ADSORPTION AND DESORPTION OF ATRAZINE

ON A MELAMINE-BASED SOIL AMENDMENT

A Thesis

by

SUSAN L. NEITSCH

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2004

Major Subject: Soil Science

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Approved as to style and content by:

Kevin J. McInnes	Scott A. Senseman
(Chair of Committee)	(Member)
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(Member)	(Head of Department)

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ABSTRACT

Adsorption and Desorption of Atrazine

on a Melamine-Based Soil Amendment. (May 2004)

Susan L. Neitsch, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Kevin J. McInnes

Adsorption kinetics and adsorption-desorption of atrazine on organoclay composites prepared with the surfactant 6-piperazin-1-yl-N,N'-bis-(1,1,3,3-tetramethyl-butyl)-(1,3,5)triazine-2,4-diamine and Houston Black clay were studied using the indirect batch equilibration procedure. The organoclay composites sorbed significantly more atrazine than the Houston Black clay. Adsorption equilibrium was reached after 72 h for the organoclay composites. Atrazine adsorption isotherms were described by linear partitioning. The K_{oc} values ranged from 605 to 5271 L kg^{-1} for the organoclay composites compared to a value of 41 L kg^{-1} for the Houston Black clay. The organoclay composite containing 20% surfactant on a total weight basis provided the most efficient adsorption of atrazine, although organoclay composites containing much lower amounts of surfactant also adsorbed significant amounts of atrazine. An average of 11% of sorbed atrazine was released during desorption. Characterization of desorption products showed only atrazine molecules being released from the organoclay composites.

To my parents.

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I am grateful to Erick Acosta and Jason Krutz for their input and advice in the laboratory.

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Pesticide use in the United States averages roughly 500 million kilograms active ingredient per year (Larson et al., 1997). Use of pesticides has benefited society with increased crop production, lower maintenance costs, and control of public health hazards. However, adverse effects of pesticides on human health and the environment is a major concern for development of a sustainable agricultural system.

Larson et al. (1997) noted that the greatest potential for unintended adverse effects of pesticides is through contamination of the hydrologic system. In particular, surface waters are prone to contamination by runoff of biological and chemical agents from agricultural lands and urban areas. Once contaminants habitate streams and rivers, they can be transported to lakes, reservoirs, and other water bodies. The presence of pesticides in a water body can affect its use for municipal water supply and recreational activities as well as its ability to support aquatic life and dependent food chains.

Larson et al. (1997) reviewed studies on the occurrence of pesticides in surface waters conducted by various government and private organizations. They noted that for most triazine and acetanilide herbicides, the amounts detected in the rivers typically represented 0.2 to 2% of the amounts applied to fields in the upstream drainage area while the total range in values was 0.1 to 10% of the amount applied.

The fate of a pesticide in the environment is controlled by retention, transformation, and transport processes (Cheng, 1990). Retention processes serve to retard or prevent pesticide movement as well as affect its availability for plant uptake or transformation. Retention depends

This thesis follows the style of the Soil Science Society of America Journal.

on the interaction between the pesticide and the soil solids. Transformation processes, which result in a change in the chemical nature of the pesticide molecule, control whether and how long pesticides may be present in the environment. Transformation processes may be purely chemical, catalyzed by soil constituents, or induced photochemically, but most pesticides are biochemically transformed. Transport processes govern where a pesticide is present in the environment. Transport processes include movement from the soil to the atmosphere via volatilization, to the groundwater via leaching, and into surface waters via overland flow.

Agricultural activities account for 70 to 80% of total annual pesticide use (Aspelin, 1994) with triazine and acetanilide herbicides comprising roughly 36% of agricultural pesticides (Larson et al., 1997). The most common triazine herbicides are atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine], cyanazine {2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl] amino]-2-methylpropanenitrile} and simazine (6-chloro-*N, N'*-diethyl-1,3,5-triazine-2,4-diamine) for weed control in corn, and metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] for weed control in soybeans. Acetanilide herbicides commonly used include alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide], metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide], and propachlor (2-chloro-*N*-isopropylacetanilide) which are used for weed control in corn, soybeans, and sorghum.

Collectively, triazine and acetanilide herbicides possess moderate to high water solubility, low soil-sorptivity, and relatively long persistence in the soil (Wauchope et al., 1992). As a consequence of these characteristics, triazine and acetanilide herbicides possess a moderate to high potential for loss from agricultural fields with runoff of storm and irrigation waters, primarily in the dissolved phase (Goss, 1992). In the water, most of these herbicides are chemically stable, that is, they do not hydrolyze, and are not likely to volatilize (Larson et al.,

1997). The probability that these chemicals will be carried by surface runoff into the stream system is increased by the application method for these compounds. Triazines and acetanilide herbicides are typically applied preemergent to bare soil or residual vegetation from the prior year's crop (Wauchope et al., 1992). Because they are surface applied rather than incorporated into the soil, the chemicals are readily available for transport by surface runoff.

Given the chemical stability of atrazine in water and the difficulty and expense associated with remediation of pesticide-contaminated water, preventing movement of atrazine into surface waters is highly desirable. A number of land management practices are used to minimize the amount of pesticide moving off application areas. One potential practice is the application of polymeric organic compounds to adsorb organic contaminants while simultaneously controlling erosion.

In the course of characterizing the properties of newly-synthesized dendrimers based on melamine (2,4,6-triamino-1,3,5-triazine) (Zhang and Simanek, 2000; Zhang et al., 2001), researchers discovered that some of the dendrimer systems sequestered triazine herbicides from solution. This observation and the economical nature of producing these dendrimers were new discoveries. Subsequent research (Acosta, 2003) identified a promising surfactant [6-piperazin-1-yl-*N*,*N'*-bis-(1,1,3,3-tetramethyl-butyl)-(1,3,5)triazine-2,4-diamine] for further study.

The objective of this research is to evaluate 6-piperazin-1-yl-*N*,*N'*-bis-(1,1,3,3-tetramethyl-butyl)-(1,3,5)triazine-2,4-diamine for possible use as a soil amendment to retain atrazine. This study characterizes the adsorption/desorption of atrazine on organoclays created with the compound and quantifies the impact of the fraction of surfactant relative to clay on atrazine adsorption/desorption. As a basis of comparison to a natural soil system, atrazine adsorption/desorption experiments were performed on soil from the upper 10 cm of a Houston Black clay (fine, smectitic, thermic Udic Haplustert) pedon.

Characterization of atrazine adsorption/desorption was done in four steps. First, the adsorption kinetics were measured over a 5-day period to determine the amount of time required for equilibration between atrazine in solution and on the solid. Atrazine isotherms were then determined for all substrates by exposing the solids to eight different atrazine solution concentrations. Next, the amount of atrazine desorbed from the solids was quantified over a 4-day period. Finally, the nature of the organic material (atrazine, fragments of the atrazine molecule or atrazine/surfactant fragments) being desorbed was determined. The first three steps used an indirect batch equilibration method to obtain experimental data while high performance liquid chromatography was used in the final step.

LITERATURE REVIEW

Dendrimers

Polymeric biomolecules, such as proteins, are responsible for the majority of tasks associated with the chemistry of living organisms. A primary goal of polymer chemistry is the synthesis of macromolecules that in some respect can mimic the functionality of these polymeric biomolecules. Due to the lack of reliable synthesis mechanisms for branched structures, polymer chemistry initially focused on the synthesis and characterization of linear polymers. This changed with the development of an iterative cascade method for the synthesis of low molecular weight branched amines by Vögtle in 1978 and the development of methods for the orderly preparation of branched polymers in the mid-1980s (Grayson and Fréchet, 2001).

Dendrimers are highly ordered, regularly branched, globular macromolecules prepared by a stepwise, iterative approach. The structure of a dendrimer can be divided into three distinct regions: (i) a core, (ii) layers of branched repeat units emanating from the core and (iii) end groups on the outer layer of repeat units (Fig. 1). Each layer of branched units in the molecule is termed a "generation" and each main branch that emanates from the core is a "dendron". Different generations of dendrimers that possess the same core, branch and end group chemistries are referred to as a "family".

Dendrimers typically have a diameter ranging from 3 to 10 nm which is comparable to the diameter of enzymes or proteins. This similarity has led a number of researchers to engineer protein-like functions into dendrimers such as catalysis, light harvesting and host-guest interactions such as small molecule transport (Simanek and Gonzalez, 2002).
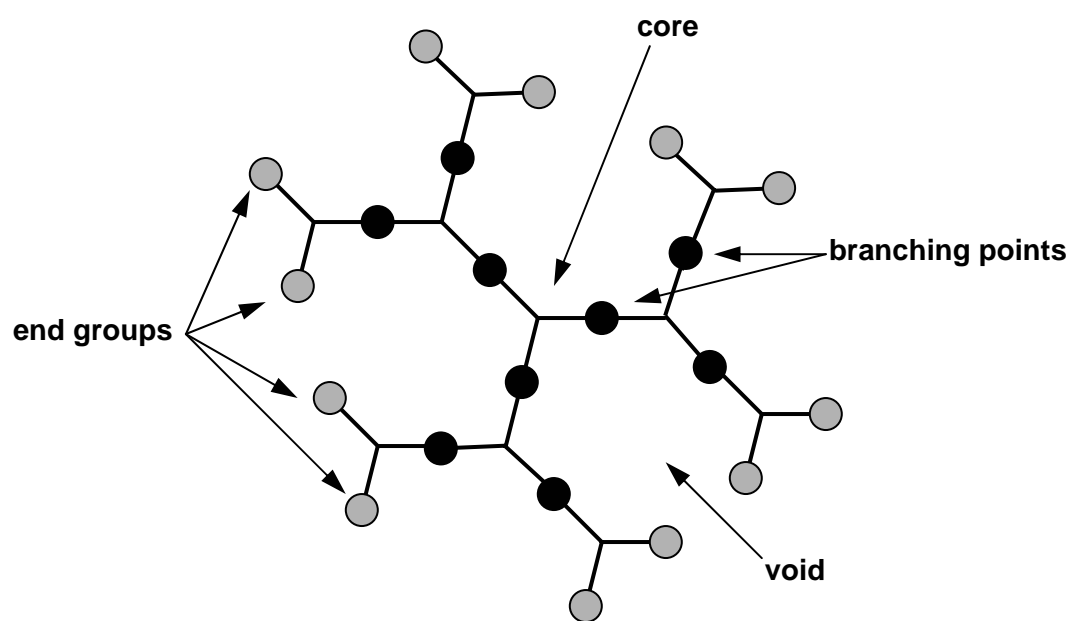
Fig. 1. Structure of a dendrimer.

An important factor in the ability of dendrimers to perform as catalysts, filters or sorbents is the access other molecules have to the interior of the macromolecule. Unbranched (linear) macromolecules have an asymmetric and relatively open conformation which allows segments from other molecules easy access to the interior of the macromolecule. In contrast, control over the macromolecular configuration is a key goal in dendrimer chemistry (Newkome et al., 2001). Regulation of molecular configuration includes controlling the overall molecular shape, internal and external rigidity, lipophilicity and hydrophilicity, degrees of void and excluded volumes, density gradients, complementary functionalities and environmental cooperativity (Newkome et al., 2001). The high level of control over macromolecular configuration gives researchers the ability to control and fine-tune the functionality of a dendrimer, a powerful tool that has potential for application in the field of environmental remediation.

Soil Amendments

Polymeric organic compounds have been added to soil to control erosion and/or increase the retention of organic contaminants. Polymeric organic compounds commonly applied to soil fall into two classes: polyacrylamides (PAMs) and polymeric surfactants.

PAMs

Of the two types of polymeric organic compounds, PAMs are the most commercially important synthetic water-soluble polymers (Bikales, 1973). The most common use of PAMs is as a flocculating agent to precipitate suspended clays in water treatment. Their use as soil conditioners (material used to improve soil physical properties) has been studied for the past 40

years (Laird, 1997) and their popularity as a soil amendment is illustrated by the large number of articles published on the topic.

PAMs are used to increase aggregate stability and infiltration rates of soils (Nadler et al., 1996; Zhang and Miller, 1996) and decrease penetration resistance and bulk density of soils (Helalia and Letey, 1988; Wallace et al., 1986a, 1986b). Unfortunately, PAMs do not considerably enhance the retention of organic contaminants (Deng, 2001), limiting their usefulness to improving soil physical properties.

Polymeric Surfactants

A surfactant or surface-active agent is a chemical that is active at the interface between two phases, such as the interface between hydrophilic and hydrophobic phases. A surfactant accumulates at the interface and modifies its surface tension. Polymeric surfactants contain both hydrophilic and hydrophobic segments in their structure which allow these compounds to greatly influence the way in which organic compounds interact with the primarily hydrophilic soil matrix.

Next to solvents, surfactants make up the largest group of adjuvants in pesticide formulations (Krogh et al., 2003). Adjuvants are compounds other than the active ingredient added to enhance the effectiveness, i.e. bioavailability, of the pesticide formulation by increasing the solubility, or the compatibility of the active ingredients. Adjuvants may also enhance adsorption, penetration and translocation of the active ingredient into the target, increase rain fastness, and alter selectivity of the active ingredient for different plants (Krogh et al, 2003).

Surfactants have been used in the synthesis of organoclay composites. Hydrophilic segments of the surfactant attach to the clay surface or become partially sorbed into interlayers

of smectitic clays (Deng, 2001; Acosta, 2003). The hydrophobic segments of these surfactants

then are available to adsorb hydrophobic organic compounds from water (Garcia et al., 2001).

A number of environmental applications for organoclays exist (Deng, 2001).

Organoclays can be incorporated into earthen landfill liners to immobilize dissolved organic

contaminants and prevent the hydraulic failure of the clay barrier which can occur when a high

concentration of organic liquid is released. Organoclays have been shown to adsorb more oil

and grease than activated carbon and can be used as extenders for activated carbon in water

treatment. Organoclays have also been used to adsorb airborne organic contaminants. Other

applications that are receiving increased attention include their use in enhanced oil recovery,

water-based drilling fluids, and cleanup of nonionic organic contaminants.

Melamine-Based Surfactants

The first dendrimer family prepared at Texas A&M University by Simanek and

coworkers (Zhang and Simanek, 2000; Zhang et al., 2001) was based on melamine (2,4,6-

triamino-1,3,5-triazine). Development of dendrimers based on melamine is of interest due to

their easy synthesis, the ability to control diversity in their composition, and their intrinsic

potential for molecular recognition (Zhang and Simanek, 2000).

In the course of characterizing the properties of dendrimers based on melamine, the

researchers discovered that some of the dendrimer systems sequestered triazine herbicides from

solution. This discovery led to a study of the relationship between dendrimer structure and

atrazine sequestration potential of corresponding organoclay composites. Acosta (2003) studied

10 different dendrimers containing a melamine core with two hydrophobic dendrons and one

hydrophilic dendron. The hydrophilic dendron was responsible for attaching, or anchoring, the

surfactant to a clay particle while the hydrophobic dendrons remained free to interact with other

organic chemicals. Acosta looked at the role of size and shape, the role of the hydrophobic functional group and the role of the hydrophilic (cationic) anchor on the ability of the melamine surfactant to sequester atrazine. He found that smaller surfactant molecules are more effective than larger molecules, that larger hydrophobic groups increase adsorption and that the hydrophilic anchor, for reasons not yet understood, can have a great impact on the ability of the surfactant to sequester atrazine.

The surfactant to be used in this research project was the most promising compound identified by Acosta's research (2003).

Pesticide Adsorption

Adsorption of a pesticide to soil is a reversible process that involves the attraction and retention of the chemical for a time that depends on the affinity of the chemical for the surface (Koskinen and Harper, 1990). It is often difficult to distinguish between true adsorption in which molecular layers form on a soil particle surface, precipitation in which either a separate solid phase forms on solid surfaces or covalent bonding with the soil particle surface occurs, and physical trapping in soil micropores.

Koskinen and Harper (1990) reviewed a number of mechanisms that contribute to sorption of an organic compound onto a soil particle. London-van der Waals forces are short-range bonds resulting when the electronic motion in each of two adjacent molecules is synchronized to produce a small net electrostatic attraction at all times. Hydrogen bonds are produced from the electrostatic attraction between an electropositive H nucleus and exposed electron pairs on electronegative atoms. Cation bridging is a weak adsorption mechanism involving the formation of a complex between an exchangeable cation and an anionic or polar functional group. Water bridging is an interaction between a proton in a hydrating water

molecule of an exchangeable cation and an organic functional group. Anion exchange is the
nonspecific electrostatic attraction of an anion to a positively charged site on the soil surface.
Ligand exchange forms a complex between an organic functional group and a metal ion (Fe or
Al) at the surface of a soil mineral. Protonation of an organic compound occurs when an organic
functional group forms a complex with a proton at the mineral surface. Cation exchange is the
electrostatic attraction of cationic functional groups by a negatively charged site at the soil
surface. Covalent bonding, an irreversible sorption mechanism, occurs when electrons are
shared between an atom in an organic functional group and an atom on the soil surface. Finally,
organic compounds may be physically trapped in the soil matrix.

More than one mechanism may be involved in sorption of a pesticide on the soil surface.
Koskinen and Harper (1990) noted that for most pesticides a rapid, reversible equilibrium is
initially established between solution and the soil surface followed by reactions which more
permanently bind the adsorbed pesticide molecules to the soil particle.

One of the main assumptions in characterizing pesticide adsorption on a solid is that
equilibrium is established between pesticide on the solid and that in solution. Assuming
equilibrium, distribution coefficients can be used to express the relationship between pesticide in
the two phases.

Two distribution coefficients are commonly used (Koskinen and Harper, 1990). When
adsorption is linearly related to solution concentration, a partition coefficient, K_d, is used. The
partition coefficient is defined as

$$K_d = [(x/m)]/[C_e] \qquad [1]$$

where *x/m* is the concentration of pesticide on the solid (mg kg^{-1}) and C_e is the pesticide

concentration in solution (mg L^{-1}). Most often, adsorption is not a linear process and in such

cases a distribution coefficient based on the empirical Freundlich relationship is a better choice.

The Freundlich distribution coefficient, K_f, is defined as

$$K_f = [(x/m)]/([C_e]^{1/n})$$ [2]

where *n* is an empirical constant, usually less than or equal to 1.

Atrazine Adsorption

The herbicide atrazine ($C_8H_{14}ClN_5$; molecular weight 215.68) is a white powder or

crystalline solid with an melting point of 171-174 °C, a vapor pressure of 0.04 mPa at 20 °C/0.19

mPa at 30 °C, and a water solubility of 28 mg L^{-1} at 20 °C/33 mg L^{-1} at 27 °C (Montgomery,

1993). Figure 2(a) illustrates the structure of atrazine.

Atrazine has functional groups capable of engaging in hydrogen bonding, van der Waals

bonding, and ligand exchange (Sparks and Swift, 2002). The extent of atrazine adsorption on a

specific soil will depend on soil properties that favor or discourage formation of these bonds.

The soil constituents involved in atrazine adsorption are soil humic substances and

smectitic clay minerals. The triazine herbicides have been shown to readily sorb to smectites

(Weber, 1970). Enhanced adsorption of triazines to smectites at low pH has been attributed to

protonation of the triazine molecule and sorption of the resulting cation via cation-exchange

(Weber, 1970; Hermosín et al., 1982). More recent studies have postulated that atrazine is

sorbed to smectitic clays through relatively weak van der Waals or hydrogen bonds (Barriuso et

al., 1994) and that mineral surface acidity can lead to protonation and hydrolysis of the sorbed molecules (Laird, 1996).

Sorption of atrazine by soil organic matter is attributed to either hydrogen bond formation or proton transfer between atrazine and the acidic functional groups (carboxyl and phenolic) of humic macromolecules (Sullivan and Felbeck, 1968; Li and Felbeck, 1972). Structural characteristics have a significant impact on the sorption capacity of humic substances because hydrogen bonding of humic acid carboxylates to atrazine are favored in a hydrophobic environment while hydrogen bonding to water will dominate in a hydrophilic environment (Wang et al., 1991; Welhouse and Bleam, 1993a,b).

Celis et al. (1997, 1998) compared atrazine adsorption of individual soil colloidal components (montmorillonite, ferrihydrite and humic acid) to adsorption on associations composed of two or more of these individual components. The researchers found that sorption to the associations was not the simple sum of sorption on individual components. Depending on the combination, adsorption of atrazine was enhanced or reduced as a result of interaction between individual constituents. They concluded that the adsorption sites for the pesticide may be reduced in number or change in character as a result of the association between soil components.
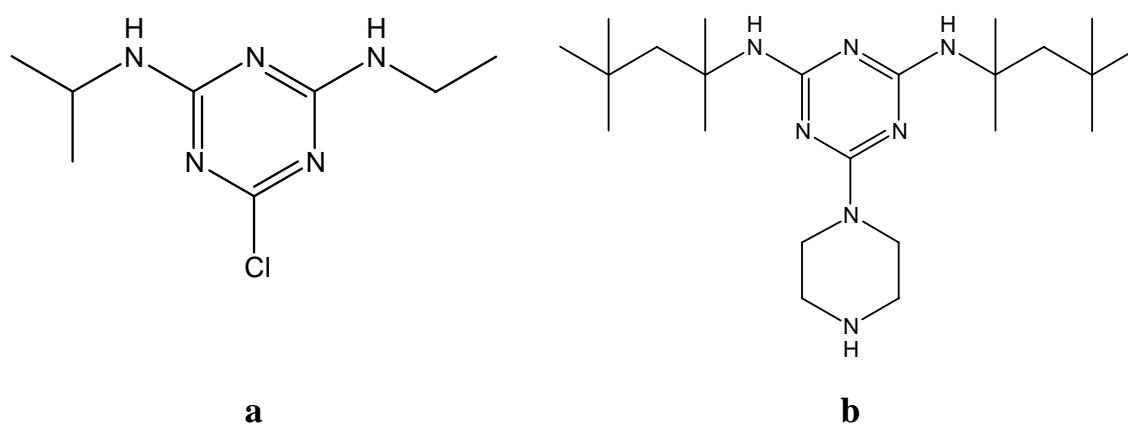
Fig. 2. Chemical structure of atrazine (a) and the surfactant 6-piperazin-1-yl-*N*,*N*′-bis-(1,1,3,3-tetramethyl-butyl)-(1,3,5)triazine-2,4-diamine (b).

MATERIALS AND METHODS

Herbicide

Both nonlabeled and ^{14}C-labeled atrazine were used in the experiments. Nonlabeled atrazine with a chemical purity of 98% was purchased from Chem Service (West Chester, PA). ^{14}C-ring-labeled atrazine with a chemical purity of 96.7%, a radioactive purity of 98.7% and a specific activity of 3.40×10^{14} Bq mol^{-1} was obtained from Syngenta Crop Protection (Greensboro, NC).

Atrazine solutions were prepared in pure methanol. Eight solutions were created with atrazine concentrations ranging from 1 mg L^{-1} to 3000 mg L^{-1}. Dilutions of 50 μL of atrazine solution in 5 mL of aqueous 10 mmol L^{-1} (0.01 M) CaCl$_2$ solution provided the desired concentrations of 0.01 mg L^{-1} to 30 mg L^{-1}. The working solutions contain 1% methanol.

Labeled and unlabeled atrazine was added to the atrazine solutions to provide 10,000 disintegrations per minute (dpm) in each mL of working solution. The only exception was the solution for the most dilute atrazine concentration, which provided only 1,000 dpm mL^{-1} of working solution.

Surfactant

The surfactant [6-piperazin-1-yl-N,N'-bis-(1,1,3,3-tetramethyl-butyl)-1,3,5-triazine-2,4-diamine] [Fig 2(b)] used in the experiments was prepared by Erick Acosta of the Simanek Group, Department of Chemistry, Texas A&M University. A summary of the surfactant synthesis is provided in the appendix (p. 62).

Organoclay Composites

The organoclay composites were created by sorbing the surfactant to Ca-saturated smectite clay. The clay used to prepare the organoclay composites was a Gonzales bentonite sample obtained from Southern Clay Products (Gonzales, TX). The clay was pretreated following the procedure detailed in the appendix (p. 66). Eighteen different organoclay composites were prepared containing 1, 2, 3, 4, 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5, 25, 30, 35, 40, 45 and 50% surfactant on a total weight basis. On a clay weight basis the surfactant concentrations were 1.0, 2.0, 3.1, 4.2, 5.3, 8.1, 11.1, 14.3, 17.7, 21.2, 25.0, 29.0, 33.3, 42.9, 53.9, 66.7, 81.8, and 100%. References to specific organoclay composites in the remainder of the text will made using percent surfactant on a total weight basis.

For each composite, 500 mg of clay was suspended in 20 mL of distilled water in a 50-mL polypropylene conical centrifuge tube. The required amount of surfactant was dissolved in 5 mL tetrahydrofuran and added to the clay suspension by pipette. The suspensions were then shaken for 24 h at 25 °C. The resulting organoclay composites were centrifuged at $15,180 \times g$ for 10 min and the supernatant decanted. The composites were washed 3 times with distilled water to remove excess surfactants. Washing was done by adding 15 mL distilled water to the organoclay sediment, shaking until all the sediment was suspended, centrifuging at $15,180 \times g$ for 10 min, and then decanting the supernatant. The composites were then freeze dried and ground to a powder.

Additional amounts of 2, 5, 12.5, 25 and 45% organoclay composites were created. To create the additional 2, 12.5 and 45% organoclay composites, 1200 mg of clay was suspended in 40 mL of distilled water in a 50-mL polypropylene conical centrifuge tube. The required amount of surfactant was dissolved in 5 mL tetrahydrofuran and added to the clay suspension by pipette. To create the additional 5 and 25% organoclay composites, 1000 mg of clay was

suspended in 40 mL of distilled water in a 50-mL polypropylene conical centrifuge tube. The

required amount of surfactant was dissolved in 5 mL tetrahydrofuran and added to the clay

suspension by pipette. All suspensions were then shaken for 24 h at 25 °C. The resulting

organoclay composites were centrifuged at $15,180 \times g$ for 10 min and the supernatant decanted.

The composites were washed 3 times with distilled water to remove excess surfactants. Washing

was done by adding 15 mL distilled water to the organoclay sediment, shaking until all the

sediment was suspended, centrifuging at $15,180 \times g$ for 10 min, and then decanting the

supernatant. The composites were then freeze dried and ground to a powder.

The amount of surfactant sorbed to the clay was measured with a Carlo Erba NA-1500

combustion unit (CE Elantech, Lakewood, NJ).

Soil Sample

The soil sample was collected from the top 10 cm of a Houston Black clay pedon (fine,

smectitic, thermic Udic Haplustert) located on the Blackland Research Center, Texas

Agricultural Experiment Station. The sample site (31° 3' 11.6" N, 97° 21' 0.9" W) was located at

the base of a 1 to 3% slope. The soil sample was air dried and ground to pass a 2-mm sieve, then

pulverized with a laboratory ring pulverizer (Armstrong Inc., Chicago, IL).

Particle size analysis of unpulverized clay using the hydrometer method (Gee and Or,

2002) established a size distribution of 13% sand (2000-50 μm), 34% silt (50-2 μm), and 53%

clay (< 2 μm). The pulverized soil sample had 1.5% organic carbon and 31.4% $CaCO_3$

equivalent (29.9% calcite and 1.4% dolomite) as determined by the Soil Characterization

Laboratory, Soil & Crop Sciences Dept., Texas A&M University. Total carbon was determined

using combustion (Nelson and Sommers, 1982). Calcium carbonate equivalent was measured

using HCl treatment and an Chittick apparatus (Drenianis, 1962). Organic carbon is calculated as

the difference between total carbon and $CaCO_3$ equivalent.

Experimental Protocols

All experiments were carried out in 35-mL glass centrifuge tubes with Teflon lined caps. To remove variation in atrazine adsorption due to sorption by the clay component, samples were weighed so that all vials contained 15 mg of clay. The sample weights used for the different organoclay composites were: 0%, 15.0 mg; 1%, 15.2 mg; 2%, 15.3 mg; 3%, 15.5 mg; 4%, 15.6 mg; 5%, 15.8 mg; 7.5%, 16.2 mg; 10%, 16.7 mg; 12.5%, 17.1 mg; 15%, 17.7 mg; 17.5%, 18.2 mg; 20%, 18.8 mg; 22.5%, 19.4 mg; 25%, 20.0 mg; 30%, 21.4 mg; 35%, 23.1 mg; 40%, 25.0 mg; 45%, 27.3 mg; 50%, 30.0 mg. The weight used for the Houston Black clay sample was 29.4 mg. Triplicate 15 mg clay-equivalent samples were weighed into centrifuge tubes and pre-equilibrated for 24 h in 5 mL of 10 mmol L^{-1} (0.01 M) $CaCl_2$ solution.

The freeze-dried organoclays did not readily wet due to their high hydrophobicity. To overcome this problem the samples were agitated twice. The first agitation was performed with the addition of the $CaCl_2$ solution, which was added in two portions. First, 2 mL of $CaCl_2$ solution were added to a centrifuge tube, which was then capped and shaken on a vortex mixer for five seconds, then the remaining 3 mL of $CaCl_2$ solution were added. Within the last 3 h of the pre-equilibration period, the centrifuge tubes were shaken on a rotary shaker for 1 h.

Once the pre-equilibration period was completed, 50 µL of the desired atrazine solution was added to each centrifuge tube by pipette. The tubes were shaken, then centrifuged for 20 min at $622 \times g$ and the supernatant decanted.

The concentration of atrazine in the decanted liquid was measured by liquid scintillation counting of 1 mL of the supernatant mixed with 10 mL of Ecolite liquid scintillation cocktail (ICN Biomedicals, Costa Mesa, CA) using a Beckman LS6500 multipurpose scintillation

counter (Beckman Instruments, Inc., Fullerton, CA). The counting time was set to obtain a 2%

precision for the dpm mean.

Centrifuge tubes containing no solid material were prepared in triplicate and processed

alongside the sample centrifuge tubes. The concentration bound to the solid was calculated as

the difference between the concentrations in solution of centrifuge tubes containing no solid

material and of the samples with the solid. Background radioactivity was accounted for by

processing centrifuge tubes with solid material to which 50 μL methanol was added in place of

the atrazine solution. Two scintillation vials were made for each centrifuge tube to account for

variability in pipette technique.

Kinetics

Kinetic studies were carried out with 0, 2, 5, 12.5, 25 and 45% organoclay composites

and Houston Black soil at a solution concentration of 2 mg L^{-1} atrazine.

The adsorption percentages were calculated:

$$\% \text{ adsorbed} = 100 \times (C_i - C_e)/C_i \qquad [3]$$

where C_i is the initial concentration in solution (mg L^{-1}) and C_e is the concentration in solution at

the end of the equilibration period (mg L^{-1}).

The concentration of atrazine sorbed, x/m, was calculated:

$$x/m = [(C_i - C_e) \cdot v_{sol}]/m_{sub} \qquad [4]$$

where x/m is the concentration of atrazine sorbed (mg kg^{-1} of total weight), v_{sol} is the total

solution volume (L), and m_{sub} is the total mass of substrate exposed to the solution (kg).

Adsorption equilibrium was determined from the kinetics data. Adsorption equilibrium was defined as the time step where the difference in the amount of atrazine sorbed from solution between the current and next time step was less than or equal to 5% (Moreau and Mouvet, 1997).

Adsorption Isotherms

Adsorption isotherm studies were carried out with all organoclay composites and Houston Black clay using solution concentrations of 0.01, 0.1, 1, 2, 5, 10, 20 and 30 mg L^{-1} atrazine. Solution concentrations were selected to represent typical concentrations found in runoff (0.01 mg L^{-1}) and the soil (2 mg L^{-1}) as well as the saturation concentration of atrazine in water (30 mg L^{-1}; Montgomery, 1993). Additional solution concentrations provided adsorption measurements over several orders of magnitude to fully characterize atrazine adsorption by the organoclay composites. Based on kinetic study results, the adsorption isotherm samples were equilibrated for 72 h.

Both the partition coefficient, K_d, and Freundlich distribution coefficients, K_f and $1/n$, were determined. The Freundlich distribution coefficients were calculated using linear regression with the linear form of the Freundlich equation (Moreau-Kervévan and Mouvet, 1998):

$$\ln(x/m) = \ln(K_f) + (1/n)\ln(C_e)$$

[5]

where K_f represents the adsorption capacity of the solid and $1/n$ represents the adsorption intensity. The partition coefficient was adjusted for organic C content (% org C) of the solid (K_{oc}) using:

$$K_{oc} = \left(K_d \big/ \% \, \mathrm{org.C}\right) \times 100 \qquad\qquad [6]$$

The Freundlich distribution coefficient was adjusted for organic C content of the solid (K_{foc}) using:

$$K_{foc} = \left(K_f \big/ \% \, \mathrm{org.C}\right) \times 100 \qquad\qquad [7]$$

Desorption

Desorption studies were carried out with 0, 1, 5, 20, 35 and 50% organoclay composite and Houston Black clay samples. The samples were equilibrated with a solution containing 10 mg L^{-1} atrazine. A high atrazine concentration was selected for equilibration to ensure that the substrates were saturated with atrazine.

Desorption studies were carried out twice. In the first study, the atrazine solution contained non-labeled and ^{14}C-labeled atrazine. Liquid scintillation analysis was used to determine the amount of atrazine desorbing from the substrates. In the second study, the atrazine solution contained only non-labeled atrazine. High performance liquid chromatography analysis was used to determine the type of material desorbing from the substrate—atrazine molecules, atrazine degradation products or larger particles made of substrate/atrazine complexes.

For both studies, sample tubes were equilibrated with the atrazine solution for 3 d. Once the equilibration period was complete, the tubes were centrifuged for 20 min at $622 \times g$ and the supernatant removed and stored. Five mL of 10 mmol L^{-1} (0.01 M) CaCl$_2$ solution was then added to the centrifuge tubes and the tubes shaken for 24 h. This procedure was performed 4

times for each sample.

In the first study, the concentration of atrazine in the supernatant was measured by liquid scintillation counting. The percentage of pesticide desorbed at each time step was calculated:

$$\% \text{ desorbed} = 100 \frac{\left\lfloor (x/m)_{t-1} - (x/m)_t \right\rfloor}{(x/m)_{t-1}} \qquad [8]$$

where $(x/m)_t$ is the concentration (mg kg^{-1}) remaining bound to the solid at time step t, and $(x/m)_{t-1}$ is the concentration remaining bound to the solid at the previous time step.

In the second study, the type of material present in the supernatant was identified using high performance liquid chromatography. Samples were analyzed on a Waters RP8 symmetry shield C8 column with a Waters HPLC instrument equipped with a photodiode array detector (Waters Inc., Milford, MA) set at the 225-nm wavelength. The injection volume was 20 μL and the flow rate was 0.3 mL min^{-1}. Two mobile phases were used in a gradient program (Table 1). They consisted of acetonitrile-water-70 mmol L^{-1} ammonium acetate buffer (10:75:15 v/v) and acetonitrile-water-70 mmol L^{-1} ammonium acetate buffer (80:5:15 v/v) for the initial and final mobile phases, respectively.

Table 1: High performance liquid chromatography mobile phase gradient profile for atrazine and atrazine metabolite separation. Initial and final mobile phases were acetonitrile-water-0.07 mol L^{-1} ammonium acetate buffer (10:75:15 v/v) and acetonitrile-water-0.07 mol L^{-1} ammonium acetate buffer (80:5:15 v/v), respectively.

Time (min)	Initial mobile phase (%)	Final mobile phase (%)
0	100	0
5	100	0
6	0	100
26	0	100
27	100	0

RESULTS AND DISCUSSION

Organoclay Characterization

The organoclays and the pure clay were analyzed for organic C and organic N. The pure clay contained 0.42% organic C and 0% organic N on a total weight basis.

Measured organic nitrogen content correlated well with values calculated assuming 100% adsorption of applied surfactant to the clay (Fig. 3). Expected and measured organic N for the 1 to 5% organoclay composites indicate that all surfactant was sorbed to the clay. For organoclay composites containing a surfactant fraction > 5%, sorption of the surfactant to the clay was slightly incomplete for most composites, but there was no trend (Fig. 4).

Measured organic carbon content differed from expected values (Fig. 5) than did organic nitrogen (Fig. 3). The difference between measured organic carbon and the value of organic carbon predicted from measured organic N and the C:N ratio (2.82:1) of the surfactant (Fig. 6) increased as the surfactant percentage decreased.

The additional organic carbon measured in the organoclay composites was attributed to tetrahydrofuran, the solvent used to dissolve the surfactant. This assumption was supported by the reductions in organic carbon for the 2%, 5% and 12.5% organoclay composites relative to other treatments. These reductions were expected since, in the second round of organoclay synthesis, a smaller amount of tetrahydrofuran relative to the amount of water was used. Tetrahydrofuran sorption was greatest on the 1% organoclay composite and decreased as the amount of surfactant increased (Fig. 6), indicating preferential sorption of the surfactant on the clay. While the differences increased with the 45% and 50% organoclay composites, the

% N meas = 0.985 x % N exp
R-square = 0.997

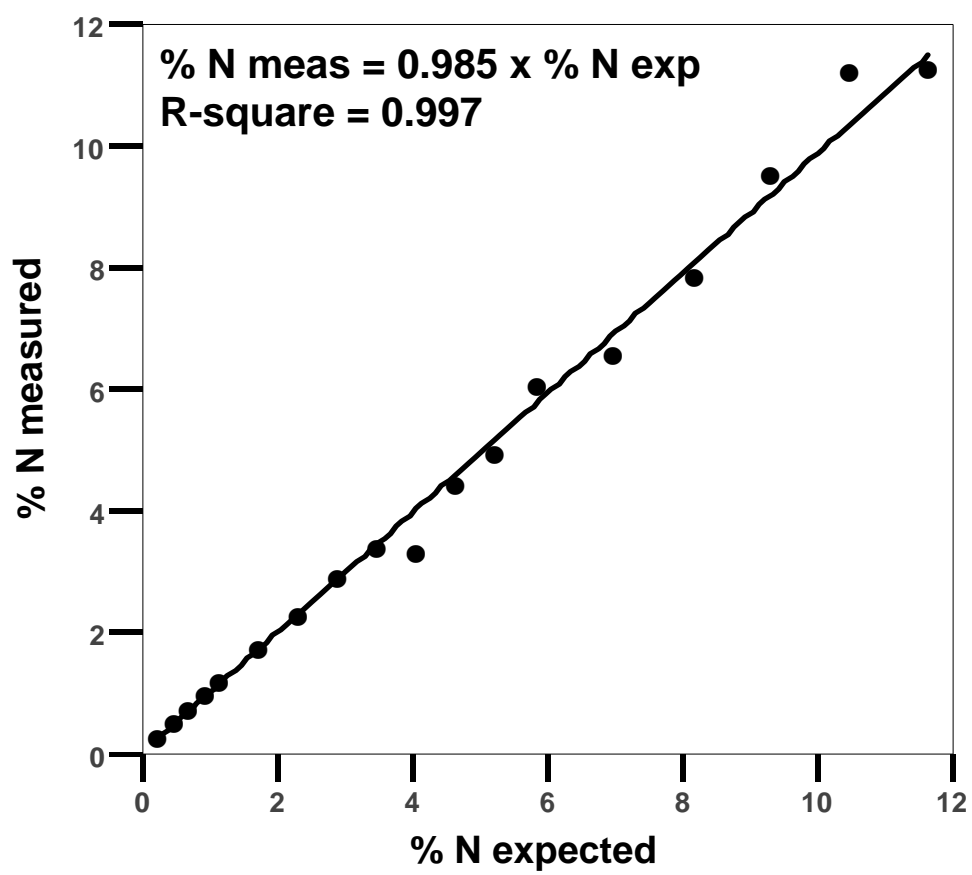**Fig. 3. Expected and measured organic N in organoclays.**

Fig. 4. Difference between expected and measured percent organic N. A difference of zero results when measured and expected percent organic N are equal, a negative difference is produced when the measured value is less than the expected value, and a positive difference indicates that the measured value is greater than the expected value.

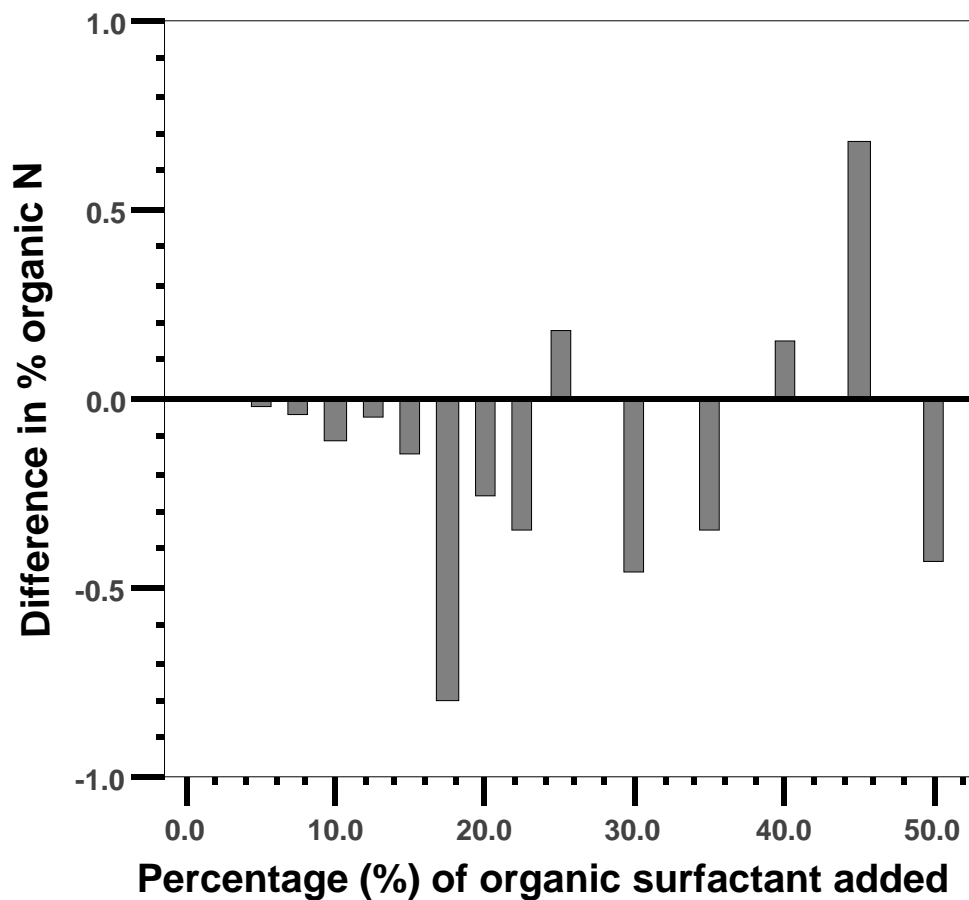**Fig. 5. Expected and measured organic C in organoclay composites.**

Fig. 6. Difference between expected and measured percent organic C. A difference of zero results when measured and expected percent organic C are equal, a negative difference is produced when the measured value is less than the expected value, and a positive difference indicates that the measured value is greater than the expected value.
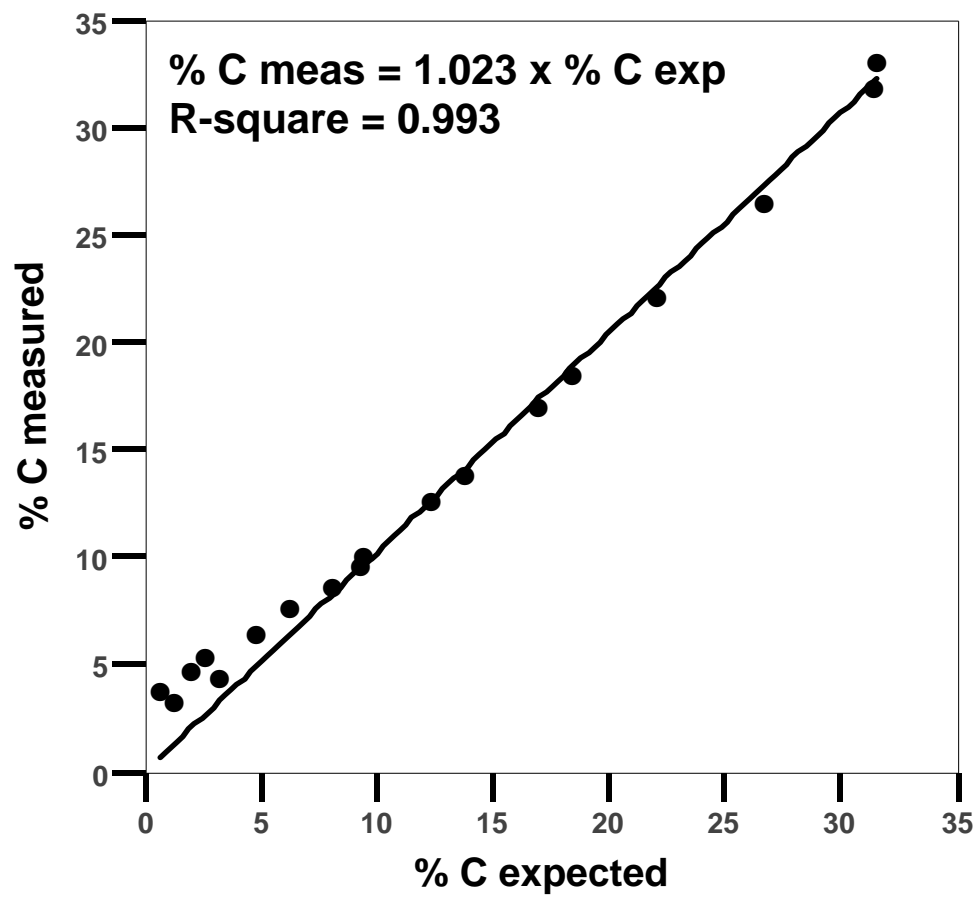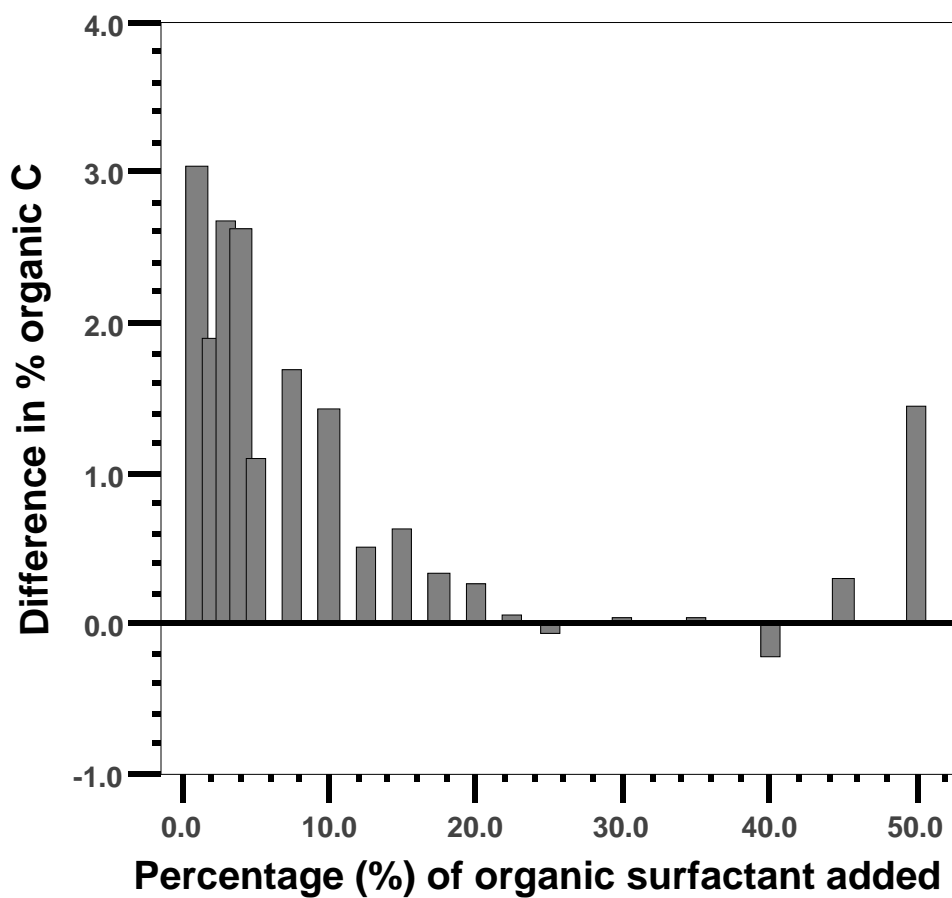
variability in test results for these two organoclay composites was much greater than that for the other samples. Differences between measured and expected percentages calculated for individual 45% composite samples were -0.23 and +0.84. For individual 50% composite samples, the differences between measured and expected percentages were +0.61 and +2.28.

Supplementary experiments were conducted to assess the impact of tetrahydrofuran on atrazine sorption by the organoclays. These experiments showed no sorption of atrazine by tetrahydrofuran and no variation in atrazine adsorption of an organoclay composite due to differences in the amount of tetrahydrofuran used during preparation of the organoclay composite. Experimental details are given in the appendix (p. 68).

X-ray diffraction analysis of the samples showed no significant change in basal spacing of the organoclay composites relative to that of the pure clay. This indicated that the surfactant and any tetrahydrofuran sorbing to the clay was doing so on the clay surface rather than in the clay interlayer. As more surfactant was added to the sample, it formed additional layers around the clay particles (appendix, p. 68).

Adsorption Kinetics

Adsorption kinetics of the 0, 2, 5, 12.5, 25 and 45% organoclay composites and the Houston Black clay sample were measured over a 5-day period. Atrazine removal increased as the amount of surfactant present in the organoclay composite increased (Fig. 7). The Houston Black clay adsorbed some atrazine, but the sorption was much less than that of the organoclay composites.
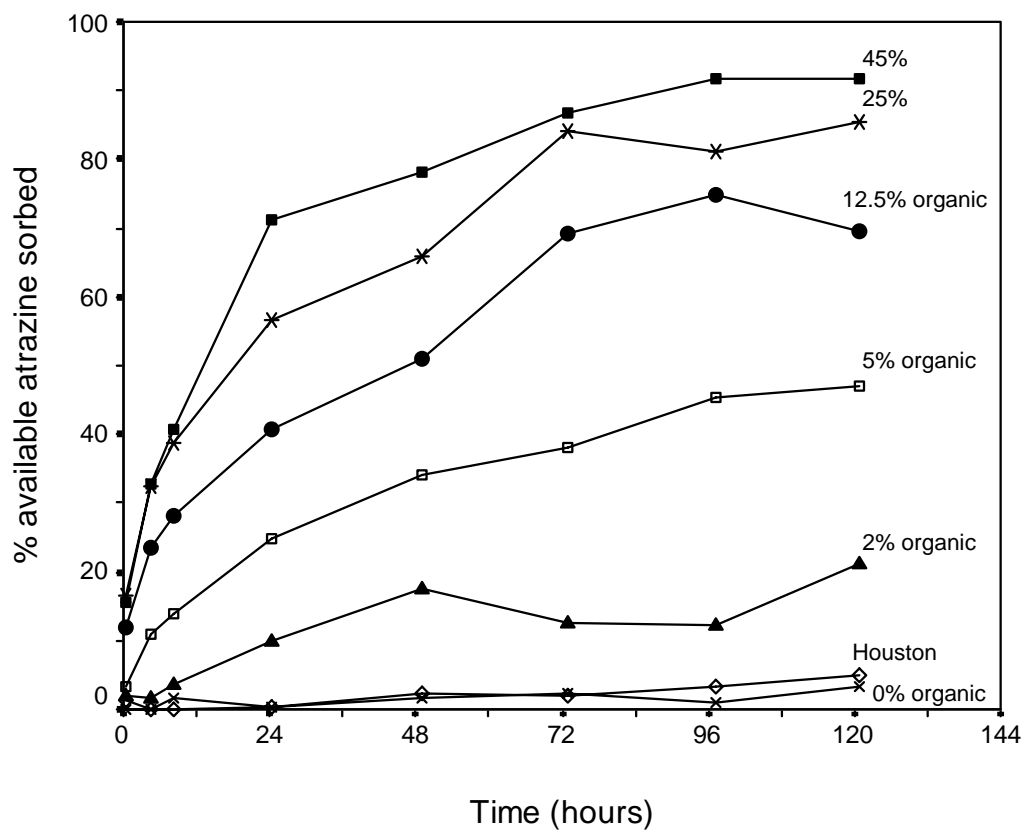
Fig. 7. Atrazine adsorption kinetics graphed as percent of atrazine removed from a 2 mg L^{-1} solution by Houston Black clay and 6 different organoclay composites. Each point is the mean of three replicates.

Table 2: Amount of atrazine sorbed for each time period.

Time period (h)	Houston Black clay	Amount of atrazine sorbed to substrate (mg kg^{-1}) with 95% CI					
		Percentage of organic surfactant added[†] %					
		0	2	5	12.5	25	45
0.5	0	0	13 (4-22)	20 (0-68)	69 (36-102)	82 (36-129)	57 (39-75)
4	0	0	11 (0-35)	69 (54-84)	138 (112-164)	163 (151-175)	120 (108-132)
8	0	11 (0-40)	24 (12-36)	88 (66-110)	163 (138-188)	194 (171-218)	149 (131-166)
24	0	2 (0-11)	66 (59-72)	158 (126-190)	238 (191-285)	282 (249-316)	261 (247-275)
48	0	11 (0-39)	116 (98-133)	215 (188-242)	298 (294-302)	329 (312-347)	286 (275-299)
72	0	16 (0-35)	81 (48-133)	241 (212-270)	404 (368-440)	421 (406-436)	318 (298-338)
96	0	6 (0-22)	81 (67-94)	288 (272-304)	436 (430-443)	405 (399-410)	337 (328-346)
120	0	22 (0-62)	139 (125-153)	299 (276-322)	405 (379-430)	428 (408-447)	336 (330-342)

[†] Percentage of organic surfactant added pertains to the percentage of the surfactant 6-piperazin-1-yl-*N,N'*-bis-(1,1,3,3-tetramethyl-butyl)-1,3,5-triazine-2,4-diamine in organoclay composites created with pretreated Gonzales clay and the surfactant. The percentages are calculated on a total weight basis.
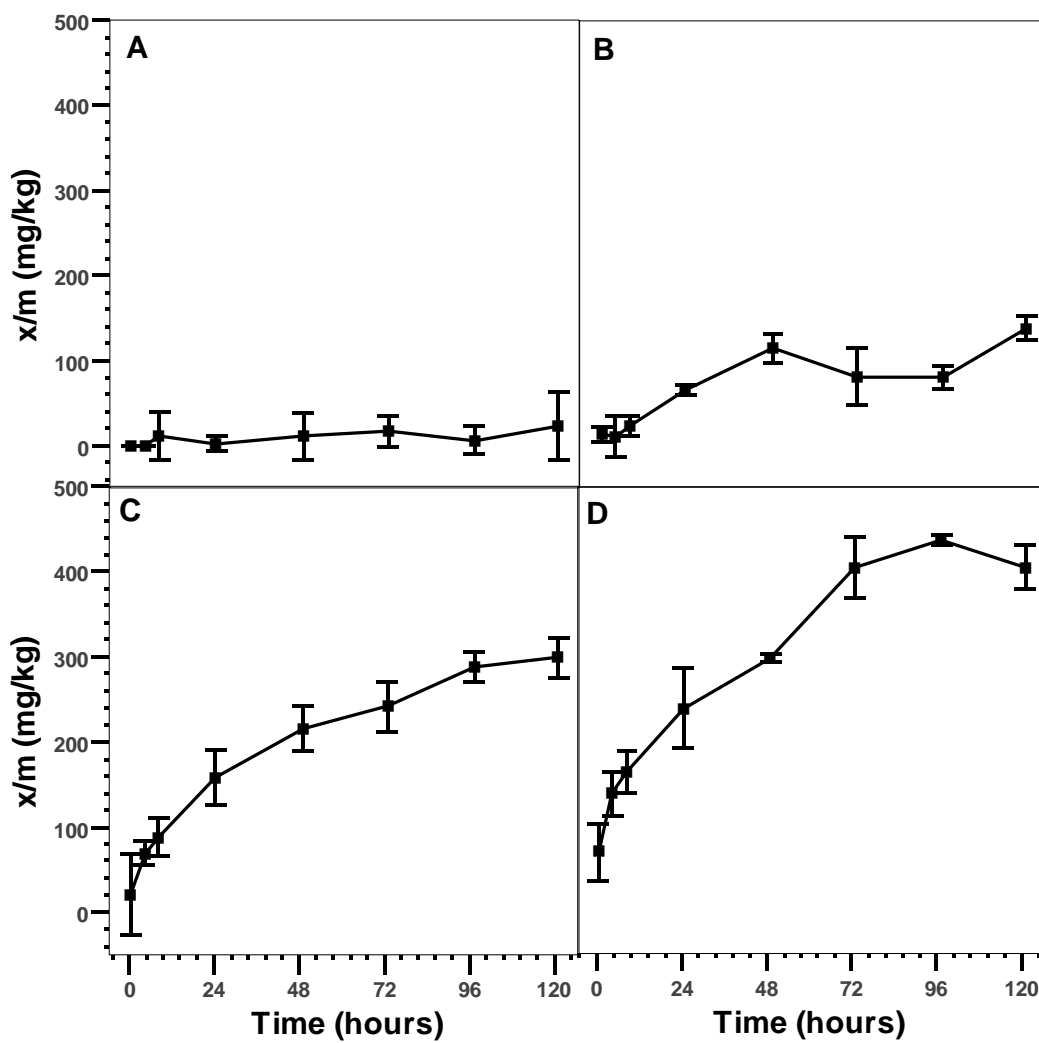
Fig. 8. Adsorption kinetics of atrazine, 2 mg L^{-1}, on organoclay composites containing 0 (A), 2 (B), 5 (C), 12.5 (D), 25 (E), and 45% (F) surfactant on a total weight basis and Houston Black clay (G). Each point is the mean of three replicates. The error bars represent the 95% confidence interval for the amount of atrazine sorbed by a given substrate.
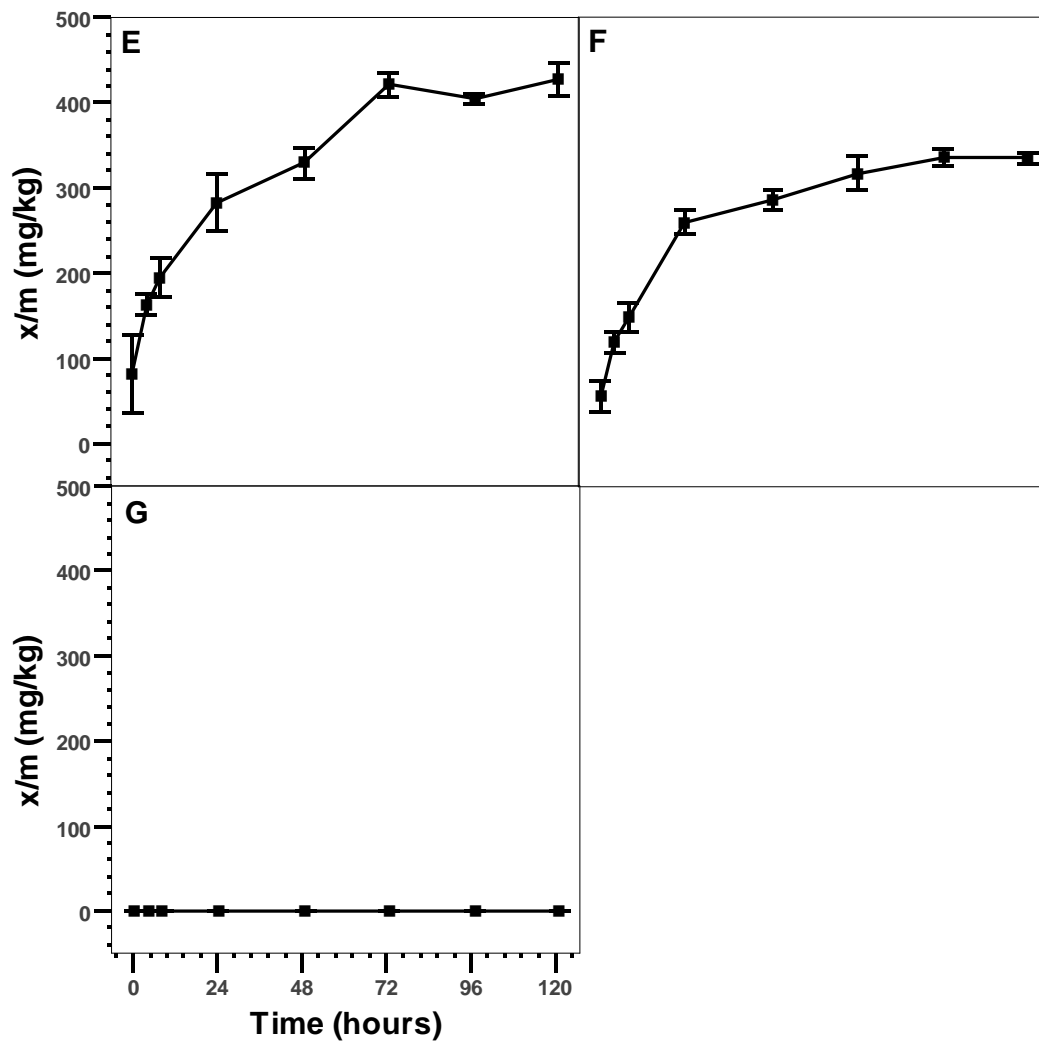
Fig. 8. Continued.

Atrazine sorption on a mass basis is summarized in Table 2 and displayed graphically in Fig. 8. For the Houston Black clay, the amount of atrazine sorption was not significantly different from zero for any time period. The amount of atrazine sorbed by the 0% organoclay composite (pure clay) was not significantly different from zero for any time period. For the five organoclay composites containing varying amounts of surfactant, adsorption of atrazine was initially rapid followed by a period of slower adsorption before finally reaching equilibrium. Equilibrium, defined as $\leq$ 5% change over a 24-h period, was reached after 72 h for all organoclay composites.

Adsorption kinetics plotted as fraction of maximum adsorbed (Table 3 and Fig. 9) emphasize the decrease in rate of adsorption with time. Of the total amount of atrazine adsorbed during the 72-h equilibration period, approximately 70% is adsorbed within the first 24 h with the remaining 30% adsorbed in the next 48 h. The presence of two stages in the adsorption kinetics suggests progressive adsorption (Moreau and Mouvet, 1997). During the initial rapid adsorption period, atrazine is adsorbing to easily accessible sites on the surface of the organoclay composite while the second, slower stage of adsorption represents adsorption on less accessible sites. The second stage of adsorption is most likely physically controlled by the diffusion of atrazine into the interior of the organoclay complex.

Table 3: Fraction of maximum amount of atrazine sorbed for each time period.

| Time period (h) | Houston Black clay | Fraction of maximum amount of atrazine sorbed to substrate with 95% CI | | | | | |
| | | Percentage of organic surfactant added[†] % | | | | | |
		0	2	5	12.5	25	45
0.5	0.26	0	0.09	0.07	0.17	0.19	0.17
	[(-0.85)-1.36]		(0.03-0.16)	[(-0.09)-0.23]	(0.09-0.25)	(0.08-0.30)	(0.12-0.22)
4	0	0	0.08	0.23	0.34	0.38	0.36
			[(-0.09)-0.25]	(0.18-0.28)	(0.28-0.41)	(0.35-0.41)	(0.32-0.39)
8	0	0.49	0.17	0.30	0.40	0.45	0.44
		[(-0.78)-1.77]	(0.09-0.26)	(0.22-0.37)	(0.34-0.47)	(0.40-0.51)	(0.39-0.49)
24	0.09	0.09	0.47	0.53	0.59	0.66	0.78
	[(-0.31)-0.50]	[(-0.31)-0.49]	(0.43-0.52)	(0.42-0.64)	(0.47-0.70)	(0.58-0.74)	(0.73-0.82)
48	0.48	0.50	0.83	0.72	0.74	0.77	0.85
	[(-0.09)-1.05]	[(-0.75)-1.76]	(0.71-0.96)	(0.63-0.81)	(0.73-0.75)	(0.73-0.81)	(0.82-0.89)
72	0.44	0.73	0.56	0.81	1.00	0.98	0.95
	[(-0.08)-0.96]	[(-0.12)-1.59]	(0.35-0.82)	(0.71-0.91)	(0.91-1.09)	(0.95-1.02)	(0.89-1.01)
96	0.70	0.29	0.58	0.96	1.08	0.95	1.00
	[(-0.08)-1.48]	[(-0.40)-0.99]	(0.48-0.68)	(0.91-1.02)	(1.06-1.09)	(0.93-0.96)	(0.98-1.03)
120	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	(0.47-1.57)	[(-0.83)-2.83]	(0.90-1.10)	(0.92-1.08)	(0.93-1.06)	(0.95-1.05)	(0.98-1.02)

[†] Percentage of organic surfactant added pertains to the percentage of the surfactant 6-piperazin-1-yl-*N,N'*-bis-(1,1,3,3-tetramethyl-butyl)-1,3,5-triazine-2,4-diamine in organoclay composites created with pretreated Gonzales clay and the surfactant. The percentages are calculated on a total weight basis.

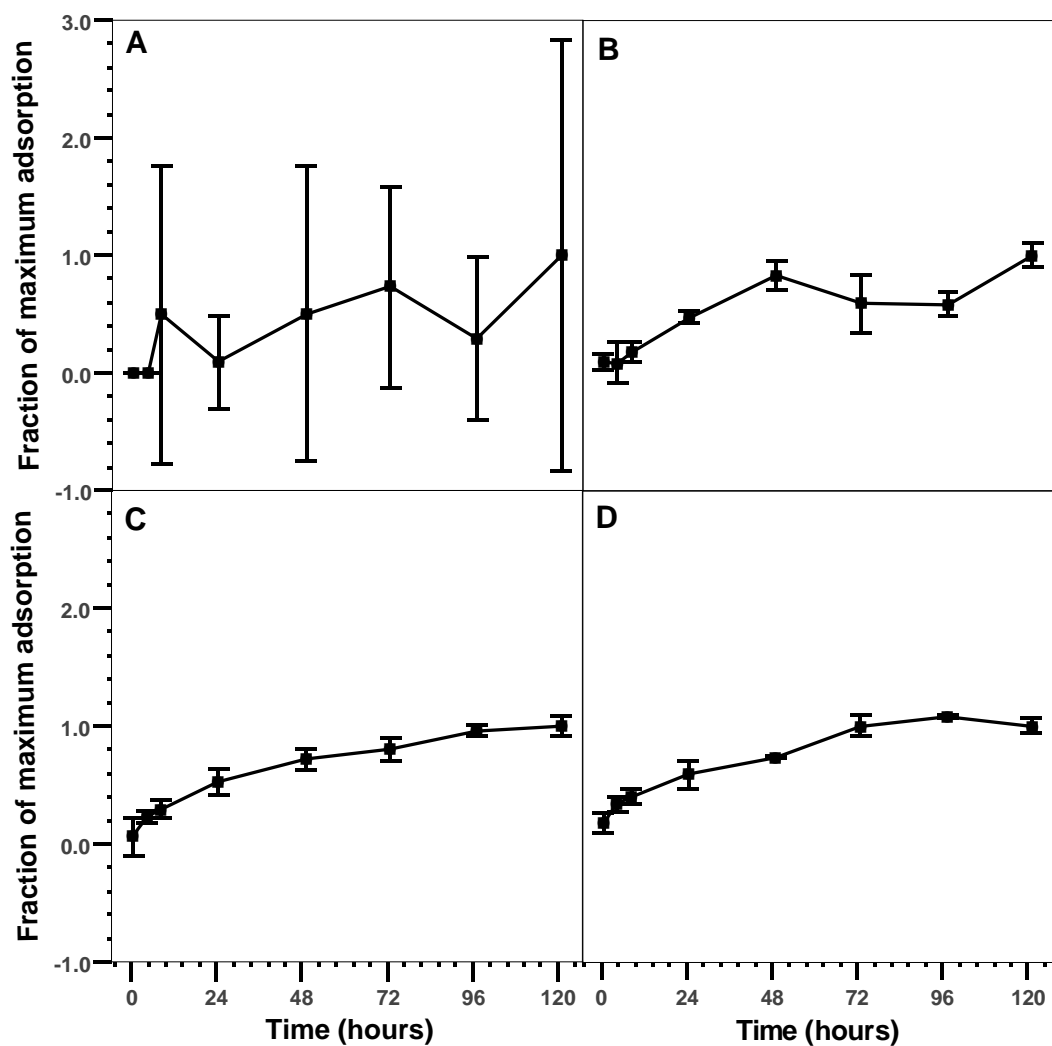**Fig. 9. Adsorption kinetics of atrazine, 2 mg L^{-1}, on 6 organoclay composites containing 0 (A), 2 (B), 5 (C), 12.5 (D), 25 (E), and 45% (F) surfactant on a total weight basis and Houston Black clay (G) plotted as fraction of maximum adsorbed. Each point is the mean of three replicates. The error bars represent the 95% confidence interval for the amount of atrazine sorbed by a given substrate.**
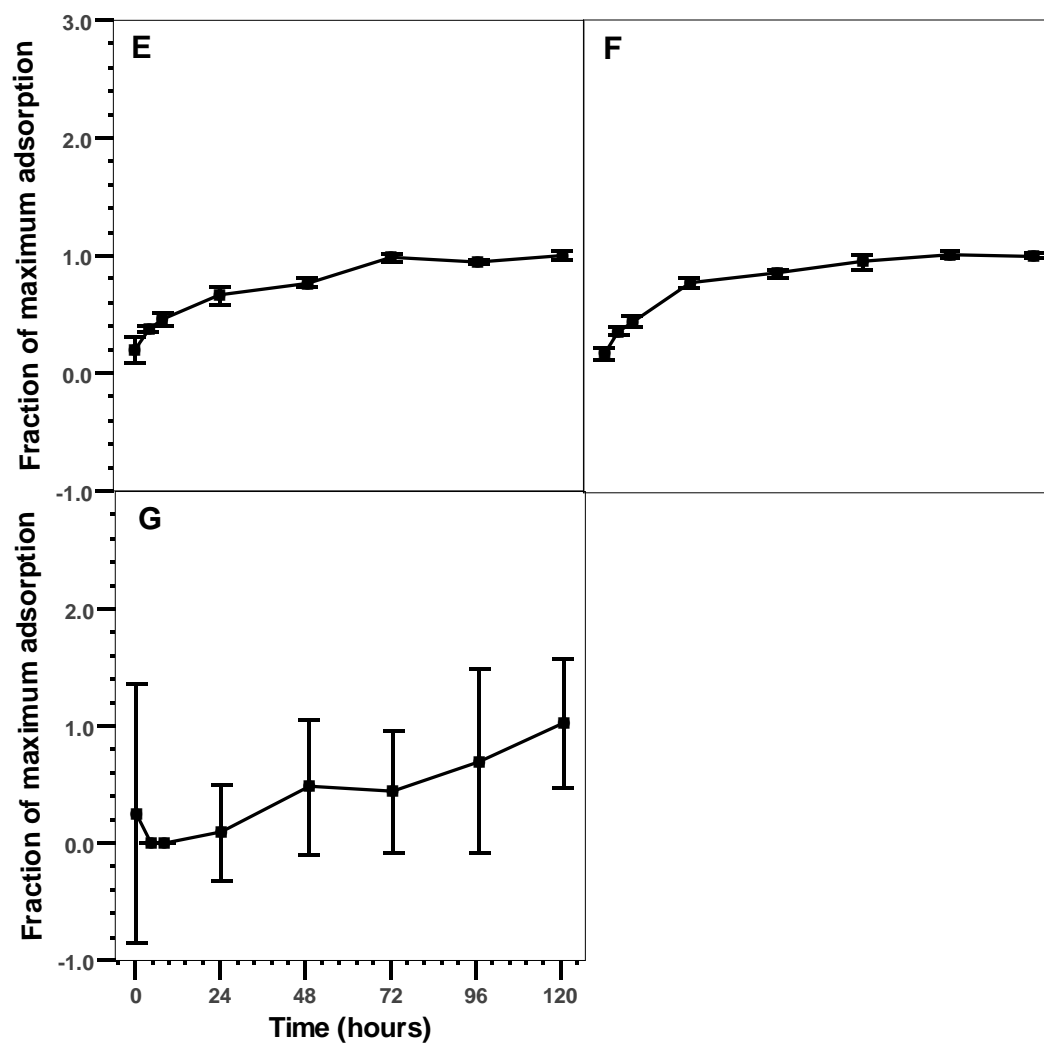
Fig. 9. Continued.

Adsorption Isotherms

The Freundlich isotherm represented atrazine adsorption by the organoclay composites (Table 4) with the correlation coefficients significant at the 0.05 level. Values for $1/n$ ranged from 0.8 to 1.17 with a decrease in value associated with an increase in percent surfactant. As $1/n$ decreases, the initial atrazine solution concentration has a more significant influence on the amount of atrazine adsorbed by the organoclay composite.

Although the isotherm slopes did vary slightly from one, they were close enough to permit use of a linear partitioning coefficient to describe atrazine adsorption by the organoclay composites (Fig. 10, Table 5). Correlation coefficients for the partition coefficient were significant at the 0.05 level.

Both partition and Freundlich distribution coefficients increased as the fraction of surfactant increased (Tables 4 and 5). When the coefficient values are adjusted for organic carbon content, values increase to a maximum value for the 20% organoclay composite then decrease for organoclay composites containing more that 20% surfactant (Fig. 11). This indicates that the organoclay composites become less efficient adsorbing atrazine at surfactant percentages greater than 20%.
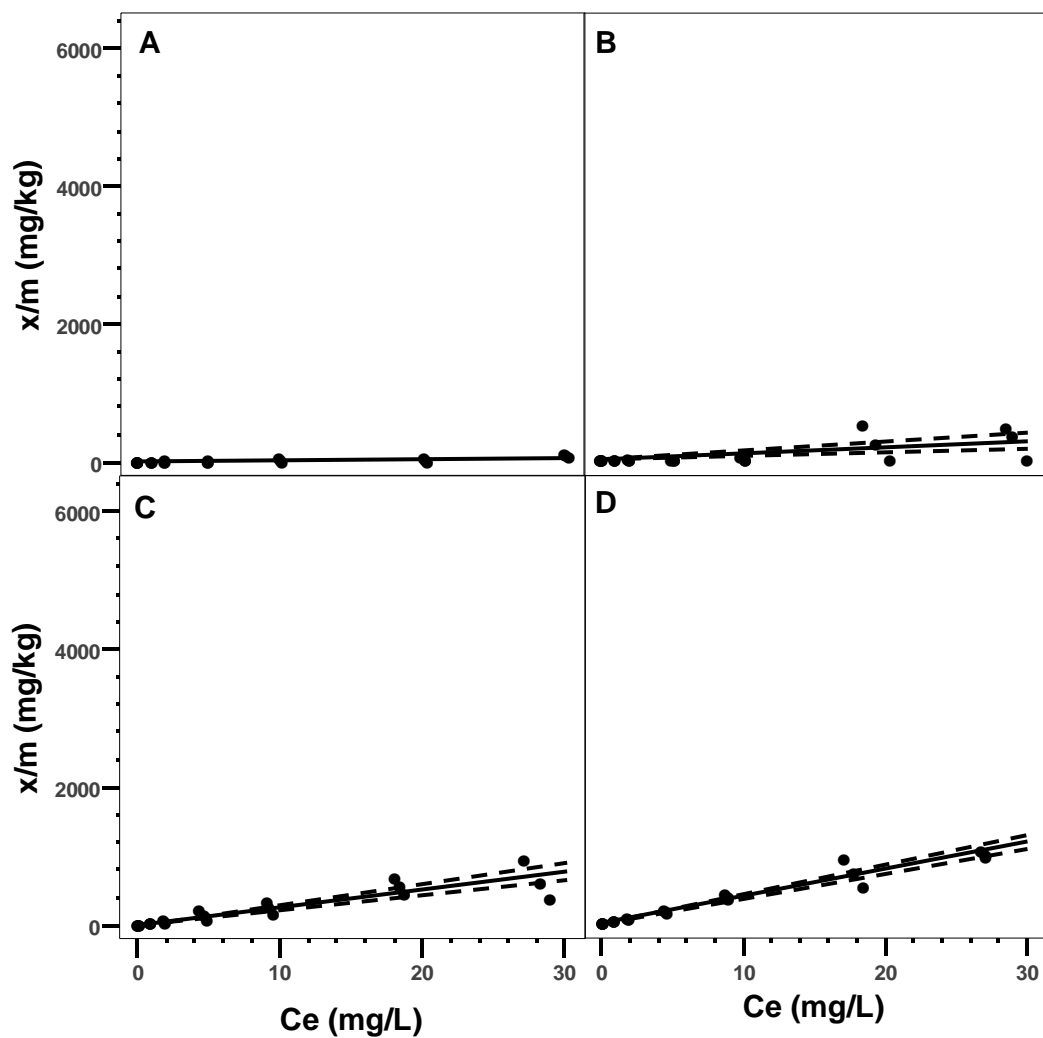
Fig. 10. Adsorption isotherms of atrazine on Houston Black clay (A) and 19 organoclay composites containing 0 (B), 1 (C), 2 (D), 3 (E), 4(F), 5 (G), 7.5 (H), 10 (I), 12.5 (J), 15 (K), 17.5 (L), 20 (M), 22.5 (N), 25 (O), 30 (P), 35 (Q), 40 (R), 45 (S) and 50% (T) surfactant on a total weight basis. The center line is the amount of atrazine sorbed calculated according to the Freundlich equation. The two dashed lines represent the 95% CI.

Fig. 10. Continued.

Fig. 10. Continued.

Fig. 10. Continued.

Fig. 10. Continued.

Table 4. Freundlich coefficients (K_f, $1/n$)

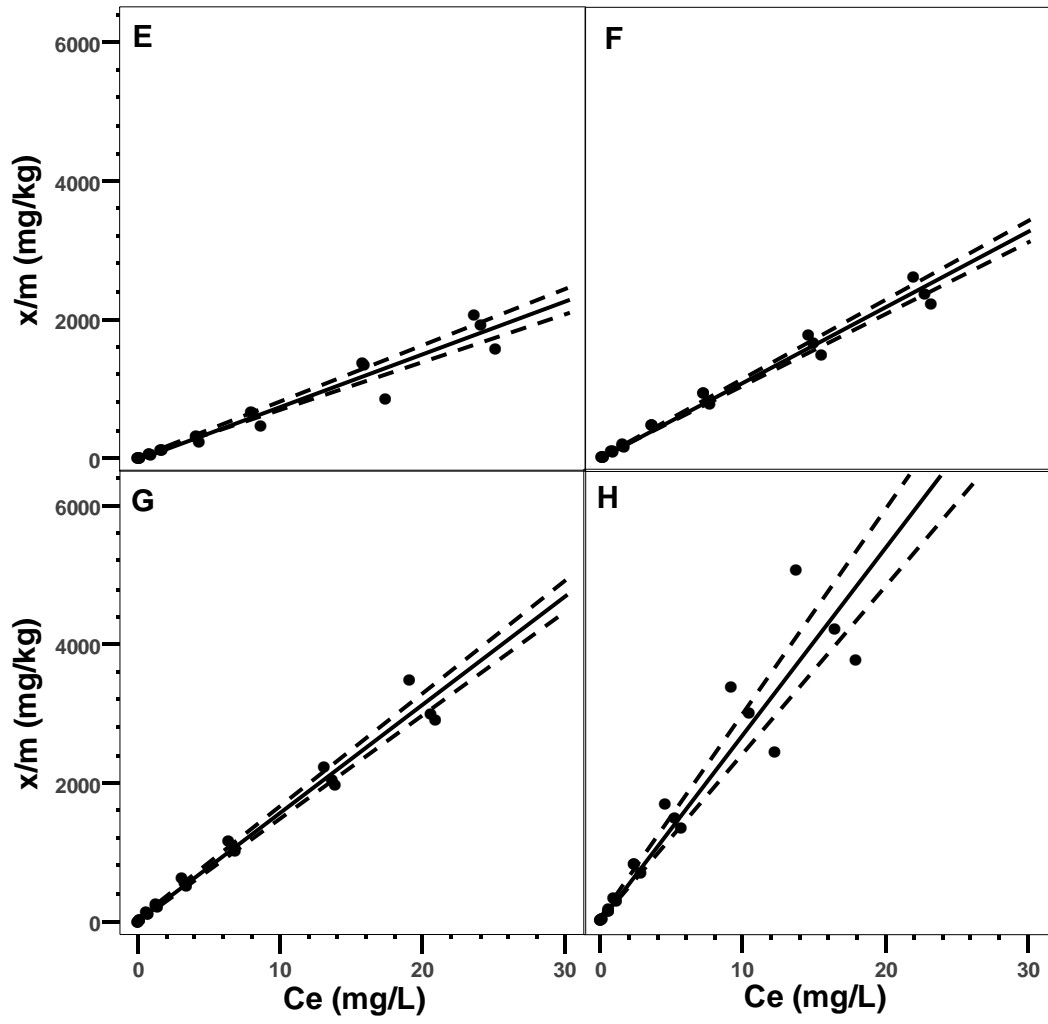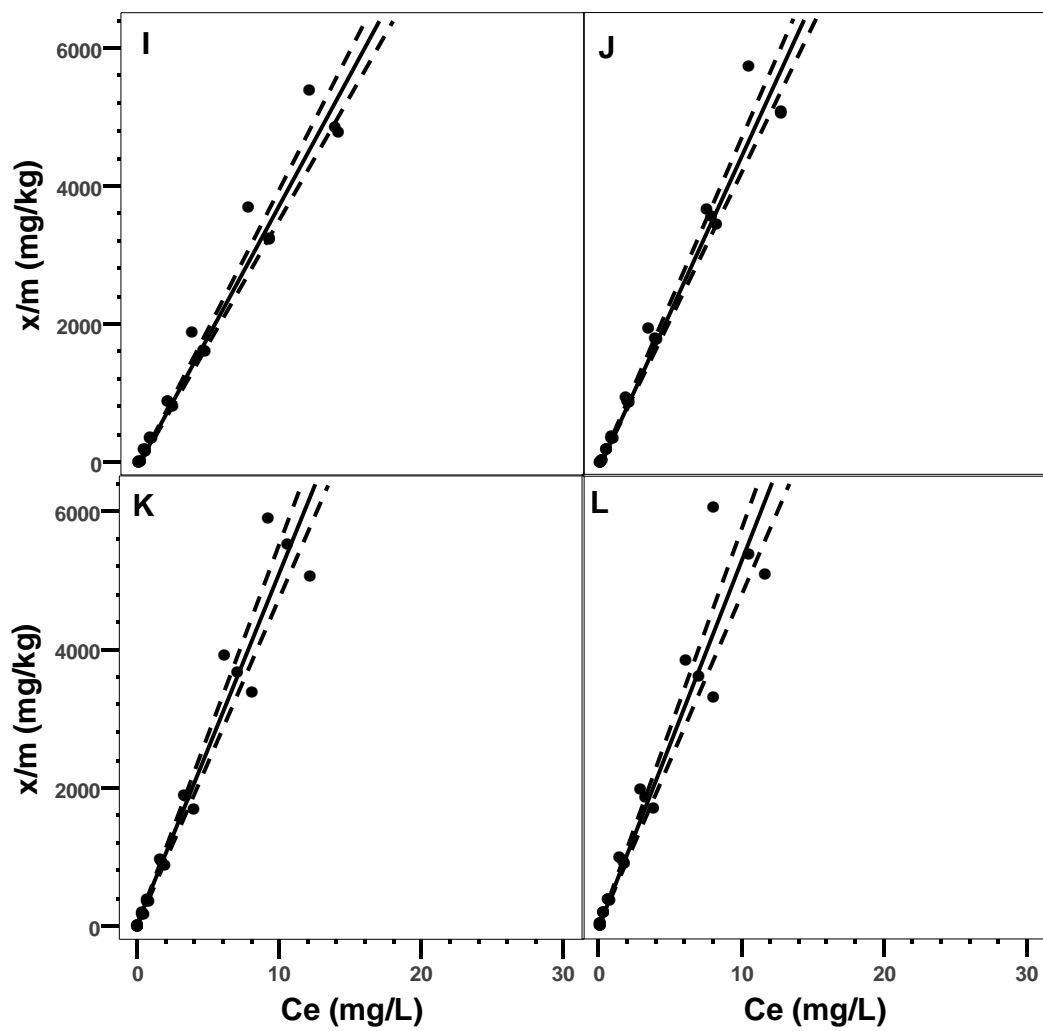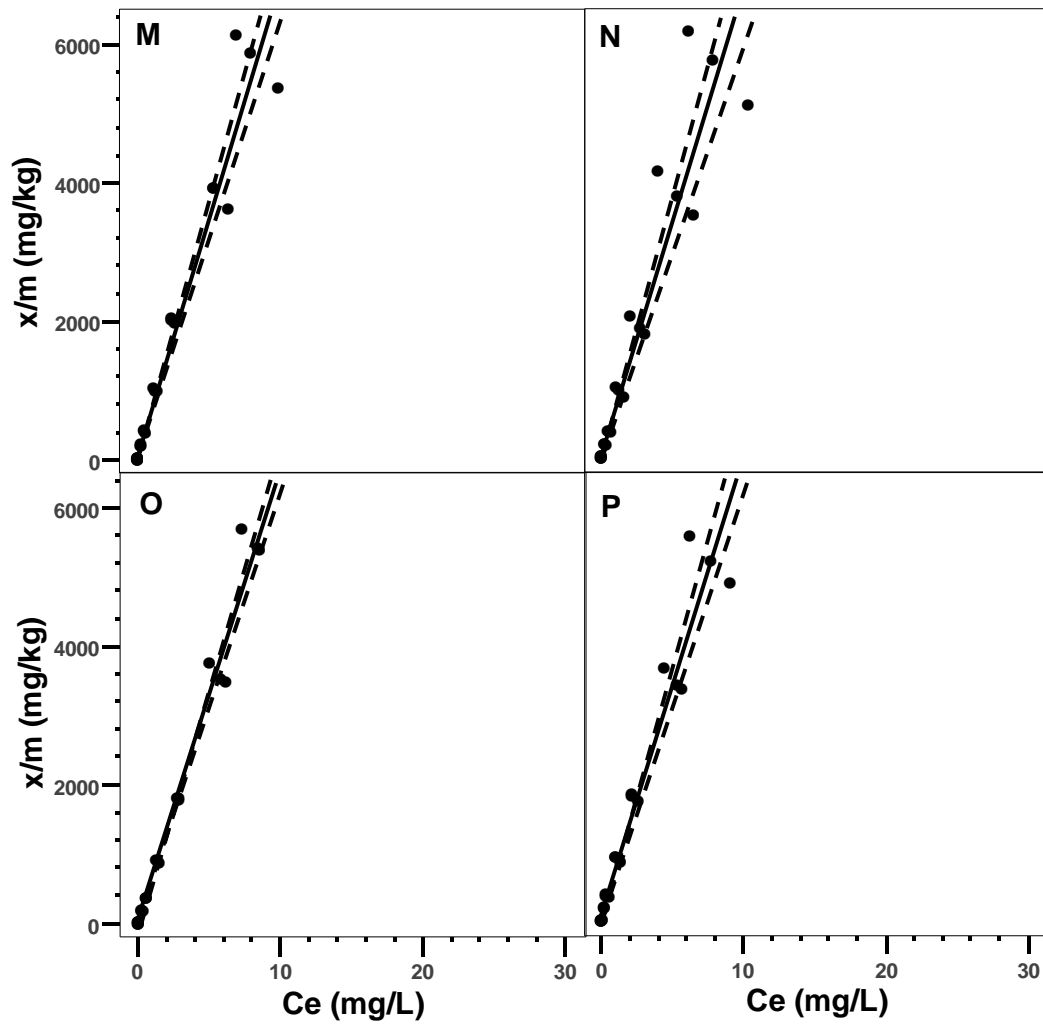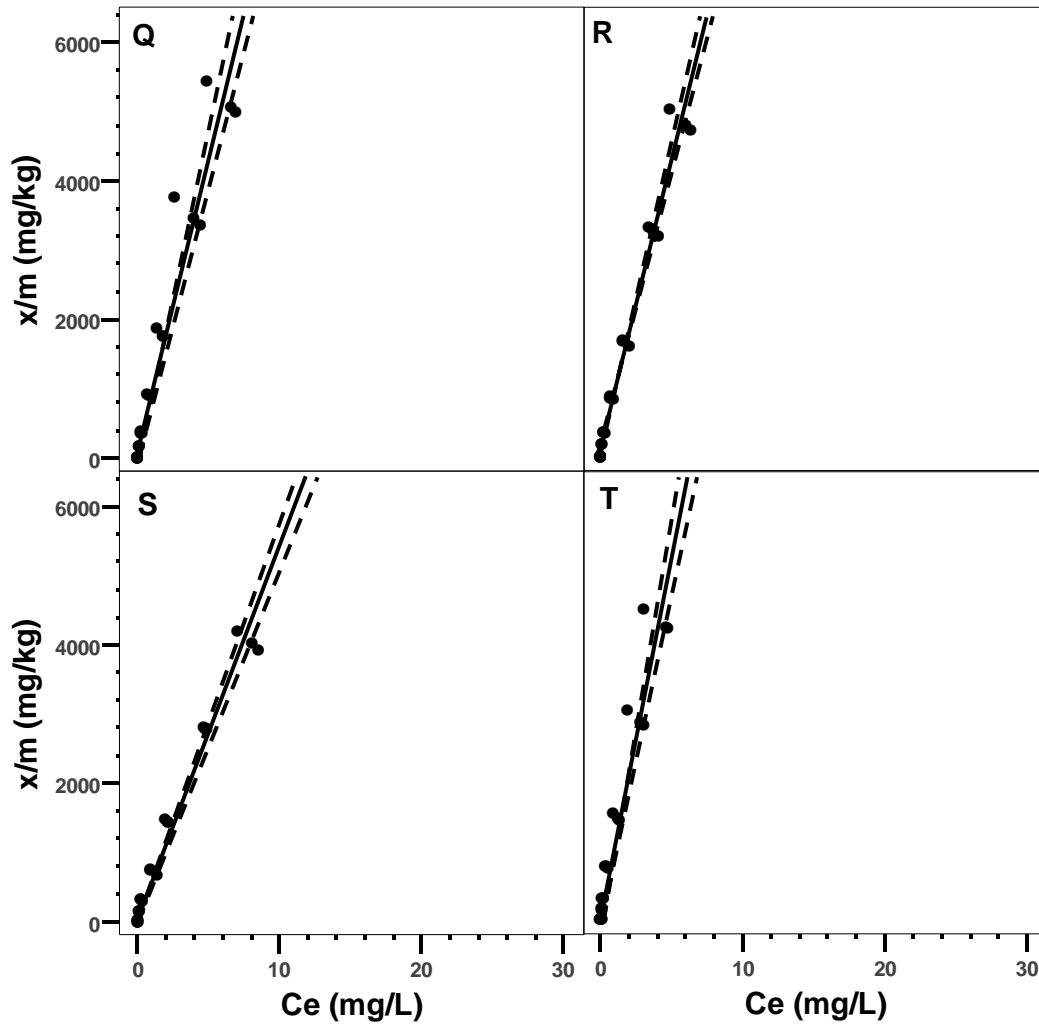| Adsorbent	K_f (L kg^{-1})[†]	$1/n$	r^2	K_{foc} (L kg^{-1})
Houston Black clay	1.92 (1.09-3.37)	0.999	0.801	35 (20-61)
0% organic[‡]	5.97 (3.53-10.1)	1.176	0.937	1421 (840-2405)
1% organic	27.0 (22.9-31.9)	0.942	0.978	660 (560-780)
2% organic	42.8 (38.7-47.4)	0.934	0.991	1186 (1072-1313)
3% organic	72.3 (67.0-77.9)	0.993	0.996	1429 (1324-1540)
4% organic	119 (111-128)	0.971	0.996	2099 (1958-2257)
5% organic	174 (164-182)	0.967	0.997	3671 (3460-3840)
7.5% organic	291 (267-317)	0.984	0.994	4242 (3892-4621)
10% organic	411 (387-437)	0.976	0.997	5099 (4801-5422)
12.5% organic	484 (462-507)	0.959	0.998	5390 (5145-5646)
15% organic	559 (524-598)	0.949	0.997	5344 (5010-5717)
17.5% organic	576 (536-618)	0.950	0.996	5766 (5365-6186)
20% organic	813 (751-881)	0.947	0.996	6235 (5759-6756)
22.5% organic	779 (710-856)	0.934	0.994	5474 (4989-6015)
25% organic	699 (655-748)	0.914	0.997	4036 (3782-4319)
30% organic	864 (789-946)	0.874	0.994	4584 (4186-5019)
35% organic	1162 (1068-1264)	0.841	0.996	5162 (4745-5615)
40% organic	1180 (1046-1130)	0.840	0.991	4392 (3893-4205)
45% organic	809 (749-873)	0.803	0.996	2514 (2328-2713)
50% organic	1519 (1337-1727)	0.853	0.991	4544 (3999-5166)

[†] Numbers in parenthesis are the 95% confidence interval (CI) for K_f; the antilogs log K_f-CI log K_f and log K_f+CI log K_f.
[‡] Percent organic refers to the percentage of the surfactant 6-piperazin-1-yl-N,N'-bis-(1,1,3,3-tetramethyl-butyl)-1,3,5-triazine-2,4-diamine in organoclay composites created with pretreated Gonzales clay and the surfactant. The percentages are calculated on a total weight basis

Table 5. Partition coefficients (K_d, K_{oc})

Solid	K_d (L kg^{-1})[†]	r^2	K_{oc} (L kg^{-1})[†]
Houston Black clay	2.27 (1.77-2.77)	0.796	41 (32-50)
0% organic[‡]	9.11 (5.42-12.80)	0.531	2169 (1290-3048)
1% organic	24.75 (20.91-28.59)	0.885	605 (511-699)
2% organic	38.33 (35.53-41.12)	0.972	1062 (984-1139)
3% organic	74.78 (69.07-80.49)	0.970	1478 (1365-1591)
4% organic	107.83 (102.72-112.94)	0.988	1902 (1812-1992)
5% organic	155.27 (147.79-162.66)	0.988	3276 (3118-3431)
7.5% organic	266.91 (239.29-294.53)	0.946	3891 (3488-4293)
10% organic	378.55 (356.97-400.13)	0.983	4697 (4429-4964)
12.5% organic	445.49 (420.24-470.74)	0.983	4961 (4680-5242)
15% organic	509.16 (471.11-547.21)	0.971	4868 (4504-5231)
17.5% organic	518.72 (470.94-566.50)	0.956	5192 (4714-5671)
20% organic	687.86 (632.91-742.80)	0.967	5271 (4850-5692)
22.5% organic	673.22 (590.98-755.47)	0.926	4731 (4153-5309)
25% organic	660.74 (631.03-690.44)	0.989	3817 (3645-3989)
30% organic	674.89 (618.64-731.15)	0.964	3580 (3282-3879)
35% organic	861.11 (778.41-943.82)	0.953	3825 (3458-4193)
40% organic	855.84 (803.21-908.48)	0.980	3185 (2989-3381)
45% organic	540.29 (507.80-572.78)	0.981	1679 (1578-1780)
50% organic	1049.44 (938.42-1160.46)	0.943	3139 (2807-3471)

[†] Numbers in parenthesis are the 95% confidence interval (CI).
[‡] Percent organic refers to the percentage of the surfactant 6-piperazin-1-yl-*N,N′*-bis-(1,1,3,3-tetramethyl-butyl)-1,3,5-triazine-2,4-diamine in organoclay composites created with pretreated Gonzales clay and the surfactant. The percentages are calculated on a total weight basis
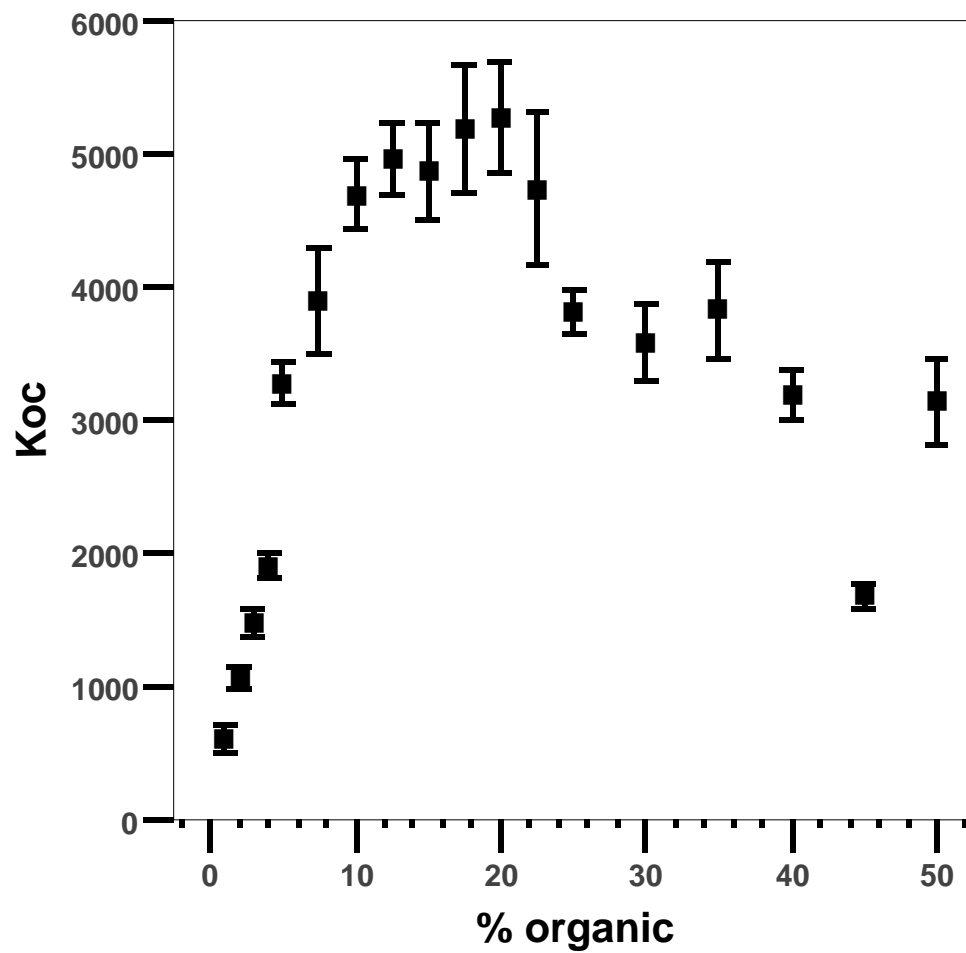
Fig. 11. *K$_{oc}$* **graphed as a function of percent organic for the organoclay composites.**

Adsorption of atrazine by the organoclay composites was significantly greater than that of the Houston Black clay. The difference in adsorption capability between the Houston Black clay and the organoclay composites became even more apparent when the partition and Freundlich distribution coefficients were adjusted for organic carbon content.

Desorption Kinetics

Desorption kinetics of the 0, 1, 5, 20, 35 and 50% organoclay composites and the Houston Black clay sample were measured over a 4-day period. Total amounts of atrazine desorbed from the solids for the 4-day period ranged from a high of 16.2% of sorbed atrazine for the 5% organoclay composite to 2% of sorbed atrazine for the Houston Black clay (Fig. 12 and Fig. 13). Percent of sorbed atrazine released during desorption averaged 10.7% for the organoclay composites. The lack of desorption implies that some covalent bonds were formed between the surfactant and atrazine, making atrazine sorption an irreversible process. Very small amounts of atrazine adsorbed to the Houston Black clay. Sorbed atrazine did not readily desorb from Houston Black clay.

Atrazine that desorbed from the organoclay composites did so primarily on the first day of the desorption study. By the third and fourth days, desorption of atrazine was less than 2.5% per day. Characterization of desorption products showed only atrazine molecules being released. Release of atrazine metabolites or surfactant molecules during desorption was negligible and not quantifiable.
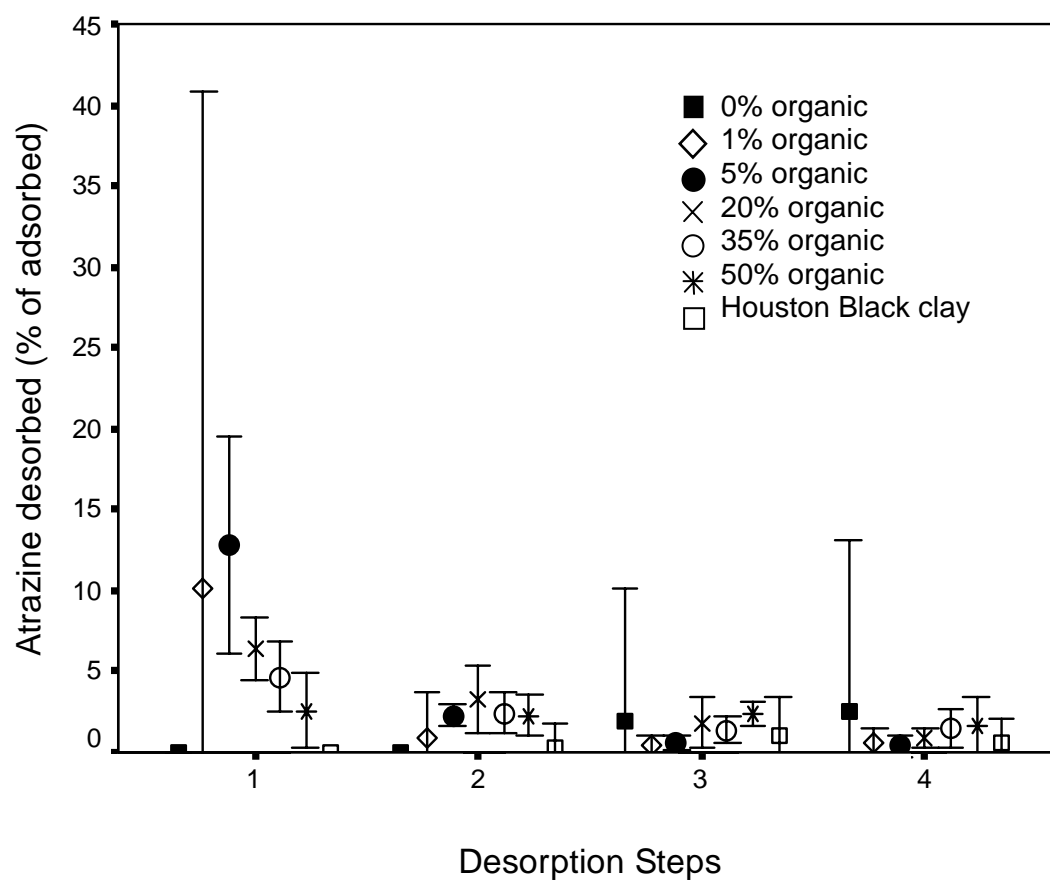
Fig. 12. Desorption as percent of initially adsorbed atrazine for 6 organoclay composites and Houston Black clay. Bars represent means of three replicates.

Fig. 13. Desorption of atrazine from 6 organoclay composites containing 0 (A), 1 (B), 5 (C), 20 (D), 35 (E), and 50% (F) surfactant on a total weight basis and Houston Black clay (G). Each point is the mean of three replicates. The error bars represent the 95% confidence interval for the amount of atrazine sorbed by a given substrate. Each desorption step was done 24 h apart.

Fig. 13. Continued.

CONCLUSIONS

This study shows that organoclay composites prepared with the surfactant 6-piperazin-1-yl-*N*,*N'*-bis-(1,1,3,3-tetramethyl-butyl)-(1,3,5) triazine-2,4-diamine are capable of adsorbing large amounts of atrazine from solution. Adsorption of atrazine by the organoclay composites was best described by linear partition isotherms.
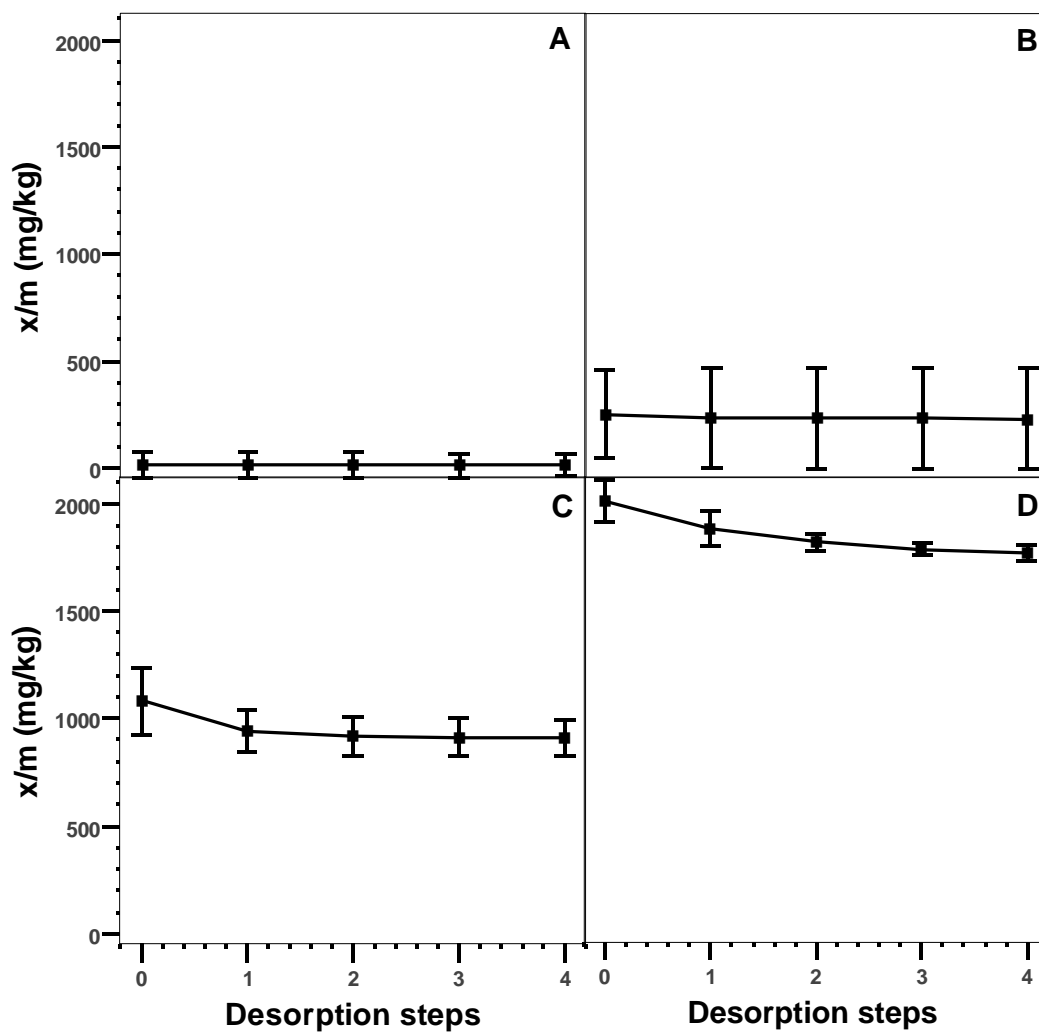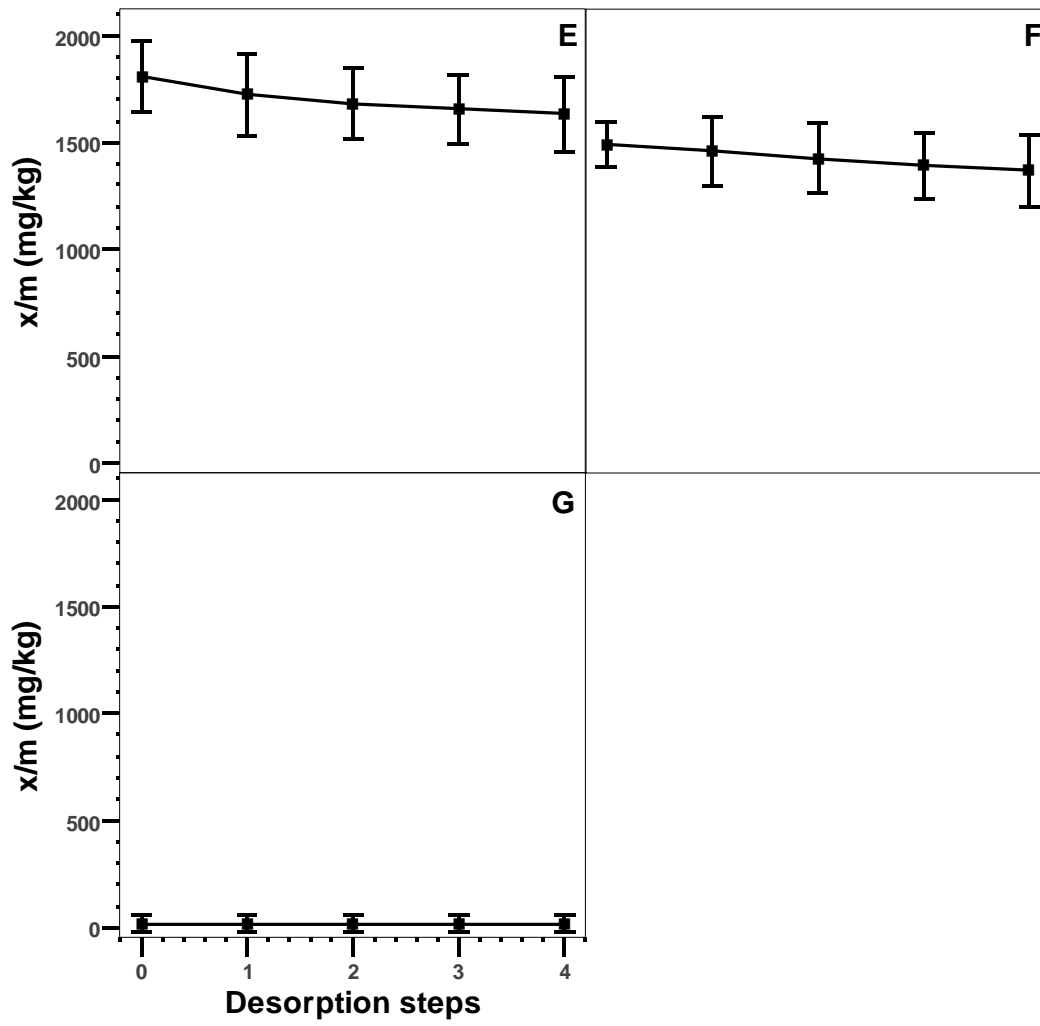
The organoclay composite containing 20% surfactant on a total weight basis provided the most efficient adsorption of atrazine, although organoclay composites containing much lower amounts of surfactant are also capable of adsorbing significant amounts of atrazine. For the 20% organoclay composite, the maximum atrazine loading observed was roughly 6,000 mg atrazine per kg organoclay composite in equilibrium with a solution containing 9 mg L^{-1} atrazine (Fig. 10). This translates to a sequestration of 60 mmol atrazine by 1 mol surfactant. In other words, seventeen molecules of the surfactant are needed to sequester one molecule of atrazine. However, it should be kept in mind that the number of surfactant molecules needed to sequester one molecule of atrazine varies with the atrazine solution concentration (Fig. 14). At lower equilibrium concentrations, more molecules of surfactant would be needed to hold a single molecule of atrazine.

Eleven percent of the total amount of atrazine adsorbed on the organoclay composites was released during desorption with the majority of the release occurring in the first two days of the desorption period. Characterization of desorption products showed only atrazine molecules being released from the organoclay composites.
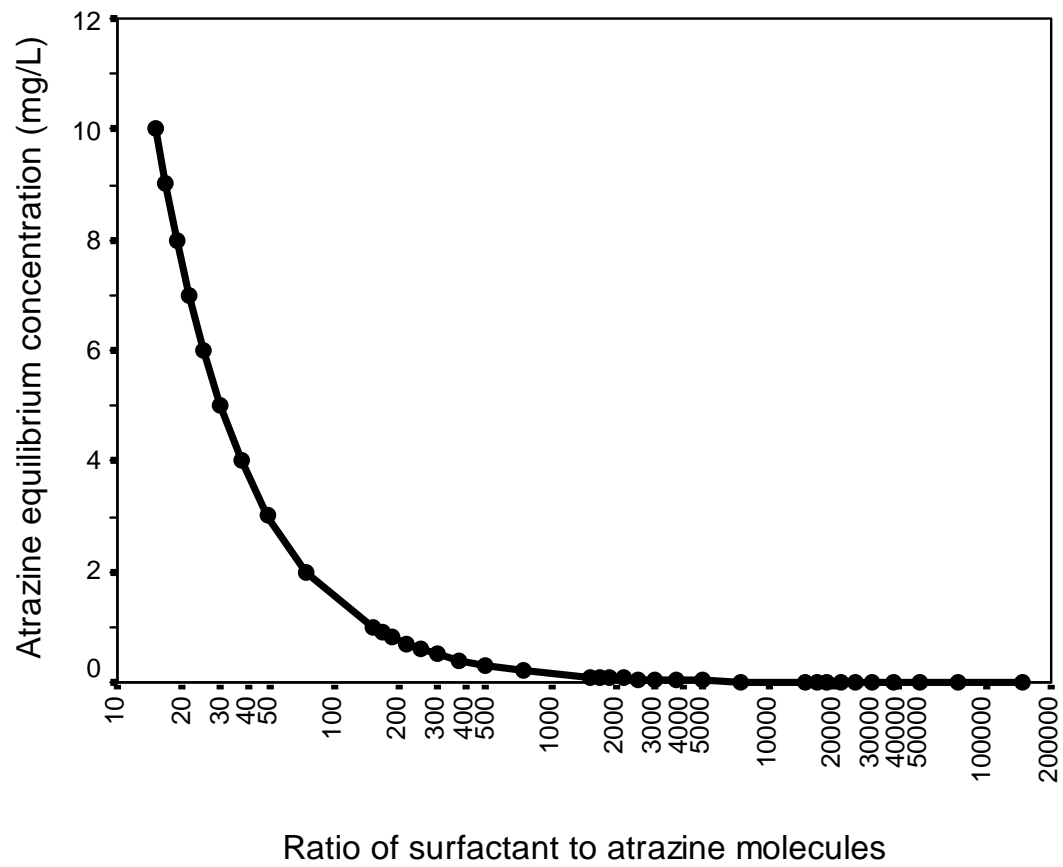
Fig. 14. Number of surfactant molecules required to sequester a molecule of atrazine at varying atrazine solution concentrations.

While the overall ability of the surfactant to sequester atrazine from solution is known, there are a number of issues which need to be addressed before this compound can be considered for use in environmental remediation efforts. Questions regarding practicality of the composites are among the most important of these issues. To estimate the atrazine removal efficiency, calculations can be performed using the mass balance equation of atrazine and the equation governing partitioning of atrazine between solution and organoclay composite.

The pesticide will partition between the organoclay composite and solution using the relationship

$$pst_{tot} = C_{solution} \cdot V_{solution} + C_{solid} \cdot M_{solid} \qquad [9]$$

where pst_{tot} is the total amount of pesticide (mg), $C_{solution}$ is the equilibrium concentration for the pesticide in solution (mg L^{-1}), $V_{solution}$ is the volume of solution (L), C_{solid} is the equilibrium concentration of pesticide on the solid (mg kg^{-1}), and M_{solid} is the mass of solid (kg). Using the partition coefficient, the equilibrium concentration of pesticide on the solid can be defined as

$$C_{solid} = K_d \cdot C_{solution} \qquad [10]$$

where K_d is the partition coefficient ((mg kg^{-1}) (mg L^{-1})$^{-1}$). Substituting equation 10 into equation 9 and rearranging to solve for the mass of the solid gives

$$M_{solid} = \frac{pst_{tot} - C_{solution} \cdot V_{solution}}{K_d \cdot C_{solution}} \qquad [11]$$

For example, assume there was 1 m^3 of water containing 15 mg L^{-1} atrazine which we wished to reduce to 1 mg L^{-1} atrazine. Given these conditions, 20 kg of 20% organoclay composite is required to reduce the solution concentration to 1 mg L^{-1} of atrazine. To reduce the solution concentration from 15 mg L^{-1} of atrazine to the drinking water standard (3 µg L^{-1}), 7,266 kg of 20% organoclay composite is needed. These are very large amounts of material and would seem to make use of the organoclay composite impractical. However, the composite does adsorb a large amount of atrazine and, if used just to reduce the atrazine load, its use may be more practical. The sequestration capacity of the organoclay composite is initially very high but drops off rapidly (Fig. 15).

To take advantage of the high sequestration capacity on "clean" organoclay composite material, one might incrementally clean the water. For example, instead of reducing the atrazine concentration from 15 mg L^{-1} to 3 µg L^{-1} in one step, assume the cubic meter of water was cleaned using 6 treatments. The first treatment required 0.73 kg of 20% organoclay composite to reduce the atrazine concentration from 15 mg L^{-1} to 10 mg L^{-1}. The second treatment required 1.45 kg of 20% organoclay composite to reduce the atrazine concentration from 10 mg L^{-1} to 5 mg L^{-1}. The third treatment required 5.81 kg of 20% organoclay composite to reduce the atrazine concentration from 5 mg L^{-1} to 1 mg L^{-1}. The fourth treatment required 13.08 kg of 20% organoclay composite to reduce the atrazine concentration from 1 mg L^{-1} to 100 µg L^{-1}. The fifth treatment required 13.08 kg of 20% organoclay composite to reduce the atrazine concentration from 100 µg L^{-1} to 10 µg L^{-1}. The final treatment required 3.39 kg of 20% organoclay composite to reduce the atrazine concentration from 10 µg L^{-1} to 3 µg L^{-1}. A total of 37.54 kg 20% organoclay composite was needed to reduce the atrazine concentration of 1 m^3 of water from 15 mg L^{-1} to 3 µg L^{-1} in 6 steps. This is much less than the 7,300 kg required to
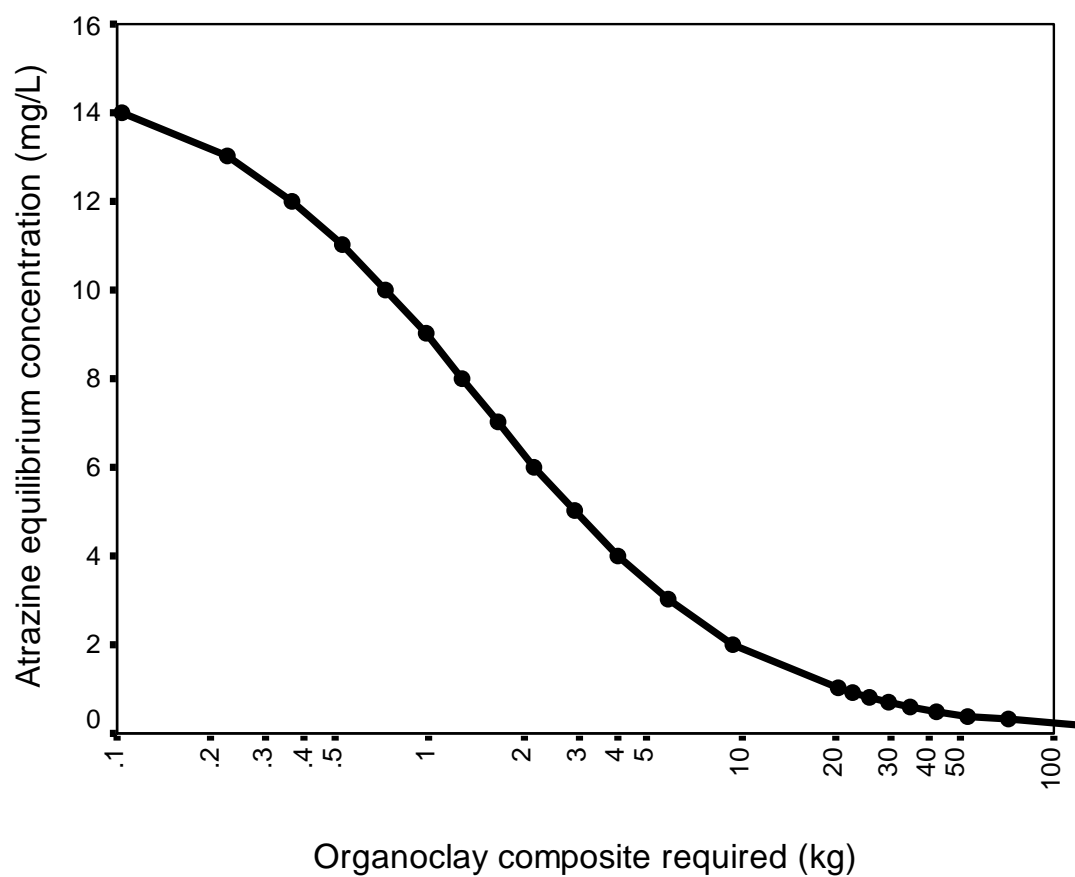
Fig. 15. Amount of 20% organoclay composite required to reduce the atrazine concentration in 1 m^3 of water from 15 mg L^{-1} to various equilibrium solution concentrations.

perform the remediation in 1 step. Smaller amounts of organoclay composite would be required if the remediation process was broken down further.

The large variation in the required amount of organoclay composite that results from changing the procedure from 1 to 6 steps is due to the difference in the adsorption potential of the organoclay composite in the different systems. As with water, whose movement in the soil is controlled by gradients in energy potential resulting from gravimetric, osmotic, and other forces, adsorption of atrazine by the organoclay composite is controlled by a gradient created between the solution and the solid. For a given solution concentration, the gradient governing atrazine adsorption will be greater for organoclay composite containing very little sorbed atrazine relative to that for organoclay composite containing a large amount of sorbed atrazine. For example, when organoclay composite is added to the cubic meter of water containing 15 mg L^{-1} atrazine, the composite will adsorb 5,000 mg of atrazine to reduce the solution concentration to 10 mg L^{-1}. In the one step process, that 5,000 mg remains in the system and serves to lower the adsorption gradient of the organoclay. To overcome the impact of the 5,000 mg atrazine on the adsorption potential, more organoclay material is required to adsorb additional atrazine from solution. In the six step process, once the 5,000 mg of atrazine is removed by the organoclay composite, the composite is removed and replaced by "clean" composite. In this scenario, the composite only has to adsorb atrazine from solution, not adsorb atrazine while retaining previously sorbed atrazine. The lower the concentration of atrazine in solution, the more sensitive the adsorption potential will be to the presence of sorbed atrazine on the organoclay composite.

In addition to the practicality of the surfactant, the stability of the surfactant in the soil environment must also be assessed. Due to the structural similarity between the surfactant and atrazine, there is a good possibility that the surfactant may be susceptible to the same

degradation mechanisms as atrazine. If the surfactant degrades in the soil environment, the

nature of the metabolites also need to be characterized.

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APPENDIX

Synthesis of the Surfactant

6-piperazin-1-yl-*N*,*N′*-bis-(1,1,3,3-tetramethyl-butyl)-(1,3,5) triazine-2,4-diamine
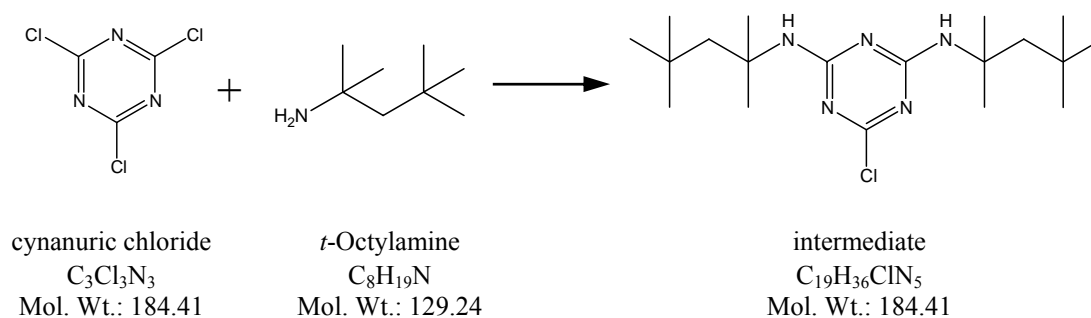
Synthesis of the surfactant (Acosta, 2003) is performed in two steps. The first step forms an intermediate compound consisting of the triazine ring with the two hydrophobic branches attached. The second step creates the surfactant by attaching the cationic anchor to the core.

Chemicals

The following chemicals and materials were used as received: cyanuric chloride (99% purity; Acros Organics, Geel, Belgium), *tert*-Octylamine (95% purity; Acros Organics, Geel, Belgium), and anhydrous piperazine (99% purity; Acros Organics, Geel, Belgium). Solvents tetrahydrofuran (99.5% purity; EM Sciences, Gibbstown, NJ), methanol (99.8% purity, EM Sciences, Gibbstown, NJ) and chloroform (99.8% purity; EM Sciences, Gibbstown, NJ) were used as received.

Procedure

The intermediate [6-chloro-*N*,*N'*-bis-(1,1,3,3-tetramethyl-butyl)-(1,3,5)triazine-2,4-diamine] is formed by reacting cyanuric chloride (trichlorotriazine) with *tert*-Octylamine [(1,1,3,3-tetramethyl-butyl) amine].

cynanuric chloride	*t*-Octylamine	intermediate
$C_3Cl_3N_3$	$C_8H_{19}N$	$C_{19}H_{36}ClN_5$
Mol. Wt.: 184.41	Mol. Wt.: 129.24	Mol. Wt.: 184.41

Cyanuric chloride (1.0015 g, 5.43 mmol) is dissolved in 20 mL of tetrahydrofuran (THF) in a 500 mL round-bottom flask. The flask is placed in an ice bath on a magnetic stirring plate and cooled to 0 °C. While the mixture is stirred continuously, *tert*-Octylamine (5 mL, 31 mmol) is added dropwise over 30 min. The removal of the first chloride ion from the triazine core and replacement with an octylamine is an exothermic reaction. The energy released from the reaction is controlled by adding the *tert*-Octylamine slowly and dissipated by keeping the flask in the ice bath. As this reaction proceeds, HCl is produced as a side product. Because amines are basic, the hydrochloric acid will react with the *tert*-Octylamine to produce a salt which precipitates out of solution as white crystals.
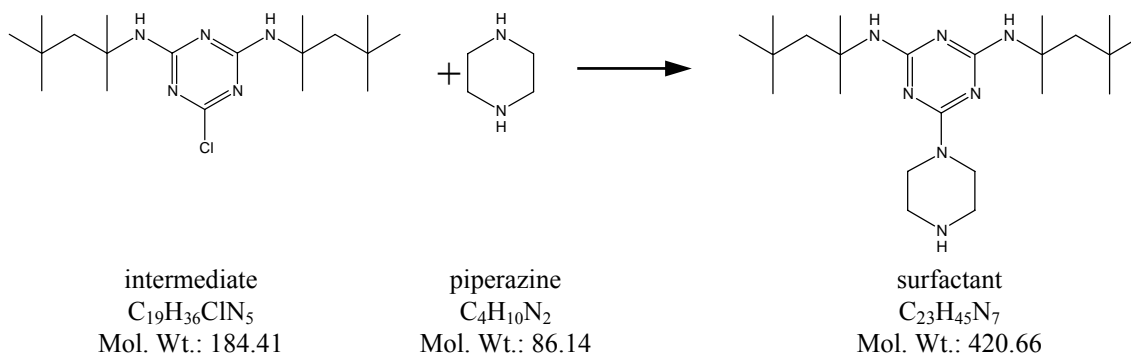
After the *tert*-Octylamine is added to the solution, the flask is removed from the ice bath, capped, and stirred at 25 °C (room temperature) for 24 h. During this period, the second chloride ion is removed from the triazine core and replaced with an octylamine. Replacement of the second Cl^- is less exothermic and the energy is dissipated without any special environmental controls. As with the first substitution, HCl is generated as a side product which subsequently reacts with *tert*-Octylamine to produce a salt.

The precipitate is separated from the solution by vacuum filtration with a Büchner funnel using No. 1 filter paper. The filtrate, which contains the intermediate and impurities dissolved in THF, is transferred from the filter flask to a round-bottom flask. The solvent is removed via vacuum distillation using a Büchi R-114 Rotovapor.

Once all the THF is removed, methanol is added to the flask. The impurities (excess *tert*-Octylamine and the salt) are highly soluble in methanol while the intermediate product is only slightly soluble. The flask is cooled in a refrigerator overnight to minimize the amount of intermediate dissolved. The intermediate (solid) is isolated by vacuum filtration with a Büchner funnel using No. 1 filter paper and dried in a vacuum desiccator overnight. A white powder is obtained (1.5852 g, 79% yield).

Identification of the intermediate was confirmed using thin-layer chromatography to compare the product with known intermediate and mass spectrometry analysis to confirm the molecular weight (ESI-MS: 370.27).

The surfactant is prepared by reacting the intermediate with piperazine.

intermediate	piperazine	surfactant
$C_{19}H_{36}ClN_5$	$C_4H_{10}N_2$	$C_{23}H_{45}N_7$
Mol. Wt.: 184.41	Mol. Wt.: 86.14	Mol. Wt.: 420.66

The intermediate (49.9 mg, 0.271 mmol) is dissolved in 25 mL THF in a 100 mL round-bottom flask. Anhydrous piperazine (338.1 mg, 3.925 mmol) is added to the flask. The flask is capped, placed on a magnetic stirrer, and stirred for 24 h at 25 °C (room temperature). The solvent is then removed via vacuum distillation using a rotovapor.

During this reaction, the chloride ion on the triazine core of the intermediate is replaced with a piperazine group. Hydrochloric acid is generated as a side product. Because amine

groups are present on both the piperazine and surfactant, hydrochloric acid can form salts with both compounds. The surfactant can also form dimers.

Column chromatography is used to separate the surfactant from the impurities with silica gel used as the adsorbent and 9:1 chloroform: methanol as the eluting solvent. Eluant is collected in vials. The vials are tested for the presence of the surfactant using thin-layer chromatography and ninhydrin tests. Eluant containing the pure surfactant is transferred to a 100 mL round-bottom flask and the solvent removed by vacuum distillation using a rotovapor. A white powder is produced (80 mg, 70% yield).

^{1}H NMR and ^{13}C NMR spectra recorded at 300 and 75 MHz respectively on a Varian spectrometer confirmed successful synthesis of the surfactant.

Preparation of Ca²⁺-saturated Smectite Clay

The clay used to prepare the organoclay composites was a Gonzales bentonite sample obtained from Southern Clay Products, Gonzales, Texas as a white powder. Preparation of the clay follows the procedure detailed in Deng (2001) which is summarized below. Pretreatment was performed to remove any particles greater than 2 μm in diameter and to saturate the clay surface with Ca^{2+} ions.

Removal of Carbonate

Twenty-five grams of the bentonite powder were placed in a 250 mL Nalgene centrifuge tube and mixed with 100 mL of 1 mol L^{-1} pH5 sodium acetate (NaOAc) solution. The mixture was heated to 90 °C in a water bath and occasionally stirred over a 1 h period. The mixture was then centrifuged at 2000 rev min^{-1} for 5 min and the supernatant decanted. Treatment with the NaOAc solution was repeated twice to ensure that all carbonate minerals were removed.

Size Fractionation

The sediment in the centrifuge tube was washed once with 1 mol L^{-1} NaCl solution followed by several washings with 1.42 mmol L^{-1} pH10 Na_2CO_3 solution to remove excess NaOAc and disperse the sample. The mixture was passed through a 325 mesh sieve to remove the sand fraction (>50 μm). The remaining clay and silt mixture was transferred to a 250 mL centrifuge tube and the height of the suspension brought to 10 cm by adding pH10 Na_2CO_3 solution. The clay (<2 μm) and silt(2-50 μm) fractions were separated by centrifuging at 750 rev min^{-1} for 3.2 min which causes the silt to deposit on the bottom of the centrifuge tube while the clay remains suspended in solution. The supernatant containing the clay was transferred to a 4-L

plastic beaker. After removing the supernatant, pH10 Na_2CO_3 solution was added to the centrifuge tube containing the silt fraction and the mixture shaken to resuspend the particles. The separation by centrifugation was repeated until the supernatant became clear.

Saturation with Calcium Ions

The clay suspension was centrifuged at 2000 rev min^{-1} for 5 min and the supernatant removed. The clay sediment was then mixed with 0.5 mol L^{-1} $CaCl_2$ solution and shaken for a minimum of 1 h. This was repeated 3 times to ensure that the clay was saturated with calcium ions.

The clay was then washed with distilled water and dialyzed against distilled H_2O until the electrical conductivity of the balance solution was < 5 μS. Once all excess salt had been removed, the clay was freeze dried, and ground to pass through a 140-mesh sieve.

Sample Characterization

Deng (2001) confirmed that the mineral composition of the clay fraction was smectite using X-Ray diffraction and Fourier-transform infrared. Cation exchange capacity for the smectite was 81.2 $cmol_c$ kg^{-1}, specific area was 786.6 m^2 g^{-1}, charge density was 1.03 $μmol_c$ m^{-2}, and the pH was 6.4 (Deng, 2001).

Impact of Tetrahydrofuran on Atrazine Sorption by Organoclays

Tetrahydrofuran was used as a solvent to dissolve the surfactant during the creation of the organoclay composites. Organic C and N characterization showed that some tetrahydrofuran sorbed to the clay. The purpose of this experiment is to assess the impact of tetrahydrofuran on atrazine sorption by the organoclays.

Sorption of tetrahydrofuran on the clay was significant for organoclay composites containing 5% or less surfactant. Consequently, the organoclay composites selected for this experiment contained smaller percentages of surfactant. Three organoclay composites containing 0%, 2% and 10% surfactant on a total weight basis were studied. Results for the 0% organoclay composite quantify the sorption capacity of tetrahydrofuran alone. The 2% organoclay composite is representative of those composites where both tetrahydrofuran and surfactant are present in significant quantities, while the 10% organoclay composite is representative of composites where tetrahydrofuran is present in trace amounts.

Organoclay Composite Preparation

Three organoclay composites were synthesized for this experiment containing 0%, 2%, and 10% surfactant on a total weight basis. Multiple batches were created for each organoclay composite using varying amounts of tetrahydrofuran.

The original organoclay composite preparation used 500 mg of clay, 20 mL of water, and surfactant dissolved in 5 mL of tetrahydrofuran. For the 2% and 10% organoclay composites, three different sets were created using the original ratio of water to tetrahydrofuran, half the original amount of tetrahydrofuran and double the original amount of tetrahydrofuran. For the 0% organoclay composite, these three sets were created as well as a set containing a

tenth the original amount of tetrahydrofuran and a set containing no tetrahydrofuran.

The organoclay composites were created by sorbing the surfactant to Ca^{2+}-saturated smectite clay. The clay used to prepare the organoclay composites was a Gonzales bentonite sample obtained from Southern Clay Products, Gonzales, Texas. The clay was pretreated following the procedure detailed in the appendix (p. 66).

For each set of 0% organoclay composite, 500 mg of clay was suspended in 20 mL of distilled water in a 50 mL polypropylene conical centrifuge tube. The following amounts of tetrahydrofuran were then added to different clay suspensions by pipette: 0 mL (none), 0.5 mL (tenth), 2.5 mL (half), 5 mL (reg), 10 mL (dbl). For each set of 2% and 10% organoclay composite, 250 mg of clay was suspended in 10 mL of distilled water in a 50 mL polypropylene conical centrifuge tube. The required amount of surfactant was then dissolve in the following amounts of tetrahydrofuran and added to different clay suspensions by pipette: 1.25 mL (half), 2.5 mL (reg), 5 mL (dbl). The suspensions were then shaken for 24 h at 25 °C. The resulting organoclay composites were centrifuged at $15,180 \times g$ for 10 min and the supernatant decanted. The composites were washed 3 times with distilled water to remove excess surfactants. This was done by adding 15 mL distilled water to the organoclay sediment, shaking until all the sediment was suspended, centrifuging at $15,180 \times g$ for 10 min, and then decanting the supernatant. The composites were then freeze dried and ground into a powder.

Adsorption Isotherm Experiment

To assess the impact of tetrahydrofuran on atrazine sorption, adsorption isotherm studies were carried out using a solution concentration of 10 mg L^{-1} atrazine containing labeled and unlabeled atrazine.

The experiments were carried out in 35-mL glass centrifuge tubes with Teflon lined

caps. To remove variation in atrazine adsorption due to sorption by the clay component, samples were weighed so that all vials had 15 mg of clay. The sample weights used for the different organoclay composites were: 0%, 15.0 mg; 2%, 15.3 mg; 10%, 16.7 mg. Triplicate 15 mg clay-equivalent samples were weighed into centrifuge tubes and pre-equilibrated for 24 h in 5 mL of 10 mmol L^{-1} (0.01 M) $CaCl_2$ solution.

The freeze-dried organoclays did not readily wet. To overcome this problem the samples were agitated twice. The first agitation was performed with the addition of the $CaCl_2$ solution, which was added in two portions. Two mL of $CaCl_2$ solution were added to a centrifuge tube, which was then capped and shaken on a vortex mixer for five seconds. After shaking, the remaining 3 mL of $CaCl_2$ solution were added. Within the last 3 h of the pre-equilibration period, the centrifuge tubes were shaken on a rotary shaker for 1 h.

Once the pre-equilibration period was over, 50 μL of 1000 mg L^{-1} atrazine solution was added to each centrifuge tube by pipette. The tubes were shaken for 3 d then centrifuged for 20 min at $622 \times g$.

The concentration of atrazine in the liquid phase was measured by liquid scintillation counting of 1 mL of the supernatant mixed with 10 mL of Ecolite liquid scintillation cocktail (ICN Biomedicals, Costa Mesa, CA) using a Beckman LS6500 multipurpose scintillation counter (Beckman Instruments, Inc., Fullerton, CA). The counting time was set to obtain a 2% precision on the dpm mean.

Centrifuge tubes containing no solid material were prepared in triplicate and processed alongside the sample centrifuge tubes. The concentration bound to the solid was calculated as the difference between the concentrations in solution of centrifuge tubes containing no solid material and of the samples with the solid. Background radioactivity was accounted for by processing centrifuge tubes with solid material to which 50 μL methanol was added in place of

the atrazine solution. Two scintillation vials were made for each centrifuge tube to account for

variability in pipette technique.

Mineralogical Analysis Using X-Ray Diffraction

X-ray diffraction was used to obtain the basal spacing for the organoclay composites.

The basal spacing of smectitic clays is affected by the nature of adsorbed ions and molecules and

XRD conditions must be carefully controlled. All samples were stored under the same

environmental conditions (in a dessicator) prior to analysis, making comparison between the

samples viable. Random powder mounts were prepared for the different composites and

analyzed on a Bruker D8 Advance diffractometer (Bruker AXS Inc., Karlsruhe, Germany).

Results

Adsorption isotherm experiments showed no sorption of atrazine by tetrahydrofuran and

no variation in atrazine adsorption of an organoclay composite due to differences in the amount

of tetrahydrofuran used during preparation of the organoclay composite (Fig. 16).

Basal spacings determined for the organoclay composites varied between 1.45 nm and

1.47 nm (Fig. 17). No significant change in basal spacing was observed relative to that of the

pure clay. This indicates that the surfactant and any tetrahydrofuran sorbing to the clay is doing

so on the clay surface rather than in the clay interlayer. As more surfactant is added to the

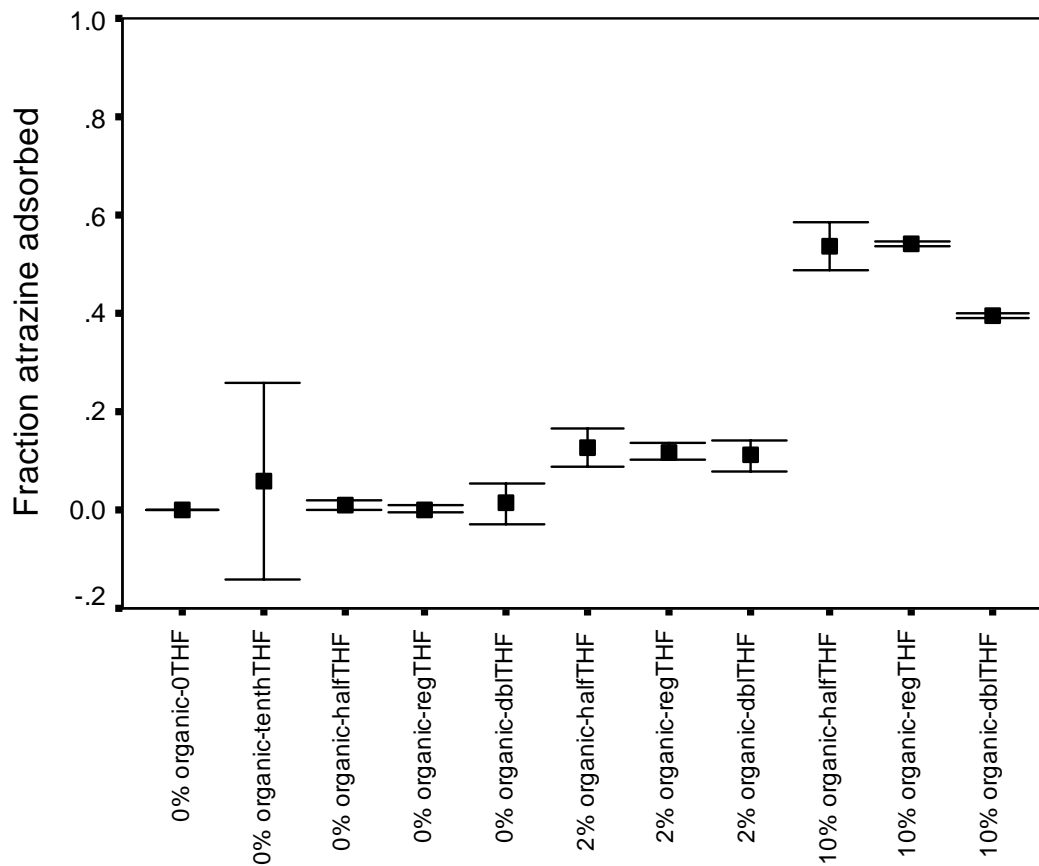sample, it forms additional layers around the clay particles.

Fig. 16. Adsorption of atrazine, 10 mg L^{-1}, on three organoclay composites containing varying amounts of tetrahydrofuran (THF). Each point is the mean of three replicates. The error bars represent the 95% confidence interval for the amount of atrazine sorbed by a given substrate.
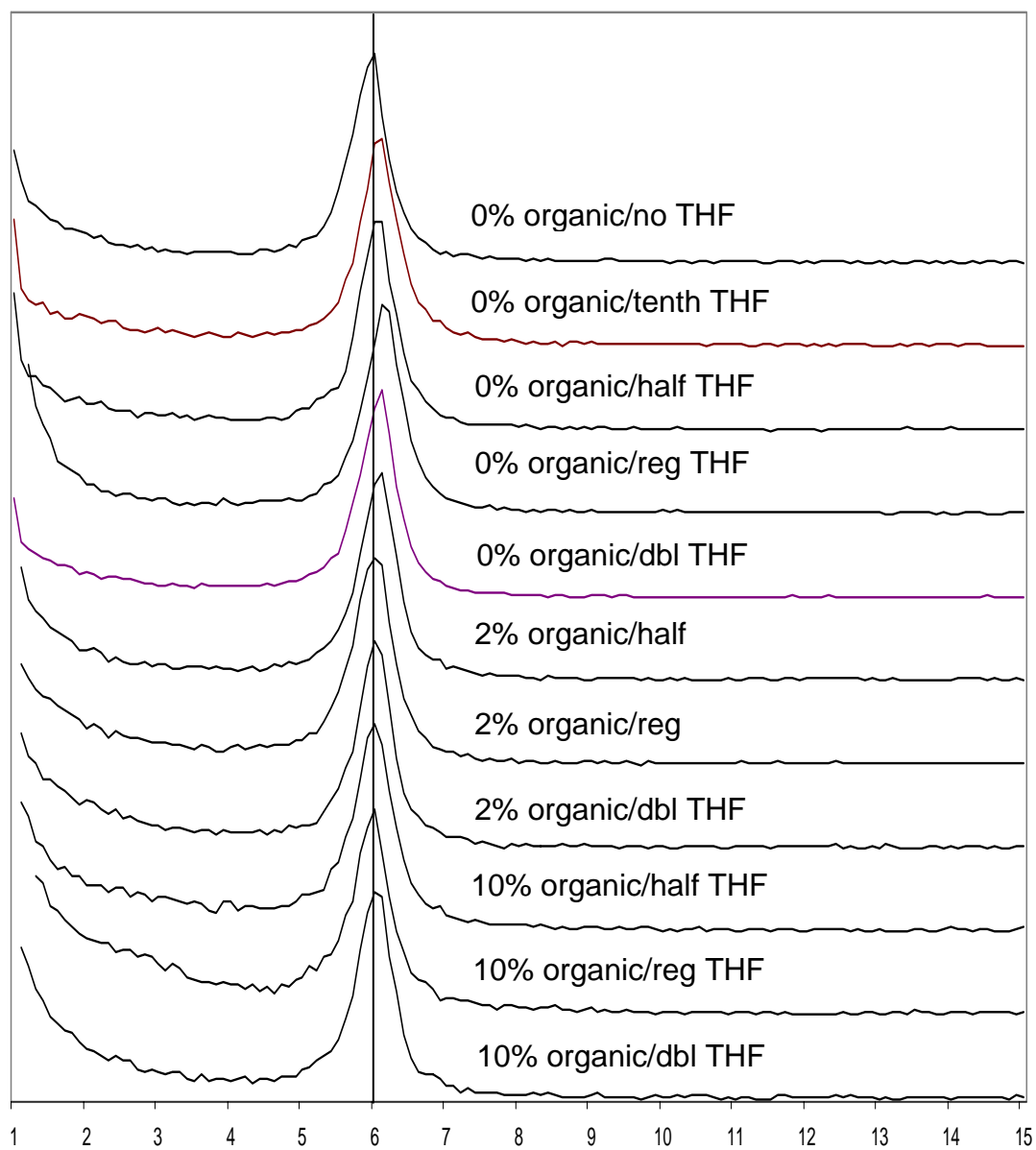
Fig. 17. XRD patterns of three organoclay composites containing varying amounts of tetrahydrofuran (THF).

VITA

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