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# The Uptake of 2,4-Dichlorophenoxyacetic Acid By An Organic Rich Soil

by

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## ABSTRACT

### The Uptake of 2,4-Dichlorophenoxyacetic Acid By An Organic Rich Soil

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University of Calgary, 1996

This thesis presents a study of the uptake of 2,4-dichlorophenoxyacetic acid (2,4-D) by Armadale soil, and includes a characterization of the soil. The affect of herbicide concentration on its uptake by the soil was examined using a modified batch slurry experiment under acidic solution conditions coupled with a micro-filtration HPLC technique. Short and long term sorption was studied, and interpreted in terms of a two-stage sorption model.

Uptake of a labile, surface sorbed fraction is very rapid and is followed by a slower accumulation of a non-labile sorbed fraction. This rate limiting step is assumed to involve diffusion of the herbicide into the interior of the soil particle. Invoking a rapid equilibrium assumption allows calculation of an experimental equilibrium constant (K = 0.0441 +/- 0.0028) for the labile uptake and the rate constant ($k_3$ = (3.1 +/- 0.7) E-6 $sec^{-1}$) for the non-labile uptake. The non-labile fraction is seen to have a definite binding capacity equal to 0.0321 +/- 0.0001 μmol 2,4-D / g soil No binding capacity was observed for the labile fraction.

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# CHAPTER 1
# INTRODUCTION

## 1-1. Sorption of Organic Chemicals by Soil

The use of agricultural chemicals has become widespread over the past several decades, and while leading to increased crop production their use has not been free from negative impact on the environment. Understanding the behaviour of these pesticides in a soil environment in terms of sorption into soil material allows better prediction of availability for uptake by plants, bio-degradation and the potential mobility of these chemicals. Migration of these pesticides from the area of application into surrounding waterways and groundwater is an active area of study.

A variety of mathematical models has been developed in order to predict migration behaviour of organic contaminants in soil and ground water systems (PESTFADE, SOILCHEM) (16, 68). All such models contain terms to describe sorption, therefore understanding of the interactions between the organic pollutant (sorbate) and the soil (sorbent) is critical to allow proper predictions of mobility to be made (33, 59).

Soil consists of a complex and variable mixture of organic matter, clay minerals metal oxides and hydroxides. Many sorption studies have focused on idealized systems where only a single component of the soil is used as a sorbent (28, 29, 41, 42, 50, 72, 73). In an effort to better understand contaminant transport in natural systems, study of sorption behaviour of whole soils will be necessary. A detailed study of the adsorption of atrazine on the fulvic acid (acid soluble fraction of soil organic matter) and humic acid (base soluble fraction of soil organic matter) fractions of Laurentian soil demonstrated that while similar trends were observed for the whole soil, the adsorption behaviour of the soil fractions was probably not strictly additive (74).

This chapter will begin with a brief discussion of sorption phenomena including the primary driving forces behind sorption and empirical models used to describe this behaviour. The current level of understanding of the mechanism of contaminant uptake will be explored in detail with particular emphasis on methods used to acquire kinetic data

### 1-1.1 Sorption from Solution

Adsorption can be defined as the accumulation of particles at a surface or interface. The manner in which the particles and the surface/interface become associated can be described by one of two operationally defined categories: physisorption and chemisorption. These terms arise from the abbreviation of physical adsorption and chemical adsorption respectively and are distinguished by the enthalpies of adsorption associated with the different processes.

In soil systems the term "surface" can have many meanings. The outer surface of soil particles will certainly participate in sorption processes, however there exists a significant amount of internal surface area in both clay minerals and organic matter particles. It is believed that these interior surfaces play an important role in the long term sorption behaviour of organic contaminants in soil systems, as will be discussed later.

Adsorption will occur spontaneously when the change in Gibb's free energy (G) for the process is negative: $\Delta G = \Delta H - T\Delta S$. This can occur if the interaction is sufficiently exothermic ($\Delta H$ is negative) or if there is a sufficient increase in disorder in the system ($\Delta S$ is positive) or due to a balance of contributions from both terms.

Forces that determine the change in enthalpy in the system include dispersion and electrostatic forces. The London-van der Waals attractive forces (transient dipole interactions) and coulombic forces fall into this category, as do the attractive forces

behind hydrogen bonding. Complex formation due to charge transfer or ligand exchange can also lead to a decrease in the enthalpy of the system.

Generally speaking, pesticides are hydrophobic compounds or contain hydrophobic portions in their molecular structure. Solvation of hydrophobic compounds by water leads to a net increase in the structure of the solvating water molecules relative to that of the bulk water in the system. Removing the pesticide from an aqueous solution allows this structure to dissipate, resulting in a net increase in the disorder, and therefore in the entropy of the system.

Physisorption is a thermoneutral process that can occur between any two species which may approach each other. The sorbent and sorbate retain their original chemical identity following sorption since they do not undergo any chemical reaction with each other. In physisorption, the sorbate is generally not held as tightly to the surface as in chemisorption. Many organic contaminants of interest may bind to soil through physisorption processes.

Chemisorption is the specific chemical interaction between the sorbate and the sorbent, usually to form a chemical bond between the two species. Chemisorption is characterized by enthalpies of adsorption that are much larger than those found in physisorption, $\Delta H_{ads}$ ~20 kJ mol$^{-}$ for physisorption compared to ~40-800 kJ mol$^{-}$ for chemisorption (2). The kinetics of chemisorption exhibit sizable activation energies. Desorption of either a chemisorbed or a physisorbed species is commonly an activated process.

### 1-1.2 Adsorption Isotherms

Sorption processes can be studied through the construction of adsorption isotherms. An isotherm consists of adsorption behaviour studied as a function of

solution concentration at constant temperature, and can be used to determine parameters such as the equilibrium constants and binding capacities that describe the system. These parameters may then be used within computer models to predict pesticide fate and effect in natural systems.

For an idealized system, limited to monolayer surface coverage from an ideal solution, where all sites are characterized by the same heat of adsorption, the preferred model to describe sorption is the Langmuir isotherm. The chemical system of interest is the equilibrium between solution solute/adsorbed solvent and solution solvent/adsorbed solute. Mathematically, the isotherm is described as:

$$\Theta = \frac{Kc}{1 + Kc} \qquad (1\text{-}1.1)$$

Where $\Theta$ is the fraction of surface covered, K is the equilibrium constant and c is the solution concentration of the solute. This isotherm also makes the assumption that all surface sites are homogeneous, such that one K describes all sorption sites accurately and that these sites are far enough removed from one another that adsorbed species do not interact with each other. If a system obeys Langmuirian behavior, a plot of $\frac{c}{n}$ versus c will produce a straight line according to the following equation:

$$\frac{c}{n} = \frac{c}{n_m} + \frac{1}{n_m K} \qquad (1\text{-}1.2)$$

Where n is the number of moles on the surface for any given concentration, and $n_m$ is the number of moles required for monolayer coverage. Using this equation the value for the equilibrium constant can be obtained.

Another commonly used isotherm for the study of sorption processes in soil is the Freundlich isotherm. The equation of the isotherm is:

$$\Theta = K c^{n} \qquad (1\text{-}1.3)$$

where $\Theta$ is again surface coverage, c is concentration and K and n are empirical parameters which describe sorption capacity and sorption intensity respectively. Since this isotherm is strictly empirical, however, parameters obtained from its use have no thermodynamic significance, although this isotherm has been used in the estimation of activation energies for many systems. (28, 29, 42)

### 1-1.3 Mechanisms of Sorption

Opinion is divided on the matter of the nature of sorptive interactions in soil. Many researchers believe that binding occurs through a partitioning mechanism, where the soil is considered to contain a discrete hydrophobic phase into which the organic contaminant essentially dissolves (13, 14). Others believe that the evidence indicates a mechanism more accurately described as an interaction between the organic contaminant and a specific site on (or in) the soil surface (7, 27, 46, 49, 54, 72, 73, 74).

The partition model, most popular for organic contaminants with low water solubility, is based on three postulates. First, it is assumed that the soil contains a physically separate organic phase into which the contaminant may dissolve. This separate organic phase is believed to consist primarily of humic substances or soil organic matter. Second, it is believed that any interaction between this second physical phase and the organic contaminant is non-specific, and best described as a non-localized solute-solvent interaction. The third postulate predicts that distribution of the organic contaminant in a soil water system is governed by the relatively low entropy of solution of a non-polar molecule in water so that the transfer to the organic phase leads to an entropy increase greater than the entropy of mixing. Systems described by the partition model can be characterized by a distribution coefficient, $K_d$.

The specific site binding model contrasts directly with the second postulate of the partition model, and proposes that binding between organic contaminants and soil particles arises due to specific interactions between functional groups. These interactions can occur due charge transfer, dipole or induced-dipole, hydrogen bonding or London-van der Waals forces as described earlier, or even through the interaction with hydrophobic sites if they are localized (26, 27, 47, 72, 73, 74).

The specific site model appears to be emerging as the favored model as a result of over a decade of research. Atrazine binding in soil has been well studied by many researchers. The binding between atrazine and humic material has been determined spectroscopically to be due to hydrogen bonding interactions (51), and non-competition between atrazine and its hydrolysis product hydroxy-atrazine has been shown (72, 73, 74). Binding site saturation has also been observed in systems where the aqueous concentrations are low, and surface coverage indicates that only a small fraction of the available carboxyl groups are involved (45, 72, 73, 74). The number of carboxyl groups is a convenient stoichiometric dimension which can be used to provide context for the measurement of binding capacities. Further supporting evidence for the specific site binding model is discussed in depth by Li (45).

### 1-1.4 Two Stage Sorption Phenomena

Originally, methods established to examine sorption processes assumed that the system reached equilibrium within a few hours to a few days (32, 50, 78). This has since been proven incorrect with a number of systems, where it may require weeks or even months to reach "chemical equilibrium" (3, 45, 53, 79). Correct description of equilibrium conditions is necessary in order to determine parameters useful for accurate modeling of contaminant migration.

In discussing non-equilibrium conditions we will exclude phenomena related to transport of the contaminant to the soil surface, although advection and dispersion are important on a field scale to predicting migration. In soil slurry experiments generally used to collect adsorption data the system is well stirred, hence this "physical non-equilibrium" is not observed.

It now appears that sorption processes in soil are at least bimodal, consisting of both a fast and a slow component. The magnitude of the slow fraction has been shown to be non-trivial, and since this fraction tends to be more resistant to desorption, its impact on clean-up procedures is very important. The impact of exposure time on the availability of a contaminant for bio-degradation can be seen in a study using lake sediments exposed to phenanthrene (1). More attention has been given recently to modeling both these short and long term processes.

A general picture has emerged that provides a minimum description of the sorption processes in soil-water systems as follows. The short term sorption process is fast since it occurs at or near the surface of the soil particle, at easily accessible sorption sites. The contaminant molecule comes into contact with the soil and is physisorbed there, making it easily desorbed, or "labile bound" (45). Longer term sorption occurs as the contaminant molecule proceeds to diffuse into interior portions of the soil particle, either along cracks or fissures, between interlayer spacing of clay minerals, or through diffusion across the gel like humic material. Since the contaminant is no longer easily accessed by solvent or biological organisms, it becomes resistant to desorption or degradation. This slow fraction has been labeled "resistant", "recalcitrant", "rate-limiting" and "non-labile" in the literature. We will prefer the term non-labile.

The overall equilibrium can be envisioned as a two stage process, the first a relatively fast process occurring between the solution and the surface of the soil particle

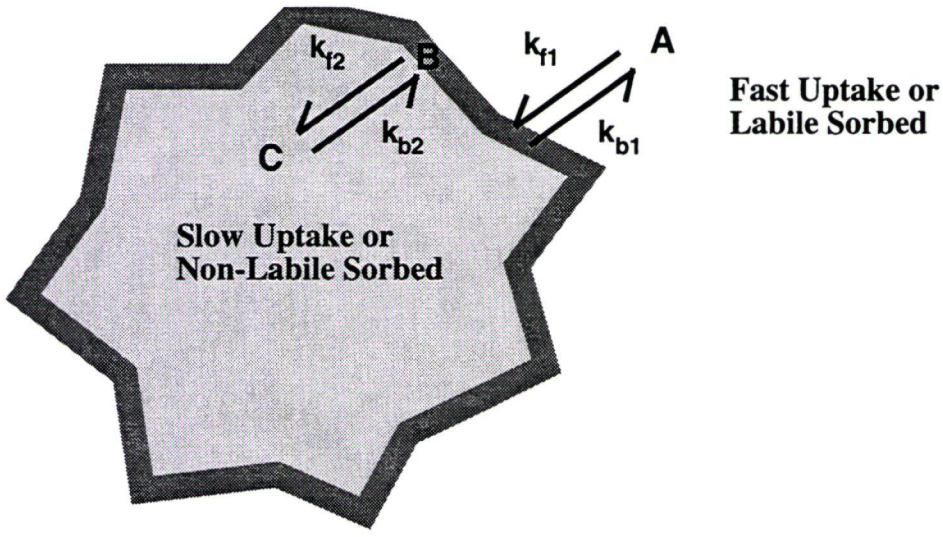


**Fig. 1-1.1, Schematic Representation of Two Stage Uptake**

and the second, a slower equilibration between the surface of the soil and its interior. These processes can be described by Figure 1-1.1 and equation 1-1.4:

$$A \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} B \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} C \qquad (1\text{-}1.4)$$

Speculation about the mechanism of the slow uptake has been prominent in the literature for several decades (3, 11, 39, 40, 42, 44, 59, 66, 78). The rate limiting step is believed to occur within the interior of the soil particle, since in a well mixed batch experiment diffusion through the bulk liquid or across the stagnant liquid film surrounding the particle is likely to be a fast process (8, 53, 59, 67, 75). Diffusion within the soil matrix and internal pores is retarded by attractive interactions between the matrix or pore wall and the solute.

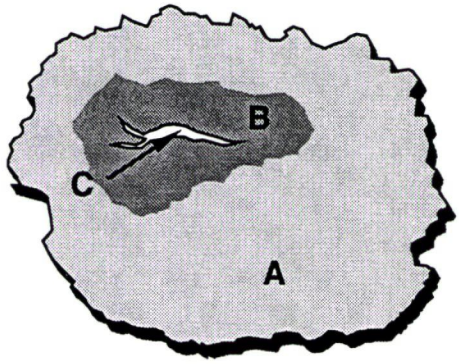


**Fig. 1-1.2, Organic Matter Diffusion Model**

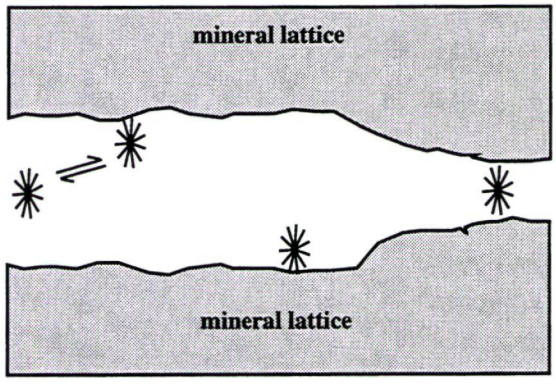


**Fig. 1-1.3, Sorption Retarded Pore Diffusion Model**

Figures 1-1.2 and 1-1.3 Adapted from Ref. (59)

Two possible models for the kinetically slow step are discussed in a recent review by Pignatello (59). The first model assumes that diffusion through natural organic matter (NOM) is the rate limiting step, with the solute passing through zones in NOM possessing varying degrees of crystallinity (Figure 1-1.2). Diffusion through amorphous zones is Fickian in nature, with concentration changes proportional to the square root of time, and generally faster than diffusion through more crystalline regions.

The behaviour of NOM has been shown to be analogous to that of polymers in that the diffusion kinetics of polymers are governed by exposure history, polydispersity, polymer structure, temperature and solute concentration (43, 59, 62, 71). While polymers are a good conceptual framework for NOM they cannot be used exclusively to model the behaviour of contaminants in soil due to the highly variable nature of NOM, its continuous particle distribution and generally unknown exposure history.

A second model describes the slow sorption process as resulting from retardation of the solute in stagnant pore water (Figure 1-1.3). This water has become less mobile due to sorption to pore walls, and acts to slow diffusion of the solute through the soil particle. The porous nature of soil can result from the existence of naturally forming aggregates, from cracks and fissures or from the interlayer spaces of clay minerals. This model applies either to soil containing porous NOM, or to clay minerals where sorption occurs in the interlayer spacing.

### 1-1.5 Techniques Used to Study Sorption Phenomena

The method chosen to study sorptive processes will vary depending on the information sought from the experiment. Generally speaking, most methods can be classed as either batch or flow methods. Batch methods involve combining the soil and solute of interest in an aqueous slurry, and providing continuous agitation either by stirring or shaking. While agitation is necessary to eliminate solution diffusion processes, it can lead to changes in the particle size distribution of the soil due to abrasion and fracturing of soil particles (24, 78). Soil is then separated from the supernatant by centrifugation or filtration, and the supernatant analyzed for free solute. Bound solute can be determined by extraction of the soil using any one of a variety of methods

including Soxhlet extraction, room temperature solvent shake, purge and trap, supercritical $CO_2$, or hot solvent extraction methods (9, 25, 36, 38, 58, 60, 61, 63, 69)

Flow methods generally involve placing the soil in a sample holder and leaching the sample with a solution containing the solute of interest. Breakthrough of this solute is then determined by collection of elution samples at frequent intervals and subsequent analysis. Flow methods can be considerably influenced by mass transfer since the sample is generally not mixed, although stirred flow methods and fluidized bed-reactors have overcome this problem (12, 15, 34, 35, 77).

### 1-1.6 Micro-filtration HPLC Technique

To distinguish between surface sorption and sorption that has occurred due to diffusion of the solute into interior soil regions would be difficult using traditional batch methods since this would require separation of the slurry into soil and supernatant fractions and subsequent extraction prior to analysis. Filtration or centrifugation may act to perturb the surface bound phase making the determination of this phase either difficult or impossible. In order to facilitate study of two-stage sorption phenomena a method combining batch slurry experiments with micro-filtration high performance liquid chromatography (MF-HPLC) has been developed (20, 21, 22). This method has been successfully applied to the analysis of the sorption and hydrolysis of atrazine on a mineral soil and by clay minerals (23, 45) as well as the kinetic uptake of wood preservatives in soil (55). This method offers a one step extraction and analysis of both the surface sorbed species (hereafter referred to as "labile sorbed") and solute that has penetrated into the soil interior (hereafter referred to as "non-labile sorbed"), as well as determination of any degradation products that may occur.

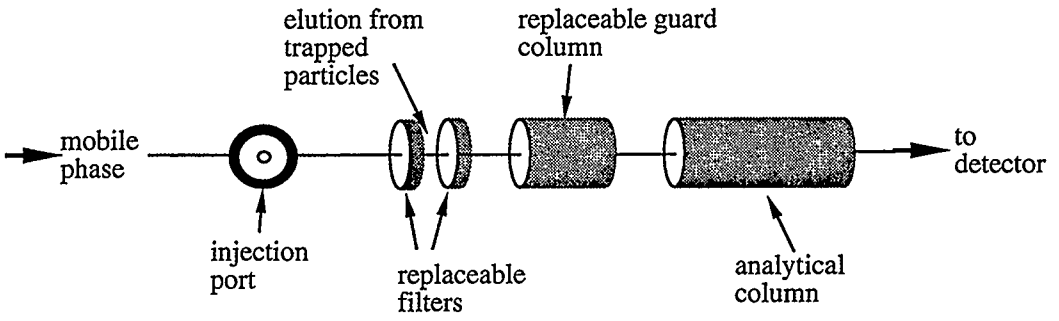


**Figure 1-1.4 Schematic Representation of MF-HPLC On-Line Extraction**

The experiment consists of a well agitated slurry containing soil, water and the solute of interest maintained at a constant temperature. Analyses consist of two types of HPLC injections; one a pre-injection filtration of the slurry to determine free solute in solution, and the second a direct injection of the whole slurry. Desorption of the solute from the soil injected onto the HPLC is accomplished by trapping this soil on an in-line filter such that it is extracted by the mobile phase (Figure 1-1.4). The difference in peak area detected between the slurry sample and the pre-injection filtered sample will give the amount of labile sorbed solute for any given time. Similarly, the amount of non-labile sorbed solute is found from the difference between the initial concentration of solute in the slurry and the amount determined by the slurry injection analysis. The amount of labile and non-labile sorbed solute found by this method can vary depending on the mobile phase of choice, and so should be thought of as operational definitions.

Advantages of the MF-HPLC technique include time and labour savings and limited operator expertise requirements since no sample preparation is required prior to injection save filtration. Analyses can be carried out on a relatively short time scale allowing

kinetic work to be done on heterogeneous samples. Depletion of the sample is minimized since aliquots used for analysis are small. The technique can, however, be prone to large standard deviations between replicate injections mainly due to the small size of the soil sample extracted in each analysis. Highly heterogeneous samples containing either a broad particle size distribution or a variety of particle types will likely be more prone to scatter in the data.

Batch experiments in general make an important underlying assumption, that is that the soil does not participate in any chemical or physical events other than that of binding with the solute. This has been shown to be incorrect in some cases as the soil particles can break apart as a result of continuous agitation (24, 78). The breakdown of the soil over time can have an important consequence on sorption studies since an increase in the number of soil particles in the system means an increase also in the available surface for sorption. Changes in surface area over time can be difficult or impossible to distinguish from slow, long-term sorption.

Certain conditions must also be met by the MF-HPLC technique to ensure results are valid. Mass balance is an essential assumption in order to allow calculation of the labile and non-labile phases. It must be assumed or verified experimentally that any amount not recovered by the in-line extraction is indeed bound by the soil, and not consumed by degradation processes that were not observed

## 1-2. Research Prospectives

Substantial progress has been made in fields relating to behaviour of natural systems, and in particular in the understanding of the interaction processes between soil and anthropogenic pollutants. Our research group has made substantial contributions to the understanding of the binding behaviour between soil and soil components and various

pesticides and metal ions. A strategy has evolved which involves collection of empirical results from a series of systems and extraction of important physicochemical data. Ultimately, a better understanding of molecular level interactions should be achieved, and better predictive modeling using computers should be possible. The research goals of this thesis originated with this strategy in mind, and will focus primarily on the interaction between 2,4-dichlorophenoxyacetic acid (2,4-D) and an organic soil, Armadale. The research includes:

(1) Discussion of a batch experiment combined with the micro-filtration high performance liquid chromatography technique developed previously (20, 21, 22) to determine equilibrium binding capacities for both labile and non-labile phases of 2,4-D bound to Armadale soil.

(2) Examination of assumptions inherent in the technique to be used, including issues such as soil particle stability over time; and that mass balance is achieved.

(3) Discussion of the sorption phenomena observed in the context of the two-stage model currently proposed in the literature, including application of the concepts of labile sorption and non-labile, intraparticle diffusion processes.

# CHAPTER 2
# CHARACTERIZATION OF ARMADALE SOIL

## 2-1. Introduction

Batch methods, as described in the previous chapter, are popular for studying sorption processes in soil. It is important to maintain adequate agitation during these experiments to avoid interference from solution diffusion processes. It has been observed, however, that vigorous stirring of the soil slurry can result in abrasion and eventual breakdown of the soil particles (24, 78). A balance must then be achieved between the need to eliminate solution diffusion and the destructive potential of the mixing action in order to provide useful mechanistic insights into the sorption process while preserving, as much as possible, the natural condition of the soil.

This chapter will focus on the characterization of Armadale soil in terms of its chemical composition, surface area and morphology. Changes occurring in the soil over time due to prolonged shaking will be investigated. Finally, a proposal to avoid problems associated with particle breakdown due to shaking will be made.

## 2-2. Experimental

### 2-2.1 Chemical Analysis

Chemical analysis of the soil was performed by Richard Rogalski of the Department of Geography, University of Calgary. Results obtained include organic carbon, organic matter, elemental analysis, particle size distribution, and cation exchange capacity.

Armadale soil organic matter and organic carbon were determined using a wet oxidation of the soil by potassium dichromate to destroy organic matter (52). Elemental analyses were performed on the barium chloride exchangeable elements, with and

without washing pretreatment using distilled water for calcium, magnesium and sodium, and without washing pretreatment for iron, aluminum and manganese (31). Cation exchange capacity (CEC) was estimated as the sum of the exchangeable elements using the barium chloride procedure without washing pretreatment. Iron, aluminum and manganese content was also determined by ammonium oxalate extraction (52). Particle size distribution was determined by sieving. These results are summarized in Tables 2-3.1 and 2-3.2.

X-ray powder diffraction analysis was done on Armadale soil to identify crystalline minerals present. Percent mineral composition was obtained using the method proposed by Bayliss (5). The results of this analysis are summarized in Figure 2-3.2 and Table 2-3.3.

### 2-2.2 Solution Particle Counting

Changes in slurry solution particle counts over time due to breakdown of soil particles were investigated using a Coulter Counter Model TA II Multichannel Particle Counter equipped with a Coulter Model PCA II Population Accessory (Coulter Electronics, Hialeah, Florida). A 1% NaCl (Fischer ACS grade) electrolyte was prepared using Millipore Milli-Q water, then filtered through 0.22 μm nylon filters (Millipore). Sampling was done in manometer mode at 500 μL, and the aperture opening was 70 μm in diameter. Aliquots of slurry were sampled using a 100 μL Hamilton 710 syringe.

Slurries were sampled over a period of 60 days. Samples were run in duplicate, with each sub-sampled three times to minimize random errors due to sample heterogeneity. Counts were recorded by the instrument 4 times per sub-sample to minimize problems associated with particle settling. Slurry samples were either shaken continuously for 60 days or left to stand undisturbed to investigate the effect of the

solvent alone on particle breakdown. Deionized water was used as the slurry solvent, and the behavior of both Armadale soil and a well characterized mineral soil, GB-843 (Land Resources Research Institute, Agriculture Canada), was investigated. Slurries were prepared by adding 0.5 g soil to 20 mL of solvent and shaking for 2 days or sonicating for 4 hours before acquiring the initial data point.

### 2-2.3 Specific Surface Area

Surface area estimates were obtained using the EGME (ethylene glycol monoethyl ether) adsorption method proposed by Carter et. al. (10). Briefly, soil samples were saturated with aqueous $CaCl_2$, rinsed well and dried at 110°C, then saturated with EGME. Samples were then placed in a vacuum desiccator containing a $CaCl_2$/EGME slurry and allowed to stand for 1 hr. The desiccator was then evacuated and the samples weighed at intervals until constant weight was attained. Surface area due to monolayer coverage of EGME can then be calculated. Surface areas of samples that were oxidized using $H_2O_2$ to remove organic matter were also measured. Oxidation was achieved by placing 8 g of soil in a beaker containing 80 mL deionized water and 5 mL 1M HCl. This slurry was then heated and stirred for 1 hr, then the pH was measured to ensure it was below 5.8. Additional acid and further heating were supplied if needed. Following this, 80 mL of 30% $H_2O_2$ was added and the soil heated to boiling to drive the oxidation. When foaming characteristic of the oxidation process subsided the sample was cooled and 20 mL of 10% $K_2CO_3$ was added to replace carbonates removed during acidification. The soil was then washed over a 0.45 μm nylon filter (Millipore) with 50 mL of distilled water, dried, and analyzed using the EGME method. All reagents were analytical grade and water was purified using a Barnstead Nanopure water system. Organic matter (OM)

and organic carbon (OC) of the soil following oxidation and sonication procedures was also determined as described in section 2-2.1. Results are summarized in Table 2-3.4.

### 2-2.4 Batch Technique

Batch experiments were run in 150 x 25 mm test tubes sealed with parafilm and placed in a wrist action shaker (Burrell, Pittsburgh, PA). Temperature control was achieved with a water bath and an immersion circulator (Cole Parmer). HPLC analyses were performed using either a Waters 501 solvent delivery system coupled to a Perkin Elmer variable wavelength UV-Vis detector (model LC-95) and an IBM 386 PC running Peak Simple software, or a Beckman model 125 solvent delivery system and 166 Variable wavelength UV-Vis detector controlled by System Gold V 8.1 software. A Rheodyne Model 7010-084 injection valve with model 7012 loop filler port was used. The analytical and guard columns chosen were Alltech column cartridges containing Absorbosil 5 μm C-18 reverse phase packing material. Replaceable 2.0 and 0.5 μm stainless steel filter frits were used for in-line filtration. Direct injection of slurries and filtrates was done using disposable Tuberculin BD-1 1cc syringes. Pre-injection filtration was done through 0.45 μm pore size, 13mm diameter PTFE filters (Millipore). The sample loop used was 20 μL in volume and made of stainless steel. Further details about the experiment have been published (21, 22, 45).

The soil used in the batch experiments has been referred to as "Armadale" in the literature (19, 64, 65, 70, 76) but has been more recently reclassified as Mossy Point Soil, and is collected from the Bg1 horizon (48). The soil, collected on Prince Edward Island, has formed on fairly course textured materials in a poorly drained environment, and covers roughly 10% of the province (76). The soil has been classified as an Orthic Gleysol. Where drainage is adequate, this soil is potentially productive for pasture,

forage and tree crops. The soil was sieved to pass a 40 mesh screen and air dried before use.

A standard stock solution of 2,4-dichlorophenoxyacetic acid (2,4-D) was made using the commercially available solid (Aldrich) which was recrystallized from toluene and dissolved in deionized water (Barnstead, Nanopure). Further standards were made from dilution of this stock. No degradation of stock solutions was seen over a period of four months.

The general kinetic procedure involved suspending 0.5 g of soil in 10 mL of deionized water and shaking for 2 days. Following this initial "wetting" period a calculated aliquot of 2,4-D was added and the slurry volume made up to 20 mL. A blank was prepared that included all of the matrix elements except soil, and was run to account for any losses of 2,4-D not due to sorption to soil. Conditions for a typical set of samples are shown in Table 2-2.1. Constant shaking in the wrist action shaker provided adequate agitation, while temperature was controlled at 25°C +/- 0.2°C. Sample volumes injected were at least 400 µL in order to provide adequate rinsing of the loop filler port and the sample loop. Two types of HPLC analyses were done alternately, one a pre-injection filtration using 0.45 µm PTFE filters (Millipore), and the other a post-injection filtration using the in-line 2.0 and 0.5 µm stainless steel filters. Slurry aliquots for post-injection filtration were drawn using the Hamilton 710 syringe, and 400 µL of slurry was injected using a disposable 1 mL syringe. The chosen eluent was made up using HPLC grade acetonitrile and deionized water (3:2), its pH was adjusted to 2.5 using trifluoroacetic acid, and it was degassed with a helium sparge. Mobile phase flow rates were 1.0 mL/minute for all runs, and analyte detection was achieved in direct UV mode at 230 nm. Detector response was linear over 3 orders of magnitude.

Batch experiments were run for a duration of three weeks. All samples were run in duplicate and results averaged. Data were smoothed using a moving window averaging routine. Experimental parameters for the HPLC analysis are summarized in Table 2-2.2.

**Table 2.2-1 Typical Parameters for Batch Slurry Experiments**

| Sample | [2,4-D] (M) | Soil (g) | Water (mL) | 100 ppm 2,4-D (mL) |
|---|---|---|---|---|
| 50-B | 2.365 E-04 | 0.0000 | 10.00 | 10.01 |
| 50-1 | 2.351 E-04 | 0.5052 | 10.05 | 9.94 |
| 50-2 | 2.370 E-04 | 0.5197 | 9.94 | 9.99 |
| 40-B | 1.880 E-04 | 0.0000 | 12.09 | 7.98 |
| 40-1 | 1.895 E-04 | 0.5184 | 11.96 | 8.00 |
| 40-2 | 1.907 E-04 | 0.5185 | 11.94 | 8.07 |
| 30-B | 1.429 E-04 | 0.0000 | 13.88 | 6.01 |
| 30-1 | 1.426 E-04 | 0.5048 | 13.96 | 6.03 |
| 30-2 | 1.409 E-04 | 0.5070 | 14.04 | 5.96 |
| 20-B | 9.461 E-05 | 0.0000 | 15.91 | 3.98 |
| 20-1 | 9.362 E-05 | 0.5019 | 16.08 | 3.97 |
| 20-2 | 9.371 E-05 | 0.5008 | 15.98 | 3.95 |
| 10-B | 4.752 E-05 | 0.0000 | 18.08 | 2.02 |
| 10-1 | 4.827 E-05 | 0.5061 | 17.94 | 2.04 |
| 10-2 | 4.649 E-05 | 0.5173 | 17.88 | 1.95 |

**Table 2-2.2 HPLC Operating Parameters (Waters 501 or Beckman)**

| | |
|---|---|
| Mobile Phase | $CH_3CN$ : $H_2O$ 3:2, pH 2.5 adjusted with trifluoroacetic acid |
| Flow Rate | 1.0 mL / minute |
| Pressure (psi) | 1600 - 2000 (new column) |
| Injection Loop | 20 µL |
| Injection Volume | 400 µL |
| Analytical Column | Alltech Absorbosil C-18 5µm, 250 x 4.6 mm |
| Guard Column | Alltech Absorbosil Guard Column Cartridge |
| Retention Time (min) | ~5.3 |
| Detector | UV at 230 nm |
| Data Acquisition | 386 IBM compatible running Peak Simple or System Gold software |

## 2-3. Results and Discussion

### 2-3.1 Chemical Analysis of Soil

Chemical analysis of the soil revealed that the organic matter and organic carbon content of Armadale soil were not changed by sonication. Exchangeable cations increased with sonication as more surface area of the soil was exposed (see Table 2-3.3). Results are summarized in Table 2-3.1. Particle size distribution results from sieving are summarized in Figure 2-3.1 and Table 2-3.2.

X-ray diffraction revealed that the crystalline mineral composition of the soil consists primarily of quartzite with small amounts of albite and illite. Table 2-3.2 and Figure 2-3.2 summarize these results.

**Table 2-3.1 Chemical Analysis of Armadale Soil**

| Analysis | Whole Armadale- Dried and Sieved | | Sonicated Armadale | |
|---|---|---|---|---|
| | meq / 100 g | RSD % | meq / 100 g | RSD % |
| Ca | 2.008 | 1.2 | 14.03 | 0.4 |
| Ca with washing pretreatment | 1.661 | 0.6 | 12.64 | 1.1 |
| Mg | 0.342 | 1.0 | 0.252 | 0.4 |
| Mg with washing pretreatment | 0.297 | 0.8 | 0.220 | 0.4 |
| Na | 0.146 | 0.2 | 0.136 | 0.1 |
| Na with washing pretreatment | 0.120 | 0.2 | 0.113 | 0.0 |
| K | 1.917 | 0.0 | 0.178 | 3.7 |
| K with washing pretreatment | 0.050 | 0.0 | 0.096 | 0.6 |
| Fe ($BaCl_2$ method) | 0.027 | - | 0.064 | - |
| Al ($BaCl_2$ method) | 2.172 | 1.2 | 1.033 | 1.8 |
| Mn ($BaCl_2$ method) | 0.003 | - | 0.002 | - |
| CEC | 6.615 | - | 15.695 | - |
| | | | | |
| | % | RSD % | % | RSD % |
| % Fe (oxalate method) | 0.22 | 0.2 | 0.09 | 0.2 |
| % Al (oxalate method) | 0.83 | 0.7 | 0.74 | 0.4 |
| % Mn (oxalate method) | 0.00 | - | 0.00 | - |
| Organic Carbon (OC) | 4.70 | - | 4.70 | - |
| Organic Matter (OM) | 8.10 | - | 8.10 | - |

**Table 2-3.2 Particle Size Distribution of Armadale Soil**

| Particle Size (mm) | Cumulative Soil (g) | % Coarser by Weight |
|---|---|---|
| 1.41 | 11.63 | 5.86 |
| 0.71 | 26.91 | 13.57 |
| 0.59 | 31.01 | 15.64 |
| 0.42 | 43.87 | 22.12 |
| 0.25 | 112.96 | 56.96 |
| 0.21 | 147.40 | 74.32 |
| 0.088 | 190.32 | 95.96 |
| 0.044 | 195.16 | 98.62 |
| < 0.044 | 198.33 | - |

**Table 2-3.3 X-Ray Powder Diffraction Analysis of Armadale Soil**

| Mineral | d (A) | Peak Intensity | Corr. Factor | Percentage * |
|---|---|---|---|---|
| Quartz | 3.35 | 260276 | 4.3 | 79.8 |
| Albite | 3.19 | 18907 | 1.7 | 14.6 |
| Illite | 10.1 | 2966 | 0.7 | 5.6 |

* given as percentage of total minerals only.

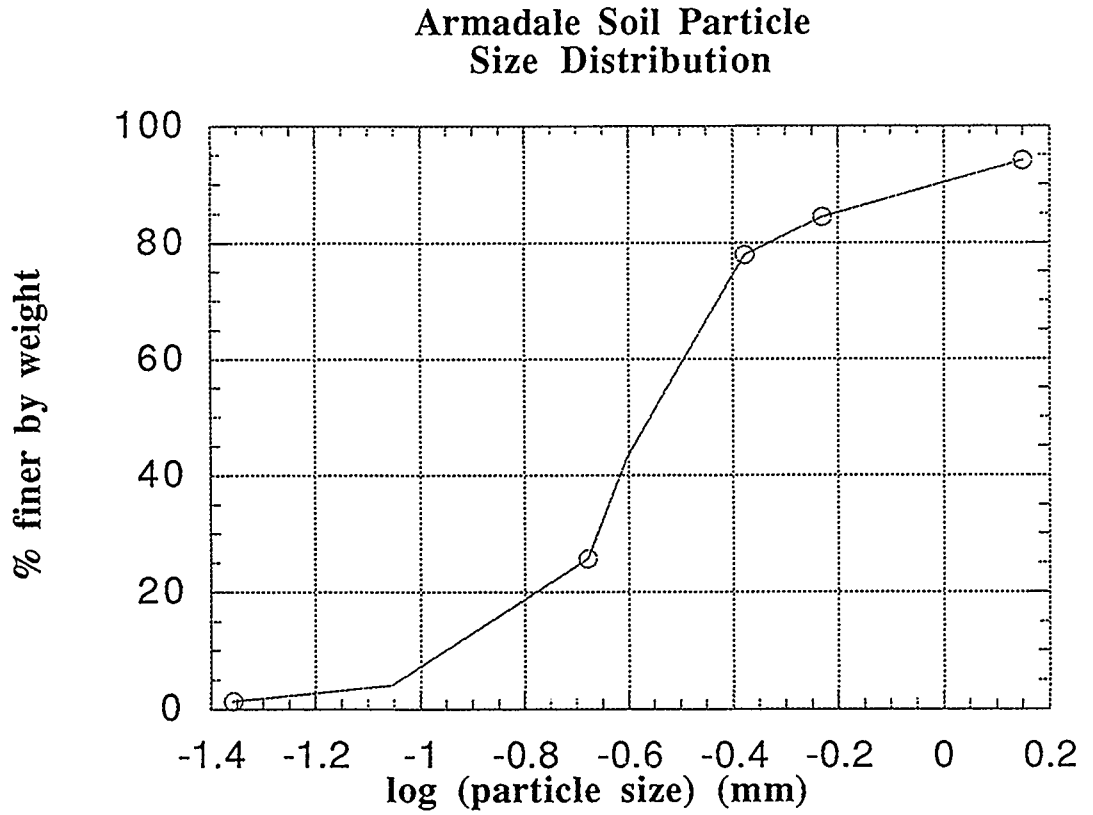


**Figure 2-3.1,** Particle size distribution of Armadale soil found from sieving.

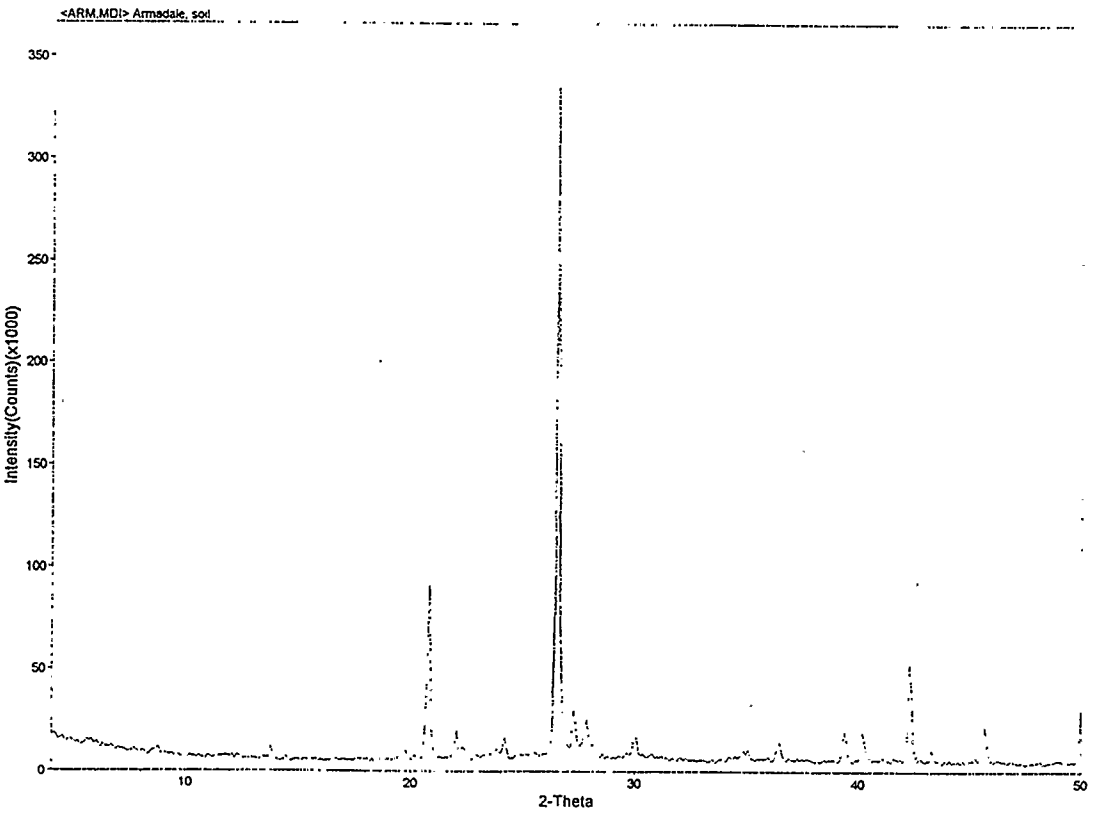


**Figure 2-3.2,** Powder X-ray diffraction spectrum for Armadale soil

### 2-3.2 Surface Area

Results of chemical analysis show that only 42.5% of the total organic matter was destroyed by oxidation using $H_2O_2$. The surface area of Armadale soil tends to increase according to the extent of organic matter or organic carbon present, and doubles following sonication for 4 hours. Results are summarized in Table 2-3.4

Questions have been raised as to the validity of using the EGME method to determine specific surface areas of high organic content soils such as Armadale soil (17). Concerns have been that EGME, due to its polar nature, causes changes to the soil organic matter structure thereby altering its natural surface area. Since many contaminants of interest in soil systems also contain polar functional groups it may be argued that EGME surface areas give a convenient measure of the available surface binding sites in soil. At the very least, the EGME method provides a useful means of comparing different soils.

**Table 2-3.4 Specific Surface Area from EGME Method, Organic Matter and Organic Carbon of Armadale Soil Following Various Pretreatments**

| Soil Pre-Treatment | Specific Surface Area +/- SD ($m^2$ / g) | OM % | OC % |
|---|---|---|---|
| Whole Armadale, dried and sieved | 10.14 +/- 1.93 | 8.10 | 4.70 |
| Sonicated Armadale | 21.08 +/- 2.62 | 8.10 | 4.70 |
| Oxidized Armadale | 7.11 +/- 0.30 | 4.65 | 2.70 |
| Oxidized, Sonicated Armadale | 7.26 +/- 0.58 | 2.75 | 1.60 |

### 2-3.3 Particle Breakdown

Batch experiments were run over a period of three weeks to monitor uptake of both labile and non-labile fractions of 2,4-D. During this time period it was observed that the appearance of the slurry was changing from a relatively clear solution with suspended particles to an opaque, "muddy" solution. It was postulated that this change could be due to the fracturing of soil particles caused by the constant shaking action. The Coulter Counter was chosen as a method of quantifying the number of particles in solution since it offered the advantage that little sample disturbance was necessary other than dilution. Maintaining the particles in an aqueous solution could prevent further breakdown that might occur during drying processes.

Many methods exist which can be used to determine particle size distributions of soils and/or colloidal material, including dynamic light scattering and sedimentation. The apparatus chosen for this study was designed to be used to count very small particles (1.4 to 28 μm range) which are dispersed in an electrolyte solution. The Coulter Counter responds to changes in solution resistance across a small aperture immersed in the electrolyte which result from particles which are drawn through this opening under an applied vacuum. These changes in resistance are recorded as voltage spikes by the instrument, with the size of the spike being proportional to the size of the particle, and the number of spikes being proportional to the number of particles present. While the method offers the advantage of conducting experiments within a solution, it does not offer a wide range of observable particle sizes.

The rate of particle breakdown observed due to shaking in the 1.4 to 28 μm range was much greater for the Armadale soil than for the GB-843 mineral soil (Figure 2-3.3). GB-843 is characterized as a "rock flour" (45), and was formed by the grinding action of glaciers upon Precambrian shield. This soil consists primarily of fine clay particles and

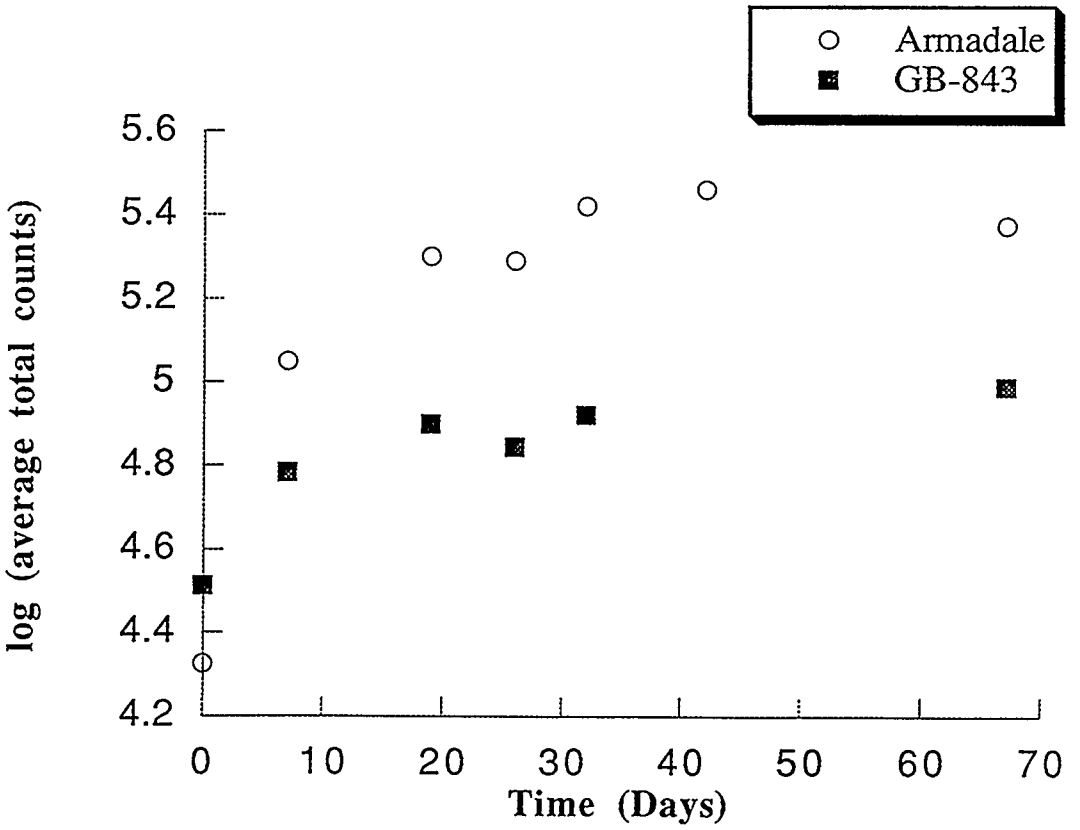


**Figure 2-3.3,** Particle breakdown over time due to shaking as seen by the increase in the total number of particles counted.

contains less than 1% organic carbon (45), providing a moderately stable solid form, resistant to further breakdown. Armadale soil, however is much higher in fragile organic matter as evidenced by the micrograph shown in Figure 2-3.4. This organic matter is highly susceptible to tearing and abrasive action, and can be shown to disintegrate completely as a result of either shaking or ultrasonic treatment (Figures 2-3.5 and 2-3.6 respectively). The overall increase in the number of particles is much greater for the organic soil than for the mineral soil for the same reason.

To determine if the observed particle breakdown was occurring due to shaking or some other phenomena, control samples were run where the soil was shaken for only two days and then allowed to stand. Samples were only shaken just prior to sampling, and their behavior monitored over 49 days under these diffusion conditions. These samples showed no significant changes in particle counts over time (Figure 2-3.7).

### 2-3.4 Effect of Sonication

Armadale soil particles were shown to break down dramatically over time due to shaking. Changes in the number of soil particles necessarily means a change in the available surface area of soil in the slurry, hence results from batch sorption experiments are difficult to interpret under these continuously varying conditions. Two options exist to avoid soil breakdown. The first is to avoid agitation of the slurry, which is unattractive since this introduces solution diffusion effects. The second option, which we will adopt, is to pulverize the soil prior to beginning the sorption study, and thereby avoid any further breakdown.

The effect of shaking after sonication was monitored using Armadale soil which had been sonicated for 4 hours, and then sampled over 60 days of continuous shaking. The first 26 days of this experiment are summarized in Figure 2-3.8, where it can be seen

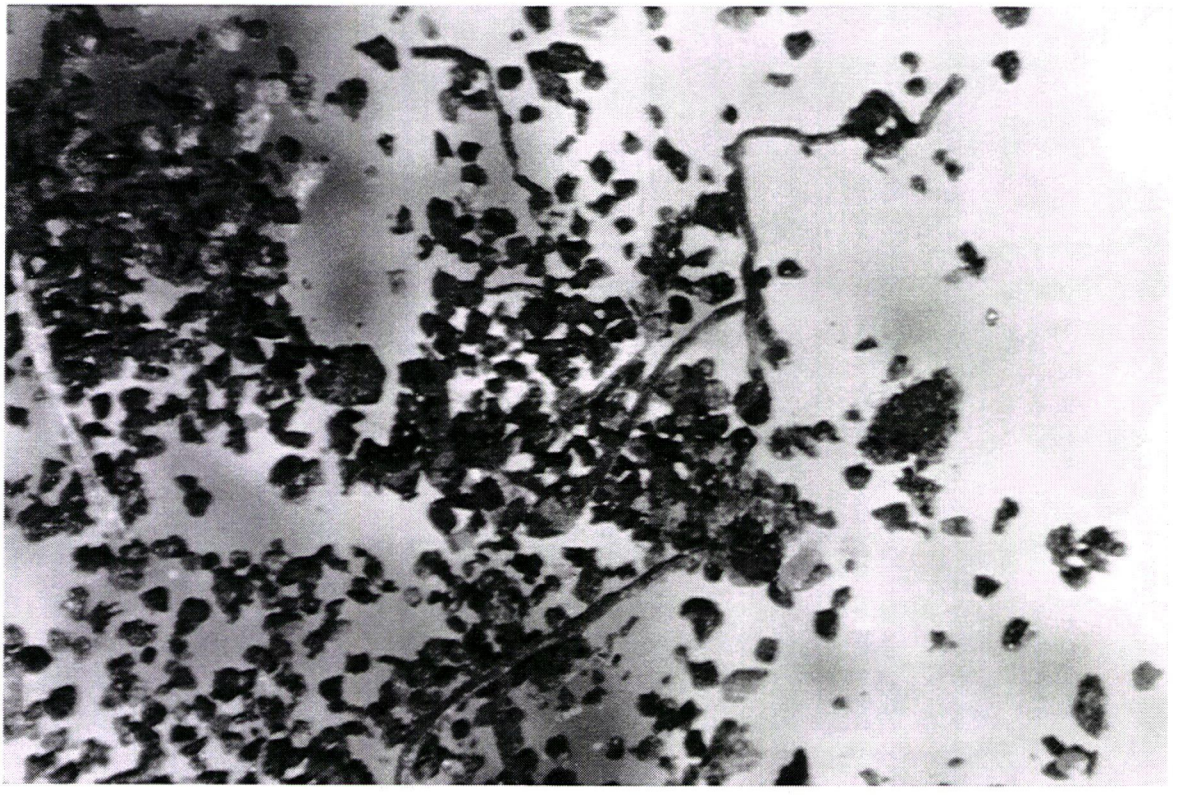

**Figure 2-3.4**, Appearance of Armadale soil after sieving through 40 mesh screen and drying. Magnification ~50x.

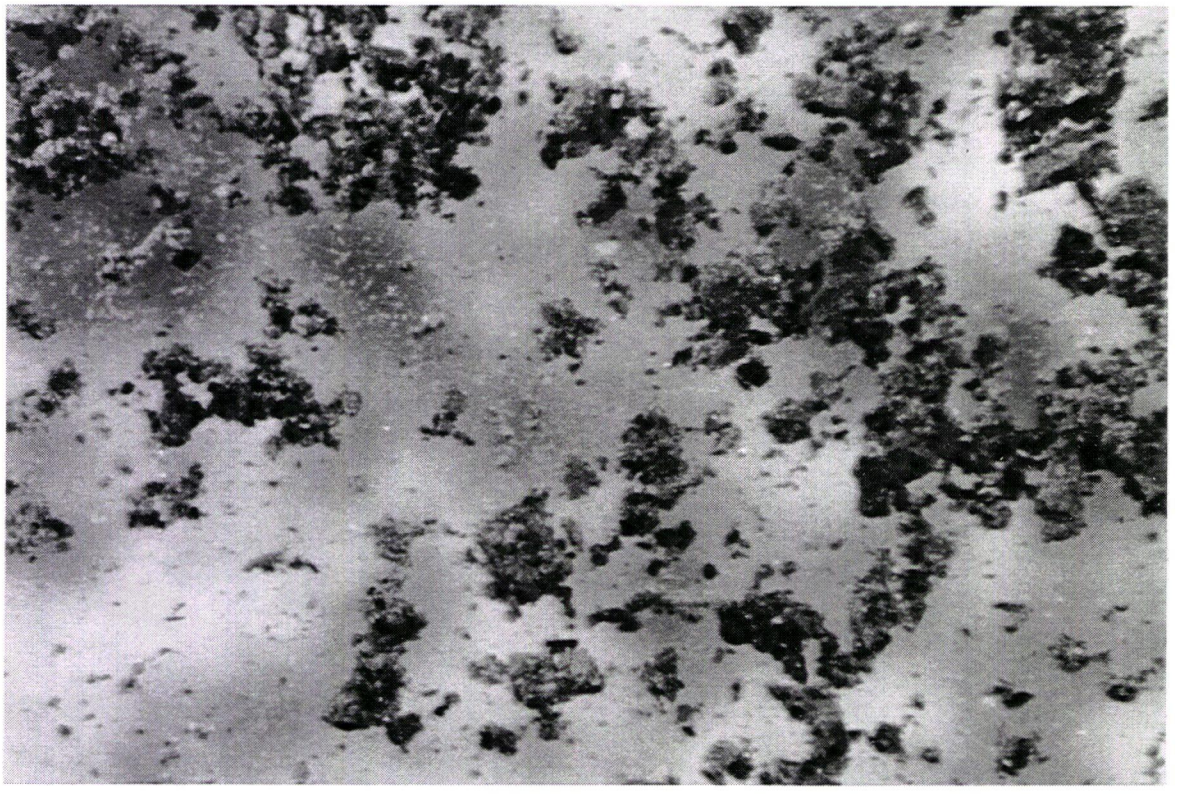

**Figure 2-3.5**, Appearance of Armadale soil following 60 days of continuous shaking in solution. Magnification ~50x.

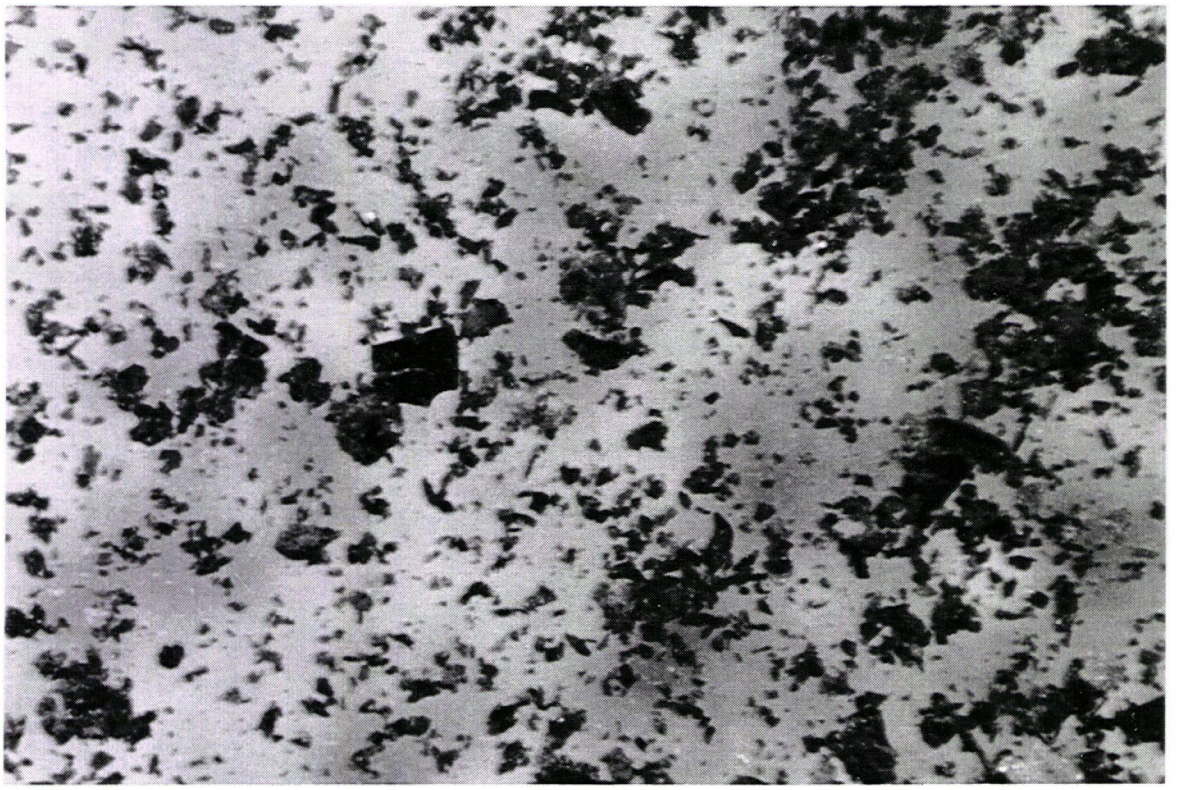

**Figure 2-3.6**, Appearance of Armadale soil following 4 hours in an ultrasound bath. Magnification ~50x.

that the soil particles do not appear to undergo any further breakdown until about 12 days of shaking. Breakdown appears to result in the loss of particles in the 20 μm range and the appearance of particles in the smaller channels. This is more easily seen in Figure 2-3.9 where the difference between final and initial counts is plotted against the particle size. Increases in counts per channel in soil subjected only to shaking appears to result from the breakup of particles larger than 28 μm, while sonicated samples appear to consist primarily of particles smaller than 28 μm prior to shaking. Little change is seen over time for diffusion only runs.

Micrographs taken of the soil suggest that it has a great deal of heterogeneity at the scale of individual soil grains. The effect of sonication on the soil can be seen in Figure 2-3.6, where the soil appears shattered, yet seems to maintain its complex morphology. It has been observed by Nagata et al (57) that decomposition of humic acids can result from sonication of soil materials. This decomposition does not result in total destruction of the humic materials, however, but simply breaks the organic polymer into smaller fragments. It would appear that sonication might act to accelerate the breakdown process without significantly altering the soil chemistry, since organic content of the soil was not changed following sonication. An experiment to explore the possibility of using sonication as a pretreatment for Armadale soil prior to sorption studies will be presented in Chapter 3.

### 2-3.5 Importance of pH Control

Due to the acidic functional group on 2,4-D, the pH of the slurry can vary with the concentration of 2,4-D added. Often a soil can possess enough buffering capacity to maintain constant pH across a wide range of conditions, however, Armadale soil was not capable of providing sufficient buffering strength at higher 2,4-D concentrations. It was

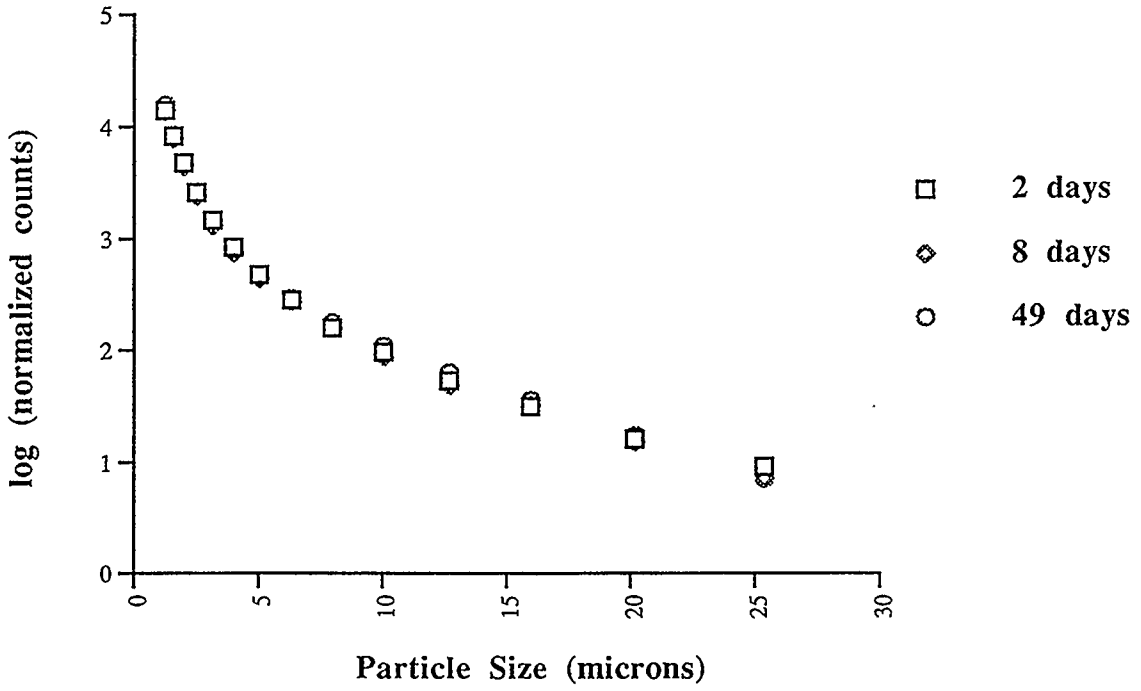


**Figure 2-3.7,** Changes over time in total number of particles counted under diffusion controlled conditions.

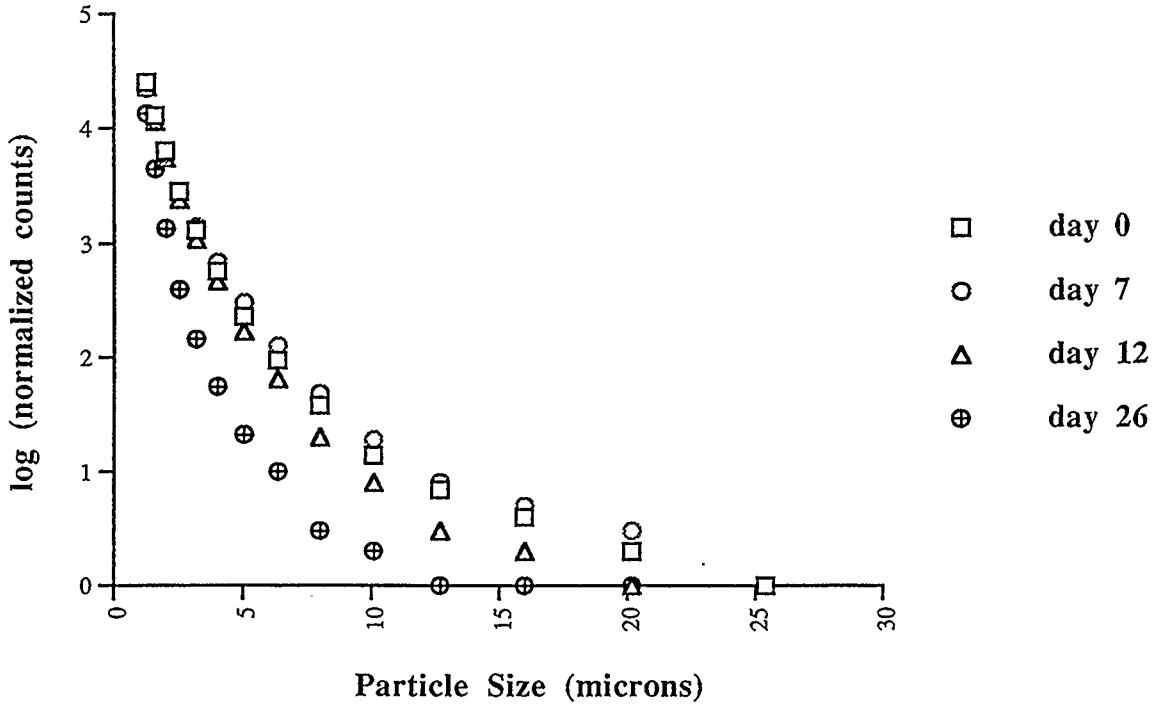


**Figure 2-3.8,** Changes over time in total number of particles counted for Armadale soil which was sonicated 4 hours then shaken continuously.

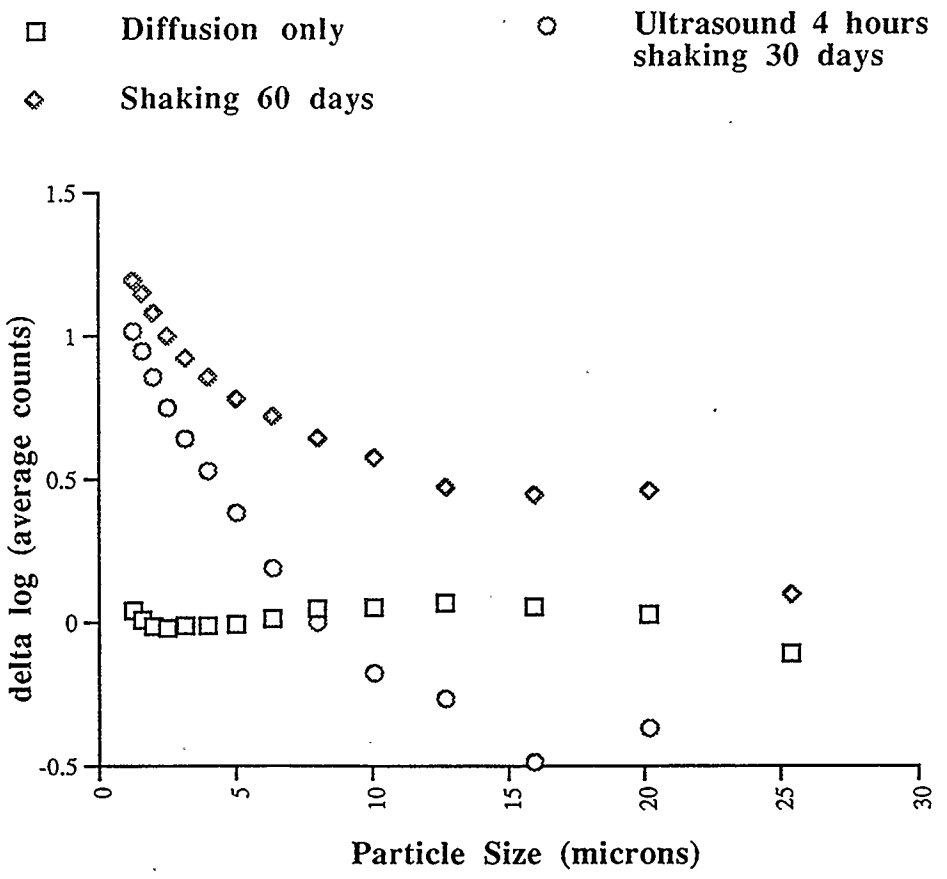


**Figure 2-3.9**, Difference between final and initial number of particles counted due to various treatments (shown here in log scale).

believed that initial concentrations as high as 300 ppm 2,4-D would be needed to completely characterize the adsorption isotherm of 2,4-D on Armadale soil since other authors had identified binding capacities on goethite which were in this range (41). Control of pH is critical in studying the uptake of 2,4-D in any system since it is widely held that the extent of sorption is determined by the amount of protonated 2,4-D available, since the molecular form is preferentially sorbed over the anion (32, 41).

Adding a buffering agent to the soil slurry can complicate interpretation of sorption results, and may lead to competition between 2,4-D and the buffer in the case of organic acids. The simplest solution to this problem appears to be to add sufficient strong acid to hold the pH at a constant, low value. Hydrochloric acid was chosen for this task, since it is not anticipated to compete with 2,4-D for sorption sites. This modification will be implemented in experiments presented in Chapter 3.

## 2-4. Summary

This chapter has focused on the chemical and morphological characterization of Armadale soil, as well as addressed changes that the soil undergoes during a typical batch sorption experiment. As a result of information presented in this chapter, a modification to the MF-HPLC procedure developed by Gamble et al (20, 21, 22) is proposed and will be explored further in Chapter 3. It was shown that:

(1) The soil particles of Armadale soil break down dramatically over time due to the continuous agitation necessary to perform a batch slurry experiment. Overall, an increase of over 1 order of magnitude was seen in the number of particles counted following 60 days of continuous shaking.

(2) Sonication of Armadale soil prior to subjecting the soil to continuous shaking provides a much more stable physical state of the soil with which to perform batch

sorption experiments. Break down of the sonicated soil as a result of prolonged shaking is not seen until after 12 days, and is less severe than in non-sonicated samples.

(3) pH control is critical when studying uptake of an acidic moiety. Since Armadale soil is not capable of buffering the soil slurry it is proposed that a strong acid such as HCl may be added to hold the pH at a constant, low value.

(4) Suggestions that the bulk chemistry of the soil may be maintained following sonication are given in that organic content of the soil remains unchanged following sonication. The appearance of whole Armadale soil and Armadale soil following 4 hours of sonication shows that the heterogeneous morphology of the soil is largely maintained.

Consequently, further investigation of sonication pretreatment for soil to be used in batch slurry experiments is necessary, and will be presented in Chapter 3.

# CHAPTER 3

# 2,4-D UPTAKE BY ARMADALE SOIL

## 3-1. Introduction

2,4-D is used primarily as a broad leaf herbicide to control unwanted brush and trees, but has also found use in the citrus industry to control premature fruit drop in orange and grapefruit groves (18). The mobility of 2,4-D in soil can be considered as moderately high compared to other herbicides, and has been classified as more mobile than atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine], but less mobile than dicamba [3,6-dichloro-2-methoxybenzoic acid] (30). It has been noted that soil organic matter plays a major role in reducing 2,4-D mobility in field conditions (56).

Sorption studies of 2,4-D have been done on many materials and indicate, for kinetically fast uptake at least, that the binding mechanism is likely physisorption with activation energies estimated at 1.6 to 3.5 kcal/mole for humic acids and clays respectively (28, 29, 42). These studies were concerned with total 2,4-D bound by the substrate, however, making no distinction between surface and intraparticle sorbed species. Further, none of these studies examined the behaviour of long term uptake of 2,4-D.

The MF-HPLC technique developed by Gamble et al allows the distinction to be made between labile sorbed species and non-labile sorbed species (20, 21, 22). The model commonly proposed considers the labile fraction to be located on the surface of the sorbent while the non-labile fraction exists in the interior of the soil particle (45, 59). The MF-HPLC method provides more information about the nature and possibly the location of the binding sites and the binding mechanism than traditional sorption methods do, and has not been applied to the study of the uptake of 2,4-D before this work.

This chapter will focus on the presentation of results obtained from the use of a modified MF-HPLC technique to study the uptake of 2,4-D by Armadale soil. Modifications from the original method include sonication of the soil prior to beginning the sorption experiment and control of slurry pH using HCl. Complete extraction of the soil via a Soxhlet method will also be described in order to determine whether mass balance of 2,4-D may be obtained, and in what state the sorbed 2,4-D exists.

## 3-2. Experimental

### 3-2.1 Batch Slurry Experiments

The general kinetic procedure for the batch sorption experiments is as described in Chapter 2, with some important differences. The new procedure involves suspending 0.5 g of soil in 10 mL of 0.02 M HCl, then either shaking for 2 days or sonicating for 4 hours prior to beginning the kinetic study. The pH of the slurry was monitored over the length of the sorption trials to ensure that equilibrium pH was constant for all concentrations of 2,4-D investigated. Conditions for a typical set of samples are shown in Table 3-2.1. All samples were run in triplicate and results averaged.

A preliminary study of the sorption of atrazine on Armadale soil was also performed using the MF-HPLC technique. In this experiment 0.5 g of soil was suspended in 10.0 mL of deionized water and sonicated for 4 hours prior to adding a calculated aliquot of atrazine and beginning the HPLC experiment. Atrazine stock solution was prepared by dissolving the white crystalline solid (donated by Ciba Geigy) in a few milliliters of methanol and then diluting with deionized water. Standards were prepared by serial dilution of the stock and were stored in the dark to prevent photo-degradation. Samples were run in parallel with blanks to ensure that no systematic losses of atrazine were occurring. HPLC operating parameters were the same as given for

**Table 3-2.1 Typical Parameters for pH Controlled Batch Slurry Experiment**

| Sample | Soil (g) | 0.02 M HCl (mL) | Water (mL) | 600 ppm 2,4-D (mL) | Equilibrium pH |
|---|---|---|---|---|---|
| H200-B1 | 0.0000 | 10.00 | 3.89 | 6.74 | 2.03 |
| H200-B2 | 0.0000 | 10.00 | 3.34 | 6.59 | 2.02 |
| H200-1 | 0.4948 | 10.00 | 3.30 | 6.61 | 2.51 |
| H200-2 | 0.5040 | 10.00 | 3.38 | 6.66 | 2.54 |
| H200-3 | 0.5046 | 10.00 | 3.31 | 6.67 | 2.53 |
| H200-4 | 0.5031 | 10.00 | 3.42 | 6.68 | 2.51 |
| H200-5 | 0.4976 | 10.00 | 3.27 | 6.61 | 2.50 |
| H200-6 | 0.5050 | 10.00 | 3.32 | 6.67 | 2.52 |
| H200-7 | 0.5023 | 10.00 | 3.30 | 6.65 | 2.50 |
| H200-8 | 0.5013 | 10.00 | 3.29 | 6.59 | 2.51 |
| H200-9 | 0.5057 | 10.00 | 3.31 | 6.67 | 2.52 |

2,4-D experiments with the exception of the detector wavelength which was set to 254 nm to monitor atrazine. Trials performed at 238 nm did not indicate the appearance of the hydrolysis product hydroxyatrazine over the length of the study.

Labile uptake in batch experiments was determined as the difference in peak area detected between slurry and filtrate injections, that is post-injection and pre-injection filtration experiments respectively. Non-labile uptake was determined as the difference in the amount of 2,4-D recovered in a post-injection filtration trial and the original slurry concentration of 2,4-D. Changes in labile and non-labile 2,4-D uptake by sonicated Armadale soil were plotted against time, and the plateaus for these two species were

determined from the graphs obtained. These plateaus were used to define sorption capacities for both the labile and non-labile components and to construct adsorption isotherms for the labile and non-labile phases of 2,4-D on Armadale soil at 25°C.

### 3-2.2 Soil Extraction

Armadale soil was separated from the slurry at the conclusion of a batch experiment by passing ~20 mL of slurry through a 0.45 μm PTFE filter (Millipore). The soil was dried in an oven at 100°C and the filtrate retained for analysis by HPLC. The volume of filtrate recovered from the filtration was determined from the mass of the filtrate collected and this parameter used to calculate the concentration of the extracted 2,4-D in terms of moles of 2,4-D per L of slurry. The soil was extracted overnight via a Soxhlet technique using approximately 1 g of soil and 150 mL of methanol. The extract was then evaporated to approximately 3 mL using a rotary evaporator and an exact quantity of toluene was added as an internal standard. The extracted 2,4-D, the retained filtrate, a standard solution of toluene in methanol and a standard solution of 2,4-D were then analyzed by HPLC using the same parameters as described for the MF-HPLC technique, and these results compared to the original concentration of 2,4-D in the slurry to determine mass balance. Blank extractions were done using a standard solution of 2,4-D in methanol to determine any losses of 2,4-D to the Soxhlet apparatus.

## 3-3. Results and Discussion

### 3-3.1 Mass Balance Experiments

Extraction of Armadale soil using a Soxhlet technique revealed recoveries of 93.2+/-1.9% of the total 2,4-D in the system while blank extractions yielded recoveries

of 92.8 +/- 3.2%. Some 2,4-D was non-recoverable even in blank trials suggesting that loss to the Soxhlet apparatus occurred. Since the recovery of 2,4-D from exposed soil and from blank trials is not significantly different, it may be concluded that 100% recovery of the non-labile phase as determined by the MF-HPLC technique is possible using this Soxhlet method, and that therefore the 2,4-D is indeed taken up by the soil and is not lost from the slurry by other mechanisms such as degradation. Mass balance may be achieved, thus calculations used in the MF-HPLC technique to determine labile and non-labile fractions are therefore feasible for this system.

### 3-3.2 Adsorption Isotherm of 2,4-D on Armadale Soil

Figures 3-3.1 through 3-3.3 show that uptake of both labile and non-labile phases is rapid for all concentrations of 2,4-D on Armadale soil. The labile phase can been seen immediately after 2,4-D is added to the slurry (Figure 3-3.1), and establishes a rapid equilibrium with the solution phase 2,4-D. Labile phase concentrations do not vary considerably over the duration of the experiment. Non-labile equilibrium is generally attained in 10 days or less as signified by a leveling off in the curve of non-labile sorption versus time. The corresponding data for these experiments are summarized in Tables 3-3.1 through 3-3.3 along with the percent recovered by the MF-HPLC technique.

A summary of the labile and non-labile sorption capacities for each concentration of 2,4-D is given in Table 3-3.4 and presented graphically in Figure 3-3.4. Comparison to literature values is difficult since the amount sorbed reported therein is generally a combination of both the surface and intraparticle sorbed species. Wang et al. (72, 73, 74) and Li (45) examined binding capacities of atrazine on Laurentian humic substances and the mineral soil GB-843 respectively. Their values, obtained from a plot of a Langmuirian isotherm, are presented for comparison in Table 3-3.5. A binding capacity

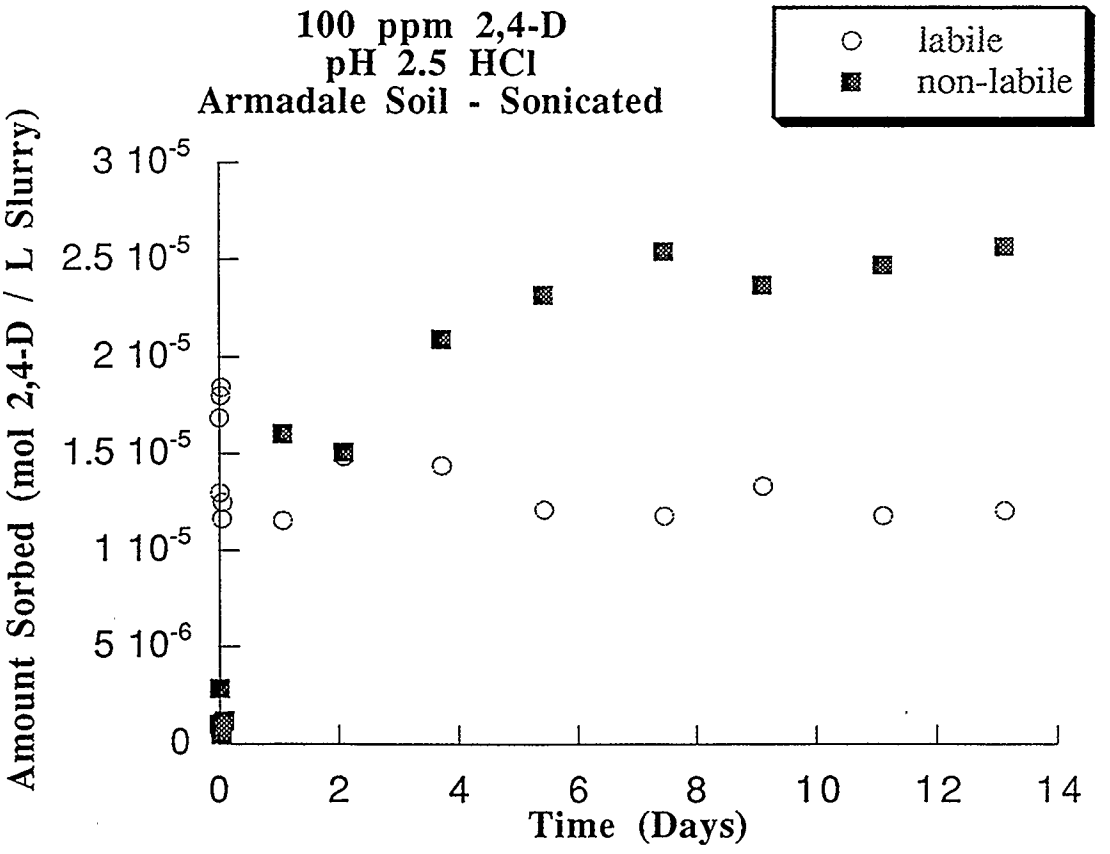


**Figure 3-3.1,** Adsorption behaviour of 2,4-D on sonicated Armadale soil $[2,4\text{-D}]_o$ = 4.503 E-4. (mol 2,4-D / L Slurry)

**Table 3-3.1 Experimental Data for 100 ppm 2,4-D Trial**

| Time (Days) | Solution (M) | % * | Labile Sorbed (M) | % | Non-Labile Sorbed (M) | % |
|---|---|---|---|---|---|---|
| 0.004 | 4.323 E-4 | 96.0 | 1.686 E-5 | 3.74 | 1.106 E-6 | 0.25 |
| 0.015 | 4.345 E-4 | 96.5 | 1.297 E-5 | 2.88 | 2.849 E-6 | 0.63 |
| 0.024 | 4.315 E-4 | 95.8 | 1.799 E-5 | 4.00 | 8.360 E-7 | 0.19 |
| 0.033 | 4.314 E-4 | 95.8 | 1.842 E-5 | 4.09 | 4.870 E-7 | 0.11 |
| 0.043 | 4.382 E-4 | 97.3 | 1.162 E-5 | 2.58 | 5.022 E-7 | 0.11 |
| 0.052 | 4.368 E-4 | 97.0 | 1.248 E-5 | 2.77 | 1.061 E-6 | 0.24 |
| 1.05 | 4.227 E-4 | 93.4 | 1.154 E-5 | 2.56 | 1.603 E-5 | 3.56 |
| 2.07 | 4.204 E-4 | 93.4 | 1.486 E-5 | 3.30 | 1.509 E-5 | 3.35 |
| 3.71 | 4.150 E-4 | 92.2 | 1.440 E-5 | 3.20 | 2.092 E-5 | 4.64 |
| 5.42 | 4.151 E-4 | 92.2 | 1.210 E-5 | 2.69 | 2.316 E-5 | 5.14 |
| 7.45 | 4.131 E-4 | 91.7 | 1.176 E-5 | 2.61 | 2.541 E-5 | 5.64 |
| 9.01 | 4.143 E-4 | 92.0 | 1.332 E-5 | 2.96 | 2.266 E-5 | 5.25 |
| 11.1 | 4.138 E-4 | 91.9 | 1.178 E-5 | 2.62 | 2.470 E-5 | 5.48 |
| 13.1 | 4.127 E-4 | 91.6 | 1.202 E-5 | 2.67 | 2.563 E-5 | 5.69 |

* shows the concentration as a percentage of total 2,4-D.

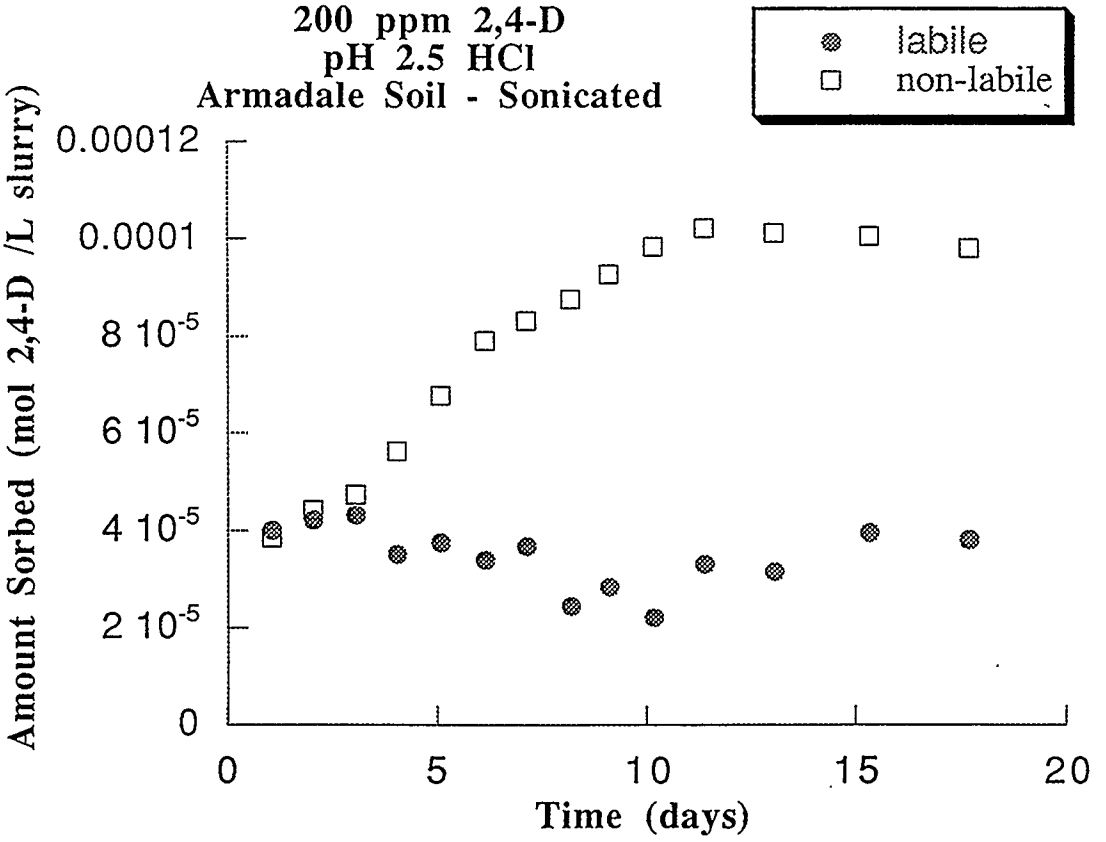


**Figure 3-3.2**, Adsorption behaviour of 2,4-D on sonicated Armadale soil $[2,4\text{-D}]_o$ = 9.033 E-4. (mol 2,4-D / L Slurry)

**Table 3-3.2 Experimental Data for 200 ppm 2,4-D Trial**

| Time (Days) | Solution (M) | % * | Labile Sorbed (M) | % | Non-Labile Sorbed (M) | % |
|---|---|---|---|---|---|---|
| 1.06 | 8.247 E-4 | 91.3 | 4.003 E-5 | 4.43 | 3.860 E-5 | 4.27 |
| 2.04 | 8.170 E-4 | 90.4 | 4.214 E-5 | 4.67 | 4.415 E-5 | 4.89 |
| 3.05 | 8.128 E-4 | 90.0 | 4.315 E-5 | 4.78 | 4.731 E-5 | 5.24 |
| 4.04 | 8.119 E-4 | 89.9 | 3.512 E-5 | 3.89 | 5.628 E-5 | 6.23 |
| 5.08 | 7.980 E-4 | 88.3 | 3.756 E-5 | 4.16 | 6.776 E-5 | 7.50 |
| 6.14 | 7.903 E-4 | 87.5 | 3.397 E-5 | 3.76 | 7.906 E-5 | 8.75 |
| 7.13 | 7.836 E-4 | 86.7 | 3.668 E-5 | 4.06 | 8.307 E-5 | 9.20 |
| 8.19 | 7.914 E-4 | 87.6 | 2.437 E-5 | 2.70 | 8.757 E-5 | 9.69 |
| 9.11 | 7.823 E-4 | 86.6 | 2.827 E-5 | 3.13 | 9.273 E-5 | 10.3 |
| 10.2 | 7.829 E-4 | 86.7 | 2.205 E-5 | 2.44 | 9.830 E-5 | 10.9 |
| 11.4 | 7.682 E-4 | 85.0 | 3.298 E-5 | 3.65 | 1.021 E-4 | 11.3 |
| 13.1 | 7.707 E-4 | 85.3 | 3.149 E-5 | 3.49 | 1.011 E-4 | 11.2 |
| 15.3 | 7.634 E-4 | 84.5 | 3.950 E-5 | 4.37 | 1.004 E-4 | 11.1 |
| 17.7 | 7.673 E-4 | 84.9 | 3.800 E-5 | 4.21 | 9.800 E-5 | 10.8 |

* shows the concentration as a percentage of total 2,4-D.

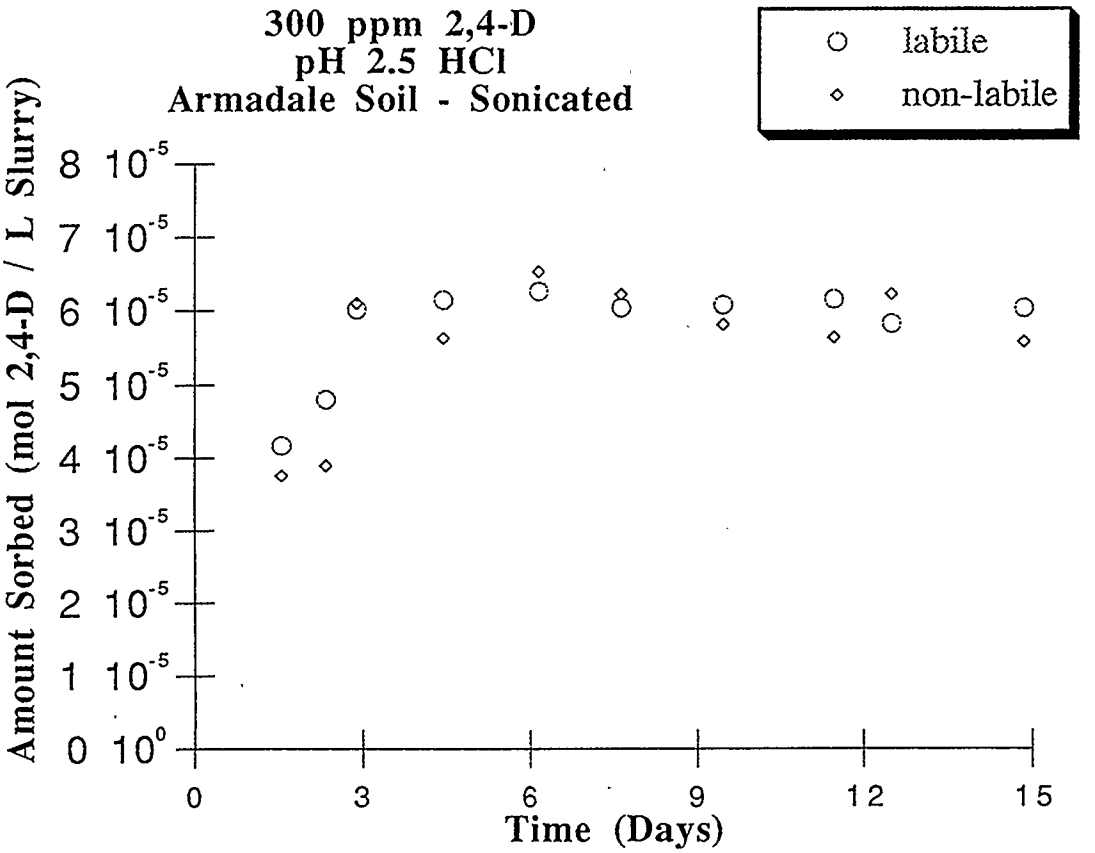


**Figure 3-3.3,** Adsorption behaviour of 2,4-D on sonicated Armadale soil $[2,4\text{-D}]_o$ = 1.357 E-3. (mol 2,4-D / L Slurry)

**Table 3-3.3 Experimental Data for 300 ppm 2,4-D Trial**

| Time (Days) | Solution (M) | % * | Labile Sorbed (M) | % | Non-Labile Sorbed (M) | % |
|---|---|---|---|---|---|---|
| 1.56 | 1.267 E-3 | 93.3 | 4.171 E-5 | 3.07 | 4.855 E-5 | 3.58 |
| 2.90 | 1.235 E-3 | 91.0 | 6.009 E-5 | 4.43 | 6.223 E-5 | 4.61 |
| 4.45 | 1.239 E-3 | 91.3 | 6.145 E-5 | 4.53 | 5.627 E-5 | 4.15 |
| 6.17 | 1.229 E-3 | 90.6 | 6.257 E-5 | 4.61 | 6.528 E-5 | 4.81 |
| 7.66 | 1.235 E-3 | 91.0 | 6.029 E-5 | 4.44 | 6.217 E-5 | 4.58 |
| 9.47 | 1.238 E-3 | 91.3 | 6.067 E-5 | 4.47 | 5.800 E-5 | 4.27 |
| 11.5 | 1.239 E-3 | 91.3 | 6.150 E-5 | 4.53 | 5.627 E-5 | 4.15 |
| 12.5 | 1.237 E-3 | 91.1 | 5.811 E-5 | 4.28 | 6.210 E-5 | 4.58 |
| 14.8 | 1.241 E-3 | 91.5 | 6.022 E-5 | 4.44 | 5.568 E-5 | 4.10 |

* shows the concentration as a percentage of total 2,4-D.

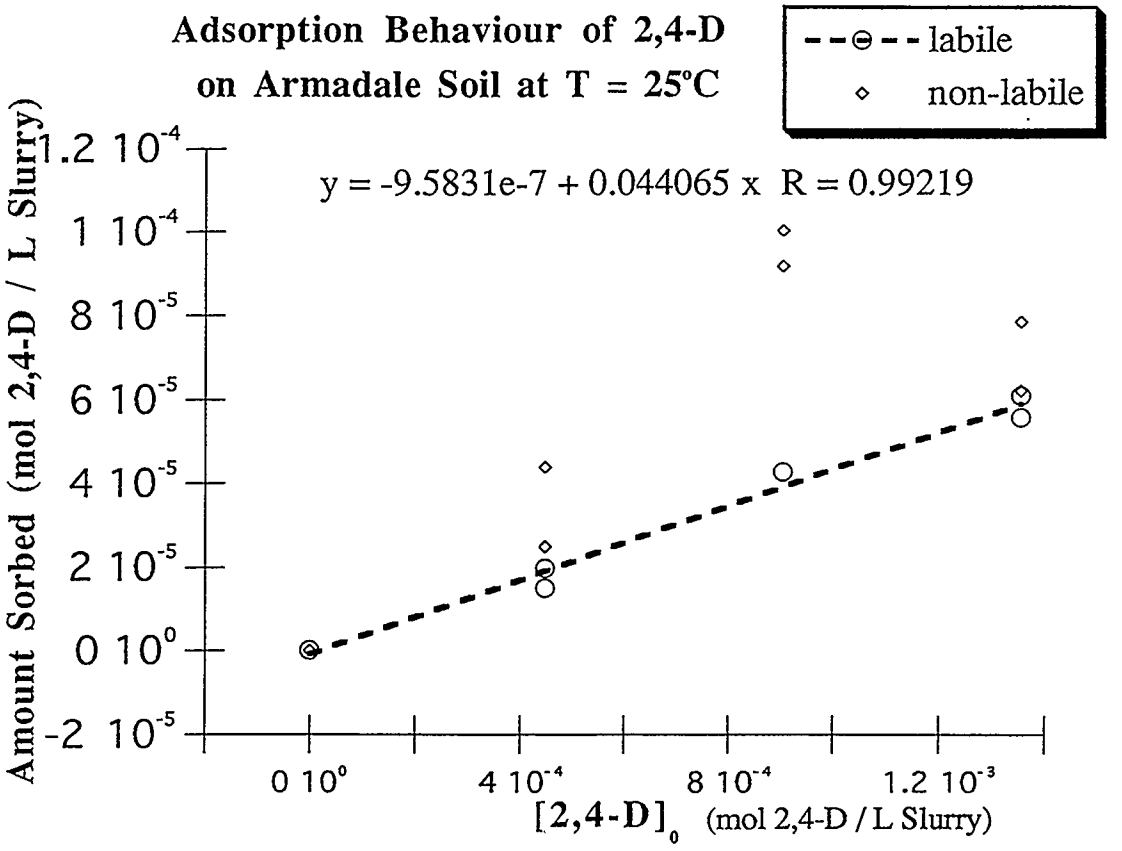


**Figure 3-3.4,** Adsorption isotherm for 2,4-D on Armadale soil.

**Table 3-3.4 Binding Capacity of 2,4-D at Different Concentrations, 25°C**

| Initial [2.4-D] (M) | Labile Sorbed (mol 2,4-D / L Slurry) | % RSD | Non-Labile Sorbed (mol 2,4-D / L Slurry) | % RSD |
|---|---|---|---|---|
| 4.503 E-4 | 1.957 E-5 | 10.1 | 4.383 E-5 | 11.9 |
| 4.503 E-4 | 1.486 E-5 | 7.81 | 2.485 E-5 | 13.2 |
| 9.033 E-4 | 4.265 E-5 | 1.67 | 1.002 E-4 | 1.68 |
| 1.357 E -3 | 6.068 E-5 | 1.21 | 7.842 E-5 | 9.60 |
| 1.357 E -3 | 5.557 E-5 | 2.13 | 6.199 E-5 | 3.42 |

**Table 3-3.5 Binding Capacities of Atrazine on Two Types of Soil**

| Sorbent | Sorbate | Binding Capacity (μmol / g) | Reference |
|---|---|---|---|
| GB-843 | Atrazine | 0.397 | Li 1993 |
| Laurentian Soil | Atrazine | 0.37 | Wang 1992 |
| Laurentian HA | Atrazine | 15.3 | Wang 1991 |
| Laurentian FA | Atrazine | 8.8 | Wang 1990 |

is not seen for the labile phase below an initial slurry concentration of 300 ppm (Figure 3-3.4), while the non-labile phase does appear to be saturated at this point. An average value of 0.802 +/- 0.200 μmol / L slurry is obtained for the non-labile 2,4-D binding capacity on Armadale soil. This can be converted to 0.0321 +/- 0.0001 μmol / g soil assuming a homogeneous slurry with a concentration of soil equal to 25 g / L. This number is small compared to the values obtained by Wang and Li for atrazine sorption to whole soils.

### 3-3.3 Continuous Shaking versus Sonication

The adsorption data presented above were collected using Armadale soil which was sonicated prior to beginning uptake experiments. This pretreatment is a modification of the MF-HPLC technique originally proposed by Gamble et al (20, 21, 22), and appears reasonable based on chemical analysis presented in Chapter 2, however, the true test of this change in procedure is a comparison between results obtained for soil which has been sonicated and soil which has only been shaken. Figure 3-3.5 shows the uptake over time of both labile and non-labile phases of 2,4-D on Armadale soil which has only been shaken. Two interesting features emerge from this graph. First, the non-labile binding capacity very nearly matches that obtained for soil which received the ultrasound pre-treatment. Second, a break appears in the graph beyond 12 days, after which the labile amount sorbed is seen to increase dramatically with time, while the non-labile amount sorbed decreases. This break corresponds to an increase in the rate of shaking of the slurry samples, and results from rapid break down of the soil particles causing a rapid increase in the available surface area. This increase in surface area provides more sites for labile sorption to occur while exposing sites which were previously on the interior of the particle, releasing non-labile sorbed 2,4-D.

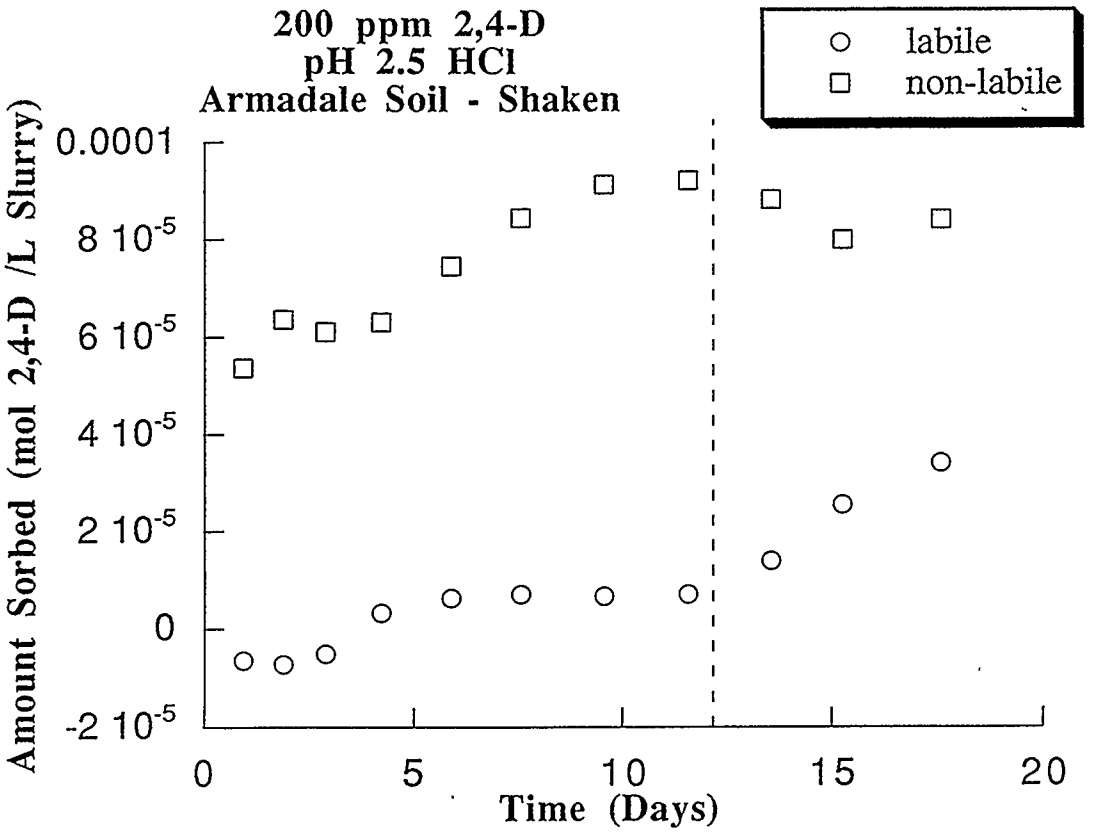


**Figure 3-3.5**, Adsorption behaviour of 2,4-D on Armadale soil which has been shaken only. $[2,4\text{-D}]_o = 9.033$ E-4. (mol 2,4-D / L Slurry)

Important conclusions may be drawn from these observations. Experimentally, they reaffirm the importance of avoiding vigorous agitation during a sorption study since the soil's physical characteristics will change with time as the soil particles and aggregates may break down with time. The fact that the non-labile sorption capacities agree between those obtained using either sonically pre-treated soil or soil which was shaken only gives weight to the plausibility of this methodological modification. From a mechanistic point of view, the decrease in the amount of non-labile sorbed after the shaking rate was increased suggests that the non-labile fraction is sorbed to sites which are located in the interior of the soil particle.

### 3-3.4 Kinetics of Uptake of 2,4-D

Two-stage uptake in batch sorption experiments has been described as a two step process in which a surface layer of adsorbed material approaches equilibrium with the surrounding solution, and the concentration gradient between the surface and the interior of the soil particle drives diffusion of the sorbate into interior soil spaces. In this process the surface sorbed state is an intermediate on which the formation of the intraparticle sorbed state is dependent. In Li's work (45), the surface sorbed state was referred to as labile sorbed, while the intraparticle sorbed state was known as non-labile sorbed.

Compared to the behaviour of atrazine studied by Li (45), the kinetics of uptake of 2,4-D are very fast, with both labile and non-labile fractions appearing in the first few days. This system can be treated as one in which the first step is a rapid equilibration between solution phase 2,4-D (A) and labile sorbed 2,4-D (B) followed by the rate limiting step which is the formation of the non-labile sorbed 2,4-D phase (C) (37). This system may be described by equation 3-3.1:

$$A \overset{K_{12}}{\rightleftharpoons} B \xrightarrow{k_3} C \qquad (3\text{-}3.1)$$

An apparent equilibrium constant, $K_{12}$, may be found from the ratio of the concentration of B to the concentration of A. Since the solution concentration does not vary by more than 2.3% over the duration of the experiment, and the amount of labile sorbed is essentially constant, the initial solution concentration of 2,4-D will be used for [A], while the labile sorption capacity for each concentration of 2,4-D will be used for [B].

The rate of uptake of the non-labile phase is given by equation 3-3.2:

$$\frac{d[C]}{dt} = k_3 [B] \qquad (3\text{-}3.2)$$

The concentration of the labile phase, [B], must be expressed in terms of C to make it possible to integrate this equation. Since $K_{12} = [B]/[A]$, we can obtain equation 3-3.3 by inverting this expression and adding [B] / [B] to both sides.

$$\frac{1}{K_{12}} + 1 = \frac{[A] + [B]}{[B]} \qquad (3\text{-}3.3)$$

The sum [A] + [B] can be expressed in terms of the total original solution concentration of 2,4-D $[A]_o$ as:

$$[A]_o = [A] + [B] + [C]$$

$$[A] + [B] = [A]_o - [C] \qquad (3\text{-}3.4)$$

Rearranging equation 3-3.3 to solve for [B], and substituting for [A] + [B] from equation 3-3.4 gives:

$$[B] = \frac{([A]_o - [C])\, K_{12}}{(K_{12} + 1)} \qquad (3\text{-}3.5)$$

Substitution for [B] into equation 3-3.2 gives an equation with only [C] as a concentration variable:

$$\frac{d[C]}{dt} = \frac{k_3 K_{12}}{(K_{12} + 1)} ([A]_o - [C]) \qquad (3\text{-}3.6)$$

A plot of the time rate of change of the uptake of the non-labile phase versus ($[A]_o$ - [C]) should give a straight line with an intercept equal to the experimental rate constant, $k_{exp}$, where $k_{exp}$ is given by:

$$k_{exp} = \frac{k_3 K_{12}}{K_{12} + 1} \qquad (3\text{-}3.7)$$

Values for d[C]/dt were found by fitting the initial uptake of the non-labile phase with a straight line for each of the concentrations of 2,4-D investigated (Figures 3-3.6 through 3-3.8, Table 3-3.6). A plot of equation 3-3.6 is given in Figure 3-3.9, showing a straight line with slope equal to $k_{exp}$. A value for $K_{12}$ of 0.04406 +/- 0.00277 can be obtained from data in Table 3-3.4, and used in equation 3-3.7 to find the rate constant for the formation of the non-labile phase, $k_3$, as:

$$k_3 = \frac{k_{exp} (K12 + 1)}{K12} = \frac{0.01308 +/- 0.00268 \ ((0.04406 +/- 0.00277) + 1)}{(0.04406 +/- 0.00277) \text{ days}}$$

$k_3 = (3.1 +/- 0.7)$ E-6 $sec^{-1}$.

It should be noted that while $K_{12}$ is the experimental equilibrium constant for the labile uptake process, this K value is not the same as the K value in the Langmuir adsorption isotherm expression. Since $\Theta$ is given by n / $n_m$, where n is the number of moles of solute adsorbed per gram of soil, and $n_m$ is the number of moles adsorbed at monolayer coverage, equation 1-1.1 may be re-written as:

$$n = \frac{n_m K c}{1 + K c} \qquad (3\text{-}3.8)$$

From this equation it may be seen that at low concentrations, when K c is much less than 1, n is proportional to c, with slope equal to $n_m$ K. Since the experimental equilibrium constant for labile sorption was found in the region of the isotherm where c is indeed

**Table 3-3.6 Data Used to Determine Experimental Rate Constant, $k_3$**

| Initial [2,4-D] (M) | $[A]_o$ - [C] | | d[C] / dt | |
|---|---|---|---|---|
| | (M) | mol 2,4-D / g soil | (M) | mol 2,4-D / g soil |
| 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 4.503 E-4 | 4.160 E-4 | 1.664 E-5 | 1.469 E-6 | 5.876 E-8 |
| 9.033 E-4 | 8.031 E-4 | 3.212 E-5 | 6.987 E-6 | 2.795 E-7 |
| 1.357 E-3 | 1.287 E-4 | 5.147 E-5 | 1.650 E-5 | 6.600 E-7 |

small, and since no binding capacity was observed, hence the value of $n_m$ is unknown, the value obtained for $K_{12}$ is equal to $n_m K$ in equation 3-3.8. To extract the value of the Langmuir constant, K, would require extension of the adsorption isotherm to concentrations higher than 300 ppm in order to determine the value of the binding capacity, $n_m$. Once studied in the region of high enough concentration to define $n_m$, the isotherm could then yield both the values of $n_m$ and K using equation 1-1.2.

Interpretation of the 2,4-D uptake behaviour by Armadale soil in the above manner is consistent with other published results (45) and agrees with the notion of a rapidly forming, surface bound phase of 2,4-D which acts as an intermediate to the formation of a more strongly bound intraparticle phase of 2,4-D. The extremely rapid kinetics of 2,4-D sorption to Armadale soil were not seen in a study of the uptake of atrazine by a mineral soil (45). To determine whether the difference was due primarily to the difference in the sorbate or the sorbent in these two systems, a preliminary study of the uptake of atrazine by Armadale soil was done. These results are summarized in Figure 3-3.10, and show the same type of two-stage uptake as seen for 2,4-D. The rapid establishment of the equilibrium between the solution phase atrazine and the labile sorbed phase on Armadale soil is not seen on the mineral soil GB-843, where both the labile and

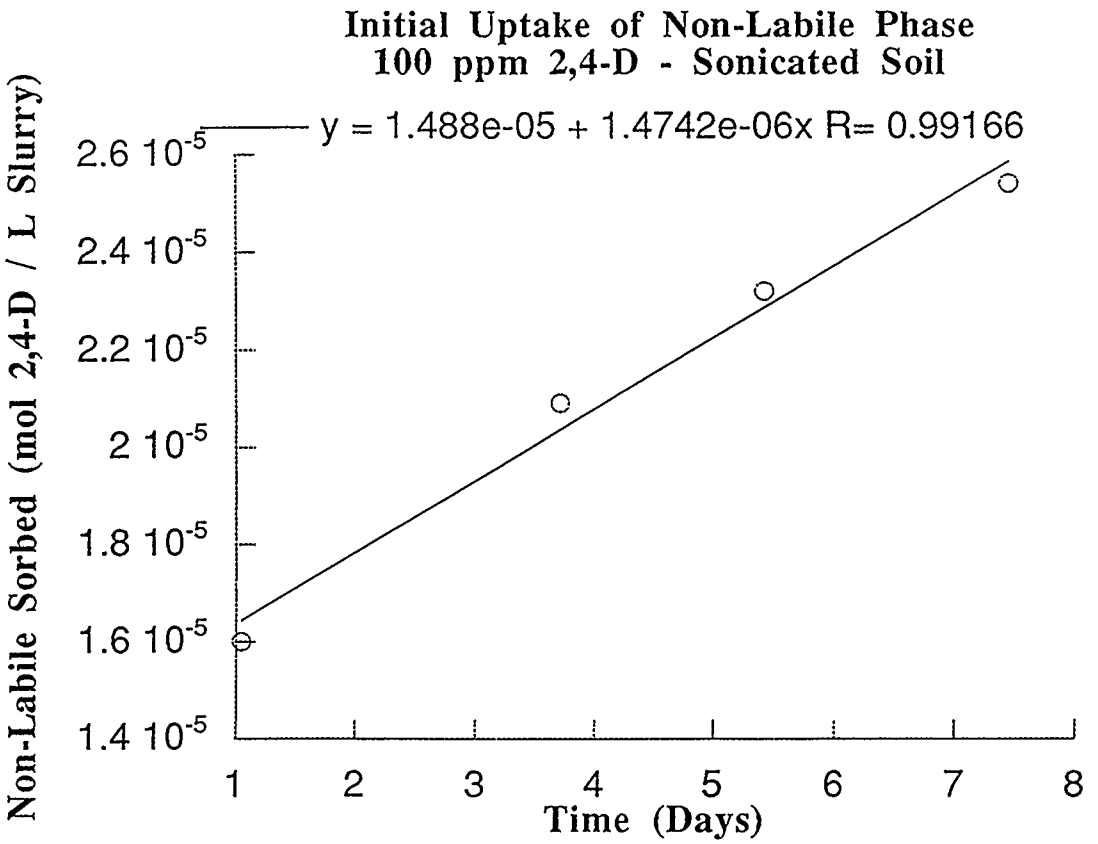


**Figure 3-3.6,** Rate of approach to equilibrium for non-labile phase.

$[2,4\text{-D}]_o$ = 4.503 E-4. (mol 2,4-D / L Slurry)

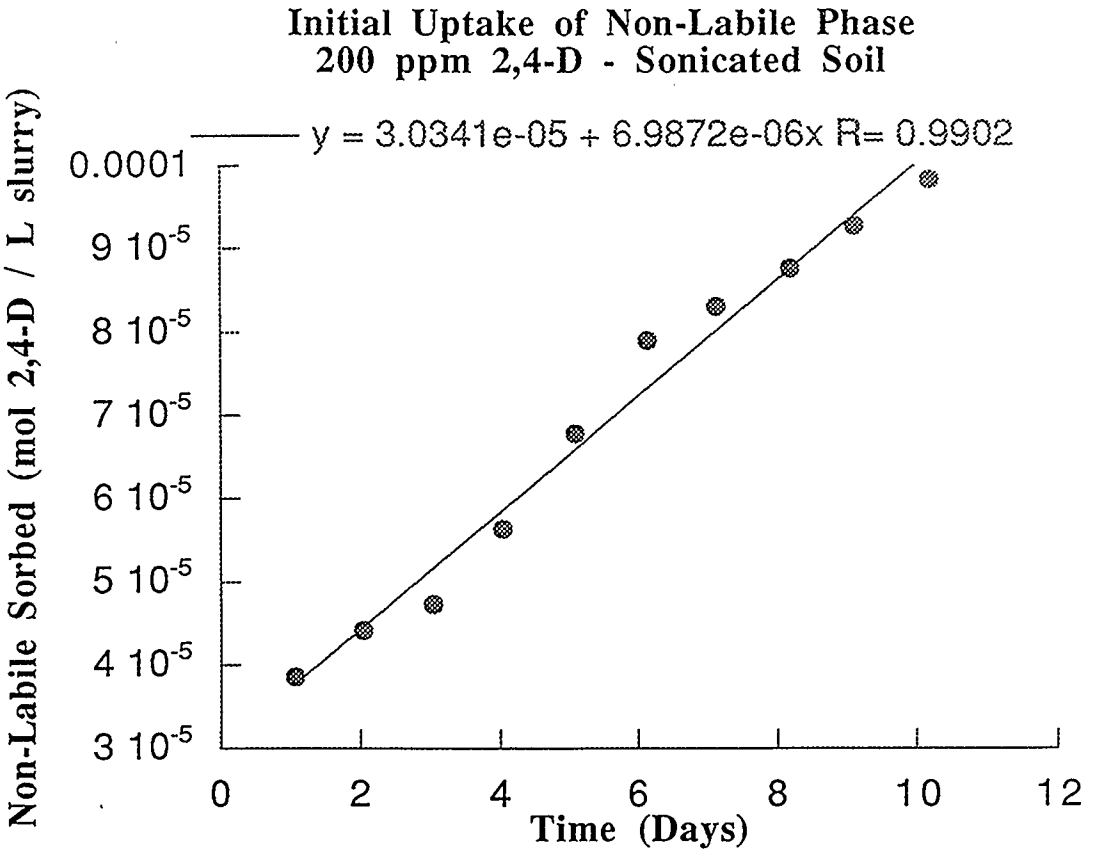


**Figure 3-3.7,** Rate of approach to equilibrium for non-labile phase.

$[2,4\text{-D}]_o$ = 9.033 E-4. (mol 2,4-D / L Slurry)

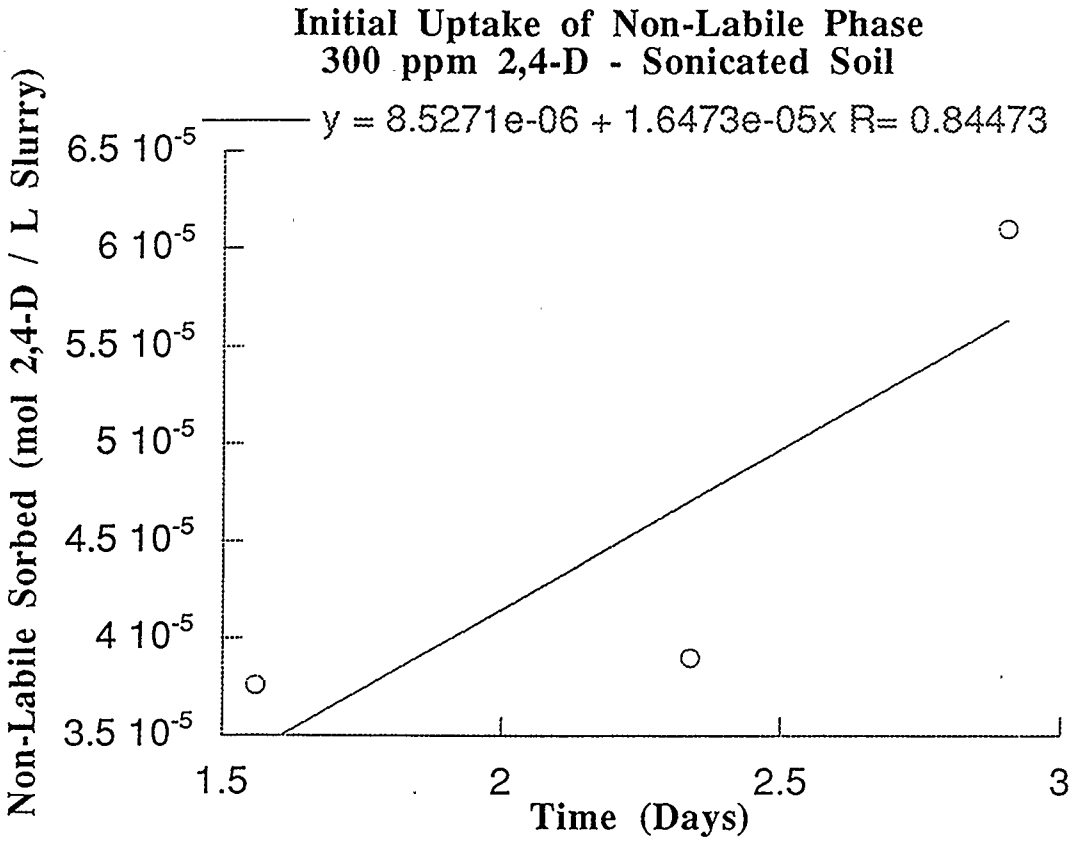


**Figure 3-3.8,** Rate of approach to equilibrium for non-labile phase.

$[2,4\text{-D}]_o$ = 1.357 E-3. (mol 2,4-D / L Slurry)

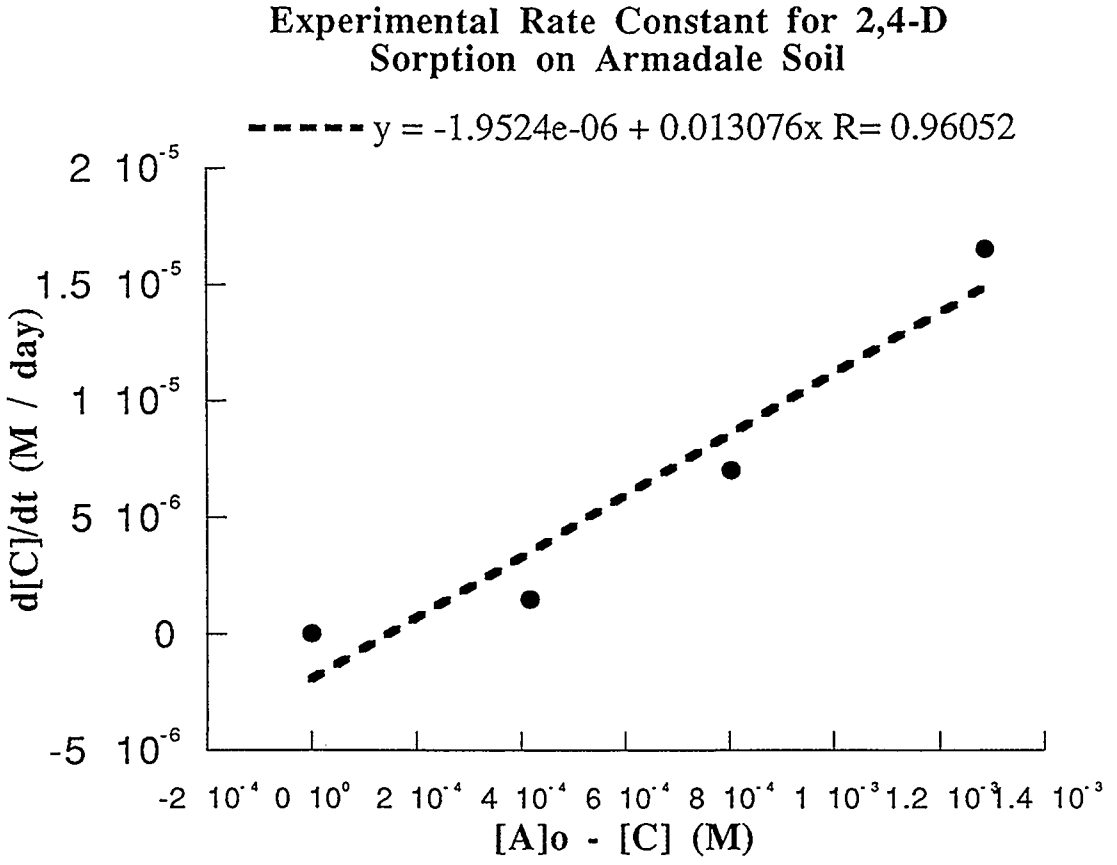


**Figure 3-3.9**, Determination of experimental rate constant, $k_3$.

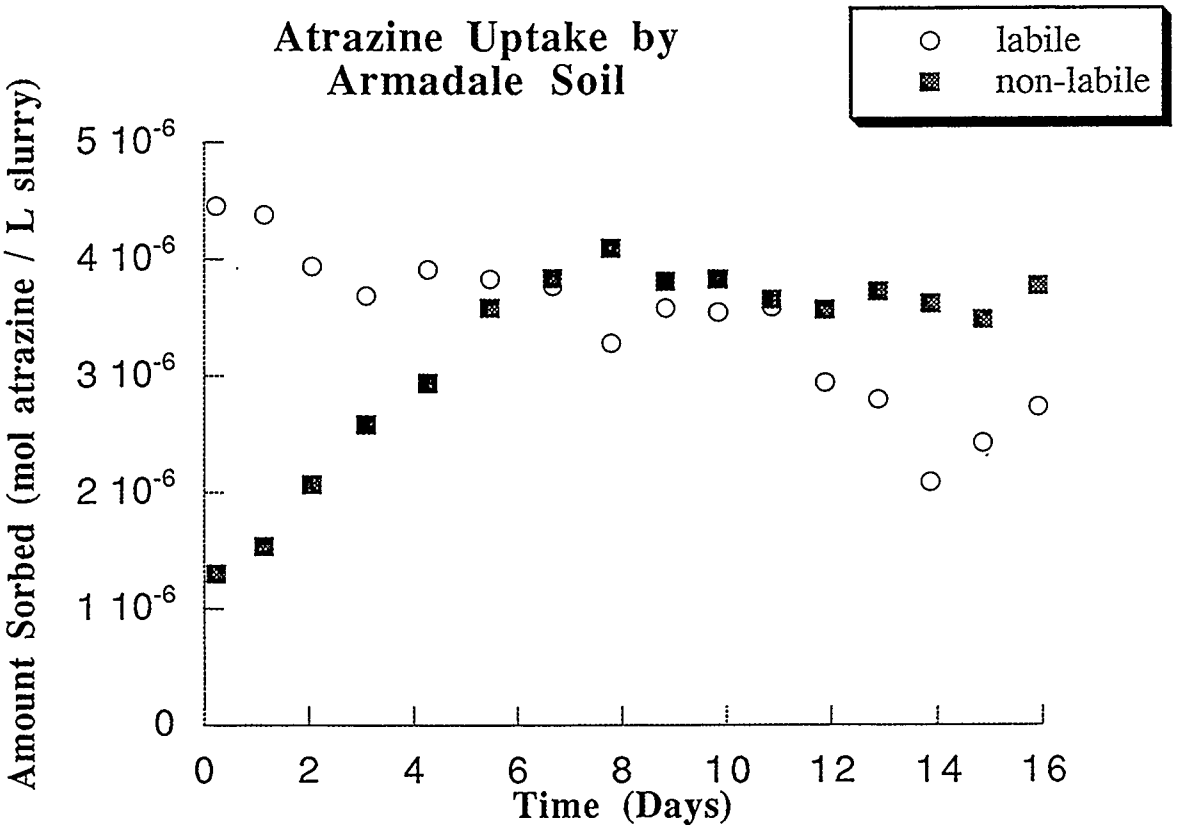


**Figure 3-3.10,** Uptake of atrazine by Armadale soil.

Initial concentration = 5.032 x $10^{-5}$ (mol atrazine / L Slurry)

non-labile kinetics are much slower. The difference in organic carbon content between the two soils (GB- 843 has less than 1% OC) is the most likely explanation for the difference in rates of sorption, although other physical and chemical differences between the soils could come into play.

The discussion above centers around the idea that 2,4-D sorption to Armadale soil is indeed the process that is being observed. A recent study using magnetic resonance imaging has shown that Armadale soil, under diffusion controlled conditions, has a half life of approximately 6 days to reach equilibrium with water and become fully wet (6). Using the expression to calculate the half life, $t_{1/2}$, for a first order reaction:

$$t_{1/2} = \frac{\ln 2}{k} \qquad (3\text{-}3.9)$$

and substituting $k_3$ for k, a value of 2.6 days is found for the half life for the uptake of the non-labile phase of 2,4-D by Armadale soil. The possibility exists that the process being observed in this research is not in fact uptake of 2,4-D, but is more accurately described as the accomplishment of complete wetting of the soil, followed by nearly instantaneous sorption of 2,4-D by the wetted soil matter. Labile and non-labile phases are then distinguished only by the depth into which the sorbate has penetrated the soil matter, as this depth would govern the relative ease with which these two phases could be extracted by the MF-HPLC technique. A faster half life would be expected in the case of 2,4-D uptake since the soil has been subjected to the ultrasound pretreatment, where soil used in the work by Belliveau was whole Armadale. The similarity between these half lives, considering the factor of two increase in surface area for the sonicated soil, requires further investigation before conclusions may be drawn regarding the true mechanism of uptake of 2,4-D.

## 3-4. Summary

Within this chapter the equilibrium state of sorption of labile and non-labile fractions of 2,4-D on Armadale soil has been examined under the modified MF-HPLC method. An understanding of the uptake mechanism has been gained. It can be seen that:

(1) Both labile and non-labile phases are present at very early times in the experiment. A binding capacity for the non-labile phase can be estimated at 0.802 +/- 0.200 μmol / L slurry for the bulk soil. No binding capacity was observed for the labile phase at initial 2,4-D solution concentrations below 300 ppm.

(2) A rapid equilibrium approximation can be made and allows calculation of an experimental equilibrium constant for the sorption/desorption of the labile phase, and a rate constant for the non-labile uptake to be found. These values are 0.04406 +/- 0.00277 and (3.1 +/- 0.7) E-6 $sec^{-1}$ respectively. The uptake mechanism appears to be one in which the labile phase is a necessary precursor to the formation of the non-labile phase.

(3) Pre-treatment of the soil by sonication prior to beginning uptake experiments does not seem to affect the final equilibrium position of the non-labile fraction. The equilibrium position for the labile phase is affected dramatically by particle breakdown. Sonication seems to provide the best conditions of soil stability over time without sacrificing soil chemistry.

(4) Mass balance may be attained for 2,4-D using a more thorough extraction technique. This suggests that the 2,4-D is sorbed in the soil in a recoverable state, and that the non-labile fraction is indeed associated with the soil and not lost to degradation processes.

To gain a better understanding of the type of binding of 2,4-D occurring in this system it would be necessary to perform more detailed investigations on: 1) temperature dependence of uptake and 2) pH dependence of uptake. These studies could answer whether the labile and non-labile phases are physically or chemically bonded to the surface, and whether the molecular form of 2,4-D, the anionic form or both contribute to binding in soil. Studies over a wide range of pH are needed to better predict the mobility of 2,4-D in a variety of soil conditions.

# CHAPTER 4

# CONCLUSION AND SUGGESTION FOR FUTURE RESEARCH

## 4-1. Conclusion

In keeping with the research strategy that has existed in our research group for several years, this thesis has focused on the examination of an aqueous soil-pesticide system in order to gain insight into the physico-chemical processes responsible for binding of the pesticide by the soil. Chapter 2 investigated the long term stability of the soil under typical batch conditions and provided chemical information about the soil. Chapter 3 focused on collection and interpretation of sorption data using the micro-filtration HPLC technique. These data were interpreted to provide an experimental rate constant to describe the non-labile sorption process and an equilibrium constant for the labile uptake. The salient features of this work include:

(1) Direct observation of particle breakdown due to the mixing of the soil slurry can occur. This breakdown results in an ever changing soil surface area in the system, therefore making interpretation of long term sorption experiments difficult.

(2) Pre-treatment of the soil by sonication results in a soil which has been nearly completely broken down, and which undergoes further break down to only a small degree. This pre-treatment does not appear to alter the chemistry of the soil or the final equilibrium position of the uptake of the non-labile fraction for the combination of soil and herbicide which was investigated.

(3) The soil Armadale has been characterized by chemical analysis with respect to cation exchange capacity, organic matter content, surface area and elemental analysis, and

mineral content. The average values for CEC, organic matter and surface area of whole Armadale soil are: 4.551 meq/100g, 8.10 % and 10.14 +/- 1.93 $m^2/g$ respectively.

(4) Both labile and non-labile fractions as determined by the MF-HPLC experiment appear to result from uptake by the soil, and are not produced by artifacts such as loss to degradation processes. This may be concluded since complete recovery of the herbicide is possible using a strong extraction technique.

(5) A binding capacity was observed for the non-labile fraction and estimated to be 0.802 +/- 0.200 µmol / L slurry. No binding capacity was observed for the labile fraction over the range of concentrations investigated.

(6) Uptake of the labile fraction occurs at a rapid initial pace, with this species appearing in the system at the earliest time measurable by the method. Using the rapid equilibrium approach for this system, an experimental equilibrium constant for the sorption/desorption of 2,4-D was found to be 0.0441 +/- 0.0028, while the rate constant for formation of the non-labile phase was found to be (3.1 +/- 10.7) E-6 $sec^{-1}$.

## 4-2. Suggestions For Future Research

(1) The proposed method of pre-treating soil by sonication prior to performing batch uptake experiments should be further investigated using other soils. It may be that soils which are rich in organic matter may be more susceptible to break down due to agitation than mineral soils, and this treatment may only be necessary for these more fragile soils. Before adopting this pre-treatment for soils other than Armadale it should be verified that sonication is indeed necessary to avoid break down of soil particles and does not alter the chemistry of the soil.

(2) Examining the effect of temperature on the binding behaviour of 2,4-D on Armadale soil could provide insight into the type of binding occurring, that is whether it

is a physical or chemical interaction. This research suggests that 2,4-D is not modified chemically by the sorption process since it is completely recoverable, but a chemical sorption process could still exist in which the soil would undergo a structural rearrangement to allow uptake to occur. Obtaining these thermodynamic parameters for this system would allow better descriptions of the binding process to be made.

(3) The pH has been held constant in this research at an equilibrium value of 2.5. Since opinion holds that the molecular form of 2,4-D is bound more strongly to soil than the ionic form, a study of the effect of pH on the distribution of labile and non-labile phases could be valuable in determining whether speciation determines the intensity of the binding interaction. This information would also be needed to better predict the mobility of 2,4-D under a range of pH conditions.

(4) Investigation of sorption behaviour at higher concentrations of 2,4-D would allow separation of the experimental equilibrium constant obtained for the labile uptake into binding capacity and Langmuirian equilibrium constant terms, provided that a binding capacity could be observed.

Continued use of the MF-HPLC technique on a variety of soil-contaminant pairs should help to further establish this technique as a valuable tool for determining the mechanism of uptake of contaminants by soil, in addition to allowing determination of experimental parameters which may be used in predicting the fate of contaminants in the environment.

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Appendix 1 - Particle Counting Data for one Ultrasound Experiment

Particle Sizes — Coulter Counter — October 26,1995
Ultra Sound Study

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Density Brine | 1.01 | | | | | | | | |
| # | Sample | | Channel | Particle Sizes µm | Counts per channel | | | | Average of 4 runs | Normalized Counts |
| 1 | ULT-3 | | 2 | 1.26 | 29333 | 27154 | 26559 | 25449 | 27124 | 27124 |
| | | | 3 | 1.59 | 13904 | 13422 | 13216 | 12738 | 13320 | 13320 |
| | soil (g) | 0.5177 | 4 | 2.00 | 6815 | 6498 | 6615 | 6325 | 6563 | 6563 |
| | volume (mL) | 19.94 | 5 | 2.52 | 3110 | 2842 | 2913 | 2929 | 2949 | 2949 |
| | | | 6 | 3.17 | 1333 | 1279 | 1328 | 1308 | 1312 | 1312 |
| | | | 7 | 4.00 | 606 | 615 | 559 | 558 | 585 | 585 |
| | Accuvette (g) | 6.4819 | 8 | 5.04 | 279 | 241 | 205 | 206 | 233 | 233 |
| | Acc. + brine | 29.4689 | 9 | 6.35 | 104 | 93 | 89 | 78 | 91 | 91 |
| | w/ sample | 29.4818 | 10 | 8.00 | 32 | 30 | 31 | 35 | 32 | 32 |
| | | | 11 | 10.08 | 10 | 15 | 11 | 9 | 11 | 11 |
| | Vol. brine mL | 22.78306 | 12 | 12.70 | 8 | 5 | 6 | 7 | 7 | 7 |
| | Vol. Sample mL | 0.012786 | 13 | 16.00 | 3 | 2 | 0 | 3 | 2 | 2 |
| | | | 14 | 20.20 | 4 | 2 | 0 | 1 | 2 | 2 |
| | Dilution factor | 1.46E-05 | 15 | 25.40 | 1 | 2 | 0 | 0 | 1 | 1 |
| | Normalization Factor | 1 | Totals | | 55542 | 52200 | 51532 | 49646 | 52232 | 52232 |

Original Dilution Factor ULT-3 1.46E-05

Volume of sample was determined from the mass difference of the sample and masses of brine and accuvette, after correction for bouyancy. All sample counts were normalized against one sample to account for differences in dilution.

Peak Areas 2,4-D

| Time | | | 200 ppm | Blank | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Day | Hour | Min | Standard | | Filtrate | Slurry | Filtrate | Slurry | Filtrate | Slurry |
| 22 | 14 | 29 | 155.42608 | 154.01582 | 150.48573 | 148.48656 | 155.97659 | 156.82722 | 144.96539 | 147.01187 |
| 23 | 10 | 52 | 157.59498 | 158.23154 | 145.69537 | 144.81451 | 146.46004 | 143.9321 | 150.65692 | 148.65343 |
| 24 | 11 | 10 | 156.68876 | 156.20300 | 143.92281 | 140.11362 | 147.07829 | 147.97722 | 152.78221 | 150.34908 |
| 25 | 10 | 59 | 157.54351 | 149.37035 | 146.43253 | 144.55629 | 151.65549 | 153.25148 | 145.57077 | 145.56477 |
| 26 | 10 | 31 | 157.98239 | 160.34358 | 144.85451 | 146.41336 | 144.55589 | 144.17174 | 155.09595 | 151.71364 |
| 28 | 10 | 14 | 158.84345 | 150.98116 | 144.87955 | 144.97699 | 140.83524 | 147.50813 | 148.35234 | 149.05476 |
| 30 | 11 | 16 | 161.76596 | 159.60313 | 144.41786 | 144.55521 | 147.78191 | 151.30437 | 140.44102 | 141.20662 |
| 31 | 10 | 33 | 161.43835 | 160.64064 | 145.77396 | 142.10260 | 143.93172 | 145.05713 | 147.81540 | 149.29796 |
| 34 | 11 | 13 | 163.82166 | 159.05875 | 141.59357 | 146.57640 | 146.76015 | 147.88219 | 148.88382 | 149.90419 |
| 36 | 10 | 59 | 163.52989 | 156.11472 | 143.43974 | 146.10507 | 150.10214 | 152.10123 | 142.06180 | 142.46886 |
| 37 | 8 | 53 | 159.73129 | 160.36148 | 147.11081 | 143.34924 | 139.54822 | 140.17650 | 141.55959 | 154.29773 |
| 39 | 13 | 52 | 163.18599 | 149.62691 | 135.57498 | 149.05937 | 143.06071 | 149.75435 | 151.74887 | 156.99228 |
| 43 | 10 | 37 | 150.37589 | 146.38599 | 116.55394 | 133.01157 | 136.20615 | 137.18509 | 128.98999 | 128.85822 |

Constants Used for Calculation: Day 0 = 22, Hour 0 = 13, Minute 0 = 30

Calculations:
Time in days = (day - day 0) + ((hour - hour 0) + ((minute - minute 0) / 60)) / 24
Area = Response Factor x Concentration, R.F. determined from standard
Unknown Concentration = Area / R.F.