

ADSORPTION COEFFICIENTS OF 2,4-DNT IN SOILS AND CLAY MINERALS

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ABSTRACT

Contamination of soil and water by explosives is widespread and often caused by various military activities. 2,4-DNT is commonly used as a military explosive. This explosive may enter to the environment from the processes in which it is made and used. Dinitrotoluenes (DNT's) are intermediates in the production of the explosive trinitrotoluene (TNT) and precursors in synthesis used in the manufacture of polyurethanes. Improper disposal practices associated with TNT manufacturing have resulted in contamination of the soils and water with dinitrotoluenes. In this study, samples of 2,4-DNT were allowed to interact with soil and clay samples to evaluate the adsorption behavior. The behavior of 2,4-DNT was evaluated in soil samples and clay fractions from the Ap and A horizon of the Jobos Series at Isabela, PR and from the University of Puerto Rico at Mayagüez, PR. The clay fraction was separated from the other soil components (sand and silt) by centrifugation.

High performance liquid chromatography (HPLC) was used to obtain adsorption coefficients (K_d values) for the interactions between 2,4-DNT-soil and 2,4-DNT-clay. The adsorption process for 2,4-DNT-soil and 2,4-DNT-clay were described by the Freundlich isotherm model. Values for the correlation factor (R^2) near one were obtained in the linear representation of the Freundlich model for the soil and clay samples. Ap horizon shows a greater maximum adsorption (11.87L/kg) than the others. The higher organic matter content of the Ap horizon (4%) may have contributed to the higher 2,4-DNT adsorption observed. In the case of the 2,4-DNT-clay interaction, the sample of the University of Puerto Rico at Mayagüez Campus showed a maximum adsorption (12.73L/kg). The higher adsorption on this clay fraction may be the result of a larger surface area (231.97m²/g).

RESUMEN

La contaminación del suelo y las aguas con explosivos es bastante amplia y es comúnmente causada por actividades militares. El 2,4-dinitrotolueno (2,4-DNT) es usado comúnmente como un explosivo militar. Este explosivo puede entrar al medio ambiente mediante los procesos en los cuales éste es fabricado y utilizado. Los dinitrotoluenos son intermediarios en la producción del trinitrotolueno y son precursores en la síntesis utilizada para la manufactura de poliuretanos. La eliminación inadecuada de desperdicios en la manufactura del TNT trae como resultado la contaminación de los suelos y agua con dinitrotoluenos. En este estudio, se evaluó el comportamiento de adsorción del 2,4-DNT interaccionando con muestras de suelos y arcillas. La adsorción fue evaluada en muestras de suelo y fracciones de arcilla de los horizontes A y Ap de la Serie Jobos de Isabela, PR y además de la Universidad de Puerto Rico en Mayaguez, PR. La fracción de arcilla fue separada de los otros componentes del suelo (arena y limo) por centrifugación.

Cromatografía líquida de alto desempeño (HPLC) fue utilizada para obtener los coeficientes de adsorción (valores de K_d) para las interacciones entre 2,4-DNT-suelo y 2,4-DNT-arcilla. El modelo de la isoterma de Freundlich fue el que mejor describió los procesos de adsorción entre ambas interacciones. Valores del coeficiente de correlación (R^2) cercanos a uno fueron obtenidos para este modelo de isoterma mostrando una tendencia lineal. El horizonte Ap mostró una mayor adsorción que los otros analizados (11.87L/kg). El alto contenido de materia orgánica del horizonte Ap (4%) pudo haber contribuido a la alta adsorción de 2,4-DNT observada. Para el caso de la interacción 2,4-DNT-arcilla, la muestra del Recinto de Mayagüez mostró una mayor adsorción (12.73L/kg). La alta adsorción en esta fracción de arcilla puede ser el resultado de una mayor área superficial (231.97L/kg).

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*To God, to my loved parents,
to my sister and my brother.*

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1. INTRODUCTION

When a landmine is buried in the ground, vapor emanating from the explosive begins to leak from the landmine into the soil. The fate of the explosives molecules, once released from the landmine, and the mechanism by which they are transported through the soil to the surface of the ground is a complex process¹. The movement of explosives molecules through soil, air, and water is influenced by the type of soil, as well as by environmental conditions, such as temperature and rainfall. There has been considerable interest in determining the fate and pathways of explosives molecules in soil and aquatic environments. When chemical explosive particles or vapor escape to the environment, they can interact chemically or physically with surfaces on their way. These interactions could lead to adsorption of the chemical explosive on soil mineral and organic components.

Dinitrotoluenes (DNT's) are nitroaromatic compounds, classified as chemical explosives, that have been detected in the soil, surface water, and groundwater near by sites that contains buried munitions wastes². DNT's are intermediates in the production of the explosive trinitrotoluene (TNT) and precursors in toluenediisocyanate synthesis used in the manufacture of polyurethanes. Dinitrotoluenes are formed by the sequential nitration of toluene and the 2,4-DNT and 2,6-DNT isomers typically occur in a 4:1 ratio. Improper disposal practices associated with TNT manufacturing have resulted in contamination of the soils and water with dinitrotoluenes. Both, 2,4-DNT and 2,6-DNT exhibit acute toxicity and low-level carcinogenicity and present an environmental health concern, whereas 2,4-DNT is listed as a U.S. EPA priority pollutant³.

Since soils usually have large surfaces areas; the probability for DNT sorption onto soil particles is vast. Sorption from aqueous solution to solid surfaces is one of the key

processes determining the distribution and fate of nitroaromatic compounds. To determine the fate and transport mechanisms of buried landmines it is essential to understand the adsorption process of 2,4-DNT on soil and clay minerals.

In this research, the adsorption behavior of 2,4-DNT was evaluated in soil and clay samples from Ap and A horizons from Jobos Series at Isabela, Puerto Rico and also a sample of the University of Puerto Rico at Mayagüez Campus. The clay samples were obtained from the same soil using the mechanical analysis method. High performance liquid chromatography (HPLC) was used to obtain adsorption coefficients (K_d values) for the interactions between 2,4-DNT-soil and 2,4-DNT-clay.

2. LITERATURE REVIEW

In the past years, researchers have dedicated great effort studying the behavior of nitroaromatic compounds on clay mineral surfaces. They developed adsorption methods in which they put in contact aqueous solutions of nitro-compounds, like DNT and TNT, with solid surfaces of clay minerals.

In 1993, Stefan B. Haderlein and René Schwarzenbach⁴ studied the sorption of a series of substituted nitrobenzenes and nitrophenols on homoionic kaolinite. These clay minerals have different surfaces sites that are representative of many minerals. Using adsorption experiments and the analysis of the equilibrium liquid-phase by reverse phase HPLC (High Performance Liquid Chromatography), they observed that the strength of adsorption depends on the structure of the compound and on the type of cation adsorbed on the siloxane surface of the clay.

In 1996, Stefan B. Haderlein, Kenneth W. Weismhr and René Schwarzenbach⁵ studied the adsorption behavior of neutral and ionizable nitroaromatic compounds such as 2,4,6-trinitrotoluenes (TNT), dinitrotoluenes and various aminonitrotoluenes on clay minerals, such as kaolinite, illite and montmorillonite. They found that the mobility of nitroaromatic compounds such as TNT may be controlled by manipulating the saturation degree of weakly hydrated cations present on clay surfaces.

In 2004, Paul B. Hatzinger, Mark E. Fuller, Darin Rungmakol, Rachel L. Schuster and Robert Steffan⁶ studied the adsorption and desorption isotherms for different explosives with a wide variety of natural and man-made adsorbents, including wheat straw, sawdust, peat moss, ground rubber tires, and clays. Among the various adsorbents tested, peat moss proved to be the most effective sorbent for the three explosives. The adsorption

coefficients (K_d^s) for TNT and RDX with peat (310 and 87 L/kg, respectively) were at least two orders of magnitude higher than that determined for adsorption of these energetic compounds with two different soil surfaces.

In 2006, Rosángela Rivera⁷ studied the TNT adsorption on Jobos soil and clay fractions. The adsorption behavior of TNT was evaluated in soil and clay samples from Jobos Ap and A horizons. High performance liquid chromatography (HPLC) was used to determine TNT adsorption. A higher adsorption was observed on the Ap horizon. The higher organic matter content of this horizon may have contributed to the higher TNT adsorption observed. The adsorption coefficient for the clay fraction of the A horizon was higher than the Ap horizon. The higher adsorption on the clay fraction of this horizon was attributed to the larger surface area.

In 2009, Xin Shi, Liangliang Ji, and Donggiang Zhu⁸ studied the roles of various soil components in sorption of organic compounds differing in polarity. Removal of whole soil organic matter decreased sorption by approximately 86% for nonpolar 1,3,5-trichlorobenzene (TCB), but only 34-54% for highly polar 1,3,5-trinitrobenzene (TNB). TNB exhibits several orders of magnitude stronger sorption compared with TCB, suggesting specific sorptive interactions for TNB with the individual model soil components. It was proposed that sorption of TCB to the bulk soil was dominated by hydrophobic partition to the condensed, non-extractable fraction of organic matter (humins/kerogen and black carbon), while interactions with soil clay minerals were an important additional factor for sorption of TNB. This finding implies that sorption of polar organic compounds such as nitroaromatics is soil specific and may involve various specific sorptive interactions whose types and intensities are dependent on the content and properties of both organic components and inorganic components. Thus, a comprehensive

model in consideration of contributions from both organic components and inorganic components is required to quantify sorption of these compounds to soil.

3. THEORY OVERVIEW

3.1 Clay Minerals

The main inorganic components of soil materials are minerals. A mineral is a natural inorganic solid that has an internal structure orderly and a definite chemical composition. It consists of a three-dimensional arrangement of atoms and/or ions that is repeated at regular intervals, which is called the crystal. These inorganic components present in the soil include primary and secondary minerals. The secondary minerals normally are found in the clay fraction (fraction with particle sizes $< 0.002\text{mm}$)⁹.

According to the Glossary of Soil Science Terms⁹, primary minerals are those that have not been altered chemically since their deposition or crystallization. Primary minerals identified in soils belong mainly to the classes of silicates, oxides of Fe, Zr, and Ti, and phosphates. Their study is essential because: a) they serve as sources of plant nutrients; b) they are, in certain cases, the precursors of secondary clay minerals; and c) they provide information about soil development. Silicates are the most abundant minerals found in soils. The building unit of the silicates is the silicon tetrahedron. Silicate structures may consist of single tetrahedral (nesosilicates), double tetrahedral (sorosilicates), rings (cyclosilicates), single or double chains (inosilicates), sheets (phyllosilicates), or framework patterns (tectosilicates).

Secondary minerals may be defined as recrystallized products of the chemical breakdown and/or alteration of primary minerals. Secondary minerals are generally characterized by smaller particle size, because the particle size of primary minerals is decreased during weathering and therefore, they are typically principal components of the clay fraction of the soils. Primary minerals including feldspar, pyroxenes, amphiboles,

micas and primary chlorite may be altered to secondary minerals such as illite, vermiculite, smectites, kaolinite, halloysite, and oxides of Fe and Al by the removal of silica and bases, and the addition of water. The most common oxides of Fe and Al, typically reported in soils are goethite, hematite, and gibbsite. These minerals sometimes referred to as sesquioxides, generally occur in soils subject to intense weathering, e.g. Oxisols and Ultisols⁹.

According to the arrangement of tetrahedral and octahedral sheets, clay minerals can be classified into two groups, 1:1 and 2:1 minerals. Kaolinite is one of the most common clay minerals in soils; this is a 1:1 aluminosilicate mineral composed of one octahedral sheet stacked above one tetrahedral sheet. The two crystal units comprising one kaolinite particle are held together by hydrogen bonds, and the space between the structural layers, therefore, has a fixed dimension.

In 2:1 minerals, an octahedral sheet is bonded to two tetrahedral sheets. The octahedral sheet is generally between the two tetrahedral sheets. This group of minerals is represented by the mica, smectite, and vermiculite groups. The 2:1 minerals provide more surface area and CEC than 1:1 minerals. Depending on the degree of charge due to isomorphous substitution, some of these clay minerals have the ability to expand their interlayer sites between two 2:1 layers (See Figure 3.1).

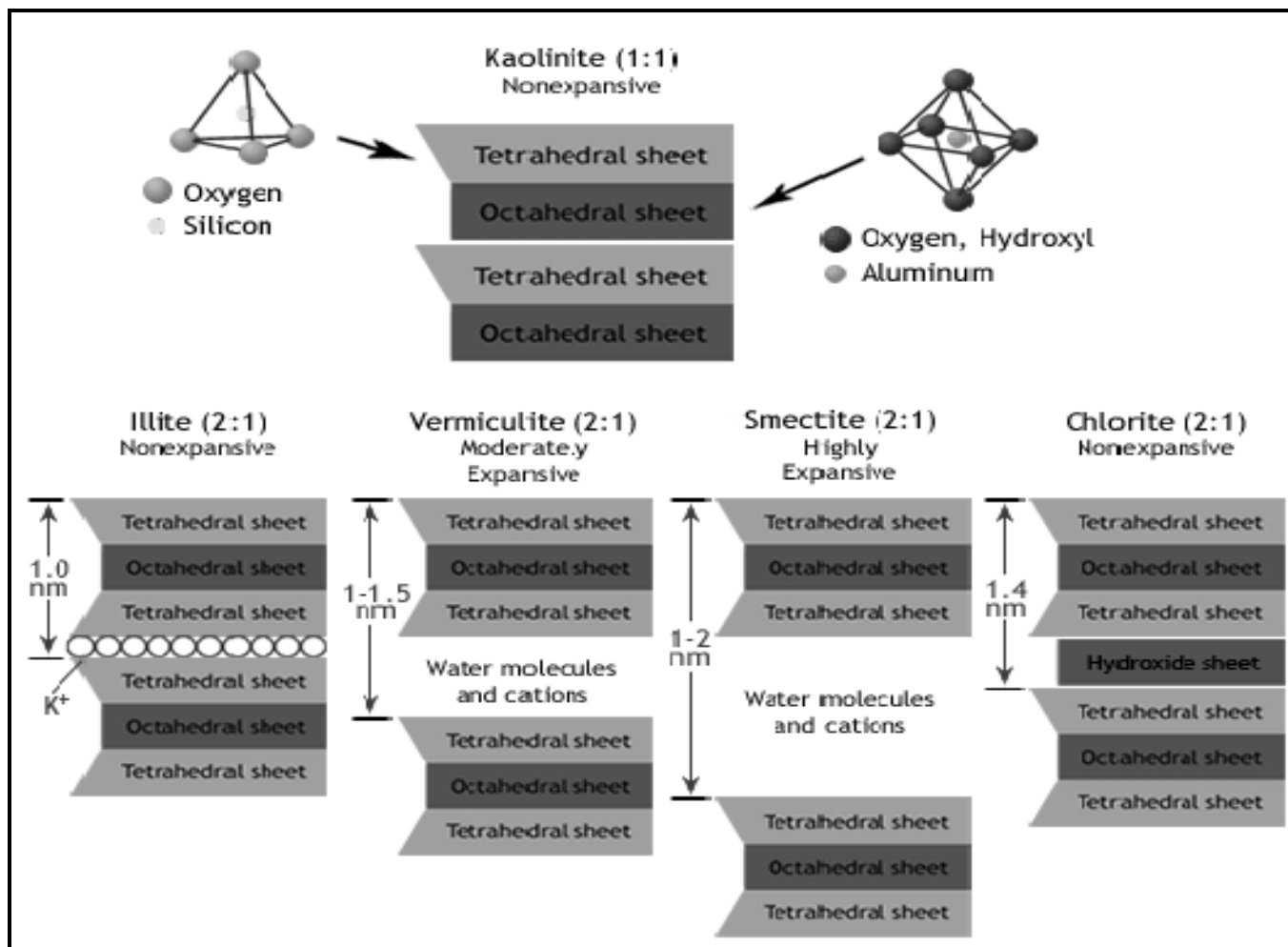


Figure 3.1 Examples of clay minerals with expanding and not expanding interlayer sites

Created by Josh Lory at www.soilsurvey.org (accessed in August 2009)

3.2 Chemical Explosives

An explosive is a material, either a pure single substance or a mixture of substances, which is capable of producing an explosion by its own energy released.¹⁰ A substance, or a mixture of substances, which is capable of undergoing a sudden transformation with the production of heat and gases.¹⁰ Explosives have been classified into high and low explosives, according to the type and velocity of the reaction involved. High explosives have been subdivided into two groups according to their function in the explosion: primary (or initiating) explosives, used to start the explosion (e.g. in blasting caps), and secondary explosives, used as the main charge. Explosives have also been classified according to their chemical structure. The most important class includes organic compounds which contain the nitro (NO₂) groups. They are subdivided according to the atom which the NO₂ group is attached. Nitro compounds contain a C-NO₂ group, nitrate esters a C-O-NO₂ group and nitramines a C-N-NO₂ group. Another classification, military versus industrial explosives, is based on the application for which an explosive is designed. In this research, the explosive studied 2,4-DNT have been classified as secondary, nitro compound and a military explosive.

3.2.1 2,4-Dinitrotoluene (DNT)

2,4-Dinitrotoluene is one of the six forms of the chemical called dinitrotoluenes (DNT's). They are pale yellow crystalline solids. It dissolves in water slightly but easily dissolves in organic solvents such as ether, acetone, benzene and toluene. DNT (Figure 3.2) has melting and boiling points at 71 °C and 300 °C, respectively (Table 3.1). Its crystal density is 1.3208 g/cm³ at 71 °C. There are no natural sources of DNT, which is usually manufactured by mixing toluene with nitric acid in the presence of concentrated sulfuric

acid. This reaction produces a mixture which consists of approximately 80% of the 2,4-isomer and 20% of the 2,6-isomer. Also produced are small quantities of other DNT isomers.

Small concentrations of DNT isomers also occur as by-products in the production of trinitrotoluene (TNT). There is some evidence that 2,4- and 2,6-DNT affect the nervous system and the blood of exposed workers. Both 2,4-DNT and 2,6-DNT cause liver cancer in animals and may be human carcinogens. DNT has been detected in the soil, surface water, and groundwater of hazardous waste sites that contain buried munitions wastes.

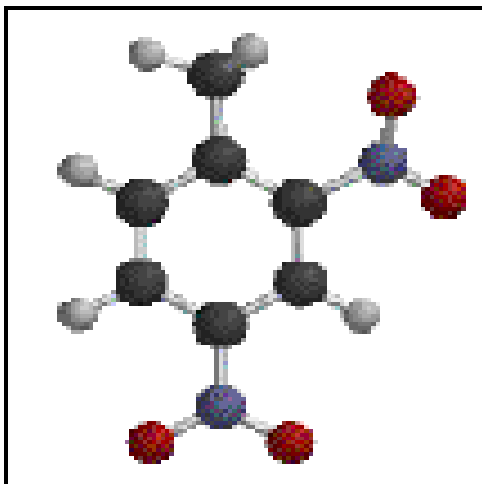


Figure 3.2 2,4-DNT (2,4-dinitrotoluene)

Table 3.1 Physical and chemical properties of 2,4-DNT

*From Reference 2

Physical and Chemical Properties of 2,4-dinitrotoluene (2,4-DNT)	
Molecular Weight	182.13 g/mol
Molecular Formula	$C_7H_6N_2O_4$
Density	1.521 g/cm^3
Solubility in water at 25°C	0.027g/100g
Melting Point	71°C
Boiling Point	300°C
Flash Point	155°C

3.3 Chromatography

The distribution equilibria involved in chromatography are described by relatively straightforward equations that involve the transfer of an analyte between the mobile and stationary phases. Thus, for the solute species A, we may write



The equilibrium constant K for this reaction is called the distribution constant, the partition ratio, or the partition coefficient, and is defined as

$$K = \frac{C_S}{C_M} \quad (3.2)$$

where C_S is the molar concentration of the solute in the stationary phase and C_M is its molar concentration in the mobile phase.

3.3.1 High Pressure Liquid Chromatography (HPLC)

High-performance liquid chromatography is the most widely used of all of the analytical separation techniques¹¹. The reasons for the popularity of the method are its sensitivity, its ready adaptability to accurate quantitative determinations, and its suitability for separating nonvolatile species or thermally fragile ones. HPLC uses high pressure to force solvent (mobile phase) through closed columns containing very fine particles that give high-resolution separations. The HPLC system in Figure 3.3 consists of a solvent reservoir, a high pressure column, a sample injection valve, a detector and a computer to control the system and display results. Many systems include an oven for temperature control of the column.

Eluent strength measures the ability of a given solvent to elute solutes from the column. The time at which a specific analyte elutes (comes out of the end of the column) is called the retention time and is considered a reasonably unique identifying characteristic of a given analyte.

Two types of partition chromatography are distinguishable based upon the relative polarities of the mobile and stationary phases¹¹. These two types are: normal phase and reversed phase. In normal-phase chromatography, the stationary phase is polar and a less polar solvent is used. Eluent strength increases as the polarity of the solvent increases. Reversed-phase chromatography employs a nonpolar stationary phase and polar solvent. Eluent strength increases as the polarity of the solvent decreases. Most separations of organic compounds can be done on reversed-phase chromatography.

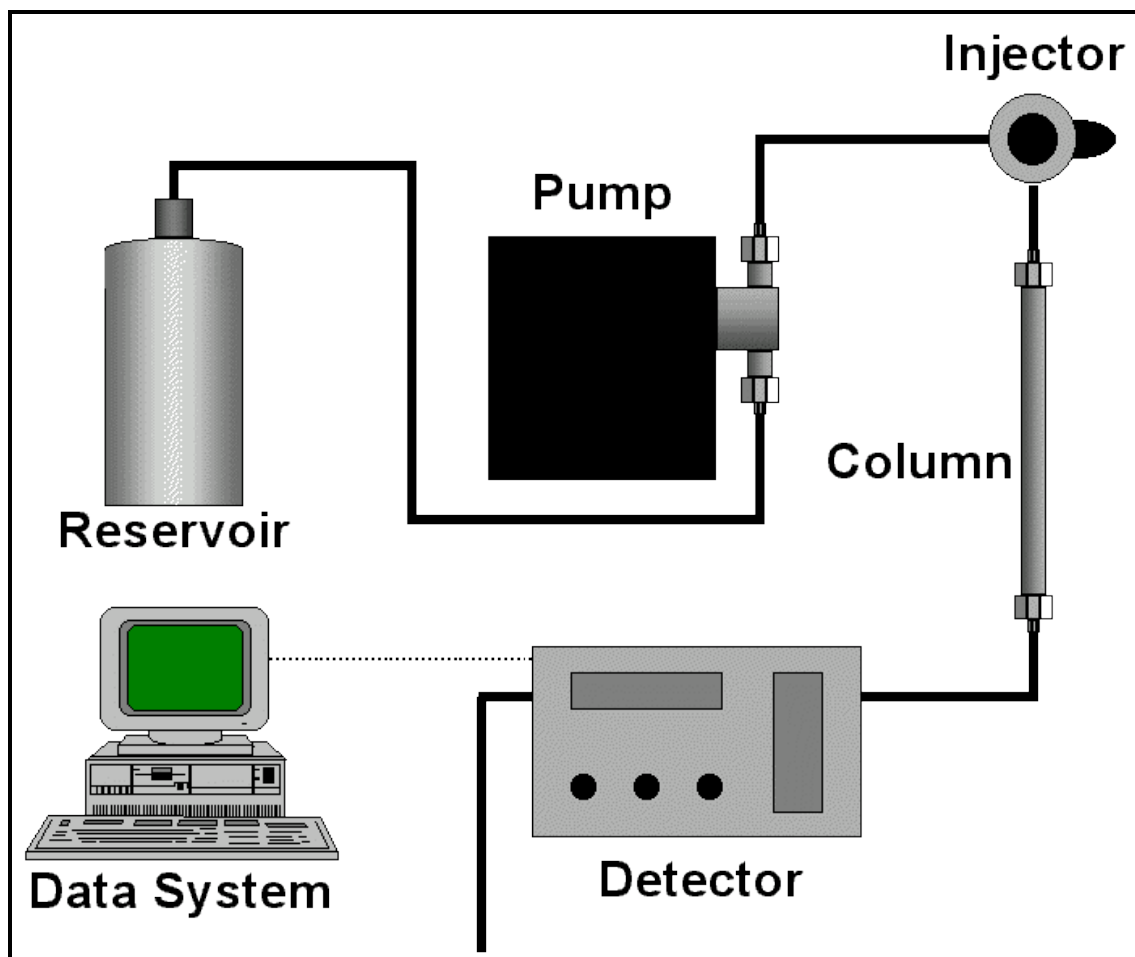


Figure 3.3 Schematic representation of an HPLC system

From: <http://www.lcresources.com> (Accessed in July 2009).

3.3.2 Variable Wavelength UV/VIS Detector (VWD)

An ideal detector of any type is sensitive to low concentrations of every analyte, provides linear response, and does not broaden the eluted peaks. It is also insensitive to changes in temperature and solvent composition. An ultraviolet detector using a flow cell is the most common HPLC detector, because many solutes absorb ultraviolet light. This detector measures the ability of a sample to absorb light. This can be accomplished at one or several wavelengths: fixed-wavelength that measures at one wavelength, usually 254 nm, the variable-wavelength that measures at one wavelength at a time, but can detect over a wide range of wavelengths, and diode array that measures a spectrum of wavelengths simultaneously.

The variable-wavelength UV detector that uses a deuterium lamp allows the detection of many compounds at any wavelength in the UV region depending on the background absorbance of the mobile phase and, of course, on whether the compound has any absorbance at a given wavelength. As a general rule, the wavelength is set to the absorbance maximum of the analyte can be detected. Using wrong wavelength may result in decreased peak heights or even no peaks at all. The VWD is good for quantitative analysis because of a stable and normally reproducible signal.

The detector measures the concentration of sample bands as they leave the column and pass through the detector flow cell. When a sample band reaches the detector, the detector responds to the difference in the mobile phase properties caused by the presence of the sample compound, giving rise to a change in detector signal, seen as a peak. The signal

displayed increases in proportion to the concentration of sample in the flow cell. The detector will also respond to other changes in the contents of the flow cell.

3.3.3 HPLC Applications

Liquid chromatography has been used frequently in biochemistry and analytical chemistry to separate, identify, and quantify compounds. During the last 10 years, HPLC has gained popularity in the analysis of explosives and their degradation products in various matrices such as pharmaceutical formulations, water, soil and air¹¹. For many of the separations that involve explosives, the isocratic runs method was used, where simple methanol-water or acetonitrile-water mixtures are used as the mobile phases.

For 2,4-DNT adsorption studies presented in this research, we used an Agilent 1100 Series HPLC from Agilent Technologies, Inc. (Figure 3.4), a Variable Wavelength Detector (VWD) with Deuterium Lamp and a temperature control module. Separation was performed with Supelcosil Column LC-18 (5 μ m, 4.0 x 150 mm) maintained at 40°C. The mobile phase composition was methanol/water at a composition of 50:50. The run was isocratic elution at a flow rate of 1.0 mL/min.



**Figure 3.4 Agilent 1100 series HPLC from Agilent technologies system used for
2,4-DNT adsorption studies**

3.4 Adsorption

The phenomenon of adsorption occurs when atoms, molecules or ions accumulate in the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption is usually described with functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). This type of functions is called isotherms. The most widely used adsorption isotherm equation employs a simple linear function. An adsorption isotherm equation is conveniently expressed in terms of the distribution coefficient, K_d :

$$x = K_d C \quad (3.3)$$

Where x is the amount of ion adsorbed per unit of mass and C is the equilibrium solution ion concentration.

3.4.1 Freundlich Adsorption Model

The first model of isotherms is due to Freundlich in 1894 and it is an adsorption isotherm, which is, a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The Freundlich adsorption isotherm is mathematically expressed as:

$$q = K_d C^{1/n} \quad (3.4)$$

where q describes the mass of adsorbate adsorbed per unit of sorbent, C is the concentration in equilibrium between the adsorbed mass and the media where the process takes place and K_d and $1/n$ are empirical constants.

The logarithmic expression of this equation gives a linear relation which allows the determination of some characteristics of the adsorption process, and the equation is expressed as:

$$\log q = \log K_d + \frac{1}{n} \log C \quad (3.5)$$

Where, $1/n$ (the slope) define the affinity and K_d define the relative adsorption.

3.4.2 Langmuir Adsorption Model

The Langmuir adsorption equation is used to model monolayer adsorption where all surface adsorption sites have the same affinity for the adsorbing species. Despite the fact that these assumptions are violated in soils, the Langmuir equation has often been used to describe ion adsorption on soil materials⁷. The equation was developed by Irving Langmuir in 1916 and it is expressed as:

$$\frac{x}{m} = \frac{KCb}{1 + KC} \quad (3.6)$$

where x/m describes the mass of adsorbate adsorbed per unit of sorbent and C is the concentration in equilibrium between the adsorbed mass and the media where the process takes place. In this equation K and b are empirical constants.

To describe the adsorption characteristics, we rearrange the Langmuir equation to the linear form equation and it is expressed as:

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{1}{b}C \quad (3.7)$$

where, the value of the slope represented by $1/b$ is the maximum adsorption of the system and the intercept value represented by $1/K$ define the retention energy.

4. METHODOLOGY

4.1 Soil fractions separation: sand, silt and clay

4.1.1 Removal of Carbonates and Organic Matter

Samples of soil from A and Ap horizons of Jobos Series at Isabela, PR and soil from University of Puerto Rico at Mayaguez Campus were obtained down to depth of 0 to 10 inches. The soil was allowed to dry at room temperature, ground and passed through a 2 mm opening sieve. To remove carbonates from the soil samples, thirty grams of each one were placed in beakers of 1000 mL and increments of 1N NaOAc were added. Then, the samples were placed in a water bath at 80.0°C and treated with additions of 5 mL of 30% of hydrogen peroxide (H_2O_2) to remove the organic matter presented in each soil samples.

4.1.2 Clay Separation

The soil samples, free of carbonates and organic matter, were transferred to a 250 mL centrifuge bottle using 100 mL of 0.25N NaCl solution. The solution was mixed using a Vortex and placed in a centrifuge IEC Model CU-500 for 5 min at 2000 rpm. A dispersive solution of 0.01M Na_2CO_3 was used to transfer each soil sample to a mixer. The soil samples with dispersive solution were mixed for 15 min and transferred to a 250 mL centrifuge bottle.¹⁴ This bottle was filled with dispersive solution and then centrifuged for 35 min at 700 rpm. The clay suspension was collected in a 1000 mL beaker (See Figure 4.1). We repeated the process until a clear suspension was obtained. The clay was allowed to settle for several weeks.

4.1.3 Sand and Silt Separation

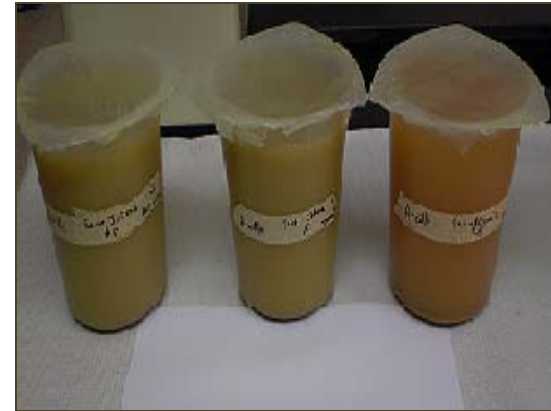
After removing the clay fraction from the centrifuge bottle, the sand and silt fractions were removed by adding distilled water to the centrifuge bottle, shaken and passed through a mesh sieve number 325. The sand particles stay in the sieve while silt particles were collected in a 1000 mL beaker and left to settle a few weeks prior to removing the excess of water (See Figure 4.2). The sand and silt fractions were dried at 100 °C for 48 hours and the weight recorded.

4.1.4 Saturation of Clay with K^+

The clay fraction with a particle size of $< 2\mu m$ was obtained saturating with K^+ by washing with 0.1M KCl solution three times in a 250 mL centrifuge bottle. The excess KCl was removed by repeatedly washing with water until no Cl^- was detected by reaction with $AgNO_3$ solution. The clay suspensions were then quick-frozen, freeze-dried, and stored in a closed container prior to use. This technique minimizes the possibility of structural changes in clay minerals that could be caused by oven-drying.



(a)



(b)

Figure 4.1 Clay Separation: (a) centrifuge used to separate the clay fraction and (b) collection of the clay suspension



(a)



(b)



(c)

Figure 4.2 Physical separation of silt and sand: (a) sand and silt, (b) sand separate by a mesh sieve and (c) silt aqueous solution.

4.1.5 Determination of pH

The soil and clay samples were mixed with distilled water in a proportion of 1:2 (e.g. 5.0 g of soil: 10 mL of distilled water). The pH measurements were obtained using a Seven Multi Mettler Toledo pH meter. After this, clay samples were dried using the freeze-drying technique.

4.2 Soil Texture

The soil was named according to their textural class and this was determined using the proportion of the different particle size fraction (clay, sand and silt). The percentage for each soil particle size fraction was calculated and the soil textural class was determined using the USDA textural triangle.

4.2.1 Soil Texture Using Hydrometer

Soil texture was determined using the hydrometer method. First, two soil samples of 50 g were weighed and one of them oven dried at 105 °C in order to determine the soil dry weight. The other soil sample was transferred to a mixer using 200 mL of a sodium metaphosphate solution. This solution containing the soil sample was mixed for 5 minutes and then transferred to a sedimentation cylinder. It was filled to a calibration mark using distilled water and agitated using a strong upward with a plunger. The hydrometer was placed into the system and its measure and the temperature were recorded after the first 40 s. After this, the hydrometer was taken out and the sodium methaphosphate solution containing the soil sample was agitated again. The reading of the hydrometer and temperature of the system was collected after 2 h. This procedure was performed for the three soils under study.

4.3 Organic Matter Content

The Walkley-Black Method¹² was used to determine the organic content in the soil samples. A sample of 0.5 g of the soil was transferred into a 500 mL Erlenmeyer flask and 10 mL of a solution 1N K₂Cr₂O₇ were added. The flask was swirled gently and then 20 mL of H₂SO₄ were added. The flask was swirled until soil and reagents were mixed and then the system was undisturbed for approximately 30 min. After that time, 200 mL of distilled water were added to the flask and this suspension was filtered. Five drops of o-phenanthroline indicator were added and then this solution was titrated with a solution 0.5 M FeSO₄. To determine the end point, the solution takes a greenish cast and then changes to dark green and finally to a brown color. This analysis was performed in duplicate. A blank determination was done in the same manner. Percent of organic matter was calculated from the % Organic Carbon (%OC) as follows:

$$\%OC = \frac{meqK_2Cr_2O_7 - meqFe(NH_4)_2(SO_4)_3}{SoilWeight(g)} \times \frac{0.003gofC}{meq} \times 100 \quad (4.1)$$

where 0.003 g is the weight of 1 meq of C.

$$\%OM = (\%OC) \left(\frac{1}{0.77} \right) \left(\frac{1}{0.58} \right) \quad (4.2)$$

where 0.77 is the %C recovered by the Walkley-Black Method, and 0.58 is the conversion factor from carbon to organic matter¹².

4.4 Cation Exchange Capacity

To determine the cation exchange capacity (CEC) of the samples under study, 5 g of each soil were placed in 50 mL centrifuge tubes. These tubes were filled with 30 mL of 0.2M NH₄Cl and then shaken for 5 minutes. The samples were centrifuged at 2500 rpm for 5 minutes and the supernatant was collected in a 250 mL volumetric flask. This process was

repeated four more times and the supernatant added to the 250 mL volumetric flask. The samples previously saturated with 0.2 M NH_4Cl were washed twice with 30 mL deionized water to remove the excess of NH_4Cl . The NH_4^+ adsorbed to exchange sites was extracted using a 0.2 M KNO_3 solution. The samples were washed five times with the 0.2 M KNO_3 solution, centrifuged and the supernatant containing NH_4^+ ions was collected in a 250 mL volumetric flask. The samples were diluted to volume and analyzed using Micro Kjeldahl. The same procedure was used to determine the CEC of the clay, but only 2 g of the clay were used.

4.5 Surface Area

For surface area analysis, 2 g of each soil were placed in an aluminum plate and placed in a furnace at 105°C for 24 hours. The dry samples were transferred to a CaCl_2 desiccator to prevent moisture adsorption and then, after 15 min the samples were weighed and 3 mL of ethylene glycol methyl ether (EGME) solution were added. They were placed inside a desiccator equipped with a vacuum outlet and allowed to equilibrate for 30 minutes. A vacuum pump was connected to the desiccator and the samples were evacuated for 45 minutes. Four hours after the evacuation, the samples were removed from the desiccator and the weight recorded. The samples were placed again in the desiccator, evacuated and the weight recorded after two hours. This procedure was repeated until constant weight of the samples was achieved. This study was performed in duplicate. We used a mass of 1 g of the clay previously saturated and dried for the analysis of clay surface area. The specific surface area (SSA) was determined using the following equation¹³:

$$\text{SSA} = \frac{\text{gramsofEGME}}{\text{gramsofsample}} \times \frac{1}{2.86 \times 10^{-4} \text{ g / m}^2} \quad (4.3)$$

4.6 X-Ray Diffraction Analysis

The identification of minerals in the clay fraction was performed by X-ray diffraction (XRD) analysis using a Siemens D5000 unit. This unit consisted of a ceramic Cu tube, graphite monochromator, computer-controlled theta-compensating slit and automated 40 sample changer equipped with the DiffracPlus software and Powder Diffraction File 2002 database. Approximately 1 g of clay from each soil was placed in a sample holder. The scans were collected from 4 to 70 degrees 2-theta, 2 second counts at 0.020 degrees steps. X-Ray analysis was done in the X-Ray Microanalysis Laboratory of the Geology Department of the University of Puerto Rico Mayaguez Campus.

4.7 Analytical Method: High Performance Liquid Chromatography

Chemical analysis was performed by RP-HPLC using an Agilent 1100 Series HPLC modules from Agilent Technologies. The HPLC modules system consisted of a Variable Wavelength Detector (VWD) with Deuterium Lamp and a temperature control module. Separation was performed with Supelcosil Column LC-18 (5 μ m, 4.0 x 150 mm). The methanol:water isocratic elution was at a flow rate of 1.0 mL/min at a composition of 50:50 was held for 8 minutes. 2,4-DNT was obtained from Cerilant with 99.0% of purity. Aqueous 2,4-DNT solutions were prepared from stock solutions in acetonitrile (0.1M). A specific volume from stock solution was added to deionized water to give the following initial 2,4-DNT concentrations 4, 8, 12, 16, 20, 24 μ g/mL.

4.8 Adsorption Studies

4.8.1 Sorption Kinetics

A stock solution of 2,4-DNT was prepared in a 5 mL volumetric flask dissolving 22.20 mg of 2,4-DNT (99.0%) crystalline in acetonitrile. In 50mL borosilicate centrifuge tubes, 10 mL of a 12 µg/mL standard aqueous solution of 2,4-DNT were combined with 2.0 g of soil and 0.2 g of the clay fraction samples. A background solution of 0.1M KCl was added to the clay samples. Centrifuge tubes were agitated on a reciprocal shaker from 1 hour to 54 hours. Then, the samples were centrifuged in an IEC Model CU-500 Centrifuge and the supernatant was filtered using a Millex-HV 0.45µm filter and analyzed by HPLC. The mass of 2,4-DNT adsorbed by the soil and clay fractions samples was calculated by difference.

4.8.1 Sorption Isotherms

Aqueous 2,4-DNT solutions were prepared from stock solution in acetonitrile. A specific volume from the stock solution was added to deionized water to give the following initial 2,4-DNT concentrations 4, 8, 12, 16, 20, and 24 mg/L. In 50 mL borosilicate centrifuge tubes, 10 mL of the aqueous 2,4-DNT solutions was combined with 2.0 g of topsoil. For the sorption study in clay, the aqueous solutions were prepared in 0.1M KCl and combined with 0.2 g of clay fraction. Centrifuge tubes were sealed and agitated on a shaker for 22 hours. After this time, the tubes were centrifuged for 30 min at 3500 rpm and the supernatant was filtered using a Millex-HV 0.45µm filter unit and then analyzed by HPLC. The mass of 2,4-DNT sorbed by topsoil was calculated by difference. All experiments were conducted in triplicate.

4.9 Acetonitrile Extraction

2,4-DNT was extracted from soil samples using the EPA SW-846 Method 8330¹⁵ acetonitrile extraction procedure. The soil was combined with 10.0 mL of acetonitrile, vortexed and placed in a sonicator bath cooled to 22°C for 18 h. Then, the samples were centrifuged and after sedimentation, 4.0 mL of the supernatant was combined with 4.0 mL of a 5 g/L CaCl₂ solution. The solutions were agitated and settled for 15 min prior to sample preparation for HPLC analysis.

5. RESULTS AND DISCUSSIONS

5.1 Soil Description

The soils used in this research were from Jobos series at Isabela, Puerto Rico and Humatas series at University of Puerto Rico, at Mayaguez Campus. The Jobos series is a highly weathered soil located at the western region of Puerto Rico, approximately 8 kilometers west of the town of Isabela. The Humatas series is formed in clayey and loamy material that weathered from igneous rocks and also, it is located at the west region of Puerto Rico, approximately 6.5 miles from the city of Mayaguez. Both soils are classified as Ultisols. This taxonomic order is extensive in Puerto Rico. Ultisols are soils in humid and tropical areas. They formed from fairly intense weathering and leaching processes that result in a clay-enriched subsoil dominated by minerals, such as quartz, kaolinite, and iron oxides. Ultisols are typically acid soils in which most nutrients are concentrated in the upper few inches. They have a moderately low capacity to retain cations.

Soil samples from the surface of each series were selected for the adsorption experiments. Ap and A horizons from the Jobos series were used for adsorption studies (See Figure 5.1). The A horizon is a surface horizon composed of minerals and organic matter¹⁴. The organic matter is accumulated from growing plants and organic matter decomposed by organisms. The A horizon is usually below the O horizon and above the B horizon. The dark color of the A horizon is due to the mixing of humus with minerals. If the A horizon is thicker than 2-3 inches, it has probably been plowed. In this cases it will have properties resulting from cultivation, pasturing, or similar kinds of disturbances, and is designated as Ap horizon.

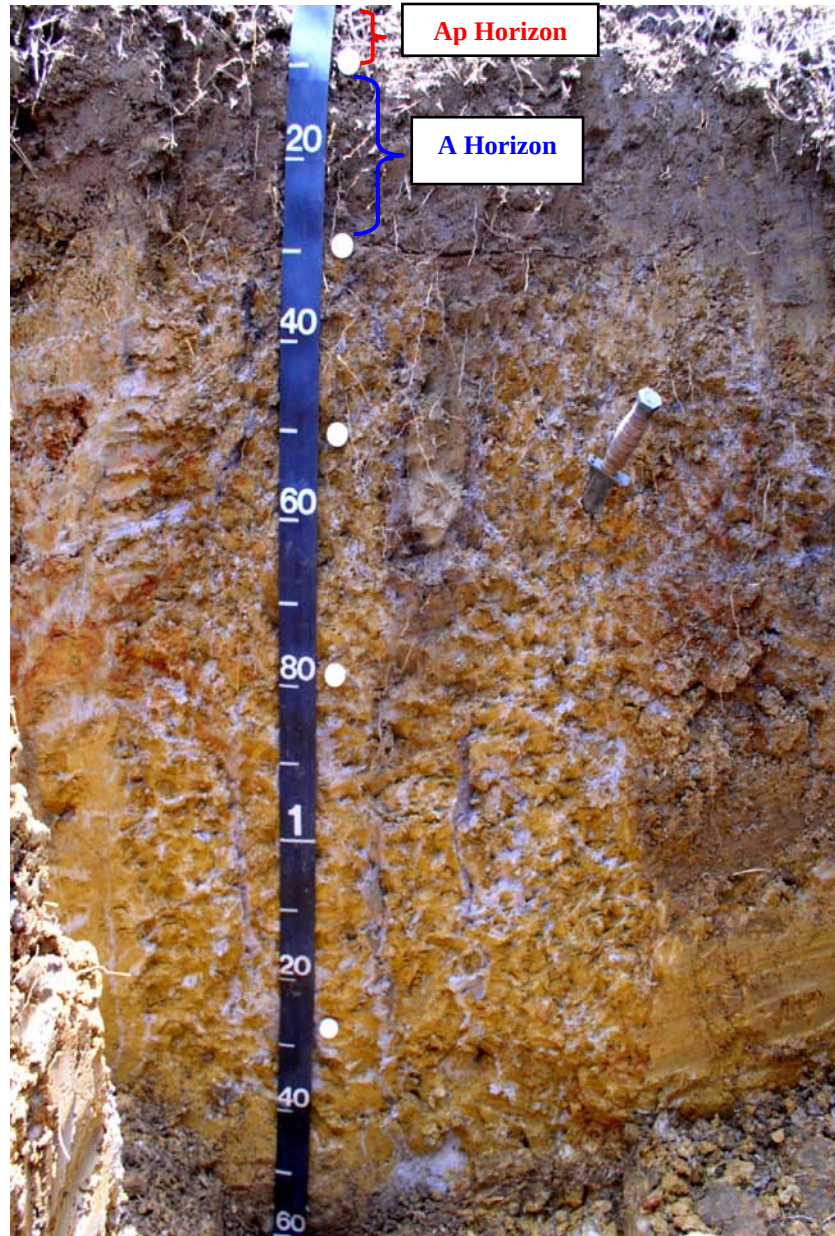


Figure 5.1 Soil profile for Jobos Series showing the distinctive horizontal layers.
*From Reference 7

5.1.2 Texture

The texture of a soil is extremely important in the sorption process. If a soil is made up of mostly clay and organic matter a significant amount of sorption will take place. Clay especially intermixed with organic particles, by far adsorbs the most out of the three main soil textures (clay, silt and sand) because of its small particle size, high surface area, and high surface charge. The soil texture was determined using the hydrometer method by measuring the grams of the soil particles (sand, silt and clay) that remain suspended in the cylinder after a specific period of time. Different sized soil particles are separated by their different sedimentation rates. Based on Stokes Law, larger particles will settle faster in a column of water, while smaller particles remain suspended¹⁴. After 40 seconds particles of sand (largest particles) quickly dropped to the bottom of the cylinder, only silt and clay particles were left suspended in the water. After two hours only clay-sized particles remained suspended.

Table 5.1 shows the distribution of soil separates for the selected soil. A 35.7%, 27.8% and 61.0% of clay were obtained in Ap horizon, A horizon and UPRM soils, respectively. According to USDA textural triangle (Figure 5.2), Ap and A horizons are classified as sandy clay loam.; soil having this texture consists of materials whose behavior is dominated by sand and clay¹⁴. In contrast, the UPRM soil is classified as clay and it is the finest textured of all the soil classes.

Table 5.1 Properties of soil samples from Ap and A horizons and UPRM used in 2,4-DNT adsorption studies.

Horizons	% Clay	% Silt	% Sand	% Organic Matter	pH	Surface Area (m ² /g)	CEC (meq/100g)
	< 0.002 mm	0.05 - 0.002 mm	0.05 - 2.0 mm				
Ap	35.7	5.6	58.7	4.21	7.63	22.58	3.62
A	27.8	3.9	68.3	0.63	7.51	18.06	2.57
UPRM	61.0	18.5	20.5	2.42	7.44	33.01	6.75

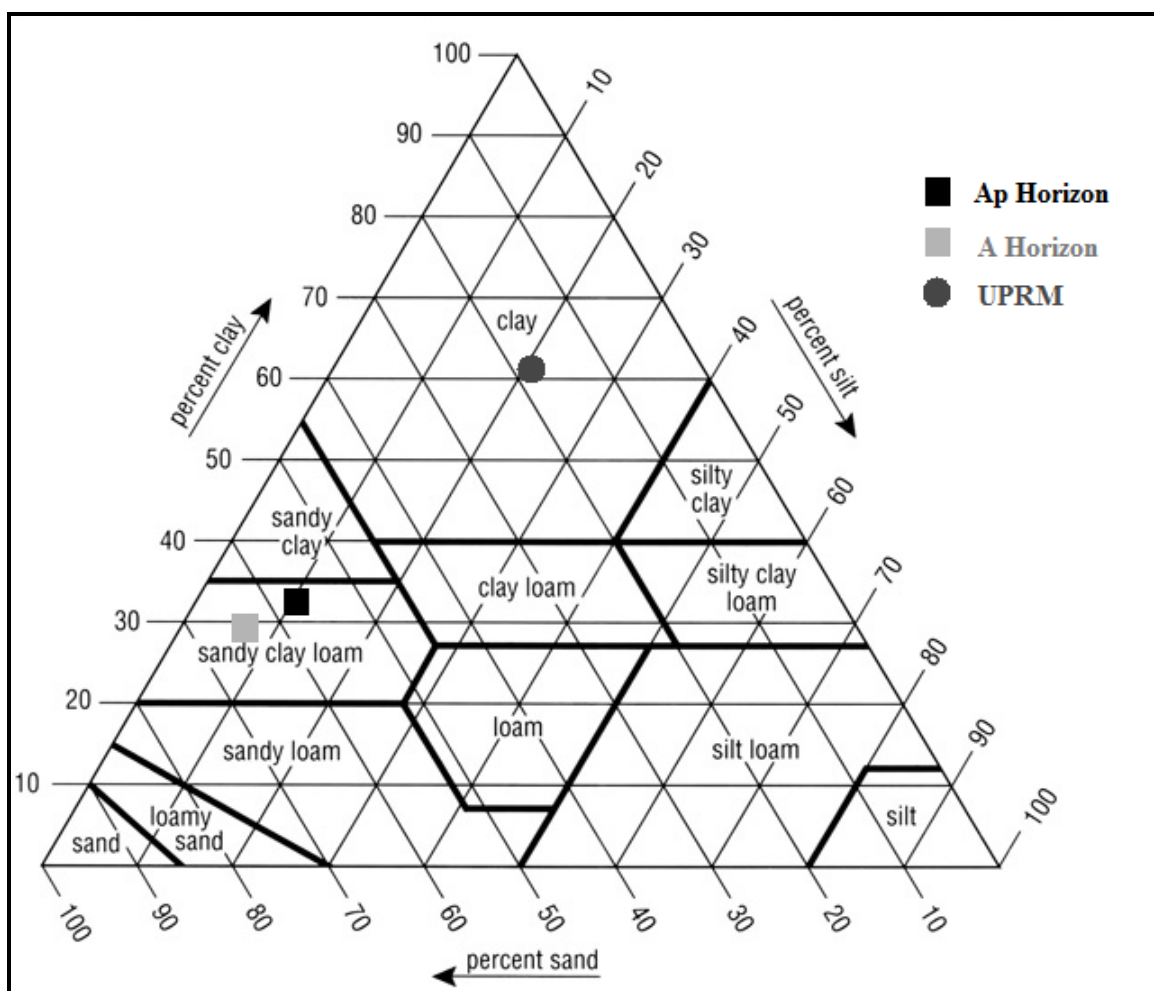


Figure 5.2 USDA Textural Triangle

From: <http://www.soils.usda.gov> (Accessed: August 2009)

5.2 Cation Exchange Capacity for Soil and Clay Samples

Cation exchange capacity, CEC, refers to the quantity of negative charges in soil existing on the surfaces of clay and organic matter. The negative charges attract positively charged ions, or cations, hence the name 'cation exchange capacity'. Cations are positively charged ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+), sodium (Na^+), hydrogen (H^+), aluminum (Al^{3+}), iron (Fe^{2+}), manganese (Mn^{2+}), zinc (Zn^{2+}) and copper (Cu^{2+}). These cations are held by the negatively charged clay and organic matter particles in the soil through electrostatic forces. The cations on the CEC of the soil particles are easily exchangeable with other cations. Thus, the CEC of a soil represents the total amount of exchangeable cations that the soil can adsorb. The main source of charge on clay minerals is isomorphous substitution; this is the substitution of one element for another in ionic crystals without changes in its structure. The negative charges associated with isomorphous substitution are considered permanent, that is, the charges do not change with pH changes. It is important to establish the soil pH because some clay minerals like kaolinite, iron oxides and aluminum oxides present pH dependent charges. This type of charge is variable and negative charges increase with increasing pH. Table 5.1 presents pH and CEC values for the soil samples at A and Ap horizons, and UPRM soil. It indicates that soil sample from UPRM has higher CEC. Results for the clay fractions, presented in Table 5.2, indicate that clay fraction from A horizon has higher CEC than clay from the other soils. The importance of cation exchange at negative sites is that it is the major retention mechanism for heavy metals and other contaminants such as nitroaromatics compounds.

Table 5.2 Properties of clay fractions samples from Ap, A horizons and UPRM used in 2,4-DNT adsorption studies.

Horizons	pH	Surface Area (m²/g)	CEC (meq/100g)
Ap	5.5-6.0	189.71	12.50
A	5.5-6.0	163.87	13.12
UPRM	5.5-6.0	231.97	11.87

5.3 Surface Area Analysis for Soil and Clay Samples

One of the most important characteristic of soils is their surface area. This can vary depending upon particle size, minerals present, exchange cation, presence of organic matter and method of determination. Smaller particles have larger surface area. The surface area gives us an estimate of the available area for cation exchange and adsorption of other species like contaminants. Cation exchange capacities tend to vary directly with surfaces areas. Of course the importance of the surface area depends upon the activity of the surface. As we can see in Table 5.1, the soil sample from UPRM has a higher surface area than Ap and A horizons. If we analyzed the clay fraction (See Table 5.2), it has a greater surface area than the soil samples. This fact is because the clay minerals have smaller particle sizes in comparison to the soil. The clay fraction from the UPRM has higher surface area than the other clay fractions (Table 5.2).

5.4 X-Ray Diffraction Analysis for the Clay Fraction

A qualitative mineralogical analysis of the clay fraction was performed in order to obtain a complete characterization by X-ray diffraction. The analysis indicated the presence of the mineral kaolinite in all samples. This clay mineral is characterized by a series of x-ray diffraction peaks at diffraction at 12.2 and 24.7 degrees 2 theta. Kaolinite is abundant in the clay fraction as product of weathering¹⁶. Its specific surface area is small in comparison with other clay minerals as vermiculite. Kaolinite has low CEC compared to other clay minerals. Hematite and goethite were also found in the clay fractions. Hematite is a common iron oxide which exhibits a characteristic peak at 33.3 degrees 2 theta. It is responsible of the red color in soils. Goethite shows a characteristic peak at 21.3, it is responsible of the yellow color in most soils, and it is the most abundant iron oxide in soils. These minerals were present in all the samples as shown in Figures 5.3, 5.4 and 5.5.

Another mineral was gibbsite; the main peak for this mineral was around 20.0 degrees 2 theta. Gibbsite is the most common aluminum oxide in soils and in our studies it was found in all the samples analyzed. Illite was found in the clay fraction of UPRM, this clay mineral is characterized by an x-ray diffraction peak of 8.8. Illite is a 2:1 clay mineral with a nonexpansive structure. Quartz was also observed in the x-ray diffraction analysis. This mineral exhibits characteristics peaks at 20.8 and 27.0 degrees 2 theta. Due to its hardness, this mineral is resistant to weathering and it has a tendency to accumulate in soils.

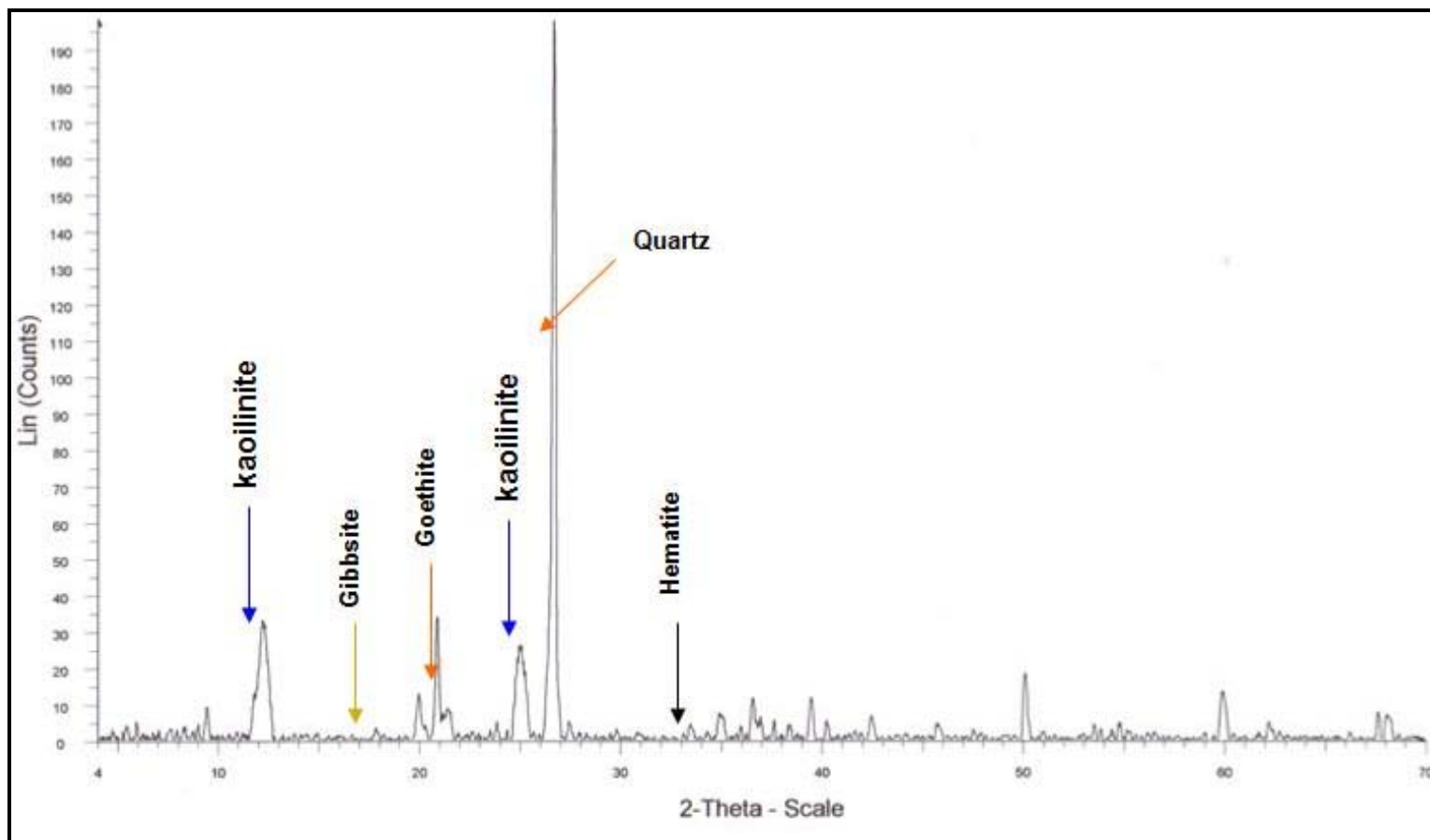


Figure 5.3 X-ray diffraction mineral characterization of the clay fraction from A horizon.

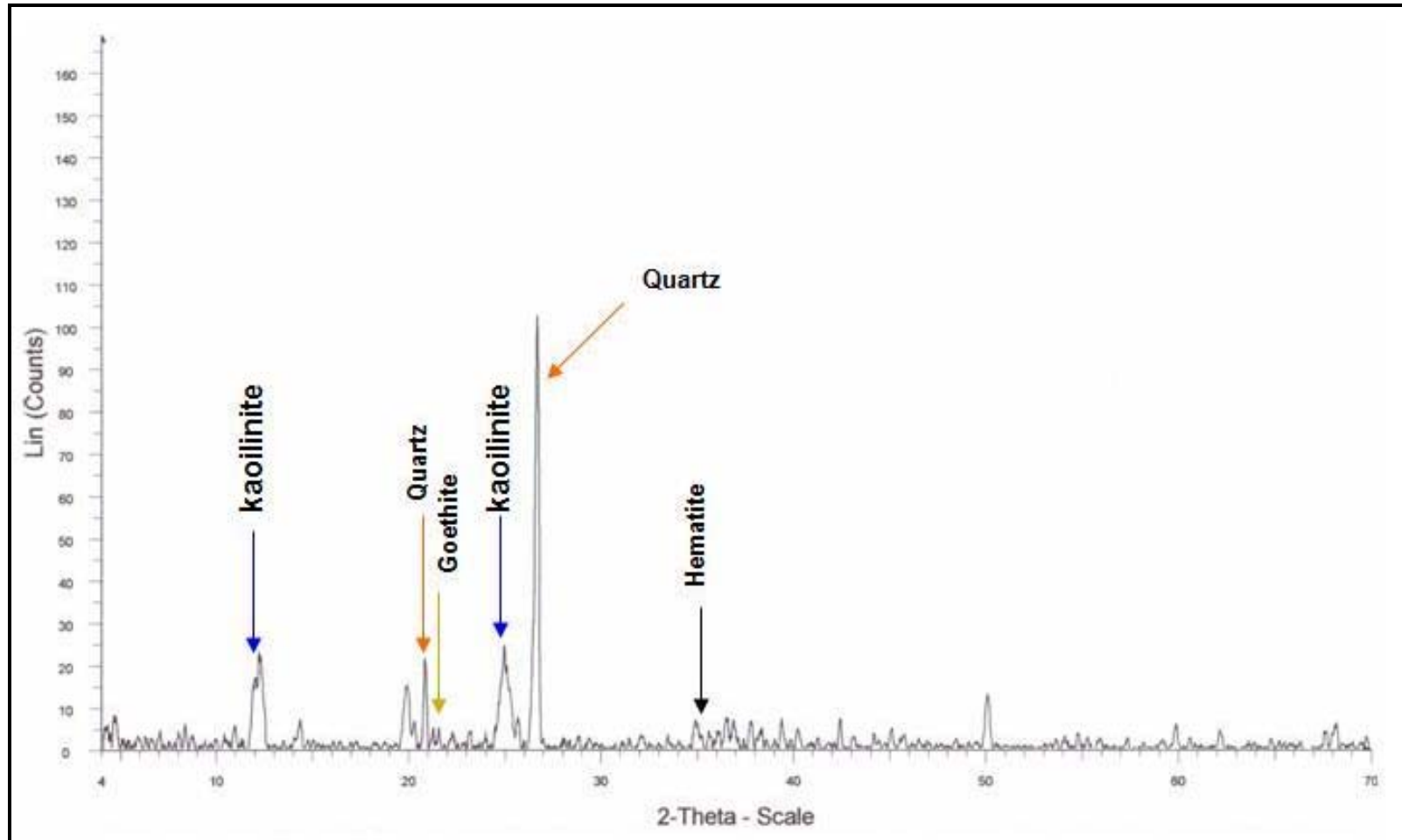


Figure 5.4 X-ray diffraction mineral characterization of the clay fraction from Ap horizon.

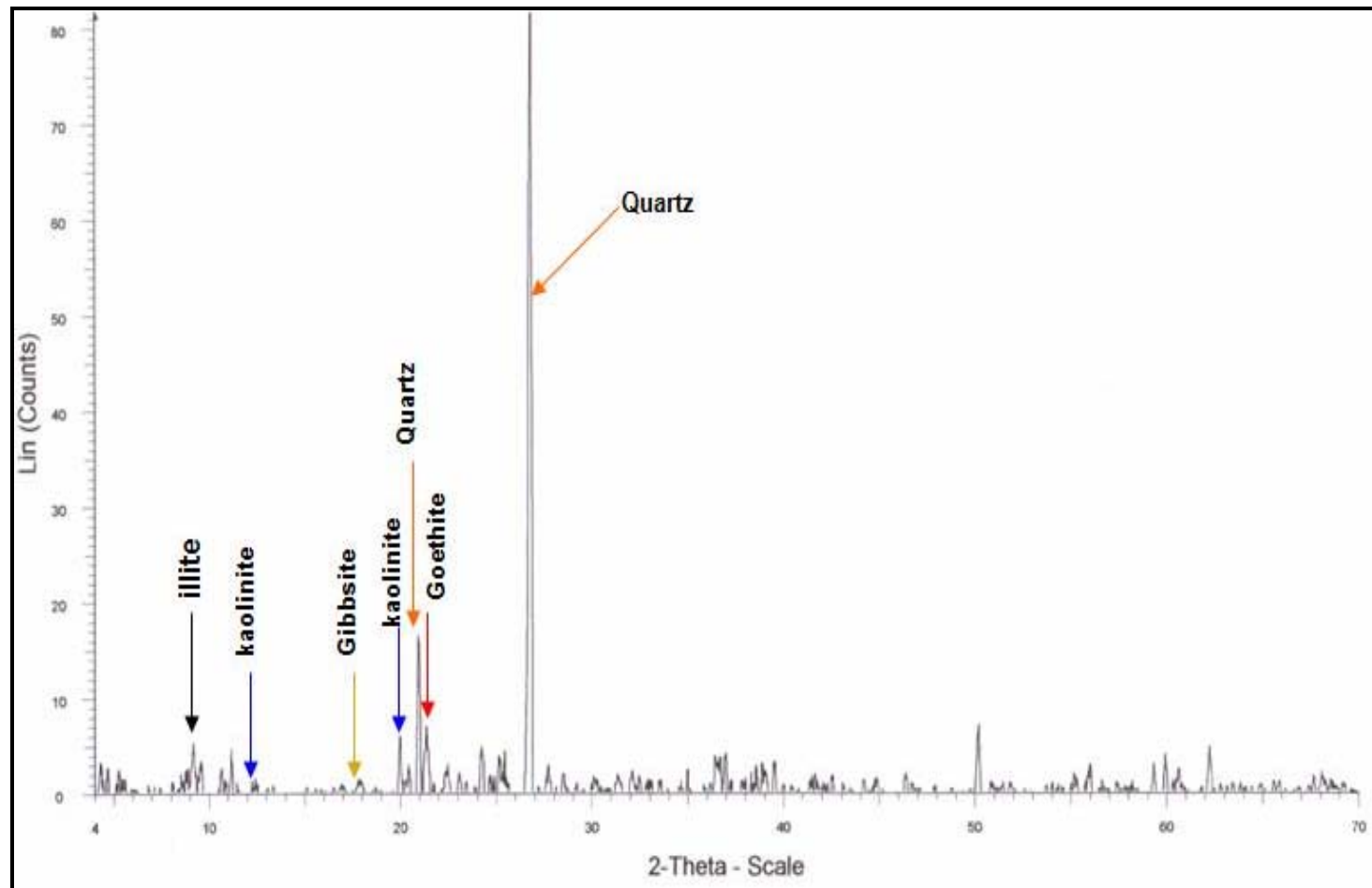


Figure 5.5 X-ray diffraction mineral characterization of the clay fraction from UPRM.

5.5 Methodology Validation for 2,4-DNT Adsorption Studies

In order to validate the proposed methodology, we evaluate the 12 ppm 2,4-DNT aqueous solution. Figure 5.6 shows two peaks, the first peak at a retention time of 1.197 corresponds to the sample solvent and the second peak at 4.833 corresponds to 2,4-DNT signal. We confirmed that the first peak that appeared at 1.197 is the sample solvent, running a blank solution which contain only 0.1M KCl in deionized water. We calculated the capacity factor (k') parameter to know if the separation of the analyte occurs in a reasonable time. This parameter is used to describe the migration rate of the analyte in the chromatographic column. The value calculated for this parameter was 3.0 which is in the accepted range of 1 to 5.

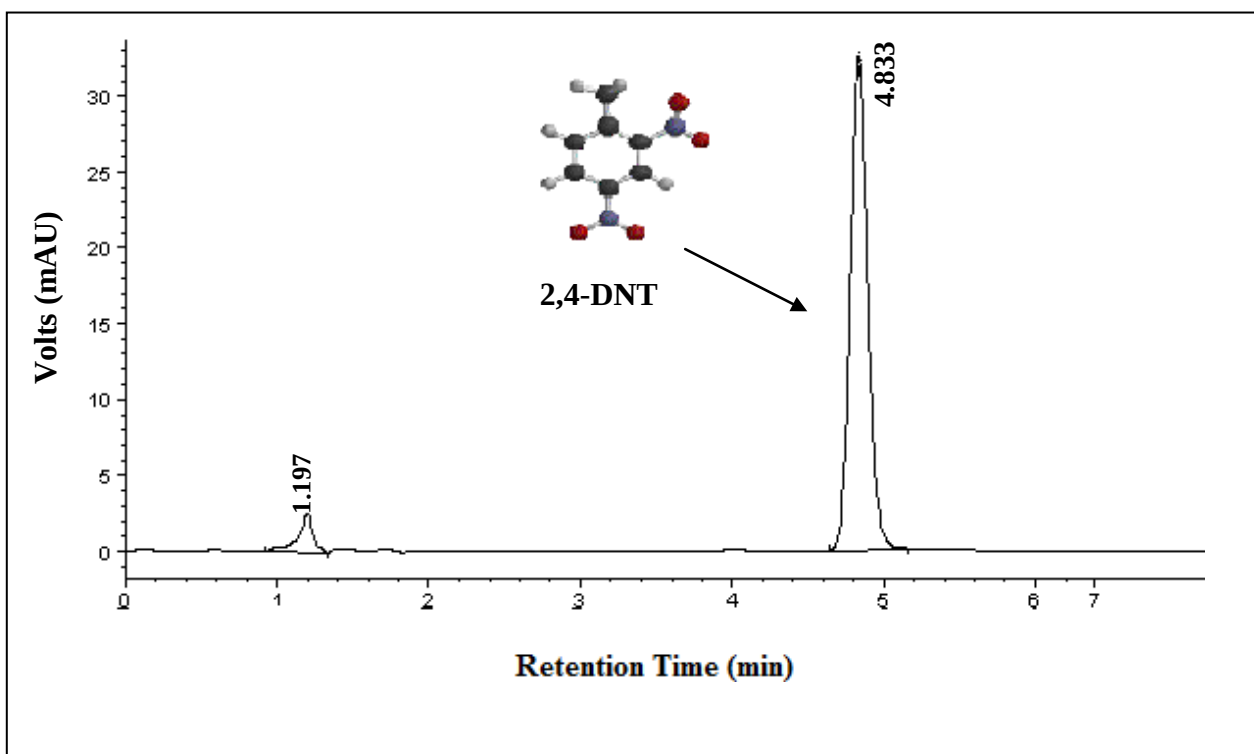


Figure 5.6 Chromatogram for 12 ppm 2,4-DNT aqueous solution

The reproducibility of the method respect to the retention time and peak area was evaluated using the 12 ppm 2,4-DNT standard solution. Relative standard deviation (% RSD) for retention time and peak area were 0.02% and 0.2%, respectively (See Tables 5.3 and 5.4). The calculated values for % RSD are good because values lower than 2% are generally considered of satisfactory precision¹¹.

In order to evaluate the limit of linearity, a calibration curve was prepared using 2,4-DNT standard solutions, in a range of concentrations of 0 ppm to 40 ppm. A 2,4-DNT concentration of 24 ppm was the highest concentration maintaining a linear relationship (See Figure 5.7). Therefore, the accepted range used for 2,4-DNT adsorption studies goes from 0 to 24 ppm. The limit of detection (LOD) of the system was 0.734 ppm and the limit of quantification (LOQ) calculated was 2.447 ppm. This concentration can be determined with acceptable accuracy and precision.

Table 5.3 Evaluation of the area for 2,4-DNT peak in aqueous solution at different concentrations.

Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Area 3 (mAU)	Average Area (mAU)	Standard Deviation	Relative Standard Deviation
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
4.00	92.7257	92.7630	92.6550	92.7145	0.0548	0.06
8.00	173.9270	173.4902	173.7141	173.7104	0.2184	0.13
*12.00	270.0581	271.1848	270.9807	270.7412	0.6003	0.22
16.00	372.1130	371.3087	371.9342	371.7853	0.4223	0.11
20.00	468.3757	466.6905	469.2990	468.1217	1.3227	0.28
24.00	578.0209	575.6469	575.0845	576.2508	1.5586	0.27

*2,4-DNT standard solution used to evaluate reproducibility

Table 5.4 Evaluation of retention time for 2,4-DNT peak in aqueous solution at different concentrations.

Concentration (ppm)	Retention Time 1 (min)	Retention Time 2 (min)	Retention Time 3 (min)	Average Retention Time (min)	Standard Deviation	Relative Standard Deviation
0.00	0.000	0.000	0.000	0.000	0.000	0.00
4.00	4.645	4.652	4.651	4.649	0.004	0.08
8.00	4.677	4.677	4.675	4.676	0.001	0.02
*12.00	4.675	4.677	4.675	4.676	0.001	0.02
16.00	4.678	4.663	4.668	4.670	0.008	0.16
20.00	4.666	4.666	4.667	4.666	0.001	0.01
24.00	4.669	4.668	4.670	4.669	0.001	0.02

*2,4-DNT standard solution used to evaluate reproducibility

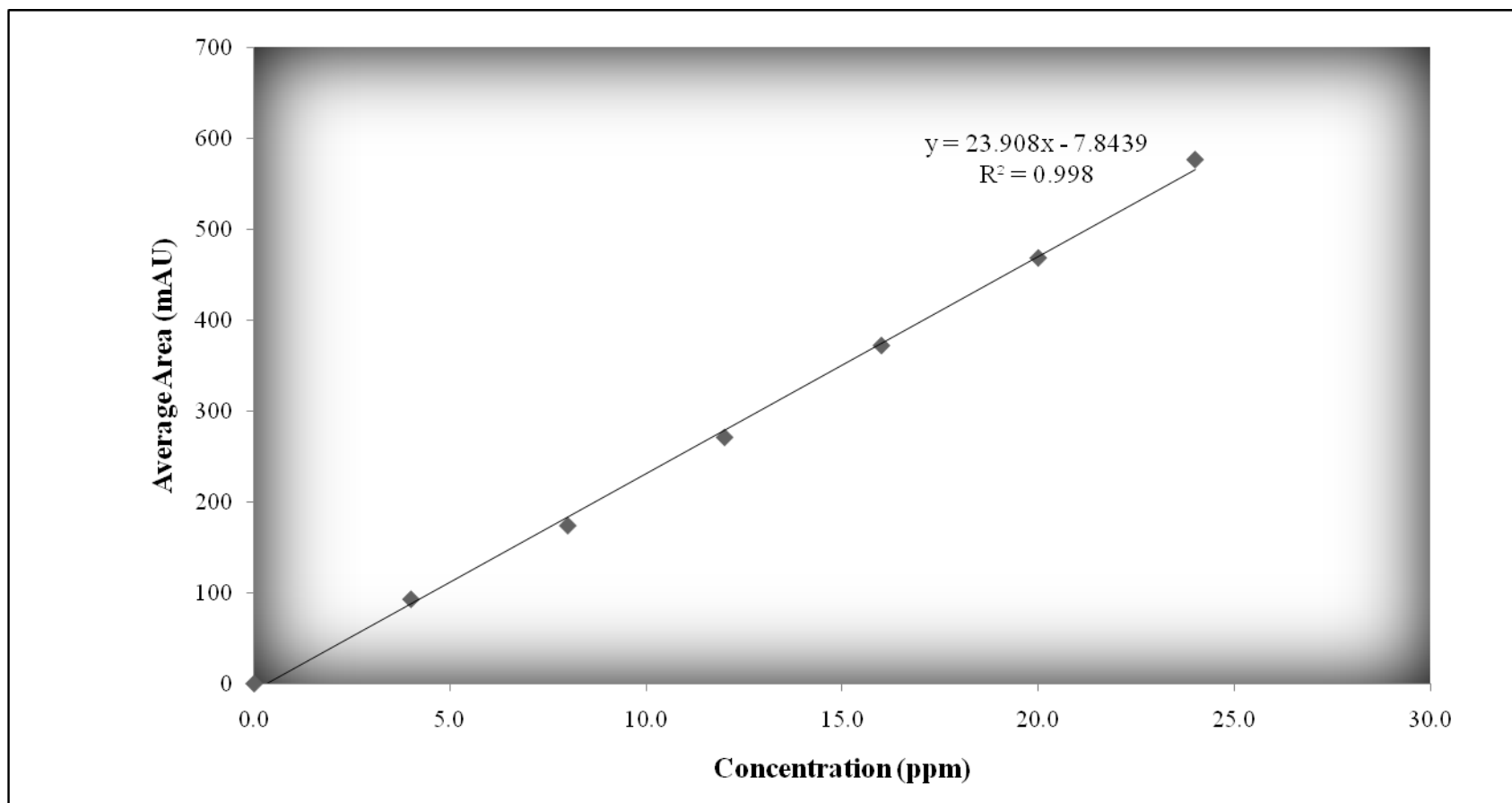


Figure 5.7 Calibration curve for 2,4-DNT in aqueous solutions

5.6 Sorption Kinetics

The result of the kinetic studies for the sorption equilibria for soil sample and clay fraction from the University of Puerto Rico at Mayaguez are presented in Figure 5.8. The study was carried out for 54 hours. The results indicated that 2,4-DNT retention was rapid and appeared to reach equilibrium within 8 hours. These results are similar for the soil and the clay fraction. Although the equilibrium was achieved between this time, we considered to make the adsorption studies with a time of equilibrium of 22 hours to observe degradation products of 2,4-DNT. The studies did not detect degradation products.

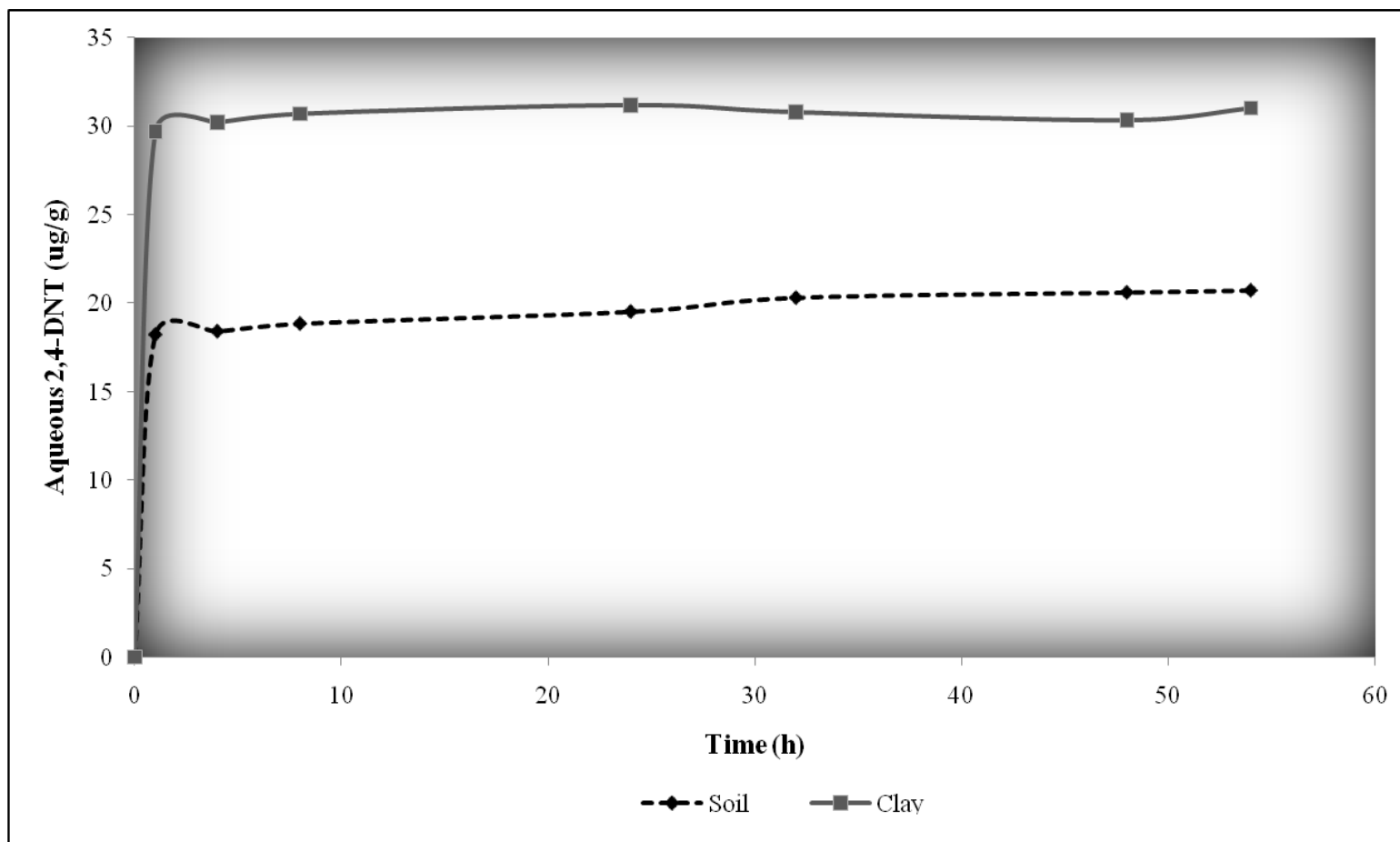


Figure 5.8 Kinetics of adsorption of 2,4-DNT on soil and clay fraction of UPRM.

5.7 Adsorption Isotherms

The 2,4-DNT adsorption on soil and clay fractions samples was modeled very well by the Freundlich isotherm (Figure 5.9). The Langmuir and Freundlich equations (see Equations 3.5 and 3.7) are linear expressions that were used to determine experimental adsorption coefficients and retention energies (see Figures 5.10 and 5.11). The experimental adsorption coefficients for 2,4-DNT-soil interactions are summarized in Table 5.6. Better linear representations of the Freundlich model for the soil samples were obtained. It was observed an adsorption coefficient (K_d) of 11.87 L/kg for Ap horizon, 1.72 L/kg for A horizon and 1.79 L/kg for UPRM soil. Ap horizon shows a greater adsorption than the other soils. The adsorption of Ap horizon can be attributed to its high organic matter (4%).

Soil organic matter (SOM), also known as humic material, is comprised of an accumulation of partially decomposed plant and animal residues as well as organic compounds formed by soil microbial activity. SOM has a greater number of binding sites because it has an extremely large surface area and is chemically reactive. They have electrical charges and exchange capacities that exceed those of the clay minerals. The chemical behavior of humic matter is in general controlled by the carboxyl and phenolic-OH functional groups. These functional groups present pH-dependent charges; they dissociate their protons making the humic molecule negatively charged. Due to the presence of these charges and the great heterogeneity of soil organic matter, a number of reactions can take place. Because SOM has a high sorption capacity, some synthetic organic compounds, such as herbicides, pesticides, and industrial waste organic compounds are readily attached to organic soil particles. Hydrogen bonding, ion-dipole interaction,

ionic bonding, water bridging, and van der Waals bonding forces can take place between humic matter and clay minerals¹⁴.

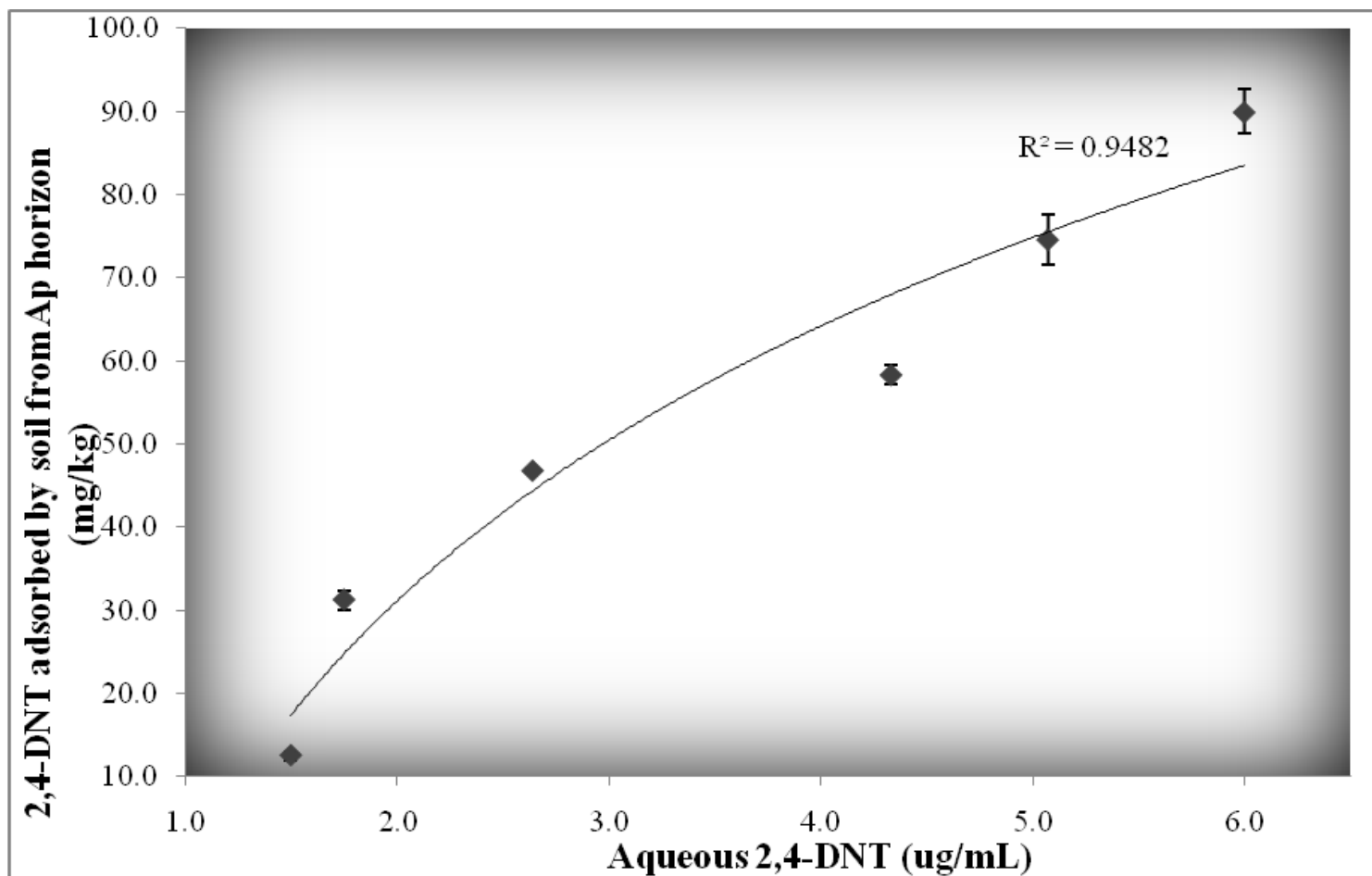


Figure 5.9 Adsorption isotherm for 2,4-DNT on soil from Ap horizon.

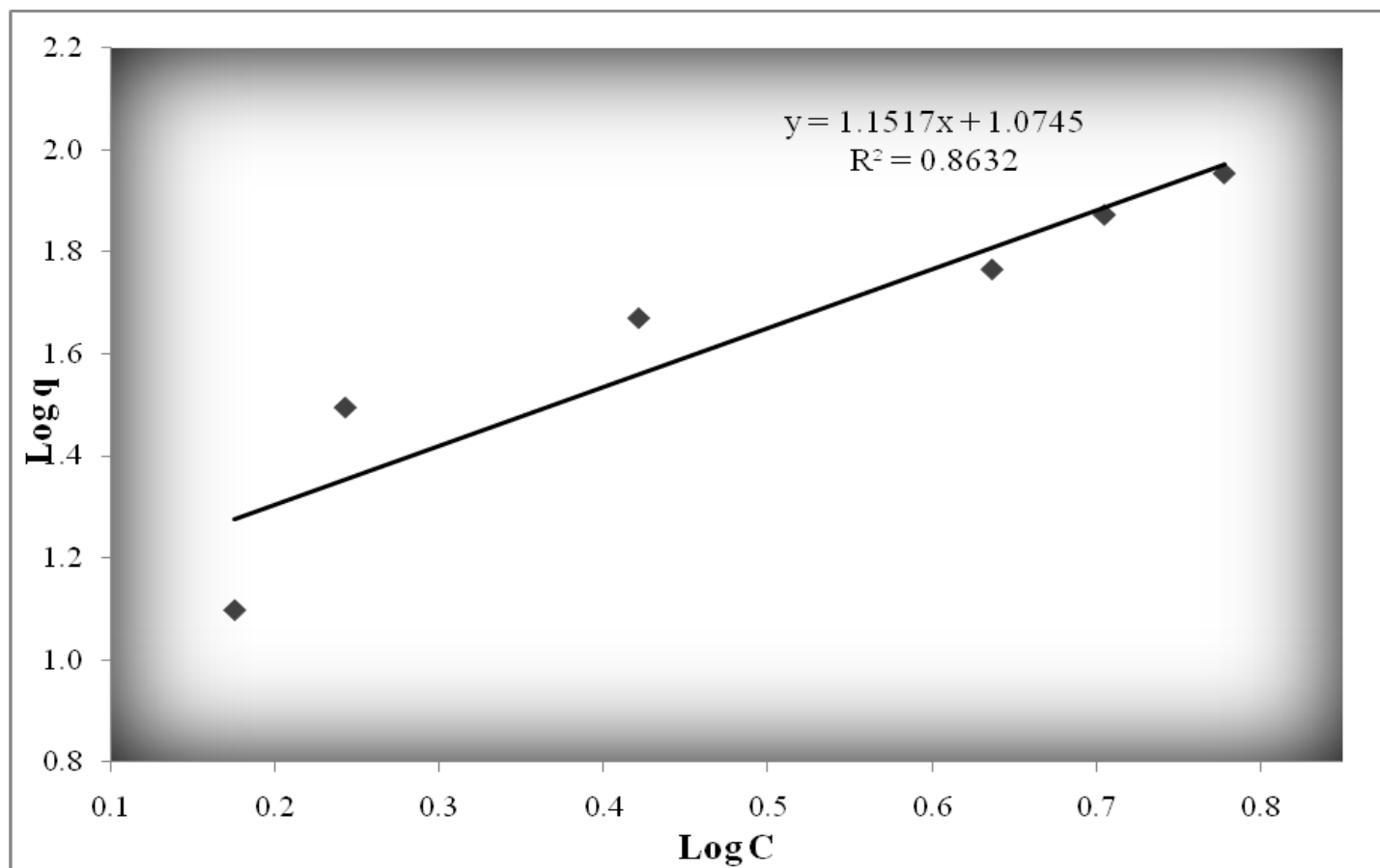


Figure 5.10 Freundlich linear isotherm for 2,4-DNT adsorption on soil from Ap horizon

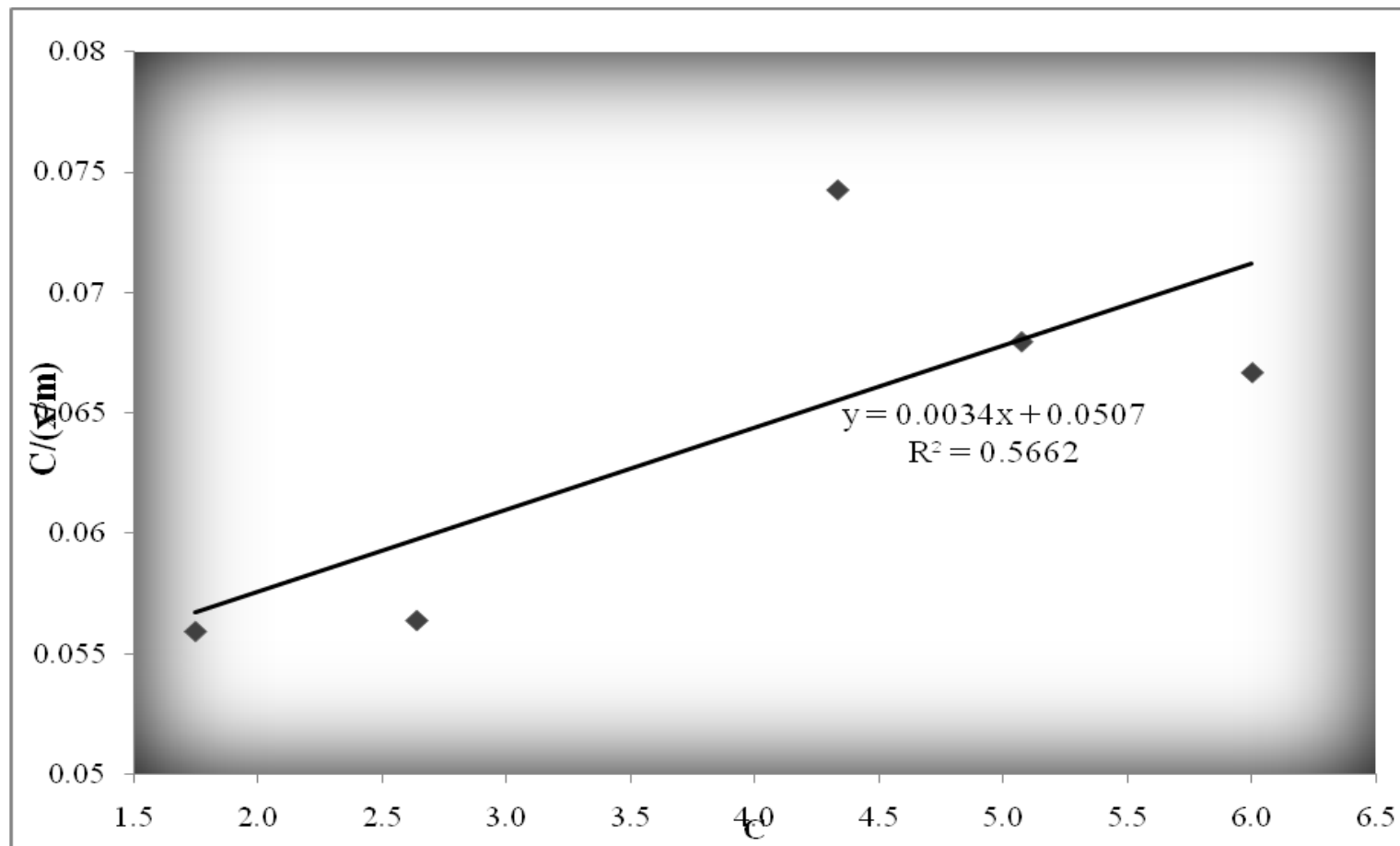


Figure 5.11 Langmuir linear isotherm for 2,4-DNT adsorption on soil from Ap horizon .

One of the adsorption isotherm obtained from the interaction of 2,4-DNT with the clay fraction is showed in Figure 5.12. For all soil and clay samples, the model of the Freundlich isotherm model was selected because a better linear representation was observed (see Figure 5.13). In contrast with the Langmuir isotherm in which the R^2 value was approximately 0.5 (see Figure 5.14). This assumption was done taking into a consideration that clay minerals are a reactive system in which more adsorption could take place. The isotherms found for these systems have a linear shape showing that a higher sorption occurs in high concentrations.

The linear representation of the Freundlich equation gives a relative adsorption of 0.92 L/kg for Ap horizon, 1.11 L/kg for A horizon and 12.73 L/kg for UPRM. The clay fraction from Ap horizon presents a lower adsorption capacity in comparison to the other clay fractions. Another characteristic associated with the adsorption of 2,4-DNT by the clay fraction is the affinity (inverse of slope) of the clay for this nitroaromatic compound. The UPRM clay fraction shows a higher affinity than the other clay fraction. This clay fraction showed a largest surface area ($231.97\text{m}^2/\text{g}$), which may have contributed to the higher adsorption of 2,4-DNT. The results are presented in the Table 5.5.

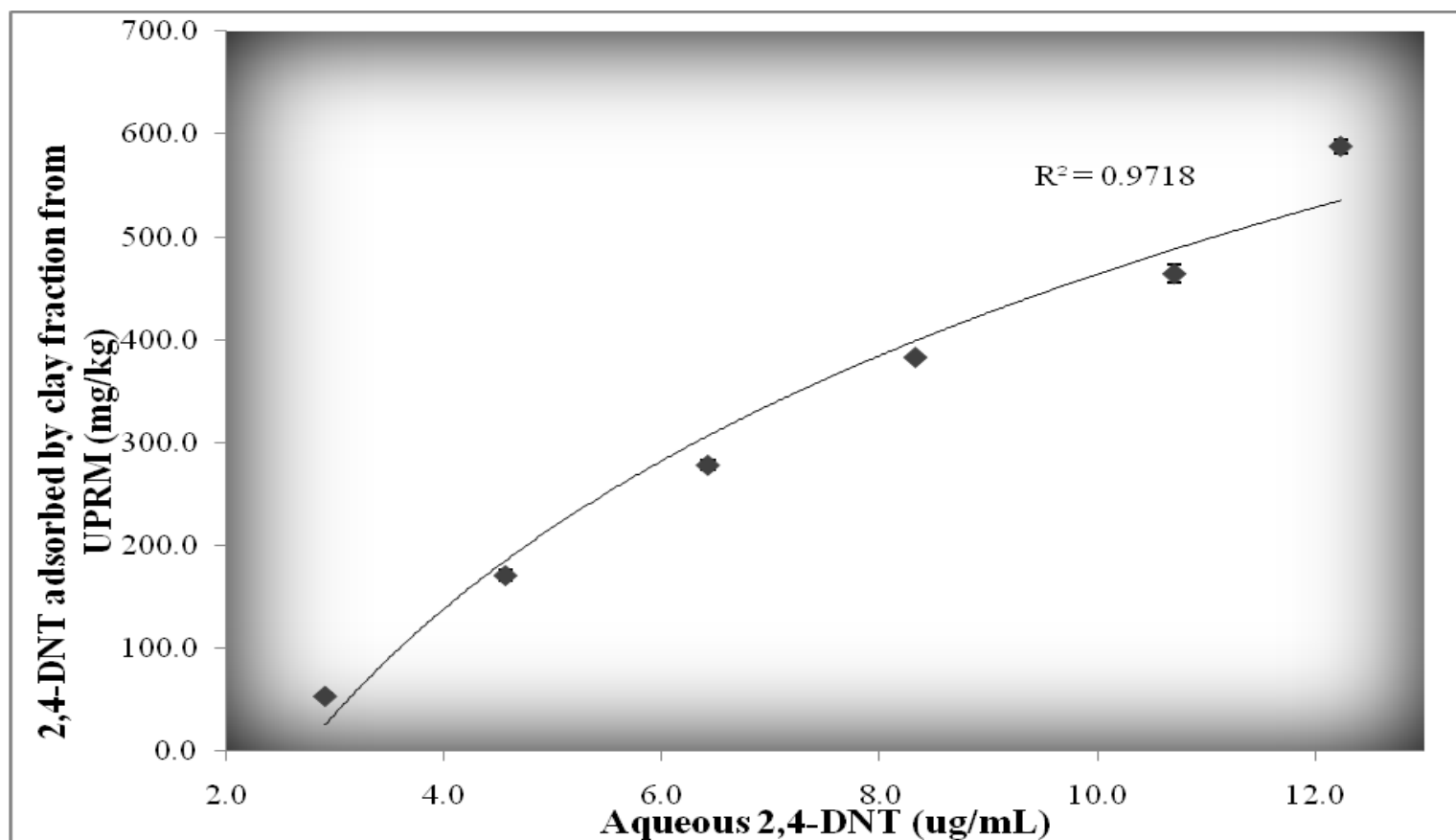


Figure 5.12 Adsorption isotherm for 2,4-DNT on clay fraction from UPRM

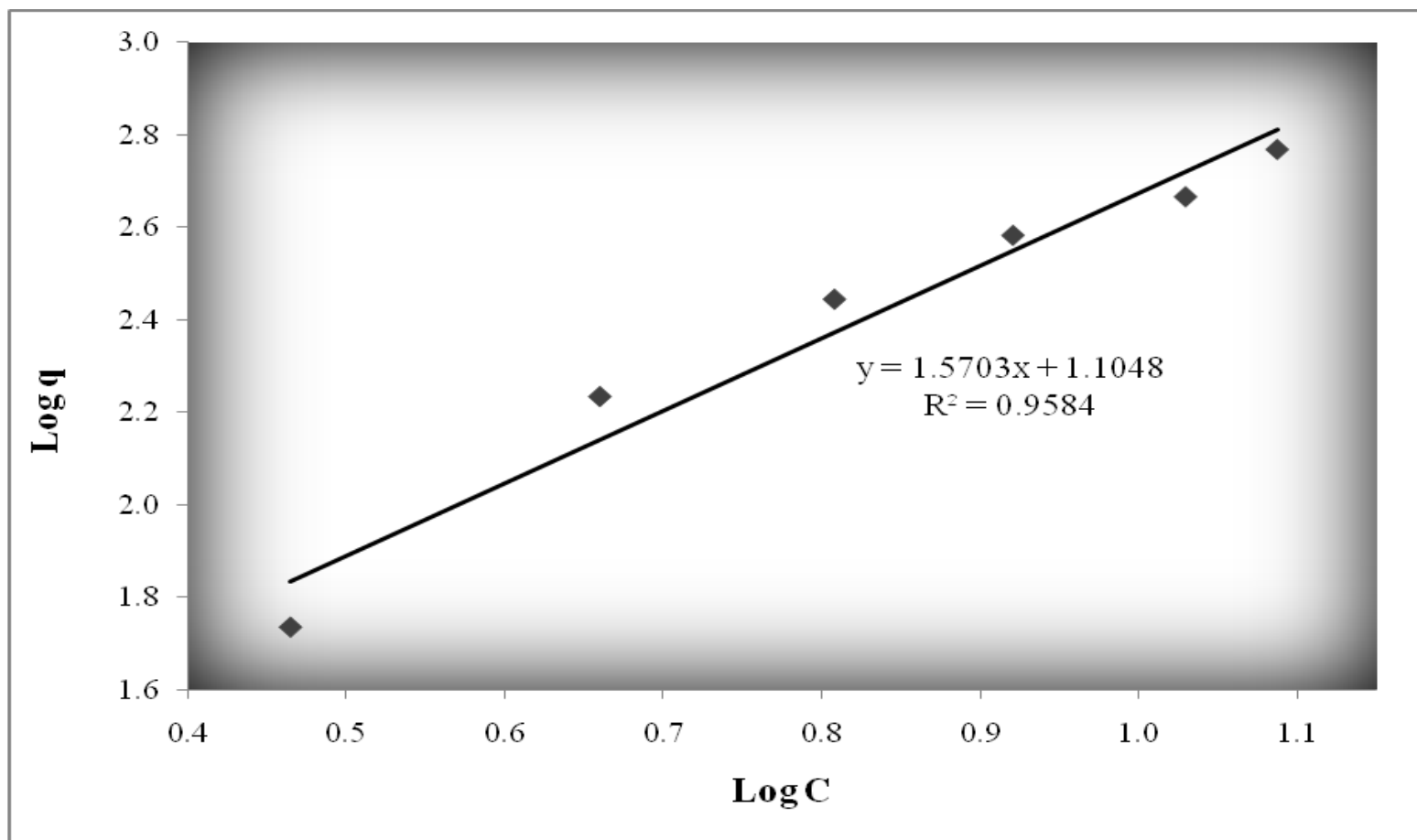


Figure 5.13 Freundlich linear isotherm for 2,4-DNT adsorption on clay fraction from UPRM.

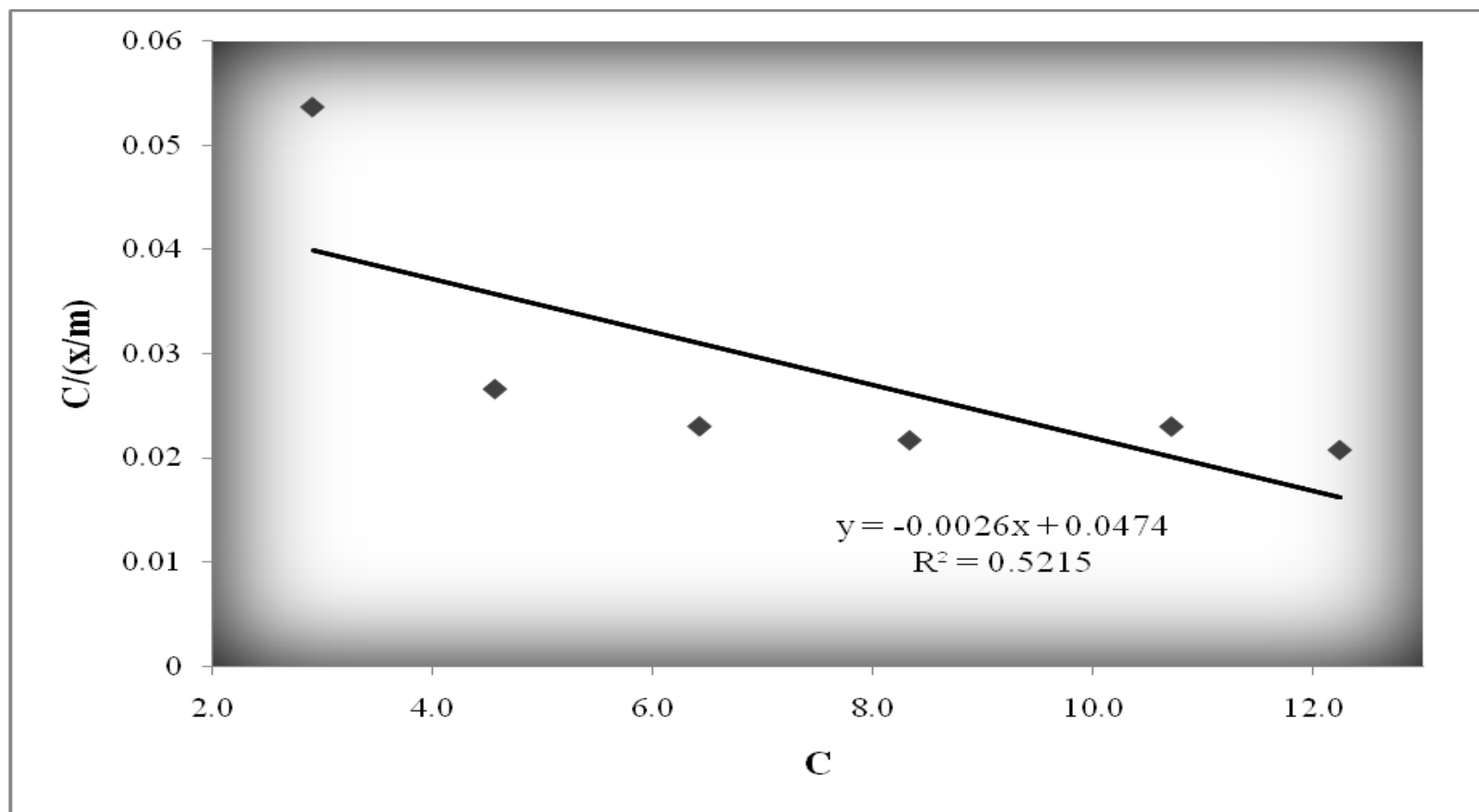


Figure 5.14 Langmuir linear isotherm for 2,4-DNT adsorption on clay fraction from UPRM.

Table 5.5 Summary of the regression parameters for 2,4-DNT adsorption on soil and clay from Ap, A horizons and UPRM.

Sample ID	Freundlich Isotherm			Langmuir Isotherm		
	Relative Adsorption (L/kg) (K_d)	Affinity (n)	R^2	Maximum Adsorption (mg/kg) (b)	Retention Constant (K)	R^2
Ap-Soil	11.87	0.87	0.863	238.10	11.33	0.107
A-Soil	1.72	0.88	0.936	133.33	1.95	0.173
UPRM-Soil	1.79	0.94	0.922	344.83	1.93	0.022
Ap-Clay	0.92	0.41	0.938	64.94	4.57	0.529
A-Clay	1.11	0.42	0.955	74.63	5.37	0.572
UPRM-Clay	12.73	0.64	0.958	384.62	21.09	0.521

The tendency to adsorb more 2,4-DNT in the clay fraction demonstrates that the cation exchange capacity (CEC) and surface area govern clay adsorptive properties. Other studies have demonstrated that explosives may adsorb specifically and reversibly to the siloxane surface of the clay mineral kaolinite, which is one of the clay minerals present in the clay fractions studied¹⁶. The adsorption of nitroaromatic compounds to phyllosilicates had been interpreted in terms of coplanar electron donor-acceptor formation with oxygen ligands at the external siloxane surface of phyllosilicates as e⁻ donors and the π -system of the nitroaromatic compound as e⁻ acceptor⁴. When clay minerals are in the soil complex matrix other factors have to be considered like soil organic matter content. This was the situation found when 2,4-DNT adsorption was evaluated in soil samples. For relatively nonpolar solutes in soil-water systems, where a significant soil organic matter (SOM) content is present, the solute partition in the SOM predominates over adsorption on mineral matter¹⁷. Also, soil organic matter can interfere with electron donor-acceptor complexes by its tendency to form surface coatings on minerals^{18,19}. Soil organic matter adsorbed at mineral surfaces might reduce the accessibility of siloxane sites decreasing adsorption of nitroaromatic compounds²⁰. Adsorption isotherms and linear representations for all the evaluated samples are presented in appendix A.

5.8 Acetonitrile Extraction

The extraction process was performed using soil samples from the second batch. Figures 5.15, 5.16 and 5.17 depict the masses of 2,4-DNT adsorbed by soil and extracted with acetonitrile after the adsorption process. An average percent of recovery of 42% was found for soil sample from Ap horizon, 84% for A horizon and 86% for the soil of UPRM. It was observed that higher 2,4-DNT adsorption resulted in less 2,4-DNT recovery. The percent of recovery found for extractable 2,4-DNT from soil samples was performed using the following equation:

$$\%of recovery = \left(\frac{(NAC_{solid} + NAC_{aqueous})}{NAC_{total}} \right) \times 100$$

Where NAC_{solid} is the 2,4-DNT recovered by acetonitrile extraction, $NAC_{aqueous}$ is the 2,4-DNT present in the aqueous phase, and NAC_{total} is the total amount of 2,4-DNT present. All the terms in this equation were expressed in units of concentration of ppm.

If a chemical remains in contact with soil particles for a long period of time, it could become less extractable. This suggests that an interaction is occurring with the surface and that molecules less accessible²¹. Adsorption kinetics studies for hydrophobic compounds have demonstrated that the initial phase in adsorption processes is rapid and frequently about half of the chemical in aqueous solution is removed by the soil in a few minutes or hours²². This first phase is followed by a considerably slower uptake, which can be of prolonged duration. These kinetic studies suggest that adsorption involves not only the external surface of particles but also a slow and continuing diffusion of the molecules to sites within the particles. The internal and remote sites continue to bind the compound with increasing time. Also, desorption studies suggest that the longer the compound remains in contact with the soil, the less is the amount released²³.

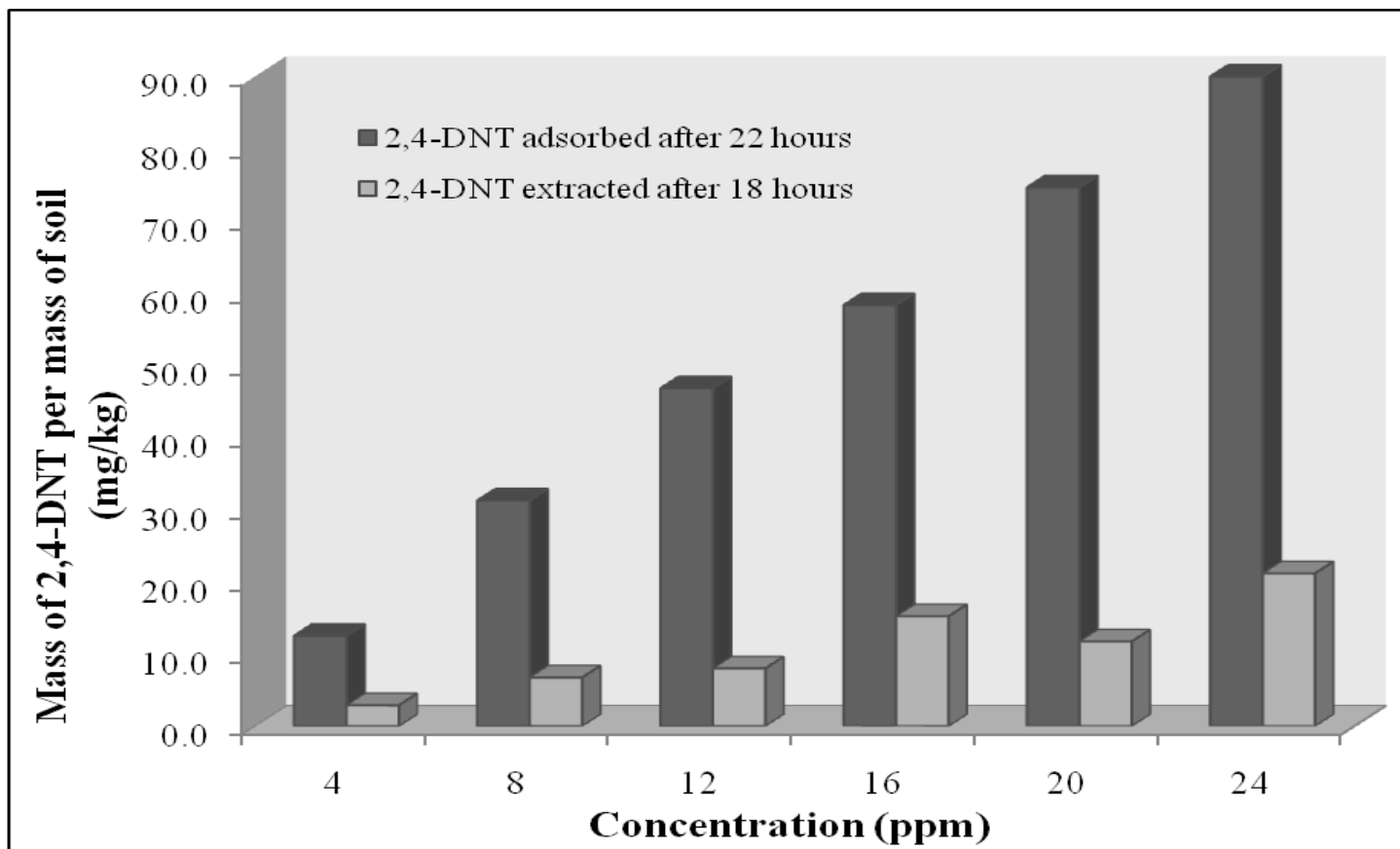


Figure 5.15 Masses of 2,4-DNT adsorbed by topsoil from Ap horizon and masses that were subsequently removed by acetonitrile extraction.

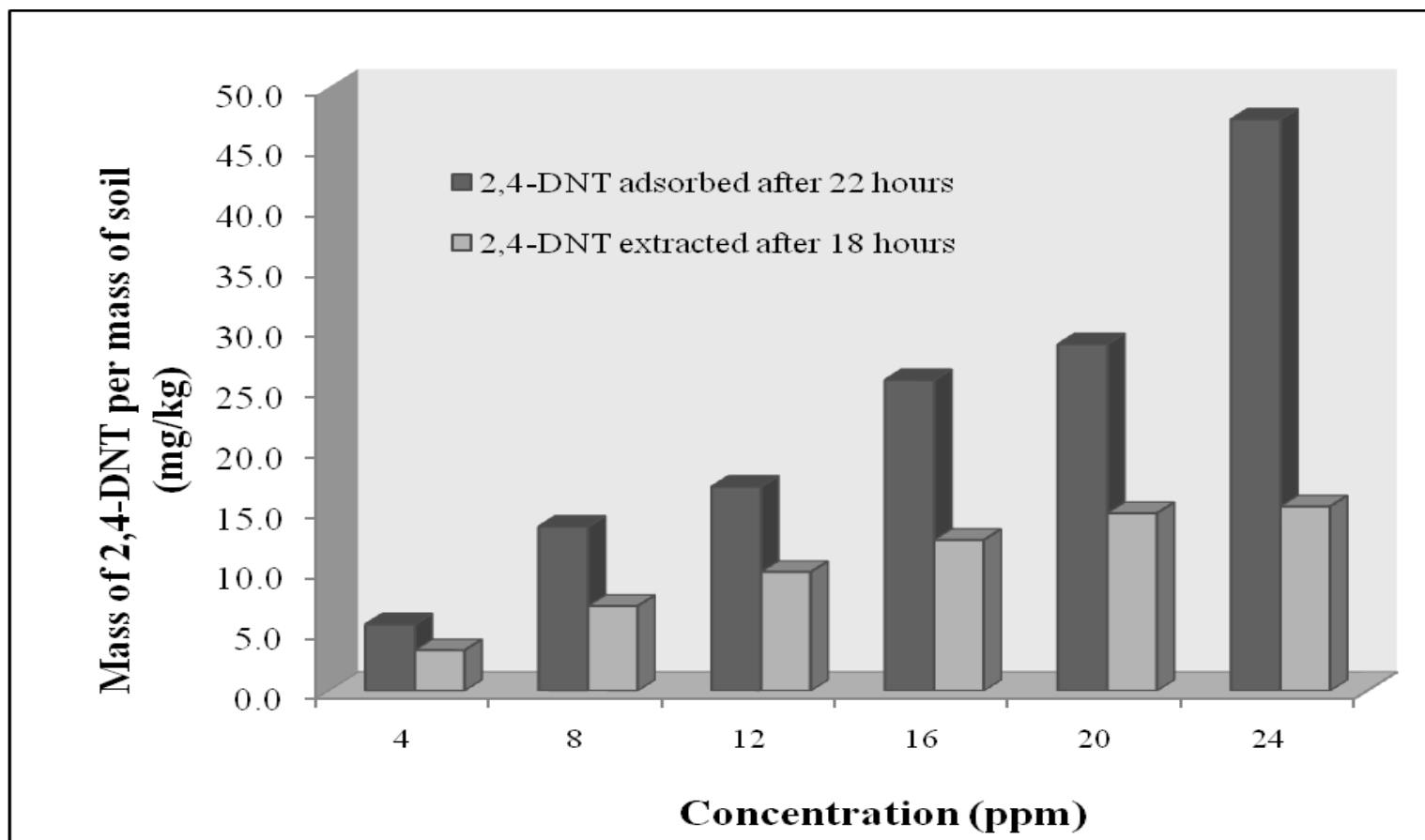


Figure 5.16 Masses of 2,4-DNT adsorbed by topsoil from A horizon and masses that were subsequently removed by acetonitrile extraction.

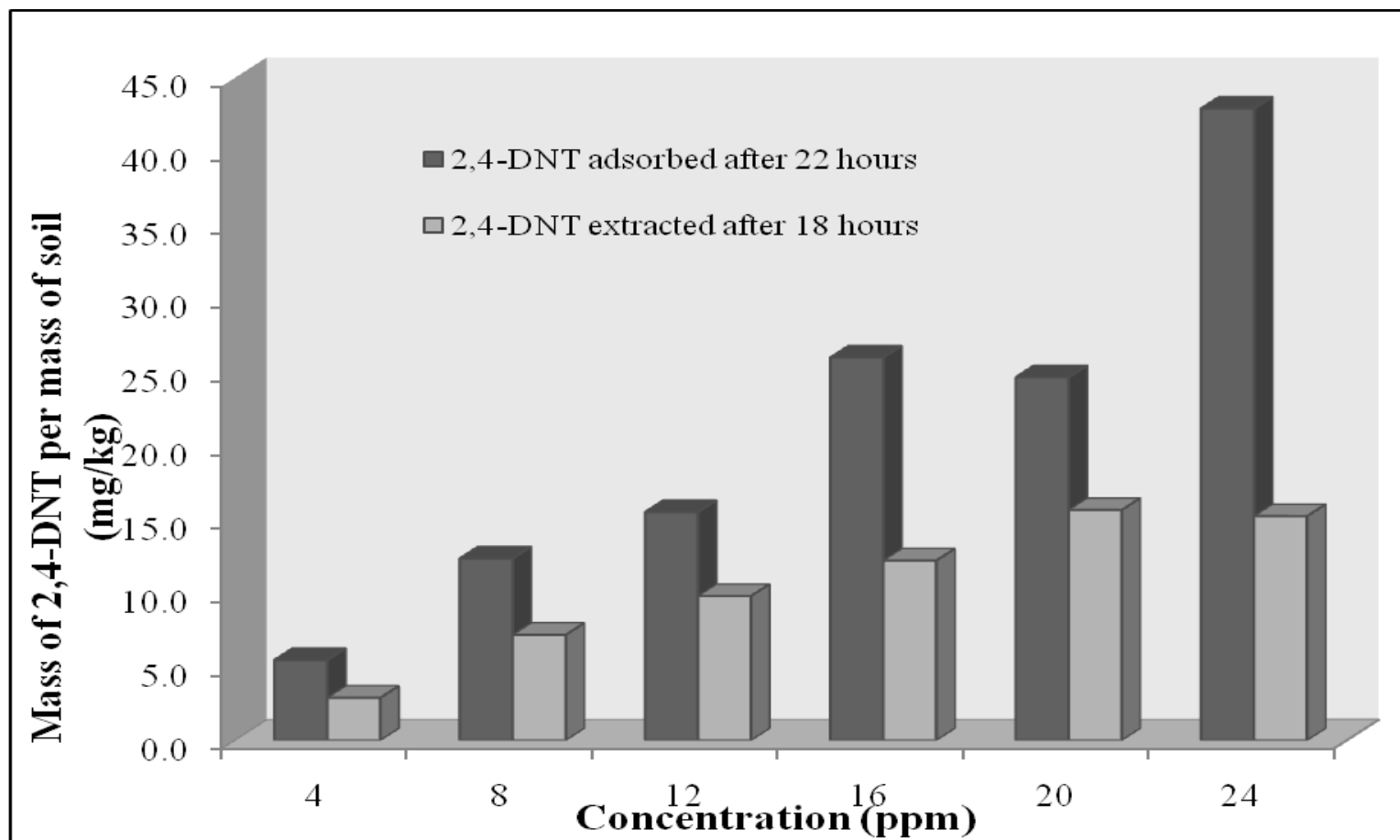


Figure 5.17 Masses of 2,4-DNT adsorbed by topsoil from UPRM and masses that were subsequently removed by acetonitrile extraction.

6. CONCLUSIONS

Adsorption coefficients for 2,4-DNT were obtained using High Performance Liquid Chromatography (HPLC). X-ray diffraction analysis revealed the presence of kaolinite, goethite, hematite, gibbsite, and quartz as clay minerals. The rates of adsorption for soil and clay fraction were similar. An equilibrium between the adsorbed and aqueous phase of 2,4-DNT was achieved between 4-8 hours. After 22 hours of adsorption process on soil and clay fraction, degradation products of 2,4-DNT were not detected.

For soil and clay samples, the Freundlich model was applied, here a linear relationship was observed between the aqueous activity and the mass adsorbed. Adsorption studies performed in soil samples demonstrated a maximum adsorption in the Ap horizon (11.87L/kg) which contains more organic matter (4%). In contrast to soil samples, when the adsorption studies were performed in the clay fractions a tendency to adsorb more in the UPRM was observed (12.73L/kg). These observations allow us to conclude that organic matter contributes significantly to the adsorption process of 2,4-DNT in soil samples rich in organic matter. On the other hand, properties like cation exchange capacity, surface area, type of exchangeable cations and clay mineral present in the samples are going to be important factors in the adsorption of clayey soils.

7. RECOMMENDATIONS

For a better understanding of the interactions between chemical explosives and soil environment, it is recommended to perform 2,6-DNT adsorption studies to compare adsorption coefficients with 2,4-DNT. Also, perform 2,4-DNT adsorption studies with soil organic matter. More research in the mineralogical field is needed to assess the contribution of iron oxides in the adsorption process.

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APPENDIX A
Adsorption Models and Linear Representations

Table A.1 Experimental results for 2,4-DNT interaction with soil from Ap horizon.

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4Ap1	4.00	36.366	36.414	36.390	1.601	16.011	23.989	11.994
8Ap1	8.00	40.757	40.717	40.737	1.788	17.885	62.115	31.058
12Ap1	12.00	62.017	61.950	61.984	2.704	27.043	92.957	46.478
16Ap1	16.00	-	-	-	-	-	-	-
20Ap1	20.00	132.393	132.151	132.272	5.734	57.341	142.659	71.329
24Ap1	24.00	129.325	129.951	129.638	5.621	56.206	183.794	91.897

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4Ap2	4.00	31.538	31.618	31.578	1.394	13.937	26.063	13.032
8Ap2	8.00	31.676	31.675	31.675	1.398	13.979	66.021	33.011
12Ap2	12.00	59.049	59.054	59.051	2.578	25.779	94.221	47.110
16Ap2	16.00	103.280	103.403	103.342	4.487	44.871	115.129	57.565
20Ap2	20.00	114.190	114.456	114.323	4.960	49.604	150.396	75.198
24Ap2	24.00	147.459	147.119	147.289	6.381	63.814	176.186	88.093

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4Ap3	4.00	33.936	34.028	33.982	1.497	14.973	25.027	12.513
8Ap3	8.00	41.381	41.378	41.380	1.816	18.162	61.838	30.919
12Ap3	12.00	60.349	60.403	60.376	2.635	26.350	93.650	46.825
16Ap3	16.00	96.187	96.163	96.175	4.178	41.781	118.219	59.109
20Ap3	20.00	104.213	104.142	104.177	4.523	45.231	154.769	77.385
24Ap3	24.00	-	-	-	-	-	-	-

Table A.2 2,4-DNT concentrations at equilibrium for three replicates, average concentration, and standard deviation for 2,4-DNT interactions with soil from Ap horizon.

Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Average concentration at equilibrium (µg/mL)	Standard Deviation
1.601	1.394	1.497	1.497	0.104
1.788	1.398	1.816	1.668	0.234
2.704	2.578	2.635	2.639	0.063
-	4.487	4.178	4.333	0.218
5.734	4.960	4.523	5.073	0.613
5.621	6.381	-	6.001	0.538

Table A.3 Adsorption of 2,4-DNT by soil for three replicates, average adsorption, and standard deviation for 2,4-DNT interactions with soil from Ap horizon.

2,4-DNT adsorbed by topsoil (mg/kg)	2,4-DNT adsorbed by topsoil (mg/kg)	2,4-DNT adsorbed by topsoil (mg/kg)	Average 2,4-DNT adsorbed by topsoil (mg/kg)	Standard Deviation
11.994	13.032	12.513	12.513	0.519
31.058	33.011	30.919	31.662	1.170
46.478	47.110	46.825	46.804	0.316
-	57.565	59.109	58.337	1.092
71.329	75.198	77.385	74.637	3.066
91.897	88.093	-	89.995	2.690

Table A.4 Experimental results for 2,4-DNT interaction with soil from A horizon.

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4A1	4.00	62.5336	63.07504	62.804	2.740	27.397	12.603	6.301
8A1	8.00	116.18393	116.38085	116.282	5.045	50.449	29.551	14.776
12A1	12.00	193.66602	193.9183	193.792	8.386	83.860	36.140	18.070
16A1	16.00	250.8981	251.2244	251.061	10.855	108.546	51.454	25.727
20A1	20.00	335.36316	335.89987	335.632	14.500	145.000	55.000	27.500
24A1	24.00	318.8555	320.83694	319.846	13.820	138.195	101.805	50.902

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4A2	4.00	68.11797	68.1946	68.156	2.970	29.704	10.296	5.148
8A2	8.00	123.87341	123.64568	123.760	5.367	53.672	26.328	13.164
12A2	12.00	205.32855	206.15376	205.741	8.901	89.010	30.990	15.495
16A2	16.00	246.49529	246.61288	246.554	10.660	106.603	53.397	26.699
20A2	20.00	323.1947	323.65759	323.426	13.974	139.739	60.261	30.131
24A2	24.00	352.86365	354.18637	353.525	15.271	152.713	87.287	43.644

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4A3	4.00	68.46176	68.56118	68.511	2.986	29.857	10.143	5.071
8A3	8.00	124.92488	125.1105	125.018	5.421	54.214	25.786	12.893
12A3	12.00	197.36223	198.39584	197.879	8.562	85.621	34.379	17.189
16A3	16.00	254.66309	255.60013	255.132	11.030	110.300	49.700	24.850
20A3	20.00	330.79749	330.72479	330.761	14.290	142.900	57.100	28.550
24A3	24.00	335.10178	335.65833	335.380	14.489	144.891	95.109	47.554

Table A.5 2,4-DNT concentrations at equilibrium for three replicates, average concentration, and standard deviation for 2,4-DNT interactions with soil from A horizon.

Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Average concentration at equilibrium (µg/mL)	Standard Deviation
2.740	2.970	2.986	2.899	0.138
5.045	5.367	5.421	5.278	0.204
8.386	8.901	8.562	8.616	0.262
10.855	10.660	11.030	10.848	0.185
14.500	13.974	14.290	14.255	0.265
13.820	15.271	14.489	14.527	0.727

Table A.6 Adsorption of 2,4-DNT by soil for three replicates, average adsorption, and standard deviation for 2,4-DNT interactions with soil from A horizon.

2,4-DNT adsorbed by topsoil (mg/kg)	2,4-DNT adsorbed by topsoil (mg/kg)	2,4-DNT adsorbed by topsoil (mg/kg)	Average 2,4-DNT adsorbed by topsoil (mg/kg)	Standard Deviation
6.301	5.148	5.071	5.507	0.689
14.776	13.164	12.893	13.611	1.018
18.070	15.495	17.189	16.918	1.309
25.727	26.699	24.850	25.759	0.925
27.500	30.131	28.550	28.727	1.324
50.902	43.644	47.554	47.367	3.633

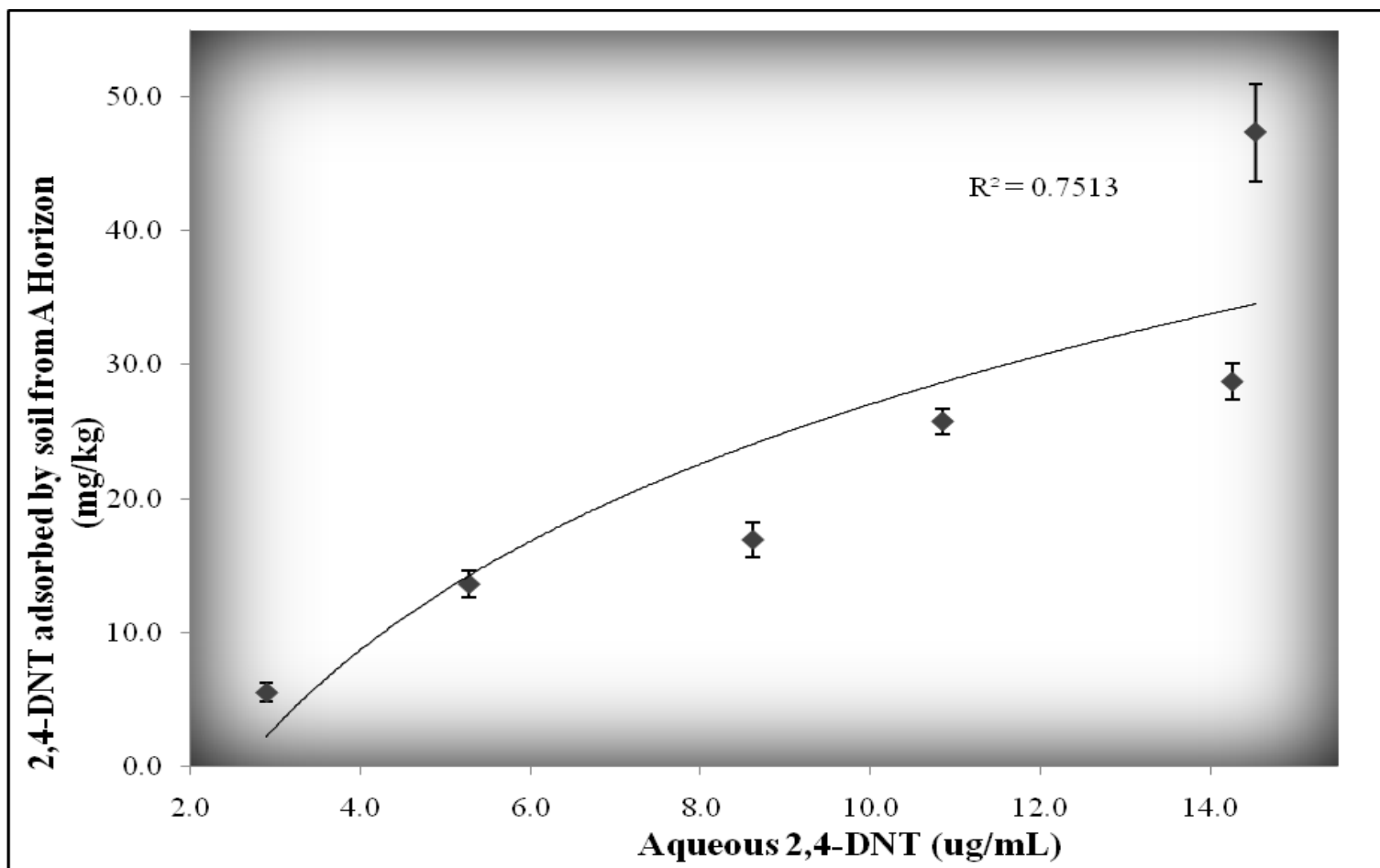


Figure A.1 Adsorption isotherm for 2,4-DNT on soil from A horizon.

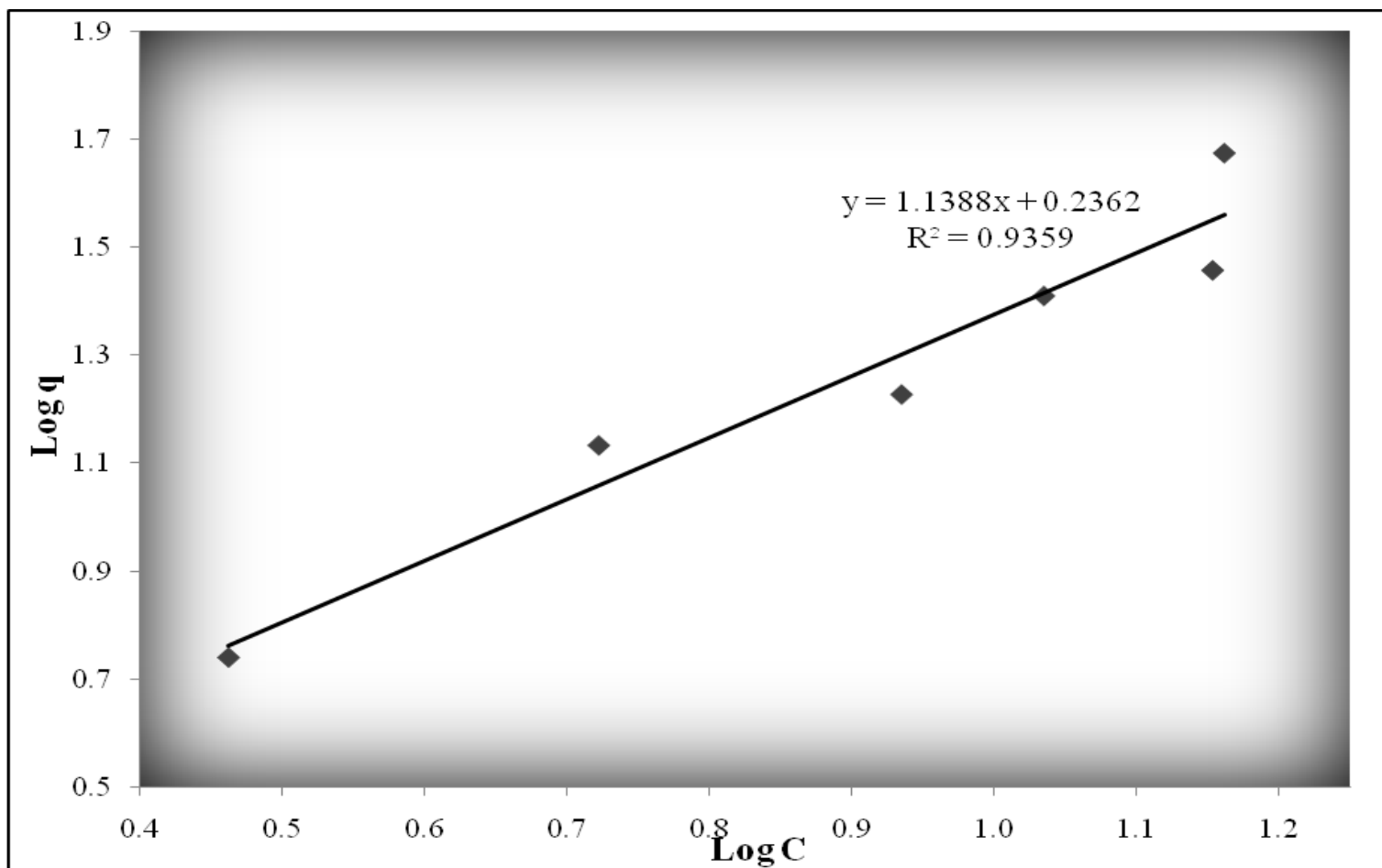


Figure A.2 Freundlich linear isotherm for 2,4-DNT adsorption on soil from A horizon.

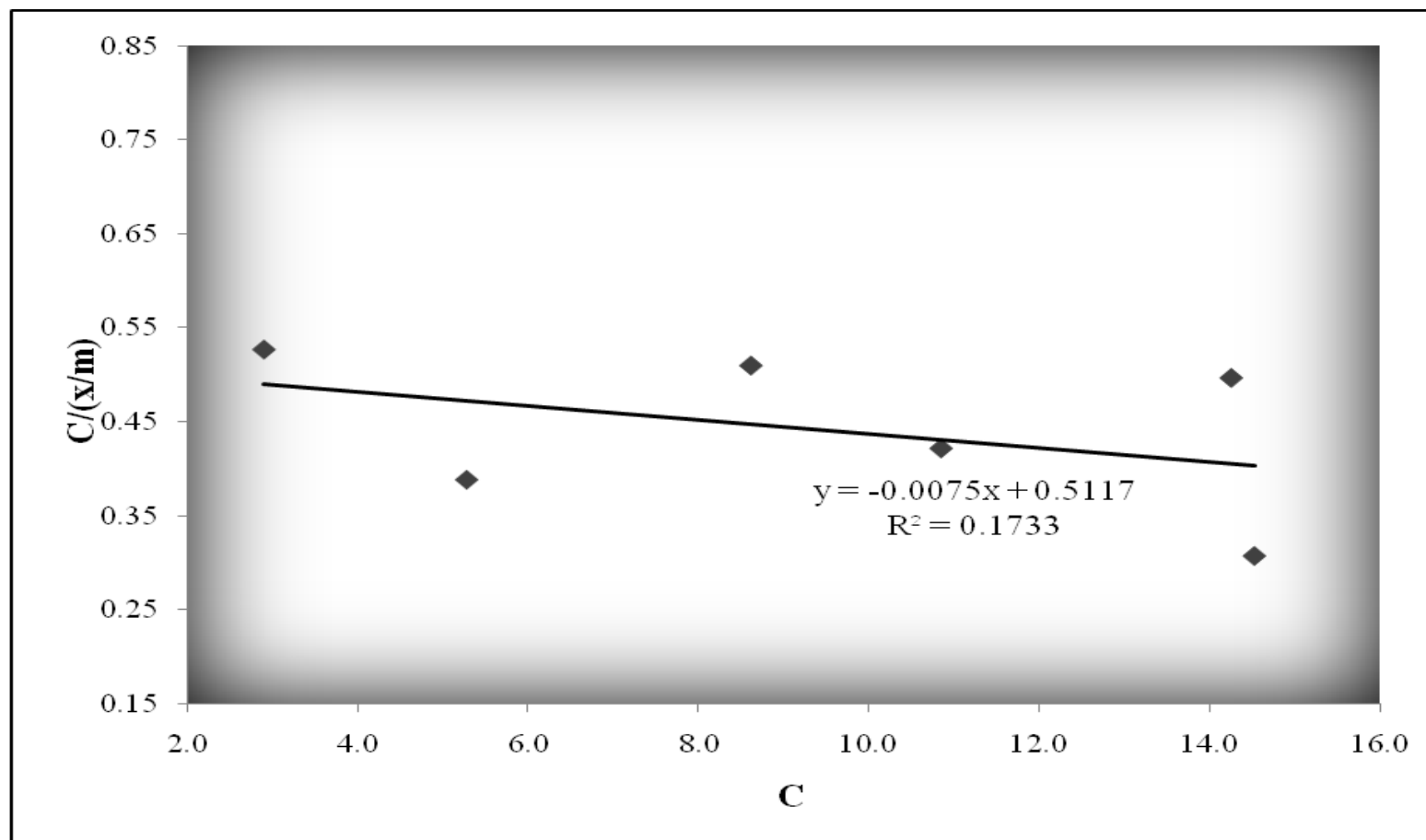


Figure A.3 Langmuir linear isotherm for 2,4-DNT adsorption on soil from A horizon.

Table A.7 Experimental results for 2,4-DNT interaction with soil from UPRM.

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4M1	4.00	66.229	66.488	66.358	2.893	28.929	11.071	5.535
8M1	8.00	125.602	125.556	125.579	5.446	54.456	25.544	12.772
12M1	12.00	206.242	206.408	206.325	8.926	89.262	30.738	15.369
16M1	16.00	249.955	250.990	250.473	10.829	108.292	51.708	25.854
20M1	20.00	347.415	344.131	345.773	14.937	149.371	50.629	25.314
24M1	24.00	353.105	354.462	353.784	15.282	152.824	87.176	43.588

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4M2	4.00	66.521	66.516	66.518	2.900	28.998	11.002	5.501
8M2	8.00	128.843	128.644	128.743	5.582	55.820	24.180	12.090
12M2	12.00	202.521	201.511	202.016	8.740	87.405	32.595	16.298
16M2	16.00	243.345	243.122	243.234	10.517	105.172	54.828	27.414
20M2	20.00	356.842	354.206	355.524	15.357	153.574	46.426	23.213
24M2	24.00	354.509	358.022	356.266	15.389	153.894	86.106	43.053

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by topsoil (mg/kg)
4M3	4.00	67.453	67.243	67.348	2.936	29.355	10.645	5.322
8M3	8.00	128.004	128.515	128.259	5.561	55.612	24.388	12.194
12M3	12.00	208.570	208.907	208.739	9.030	90.302	29.698	14.849
16M3	16.00	255.184	255.987	255.586	11.050	110.496	49.504	24.752
20M3	20.00	345.052	345.090	345.071	14.907	149.069	50.931	25.466
24M3	24.00	359.970	361.081	360.526	15.573	155.730	84.270	42.135

Table A.8 2,4-DNT concentrations at equilibrium for three replicates, average concentration, and standard deviation for 2,4-DNT interactions with soil from UPRM.

Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Average concentration at equilibrium (µg/mL)	Standard Deviation
2.893	2.900	2.936	2.9094	0.0229
5.446	5.582	5.561	5.5296	0.0735
8.926	8.740	9.030	8.8990	0.1468
10.829	10.517	11.050	10.7986	0.2675
14.937	15.357	14.907	15.0671	0.2519
15.282	15.389	15.573	15.4150	0.1470

Table A.9 Adsorption of 2,4-DNT by soil for three replicates, average adsorption, and standard deviation for 2,4-DNT interactions with soil from UPRM.

2,4-DNT adsorbed by topsoil (mg/kg)	2,4-DNT adsorbed by topsoil (mg/kg)	2,4-DNT adsorbed by topsoil (mg/kg)	Average 2,4-DNT adsorbed by topsoil (mg/kg)	Standard Deviation
5.535	5.501	5.322	7.429	0.213
12.772	12.090	12.194	13.421	0.230
15.369	16.298	14.849	22.219	1.726
25.854	27.414	24.752	25.842	1.899
25.314	23.213	25.466	30.147	0.762
43.588	43.053	42.135	39.172	1.473

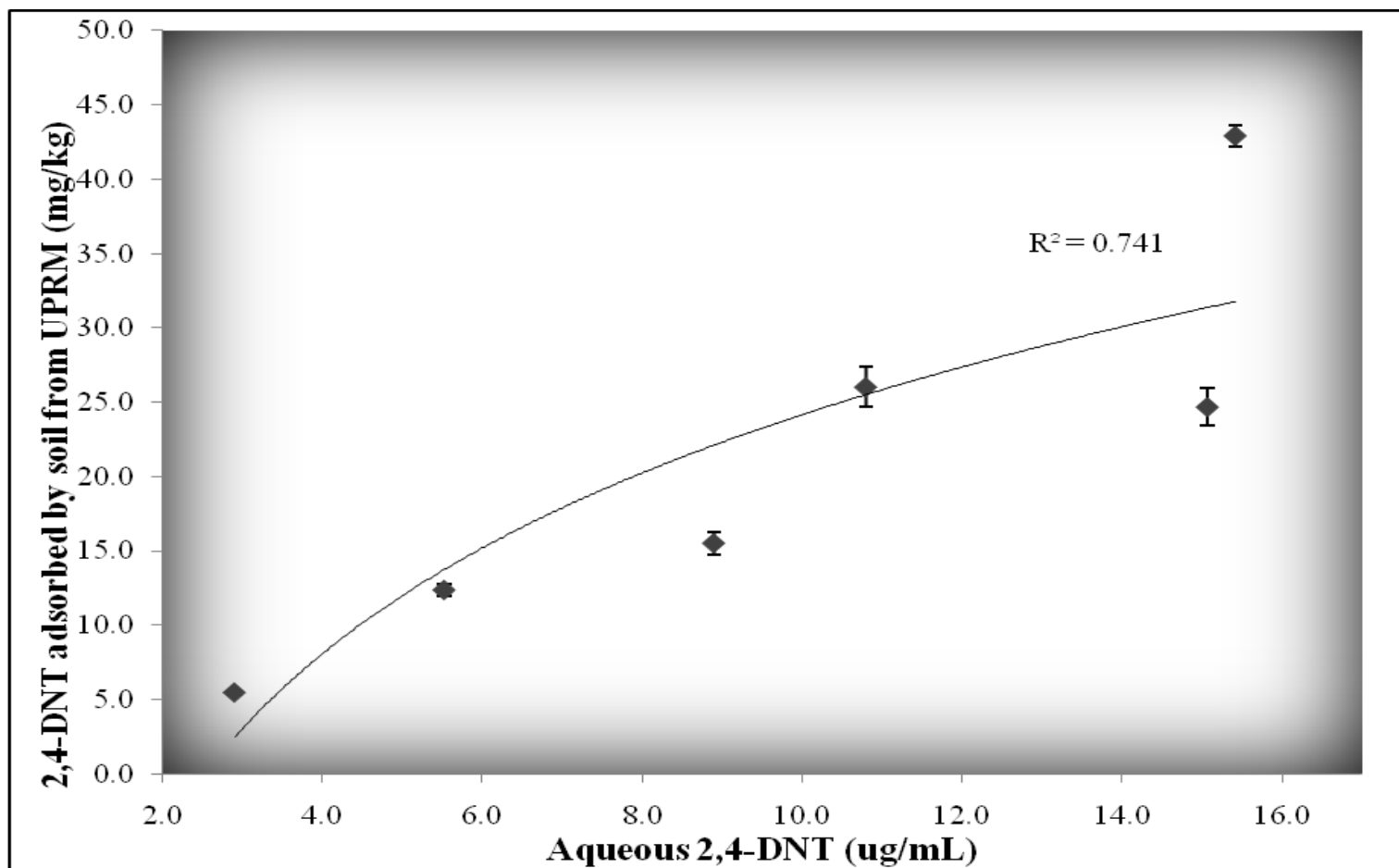


Figure A.4 Adsorption isotherm for 2,4-DNT on soil from UPRM.

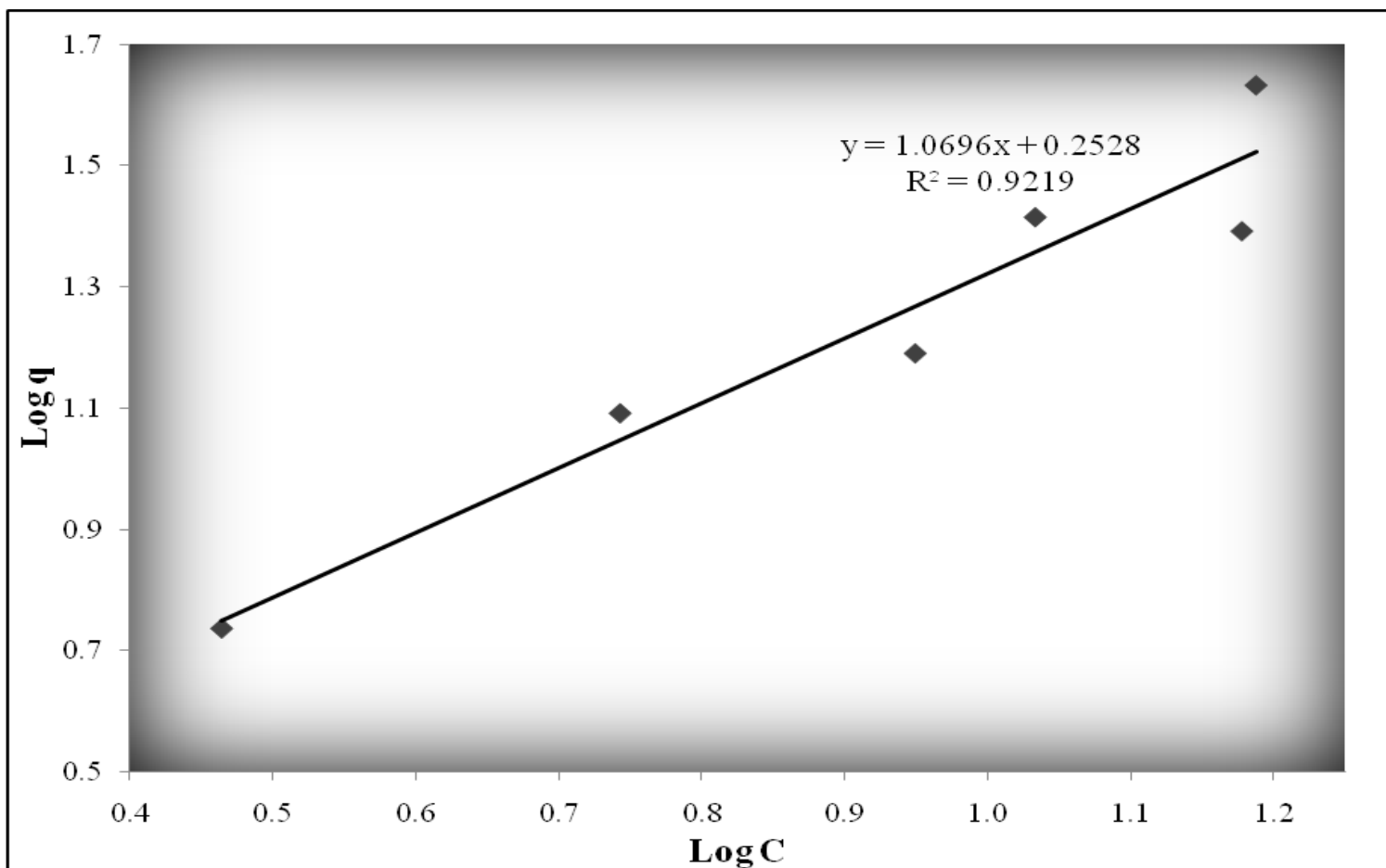


Figure A.5 Freundlich linear representation for 2,4-DNT adsorption on soil from UPRM.

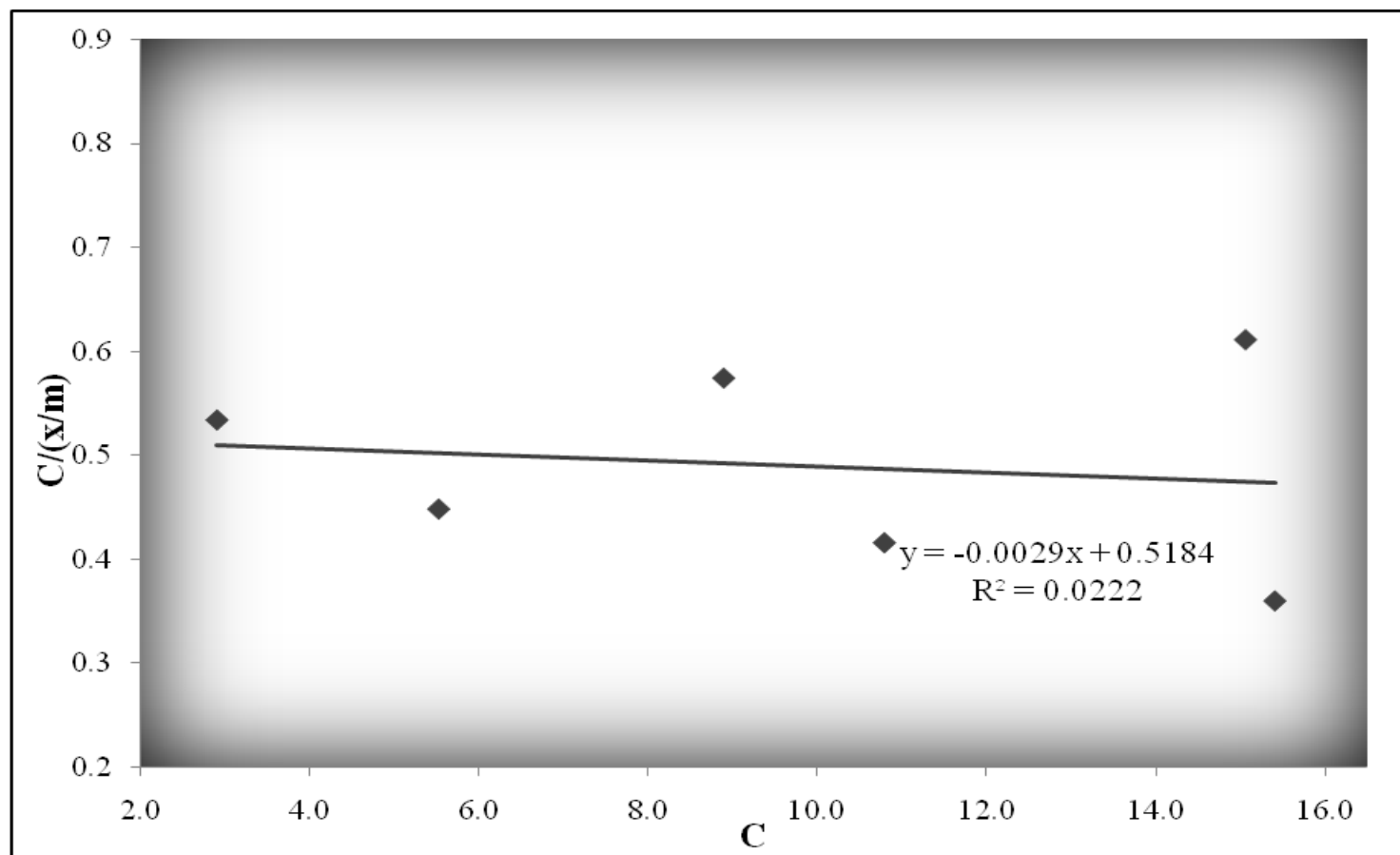


Figure A.6 Langmuir linear isotherm for 2,4-DNT adsorption on soil from UPRM.

Table A.10 Experimental results for 2,4-DNT interaction with the clay fraction from UPRM.

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-M1	4.00	33.091	32.860	32.975	2.936	29.361	10.639	53.167
8A-M1	8.00	74.106	74.137	74.122	4.567	45.666	34.334	171.501
12A-M1	12.00	120.299	120.194	120.246	6.394	63.942	56.058	280.009
16A-M1	16.00	169.499	169.860	169.679	8.353	83.530	76.470	381.207
20A-M1	20.00	227.806	227.900	227.853	10.658	106.581	93.419	466.164
24A-M1	24.00	271.661	271.263	271.462	12.386	123.861	116.139	580.407

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-M2	4.00	33.079	33.049	33.064	2.940	29.397	10.603	52.779
8A-M2	8.00	71.468	71.518	71.493	4.462	44.624	35.376	176.792
12A-M2	12.00	123.827	123.659	123.743	6.533	65.328	54.672	273.225
16A-M2	16.00	168.541	168.669	168.605	8.310	83.104	76.896	383.139
20A-M2	20.00	233.637	233.585	233.611	10.886	108.862	91.138	454.552
24A-M2	24.00	264.036	265.082	264.559	12.113	121.125	118.875	593.779

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-M3	4.00	31.262	31.243	31.252	2.868	28.679	11.321	56.465
8A-M3	8.00	77.045	76.994	77.020	4.681	46.814	33.186	165.270
12A-M3	12.00	119.121	119.381	119.251	6.355	63.548	56.452	281.557
16A-M3	16.00	169.055	169.371	169.213	8.334	83.345	76.655	381.558
20A-M3	20.00	225.541	226.306	225.923	10.582	105.816	94.184	470.683
24A-M3	24.00	267.065	266.763	266.914	12.206	122.059	117.941	588.237

Table A.11 2,4-DNT concentrations at equilibrium for three replicates, average concentration, and standard deviation for 2,4-DNT interactions with the clay fraction from UPRM.

Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Average concentration at equilibrium (µg/mL)	Standard Deviation
2.936	2.940	2.868	2.915	0.040
4.567	4.462	4.681	4.570	0.110
6.394	6.533	6.355	6.427	0.093
8.353	8.310	8.334	8.333	0.021
10.658	10.886	10.582	10.709	0.158
12.386	12.113	12.206	12.235	0.139

Table A.12 Adsorption of 2,4-DNT by soil for three replicates, average adsorption, and standard deviation for 2,4-DNT interactions with the clay fraction from UPRM.

2,4-DNT adsorbed by clay fraction (mg/kg)	2,4-DNT adsorbed by clay fraction (mg/kg)	2,4-DNT adsorbed by clay fraction (mg/kg)	Average 2,4-DNT adsorbed by clay fraction (mg/kg)	Standard Deviation
53.167	52.779	56.465	54.137	2.026
171.501	176.792	165.270	171.187	5.767
280.009	273.225	281.557	278.264	4.432
381.207	383.139	381.558	381.968	1.029
466.164	454.552	470.683	463.800	8.321
580.407	593.779	588.237	587.474	6.719

Table A.13 Experimental results for 2,4-DNT interaction with the clay fraction from Ap horizon.

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-Ap1	4.00	53.282	53.551	53.417	3.746	37.461	2.539	12.662
8A-Ap1	8.00	108.779	109.138	108.958	5.947	59.469	20.531	102.500
12A-Ap1	12.00	160.450	160.542	160.496	7.989	79.891	40.109	199.747
16A-Ap1	16.00	219.929	220.163	220.046	10.349	103.487	56.513	282.140
20A-Ap1	20.00	283.287	282.924	283.106	12.847	128.474	71.526	356.558
24A-Ap1	24.00	332.793	332.736	332.765	14.815	148.152	91.848	458.097

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-Ap2	4.00	52.386	52.525	52.456	3.708	37.080	2.920	14.583
8A-Ap2	8.00	111.690	111.665	111.678	6.055	60.547	19.453	97.266
12A-Ap2	12.00	164.219	164.235	164.227	8.137	81.369	38.631	193.154
16A-Ap2	16.00	214.358	214.400	214.379	10.124	101.242	58.758	293.204
20A-Ap2	20.00	280.647	281.030	280.839	12.758	127.576	72.424	361.396
24A-Ap2	24.00	327.788	327.049	327.419	14.603	146.033	93.967	468.195

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-Ap3	4.00	51.414	51.560	51.487	3.670	36.697	3.303	16.459
8A-Ap3	8.00	109.939	110.642	110.290	6.000	59.997	20.003	99.715
12A-Ap3	12.00	163.134	163.910	163.522	8.109	81.090	38.910	193.775
16A-Ap3	16.00	219.302	218.866	219.084	10.311	103.106	56.894	283.336
20A-Ap3	20.00	281.465	281.576	281.521	12.785	127.846	72.154	360.228
24A-Ap3	24.00	326.502	328.348	327.425	14.604	146.036	93.964	469.586

Table A.14 2,4-DNT concentrations at equilibrium for three replicates, average concentration, and standard deviation for 2,4-DNT interactions with the clay fraction from Ap horizon.

Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Average concentration at equilibrium (µg/mL)	Standard Deviation
3.746	3.708	3.670	3.708	0.038
5.947	6.055	6.000	6.000	0.054
7.989	8.137	8.109	8.078	0.079
10.349	10.124	10.311	10.261	0.120
12.847	12.758	12.785	12.664	0.264
14.815	14.603	14.604	14.674	0.122

Table A.15 Adsorption of 2,4-DNT by soil for three replicates, average adsorption, and standard deviation for 2,4-DNT interactions with the clay fraction from Ap horizon.

2,4-DNT adsorbed by clay fraction (mg/kg)	2,4-DNT adsorbed by clay fraction (mg/kg)	2,4-DNT adsorbed by clay fraction (mg/kg)	Average 2,4-DNT adsorbed by clay fraction (mg/kg)	Standard Deviation
12.662	14.583	16.459	14.568	1.898
102.500	97.266	99.715	99.827	2.619
199.747	193.154	193.775	195.559	3.640
282.140	293.204	283.336	286.227	6.072
356.558	361.396	360.228	365.985	13.277
458.097	468.195	469.586	465.293	6.271

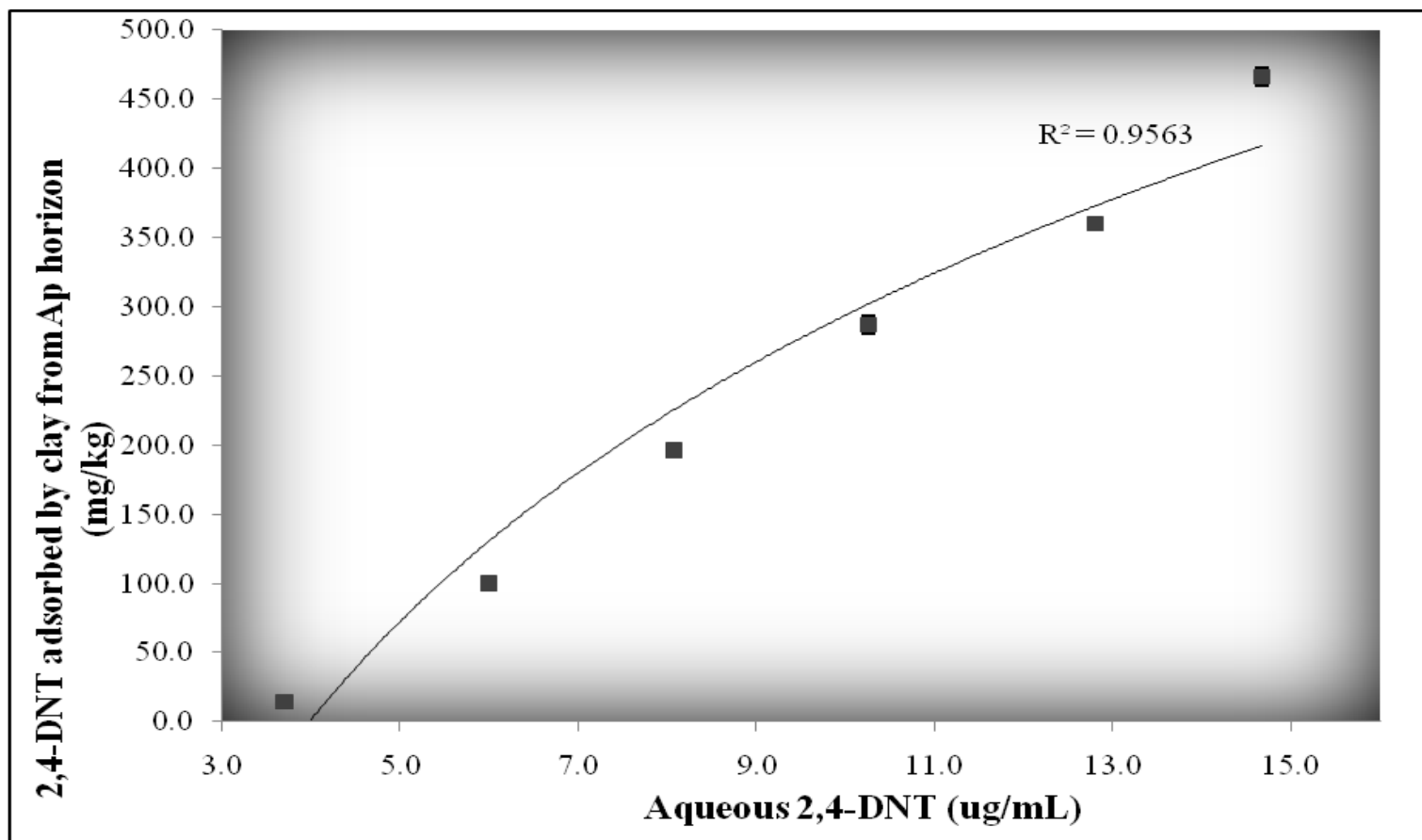


Figure A.7 Adsorption isotherm for 2,4-DNT on clay from Ap horizon.

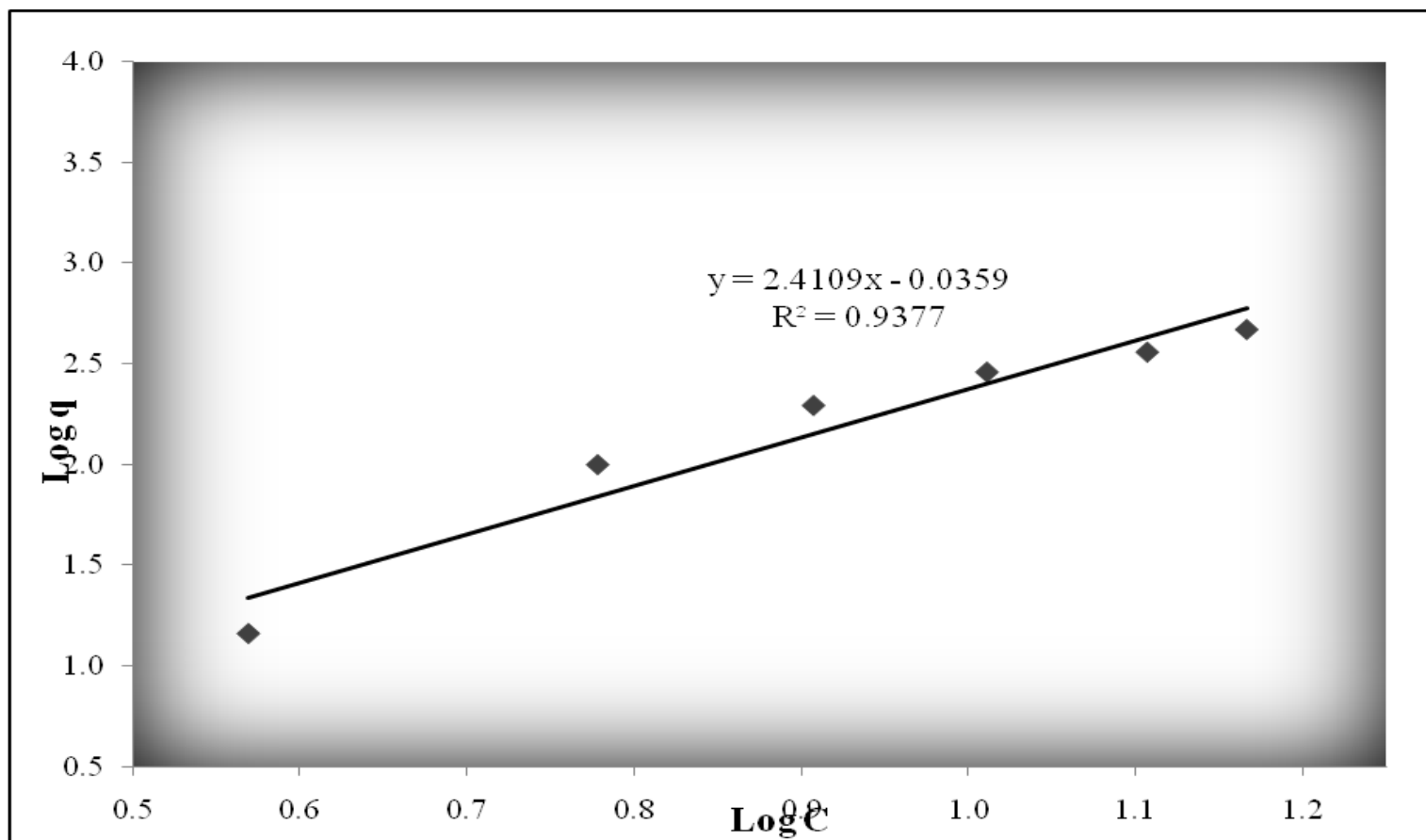


Figure A.8 Freundlich linear isotherm for 2,4-DNT adsorption on clay from Ap horizon.

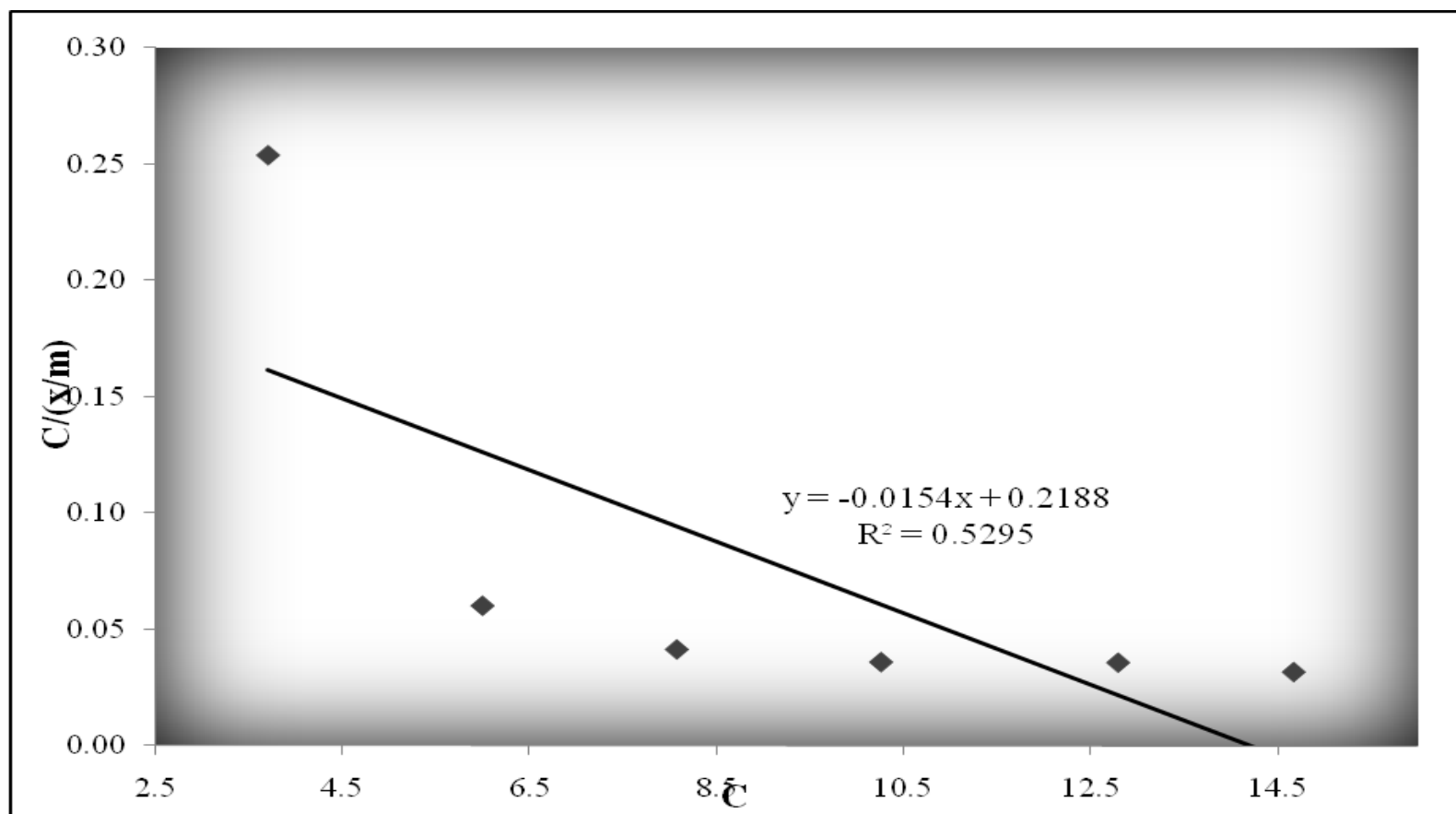


Figure A.9 Langmuir linear isotherm for 2,4-DNT adsorption on clay fraction from Ap horizon.

Table A.16 Experimental results for 2,4-DNT interaction with the clay fraction from A horizon.

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-A1	4.00	51.010	50.952	50.981	3.650	36.496	3.504	17.485
8A-A1	8.00	108.691	108.864	108.777	5.940	59.398	20.602	102.652
12A-A1	12.00	164.201	164.463	164.332	8.141	81.411	38.589	192.561
16A-A1	16.00	211.310	210.157	210.733	9.980	99.797	60.203	300.414
20A-A1	20.00	275.964	275.907	275.936	12.563	125.633	74.367	370.905
24A-A1	24.00	315.668	315.508	315.588	14.135	141.345	98.655	493.273

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-A2	4.00	50.934	50.876	50.905	3.647	36.466	3.534	17.600
8A-A2	8.00	106.095	105.920	106.007	5.830	58.300	21.700	108.337
12A-A2	12.00	162.038	161.889	161.963	8.047	80.472	39.528	197.146
16A-A2	16.00	204.683	204.725	204.704	9.741	97.408	62.592	312.179
20A-A2	20.00	270.355	270.335	270.345	12.342	123.418	76.582	381.384
24A-A2	24.00	313.222	314.201	313.711	14.060	140.602	99.398	495.505

Sample ID	2,4-DNT Initial Concentration (ppm)	Area 1 (mAU)	Area 2 (mAU)	Average Area (mAU)	Concentration at equilibrium (µg/mL)	Mass in aqueous solution (µg)	Adsorbed Mass (µg)	2,4-DNT adsorbed by clay fraction (mg/kg)
4A-A3	4.00	50.798	50.844	50.821	3.643	36.433	3.567	17.782
8A-A3	8.00	107.370	107.361	107.366	5.884	58.838	21.162	105.387
12A-A3	12.00	161.775	162.336	162.056	8.051	80.509	39.491	196.963
16A-A3	16.00	209.910	210.143	210.026	9.952	99.517	60.483	301.210
20A-A3	20.00	269.943	268.064	269.003	12.289	122.886	77.114	385.375
24A-A3	24.00	311.063	311.404	311.234	13.962	139.620	100.380	499.901

Table A.17 2,4-DNT concentrations at equilibrium for three replicates, average concentration, and standard deviation for 2,4-DNT interactions with the clay fraction from A horizon.

Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Concentration at equilibrium (µg/mL)	Average concentration at equilibrium (µg/mL)	Standard Deviation
3.650	3.647	3.643	3.646	0.003
5.940	5.830	5.884	5.885	0.055
8.141	8.047	8.051	8.080	0.053
9.980	9.741	9.952	9.891	0.131
12.563	12.342	12.289	12.398	0.146
14.135	14.060	13.962	14.052	0.087

Table A.18 Adsorption of 2,4-DNT by soil for three replicates, average adsorption, and standard deviation for 2,4-DNT interactions with the clay fraction from A horizon.

2,4-DNT adsorbed by clay fraction (mg/kg)	2,4-DNT adsorbed by clay fraction (mg/kg)	2,4-DNT adsorbed by clay fraction (mg/kg)	Average 2,4-DNT adsorbed by clay fraction (mg/kg)	Standard Deviation
17.485	17.600	17.782	17.622	0.150
102.652	108.337	105.387	105.459	2.843
192.561	197.146	196.963	195.556	2.596
300.414	312.179	301.210	304.601	6.575
370.905	381.384	385.375	379.222	7.473
493.273	495.505	499.901	496.226	3.372

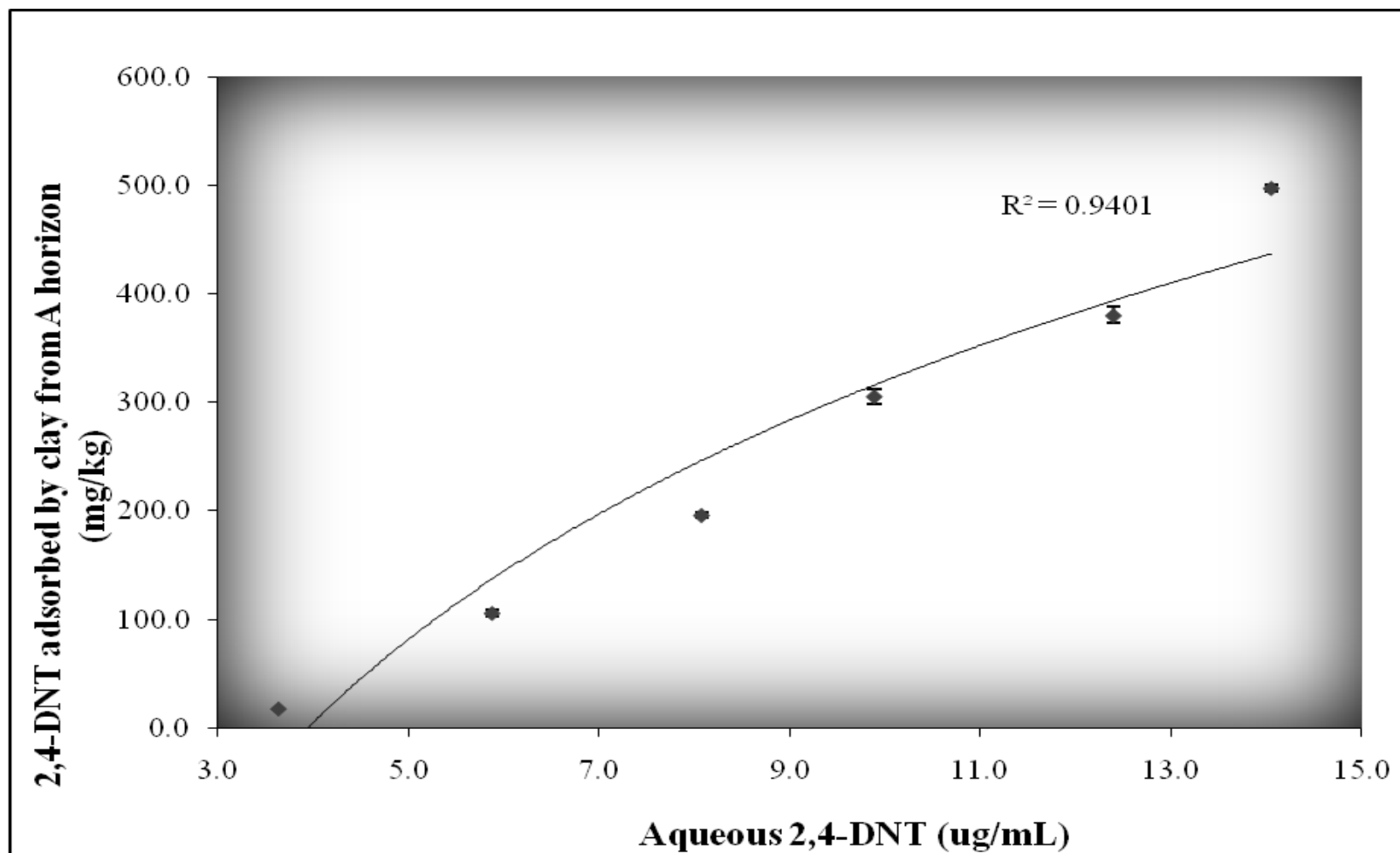


Figure A.10 Adsorption isotherm for 2,4-DNT on clay from A horizon.

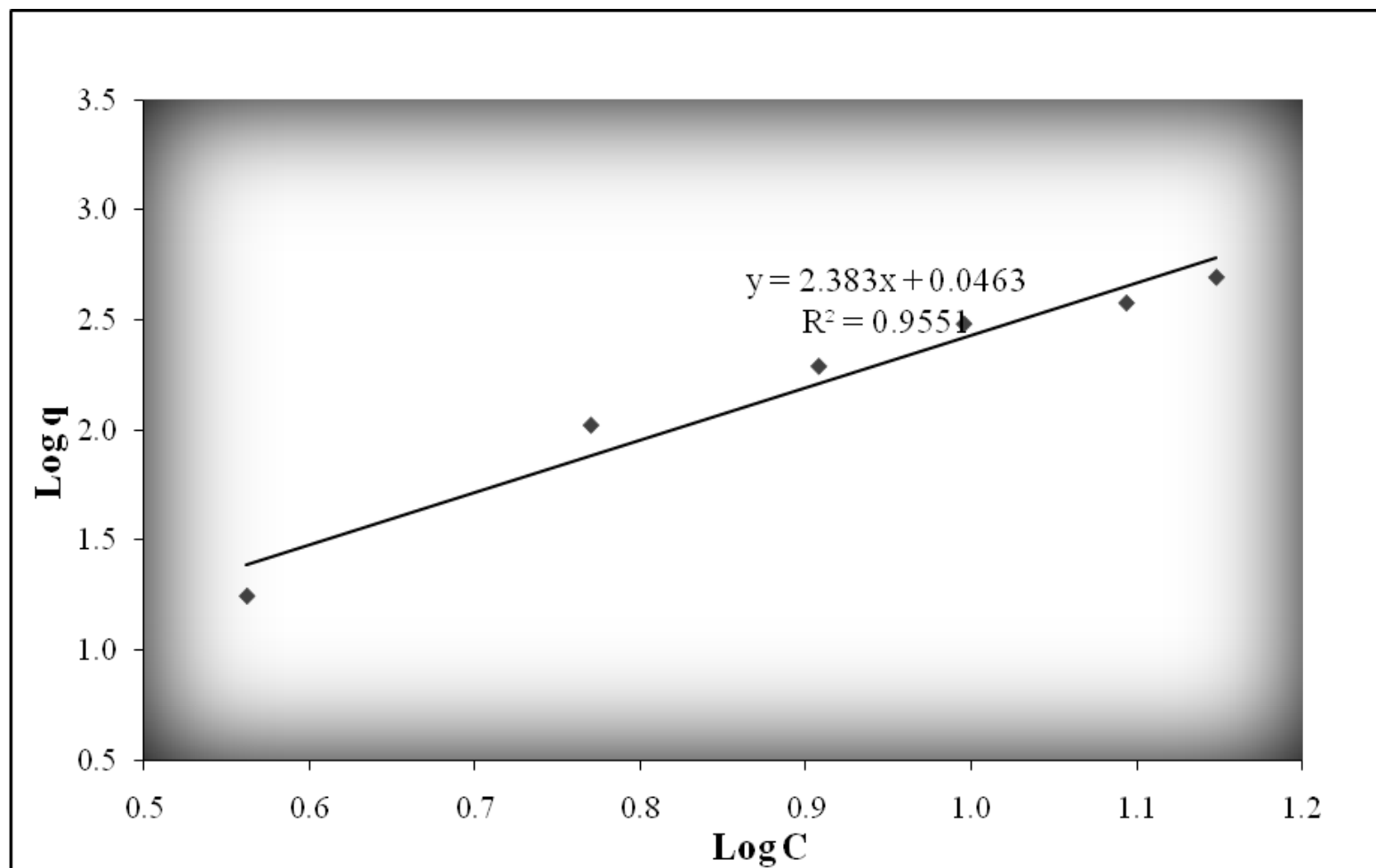


Figure A.11 Freundlich linear isotherm for 2,4-DNT adsorption on clay from A horizon.

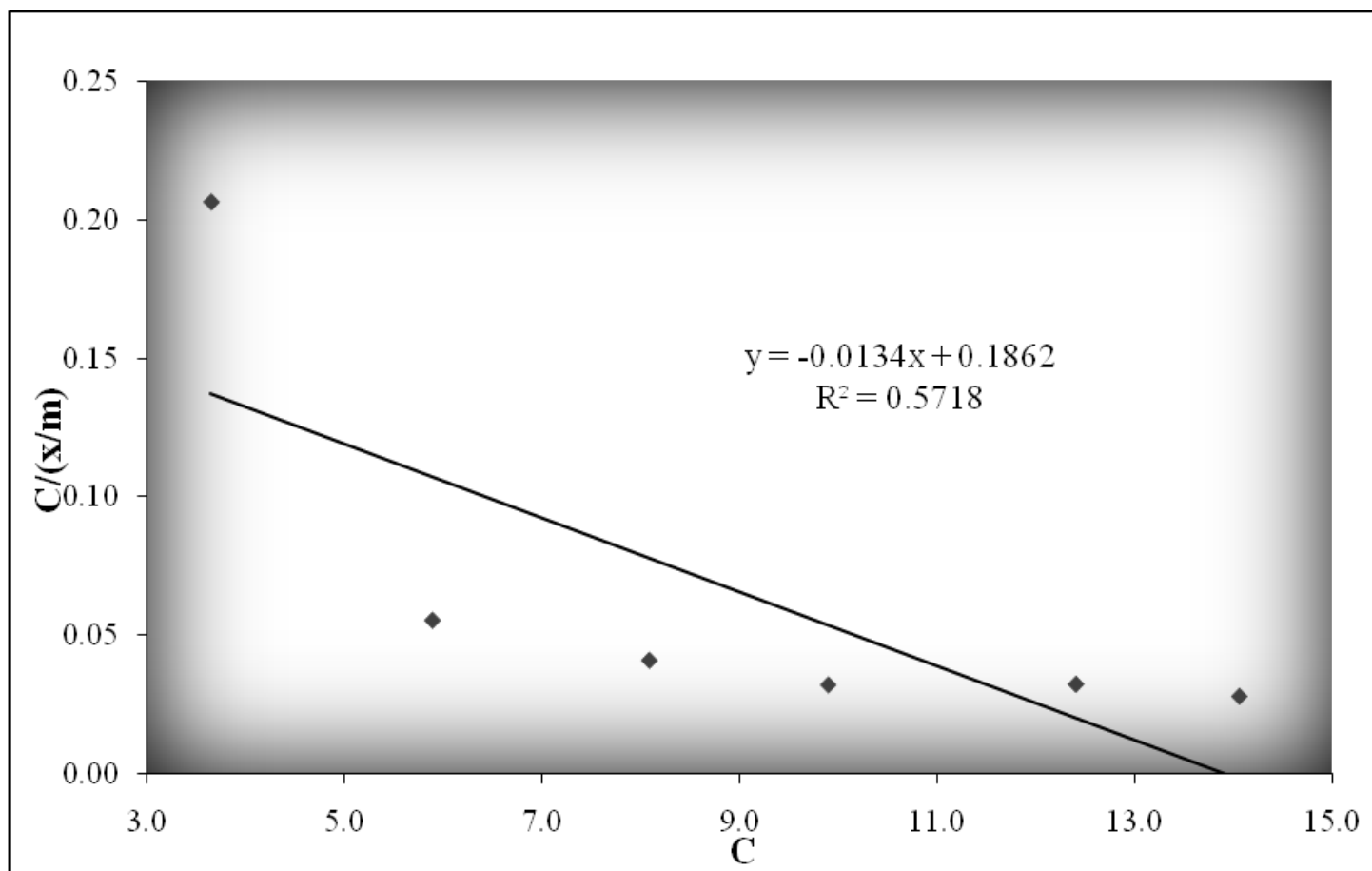


Figure A.12 Langmuir linear isotherm for 2,4-DNT adsorption on clay from A horizon.