine is frequently found in lakes, rivers, and groundwater at concentrations exceeding the 3 µg L\textsuperscript{-1} federal drinking water standard (Scribner et al., 2000; Shelton, 1989). Concerns over atrazine’s potential to disrupt endocrine function in mammals (Islam et al., 2002) and aquatic life (Le Pennec and Le Pennec, 2001; Moore and Lower, 2001) has led to its classification by the U.S. Environmental Protection Agency as a restricted-use pesticide (USEPA, 2002).

Atrazine interacts with soil via mixed-mode bonding (Lerch et al., 1997). The dominant interactions are hydrogen bonding (Bailey et al., 1968; Weber, 1970), cation exchange (Barriuso et al., 1994), van der Waals attractions, and hydrophobic associations (Laird and Koskinen, 2002). These observations are primarily based on experiments utilizing separate clay and humic materials, either commercially obtained or isolated from soils. These materials are viewed as the dominant reactive fractions in soils. The prevailing belief is that organic matter drives atrazine sorption in soils. However, such correlations are not universally verifiable (Laird and Koskinen, 2002, and references therein).

Atrazine is poorly soluble in water and impossible to concentrate in aqueous solution without co-solubilizing agents. Commercially available atrazine formulations contain a variety of materials to overcome this limitation, as well as to promote its distribution and
stability in the environment. Next to co-solvents, nonionic surfactants make up the largest component of pesticide formulations. Nonionic polyoxyethylene oxide (PEO) alcohols are commonly added to s-triazine formulations (Edwards, 1998). The combination of hydrophobic and hydrophilic groups on PEO allows the surfactant to adsorb to a broad array of sorbents, from highly polar aquifer materials (Kibbey and Hayes, 1997) to hydrophobic polystyrene beads (Geffroy et al., 2000). Favorable adsorption of one surfactant functional group leaves the other group exposed to the bulk solution. Thus, the solid-solution interface is modified by adsorption of the surfactant. For example, polar silica sorbent exhibited marked hydrophobicity after adsorption of PEO phenol alcohols (Somasundaran et al., 1991).

Since PEOs represent a major component of atrazine formulations, it follows that the surfactant may play a role in atrazine sorption on soils. There is very little information on this subject in the scientific literature. Abu-Zrieg et al (1999) and Iglesias-Jiminez (1996) observed enhanced atrazine sorption in soil with high concentrations of nonionic surfactants Rexonic, Rexol, and Tween 80. This information suggests some form of cooperative interaction between atrazine and the surfactants. On the other hand, nonionic surfactants can enhance atrazine mobility in soils and clays (Huggenberger et al., 1973; Prima et al., 2002; Sanchez-Camazano et al., 1995), suggesting that nonionic surfactants inhibit atrazine sorption.

The purpose of our paper is to investigate the sorption of emulsified atrazine on soil. Two types of formulations were used in this work: the commercial formulation Aatrex 4L (containing 43 % atrazine and 57% unidentified “inert” ingredients by weight) and a laboratory synthesized aqueous concentrate using the PEO alcohol Brij 35 (C_{12}EO_{23}, where EO = OCH_2CH_2). Brij 35 is a high hydrophile-lipophile balance (HLB), highly water-soluble polymer. Since PEO alcohols are commonly used in s-triazine formulations, Brij 35 was an appropriate candidate to simulate the aqueous atrazine emulsion.
Materials and Methods

Sample Preparation

Surface-horizon samples of three smectitic soils, Sparta (sandy, mixed, mesic, Entic Hapludoll), Sperry (fine, montmorillonitic, mesic Typic Argialboll), and Zook (fine, montmorillonitic, mesic, Cumulic Haplaquoll), were collected from Story and Marshall counties in Iowa. Some physical and chemical characteristics of these samples are presented in Table 5-1. Samples of the smectitic soils were sealed in airtight bags immediately after collection and stored at 4°C. These samples, stored in the field-moist state, represented the “never-dried” or ND samples. Sub-samples of the three ND smectitic soils were air-dried, crushed in an agate mortar, and passed through a 2-mm sieve before use. These latter samples are referred to as “air-dried” or AD soils (Table 5-2). Percent water of AD and ND samples was determined gravimetrically.

Reagents

Atrazine (99% pure) was obtained from Chem Service (West Chester, Pennsylvania, USA). Polydisperse Brij 35 was obtained from Sigma Chemical Co. (St. Louis, Missouri, USA). Both chemicals were used as received. A.C.S-certified, HPLC-grade methanol was obtained from Fisher Scientific (Madison, Wisconsin).

Preparation of Atrazine Emulsions

Aqueous atrazine – Brij 35 emulsions were prepared as follows: 3 mg of solid atrazine was dissolved in 4 ml of methanol. The dissolved atrazine-methanol solution was then added to a 100-ml volumetric flask containing aqueous Brij 35 of varying concentrations, and diluted to volume. The atrazine –Brij emulsion was prepared at least 2 h before use. Aatrex 4L (a suspension concentrate) was diluted to a 4% solution using a 4% methanol solution. This solution was centrifuged (6722 x g for 10 min) to remove excess white precipitate of an unknown chemical composition. Even after centrifugation, the supernatant retained a somewhat “cloudy” appearance. The 4% Aatrex solution was
Table 5-1. Selected physical and chemical characteristics of three smectitic soils.

<table>
<thead>
<tr>
<th>soil</th>
<th>clay/silt/sand</th>
<th>Org. C</th>
<th>pH</th>
<th>Sum of Exchangeable Cations*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>g kg⁻¹</td>
<td></td>
<td>cmolc kg⁻¹</td>
</tr>
<tr>
<td>Sparta</td>
<td>15</td>
<td>32</td>
<td>53</td>
<td>1600</td>
</tr>
<tr>
<td>Sperry</td>
<td>25</td>
<td>73</td>
<td>2</td>
<td>2100</td>
</tr>
<tr>
<td>Zook</td>
<td>43</td>
<td>42</td>
<td>15</td>
<td>2100</td>
</tr>
</tbody>
</table>

Exchangeable Cations‡

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Ba</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sparta</td>
<td>0.2</td>
<td>0.0</td>
<td>12.2</td>
<td>0.5</td>
<td>2.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Sperry</td>
<td>0.1</td>
<td>0.1</td>
<td>11.1</td>
<td>0.9</td>
<td>3.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Zook</td>
<td>0.1</td>
<td>0.1</td>
<td>24.7</td>
<td>0.4</td>
<td>4.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

‡: Obtained by adding 30 ml of 0.2 M NH₄Cl to a 50 ml polypropylene centrifuge tube containing 4 g of air-dried soil. The tubes were shaken for 1 hr on a side-to-side shaker, and then centrifuged for 10 min at 9000 rpm. Clear supernatant was collected, and then the soil was rewashed with NH₄Cl soln for a total of three times. Supernatant from the three consecutive washes was analyzed by ICP.

†: 1:1 water:soil.
Table 5-2. Percent gravimetric moisture of air-dried (AD) and never-dried (ND) smectitic soils.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Sample handling</th>
<th>Percent water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sparta</td>
<td>AD</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>8.8</td>
</tr>
<tr>
<td>Sperry</td>
<td>AD</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>11.5</td>
</tr>
<tr>
<td>Zook</td>
<td>AD</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>15.8</td>
</tr>
</tbody>
</table>

analyzed by HPLC (see Chapter 2) and was determined to contain an atrazine concentration of 46.7 mg L\(^{-1}\). We also constructed an aqueous atrazine emulsion to be used at a fixed mass ratio (wt/wt) of atrazine/Brij 35 (0.76:1). This simulated formulation contained 46.7 mg L\(^{-1}\) atrazine, 61.4 mg L\(^{-1}\) Brij 35, and 4% methanol.

**Sorption Experiments of Emulsified Atrazine**

Both AD and ND soil samples (4 g) were added to 30-ml Nalgene Teflon tubes, suspended in 20 ml of either 10 mM CaCl\(_2\) or 20 mM KCl, and equilibrated on a rotary shaker for 24 h. Afterwards, the tubes were opened and aliquots of atrazine-Brij 35 emulsions were added. Final atrazine concentration ranged from 2.1 to 10.5 mg L\(^{-1}\). The tubes were then closed and equilibrated for an additional 24 h. The tubes were centrifuged at 7500 rpm (6722 x g) and the clear supernatant was analyzed for atrazine by reverse-phase HPLC (see Chapter 2). Atrazine sorption was calculated by difference. For quality-control purposes, we attempted to extract sorbed atrazine from the soils using a 60:40 dimethyl sulfoxide – 10 mM CaCl\(_2\) (adjusted to pH 9.5), but failed because of the extractant’s ability to dissolve substantial amounts of humic material, which adversely affected the RP-HPLC
analysis. However, no hydroxyatrazine or other degraded atrazine products were detected in solution.

**Analysis of the Surfactant in Aatrex 4L**

A 75 mg L\(^{-1}\) solution of Aatrex 4L was analyzed by HPLC employing evaporative light scattering detection as described in Chapter 3. Average EO distribution was calculated using calculations described by Yuan and Jafvert (1997).

**Results and Discussion**

**Atrazine Sorption as Influenced by Brij 35**

We tested the influence of Brij on atrazine sorption. It was hypothesized that concentrations of Brij 35 (Bj) that exceed its CMC would inhibit atrazine sorption through the formation of micelles in solution (Sun et al., 1995). In our hypothesis, the micelles would act as an additional phase to compete for the equilibrium distribution of atrazine. Atrazine sorption was tested on air-dried samples of the smectitic soils, suspended in 10 mM CaCl\(_2\). We attempted to analyze the atrazine sorption isotherms (Figure 5-1) by fitting the data to the Freundlich equation. However, many of the isotherms deviated from linearity, possessing \(n\) values either greater than, or much less than 1 (Table 5-3). Therefore, comparisons of \(K_F\) values were not appropriate. Instead, the Freundlich fits were used to generate predictions of the sorbed quantities of atrazine at 40 \(\mu\)mol L\(^{-1}\), called \(C_s\), to make comparisons of atrazine sorption.

The data show that atrazine sorption was clearly affected by the presence of Bj. In the absence of Bj, we did not observe any consistent relationships between atrazine sorption and soil characteristics (Table 5-1). For example, the Zook soil (possessing the highest CEC and clay content) adsorbed the most atrazine, and yet, the Sparta soil (possessing the lowest CEC, clay content, and organic carbon) sorbed more atrazine than did the Sperry soil. However, in the presence of Bj, surfactant concentrations ranging from 50 to 2100 mg L\(^{-1}\)
Figure 5-1. Atrazine sorption by AD Sparta soil, suspended in 10 mM CaCl₂, as influenced by different additions of Brij 35.
Table 5-3. Regression coefficients calculated from the nonlinear fit of the atrazine sorption data on the AD Sparta, Sperry, and Zook soils (suspended in 10 mM CaCl₂) to the Freundlich equation. These equations were used to predict atrazine sorption at 40 μmol L⁻¹ atrazine in solution.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Brij 35 added (mg L⁻¹)</th>
<th>$K_F$</th>
<th>$n$</th>
<th>$r^2$</th>
<th>$C_S$ † (μmol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.73</td>
<td>0.99</td>
<td>76.97</td>
</tr>
<tr>
<td></td>
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<td>0.64</td>
<td>1.00</td>
<td>74.51</td>
</tr>
<tr>
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</tr>
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<td>61.49</td>
</tr>
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<td>96.52</td>
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<tr>
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<td>4.55</td>
<td>0.74</td>
<td>0.98</td>
<td>69.52</td>
</tr>
</tbody>
</table>

† Predicted sorbed atrazine concentration at an equilibrium atrazine concentration of 40 μmol L⁻¹.
Figure 5-2. Atrazine sorption on the Sparta soil as influenced by cation background, sample handling, and Brij 35.
Table 5-4. Regression coefficients calculated from the nonlinear fit of the atrazine sorption data on the Sparta soil to the Freundlich equation. These equations were used to predict atrazine sorption at 40 μmol L\(^{-1}\) atrazine in solution.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Handling</th>
<th>Brij 35 added (mg L(^{-1}))</th>
<th>(K_F)</th>
<th>(n)</th>
<th>(r^2)</th>
<th>(C_S^\dagger) (μmol kg(^{-1}))</th>
</tr>
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<tbody>
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<td></td>
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<td>36.92</td>
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\(\dagger\) Predicted sorbed atrazine concentration at an equilibrium atrazine concentration of 40 μmol L\(^{-1}\).

* Enhanced atrazine sorption.
Table 5-5. Regression coefficients calculated from the nonlinear fit of the atrazine sorption data on the Sperry soil to the Freundlich equation. These equations were used to predict atrazine sorption at 40 μmol L\(^{-1}\) atrazine in solution.

<table>
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<th>(K_F)</th>
<th>(n)</th>
<th>(r^2)</th>
<th>(C_S^\dagger) (μmol kg(^{-1}))</th>
</tr>
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<tr>
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<td>0.60</td>
<td>1.26</td>
<td>0.99</td>
<td></td>
<td>62.24 *</td>
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</tbody>
</table>

\(\dagger\) Predicted sorbed atrazine concentration at an equilibrium atrazine concentration of 40 μmol L\(^{-1}\).

* Enhanced atrazine sorption.
Table 5-6. Regression coefficients calculated from the nonlinear fit of the atrazine sorption data on the Zook soil to the Freundlich equation. These equations were used to predict atrazine sorption at 40 μmol L\(^{-1}\) atrazine in solution.

<table>
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<th>Brij 35 added (mg L(^{-1}))</th>
<th>(K_F)</th>
<th>(n)</th>
<th>(r^2)</th>
<th>(C_S^{\dagger}) (μmol kg(^{-1}))</th>
</tr>
</thead>
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</tr>
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<td>83.24 *</td>
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<td>0.84</td>
<td>1.00</td>
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</tr>
<tr>
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<td>0.99</td>
<td>63.02</td>
</tr>
<tr>
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<td>200</td>
<td>2.54</td>
<td>0.99</td>
<td>1.00</td>
<td>96.28</td>
</tr>
<tr>
<td></td>
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<td>2100</td>
<td>5.84</td>
<td>0.80</td>
<td>1.00</td>
<td>111.85 *</td>
</tr>
</tbody>
</table>

\(\dagger\) Predicted sorbed atrazine concentration at an equilibrium atrazine concentration of 40 μmol L\(^{-1}\).

* Enhanced atrazine sorption.
inhibited atrazine sorption on all three soils. At first glance, it appears that our initial hypothesis was correct, and that Bj micelles competed for atrazine in solution. However, Bj sorption on a reference smectite, Panther Creek (PC) bentonite (see Chapters 3 and 4), was shown to also inhibit atrazine sorption, yet there was < 5 mg L\(^{-1}\) in solution, not enough to form micelles. X-ray diffraction studies demonstrated that the surfactants inhibited atrazine sorption by competing for interlayer sorption sites on the reference clay. We hypothesize that Bj was highly adsorbed by the soils, as well (Yuan and Jafvert, 1997), preventing interactions between atrazine and soil surfaces.

Having shown the influence of Bj on atrazine sorption by AD soils, we conducted experiments to determine if changes in cation background and sample handling would impact the ability of the surfactant to suppress atrazine sorption. Experiments in Chapter 2 showed that air-drying and K-saturation enhanced atrazine sorption on PC, but the trends were more variable with soil samples. Atrazine sorption was tested on air-dried and never-dried (ND) soils, suspended in either 10 mM CaCl\(_2\) or 20 mM KCl. Example sorption isotherms are presented in Figure 5-2. Freundlich fits and predicted C\(_s\) are presented in Tables 5-4 through 5-6. Similar to the results in Figure 5-1, atrazine sorption was inhibited by Bj concentrations ranging from 50 to 2100 mg L\(^{-1}\), yet, evidence of enhanced atrazine sorption at 2100 mg L\(^{-1}\) Bj was obtained in some of the soil systems (indicated in Tables 5-3 through 5-5 with *). In addition, some of these isotherms that demonstrated enhanced atrazine sorption were convex (concave upward) in shape (Freundlich \(n\) values > 1). Such convex isotherms indicate cooperative sorption of solutes (Giles et al., 1960). In this case, the shape of the isotherm suggested that the sorption of atrazine promoted the sorption of more atrazine molecules from solution (Sposito, 1984). While cooperative interactions between atrazine molecules in aqueous systems are unlikely (Wellhouse et al., 1993), cooperative interactions between atrazine and Bj are likely. In fact, convex-shaped sorption isotherms were only evident at the higher Bj concentrations (200 – 2100 mg L\(^{-1}\)). This trend indicates that differences in the type of cation in the background solution and sample handling may have lowered the
concentration at which the soil was saturated with Bj. As a result, atrazine sorption was promoted by the formation of surface micelles on the soil's exterior sites (See Chapter 4).

The promotion of atrazine sorption through the formation of surface micelles of nonionic surfactants has not previously been reported, although the impact of nonionic surfactants on atrazine sorption has been recognized. For example, Abu-Zrieg et al. (1999) and Iglesias-Jiminez et al. (1996) observed only enhanced atrazine sorption by soil in the presence of some proprietary nonionic surfactants in household detergents (Rexol and Rexonic), and Triton X-100. Lee et al. (2000) and Sun et al. (1995) showed that the sorption of trichlorobenzene, benzene, toluene, and xylene by soil was greatly enhanced by Triton X-100. In our study, the potential for nonionic surfactants to inhibit sorption at low concentrations (where the concentration of surfactant in solution is << CMC) of these solutes is a new contribution. We hypothesize that these discrepancies are linked to the differences in the sorption behavior of the nonionic surfactants on soil. The sorption of Bj on reference smectites is greater than that of Triton X-100, but Triton X-100 sorption is more extensive on soils (see Appendix 4, Figure A4-4). Triton X-100, with its bulky aromatic constituent on the hydrophobic moiety, may be less effective at blocking potential sorption sites, yet, it may extensively sorb onto soil organic matter.

The mechanisms described above for enhanced sorption of atrazine assume cooperative interactions between atrazine and Bj on the soil surface. However, it should be noted that enhanced atrazine sorption was not consistently related to convex shape of sorption isotherms. For example, Zook soil showed evidence of enhanced atrazine sorption at 2100 mg L⁻¹ Bj (Table 5-5), yet the isotherms were concave.

**Sorption of Aatrex 4L**

Experiments were conducted to evaluate the sorption of atrazine originating from the commercial formulation Aatrex 4L. Our purpose for conducting these experiments was to compare atrazine sorption from the commercial formulation to sorption from our laboratory-simulated formulation. If Bj was representative of the surfactant in Aatrex 4L, then atrazine
Figure 5-3. Sorption of atrazine (originating from 4% Aatrex 4L solution) on (a) AD Ca, (b) ND Ca, (c) AD K, and (d) ND K Sparta, Sperry, and Zook soils.
Figure 5-4. Sorption of atrazine (originating from laboratory-simulated atrazine formulation) on (a) AD Ca, (b) ND Ca, (c) AD K, and (d) ND K Sparta, Sperry, and Zook soils.
Table 5-7. Regression coefficients calculated from the linear fit of the atrazine sorption data on Sparta, Sperry, and Zook soils. Atrazine was added as part of Aatrex 4L or laboratory-simulated formulations.

<table>
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<th>Soil</th>
<th>Cation</th>
<th>Handling</th>
<th>Formulation</th>
<th>$K_F$</th>
<th>n</th>
<th>$r^2$</th>
<th>$C_S$ † (µmol kg(^{-1}))</th>
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<tbody>
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† Predicted sorbed atrazine concentration at an equilibrium atrazine concentration of 30 µmol L\(^{-1}\).
Figure 5-5. Surfactant EO distribution profiles of Brij 30, Brij 35, and Aatrex 4L.
sorption from the two formulations should be similar. Since the ratio of atrazine/surfactant is fixed, we attempted to replicate this ratio in the simulated formulation. Sorption data (Figure 5-3 and 5-4) showed that trends in atrazine sorption were variable with the different treatments. However, the convex sorption isotherms were mostly observed for soils suspended in CaCl\textsubscript{2} background solution while the sorption isotherms for soils in KCl background were generally concave shaped. Where convex sorption isotherms were obtained, $n$ values from the Aatrex systems (Table 5-7) were greater than $n$ values for the lab-simulated formulation. Since convex shape of the isotherms suggests that atrazine was cooperatively sorbed, we hypothesized that differences in the sorption behavior of Aatrex and our laboratory-simulated formulation were related to differences in the type of surfactant included in the formulation.

To test this hypothesis, we analyzed the surfactant in the Aatrex 4L formulation by HPLC-ELSD to determine the distribution of PEO used in the commercial formulation (Figure 5-5). The surfactant used in Aatrex 4L possessed a smaller EO homolog size distribution (average EO size = 6.9) than Brij 35 (average EO size = 21.6). The retention times in the surfactant’s chromatograph (see Appendix 4, Figure A4-2, and Appendix 2, Figures A2-1 through A2-3) suggest that this surfactant is the lauryl PEO, Brij 30 (C\textsubscript{12}EO\textsubscript{6}), which we determined has an average EO size = 6.7. Thus, the differences in Figures 5-3 and 5-4 may be attributed to the type of surfactant controlling atrazine sorption. Preliminary comparative sorption work (Appendix 4, Figure A4-3) showed that high affinity sorption (indicative of intercalation) of Brij 30 was substantially less than that of Brij, allowing Brij 30 in solution to reach its CMC a relatively low surfactant additions. This allowed surface micelle formation to occur more extensively in the Brij 30 system, and hence, provide sites for cooperative sorption of atrazine.
Conclusions

Atrazine sorption on soils was greatly influenced by Brij 35. In the presence of Brij 35, atrazine sorption was decreased at lower surfactant concentrations, and (with some exceptions) was enhanced at higher Brij 35 concentrations. Effects of soil sample handling and cation background solution (for resuspending soils) were less predictable, but may have lowered the concentration of Bj required to saturate the soil surface. Atrazine sorption on soils was influenced by surfactant EO homolog size and concentration. Some of the sorption isotherms of atrazine from the commercial Aatrex 4L formulation suggested cooperative sorption through formation of surface micelles. We hypothesized that this behavior was linked to the sorption behavior of the short PEO, Brij 30, which we determined was the surfactant used in the commercial formulation.
CHAPTER 6. GENERAL CONCLUSIONS OF THE DISSERTATION

This work presented in this dissertation contributes to knowledge regarding mechanisms governing atrazine sorption by smectite, and the importance of formulation components in commercial formulations on atrazine sorption. Evidence in Chapter 2 demonstrated linkages between the hydrated status of Panther Creek Bentonite smectitic interlayer (i.e., expanded vs. collapsed) and atrazine sorption. It was concluded that the basal spacing of K-saturated, air-dried PC could remain irreversibly collapsed even after prolonged rehydration times. A strong relationship was demonstrated between this collapse and the clay’s increased sorption affinity for atrazine. It was hypothesized that atrazine sorption affinity was higher in the collapsed clay because (1) favorable removal of the weakly polar solute from the aqueous phase to a more “dehydrated” phase (only 1 – 2 layer hydrates compared to 3 – 4 layer hydrates in the expanded interlayer) and (2) increased possibility for the solute’s alkylamino sidechains to interact simultaneously with hydrophobic nanosites on opposing basal surfaces. (In the expanded interlayer, atrazine would only be able to interact with one basal surface and interlayer water.) While this pattern was clearly established for PC, it proved less successful in predicting sorption trends by soils. This may be, in part, a result of interactions involving humic materials, which were unaffected by air-drying. However, it can be debated that the humic materials used in this study may not accurately represent soil humics, both in composition and in function due to the clay-humic complexes by which these materials exist in soils.

Chapters 3 and 4 contained investigations into the adsorption of the nonionic, polyoxyethylene oxide (PEO) surfactant, Brij 35, and its effect on atrazine sorption. Evidence showed that Brij was strongly adsorbed on the clay. Brij was preferentially intercalated into the smectite interlayer, not only destabilizing the clay suspension, but also allowing the surfactant to successfully compete with atrazine for sorption sites. When the
interlayers were filled, however, Bj sorbed to external sites on the clay and enhanced atrazine sorption through the formation of micelles on the surface. This pattern of inhibition at low surfactant concentration, followed by enhancement at high Bj surfactant concentration is unique to the sorption literature.

In Chapter 5, the effects of cation saturation and sample handling on atrazine sorption by smectitic soils were evident; yet, these treatments clearly played a secondary role to the influence of Bj. Furthermore, the sorption behavior of atrazine in the presence of Bj, was noticeably different from the sorption behavior of atrazine originating from the proprietary atrazine formulation, Aatrex 4L. The surfactant in Aatrex 4L was identified as Brij 30, a shorter, relatively more hydrophobic PEO surfactant. Conclusions from the atrazine sorption data on the smectitic soils in the presence of Bj, combined with further discussions using the scientific literature, suggest that sorption of atrazine in commercial formulations may be regulated by the sorption behavior of the formulation’s surfactant. This evidence implies that manufacturers should consider the potential for a particular surfactant, included in a commercial formulations to promote the sorption or mobility of a pesticide in soil.

Finally, some evidence was presented supporting the abiotic degradation of Brij 35 due to sorption (Chapter 3). Chromatographic evidence suggested the clay preferentially adsorbed longer EO homologs. Yet, additional evidence tentatively pointed to the possible oxidation and carboxylation of these larger EO homologs molecules following sorption. This mechanism may be responsible for the substantial difference between the CMC of Brij 35 in water and the EMC of the residual Brij 35 polymers following sorption. This information is important for two reasons: First, it challenges the commonly held view that PEO surfactants are mainly decomposed in the environment by biodegradation, because they may be readily degraded abiotically upon contact with soil. Furthermore, spectroscopic evidence challenges the claim that PEO surfactants can be safely discharged into the environment. The appearance of a broad shoulder in the carbonyl range of the IR spectra of adsorbed Brij 35 points to the possible formation of PEO-aldehydes. These substances have non-negligible toxicities, acting as skin sensitizers in humans, with unknown effects on other animal life.
More research is needed to confirm the existence of sorption-induced, abiotic degradation of PEO surfactants, and to identify the species produced by this degradation for their possible toxicity problems.
Figure A 1-1. Schematic showing the transmission cell used for XRD analysis of clay suspensions.
APPENDIX 2. SUPPLEMENTAL MATERIAL FOR CHAPTER 3

Table A 2-1. Reported CMC values for Brij 35.

<table>
<thead>
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<th>Reference</th>
<th>Reported CMC mg L(^{-1})</th>
<th>Method of CMC determination</th>
</tr>
</thead>
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<tr>
<td>Yuan and Jafvert (1997)</td>
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</tr>
<tr>
<td>Prima (1997)</td>
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<td>Iodine assay</td>
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<td>Zheng and Obbard (2002)</td>
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<td>See ref #2 in paper</td>
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<td>Toerne et al. (2001)</td>
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<td>Sanchez-Camazano et al. (2003)</td>
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<td>Berthod et al. (2001)</td>
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<tr>
<td>Ross and Oliver (1959)</td>
<td>60</td>
<td>Iodine(V) assay</td>
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Average = 92.3 mg L\(^{-1}\)
Figure A 2-1. Chromatograph of 2000 mg L$^{-1}$ Brij 35 in water.
Figure A 2-2. Chromatograph of 200 mg L\(^{-1}\) Laureth 10 in water.

Figure A 2-3. Chromatograph of 100 mg L\(^{-1}\) Brij 30 in water.
Table A 2-2. Sample calculations for determining Brij 35 homolog distribution from HPLC – ELSD analysis.\textsuperscript{§}

<table>
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<tr>
<th>Retention time (min)</th>
<th>Peak area (min)</th>
<th>Peak area (min)</th>
<th>Fraction of total peak area</th>
<th>EO #\textsuperscript{†}</th>
<th>M(EO)\textsuperscript{‡}</th>
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Total peak area 79168.6 Avg. EO 22.62897

\textsuperscript{†} As determined using a 99% pure lauryl PEO (EO = 8) standard.

\textsuperscript{‡} EO mass fraction = (EO\#) x (fraction of total peak area).

\textsuperscript{§} As presented by Yuan and Jalvert (1997).
Raw Settling Data

Figure A 2-4. Settling curves for AD CaPC clay suspension in the presence of added 0 – 6300 mg L\(^{-1}\) Brij 35. Absorbance was measured at 600 nm.

Figure A 2-5. Settling curves for ND CaPC clay suspension in the presence of added 0 – 6300 mg L\(^{-1}\) Brij 35. Absorbance was measured at 600 nm.
Figure A 2-6. Settling curves for AD KPC clay suspension in the presence of added 0 – 200 mg L\(^{-1}\) Brij 35. Absorbance was measured at 600 nm.

Figure A 2-7. Settling curves for AD KPC clay suspension in the presence of added 2100 – 6300 mg L\(^{-1}\) Brij 35. Absorbance was measured at 600 nm.
Figure A 2-8. Settling curves for ND KPC clay suspension in the presence of added 0 – 200 mg L\(^{-1}\) Brij 35. Absorbance was measured at 600 nm.

Figure A 2-9. Settling curves for AD KPC clay suspension in the presence of added 2100 – 6300 mg L\(^{-1}\) Brij 35. Absorbance was measured at 600 nm.
Figure A 2-10. Comparison of Brij 30, Laureth 10, and Brij 35 sorption on ND CaPC.
Figure A 2-11. (top) EMC determination of residual Brij 35 polymers in solution following sorption on ND CaPC. EMC = 562 mg L\(^{-1}\). (bottom) CMC determination (by surface tensiometry) of Brij 35 in 10 mM CaCl\(_2\). CMC = 60 mg L\(^{-1}\).
Possible Relationships between Exchangeable Cations and Sorption-Catalyzed Abiotic Degradation of Brij 35

Currie et al (2004) shows how silver ions enhance the oxidation of Brij 30 arranged in a liquid crystal. These findings were not observed in a microemulsion. The above plot is the EMC determination of Bj following sorption on ND CaPC. The EMC is approximately 562 mg L\(^{-1}\) (in spite of the substantial error in this measurement) or 376 mg L\(^{-1}\) higher than the EMC of Bj on ND KPC. This difference is important because Bj sorption was very similar on both clays (see Figure 3-1). Apparently, Ca saturation may enhance Bj oxidation relative to K-saturation.
APPENDIX 3. SUPPLEMENTAL MATERIAL FROM CHAPTER 4

Organoclays and NOC Sorption

Figure A 3-1. Summary plot comparing the trends in relative sorption affinity of neutral organic compounds on HDTMA-saturated smectite clays. Data for alkylated benzene derivatives were taken from Jaynes and Boyd, (1991b) and for chlorinated derivatives from Sheng et al. (2001). Sorption constants for both studies were calculated differently, and thus, are not directly comparable (e.g., sorption affinity constant for propylbenzene cannot be compared to constant for chlorobenzene). However, both studies included constants for benzene. Thus, a comparison of alkylated vs. chlorinated benzene derivatives is not valid; yet, the trends in the sorption constants relative to benzene are comparable.
A closer look at the work of Jaynes and Boyd (1991b) and Sheng et al. (1996) reveals an interesting relationship between the sorption of a nonpolar molecule on low-charge HDTMA-modified smectite and the shape of solute molecule (Fig. A 3-1). One may observe that the stronger sorption affinity was correlated with the asymmetry of the probe molecule (relative to benzene). In other words, sorption affinity increased with increasing alkylation or halogenation of benzene, as amphiphilic groups were spatially separated from each other, and the molecule lacked a center of inversion. An examination of the resonance structures of these neutral organic chemicals may reveal a corresponding increase in sorption to the development of stronger molecular dipoles. The notable exceptions are o-xylene and trichlorobenzene, in which spatial separation of lipophiles and hydrophiles is not as distinct.

Additional Plots Not Included in Chapter 4

Figure A 3-2. Dissolved carbon in solution following atrazine sorption experiments on ND CaPC after Brij 35 additions of 50, 200, and 2100 mg L$^{-1}$. 
Addition of 2100 mg L\(^{-1}\) of Brij 35 shows a large increase in dissolved C in the supernatant. The quantity of Brij 35 added is not sufficient to account for the magnitude of this rise. Unfortunately, the compounds in solution were never identified. Yet, it seems that this C may represent MeOH in solution. At lower concentrations of Brij 35, MeOH appears to adsorb to the clay, but at the higher concentrations (where the clay begins to become saturated with Brij 35, MeOH must compete with the surfactant for sorption sites. Apparently, the large increase in C shows that the surfactant is preferred by the clay over MeOH.

Figure A 3-3. Plots showing the predicted transition of Brij 35 from adsorption on external sites to internal sites, and surface micelle formation. Trend lines represent a linear fit through the data.
Figure A 3-4. Sorption of atrazine (added at a constant 5.1 mg L$^{-1}$) in the presence of increasing concentrations of Brij 35, ranging from 3500 – 6500 mg L$^{-1}$. 

Residual Brij 35 in solution (mg L$^{-1}$)
Illustrations Showing Atrazine – Brij 35 Interactions

Figure A 3-5. PEO-organoclay model: Breaking the atrazine-Brij 35 emulsion and subsequent sorption of formulation components and reduction of clay interlayer basal spacing.
Figure A 3-6. Schematic illustrating possible association of Brij 35 molecules with the clay interlayer. In this model, atrazine is sterically or otherwise hindered access to clay interior hydrophobic domains by the Brij 35.
Figure A 4-1. Atrazine sorption on air-dried soils in 10 mM CaCl₂ background solution for (a) 0, (b) 50, (c) 200, and (d) 2100 mg L⁻¹ added Brij 35.
Table A 4-1. Selected physical and chemical characteristics for soils in Figure A 4-1.

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<th>%clay</th>
<th>%silt</th>
<th>%sand</th>
<th>%Org. C</th>
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†Sm = smectite, V = vermiculite, IMV = interstratified mica-vermiculite, HIV = hydroxyl interlayer vermiculite, K = kaolinite, F = fluorite, Q = quartz, Go = goethite
Figure A 4-2. Chromatograph of 75 mg L⁻¹ Aatrex 4L.
Figure A 4-3. Comparison of high affinity sorption of Brij 35, Laureth 10, and Brij 30 on ND CaPC.
Figure A 4-4. Comparison of Brij 35 and Triton X-100 sorption on (bottom) reference smectites and (top) soils. Closed symbols represent Triton X-100 and open symbols represent Brij 35. Surfactant sorption is shown on a Tiachung (TCS) soil (Lee et al., 2000), Oshtemo soil (Sun et al., 1995), a soil defined as EPA 3 (Yuan and Jafvert, 1997), Ca-saturated Wyoming Bentonite (Lee et al., 2000), and ND CaPC (from Chapter 3). Plots were replicated from published literature using DataThief II software by Bas Tummers.
REFERENCES


Castillo, M., F. Ventura, and D. Barcelo. 1999. Sequential solid phase extraction protocol followed by liquid chromatography-atmospheric pressure chemical ionization-mass


