EVALUATION OF ECONOMICAL SORBENTS FOR THE REMOVAL OF METOLACHLOR FROM CONTAMINATED WASTEWATER

by

Lynn E. Hutchinson

Thesis submitted to the Faculty of the

Virginia Polytechnic Institute and State University

in Partial fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Environmental Science and Engineering, Civil Engineering

APPROVED:

Duane F. Berry
D.F. Berry, Co-Chairman

Dave E. Mullins
D.E. Mullins, Co-Chairman

Andrea M. Dietrich
A.M. Dietrich, Committee Member

September, 1991
Blacksburg, Virginia

EVALUATION OF ECONOMICAL SORBENTS FOR THE REMOVAL OF METOLACHLOR FROM CONTAMINATED WASTEWATER

by

Lynn E. Hutchinson

Committee Co-Chairman: Duane F. Berry
Crop Soil and Environmental Sciences

Committee Co-Chairman: Donald Mullins
Entomology

(Abstract)

The sorption of unformulated (98% pure) and formulated (86% pure + adjuvants) metolachlor to peat, rubber, and steam-exploded wood was studied. The concentration of pesticide ranged from 50 mg/L to 400 mg/L. Equilibrium concentrations for the batch reactors were reached within 24 hr. The sorption data for both unformulated and formulated metolachlor were best described by the Freundlich isotherm model. Metolachlor was preferentially sorbed in the following order: rubber > peat > wood fibers, with removal efficiencies of 80-85%, 70-80% and 50-65%, respectively. Differences in slopes of the isotherm lines and K values were negligible for each sorbent-type tested for both unformulated and formulated metolachlor. These results suggest that the presence of surfactants did not affect the sorption capacity of the sorbents at the concentration levels tested. However, isotherm plots showed S-shaped curve

behavior for all of the sorbents in the presence of unformulated metolachlor, while a C-shaped curve was seen when the sorbents were mixed with formulated metolachlor. This suggests that different bonding mechanisms may be involved for the sorption of unformulated and formulated metolachlor to the sorbents.

Various procedures were studied to improve removal efficiencies of formulated metolachlor. Sorption of metolachlor to peat was enhanced by hydrating the peat and pre-treating the peat with HCl. Circulation of formulated metolachlor through a rubber-packed column showed the greatest removal, with only 6 mg/L of the initial 400 mg/L remaining in solution. Removal efficiencies of steam-exploded wood fibers were not improved by any of the methods investigated.

ACKNOWLEDGMENTS

I would like to thank my family for their encouragement and inspiration. They have taught me to strive for my best in whatever I do. Their support has made my graduate education possible.

I would like to express my appreciation to Dr. Berry for his guidance and patience throughout this research project, and my other committee members, Dr. Mullins and Dr. Dietrich, for their wisdom and input. I would also like to recognize the Center for Innovative Technology and Biobased Materials at VPI&SU, and the USEPA in Cincinnati for providing funding for this project.

A special note of thanks goes to Hubert Walker who always offered his help, and was invaluable in locating laboratory supplies. In addition, I would like to thank Julie Petruska for locating a peristaltic pump in my time of need. Finally, I would like to thank my friends for making my graduate education more enjoyable and providing encouragement when things were not going as anticipated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

1.0 INTRODUCTION

Recent groundwater quality studies have identified numerous pesticide pollutants in water (Baker, 1991; Hall and Lietman, 1991). Myrik (1990) and Norwood (1990) have cited improper handling of pesticides at agricultural mixing and handling sites as a potential source for soil and groundwater contamination. Clearly, pollution of water and land resources with pesticide chemicals is unacceptable, and emphasizes the need for improved disposal technology.

Several researchers have reported on pesticide disposal methods such as, use of a trickling filter and activated sludge unit, soil mounds, slurry phase biological waste treatment, incineration, and landfilling (Norwood, 1990; Bridges, 1988; Dennis and Kobylinski, 1983). However, few of these methods are appropriate for the small farm operator, due to their high cost and difficulty of operation.

Development of an inexpensive and simple pesticide disposal system has been problematic. Pesticides are commonly applied to crops in the form of wettable powders,

granular products, emulsifiable concentrates, water miscible concentrates, and flowable powders (Himmel et al., 1990). These formulations combine the active pesticidal chemical with inert adjuvants. The surfactant-adjuvants enhance the water solubility of the pesticide, and increase the persistence of the chemical and its ability to reach the target organism. The type of formulation used by each manufacturer may differ for the same pesticide.

Historically, few regulations controlled the use of approximately 1200 different inert ingredients used in pesticide formulations (Thomas, 1990). In October 1989, the Control of Substances Hazardous to Health (COSHH) regulations were enacted by the USEPA. This legislation places increased responsibility on chemical manufacturers to test the toxicity of the inert ingredients. Despite increased regulatory pressures, little if any research has been conducted on the affects of inert adjuvants on disposal methods. "Development of pesticidal waste disposal methods must take into account current and future trends in pesticide formulation chemistry," (Mullins et al., 1991).

The purpose of this research project was to: (1) evaluate economical sorbents for the removal of metolachlor from contaminated water, (2) determine if the

presence of surfactants affects the pesticide sorptive capacity of the sorbents, and (3) determine if modifications to the sorbent material, aqueous phase, or treatment process can improve removal efficiency. Sorbent materials tested include peat moss, steam-exploded wood fibers, and rubber.

Peat was chosen due to its low cost ($0.05/lb (Mullins et al., 1991),) and proven ability to remove wastes from water (Cancela et al., 1990; McKay and Allen, 1990; Hetzel et al., 1989; Mathan and Viraraghavan, 1989; Mullins et al., 1989; McKay et al., 1987; Coupal and Lalancette, 1976). In addition, peat can be chemically modified to enhance its sorptive capacity (Baes and Bloom, 1988; MacCarthy and Djebbar, 1986; Smith et al., 1976; Khan, 1969). Steam-exploded wood fibers, produced by autohydrolysis of yellow popular wood, is a lignocellulosic material that has the ability to be enzymatically hydrolyzed (Dekker, 1988, Overend and Chornet, 1987). It was chosen for this study because of its low cost ($0.07/lb,) and its ability to sorb pesticides (Mullins et al., 1991; Judge et al., 1991). Little research has been done using rubber has a sorbent; however, it was included in this study because of its hydrophobic characteristics. Used tires could be used as a source for rubber. If the pesticide can be desorbed and

biologically degraded, the rubber sorbent could be recycled in the treatment process. If biodegradation of the sorbed pesticide is not feasible, the rubber material could be incinerated. In either case, using tires as a source for rubber could be beneficial in conserving landfill space.

Mullins et al. (1991) are developing a two-phase pesticide disposal method. These phases include removal of the pesticide from contaminated water through filtration/sorption, followed by decomposition of the sorbent and pesticide through composting in a bioreactor. Composting/biodegradation has been identified as an effective means to dispose of hydrocarbon and pesticide wastes (Felsot and Dzantor, 1990; Thomas and Ward, 1990; Hetzel et al., 1989; Mullins et al., 1989; Petruska et al., 1985). It is hypothesized that this research project will identify one or more sorbent materials that can remove metolachlor from contaminated water to trace levels (<.02 mg/L). This information can then be incorporated into the two-phase pesticide disposal method.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 HISTORY OF PESTICIDE DEVELOPMENT

Pesticides are chemical agents that are designed to kill or repel unwanted weeds, microbes and insects. The use of pesticides dates back to biblical times, when armies used salt and ash on their enemies' fields to destroy their crops. Homer is noted for observing the pest repellant characteristics of sulfur in 1000 BC. In 100 BC, the Romans used a plant called hellebore to kill rats, mice and insects. The toxic properties of this plant were later attributed to alkaloids. The Chinese were the first to utilize the toxic properties of arsenic to control garden insects in 900 AD. In 1649, South Americans used rotenone to paralyze fish. The first use of a pesticide in the United States (then a British colony) can be traced back to 1690 when extracts were taken from tobacco and used as a contact insecticide. Pyrethrum, an insecticide commonly used on domestic pets for control of fleas and ticks, was discovered in 1858. The first synthetic pesticide, 4,6-dinitro-o-cresol, was developed in 1892 (Knowles, 1988). Since this time the market has been inundated with a multitude of synthetic pesticides.

The development of pesticides has revolutionized the agricultural industry. Crops which would have been destroyed by insect infestations or dominated by an unwelcome species of fauna, now flourish with a high productivity rate. Insecticides combat insects vectors that can transmit disease to both humans and animals. The development of DDT has saved the lives of an estimated 1.5 billion people from 37 different countries who would have fallen victim to the mosquito-borne disease malaria (Weigmann, 1988). The disease Schistosomiasis afflicts people in 73 different countries. It is caused by an parasitic fluke which colonizes the blood veins of mammals. The development of a molluscicide has helped control this parasite by killing the snail which acts as an intermediate host for the fluke (Knowles, 1988). The public was eager for solutions to the complex problems caused by unwanted pests. It is easy to understand why the negative consequences of pesticide use were initially overlooked.

Pesticides are "biologically toxic by necessity" (Weigmann, 1988). It is unrealistic to think that pesticides are only detrimental to the targeted organism. It was only when animals began to display chromosomal abnormalities and reproductive failures from pesticide exposure that society begin to question the indiscriminate

use of these chemical agents. The use of dieldrin in Illinois to eliminate the Japanese Beetle virtually destroyed the ground squirrel, cottontail and muskrat populations, while endangering the fox squirrel, woodchuck, mole, shrew, opossum and mouse populations (Knowles, 1988).

Rachael Carson's 1962 novel, Silent Spring, is often credited with alerting the public to the detrimental environmental impacts resulting from use of pesticides. In some cases, natural enemies of the targeted organism were destroyed while many pests developed resistance to the chemical agents. Farmers who successfully rid their crops of one pest, were disappointed to discover that the pest's niche was quickly taken over by other unwanted organisms. In addition, entire food chains were contaminated with certain hydrophobic pesticides. These chemicals bioaccumulated in the fatty tissue of organisms and biomagnified as the chemical passed from one species to another as a result of predation. Even when the public became aware of the possible hazards of specific pesticides, the products remained on the market until their use was reviewed by the EPA. Despite the negative side affects to pregnant women, it took nine years of study before the EPA was convinced to ban the use of the herbicide 2,4,5-T (Hales and Williams, 1986).

Today our society is "older and wiser". It has come to realize that responsible use of hazardous chemicals is essential to the well-being of the environment, as well as mankind. Weigmann (1989) suggests that current problems with pesticides result not from misuse, but from long-term, repeated applications to the same geographical region. Others could argue, that repeated applications are a misuse of pesticides. In the late 1970's, pesticide manufacturers began to develop chemicals that were less persistent than the organochlorine compounds previously manufactured. It was thought that these new chemicals were the solution to society's environmental problems. However, because of improved analytical and sampling techniques, scientists have since discovered that these pesticides are also contaminating our soil, water and air.

Hall and Lietman (1991) reported that atrazine, simazine, cyanizine, alachlor, and metolachlor were detected in ground water in Lancaster Valley, PA. Baker (1991) estimated that 0.05% to 0.06% of Ohio residents are consuming water contaminated with alachlor and atrazine at concentrations above the lifetime health advisory limits. Often, the chemicals are found far from the application site (Kissel, 1990). A recent study conducted by the USEPA discovered that the great lakes are currently being contaminated with DDT. The pesticide is being transported

through air currents from Mexico, where DDT is still legally used (Stroebel, 1991).

2.2 SURFACTANT CHEMISTRY

The chemical agent, or active ingredient is enmeshed in a number of surfactants, or inert ingredients. Surfactants, or surface active agents, are substances which have the ability to adsorb onto surfaces or interfaces and alter the free energy of those surfaces or interfaces (Rosen, 1978). This allows surfactants to lower interfacial tension and change the wetting characteristics when it adsorbs to the surface of organic pesticides (Rosen, 1978). The combined product of the active ingredient with the inert agents are termed formulations. Each manufacture may use the same pesticide but different surfactants or emulsifying agents to produce their own formulation of the pesticide. The ingredients of these formulations are normally patented and protected by law.

Surfactants possess both a hydrophobic and hydrophillic tail. In addition, they can be anionic, cationic, or nonionic. Anionic surfactants are usually alkaline earth metal salts of carboxylic, sulfuric, or phosphoric acids. Cationic surfactants are usually

quaternary nitrogen compounds (McIntire, 1990). Both anionic and cationic surfactants usually possess a counterion which acts to partially neutralize the surface charge of the micelle (McIntire, 1990). Nonionic surfactants are polyethylene (POE) or polypropylene surfactants. These are aromatic compounds with alkyl chain groups. 2-octylphenol and nonylphenol comprised 70% of the 1.72 billion pounds of nonionic surfactants produced in the United States in 1986 (Edwards et al., 1991). The majority of pesticides are emulsified with a blend of nonionic and anionic surfactants. Use of nonionic surfactants minimizes ionic interactions with target organisms and the environment, while reducing affects of hard water salts on the adjuvants' effectiveness (Smith, 1977).

When creating a formulation, chemists must consider the stability of the formulation. Factors to be considered are: the solubility of the hydrophillic portion of the emulsion verses the hydrophobic nature of the pesticide; the temperature affects; the dehydrating effect of fertilizer salts; flowability of the suspended or dissolved formulations; reactivity with clay and organic matter, and the effect the formulation has on the size of effective drops in a spray (Himmel et al., 1990).

The physical and chemical properties of formulations act to enhance the effect of the pesticide and bioavailability to the targeted organism (Himmel et al., 1990). Many pests dwell on the bottom surfaces of leaves were direct spray contact with the organism is difficult. Surfactants can increase residue time and adherence of pesticides to the waxy cuticle of plant leaves, where the chemical can then penetrate through the lipid membranes and eventually reach the target insect. Surfactants can also increase the number of effective drops in a spray, as well as, increase the concentration of pesticide in each drop (Kissel, 1990). Surfactants, can also form a micelle structure around an ordinarily hydrophobic compound and make it more miscible in water. Because of this property, manufacturers produce a pesticide concentrate that can later be diluted by the applicator.

When present at low concentrations, surfactants are dissolved in the aqueous phase in the form of a monomer. The hydrophobic portion of the surfactant monomers accumulates at the liquid-air interface, and causes a decrease in surface tension. As more surfactant is added, the surface tension will continue to decrease. When the liquid-air interface becomes saturated, additional surfactant is solubilized by the bulk solution. If the concentration of adjuvant continues to increase, the

monomers will coalesce into a micelle structure. The formation of this configuration occurs at the "critical micelle concentration." When micelles are present, no decrease in surface tension occurs upon subsequent surfactant addition.

Organic compounds present in the bulk solution will associate with the surfactant in the micelle structure. This association enhances the solubility of the pesticide. The structure of the micelle differs with the nature of the compounds present. With nonpolar compounds, the surfactants will encircle the hydrophobic compound and form a hydrophillic ring around it. Semi-polar compounds will align within the ring structure, enmeshed between the surfactant molecules. Polar compounds will also be positioned amidst the surfactant molecules, but they will have hydrophillic tails which are directed to the outside of the ring structure. With ionic surfactants the sphere of hydration may encompass a portion of the nonpolar chain, which may decrease the ability of a surfactant to increase the solubility of a hydrophobic compound (Kile and Chiou, 1989). The hydrophillic oxygen containing chain of nonionic surfactants is the only portion of the compound to become hydrated.

The process of micellation is always in dynamic equilibrium. Micelles continually disperse and reform,

with the average life span of a single micelle being only 10us (McIntire, 1990). The size distribution of micelles is dependent upon the number and weight of surfactant and organic compounds in the aqueous solution. In general, the size of micelles follows a Poisson Distribution (McIntire, 1990).

There are five general classifications of formulations, wettable powders, granular products, emulsifiable concentrates, water miscible concentrates, and flowables (Himmel et al., 1990). Wettable powders are made by adsorbing technical grade pesticide (approximately 85% pure) onto fine clay particles containing wetting agents. The wettable powder is suspended in water prior to application. Granular products come in either pellets or grains. They can be further classified into disintregratable and nondisintegratable. In general, granular products are preferred over wettable powders because they allow more uniform application, minimize dust, are less susceptible to phytotoxicity, and persist longer (Himmel et al., 1990). However, the popularity of granular products is decreasing due to recent bird kills which have been linked to carbofuran (Dillaha, 1990).

The majority of pesticides are sold as emulsifiable concentrates (water in oil dispersions,) (Ware, 1989). On average, emulsifiable concentrates contain 1-4 lb per

gallon of active ingredient with the remaining portion comprised of adjuvants (Smith, 1988). The process of emulsification allows the oil phase to divide into smaller units within the bulk solution. The presence of surfactants in emulsifiable concentrates enhances this process. An advantage of emulsifiable concentrates is that the pesticide can be diluted up to 5000 times its original concentration. Pesticide application concentrations can far exceed the solubility of the pure chemical. In addition, emulsifiable concentrates have a reduced surface tension which enhances atomization and application rate. Flowables are formed by suspending particulate material containing the active ingredient in oil with emulsions. When water is added, a viscous fluid is formed (Himmel et al., 1990).

2.3 PESTICIDE SORPTION

2.3.1 Sorption Theory

Adsorption is the association of a gas, vapor or dissolved material with the surface of a solid matrix, while absorption is the incorporation of the component into the solid's interior structure. The term sorption is used when both of these mechanisms occur simultaneously, or when adsorption or absorption cannot be distinguished. Sorption is categorized into three types: physical, chemical, and ion exchange. Physical sorption is attributed to dispersion forces. "Dispersion forces exist in all types of matter and always act as an attractive force between adjacent atoms and molecules no matter how dissimilar," (Faust and Aly, 1983). These forces results from instantaneous dipole-dipole interactions. Physical adsorption does not involve the transfer or sharing of electrons; it is completely reversible, and has a low energy of adsorption. In addition, physical sorption is not site-specific; molecules can cover the entire surface of the absorbent (Faust and Aly, 1983).

In contrast, chemical sorption involves the formation of chemical bonds between the absorbate and the surface. The interaction is exothermic, and has a high energy of adsorption (Lu, 1989). Generally, this process is

irreversible, and the sorbent/sorbate structure should be viewed as a new chemical entity (Clark, 1974).

Ion exchange is the interchange of anions or cations from the sorbent with other species found in the bulk solution. The process is always occurring in equilibrium with the solution phase. The higher the charge of the ion the more strongly the electrostatic forces hold the ion to the sorbent; and, the more readily it displaces lower charged species from the solid material.

2.3.2 Factors Affecting Sorption

The physical characteristics of a sorbent material can affect the ability of a sorbate to effectively sorb to the solid phase (Faust and Aly, 1983, Bailey and White, 1970). The adsorption capacity, or the amount of solute sorbed per unit weight of sorbate, is a function of the surface area of the solid. The greater the surface area, the greater the number of sites available for sorption. In addition, the porosity of the solid phase affects the sorption capacity by increasing surface area. However, the contribution of micropores to increased sorption capacity is dependent on the molecule size of the sorbate. Sites may be excluded if the sorbate is larger than the micropore.

The particle size of non-porous sorbents influences the surface area of the solid. Smaller particle sizes are generally preferred in sorption processes. However, with porous materials such as activated carbon, the majority of sorption sites lie in the internal pore area; therefore, the sorptive capacity is independent of particle size (Faust and Aly, 1983).

The physio-chemical nature of the sorbate also influences the overall sorption reaction. Bailey and White (1970) identified four factors which affect the chemical character of the adsorbate: 1) nature of the functional groups, 2) nature of the substituent groups, 3) position of the substituent group with respect to the functional groups, and 4) presence and magnitude of unsaturation in the molecule. The functional and substituent groups of the sorbate affects the compound's polarity, whether it is acidic, basic or amphoteric, its ability to hydrogen bond, and its ability to form a chelate structure with a transition metal. The presence and position of substituent groups affect intramolecular hydrogen bonding, and the sphere of hydration around the molecule.

In general, the higher the molecular weight of a compound, the greater tendency it has to sorb. The longer chain length of a sorbate, the more lipophillic the

compound. Branching of a chain usually decreases adsorptivity (Faust and Aly, 1983). The presence of -OH, $-CH_2OH$, -COOH, -COC, -C=O, and $-NH_2$ groups can adversely effect sorption by hydrogen bonding with water molecules. The presence of $-OCH_3$, and $-CH_3$ groups enhance the tendency of the compound to sorb (Bailey and White, 1970; Al-Bahrani and Martin, 1976). Polycylic compounds usually exhibit a greater affinity for the same sorbent then monocyclic compounds. Al-Bahrani and Martin (1976) noted that sorption is not always inversely related to the compound's water solubility. Decreased water solubility does not necessarily increase sorption to activated carbon.

Temperature also effects adsorption. Because sorption is an exothermic process, a rise in temperature will decrease adsorption rate and enhances desorption (Faust and Aly, 1983).

2.3.3 Sorption Kinetics

Sorption of a solute from an aqueous solution to a surface occurs in three phases: 1) film diffusion; 2) intraparticle diffusion; and 3) surface sorption (Weber and Morris, 1963). Film diffusion is the accumulation of a compound on the exterior surface of a particle. Movement of the sorbate from the exterior surface through

the pore space of a sorbent is termed intraparticle diffusion. When the sorbate adheres to a interior site, surface sorption has occurred. The later step is usually very rapid and does not limit the rate of sorption. The slower of the first two phases determines the rate-limiting step. Sorption capacity versus the square-root of time can be plotted from experimental data to determine the rate-limiting step of a sorption process. Review of the literature reveals a controversy over the interpretation of this plot. Weber and Morris (1963) stated that variation of the rate is directly proportional to the concentration when the sorption process is controlled by film diffusion. Intraparticle diffusion will not show a linear relationship. This interpretation is supported by Faust and Aly (1983) and Sweitzer (1979). Cloutier et al. (1985) and Poots et al. (1976) directly contradict this hypothesis. "If a linear plot of the mass of solute absorbed verses the square root of contact time is obtained, the controlling mechanism for adsorption is one of intraparticle diffusion," (Cloutier et al., 1985). Weber and Morris (1963) noted that film diffusion often initially controls the reaction rate; as the exterior surface becomes saturated with the sorbate, intraparticle diffusion becomes the rate determining step.

2.3.4 Equilibrium Sorption Isotherm Models

When the rate of sorption equals the rate of desorption, the net gain and loss of material from the bulk phase is zero; and, the system is said to be thermodynamically stable or in a state of dynamic equilibrium. Adsorption isotherms describe the sorption capacity as a function of the equilibrium concentration. Several isotherm models have been developed to describe this relationship. These models can be used to evaluating or compare sorbents for use in a sorption process. Each model is based on some fundamental assumptions. "Any particular model may fit experimental data accurately under one set of conditions, but fail entirely under another," (Weber, 1985). The fitting of data to one of the models does not provide proof of a sorption mechanism.

2.3.4.1 Langmuir Model

The Langmuir model was developed to describe the adsorption of gases onto a solid surface. It assumes that the adsorption energy is constant and that the surface is covered by homogeneous sites. The sorption is localized. In addition, there is no interaction between the sorbate molecules, so the adsorption capacity is maximized when

the sorbent becomes saturated in a monolayer. The Langmuir model is described by the following equation:

$$Se = \frac{QbCe}{1 + bCe} \qquad (1)$$

where Se = Amount of solute sorbed per unit weight of sorbent.
Q = Maximum sorption capacity.
b = Constant related to entropy.
Ce = Solution phase equilibrium concentration.

Equation (1) can be linearized in one of three forms to obtain parameter estimates from experimental data:

$$\frac{Ce}{Se} = \frac{1}{Qb} + \frac{Ce}{Q} \qquad (2)$$

$$\frac{1}{Se} = \frac{1}{Q} + \frac{1}{bQCe} \qquad (3)$$

or

$$Se = Q - \frac{Se}{bCe} \qquad (4)$$

For equation (2), plotting Ce/Se verses Ce gives a straight line with slope equal to 1/Q, and intercept equal to 1/Qb. Using equation (3), gives a straight-line when 1/Se is plotted verses 1/Ce. The slope of this line is 1/bQ and the intercept is Q. If Se is plotted verses Se/Ce as with equation (4), the slope of the straight-line is 1/b and the intercept is equal to Q.

In many cases the Langmuir model fails to describe the data accurately, because the basic assumptions of this

model are not seen in many sorption systems. This is especially true when dealing with sorption of organic compounds in soil environments. Thus, other models have been developed to describe sorption phenomena.

2.3.4.2 Freundlich Model

The Freundlich equation is often used to describe sorption when the data does not fit the Langmuir equation. Basic assumptions of this model are that the heat of adsorption decreases logarithmically as the fraction of the surface covered increases, the surface of the sorbent is heterogeneous; and, there is an interaction between sorbate molecules which can create a multilayering affect (Bailey and White, 1970). The Freundlich equation is considered to be an empirical model. The equation for the Freundlich Model is:

$$Se = KCe^{1/n} \qquad (5)$$

where Se = Amount sorbed per unit weight of sorbent.
K = Experimental constant, partition coefficient.
Ce = Solution equilibrium concentration.
n = Experimental constant, intensity of reaction.

This equation can be linearized through a log transformation:

$$\log Se = \log K + 1/n \log Ce \qquad (6)$$

The experimental constants can be determined from a straight-line plot. The partitioning coefficient (K) is equal to the anti-log of the intercept of the log plot, and is functionally defined as the value when Ce equals one (Hermosin and Cornejo, 1987; Faust and Aly, 1983). It is used as a relative indicator of adsorption capacity. The larger the K value the better affinity the sorbent has for the solute. The slope of the log plot is equal to 1/n, and can be used to solve for n. The value of n is associated with the energy of the reaction. The larger the number of n, the stronger the attraction between solute and sorbent. Reynolds uses The value of n, and the theoretically predicted value of Se when Ce=Co on the log plot to evaluate the sorptive ability of activated carbon. The larger these values are the more economically feasible the use of the activated carbon (Reynolds, 1982).

2.3.4.3 Brunauer, Emmett, an Teller (BET) Model

The BET model was developed as an extension of the Langmuir model to incorporate multilayer formations. It assumes that:

A given layer need not be complete before subsequent layers can form, that the first layer of molecules adhere to the surface with an energy comparable to the heat of adsorption for monolayer attachment, and that subsequent layers are essentially condensation reactions (Weber, 1985).

The equation describing the BET model is:

$$Se = \frac{BCeQ}{(Ce-Cs)\ [1 + (B-1)(Ce/Cs)]} \qquad (7)$$

where Se = Amount of solute absorbed per unit weight of sorbent.
Ce = Solution equilibrium concentration.
B = Experimental constant, energy of adsorption.
Cs = Solubility limit of solute.
Q = Maximum sorptive capacity of sorbent.

The linearized form of the equation is:

$$\frac{Ce}{(Cs - Ce)Se} = \frac{1}{BQ} + \frac{B-1}{BQ} * \frac{Ce}{Cs} \qquad (8)$$

Plotting 1/Se verses Ce/Cs, is a straight line with a slope of (Q-1)/QB, and a y intercept of 1/BQ.

2.3.4.4 Linear Model

All of the models discussed above reduce to the Linear model in dilute solutions (Weber, 1985; Faust and Aly, 1983). Use of a Linear model is limited to the concentration range of the data set, and should not be used to predict sorption capacity beyonds this range. The linear model is often used when the value of 1/n in the Freundlich model is equal to 1.

The Linear isotherm equation is:

$$Se = KCe \qquad (9)$$

where Se = Amount of solute sorbed per unit weight of sorbent.
Ce = Solution equilibrium concentration.
K = Experimental constant, Partitioning coefficient.

K is mathematically defined as the slope of the linear line.

The linear model can be used to describe the interaction between the solute and the solid. Giles has developed a system of classification based on the shape of the isotherm line when plotted using the Linear Model (Stevenson, 1982). If the isotherm line is L-shaped, the solid has a high affinity for the solute. If the line is S-shaped, the solid has a high affinity for the solvent. Peter and Weber (1982) stated that if an S-Shaped isotherm is obtained, the sorbate is probably sorbing in a vertical position to the surface with multimolecular layers; and, the bonding is monofunctional. A C-shaped curve signifies that the solute is constantly partitioning from the solvent phase to the solid. New sites become available as the solute sorbs to the solid's surface. A H-type of flat shaped curve occurs when the solute has an extremely high affinity for the solid. If this type of curve is obtained, it is possible that chemical sorption is occurring.

2.4 LEGISLATION GOVERNING USE AND DISPOSAL

The Federal Insecticide Act (FIA) of 1910 was enacted by the Federal Government to control manufacturing and use of pesticides. The original Act was based on the efficiency of a pesticide, and was designed to protect the consumer from purchasing misrepresented products. In 1947, a new act, The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), authorized the creation of a pesticide registration program. In order to register a pesticide, data on the product's effectiveness was required.

The 1972 Amendments to FIFRA switched the focus of the Act from pesticide effectiveness to the chemical's toxicity. The responsibility for regulating pesticides was placed under the jurisdiction of the United States Environmental Protection Agency (USEPA). The amendments authorizes the USEPA to: 1) evaluate the risks of pesticides through the registration program, 2) certify and classify certain pesticides for restricted application, 3) suspend or cancel pesticides which pose an undue risk, 4) establish regulations and enforce them though inspections and labeling notices, and 5) publish regulations and recommended disposal procedures for the elimination of unwanted pesticides.

The registration program mentioned above was divided into three components including: (1) registration of new pesticides, (2) reregistration of old pesticides, and (3) special review. In order to register a new pesticide, manufacturers are required to provide data on human health effects and environmental impact. The law requires that pesticides undergo extensive testing to determine if they are oncogenic, mutagenic, or teratogenic agents. Decomposition products resulting from the metabolism of the parent compound must be identified and their health affects determined. In addition to laboratory experiments, small field plot studies are also required. It is estimated that the costs of these tests range from $10-$15 million for each pesticide (Auerbach, 1988).

If a chemical was previously registered under the 1947 Act, manufacturers are required to submit similar data for reregistration. The manufacture is not required to remove the pesticide from the market until the EPA has reviewed the data collected. When the program began, an estimated 600 pesticides had to be reregistered. As of 1980, a total of 200 had been reevaluated for reregistration. The USEPA contends that the other 400 chemicals do not represent a large threat to the environment, because the 200 reviewed represent 90% of the

pesticides commonly used in the United States (Auerbach, 1988).

The special review program is designed to authorize the EPA to reevaluate a pesticide that has already been registered, but new information has lead the USEPA to believe that the chemical may pose an unacceptable risk. Under this program, the EPA can require the manufacturer to conduct additional tests. After reviewing the data, the USEPA has two methods of revoking registrations. For a routine cancellation, the USEPA will propose the suspension of the pesticide, but the chemical remains available to the consumer. A public comment period follows, and then the formal decision is rendered. The manufacturer has the right to appeal a decision during which time the pesticide will remain on the market. If the USEPA feels that the potential hazard of a pesticide is extreme, they may issue an emergency suspension. The chemical is immediately withdrawn from the market until a final decision is reached. As a result of the special review process, ethylene dibromide, 2,4,5-T, and dinoseb have been cancelled. Chlordane was also subjected to special review, but the manufacture withdrew the product from the market before a formal decision could be reached by the USEPA (Auerbach, 1988).

From 1972 to 1988, many jurisdictional problems arose regarding registration of pesticides. Pesticides were being licensed under FIFRA which violated other federal laws. FIFRA allows the risk of pesticide usage to be weighed against its benefits (Stiles, 1988). Other laws, such as the Delaney Clause of the Federal Food, Drug, and Cosmetic Act which states that no trace of a carcinogenic chemical can be found in food, and the Endangered Species Act which states that it is illegal to harm a single endangered species, consider only the risk aspect of a chemical. Congress struggled for many years to resolve these conflicts, with no decision being reached. Finally, in 1988, FIFRA was again amended to reject registration of pesticides that did not comply with both FIFRA requirements and the Delaney Clause. In addition, Congress charged the EPA to complete reevaluation of the 600 pesticides within nine years.

Under the restricted use program, application of a pesticide may be limited if the chemical is found to be acutely toxic, or because it creates an ecological hazard. Pesticides placed in the restricted use category are not removed from the market, because their limited use is still beneficial. Each state is required to establish a training, licensing, and certification program for users of restricted pesticides.

As directed by the 1972 Amendments, the EPA established several guidelines for disposing of pesticides. Applicators should triple rinse containers, and then recycle, reuse or appropriately discard of the containers. Paper and plastic containers may be burned. Dilute solutions should be reused, or placed in evaporation ponds. Cancelled and suspended products should be returned to the USEPA for disposal, and household products (1-5 gallons) should be wrapped securely and placed in the trash (Krueger, 1988). These guidelines are merely recommendations and are not enforceable regulations at this time.

Despite these guidelines, problems with pesticide disposal continue to exist. For example, the containers used for shipping and storage of pesticides are made of a diversity of materials, (plastic, metal, paper, and glass,) making development of one disposal method impractical. Once rinsed, the containers are not considered hazardous waste, but some landfill owners are refusing to accept them due to potential future liability (Krueger, 1988). Sending the containers to a registered, hazardous-waste landfill is costly; and, many pesticide users refuse to incur such an expense when the containers are not considered legally hazardous.

Although it is recommended that cancelled and suspended pesticides be sent to the USEPA for disposal, the problems with their ultimate disposal still exist. The USEPA is not equipped to dispose of these products itself, and must contract out the work. Due to the required selection process, it takes the EPA at least two years to decide what company will handle the disposal (Krueger, 1988). Despite being banned in 1985, EDB was still sitting in a Liberty, Missouri warehouse in 1988. Due to its volatility and caustic nature, much of the pesticide has evaporated and corroded through the storage containers. There are no regulations preventing this type of storage, because at this time a banned pesticide is not considered a hazardous waste under the Resource Conservation and Compensation Act (RCRA) (Stiles, 1988). A total of $70 million has been allocated in the USEPA budget for disposal of banned pesticides. Legislators realized that this is not nearly enough, so the 1988 Amendments now require that manufacturers share in disposal costs.

2.5 PESTICIDE DISPOSAL: PROBLEMS AND RESEARCH

Following the application, it is common practice to rinse the field application equipment and pesticide containers with clean water. This rinsate is laden with pesticide. Little data is available on the actual concentration of rinse solutions following the wash down of aerial applicator spray booms (Krueger, 1988). However, "Large amounts of dilute solutions are generated every day, and these are suspected of threatening groundwater," (Krueger, 1988).

Currently, There are no USEPA certified methods for disposing of dilute solutions, but existing practices include sending the collected water to an evaporation pond, registered landfill or incineration facility (Krueger, 1988). The cost of disposing of dilute solutions at these types of facilities is quite high, and can lead to additional contamination problems. Many evaporation ponds have been outlawed in some geographical regions, while others have been named to the list of Superfund sites (Krueger, 1988). With no official disposal regulations many farmers release the rinsate somewhere on the farm grounds, often only a few feet from groundwells. It is clear that this method of disposal is unacceptable and new economical and convenient methods must be developed.

Development of disposal methods for dilute pesticide solutions may be the USEPA's biggest challenge. The problem warrants extensive research. Unlike many hazardous wastes, disposal of dilute pesticide solutions pose some unique problems. To begin, the waste is usually of low concentration but large volume. In addition, many pesticide waste generators over a wide geographical region contribute to the problem. A disposal method in one area may not be applicable in another. For example, above ground evaporation ponds are an effective means of disposal in Florida, but inappropriate in states where winter temperatures are below freezing. The interaction of the surfactants with the pesticide may create additional problems in developing disposal methods. The addition of surfactants to a pesticide causes the formation of micelles which may significantly alter the fate of the chemical agent, by increasing water solubility, altering sorption properties, or by providing an alternate carbon and energy source to microbes.

It is evident that additional research is needed to address the problems of pesticide disposal. One group of researchers has been experimenting with use of ozonation to chemically decompose pesticides into by-products which are more readily mineralized by microorganism (Kearney et al., 1989). Miller et al., (1989) reported successful

chemical degradation of pesticides with the use of ultra-violet radiation. Past researchers tried to isolate bacterial enzymes to hydrolyze organophosphorus pesticides (Munnecke, 1980). It was hoped that these enzyme systems could work in conjunction with a sorption system; the enzyme could be affixed to a matrix and the contaminated water passed through it. Felsot and Dzantor (1990) report that Reineke and Knackmuss (1979), as well as Kellogg et al. (1981) have been developing genetically engineered microbes which carry the DNA code for production of pesticide degrading enzymes. Recent literature in the areas of enzymatic degradation of pesticides and genetically engineered microbes could not be located, suggesting that these methods may not be appropriate. Current research in the area of pesticide disposal is directed toward sorption and/or bioremediation strategies. Several researchers have found that because of peat's hydrophobic and hydrophillic nature, it can be used as a sorptive media for the removal of a variety of contaminants from polluted waters. Peat contains lignin, cellulose, and humic and fulvic acids (Fuchsman, 1986; McKay and Allen, 1985; Dempsey and O'Melia, 1983; Coupal and Lalancette, 1976). Lignin possesses polar functional groups such as -OH, -COH, -C=O, -COOH, and -O-. Polar organic molecules and dissolved transition metals exhibit

a high affinity for these polar functional groups. This explains some of peat's ability to sorb contaminants from wastewater (Coupal and Lalancette, 1976). Humic and fulvic acids possess highly reactive acidic carboxylic and phenolic functional groups (Dempsey and O'Melia, 1983). At neutral pH, these functional groups are normally in the anion form which allows for complexation and/or ion exchange with metals. Complexation or chelation occurs when, "Two or more coordinate positions about the metal ion are occupied by donor groups of a single ligand to form an internal ring structure," (Stevenson, 1982). Peat has a lower affinity for alkaline earth metals than it does for heavy metals (Baes and Bloom, 1988). As the heavy metals are sorbed to peat's surfaces, the alkaline earth metals are released into the aqueous phase; thus, an ion-exchange system is created. This has obvious significance in the use of peat to remove heavy metals from wastewater. Humic and fulvic acid also possess hydrophobic aliphatic side chains which can attract nonpolar organic compounds (Stevenson, 1982). Under appropriate pH values, amino acid groups can become protonated creating positively charged sites that anionic pesticides can interact with (Stevenson, 1982). In summary, pesticides can bind to peat through protonation,

H-bonding, van der Waal's forces, ligand exchange, and ion exchange.

Coupal and Lalancette (1976) found that peat can be used to remove heavy metals such as Hg, Cd, Zn, Cu, Fe, Ni, Cr^{6+}, Cr^{3+}, Ag, Pb, Sb from contaminated wastewater. In addition, they found that cyanide, phosphates, oil, detergent, and dyes could be removed by contact with peat. Mathavan and Viraghavan (1989) studied the use of peat in the treatment of oily waters. They found that the oil binding capacity of peat was 7.5 to 7.8 times its air dry weight. Oil removal efficiencies were reported at 21 to 98%, depending on the emulsion studied. Cancela et al. (1990) found that sorption of cyanazine to peat varies according to the cationic functional groups present on the peat. Adsorption to H^{+}-peat > Cu^{2+}-peat > Ca^{2+}-peat > Co^{2+}-peat > Mg^{2+}-peat > K^{+}-peat. Experiments with Diazinon contaminated waters have found that the chemical can be absorbed to peat (Hetzel et al., 1989; Mullins et al., 1989).

McKay et al. (1978) conducted a series of isotherm studies on four different dyes. Decolorizing carbon had the highest adsorptive capacity, but peat and wood were found to have high adsorptive capacities as well. McKay and Allen (1983) developed a mathematical model for the fixed bed adsorption of telon blue dye on peat. This

model can be used to predict breakthrough curves. These researchers noted that the dye may not completely penetrate into the internal pore space of peat which creates difficulty with assessing particle size affects in the mathematical model. McKay and Allen (1984) reported that the cationic groups of dyes have a strong affinity for peat because of peat's anionic groups. Poots et al. (1976) also found that peat is an effective sorbent for the removal of acid blue dye from water. They reported an equilibration time of 2 hr.

Treatment of peat with sulfuric acid as been found to improved its sorptivity. Smith et al. (1977) found that, "Peat has considerable potential for the removal of cationic species from water over a wide range of concentrations." In addition they stated, sulfuric acid-treated peat has good physical characteristics up to a pH of 8. MacCarthy and Djebbar (1986) stated that problems associated with leaching of organic matter and the impermeability of peat could be reduced by treatment with sulfuric acid. This chemically-modified peat was successful in removing paraquat, diquat and amitrole from water (MacCarthy and Djebber, 1986). These researchers reported, "A capacity of 1 mol(+) kg^{-1} for these three pesticides."

Cloutier et al. (1985) studied the removal of 2,4-D from contaminated wastewaters under a variety of initial solute concentrations, pH values, particle size of adsorbent, temperature, and ratios of weight of adsorbent to solution volume. They found that the adsorption capacity for peat increases with higher initial concentrations of 2,4-D, lower pH values, finer particle sizes, and higher peat concentrations.

Other sorption processes have been studied for the removal of pesticides from contaminated waters. Dennis and Kobylinski (1983) found that pesticide contaminated wastewater could be decontaminated by recirculation through activated carbon. Three, 400 gallon mixtures of seven pesticides formulations (baygon, dimethoate, diazinon, ronnel, malathion, dursban, and 2,4-D,) were passed through 45 lbs of granular activated carbon. Initial concentrations of pesticide in the mixtures were 20 mg/L, 60 mg/L and 100 mg/L. After 20 hr, less than 1% of the initial concentration of most of the pesticides remained in solution.

Bioremediation methods are being evaluated as a means to degrade pesticides in contaminated soils or pesticide laden sorbents. Mullins et al. (1989) suggested that nutrient-enriched peat might be a useful method for neutralizing peat-absorbed pesticide wastes. They

reported that degradation pits treated with diazinon concentrations ranging from 4000 to 32000 mg/kg contained less than 1 to 7 mg/kg after 18 weeks. Hetzel et al. (1989) found that 4000 to 32,000 mg/kg of diazinon sorbed to peat could be effectively degraded to less than 0.2% after 8 weeks and 0.02% after 18 weeks by placing the material in a degradation/composting pit. Felsot and Dzantor (1990) studied the effects of diluting contaminated soil to enhance biodegradation of land applied waste soil. They found that 75% of alachlor was detoxified in 42 days when diluted by 90% to 6.5 mg/Kg with an uncontaminated soil. This is compared to only 30% degradation at a 50% dilution rate. Analysis of soil dehydrogenase activity found that this enzyme was inhibited in undiluted soil samples; however, activity was restored in the diluted samples. These results suggest that high levels of alachlor are toxic to microorganisms. Felsot and Dzantor also studied the effect of surfactants on the biodegradation rate of alachlor. They found no significant difference in degradation rates between the technical grade and emulsifiable concentrate at 10, 100 and 1000 mg/kg.

2.6 METOLACHLOR

Metolachlor poses a challenge to disposal research due to its high water solubility (530 mg/L). Metolachlor is a chloroacetamide herbicide. Its structure is:

> a mixture of four stereoisomers, the isomerism of which is based on a combination of chiral center in the aliphatic side chain and a chiral axis between the phenyl and the nitrogen atom (Figure 1)(Lebaron et al., 1988).

It was developed for use on corn, soybean, sorghum, peanut, and cotton crops to control growth of grass and broadleaf weeds. Its mechanism of herbicidal action is unknown. Once applied it impairs or inhibits plant growth.

Concern over water contamination with this chemical has risen, due to metolachlor's increased popularity and use under conservation tillage practices (Chesters et al., 1989). Because metolachlor is relatively stable, is has a longer activity period than other chloroacetamides.

The half-life of soil-bound metolachlor is between three weeks and two months (Lebaron et al., 1988). There are various pathways for potential loss of soil-bound metolachlor. An unpublished study by Ciba-Geigy found that only 0.6-1.4% of metolachlor would volatilize within 24 hours of application (Lebaron et al., 1988). Lebaron et al. (1988) stated that Burkhardt (1977) reported that the volatility rate of the herbicide is dependent upon the nature of the surface and the velocity of air currents.

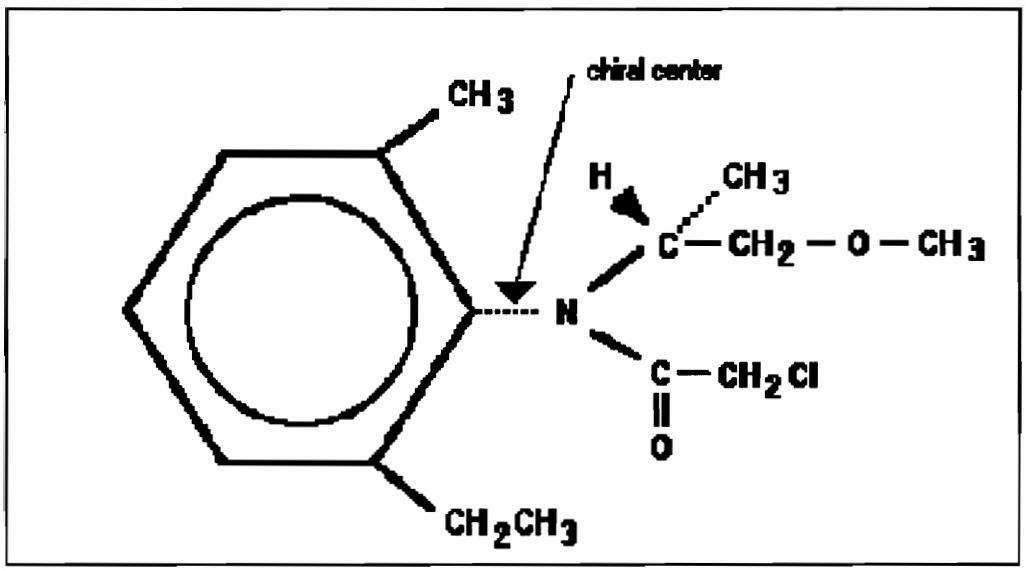

Figure 1. Structure of metolachlor.

In another unpublished Ciba-Geigy report, Parochetti (1974) discloses that while only 0.1% of metolachlor is volatilized from soil surfaces in eight days, 50% is lost from the surface of glassware, and up to 36% is lost from straw (Lebaron et al., 1988). In view of these studies, metolachlor is considered a non-volatile compound. In addition, loss due to photolysis or hydrolysis under a wide range of pH appears to be negligible (Lebaron et al., 1988).

The major mechanism responsible for reducing soil-bound metolachlor is biodegradation. The soil fungus Chaetomium globosum was found to degrade up to 45% of the metolachlor after six days; however the fungus was not able to utilize the herbicide as a carbon or energy source (Tiedje and Hagedorn, 1978). Liu et al. (1988) reported that 18.4% of the herbicide was completely transformed to $^{14}CO_2$ when added to a previously metolachlor-contaminated soil. A sterile soil showed only 3.5% mineralization. Up to 30% of the $^{14}CO_2$ was incorporated into transformation by-products. Krause et al. (1985) studied the biodegradation of metolachlor by a soil actinomycete. His studied identified eight possible metabolites. However, there was no evidence of aromatic ring cleavage. When analyzed by a mass spectrophotometer, all metabolites had a characteristic pattern for monochlorine. This indicates

that the actinomycete was unable to dechlorinate metolachlor. In addition, the study found an increased rate of degradation upon addition of 0.4% sucrose and 0.04% yeast extract to the growth medium. Results of these studies seem to suggest that metolachlor is more rapidly degraded by a biological consortium than a pure culture.

Under anaerobic conditions, Lebaron et al. (1988), and Krause et al. (1985) reported that McGahen and Teidje (1980) obtained 100% reduction of metolachlor from contaminated sediments in eight days (Lebaron et al., 1988; Krause et al., 1985). Despite this laboratory study, metolachlor has been identified as a groundwater contaminant. Therefore, it is highly unlikely that complete degradation actually occurs rapidly, if at all, in the natural environment.

Major transformation pathways for microbial degradation include dechlorination with hydroxylation, dehydrogenation of the 6'-methyl, dealkylation, demethoxylation, and formation of indoline and oxoquoline compounds (Lebaron et al., 1988).

Ideally, society would like to completely discontinue the use of pesticides in favor of less hazardous alternatives; however, there does not appear to be an effective alternative. If pesticides are not used,

society would suffer from damaged crops and life-threatening plagues. Use of pesticides will remain a trade-off of different adverse affects. This emphasizes the need for effective management strategies. However, it is clear that establishment of successful "best management practices," is contingent upon the development of appropriate pesticide disposal methods for agriculture.

CHAPTER 3

3.0 METHODS AND MATERIALS

3.1 INTRODUCTION

Batch sorption studies were conducted to evaluate the effectiveness of three economical sorbent materials for the removal of metolachlor from an aqueous phase. Materials investigated include peat moss, steam-exploded wood fibers, and rubber. Granular activated carbon represented "best available technology," and was used to compare the other sorbent materials.

Following this, several experiments were conducted where the sorbent, aqueous phase, or treatment process was modified. This was done to investigate the effect of the method modification on metolachlor removal efficiency.

3.2 PREPARATION OF MATERIALS

3.2.1 Standard Test Solutions

A 50,000 mg/L stock solution of unformulated metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methylethyl)-acetamide] (Chem Service, 98% purity) was prepared using 15 mL of Fisher Scientific HPLC-grade methanol. To prepare the test solutions, the appropriate volume from the stock solution was added to 500 mL volumetric flasks. The flasks were placed under a hood for 24 hr to allow the methanol to evaporate. After 24 hr, the remaining methanol was evaporated by sparging with nitrogen gas. No loss of metolachlor was anticipated due to its low volatility (Hartley and Kidd, 1987). All test solutions were prepared by diluting with ultra-purified water from a Vaponics ion exchange system. The solutions were capped and mixed for 48 hr on Thermolyne Nouva II stir plates, to ensure complete solubility of the compound. All solutions were stored at 10°C and brought to room temperature prior to use.

The emulsifiable concentrates or dispersions of formulated metolachlor (marketed as Dual) were prepared from a 5000 mg/L stock solution made with ultra-purified water. The formulated metolachlor was supplied by Ciba-Geigy Corp. (86.4% purity) A correction factor for the purity of the supplied chemical was used in preparing the

stock solution. Because the test solutions were prepared in deionized water, methanol evaporation was not applicable. The suspensions were placed on a stir plate for only two hours. They were also stored at 10°C.

3.2.2 Sorbent Material

Steam-exploded wood fibers were obtained from The Center for Innovate Technology and Biobased Materials at Virginia Polytechnic and State University. It was derived through autohydrolysis of yellow popular wood. The chemical characteristics of the yellow popular wood were altered using a masonite process gun (Overend and Chornet, 1987). The material was oven-dried overnight at 60°C. It was then manually sieved through Newark standard testing sieves to obtain a uniform particle size of 1-2 mm. This particle size was chosen to eliminate ultra fines which may clog filtration systems.

The sphagnum peat moss was obtained from Canada through Southern Importing Inc. in South Carolina. Cloutier et al. (1985) reported a specific surface area for sphagnum peat moss of 220 m^2/g, a bulk density of 136.5 kg/m^3, a dry basis density of 66.2 kg/m^3, a porosity of 95%, humidity of 51.5%, and a heat of combustion calculated on a dry basis of 5300 kcal/kg. McKay and

Allen (1984) reported a moisture content of 14.5% by weight, and an ash content of 1.89% by weight. The sphagnum peat moss was sieved in a similar manner to the steam-exploded wood fibers. The t-butyl rubber supplied by Fisher Scientific was mechanically ground through a 20 mesh screen in a Wiley Intermediate Mill to obtain a 0.86 mm size particle. Calgon Filtrasorb 200 with a particle size of 0.86 mm was used as a source of granular activated carbon.

Differences in particle size were unavoidable. The largest mesh size available on the mechanical grinding apparatus is 20 mesh. The nature of the wood fibers and peat are such that passing them through such a small pore size resulted in a fine dust. Although dust particles would have a greater sorptive capacity because of the increased surface area, the dust would clog the filter in laboratory and field-scale models.

3.2.3 Analytical Methods

Samples were chromatographed on a high-performance liquid chromatograph (HPLC) system (LDC Analytical, Riviera Beach, FL) consisting of a CM 3400 pump, a 7125 Rheodyne valve, and a 3100 variable-wavelength spectrophotometer. The signal output from the

spectrophotometer was recorded using 3396A Hewlett Packard integrator. The concentration of metolachlor was determined by manually measuring the height of the metolachlor peak and comparing it with an external standard of 10 mg/L. A 2 mg standard was used to analyze the activated carbon and rubber-packed column samples. Methanol and water (85:15 vol/vol) was eluted at a flow rate of 1 mL/min. The wavelength was set at 220 nm. A Supelcosil, LC-18-DB column, with a particle size of 5um and length of 15cm, was used to separate metolachlor. The retention time for metolachlor was 2.90 minutes. Calibration curves were linear in the concentration ranges of 5-50 mg/L, 0.5-5 mg/L, and 0.02-0.5 mg/L for three replicates. The detection limit for metolachlor was 0.02 mg/L ($r^2 \geq 0.96$).

All glassware and plastics were tripled rinsed with acetone, immediately after use. This was followed by soaking the dishware in Alconox soap and rinsing with tap, and then deionized water. A final acetone rinse was used before oven drying at 100°C.

3.3 DEVELOPMENT OF STANDARD TEST METHOD

Prior to HPLC analysis, samples were filtered through a 0.2 um membrane filter to remove any fine particulate matter from the solution prior to injection. Initial observations revealed that filtered solutions showed appreciable metolachlor losses using a variety of membranes including Gelman Sciences' 0.45um Acrodisc 3 CR PTFE, 0.45um Acrodisc CR PTFE, 0.2 Acrodisc 13 CR PTFE, 0.45 Nylon Acrodisc, 0.45um LC13 PVDF, and 0.2 LC13 PVDF. Apparently, metolachlor has a high affinity for the membranes tested. Experimentation showed that losses through a Gelman 0.2um LC13 PVDF membrane could be minimized if samples were diluted 9:1 with methanol. Recoveries of 25 mg/L methanol diluted samples were 96 $\pm$ 2.30% (n=3) for the unformulated metolachlor, and 101 $\pm$ 2.08% (n=3) for the formulated metolachlor.

Before diluting the aliquot sample with methanol, the sorbent had to be separated from the bulk solution. If this was not done, metolachlor could have been extracted from the sorbent resulting in higher metolachlor concentrations in solution. Two methods were found to be equally effective in separating the solid phase from bulk solutions with minimal metolachlor loss. They were centrifugation (13,000xg) and filtration through a 0.45 um glass-fiber filter. Filtration of 25 mg/L metolachlor solutions through glass-fiber filters permitted 98 $\pm$ 0.71%

(n=3) of formulated metolachlor to be recovered, while recoveries of unformulated metolachlor were 98.0 ± 0.00% (n=3). Approximately 100% recoveries for both unformulated and formulated metolachlor were obtained for the range investigated (25 mg/L to 5000 mg/L.) Initially, the glass fiber filtration method was used for the separation process. It was subsequently determined that centrifugation was a more convenient way to remove the particulate matter up to a concentration of 450 mg/L formulated metolachlor. Above this concentration, a visible white precipitate formed in the bottom of the conical centrifuge tube. Analysis of the supernatant showed a loss of metolachlor from the dispersion. It is hypothesized that the loss of metolachlor resulted from a precipitation of a surfactant-metolachlor complex.

Because of the decreased time and ease of processing samples, centrifugation was used to separate the sorbent from the bulk solution in later experiments. The separation method used for each experiment has been designated in the following methods. The two methods were graphically compared to determine the compatibility between procedures. There was essentially no difference in recoveries between the two methods.

Following the separation and dilution process, the sample was vortexed at high speed for 30 seconds. Two to

three milliliters of the methanol-diluted aliquot sample were poured into a plastic syringe. Pressure was applied manually to cause the solution to pass through the Gelman 0.2 um PVDF filter. The effluent was collected in a test tube, capped, and refrigerated at 10°C until analyzed on the HPLC. One Gelman filter membrane filter was used for triplicate samples. Between filtrations, the syringe and Gelman membrane were rinsed with 3 mL of methanol.

3.4 PRELIMINARY EXPERIMENTS

3.4.1 Hydrolysis Experiments

Hydrolysis experiments were conducted to determine the stability of unformulated metolachlor over time in an acidic, a basic and a neutral solution. One hundred milliliters of deionized water were added to each of three separate 250 mL glass Erlenmeyer flasks. Solution pH's were adjusted using 1M HCl or 1M NaOH. Final pH readings of the three samples were 12.6, 5.97 and 1.87. To each flask, 0.1 mL of a 50,000 mg/L unformulated stock solution was added. The final solution concentration of each sample was measured at 50 mg/L.

Teflon-coated stir bars were added to each flask; and, the headspace sparged with nitrogen gas, and sealed with a teflon-coated rubber stopper. The addition of nitrogen created an anaerobic environment, eliminating aerobic biodegradation as a pathway for loss of material. Degradation under anaerobic conditions was assumed to be negligible due to the short time frame of the experiments. The flasks were placed on Thermolyne Nuova II stir plates with a stir speed of 5. The experiment was conducted at ambient temperature (26.7°C); and, the samples were kept in a light-protected environment.

After 24 hr, a 1 mL aliquot was taken from each flask and set aside. The pH's of the solutions were measured; the headspace was resparged with nitrogen gas and sealed with the teflon-coated rubber stopper; and, the flasks were returned to the stir plates. This procedure was repeated for six consecutive days.

The pH's of the acidic and basic aliquots were neutralized with 1 mL of 1 M HCl and 1 M NaOH, respectively. The aliquots were then centrifuged, diluted with methanol, filtered and analyzed on the HPLC.

3.4.2 Kinetic Studies

A kinetic study was conducted on both unformulated and formulated metolachlor to determine the time required for the batch system to reach equilibrium. A Mettler PC 2200 two-place balance was used to measure 6.25 g of peat into three separate 250 mL flasks. Following peat addition, 250 mL of a 200 mg/L unformulated metolachlor solution were added to each flask. The flasks were sparged with nitrogen and sealed with teflon-coated rubber stoppers. The solutions were placed on a Eberbach shaker table operated at 200 RPM.

After 10 minutes, 25 mL of the solution/sorbent mixture was poured into a plastic syringe and filtered through a Gelman Science 13 mm plastic filter case containing a 1.5 cm diameter glass fiber filter disc. Care was taken to remove an equal proportion of solution and sorbent material. A 0.5 mL aliquot of the filtrate was diluted with 4.5 mL Fisher Scientific HPLC-grade methanol. The samples were then filtered through the 0.2 um membrane and analyzed. Additional samples were taken at 30 minutes, 1 hr, 3 hr, 6 hr, 12 hr, and 24 hr. This procedure was repeated for rubber, steam-exploded wood fibers, and activated carbon. The kinetic study for formulated metolachlor was conducted in a similar fashion. Triplicate samples were used for all experiments.

3.4.3 Determining Critical Micelle Concentration

A 500 mg/L formulated metolachlor dispersion was prepared from the stock solution. From this, dilutions were made to obtain 50 mL of 5 through 500 mg/L formulated metolachlor. Each solution was poured into the bottom of a glass Petri dish. The surface tension of the solution was measured in dynes/cm using a Fisher Scientific Model 21 Tensiomat. This instrument was operated using du Nouy method. A platinum-iridium ring of precisely known

dimensions was suspended from a counter-balance lever arm just below the liquid-air interface. It was held level by torsion applied to a taut stainless steel wire. As the torsion was increased the lever arm rose carrying a film of liquid. The force necessary to break the ring away from the surface film was measured.

The instrument was calibrated using deionized water. The surface tensions of the various solutions were plotted against a log-scale of the dispersion concentrations to determine the critical micelle concentration.

3.5 BATCH SORPTION ISOTHERMS

The purpose of this experiment was to characterize the capacity of peat, rubber, and steam-exploded wood fibers to sorb unformulated and formulated metolachlor. In addition, the sorption behavior of unformulated and formulated metolachlor was compared. The data collected was fit to several sorption isotherm models, (Linear, Freundlich, and Langmuir) to determine which best described the experimental data. The experiments were conducted at concentrations below the 530 mg/L solubility limit of unformulated metolachlor (Hartley and Kidd, 1987).

As defined in Section 2.3.4, an isotherm compares the amount of chemical sorbed per unit weight of sorbent (sorption capacity) to the equilibrium concentration. Isotherm data can be generated either by varying the concentration of the sorbate while maintaining the weight of the sorbent, or by varying the weight of the sorbent and holding the concentration of sorbate constant. Both methods were implemented in this study. The first method was used in Experiment A (Section 3.5.1) to contrast unformulated and formulated metolachlor sorption. In Experiment B (Section 3.5.2), the later procedure was used to determine if sorption of unformulated metolachlor to

the various materials was concentration, weight, or volume dependent.

3.5.1 Experiment A: Varying the Concentration

Solutions of 50, 100, 200, 300, and 400 mg/L of unformulated and formulated metolachlor were prepared from the stock solution as described in the preparation of test solutions (Section 3.2.1). The concentrations of each solution were determined to be 45 mg/L, 95 mg/L, 220 mg/L, 280 mg/L, 395 mg/L for unformulated metolachlor, and 45 mg/L, 95 mg/L, 175 mg/L, 255 mg/L, 350 mg/L for formulated metolachlor (n=1). The discrepancy between the target solution concentration and actual concentration for the formulated compound is attributed to the inaccuracy of applying the percent purity of the chemical formula to the aliquot taken to prepare the stock solution.

From each of the prepared solutions, 25 mL were added to a 60 mL serum bottle containing 0.75g of the sorbent. Experimental controls were prepared by adding 25 mL to the serum bottles without any sorbent. The investigation was conducted with triplicate samples for each concentration of metolachlor. The head space of each serum bottle was sparged with nitrogen gas, and the bottles sealed with teflon-coated rubber stoppers.

The serum bottles were placed on a shaker table operated at 200 RPM in a room with a starting temperature of 25°C. The shaker table was covered with aluminium foil to prevent any photolytic decomposition of the compound. After reaching equilibrium, as determined through the kinetic studies, the bottles were removed from the shaker table. Because of the heat generated by the shaker table during the 24 hour period, the final solution temperatures were measured at 37.5°C.

Using a glass pipette, two pipette volumes of liquid sample were withdrawn from the serum bottle and discarded. Subsequent volumes were used to fill Fisherbrand 1.8 mL plastic conical centrifuge tubes. By discarding the initial two volumes of sample from the glass pipette, all sorption sites on the pipette were saturated preventing any material from being lost from the sample.

The samples were centrifuged for 5 minutes, and a 0.5 mL aliquot of the supernatant was taken. To this aliquot, 4.5 mL of HPLC grade methanol was added (1:10 dilution). The diluted solutions were passed through a Fisher Scientific LC13 PVDF 0.2 um Acrodisc before it was analyzed using HPLC. The procedure was repeated for each sorbent. The entire experiment was duplicated using the emulsified formulation.

The amount of metolachlor bound to the serum bottle was determined. All liquid was decanted from the bottles. Residual liquid was suctioned from the bottle, using a hydraulic vacuum system. Fisher Scientific HPLC grade methanol was passed through a 0.2 um Schleicher and Schuell Nylon-66 47 mm filter to remove any particulates. Three milliliters were added to each serum bottle, and swished around the side-walls of the serum bottle to remove any bound metolachlor. A sample was directly removed from the serum bottle using a plastic syringe and analyzed with HPLC. The amount of metolachlor sorbed to the glassware for both the unformulated and formulated compound was less than 1% for all samples. Woodburn et al. (1989) also found that sorption of polyaromatic hydrocarbons to glassware was insignificant.

The amount of metolachlor bound to each sorbent, and the sorption capacity per unit weight of the matrix was determined based on the final solution concentration, and correcting for 1% estimated glassware loss (Section 3.5.3). Sorbed metolachlor was determine by calculating the difference between initial and final metolachlor concentrations (Woodburn et al., 1989). After computing the amount sorbed, the experimental data was plotted and compared to theoretical sorption models (Linear,

Freundlich and Langmuir) to determine which accurately described the sorption behavior of the matrix.

The percent remaining in solution was also calculated to determine if there was a difference in the percent of metolachlor removed from solution at different nominal solution concentrations. A comparison was also made between the percent unformulated and formulated metolachlor remaining in solution for each sorbent material.

3.5.2 Experiment B: Varying Weight and Volume of Sorbent

Twenty-five milliliters of a 400 mg/L dispersion of formulated metolachlor were added to serum bottles containing 0.25 g, 0.50 g, 0.75 g, 1.00 g, and 1.25 g of peat. Serum bottles with no peat added were used as experimental control. The samples were then processed using the standard methods (Section 3.3), including centrifugation. The procedures were repeated for rubber and steam-exploded wood fibers. Surface tension measurements were taken for the steam-exploded wood fibers and rubber samples, with a Fisher Scientific Model 21 Tensiomat. In addition, an experiment was conducted in which the weight of the sorbent was maintained at 0.75 g,

but the volume of 400 mg/L formulated metolachlor was increased to 50 mL. This was done in order to evaluate the effect of volume change on the sorption process. The ratio used is equivalent to 25 mL of formulated metolachlor and 0.38 g of sorbent.

3.5.3 Data Handling

The equilibrium concentration for each sample was computed, by contrasting peak height with the height of the 10 mg/L standard. The relationship can be summarized as follows:

$$Ce = [(H_s * C_d)/ H_d] * DF \qquad (10)$$

where Ce = Equilibrium concentration (mg/L).
H_s = Height of sample.
C_d = Concentration of standard (mg/L)
H_d = Height of standard.
DF = Dilution Factor.

The amount of metolachlor sorbed was calculated as follows:

$$A = [V*(C_o - Ce) - (I*V*0.01)] \qquad (11)$$

where A = Amount of metolachlor sorbed (mg).
V = Volume of solution (L).
Co = Initial solution concentration (mg/L).
Ce = Equilibrium concentration (mg/L).
(I*V*0.01) = Estimated glassware loss (mg).

Recoveries of metolachlor from controls were computed without correcting for glassware loss so that actual and not projected recovery could be reported.

The values calculated for Se and Ce, were used to construct Linear isotherms using equation 9 (Section 2.3.4.4). The data was transformed to fit the linear forms of the Freundlich model (equation 6, Section 2.3.4.2,) and the Langmuir model (equation 3, Section 2.3.4.1.) Regression analysis, was done using Numbers Cruncher Statistical System. Values for the experimental constants K and n, were derived from the anti-log of the intercept on the Freundlich log plot, and the slope of the regression line, respectively. Analysis of covariance compared the slopes of the regression lines for the Linear and Freundlich isotherm models.

The percent of metolachlor remaining in solution was computed as follows:

$$\%\text{Remaining} = (Ce/Co)*100 \qquad (12)$$

This was plotted against the nominal starting solution concentration.

3.6 MODIFICATIONS OF SORBENT MATERIAL

3.6.1 Salt and Acid Treatment

Fifteen grams of oven dried peat (65^{o}C) were placed in a 250 mL polyethylene container, along with 200 mL of 1 M HCl. The mixture was agitated on a shaker table operating at 200 RPM for 24 hr. The mixture was filter through a 1um glass fiber filter under vacuum pressure to separate the HCl from the peat. The peat was returned to the container and successively rinsed with 200 mL of deionized water, until the pH of the eluent approached neutrality. (This was accomplished with five rinses.)

The HCl washed peat was split into four fractions. One fraction received no further treatment. The remaining three fractions were washed five times with either 200 mL of 0.5 M $CaCl_2$, 0.5 M NaCl, or a saturated solution of $Ca(OH)_2$ (approximately 0.0468 M). The first wash was agitated for 24 hr. Successive rinses were vacuum filtered after one hr of agitation. Following the chemical treatment, the peat was rinsed three times with deionized water. All eluents were preserved for metal analysis by Flame Atomic Absorption and for pH measurements. These procedures confirmed the loading of the Na^{+} and Ca^{2+} onto the peat surfaces.Sorption studies were conducted with the hydrated peat samples. The same volume to weight ratio used in the dry isotherm studies (0.75 g/25 mL) was maintained by using 3.0 g of wet material

and 25 mL of 400 mg/L formulated metolachlor. It was previously determined that 3.0 g of wet material was approximately equal to 0.75 g of dry material.

3.6.2 Particle Size Analysis

Batch sorption studies were conducted for formulated metolachlor using peat and steam-exploded wood fibers to determine the effect of particle size on sorption. A particle size of less than 1 mm was compared to 1-2 mm sized particles. Particles of less than 1 mm were obtained by collecting the material that passed through a 1 mm Newark standard sieve. The 1-2 mm sized particles were prepared as described in Section 3.2.2. A batch study was conducted using the standard method (Section 3.3), with 0.75 g of sorbent, and 25 mL of 400 mg/L formulated metolachlor.

3.6.3 Wet and Dry Sorbent

An investigation was conducted to determine if there was a difference in the affinity of metolachlor between oven-dried and hydrated materials. Fifteen grams of peat and wood fibers were placed in 250 mL Nalgene containers filled with 200 mL of deionized water. Fifteen grams of rubber was placed in a 250 mL flask with 100 mL of methanol.

All containers were placed on the shaker table for 24 hr. After 24 hr, the peat and wood fibers were separated from the liquid phase by vacuum filtration. A 5 cm diameter glass fiber filter and nylon Buchner funnel were used. Both materials were vacuum filtered until no additional liquid was removed using the vacuum pressure. The rubber was also placed under vacuum to remove the methanol, but it was rinsed additionally with five funnel volumes of deionized water (approximately 25 mL.)

Triplicate 3 g samples of each sorbent were dehydrated in an oven set at 65°C, then weighed to determine their dry weights. Following this, the appropriate amount of wet sorbent was placed in a serum bottle, along with 25 mL of 400 mg/L formulated metolachlor. A batch study was then conducted using the standard methods (Section 3.3).

3.7 OTHER EXPERIMENTS

3.7.1 Demulsification Research conducted with other pesticide formulations has shown that the addition of crystalline $Ca(OH)_2$ to a pesticide/sorbent mixture has improved removal of the chemical from the solution phase (Mullins et al., 1991). It was hypothesized that sorption was enhanced by demulsification of the surfactant/pesticide complex. A similar experiment was conducted with metolachlor to determine if $Ca(OH)_2$ could effectively demulsify the micelle structure, and increase sorption.

Twenty-five milliliters of 400 mg/L formulated metolachlor were added to 12 serum bottles. Six of the serum bottles contained 0.75 g of peat. The other 6 serum bottles were empty. The bottles containing peat were slightly agitated to uniformly distribute the matrix within the liquid. Following agitation, 0.30 g of $Ca(OH)_2$ (Fisher Scientific) was added to 3 of the serum bottles with sorbent and 3 without. The other 6 bottles received no additional treatment. The experiment continued with the standard method of degassing, capping, shaking, centrifugating, diluting and filtering. In addition, the pH and surface tension of the solution phase was measured following the 24 hr contact period. This procedure was repeated for both the steam-exploded wood fibers and rubber.

3.7.2 Phosphatase Addition

Many anionic surfactants are comprised of alkaline earth metal salts of phosphoric acids (McIntire, 1990). This experiment was conducted to see if the surfactant in formulated metolachlor could be enzymatically degraded to break the surfactant-pesticide micelle association, and to increase the amount of binding sites on the sorbent by eliminating competition by the surfactant. Two milligrams (25 activity units) of phosphatase from Eschericha Coli bacteria was obtained from Aldrich Chemical Co. The enzyme was solubilized directly in the container with the addition of 2 mL of deionized water.

A 400 mg/L solution of formulated metolachlor was prepared (Section 3.2.1). The pH of half of this solution was adjusted to 10.4 using a saturated $Ca(OH)_2$ solution. This pH adjustment was made because the reported maximum activity of phosphatase was 10.0. Twenty-five milliliters of the pH-adjusted solution was placed into serum bottles containing peat, wood, and rubber. It was also added to serum bottles containing no sorbent material. Twenty-five milliliters of the unadjusted solution was placed into serum bottles containing one of the 3 sorbents. Six serum bottles were filled for each sorbent material.

Using a Eppendorf Pipetteman, 0.08 mL of the phosphatase solution was added to the serum bottles

containing the pH-adjusted formulated metolachlor. The same amount was added to half of the unadjusted serum bottles. This was done to compare the effects of phosphatase activity at optimal and suboptimal levels, to the no phosphatase controls. After 24 hours, the samples were processed using the standard method (Section 3.3). Surface tensions measurements were taken on all of the samples.

3.7.3 Reuse and Recontact

Batch sorption studies were conducted using a 400 mg/L formulated metolachlor dispersion to determine if metolachlor remaining in solution following the 24 hr contact period could be removed upon additional contact with fresh sorbent, and if the used sorbent material could be reused in the treatment process. Sorption studies were conducted using the standard procedures (Section 3.3). After an aliquot was taken to determine the equilibrium concentration, the remaining solution phase was decanted from the serum bottle, through a nylon funnel containing glass wool, into a graduated cylinder. The volume was recorded, and the solution poured into an empty serum bottle. Care was taken to remove as little sorbent as possible with the solution phase. Sorbent was then added to each serum bottle at a 0.75 g/25 mL ratio. The solutions

were recontacted with fresh sorbent for 24 hr. Equilibrium concentrations before and after the recontact were compared. The serum bottles contain the used sorbent were placed in a Fisher Isotemp Model 338F Oven at 37°C. Once the sorbents were dehydrated, 25 mL of fresh 400 mg/L formulated metolachlor were added to each bottle. The mixture was placed on the shaker table, and analyzed for equilibrium concentrations after 24 hr. From the equilibrium concentration, the amount of metolachlor sorbed during the first and second contact was computed using the method outlined in Section 3.5.3. Surface tension measurements were taken before and after the contact with the fresh formulation.

3.8 RUBBER-PACKED COLUMN STUDY

A flow-through column study was conducted with rubber to see if this type of reactor could effectively remove metolachlor from the aqueous phase. A 47.5 cm glass column with a 2.5 cm diameter was packed with 185 g of rubber. This was done by gradually adding a slurry of rubber and water to the top of the column with a vacuum pressure applied through the bottom of the column. It was essential that the rubber be packed tightly in the column. Otherwise, the excess space would allow the rubber to float in the column under saturated conditions. Each end of the column was packed with 3.75 cm of glass wool. The column was sealed with rubber stoppers. Oxygen was displaced from the column by sparging it with carbon dioxide gas.

Column saturation was achieved by pumping deoxygenated distilled water through the column in an upflow direction. A Masterflex Pump Controller peristaltic pump equipped with a Masterflex Model 7014 pumphead was used to generate hydraulic flow. The void volume of the column was 60 mL. Fisher brand tubing with 1 cm diameter was used to deliver the pesticide through the rubber inlet to the column. All sorption sites on the tubing were saturated by running a concentrated solution of formulated metolachlor through the tubing until the concentration of dispersion exiting the

column equalled the concentration entering. A glass tube was used for the outlet port.

A flow rate of 250 mL/hr was used based on Reynolds (1982) recommendation for test columns, and the weight of the rubber in the column. This allowed a volume of 6 L to be processed through the column in a 24 hr period. This is comparable to the weight to volume ratio of the batch studies. The concentration of the pesticide used was 400 mg/L formulated metolachlor. Samples were taken every hour for 24 hr (4.17 void volumes).

The 6 L of effluent was then divided. Half of it was recirculated through the rubber-packed column to see if the residual pesticide could be removed. The other half of the effluent was run through a 15 cm glass, activated-carbon-packed column, with a 3 cm diameter. An upflow current was maintained through the 7.26 g of activated carbon at 250 mL/hr. The column has a calculated void volume of 10 mL; however, saturated conditions were not obtained. The pesticide-saturated tubing, used to circulate the herbicide through the rubber column, was used with this system at both the influent and effluent conjunctions.

CHAPTER 3

4.0 RESULTS

4.1 PRELIMINARY STUDIES

4.1.1 Hydrolysis Experiment

This experiment was conducted to determine the stability of metolachlor over time at a pH of 1, 5, and 13. Experimental protocol is described in Section 3.4.1. Figure 2 illustrates the concentration of unformulated metolachlor in solution over time versus adjusted pH. No change in concentration was observed with time. This suggests that metolachlor is stable for at least 6 days within a wide range of pH.

4.1.2 Kinetic Studies

Kinetic experiments were conducted on 200 mg/L of unformulated and formulated metolachlor to determine the time required for the sorbent/pesticide mixture to reach equilibrium. Experimental procedure is reported in Section 3.4.2. Figures 3 and 4 display the average concentration of formulated or unformulated metolachlor in contact with the different sorbent materials at different time intervals. The complete data set for this experiment can be found in the Appendix (Tables 1 and 2).

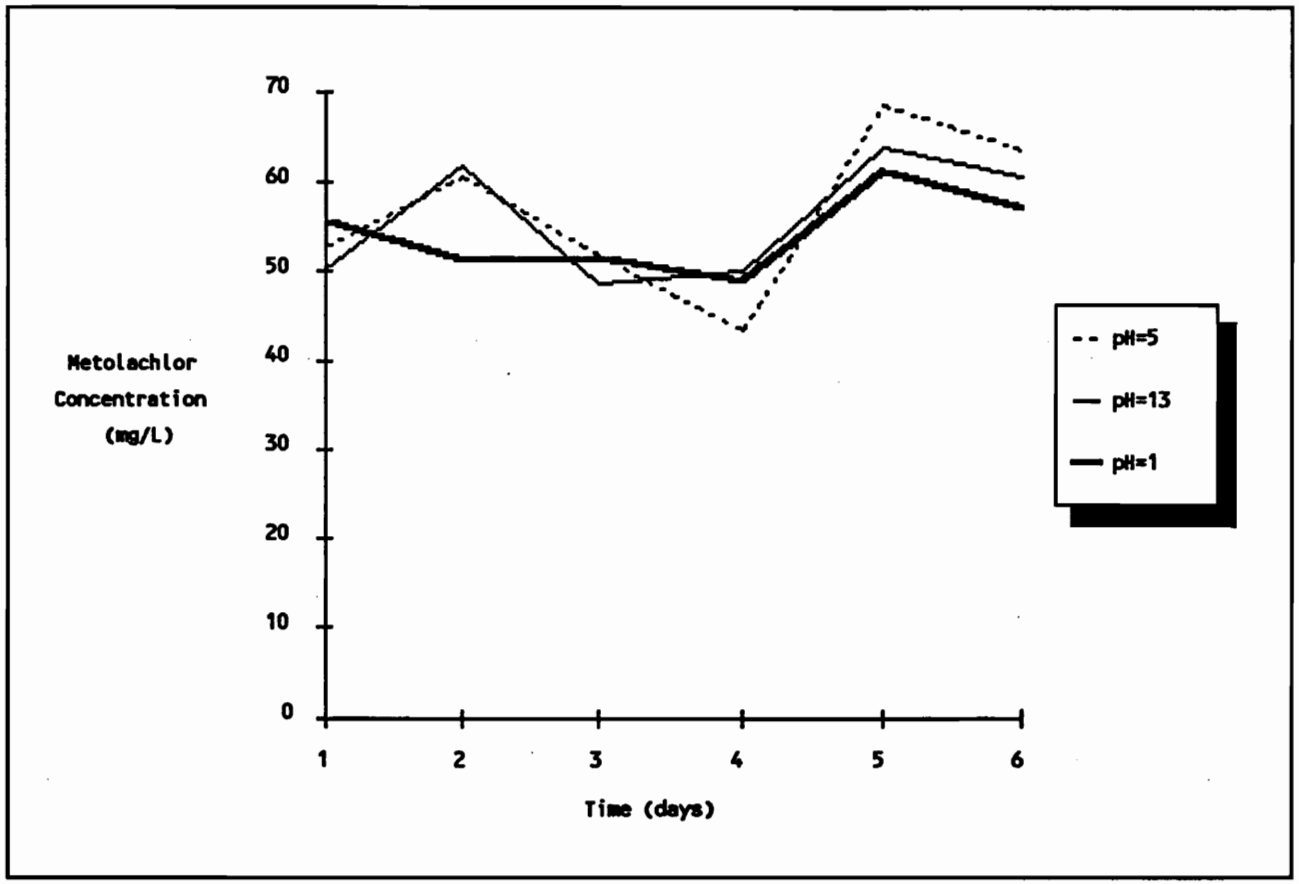

Figure 2. Stability of unformulated metolachlor over time in a basic, neutral, and acidic solution. Sample size was equal to one at each pH value. Initial unformulated metolachlor concentration equaled 200 mg/L. Initial sample volume equaled 100 mL.

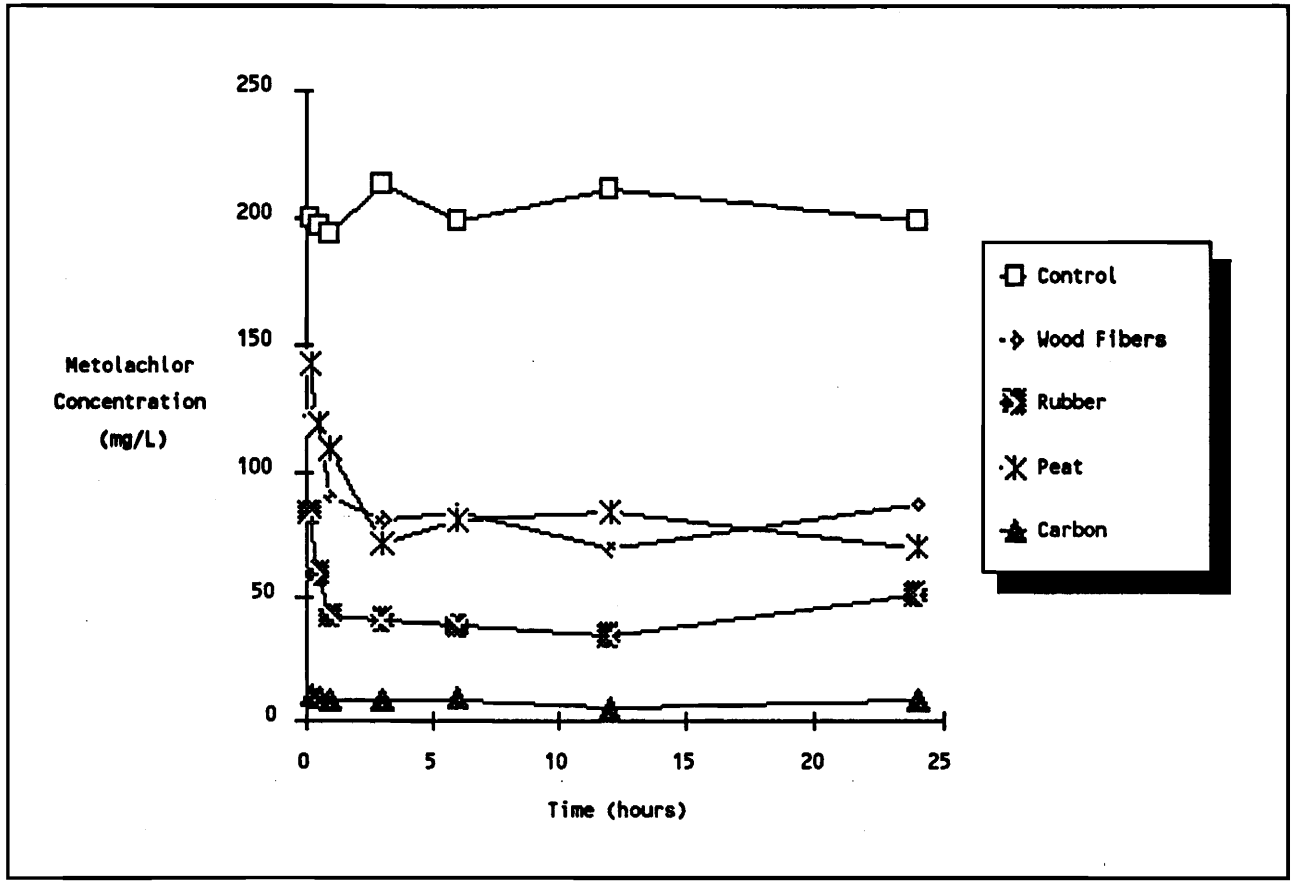

Figure 3. Kinetic Study of unformulated metolachlor sorption to different materials. Sample size was equal to 3 for each sorbent type. Initial metolachlor concentration equaled 200 mg/L. Initial sample volume was 250 mL. Weight of sorbent equaled 6.25 g. Standard deviations are listed in Appendix (Table 1).

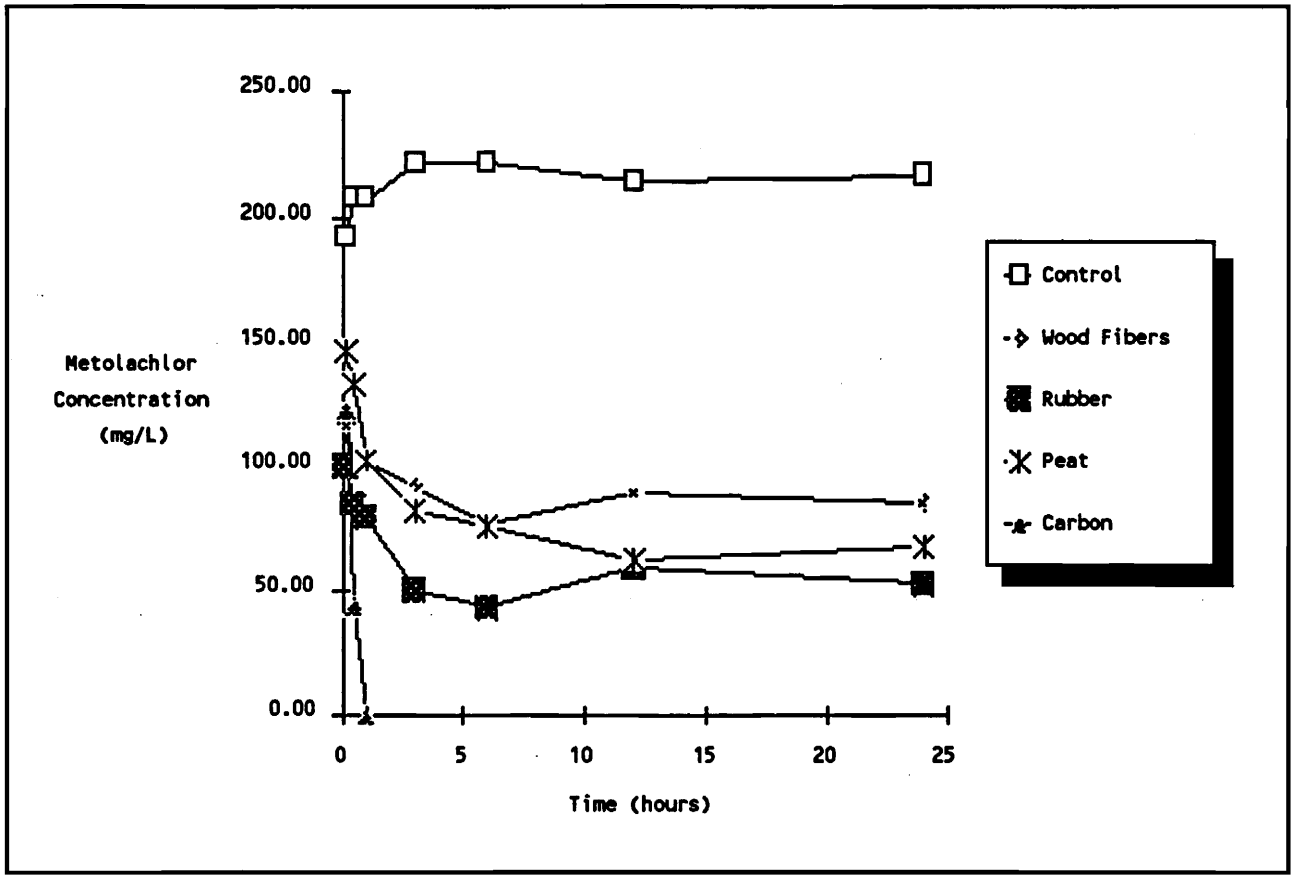

Figure 4. Kinetic Study of formulated metolachlor sorption to different materials. Sample size was equal to 3 for each sorbent type. Initial unformulated metolachlor concentration equaled 200 mg/L. Initial sample volume equaled 250 mL. Weight of sorbent equaled 6.25 g. Standard deviations are listed in Appendix (Table 2).

Equilibrium between the solution and solid phase was reached within 24 hours for all sorbents tested (Figures 3 and 4). One notable exception was observed. When mixed with activated carbon, the concentration of formulated metolachlor fell below detection limits after 30 minutes. Therefore, the equilibration time for this treatment could not be determined. There appeared to be little difference in the equilibration time, or equilibrium concentrations for sorption of unformulated or formulated metolachlor to peat. This was also observed with rubber and steam-exploded wood fibers. Equilibrium concentrations for unformulated and formulated metolachlor are listed in Table 1 (n=3).

4.1.3 Critical Micelle Concentration

Surface tension at the liquid/air interface can be used to estimate surfactant concentration. Lower surface tension values indicate higher surfactant concentrations. When the surface tension reaches a stable minimum, the critical micelle concentration has been reached. The procedure for measuring surface tension is described in Section 3.4.3. Figure 5 shows surface tension (dynes/cm) plotted versus metolachlor concentration for formulated metolachlor. A characteristic decrease in surface tension

Table 1.
Equilibrium Concentrations (mg/L) of
Formulated and Unformulated Metolachlor at 37°C[1,2,3]

SORBENT	EQUILIBRIUM CONCENTRATION mg/L	STANDARD DEVIATION
Unformulated Metolachlor		
Peat	67.51	4.55
Rubber	50.73	0.82
Wood Fibers	86.93	1.56
Activated Carbon	7.64	2.63
Formulated Metolachlor		
Peat	69.92	4.27
Rubber	52.43	6.87
Wood Fibers	85.34	4.41

1 initial solution concentration = 200 mg/L
2 0.75g of sorbent/ 25 mL herbicide used
3 sample size n=3

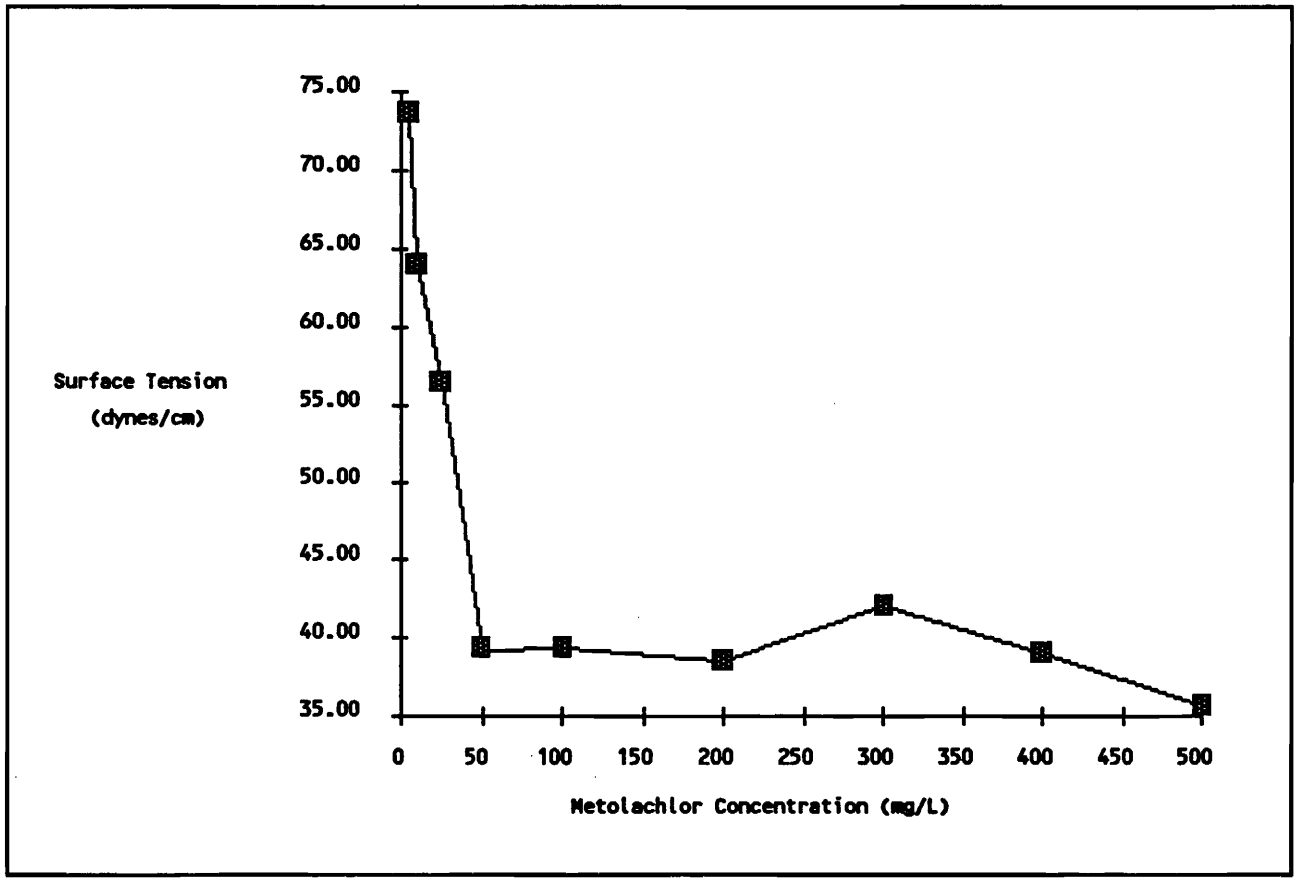

Figure 5. Surface tension versus concentration of formulated metolachlor for determination of critical micelle concentration. Three measurements were made at each concentration range. Standard deviations between triplicate samples were insignificant.

was observed relative to an increase in formulated metolachlor concentration. At 50 mg/L, the surface tension stabilized to approximately 39 dynes/cm. This defines the critical micelle concentration range (CMC) between 25 mg/L and 50 mg/L metolachlor. An estimated surfactant/adjuvant concentration was calculated between 3.4 mg/L and 6.75 mg/L based on the 86.5% purity of the metolachlor formulation.

Tables 2 and 3 show the surface tension of unformulated and formulated solution/dispersions following contact of 400 mg/L metolachlor with each of the sorbents. Surface tension for all of the unformulated metolachlor treatments were approximately 61 dynes/cm regardless of the final solution concentration. Surface tensions of the formulated metolachlor treatments for peat and rubber were also around 61 dynes/cm. Steam-exploded wood fibers samples had lower surface tensions when treated with formulated metolachlor then with unformulated metolachlor.

Table 2.
Surface Tension of Supernatant Following Mixing of
400 mg/L of Unformulated Metolachlor
with 0.75 g of Sorbent

SAMPLE	EQUILIBRIUM CONCENTRATION (mg/L)	SURFACE TENSION (dynes/cm)
Peat A	142	61.6
Peat B	114	60.5
Peat C	104	60.7
Average	120 ± 20	60.9 ± 0.6
Rubber A	65	58.9
Rubber B	77	60.2
Rubber C	71	60.2
Average	71 ± 6	59.8 ± 0.8
Wood Fibers A	179	59.8
Wood Fibers B	144	60.9
Wood Fibers C	144	61.0
Average	156 ± 7	60.6 ± 0.7
No Sorbent A	406	60.7
No Sorbent B	392	60.5
No Sorbent C	396	60.9
Average	398 ± 5	60.7 ± 0.2

Table 3.
Surface Tension of Supernatant Following Mixing of
400 mg/L of Formulated Metolachlor
with 0.75 g of Sorbent

SAMPLE	EQUILIBRIUM CONCENTRATION (mg/L)	SURFACE TENSION (dynes/cm)
Peat A	96	60.1
Peat B	102	61.1
Peat C	93	59.9
Average	97 ± 5	60.4 ± 0.6
Rubber A	59	60.3
Rubber B	70	61.2
Rubber C	61	59.9
Average	63 ± 6	60.5 ± 0.7
Wood Fibers A	139	53.4
Wood Fibers B	131	55.6
Wood Fibers C	152	54.7
Average	141 ± 11	54.6 ± 1.1
No Sorbent A	396	40.1
No Sorbent B	411	40.1
No Sorbent C	411	39.9
Average	406 ± 9	40.0 ± 0.1

4.2 SORPTION ISOTHERMS

Batch sorption isotherm studies were conducted on both unformulated and formulated metolachlor to evaluate the effectiveness of each sorbent in removing this herbicide from the aqueous phase, and to assess the effect of surfactants on the sorption characteristics of metolachlor. The procedures for this study are described in Section 3.5.1 (Experiment A) and Section 3.5.2 (Experiment B). In Experiment A, the concentration of metolachlor was varied, while the weight of the sorbent was held constant. This was conducted for both unformulated and formulated metolachlor. In Experiment B, the weight of sorbent was varied, but a single metolachlor concentration of 400 mg/L was used. This experiment was carried out using only formulated metolachlor.

A single isotherm model can be used to compare the efficiency of different sorbents. In this study, the data was transformed to fit the Linear, Langmuir, and Freundlich isotherm models. Linear regression analysis was done to determine the best straight line fit for each transformed data set. Original data is provided in the Appendix (Tables 3-12). An F-test was used to determine if there was a lack-of-fit in the estimated regression line for all of the sorption isotherm models. The null

hypothesis for the F-test was that the regression was linear in the x term, the alternate hypothesis was that the regression was nonlinear in x. The null hypothesis was rejected if $p > 0.05$. P values for all of the regression lines were less than 0.001. This indicates that the experimental data did not suggest the need to consider terms higher than first order in the estimated regression lines. Sample coefficient of determinations (r^2) (Table 4) confirmed that there was a satisfactory linear relationship for all data fit to the Linear, Langmuir, and Freundlich isotherm models.

Using the r^2 values, the Freundlich equation was chosen as the most appropriate model for comparison of the sorbent materials. Sample coefficient of determinations (r^2), straight-line equations, and Sums of Squares Errors for the regression analysis using the Freundlich isotherm model are shown in Table 5.

Figures 6, 7, and 8 show experimental data fit to the Freundlich isotherm model. (It was not possible to plot sorption isotherms for mixing of formulated metolachlor with activated carbon, because equilibrium concentrations were below detection limits.) From the slope and intercept of each regression line, values for the experimental constants K and n were determined. These

Table 4.
Coefficient of Determinations from Linear Regression Analysis

Sorbent Material	Linear Model	Langmuir Model	Freundlich Model
Unformulated Metolachlor Exp - A			
Peat	0.92	0.92	0.98
Rubber	0.87	0.96	0.87
Wood Fibers	0.89	0.79	0.93
Carbon	0.57	0.63	0.68
Formulated Metolachlor Exp - A			
Peat	0.97	0.98	0.99
Rubber	0.99	0.98	0.99
Wood Fibers	0.97	0.79	0.99
Formulated Metolachlor Exp - B			
Peat	1.00	0.69	1.00
Rubber	0.96	1.00	0.97
Wood Fibers	0.86	0.86	0.80

Table 5.
Linear Regression Analysis using the Freundlich Equation

SORBENT	REGRESSION EQUATION	COEFFICIENT OF DETERMINATION	SUMS OF SQUARES ERROR
	Unformulated Metolachlor - Exp A		
Peat	y = -0.73 + 0.84x	0.98	0.22
Rubber	y = -0.85 + 1.03x	0.87	0.07
Wood Fibers	y = -1.25 + 0.93x	0.93	0.09
Carbon	y = 0.10 + 0.55x	0.68	0.14
	Formulated Metolachlor Exp - A		
Peat	y = -0.80 + 0.86x	0.99	0.02
Rubber	y = -0.73 + 0.99x	0.99	0.01
Wood Fibers	y = -1.03 + 0.83x	0.99	0.02
	Formulated Metolachlor Exp - B		
Peat	y = -1.14 + 1.08x	1.00	0.00
Rubber	y = -1.43 + 1.35x	0.97	0.00
Wood Fibers	y = -1.14 + 1.01x	0.80	0.01

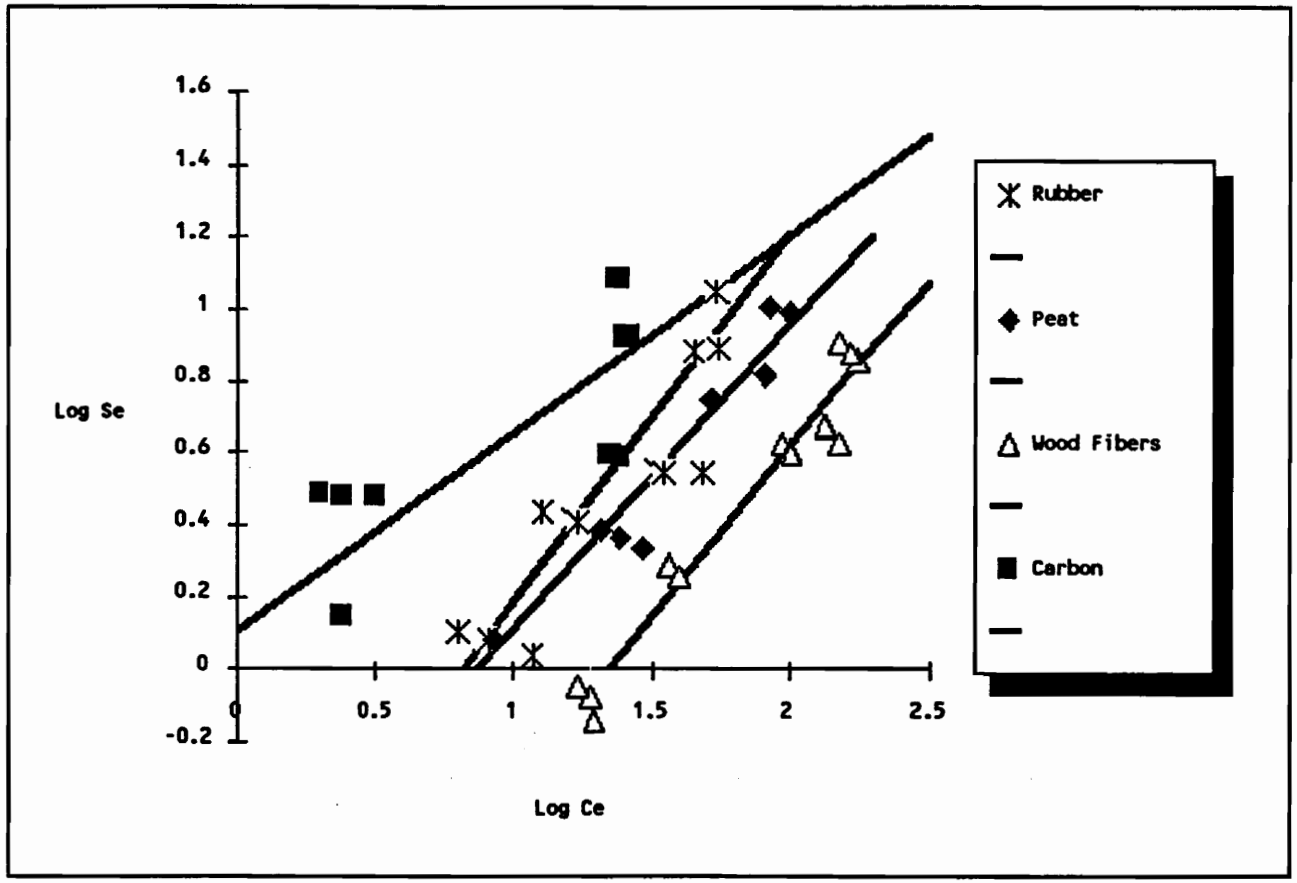

Figure 6. Freundlich isotherm plot of unformulated metolachlor sorption to different materials. Three samples were used at each solution concentration. Metolachlor concentrations used were 45 mg/L, 95 mg/L, 220 mg/L, 280 mg/L, and 395 mg/L. Sample volume equaled 25 mL. Weight of sorbent equaled 0.75 g. Se is equal to the amount of metolachlor sorbed (mg/g), and Ce is equal to the equilibrium concentration (mg/L).

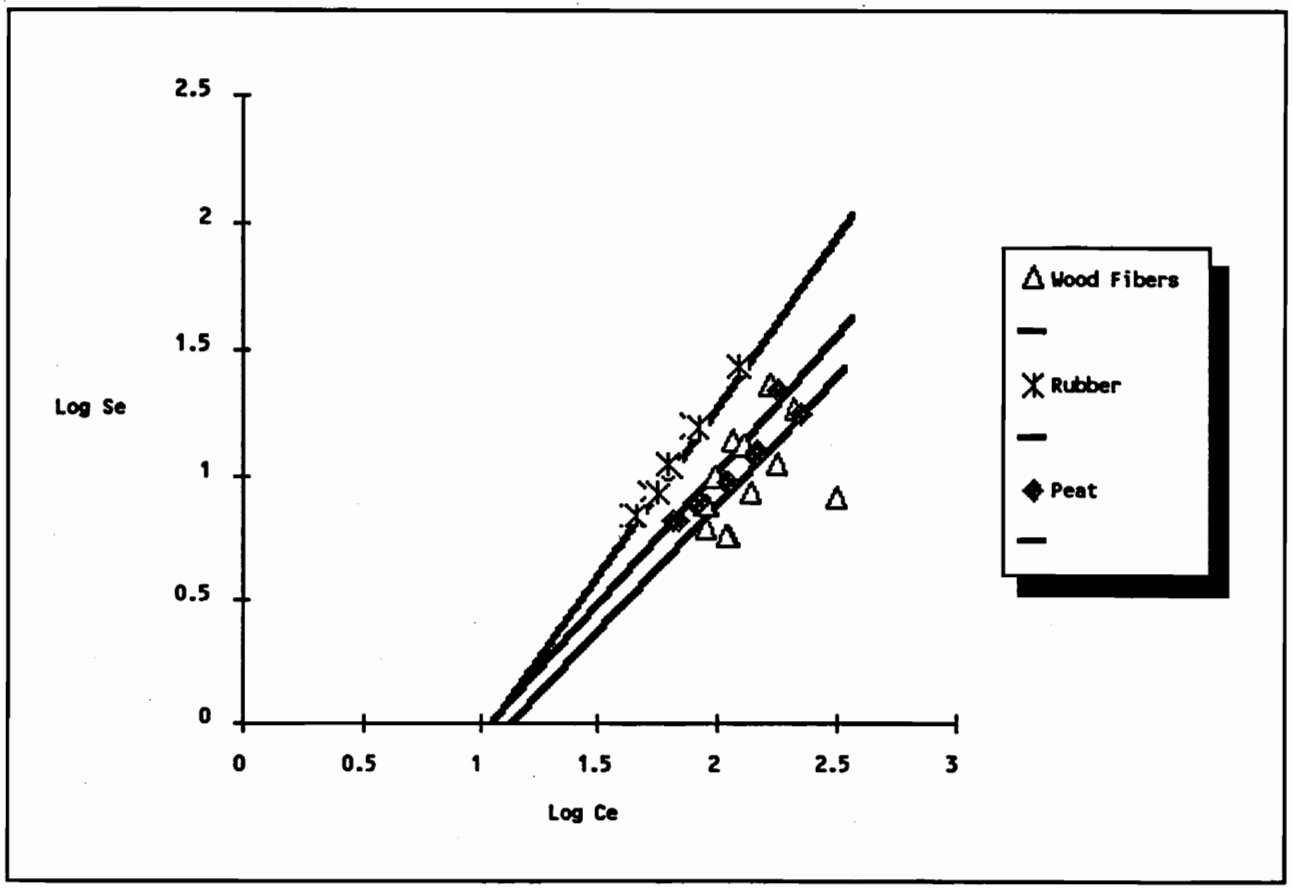

Figure 7. Freundlich isotherm plot of formulated metolachlor sorption to different materials. Three samples were used at each solution concentration. Metolachlor concentrations used were 45 mg/L, 95 mg/L, 175 mg/L, 255 mg/L, and 350 mg/L. Sample volume equaled 25 mL. Weight of sorbent equaled 0.75 g. Se is equal to the amount of metolachlor sorbed (mg/g), and Ce is equal to the equilibrium concentration (mg/L).

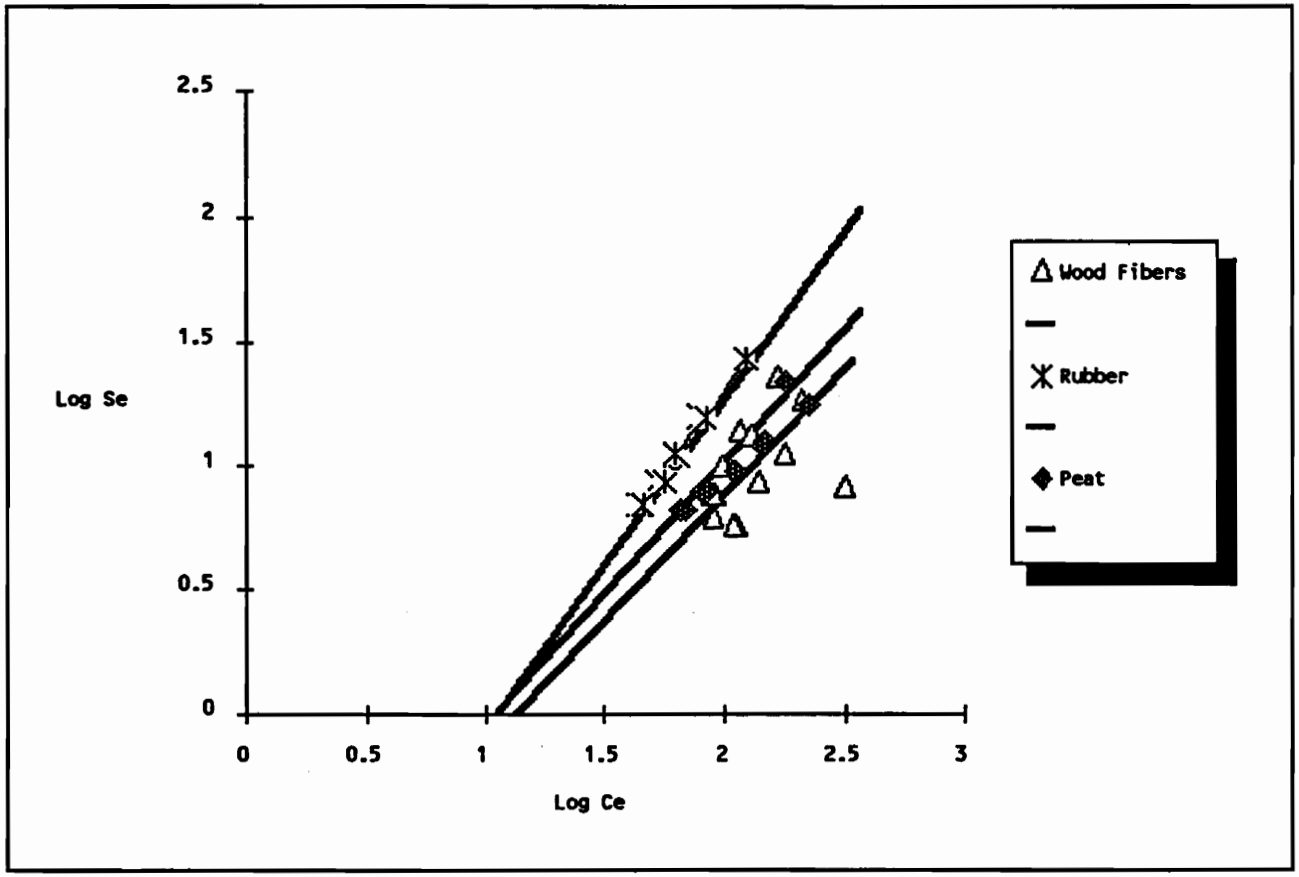

Figure 8. Freundlich isotherm plot of formulated metolachlor sorption to different weights of materials. Three samples were used at each solution concentration. Metolachlor concentrations used were 430 mg/L for the peat and wood fiber samples, and 370 mg/L for rubber. Sample volume equaled 25 mL. Weights of material used equaled 0.25 g, 0.50 g, 0.75 g, 1.00 g, 1.25 g. Se is equal to the amount of metolachlor sorbed (mg/g), and Ce is equal to the equilibrium concentration (mg/L).

values were substituted into the Freundlich equation to predict the value for Se when Ce=400 mg/L (Table 6).

Researchers use the K value to compare sorbents (Candela, 1990; Hermosin and Cornejo, 1987). Based on the K values reported for unformulated metolachlor (Experiment A, Table 6), activated carbon was the most efficient sorbent. Peat was the next most effective sorbent, followed by rubber, and then steam-exploded wood fibers. Reynolds (1985) stated that the Se value can be used to evaluate the efficiency of activated carbon in sorbing different chemicals. It is believed that this parameter can also be useful in comparing different sorbent materials (Section 5.2). Based on the Se value, rubber was the best sorbent, followed by activated carbon, peat, and then steam-exploded wood fibers.

Rubber had the highest K and Se value for formulated metolachlor in both Experiments A and B. The K value for peat was numerically greater then steam-exploded wood fibers in Experiment A, but equal in Experiment B. The Se value for peat was numerically greater than steam-exploded wood fibers' in both experiments.

In order to compare the sorption of formulated and unformulated metolachlor, the percent of metolachlor remaining in solution/dispersion was calculated, using the

Table 6.
Experimental Constants using the Freundlich Model.

Sorbent	Freundlich Equation	K value	Intensity of Reaction (n)	Se(mg/g) when Ce= 400 mg/L
Unformulated Metolachlor Exp - A				
Peat moss	$Se = 1.14Ce^{1.03}$	0.14	0.97	67.02
Rubber	$Se = 0.19Ce^{0.84}$	0.18	1.19	27.60
Wood Fibers	$Se = 0.06Ce^{0.93}$	0.05	1.07	13.15
Carbon	$Se = 1.26Ce^{0.55}$	1.26	1.81	34.00
Formulated Metolachlor Exp - A				
Peat Moss	$Se = 0.19Ce^{0.99}$	0.19	1.01	71.58
Rubber	$Se = 0.16Ce^{0.86}$	0.16	1.16	27.66
Wood Fibers	$Se = 0.09Ce^{0.83}$	0.09	1.20	13.00
Formulated Metolachlor Exp - B				
Peat Moss	$Se = 0.03Ce^{1.35}$	0.03	0.74	97.70
Rubber	$Se = 0.07Ce^{1.08}$	0.07	0.93	45.22
Wood Fibers	$Se = 0.07Ce^{1.01}$	0.07	0.99	29.72

procedure outlined in Section 3.5.3. The percent of metolachlor remaining in solution was graphed versus the nominal starting solution concentration for the formulated and unformulated compound from Experiment A (Figure 9). There was no visible trend to indicate that the surfactant enhanced or retarded sorption of metolachlor. A one way analysis of variance (ANOVA) determined that there was a difference in percent metolachlor (unformulated vs. formulated) remaining in solution after contact with the 3 different test sorbents (æ=0.05, $p < 0.001$); however, there was no difference in the percent remaining in solution between each sorbent type, ($p = 0.44$, 0.51, and 0.25 for peat, rubber, and wood fibers, respectively.) Using Duncan's multiple-range test and Newman/Keuls's range test (æ=0.05), differences in sample means were confirmed for each sorbent type; however, there was no evidence that the sample means differed for the formulated and unformulated compound within the same sorbent type.

An analysis of covariance was conducted to compare Freundlich isotherm slopes for the sorption of the two types of metolachlor to the same sorbent (Table 7). No significant difference was found between the slopes for the same sorbent. This provides further evidence that the presence of the surfactant did not affect the sorption capacity of the sorbent.

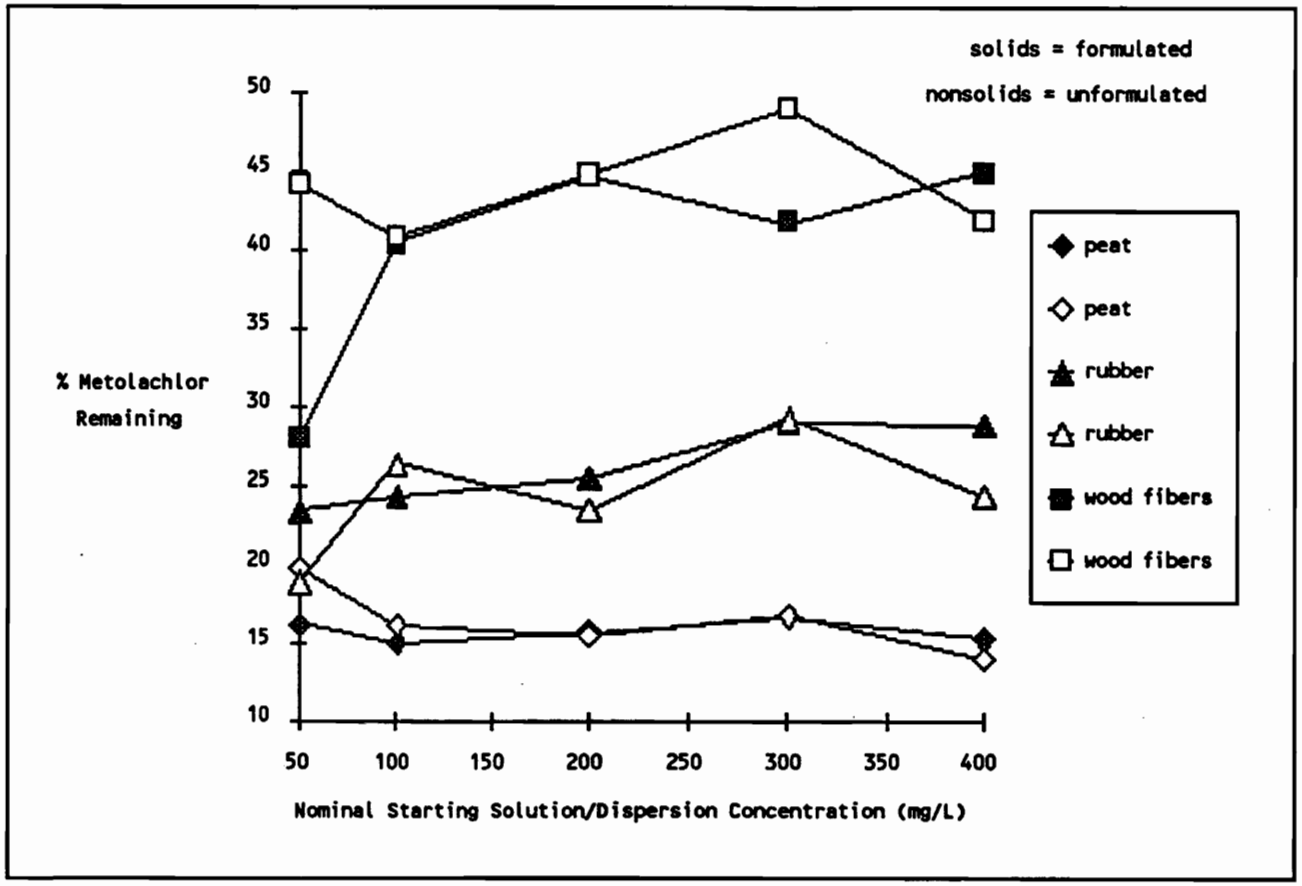

Figure 9. Average percent of metolachlor remaining in solution/dispersion following mixing of unformulated or formulated metolachlor with sorbent. Data displayed from Experiment A (varied concentration, constant weight) only. Three samples were used at each solution concentration. Metolachlor concentrations used for the unformulated were 45 mg/L, 95 mg/L, 220 mg/L, 280 mg/L, 395 mg/L, and for the formulated 45 mg/L, 95 mg/L, 175 mg/L, 255 mg/L and 350 mg/L. Sample Volume equaled 25 mL. Weight of sorbent equaled 0.75 g.

Table 7.
Comparison of Freundlich Isotherm Slopes
for Sorption of Unformulated and Formulated Metolachlor
to the Same Sorbent using Analysis of Covariance[1,2,3]

Comparison	df	p-value	Decision
Peat vs. Peat	26	0.03	reject H_0
Rubber vs. Rubber	26	0.22	reject H_0
Wood Fiber vs. Wood Fiber	25	0.02	reject H_0

1 test H_0: $b_1 = b_2$

H_A: $b_1 <$ or $> b_2$

2 reject if absolute value of t is > 2.056

3 reject if absolute value of t is > 2.060

To determine if similar binding mechanisms were present for sorption of unformulated and formulated metolachlor, the data was plotted using the Linear isotherm model (Figures 10, 11, and 12). According to Giles system of classification (Stevenson, 1982), unformulated metolachlor displayed a conventional S-type curve for all of the sorbent materials. Formulated metolachlor in Experiment A and B followed a C-curve pattern. This suggests that although the sorption capacity of the sorbent materials was not affected by the presence of surfactants, different binding mechanisms for sorption of unformulated and unformulated metolachlor may have occurred.

To approximate the surfactant concentration and determine if micelles were present following treatment of the sorbents with formulated metolachlor, surface tensions of the rubber and steam-exploded wood fibers samples (Experiment B) were measured. Surface tension of the all the rubber-treated samples increased to approximately 60 dynes/cm (Figure 13). No additional increase in surface tension was observed despite an increase in rubber mass. Surface tension of the steam-exploded wood fiber samples increased only slightly despite a large decrease in metolachlor concentration (Figure 14). Surface tension of experimental controls were between 39-45 dynes/cm.

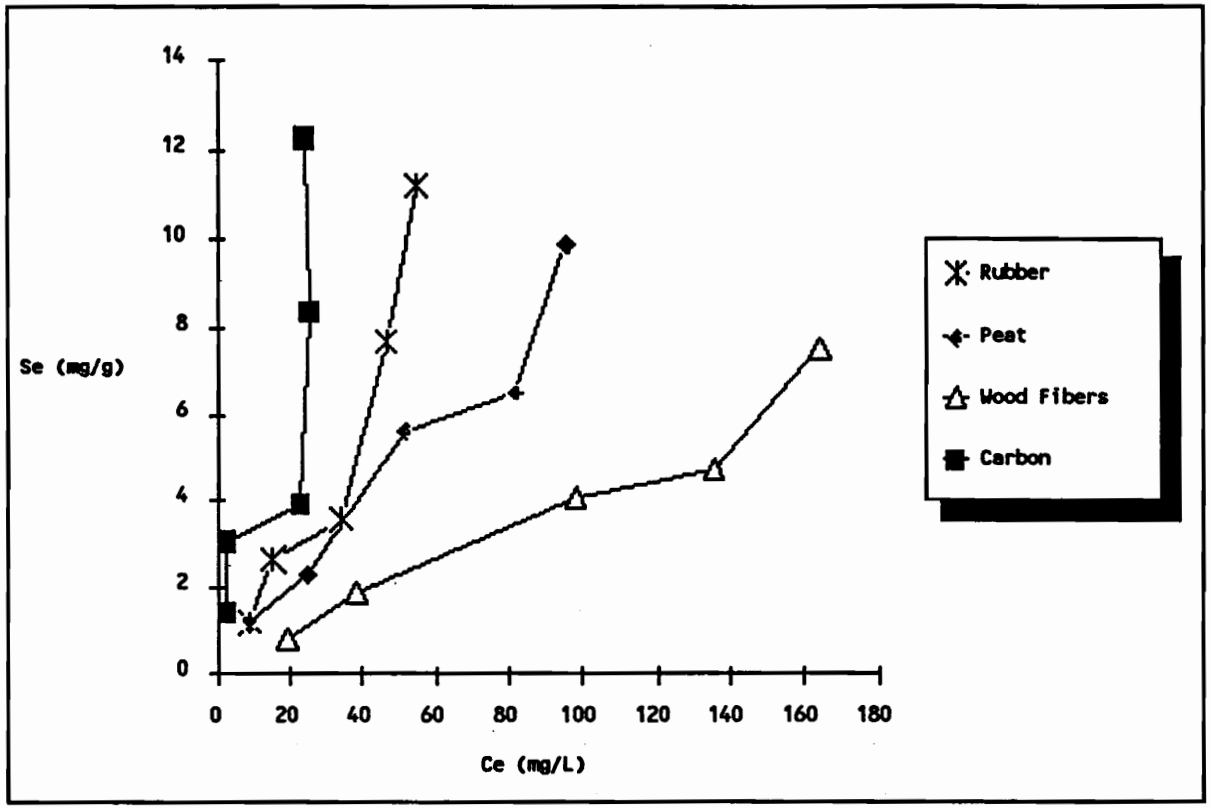

Figure 10. Linear isotherm plot of unformulated metolachlor sorption to different materials. Three samples were used at each solution concentration. Metolachlor concentrations used were 45 mg/L, 95 mg/L, 220 mg/L, 280 mg/L, and 395 mg/L. Sample volume equaled 25 mL. Weight of sorbent equaled 0.75 g. Se is equal to the amount of metolachlor sorbed (mg/g), and Ce is equal to the equilibrium concentration (mg/L).

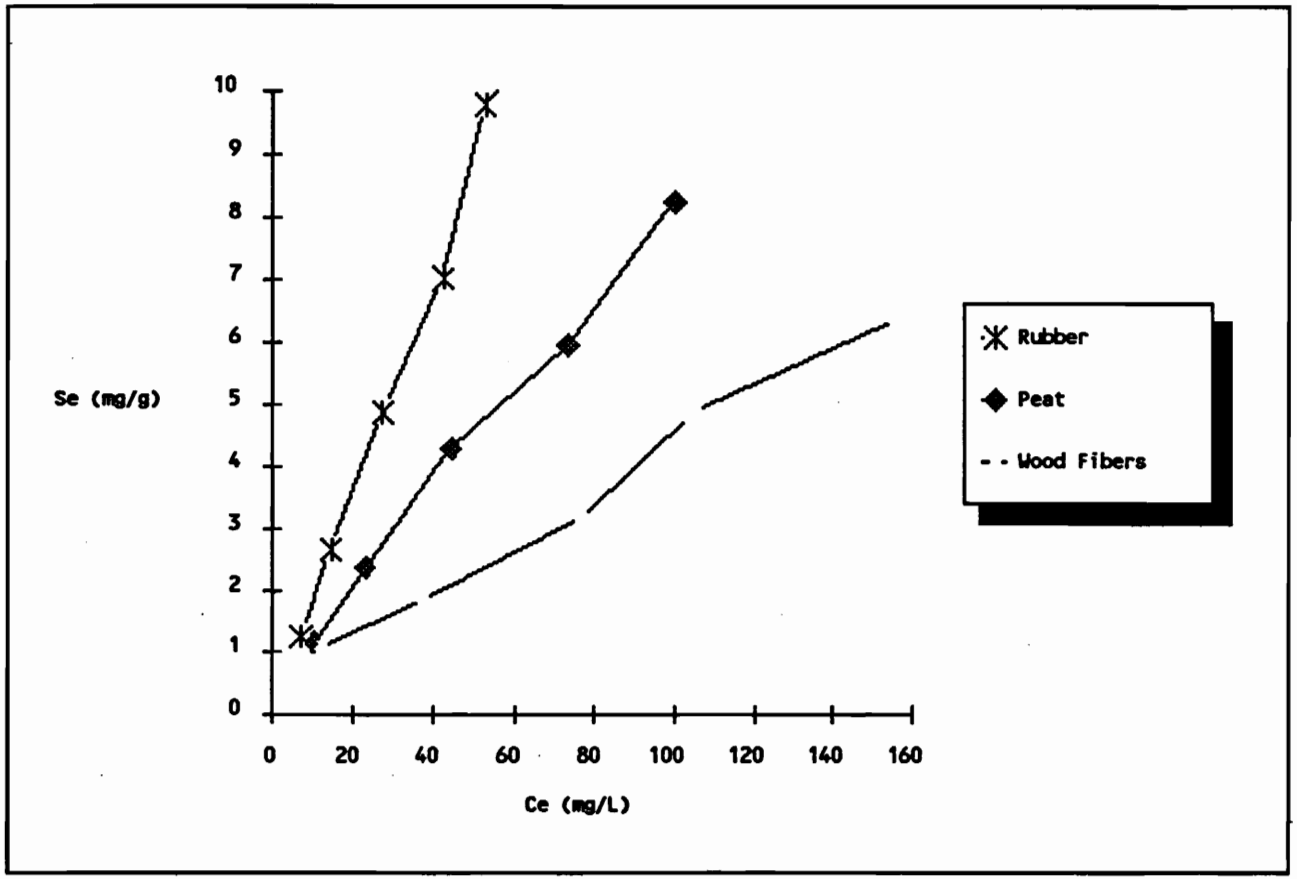

Figure 11. Linear isotherm plot of formulated metolachlor sorption to different materials. Three samples were used at each solution concentration. Metolachlor concentrations used were 45 mg/L, 95 mg/L, 175 mg/L, 255 mg/L, and 350 mg/L. Sample volume equaled 25 mL. Weight of sorbent equaled 0.75 g. Se is equal to the amount of metolachlor sorbed (mg/g), and Ce is equal to the equilibrium concentration (mg/L).

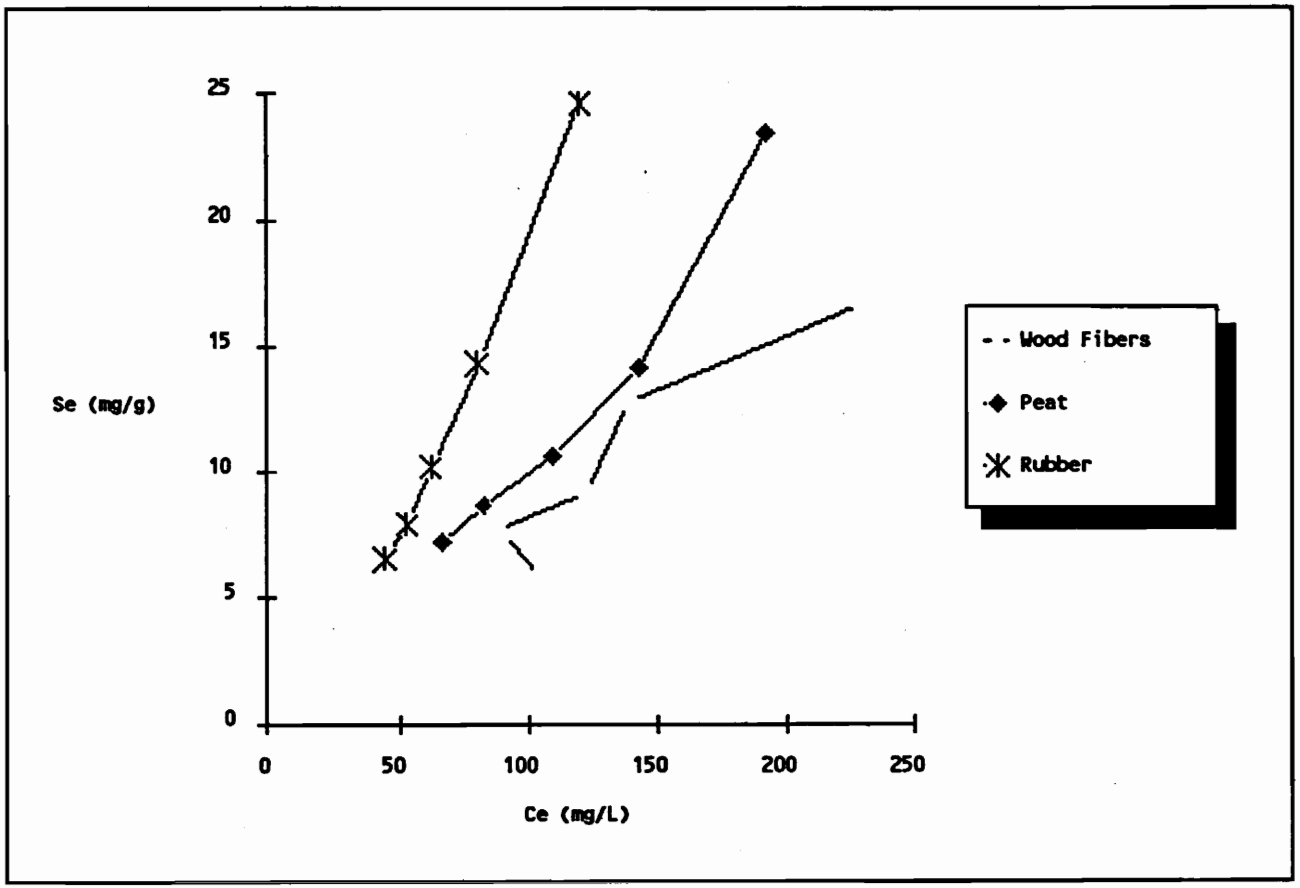

Figure 12. Linear isotherm plot of formulated metolachlor sorption to different weights of materials. Three samples were used at each solution concentration. Metolachlor concentrations used were 430 mg/L for the peat and wood fiber samples, and 370 mg/L for rubber samples. Sample volume equaled 25 mL. Weights of material used equaled 0.25 g, 0.50 g, 0.75 g, 1.00 g, 1.25 g.

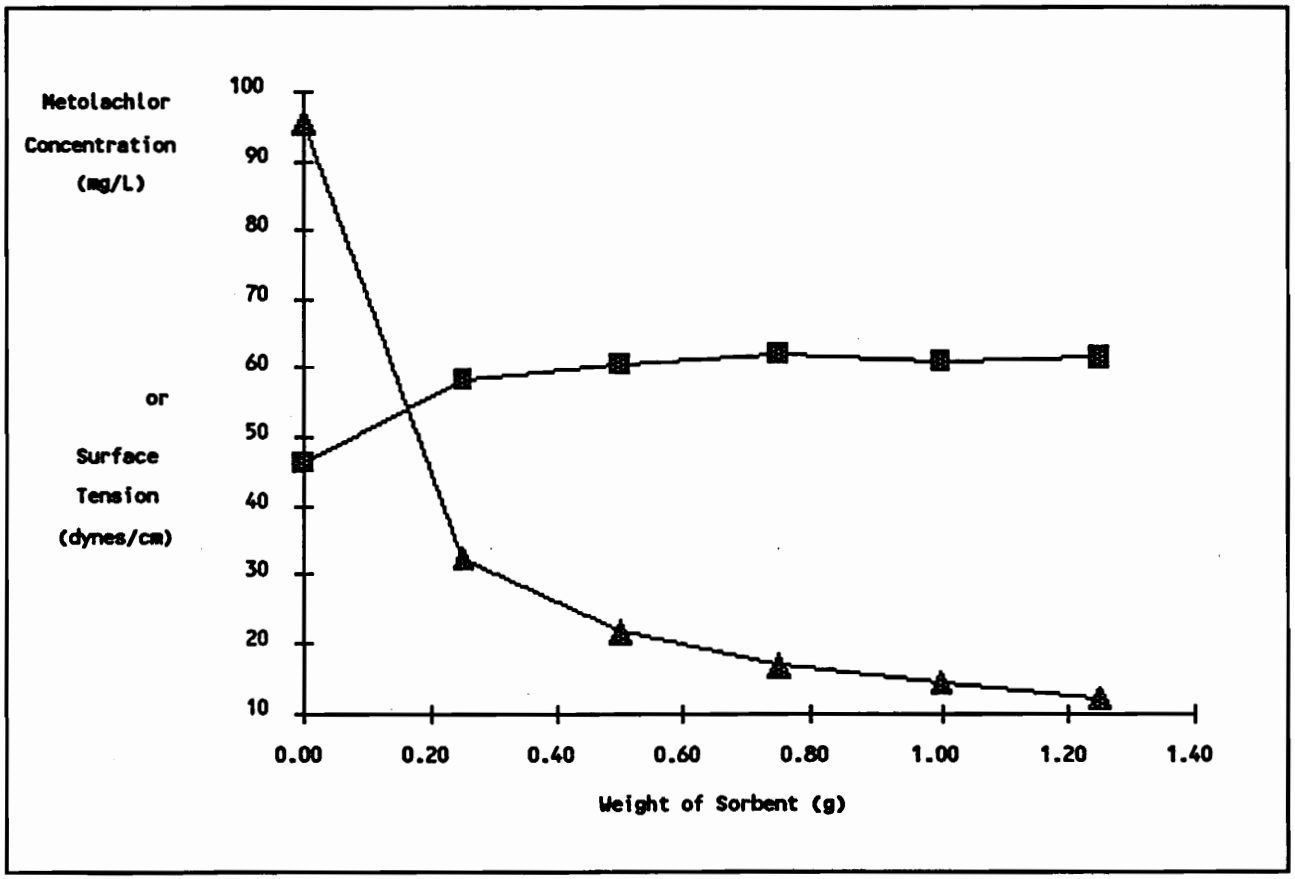

Figure 13. Surface tension and concentrations of supernatant following mixing of formulated metolachlor with different amounts of rubber. Sample size equaled 3 for each weight of rubber. Initial metolachlor concentration equaled 370 mg/L. Sample volume equaled 25 mL. Standard deviations for both measurements were insignificant.

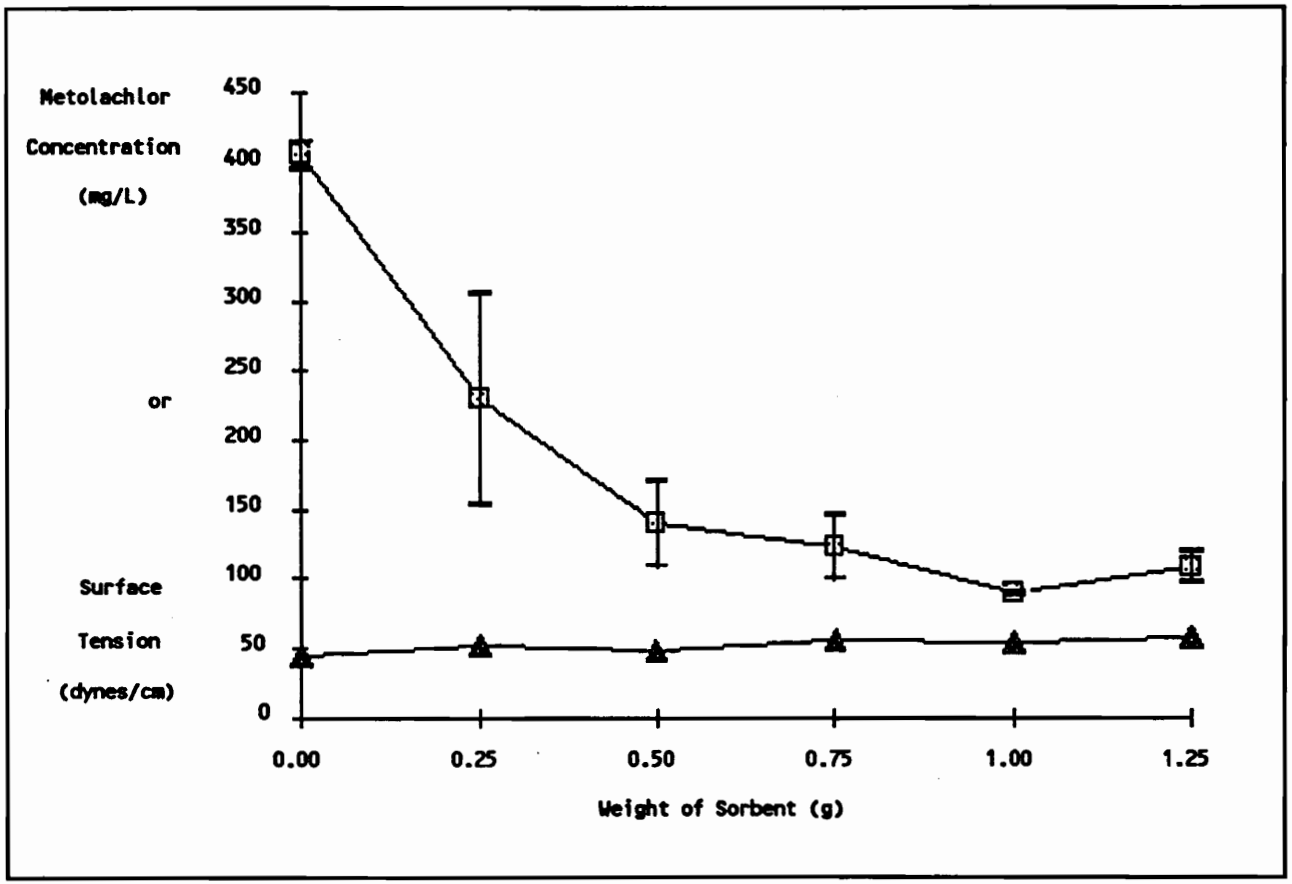

Figure 14. Surface tension and concentrations of supernatant following mixing of formulated metolachlor with different amounts of steam-exploded wood fibers. Sample size equaled 3 for each weight of wood fibers. Initial metolachlor concentration equaled 370 mg/L. Sample volume equaled 25 mL. Standard deviations for all surface tension measurements were insignificant.

4.3 MODIFICATIONS OF SORBENT MATERIAL

Although the sorption isotherms showed that all of the sorbents had some capacity to remove metolachlor from solution, trace levels of the pesticide were not obtained. Modifications to the sorbent, aqueous phase, and treatment method were made in an effort to improve removal efficiency.

4.3.1 Salt and Acid Treatment

This experiment was conducted to determine if the washing of peat with acid, or loading the negatively charged surface sites with alkaline earth metals could improve the sorption capacity of the material, by the formation of chelate structures, or by establishing an ion exchange system. The procedure used to modify the peat is outlined in Section 3.6.1. The average percent metolachlor remaining in solution following contact with different types of modified peat is shown in Figure 15. Experimental data is provided in the Appendix (Table 13).

Initial pH for all of the dispersions were between 4.5 and 4.8, with the exception of $Ca(OH)_2$ which had an initial pH of 10.5. Final pH readings were 2.77, 4.37, 7.91, 4.50, and 4.65 for the HCl, $CaCl_2$, $Ca(OH)_2$, NaCl, and control (untreated) treatments, respectively.

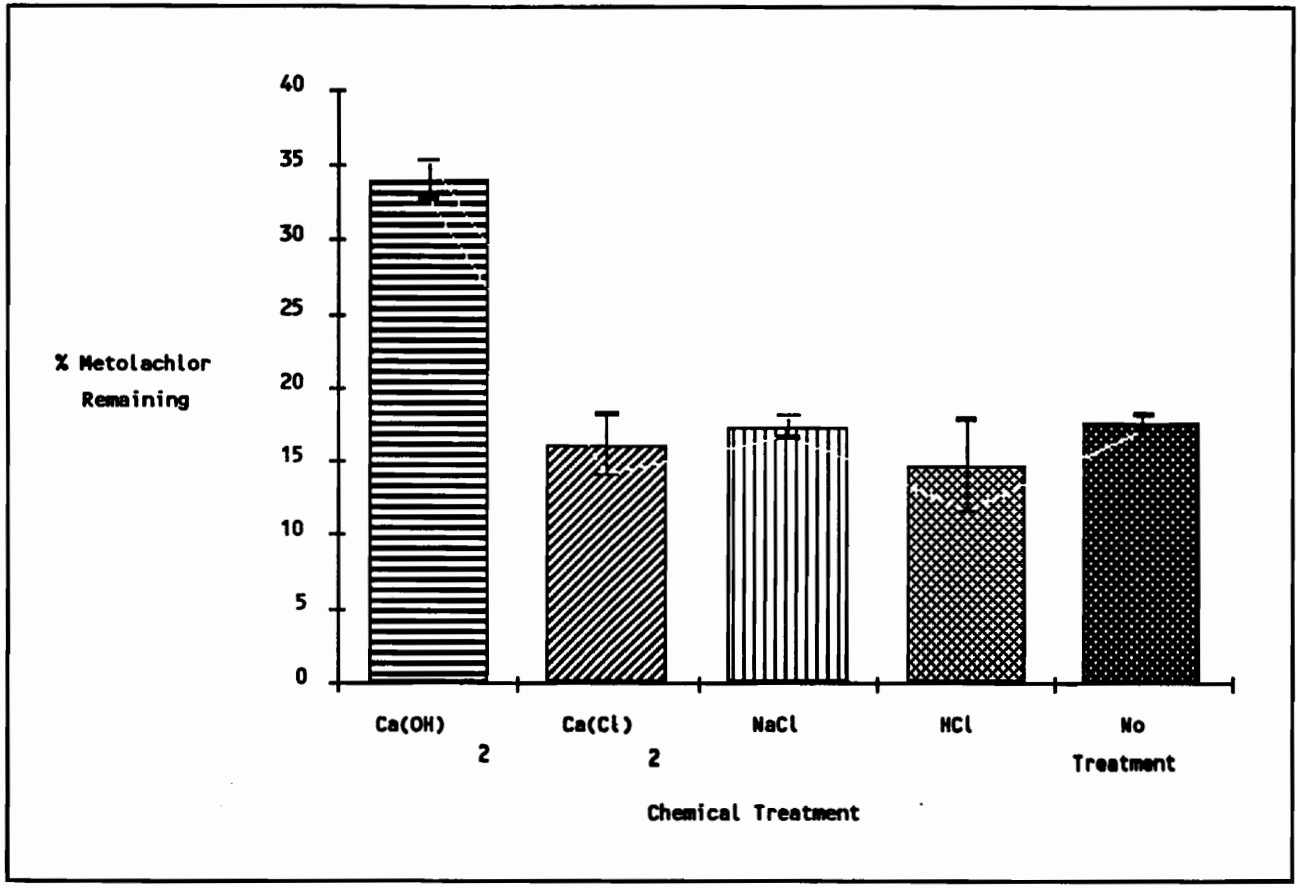

Figure 15. Efficiency of chemically modified peats in removal of metolachlor from water. Sample size equaled 3 for each modified peat. Metolachlor concentration equaled 365 mg/L. Sample volume equaled 25 mL. Weight of sorbent equaled 3.0 g wet weight (0.75 g dry weight).

Through statistical analysis, an ANOVA detected a difference in the sample means ($p < 0.001$). Using Duncan's multiple-range test (æ=0.05) a significant difference was detected between the untreated control and the HCl and $Ca(OH)_2$ treatments. The HCl treated peat performed slightly better than the untreated peat, while the $Ca(OH)_2$ treated peat performed far worse.

4.3.2 Particle Size

Particle size affects the sorption capacity of a sorbent by changing the surface area and number of binding sites. This experiment was conducted to assess the affect of particle size on the sorption of formulated and unformulated metolachlor to peat moss and steam-exploded wood fibers. Experimental protocol is described in Section 3.6.2. The average percent of metolachlor remaining in solution when a 400 mg/L solution of formulated metolachlor is mixed with different particle sizes of peat and steam-exploded wood fibers is shown in Figure 16. Average final dispersion concentrations of metolachlor were 78.51 $\pm$ 13.69 mg/L, and 151.80 $\pm$ 32.0 mg/L for the 1-2 mm sized particles for peat and steam-exploded wood fibers, respectively. For the <1 um sized particle, final concentrations were 69.73 $\pm$ 2.52 mg/L, and 126.49 $\pm$ 6.32 mg/L.

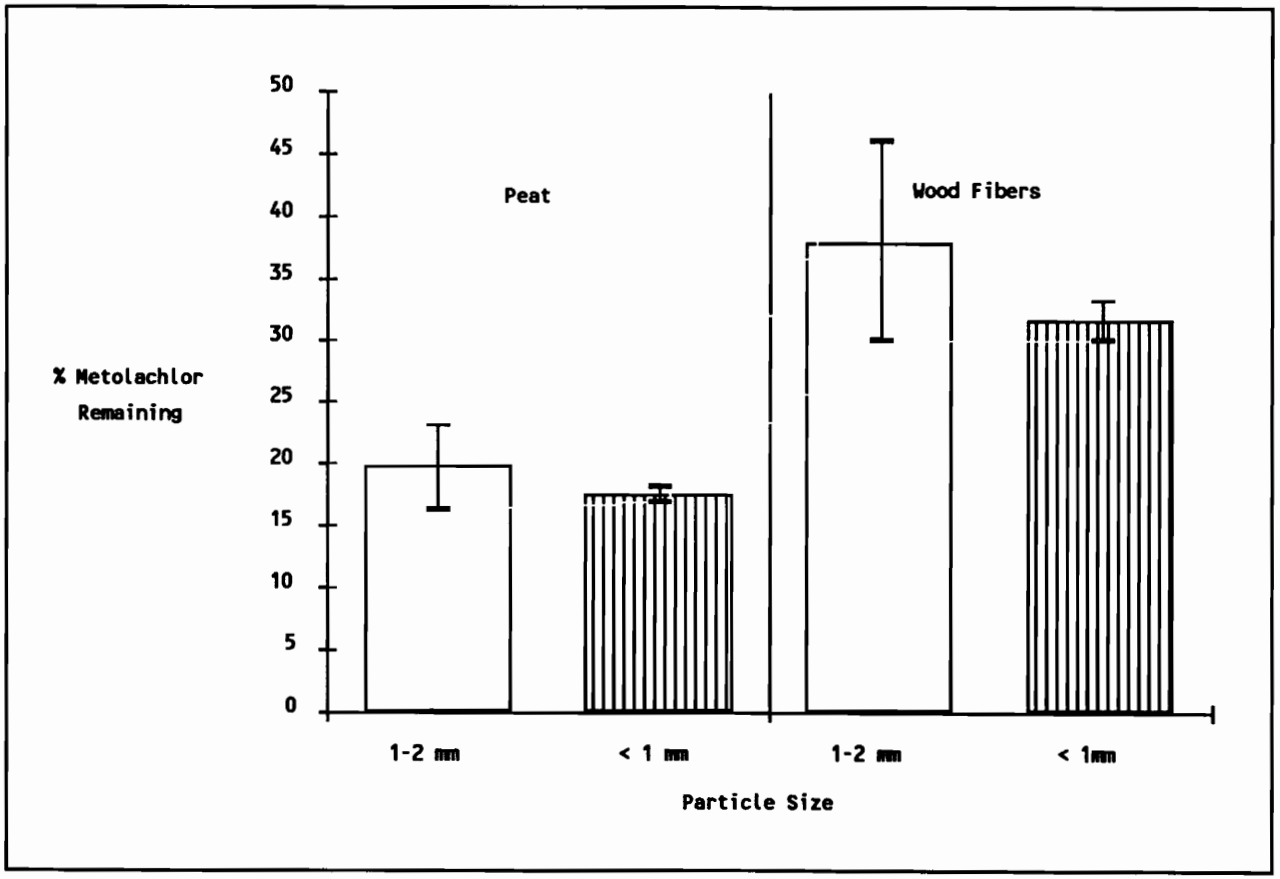

Figure 16. Efficiency of different particle sizes of peat and steam-exploded wood fibers in removal of formulated metolachlor from water. Sample size equaled 3 for each particle size. Metolachlor concentration equaled 400 mg/L. Sample volume equaled 25 mL. Weight of sorbent equaled 0.75 g.

A two-tailed T-test for equal variances failed to show a difference in metolachlor removal between the two test particle sizes (p=0.33, n=3). The 95% confidence interval on the means were [11.13, 28.14] mg/L, [15.87,18.99] mg/L for the 1-2 mm and <1 mm particles, respectively.

The <1 mm steam-exploded wood fibers particles had an average of 6% more metolachlor remaining in dispersion, than the 1-2 mm size particle. Statistical analysis failed to show a difference in the amount of metolachlor remaining in solution between the two particle sizes (p=0.25, n=3). The 95% confidence interval for the mean percent remaining in solution for the smaller particle was [18.08, 57.82] mg/L. The larger particle size had a 95% confidence range of [27.69, 35.54] mg/L.

4.3.3 Wet and Dry Sorbents

This experiment was conducted to determine if hydrating the sorbent prior to mixing with the pesticide affected the equilibrium solution concentration. Section 3.6.3 details the experimental protocol. The percent of metolachlor remaining in solution following contact of 400 mg/L formulated metolachlor with either wet or dry sorbent is shown in Figure 17. Hydrated peat removed approximately 6% more metolachlor from solution than the

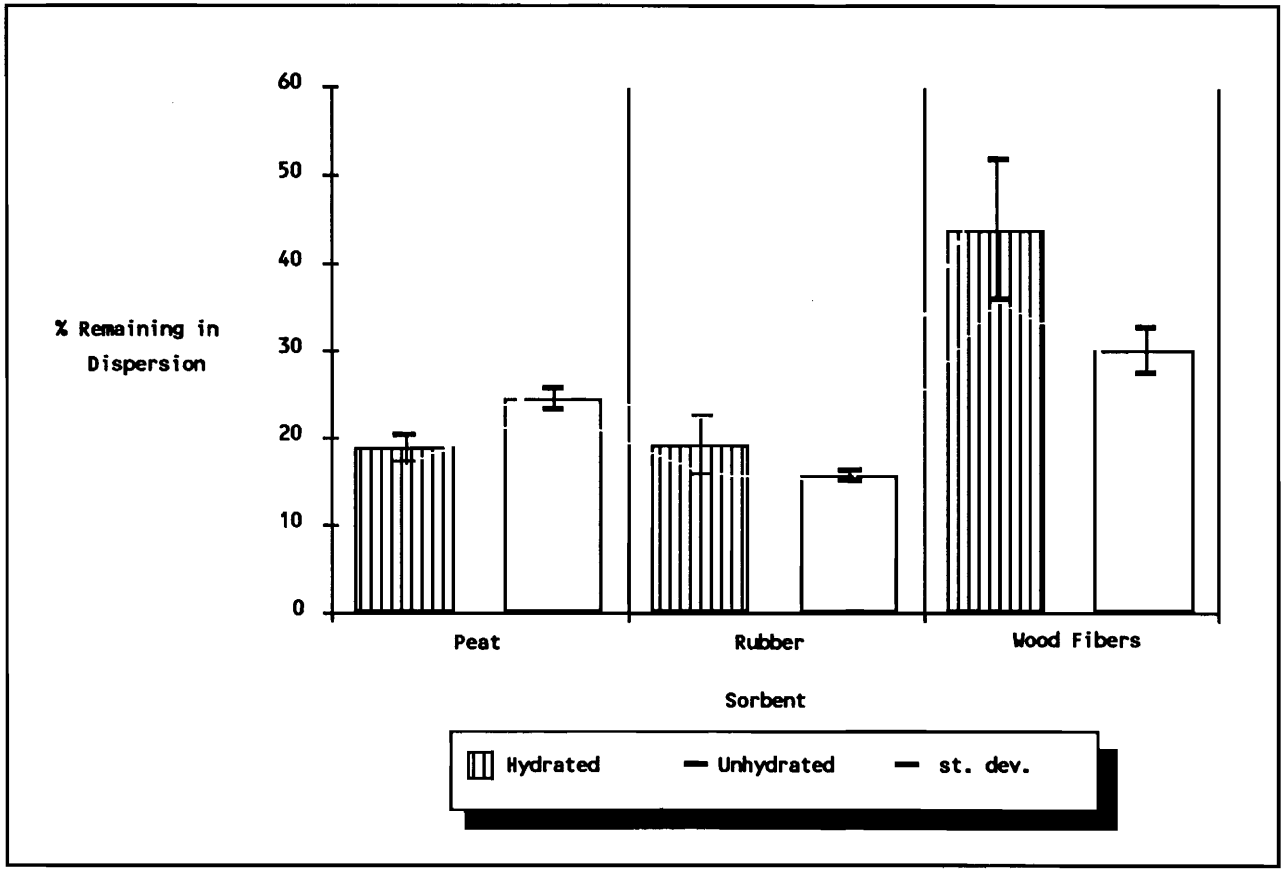

Figure 17. Efficiency of hydrated and dehydrated sorbents in removal of formulated metolachlor from water. Sample size equaled 3 for each particle size. Metolachlor concentration equaled 400 mg/L. Sample volume equaled 25 mL. Weight of dry sorbent equaled 0.75 g for all sorbent types. Weight of hydrated sorbent equaled 3.0 g, 0.95 g, and 1.40 g for the peat, rubber, and wood fibers.

dry material. The methanol soaked rubber, did not improve the affinity of the matrix for metolachlor. The hydrated steam-exploded wood fibers removed approximately 13% less metolachlor from the solution than the dry fibers. T-tests comparing the sorbent type to the wet and dry treatments, confirmed that the average percent remaining in solution differed for both peat and steam-exploded wood fibers ($p < .001$ and $p=0.04$, respectively, $n=3$). There was no evidence that treatment of rubber with methanol affected sorption ($p=0.15$, $n=3$).

There was no observed difference in the surface tension between the wet and dry samples for either the peat or rubber samples. The hydrated steam-exploded wood fibers had an average surface tension which was 3.5 dynes/cm higher than the untreated fibers.

4.4 OTHER EXPERIMENTS

4.4.1 Demulsification

$Ca(OH)_2$ is used in industry as a demulsifying/coagulating agent. Its use was evaluate in this study to see if the removal efficiency of the sorbents could be enhanced with the addition of this demulsifying agent. The percent of metolachlor remaining in dispersion following the addition of crystalline $Ca(OH)_2$ to 400 mg/L formulated metolachlor is shown for each sorbent in Figure 18. Experimental data is listed in the Appendix (Table 14).

The peat and steam-exploded wood fibers displayed an increased in solution phase metolachlor of 45-50% over the no treatment samples. There was a 5% average decrease in metolachlor concentration in the $Ca(OH)_2$ treated, rubber samples. Statistical analysis with Duncan's multiple-range test and Newman Keul's range test found that there was a significant difference in the percent of metolachlor remaining in all dispersions, with one exception. No significant difference was seen in the amount of metolachlor remaining in dispersion for the $Ca(OH)_2$ treated wood fiber and $Ca(OH)_2$ treated peat samples (α=0.05, n=3). Surface tension measurements of the rubber samples were lower for the $Ca(OH)_2$ treatments than the no treatments.

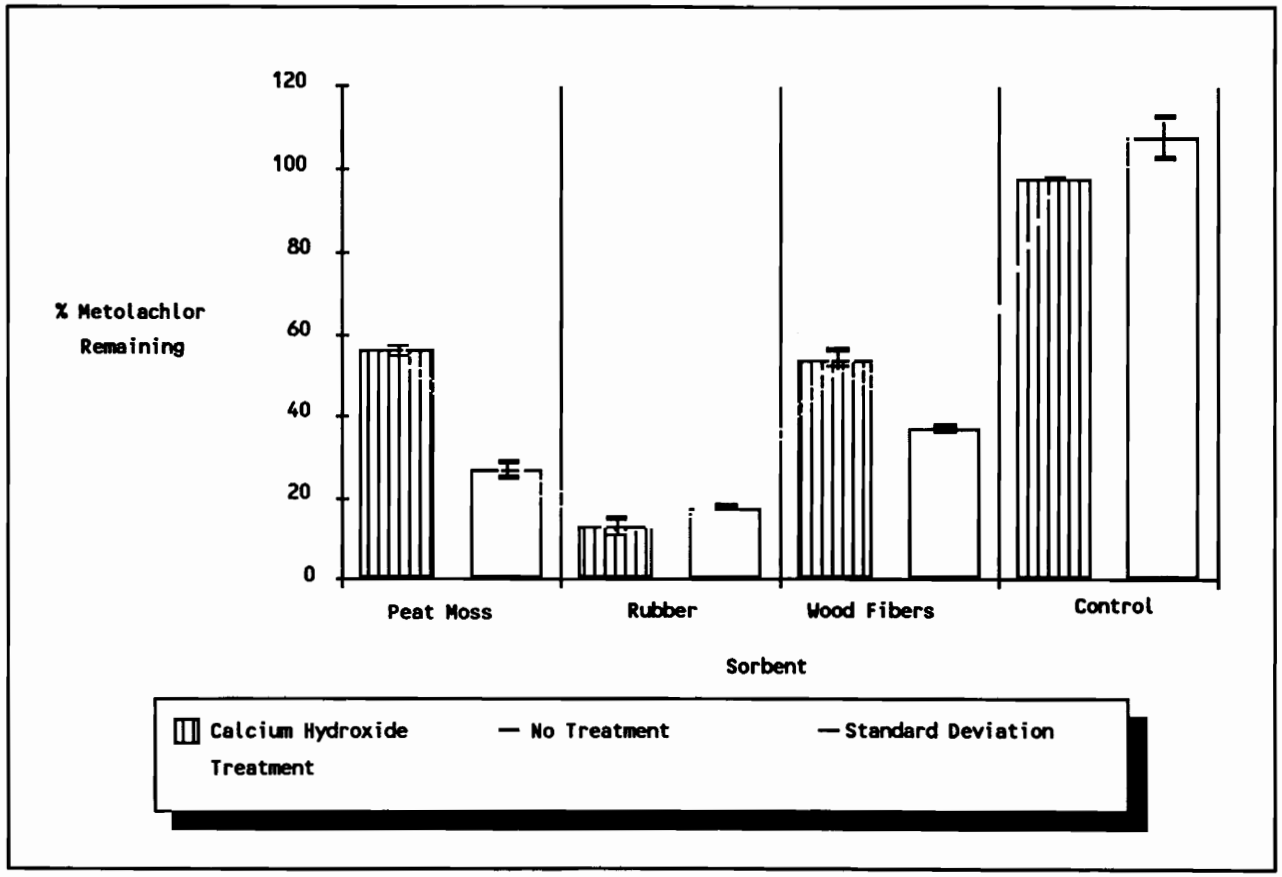

Figure 18. Effect of crystalline calcium hydroxide addition on removal of formulated metolachlor from water. Sample size equaled 3. Metolachlor concentration equaled 375 mg/L. Sample volume equaled 25 mL. Weight of sorbent equaled 0.75 g.

4.4.2 Phosphatase Treatment

An ICAP analysis of formulated metolachlor dispersion was conducted. Results showed that the formulation contained phosphorous, sulfur, potassium, and sodium. Based on this information, it was hypothesized that the addition of phosphatase to the sorbent/pesticide mixture may cause a decomposition. of the surfactant, leading to enhanced sorption of metolachlor to the sorbents. Two contacts of fresh formulation were made with the sorbents. Experimental procedure is detailed in Section 3.7.1. The amount of metolachlor sorbed to each material following two separate contacts with formulated metolachlor under the various conditions are listed in the Tables 8 and 9. The total amount sorbed to each sorbent after two sorbent contacts is listed in the Appendix (Table 15). No trends between the different treatments are evident with any of the sorbents after the first contact. However, there was an unusually high loss of material from the enzyme-amended experimental controls. T-tests were done to compare the equilibrium metolachlor concentration for each treatment within each sorbent or control group. The resulting p values are listed in Table 10. A difference in mean metolachlor concentration was detected between the pH-adjusted and no-enzyme addition controls.

Table 8.
Effect of Phosphatase Addition on the Amount (mg) of 400 mg/L Formulated Metolachlor Sorbed to 0.75 g of Sorbent (First Contact)

SAMPLE	ADJUSTED PH	NO ADJUSTED PH	NO ENZYME
Peat A	7.03	7.49	7.49
Peat B	7.63	7.54	7.35
Peat C	7.68	7.45	7.59
Average	7.45 ± 0.36	7.49 ± 0.05	7.48 ± 0.12
Rubber A	8.37	8.97	8.42
Rubber B	8.42	8.33	8.14
Rubber C	8.33	8.37	8.37
Average	8.37 ± 0.05	8.56 ± 0.36	8.31 ± 0.15
Wood Fibers A	6.43	6.43	6.43
Wood Fibers B	6.98	6.20	6.61
Wood Fibers C	6.47	5.78	6.10
Average	6.63 ± 0.31	6.14 ± 0.33	6.38 ± 0.26
No Sorbent A	1.11	0.19	0.09
No Sorbent B	1.94	0.74	-0.28
No Sorbent C	1.39	0.93	-0.74
Average	1.48 ± 0.42	0.62 ± 0.38	-0.31 ± 0.42

Table 9.
Effect of Phosphatase Addition on the Amount (mg) of 400 mg/L Formulated Metolachlor Sorbed to 0.75 g of Sorbent (Second Contact)

SAMPLE	ADJUSTED PH	NO ADJUSTED PH	NO ENZYME
Peat A	5.18	5.69	6.20
Peat B	4.90	5.78	6.20
Peat C	5.27	5.59	6.10
Average	5.12 ± 0.19	5.69 ± 0.10	6.17 ± 0.06
Rubber A	6.80	7.03	6.04
Rubber B	6.98	7.03	6.31
Rubber C	7.03	6.84	5.57
Average	6.94 ± 0.12	6.97 ± 0.11	5.97 ± 0.37
Wood Fibers A	2.84	3.72	4.62
Wood Fibers B	6.21	3.77	4.67
Wood Fibers C	2.75	3.91	4.81
Average	2.93 ± 0.12	3.80 ± 0.10	4.70 ± 0.10
No Sorbent A	0.93	1.76	-0.28
No Sorbent B	4.26	0.37	-0.28
No Sorbent C	3.70	2.04	0.28
Average	2.96 ± 1.78	1.39 ± 0.89	-0.09 ± 0.32

Table 10.
Statistical Analysis of Phosphatase Experiment
Using Two Sample T-Tests

		FIRST CONTACT		SECOND CONTACT	
SORBENT	TEST	P VALUE	DECISION	P VALUE	DECISION
Peat	1 vs. 2	0.85	accept H_o	0.01	reject Ho
Peat	1 vs. 3	0.90	accept H_o	0.00	reject H_o
Peat	2 vs. 3	0.83	accept H_o	0.00	reject H_o
Rubber	1 vs. 2	0.47	accept H_o	0.76	accept H_o
Rubber	1 vs. 3	0.52	accept H_o	0.79	accept H_o
Rubber	2 vs. 3	0.33	accept H_o	0.70	accept H_o
Wood Fibers	1 vs. 2	0.13	accept H_o	0.01	reject H_o
Wood Fibers	1 vs. 3	0.35	accept H_o	0.01	reject H_o
Wood Fibers	2 vs. 3	0.37	accept H_o	0.79	accept H_o
No Sorbent	1 vs. 2	0.06	accept H_o	0.24	accept H_o
No Sorbent	1 vs. 3	0.02	reject H_o	0.04	reject H_o
No Sorbent	2 vs. 3	0.42	accept H_o	0.05	reject H_o

Test H_o: The mean equilibrium concentration$_1$ is equal to mean equilibrium concentration$_2$

H_A: The mean equilibrium concentration$_1$ is not equal to mean equilibrium concentration$_2$

Reject H_o if : $p \leq 0.05$

1 = adjusted pH
2 = no adjusted pH
3 = no enzyme

No additional enzyme was added to these experimental trials when they were contacted with formulated metolachlor for the second time. The same no sorbent control samples that were used in the first contact, were reused for the amended phosphatase tests; however, fresh 400 mg/L formulated metolachlor was used for the no-enzyme control. The pH-adjusted phosphatase sample units for peat and steam-exploded wood fibers appeared to have been less effective in removing metolachlor from the aqueous phase. An average of 25% more metolachlor remained in dispersion with the peat, and 15% more with the steam-exploded wood fibers when compared to the no-enzyme treatments. An average of 11% more metolachlor was detected in the peat, no-adjusted-pH treatment when compared to the peat, no-enzyme treatment. There was a notable loss of 30% and 15% metolachlor from the pH-amended controls. T-tests confirmed that there was a difference in average final concentration between all three treatments of peat, and the pH-amended treatments and no-enzyme samples for both steam-exploded wood fibers and the controls (Table 10).

Surface tension measurements for the first and second contact of formulated metolachlor with the sorbents can be found in Tables 11 and 12. Surface tensions for the peat samples appeared to be the same regardless of the

Table 11.
Effect of Phosphatase Addition on Surface Tension (dynes/cm) of Supernatant after Mixing of 400 mg/L Formulated Metolachlor with 0.75 g of Sorbent (First Contact)

SAMPLE	ADJUSTED PH	NO ADJUSTED PH	NO ENZYME
Peat A	60.2	61.2	60.1
Peat B	61.2	60.5	61.1
Peat C	60.3	60.3	59.9
Average	60.6 ± 0.6	60.7 ± 0.5	60.4 ± 0.6
Rubber A	60.5	60.3	60.3
Rubber B	61.0	59.5	61.2
Rubber C	62.0	61.8	59.9
Average	61.2 ± 0.8	60.5 ± 1.2	60.5 ± 0.7
Wood Fibers A	55.5	54.4	53.4
Wood Fibers B	55.5	55.3	55.6
Wood Fibers C	55.4	54.4	54.7
Average.	55.5 ± 0.1	54.7 ± 0.5	54.6 ± 1.1
No Sorbent A	49.0	40.5	40.1
No Sorbent B	48.4	42.3	40.1
No Sorbent C	49.4	41.8	39.9
Average	48.9 ± 0.5	41.5 ± 0.9	40.0 ± 0.1

Table 12.
Effect of Phosphatase Addition on Surface Tension (dynes/cm) of Supernatant following Mixing of 400 mg/L Formulated Metolachlor with 0.75 g of Sorbent (Second Contact)

SAMPLE	ADJUSTED PH	NO ADJUSTED PH	NO ENZYME
Peat A	53.5	60.1	57.6
Peat B	58.4	60.5	58.8
Peat C	58.7	60.4	54.6
Average	56.9 ± 2.9	60.3 ± 0.2	57.0 ± 2.2
Rubber A	57.0	58.9	58.2
Rubber B	59.5	57.8	58.0
Rubber C	59.5	59.4	59.4
Average	58.7 ± 1.4	58.7 ± 0.8	58.5 ± 0.8
Wood Fibers A	52.0	52.6	53.2
Wood Fibers B	53.2	51.7	53.5
Wood Fibers C	52.6	51.0	53.7
Average	52.6 ± 0.6	51.8 ± 0.8	58.5 ± 0.3
No Sorbent A	48.0	45.0	43.4
No Sorbent B	48.2	43.8	44.5
No Sorbent C	47.2	43.2	43.2
Average	47.8 ± 0.5	44.0 ± 0.9	43.7 ± 0.7

treatment. This was also true for the rubber and steam-exploded wood samples, as well. However, there was a much higher surface tension with the adjusted-pH, no sorbent controls when compared to the no-enzyme control.

4.4.3 Recontact and Reuse

This experiment was conducted to determine if concentrations below the equilibrium concentration could be obtained by recontacting the supernatant with additional unused sorbent; and if, a maximum sorption capacity of the sorbent was reached upon initial contact with formulated metolachlor, or if the sorbent could be recycled in the sorption process. Experimental procedures are described in Section 3.7.3. Metolachlor concentrations following two mixings of the solution phase with sorbent are listed in Table 13.

Peat was able to remove an additional 61% of the metolachlor from the aqueous phase. Rubber removed an additional 75%, and steam-exploded wood fibers 60%. The final concentration of the steam-exploded wood fiber treatments after the repeated contact was approximately equal to the final solution concentration following the initial contact with rubber. The amount of metolachlor sorbed to each material following repeated contacted with

Table 13.
Metolachlor Concentration (mg/L) following
Two Separate Contacts of the Same Formulated Metolachlor Dispersion
with 0.75 g of New Sorbent

SAMPLE	FIRST CONTACT	SECOND CONTACT
Peat A	96	28
Peat B	102	26
Peat C	93	30
Average	97 ± 2	28 ± 2
Rubber A	59	15
Rubber B	70	17
Rubber C	61	17
Average	63 ± 1	16 ± 1
Wood Fibers A	139	56
Wood Fibers B	131	48
Wood Fibers C	152	63
Average	141 ± 7	56 ± 10
No Sorbent A	396	411
No Sorbent B	411	411
No Sorbent C	430	389
Average	412 ± 13	40 ± 17

formulated metolachlor is displayed in Figure 19. Experimental data is provided in the Appendix (Table 16). Peat was able to remove 75% of the initial 10 mg of metolachlor present in the dispersion. Rubber and steam-exploded wood fibers were able to remove 83% and 64%, respectively. Peat and rubber removed 13-14% less metolachlor from the initial dispersion upon recontact. Steam-exploded wood was 16% less efficient. The average surface tension of the peat and rubber treatments was slightly lower after the second contact. The surface tension of the steam-exploded wood fiber treatments remained the same after two contacts. (See "no enzyme" in Tables 11 and 12.)

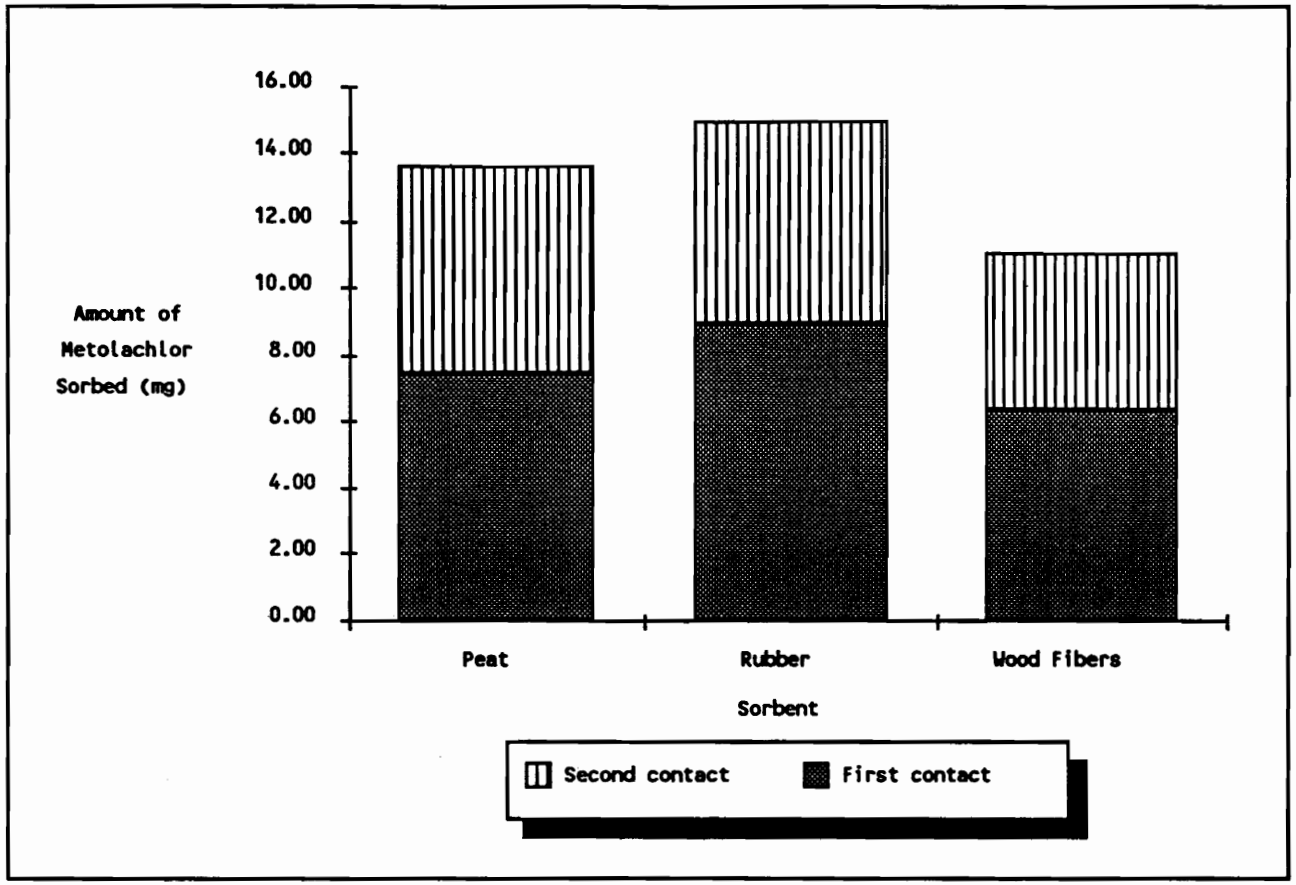

Figure 19. Average amount of metolachlor sorbed following repeated mixing of formulated metolachlor with the sorbent. Sample size equaled 3. Metolachlor concentration equaled 375 mg/L. Sample volume equaled 25 mL. Weight of sorbent equaled 0.75g.

4.5 RUBBER COLUMN STUDY

This experiment was conducted to determine if use of a continuous flow column system was an efficient treatment process to remove formulated metolachlor from the aqueous phase. Experimental protocol is provided in Section 3.8. Figure 20 displays the change in concentration of metolachlor versus the volume of dispersion treated, following downward flow of formulated metolachlor (400 mg/L) through a rubber-packed glass column. The effluent concentration after treating 250 mL (1 hr) was below detection limits (0.02 mg/L). The concentration after treating 6000 mL (24 hr) was 6.10 mg/L. Effluent concentrations between these volumes were variable.

Recirculation of 2000 mL of the effluent (9.00 mg/L metolachlor) through the rubber-packed column did not appear to remove any additional material from the aqueous phase (Figure 21). The concentration after retreating 1000 mL (4 hr) did fall below detection limits; however, the concentrations before and after this sample volume were consistent with those obtained throughout the experiment.

The concentration of metolachlor in dispersion following the re-treatment of 2000 mL of the effluent by flow through an activated carbon-packed column ranged between 1.11 mg/L and 1.83 mg/L (Figure 22). There was

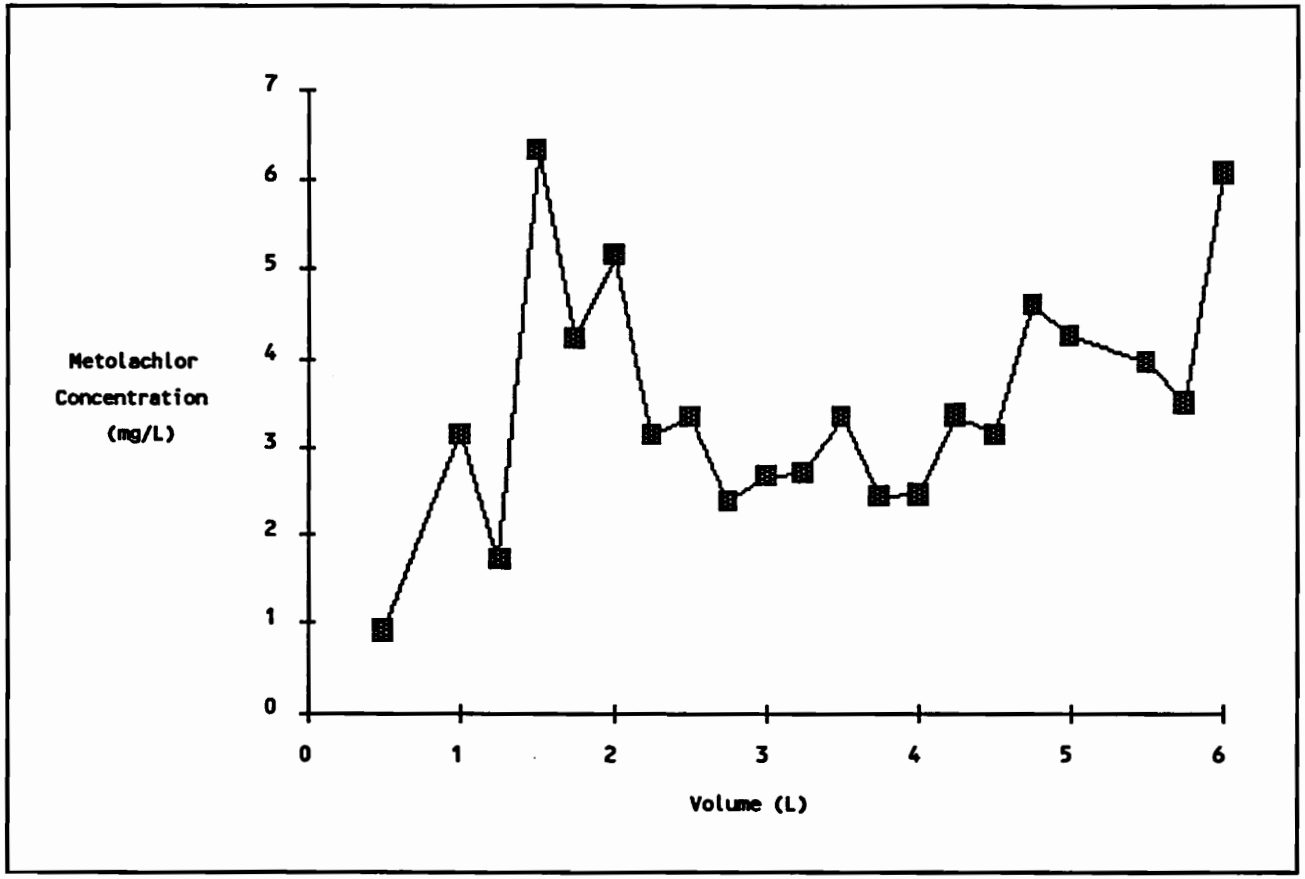

Figure 20. Effluent concentration following flow of formulated metolachlor through a rubber-packed column. Sample size equaled 1. Initial metolachlor concentration equaled 400 mg/L. Flow rate equaled 250 mL/hr. Void volume equaled 60 mL. I.D. equaled 2.5 cm. Weight of rubber equaled 185 g.

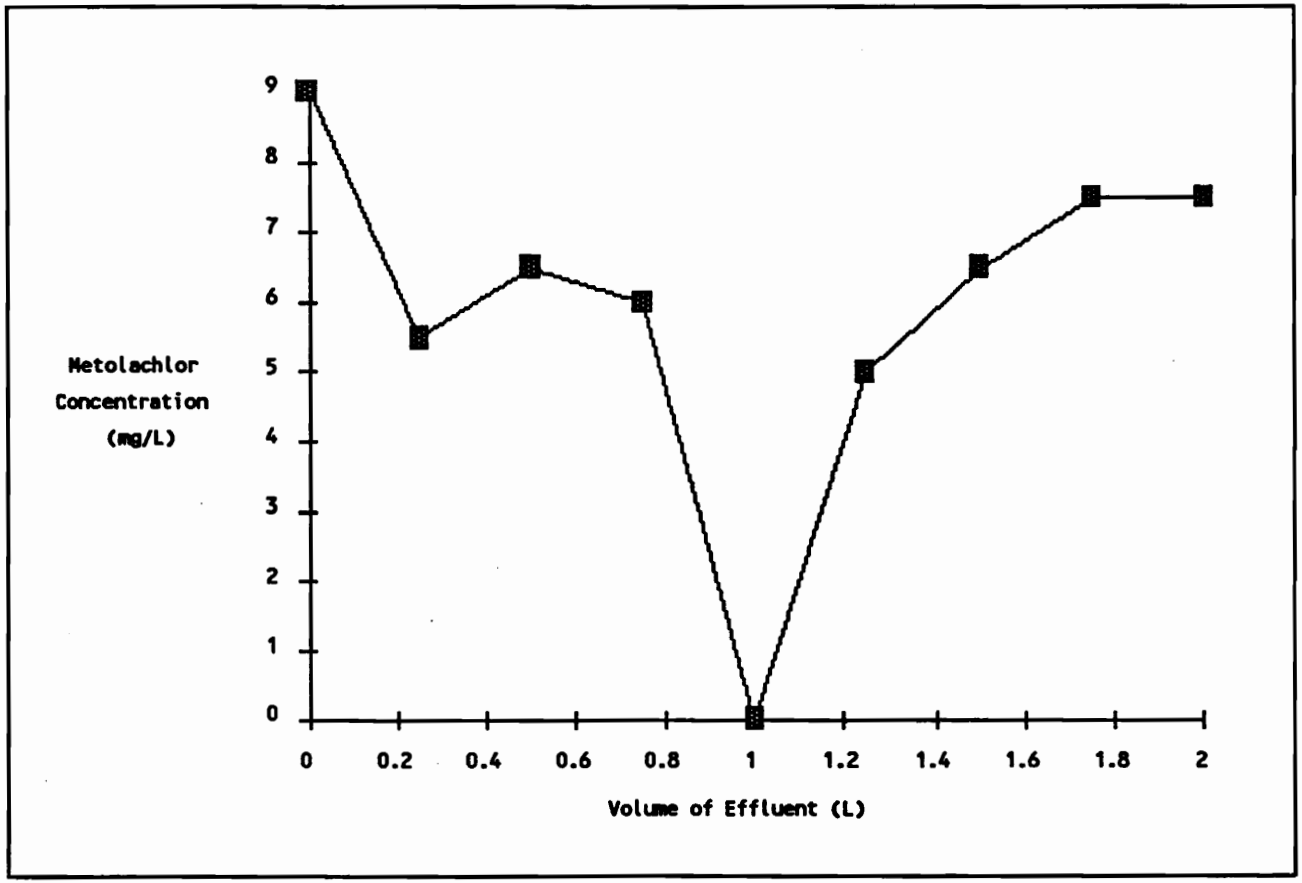

Figure 21. Metolachlor concentration following recirculation of effluent through a rubber-packed column. Sample size equaled 1. Initial metolachlor concentration equaled 400 mg/L. Flow rate equaled 250 mL/hr. Void volume equaled 60 mL. I.D. equaled 2.5 cm. Weight of rubber equaled 185 g.

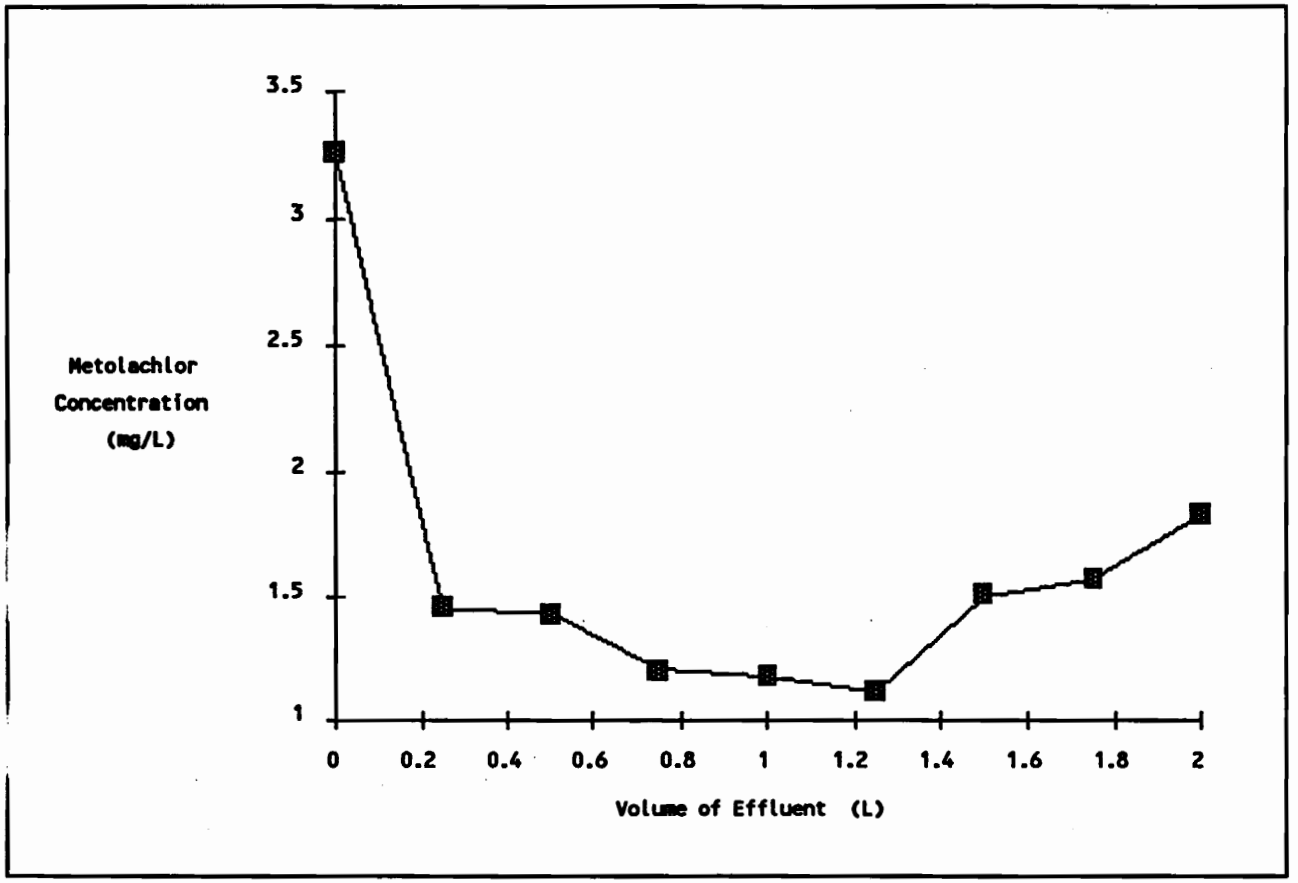

Figure 22. Metolachlor concentration following circulation of rubber-packed column effluent through a activated carbon-packed column. Sample size equaled 1. Initial metolachlor concentration equaled 400 mg/L. Flow rate equaled 250 mL/hr. Void volume equaled 10 mL. I.D. equaled 3 cm. Weight of activated carbon equaled 7.26 g.

approximately a 50% reduction from the starting solution concentration of 3.2 mg/L.

Chapter 5

5.0 DISCUSSION

5.1 PRELIMINARY STUDIES

5.1.1 Hydrolysis

Abiotic hydrolysis of a pesticide plays an important role in the fate of the chemical in the environment. Researchers have shown that atrazine is susceptible to acid hydrolysis in soil (Gamble et al., 1983; Perdue and Wolfe, 1982). The effect of pH on metolachlor was studied to determine the stability of the herbicide. Results of this study demonstrate that metolachlor is stable for at least 6 days in a wide range of pH. This confirms the unpublished information reported in Lebaron et al. (1988) that half life of metolachlor at 20^{o}C was greater than 200 days at pH 1,5,7, and 9, and 97 days at pH 13.

5.1.2 Kinetic Studies

Before a sorbent material is evaluated using sorption isotherm models, the time required for the sorbate to reach an equilibrium concentration should be determined. This time could vary depending on the nature of the sorbent, and

the characteristics of the sorbate. Wauchope and Myers (1985) found that the adsorption of atrazine and linuron to freshwater sediments occurred very rapidly, within 3 to 6 minutes. Cancela et al. (1990) found that cyanazine reached an equilibrium state with peat within 1 hour. This investigation of unformulated and formulated metolachlor sorption to the various sorbents showed that equilibrium was reached within 24 hours, for all of the sorbent materials.

5.2 SORPTION ISOTHERMS

Transforming experimental data to fit one of the sorption isotherms models can be used to determine the feasibility of using a particular sorbent in a treatment process, or to compare efficiencies of one or more sorbents. Experimental constants, K and n, are often used to assess a sorbent's efficiency. Reynold (1985) stated that the larger the n value, and the value of Se when Ce=Co, the more economically feasible the use of activated carbon for a particular chemical compound. Cancela et al. (1987) used K values to distinguish between sorbents. Larger K values indicated better sorptive capacity.

Use of K, n and Se values to evaluate isotherms pose some functional problems. First Reynold's use of the Se value, while mathematical sound, is questionable in practice. Ce would never equal Co unless no sorption occurred. If there was no sorption, the Se value would always be equal to zero. It would be more accurate to chose the largest Ce value in common between two isotherms and use this to compute a Se value. In addition, Reynold's (1985) use of the n value contradicts his use of the Se value. With all isotherms, the steeper the slope the greater the projected sorption capacity when Ce=Co, and the smaller the n value. When a large Se value is obtained, activated carbon would be rated as having good sorptive properties;

yet, the same sorbent would receive an unfavorable rating if the n value is used.

In addition, the approach used to generate the isotherm data can cause a different interpretation based on Reynold's criteria. If the weight of the sorbent is varied and the concentration of the sorbate held constant, a steep isotherm slope will result if there is little change in the equilibrium concentration as the amount of sorbent is increased. If the equilibrium concentration is very low, the sorbate has a high affinity for the sorbent. However, if a steep slope is obtained with high equilibrium concentrations, sorption is unfavorable. In the later case, sorption of the sorbate to the sorbent could be a function of the compound's solubility. A shallow slope tends to indicate favorable sorption, and that sorption is a function of the number of sorption sites available.

Conversely, if a steep slope is obtained when the sorbate concentration is changed relative to a constant weight of sorbent, favorable sorption has occurred. A shallow slope would indicate unfavorable sorption. Unless there is nearly complete removal, both steep and shallow curves could be obtained when the solubility or polarity of the sorbate controls the sorption capacity. If an increase in sorptive capacity is initially seen, and then no increase in sorptive capacity occurs despite an increased nominal

solution concentration, the sorbent has probably been saturated. Flat slopes with a low sorptive capacity indicate a lack of affinity for the sorbent. It is clear that Reynold's generalization of the n value does not always accurately depict activated carbon's sorptive capacity.

Transformation of the data in this experiment was best described by the Freundlich equation. Many researchers report that pesticides are best described by the Freundlich isotherm (Boesten and Van der Pas, 1988; Hermosin and Cornejo, 1989; Weber and Peter, 1982). No significant difference was found between the slopes in Experiments A and B. All slopes were near the value of 1, indicating an acceptable sorptive capacity for all of the sorbents. Because the slopes in Experiment A (varied concentration, constant weight) were slightly less than 1, and slightly greater than 1 in Experiment B (varied weight, constant concentration), sorption is probably a function of the solubility or polarity of metolachlor. Faust (1983) suggests that steep slopes indicate a high sorptive capacity at high equilibrium concentrations that rapidly diminish at lower Ce values. Flat or shallow slopes denote that little change occurs in sorptive capacity regardless of the equilibrium concentration.

K values are most often defined when log Ce = 1, or as the anti-log of the intercept of the Freundlich plot (Ce=0).

Three problems result from computing and using the K value. First, calculating K when Ce=0 may require extrapolation beyond the data set. It is suggested that data be collected so that the investigated range includes a value for Ce=1. This is not always possible due to lack of removal of polar compounds or measurement problems due to detection limits of the instrument. The metolachlor isotherms in this study covered a narrow equilibrium concentration range. The solubility limit of metolachlor limited the upper portion of the range, while the detection limits and polar nature of the compound limited the lower range. However, the range investigated is probably most applicable to pesticide disposal. Most rinsate solutions or surface runoff will probably have concentrations between 50 and 400 mg/L. Bowman suggests that extrapolation to compute K should be avoided. A Se value and Ce value within the range should be used to solve for K (Hermosin and Cornejo, 1987). The K values obtained in this study were not computed in this fashion, because of the emphasis on conventional methods. Bowman's method may be a more accurate way to express the K value; but, it increases the inconsistency in K values computed by different researchers.

Lack of consistency in experimental units to compute K values is another problem in interpreting isotherm data. Hermosin and Cornejo (1987) suggest that sorption data be

expressed in molar units. Candela et al. (1990) report K values for cyanazine sorption to peat and montmorillonite clay in ug/g units. Discrepancies in K units often prohibits the comparison of K values between researchers. Hermosin and Candela's proposal that researchers adopt a common method for interpreting pesticide isotherm data is sound; however, his suggestion that all scientist use molar units is debatable. Current legislation is written based on mg/g or mg/L quantities. In addition, these units probably provide a better conceptual understanding to most people.

While K may provide a good indication of a sorbent's capacity at low equilibrium concentrations, it does not describe sorption at higher Ce values. In experiment B, the K values for peat and steam-exploded wood fibers were equal, while rubber's was slightly lower. Because of the steep slope of the isotherm line, sorption to rubber quickly intersects the other isotherm lines yielding higher predicted values for Se.

To compensate for the proceeding problems, it may be useful to limit the use of K and Se, when evaluating isotherms. If low equilibrium values are desirable, the K value should be used to assess the effectiveness of the sorbents. If high equilibrium values are acceptable, Se should be used to identify the most economical sorbent.

Sorbents with large K or Se values would be preferred regardless of the method used to generate the data.

Using this criteria to evaluate the different sorbents used to remove unformulated metolachlor from the aqueous phase, suggests that activated carbon was most effective in removing the pesticide from water at low equilibrium concentrations. Peat and rubber appeared comparable, with a possibility that peat may be slightly more effective. The lowest K value was seen with steam-exploded wood fibers. At higher equilibrium concentrations, rubber appeared to outperform all other sorbents. Activated carbon and peat had a similar sorptive capacity for metolachlor. Steam-exploded wood fibers had the lowest sorption capacity.

Experiment A and B, established that rubber, peat, and steam-exploded wood fibers were equally effective in removing formulated metolachlor from water at low equilibrium concentrations. At high solution concentrations, rubber had the highest sorption capacity, followed by peat and then the wood fibers. The overlap of data points in Figure 13 suggests that no difference exists between peat and the wood fibers' ability to remove formulated metolachlor from the aqueous phase.

Slopes of isotherm plots can be useful in identifying the best treatment process for each sorbent. Bernardin (1985) suggests that a float or shallow slope indicates that

sorption is independent of equilibrium concentration, and may be treated with either a batch or column reactor. Steep slopes indicate that sorption capacity is dependent on equilibrium concentration, and treatment should be conducted in a column reactor.

Based on Bernardin's standards and the values obtained for K and Se, it appears that a rubber column would be an effective initial treatment step in the removal process. An additional column, packed with peat or activated carbon, should be used as the final treatment step.

If the K and n values are used to compare the sorption capacity of formulated to unformulated metolachlor, no difference in sorption capacity is observed. This confirms the analysis of covariance, which found no difference in the isotherm slopes between unformulated and formulated for each sorbent type.

Edwards et al. (1991) reports that solubilization of hydrophobic compounds is a linear function of the surfactant concentration above the critical micelle concentration. It is believed that this enhanced solubility will increase subsurface movement and groundwater contamination (Chiou et al. 1991; Edwards et al., 1991; Kile and Chiou, 1989). For very hydrophobic compounds such as DDT, increased solubilization may occur when nonionic surfactants are present as monomers. Kile and Chiou (1989) equate the

slight solubility enhancement of non-polar compounds by nonionic surfactants to that seen with dissolved humic and fulvic acids. Kile and Chiou (1990) state that the enhancement effect of emulsified systems is 1.5-3 orders of magnitude higher than a monomeric system, because the large size aggregates allow the micelles to act as a bulk organic phase. Because of the ability of surfactants to solubilize hydrophobic compounds, they have been incorporated into soil remediation strategies to extract oils and hydrocarbons from contaminated soil (Vigon and Rubin, 1989; McDermott et al., 1989).

Initially, it is difficult to understand why no solubility enhancement was seen with formulated metolachlor. However, experiments conducted by Kile and Chiou (1989 and 1990), Chiou et al. (1991), and Edwards et al. (1991) showed the solubility enhancement of surfactants in a pure aqueous phase. Their attempts to relate their findings to a soil and water system may be unfounded. Moore (1989) observed the effects of surfactants on the biodegradation of toluene in soil, finding that the concentration of surfactant required to reach a minimum surface tension in microcosms was two orders of magnitude higher than the critical micelle concentration in distilled water. Vigon and Rubin (1989) observed that adsorption of applied surfactant resulted in suboptimal decontamination of anthracene polluted soils.

Higher doses of surfactant increased desorption rates. These studies seem to suggest that the soil's demand for surfactant must be exceeded before solubility enhancement of hydrocarbons will occur.

Based on the findings of this study, it would appear that the materials investigated effectively sorbed the surfactant, reducing the aqueous phase concentration of surfactant below the critical micelle concentration. Results of surface tension measurements following contact of 400 mg/L unformulated and formulated metolachlor with each sorbent further confirms this hypothesis. Surface tensions of peat and rubber are the same for formulated and unformulated metolachlor indicating that the micelles are no long present in the formulated system. The surface tension of steam-exploded wood fibers following contact with formulated metolachlor is slightly lower than the unformulated compound. This suggests that the wood fibers may not be as effective in removing the surfactant from the aqueous phase, thus allowing more metolachlor to remain in solution. The surface tension of the control increased slightly in some experiments, and not in others. Lissant (1983) stated that mechanical agitation may break an emulsion. The increase in surface tension in some of the controls was most likely due to the turbulence created by the shaker table.

Although there was little difference in the Freundlich isotherms for the formulated and unformulated compound, there was a disparity in the shapes of the Linear isotherm plots. This suggests that while the sorbents were equally effective in removing unformulated or formulated metolachlor from the bulk solution, the mechanism of binding is different. Unformulated metolachlor sorption to all of the matrices resulted in a S-shaped curve. The isotherms for formulated metolachlor were more C-shaped. An S-shaped isotherm curve results when water competes for binding sites on the solid's surface. Peter and Weber (1982) stated that if an S-Shaped isotherm is obtained, the sorbate is probably sorbing in a vertical position to the surface with multimolecular layers; and, the bonding is monofunctional. A C-shape curve indicates that a constant partitioning of the solute to the sorbent occurs, with new sites becoming available as the solute sorbs (Stevenson, 1982; Weber and Peter, 1982).

Weber and Peter (1982) studied the adsorption of technical-grade metolachlor and alachlor to Ca-organic matter and Ca-montmorillonite. They found that the isotherms for sorption of both chloroacetamides to Ca-organic matter were L-shaped, and S-shaped on Ca-montmorillonite. An L-shape indicates that the solid has a high affinity for the sorbate. Weber and Peter hypothesize

that the sorption of the herbicides to Ca-organic matter occurs in a planar fashion, through multifunctional H-bonds between the carbonyl oxygen atoms of the chemical and the hydrogen atoms of carboxyl and hydroxyl groups of the organic matter, and through charge transfer bonds between the aromatic nucleus of the chloroacetamides and aromatic rings of the organic matter surfaces. Sorption to Ca-montmorillonite occurs in a random position, with monofunctional bonding between the carbonyl oxygen atoms of the herbicides and calcium atoms on the clay surfaces. Weber and Peter also note that the percent adsorption of the chloroacetamides increases with increasing concentration.

Based on Weber and Peter's findings, it was expected that adsorption of metolachlor to peat and steam-exploded wood fibers would exhibit an L-shape isotherm curve. The equilibrium concentrations of metolachlor and alachlor in Weber and Peter's study ranged from < 0.001 mg/L to approximately 11 mg/L. This concentration range is significantly lower than the range in this study. It is likely that the binding mechanisms are initially similar to those described by Weber and Peter for organic matter; however, once the surface of the peat and wood fibers become saturated, sorption is limited to multilayering interactions between metolachlor molecules. This results in the observed S-shape. No increase in percent removal was seen at higher

concentrations. This reinforces that idea that the polarity of metolachlor limits sorption, and that the solvent is competing for sorption sites.

A Thermo Jarrell-Ash (Franklin, MA) inductively coupled argon plasma (ICAP) spectrophotometer was used to determine the concentration of P, K, Ca, Mg, Na, and S in a 400 mg/L formulated metolachlor solution. Concentrations of Ca and Mg were below the instruments 0.01 mg/L detection limit. Phosphorous was reported at 0.38 mg/L, sulfur at 0.23 mg/L, potassium at 0.14 mg/L and sodium at 0.14 mg/L. Based on the ICAP analysis, coupled with information provided by the 1982 U.S patent 4,313,847 for surfactant compositions for pesticides, it is believed that the primary component of surfactants in the formulation is a polyoxyalkylene alkyl or alkyllaryl ether phosphate ester prepared by reacting a nonyl- or octylphenol with ehtylene oxide to produce polyoxyethylene nonyl- (or octyl) phenol. This is then reacted with a phosphorylating agent to prepare the ester. Secondary components include polyoxyalklene alkyl amine, and nonionic polyoxyalkylated surfactants (Chasin and Zaucha, 1984). Based on the S, Na and K content of Dual, it is likely that some of the surfactants are salts of sulfated esters of fatty alcohols or alkylbenzenesulfonates. With these components present in formulated metolachlor, it is likely that the majority of binding sites on the sorbents

are filled by electrostatic interactions and H-bonding between the surfactant and the sorbent. Sorption of metolachlor directly to the sorbent is probably minimal. Metolachlor is most likely drawn to the solid through interaction with the surfactants in subsequent layers, resulting in a C-Shape isotherm curve.

5.3 MODIFICATION TO SORBENT MATERIAL

5.3.1 Salt and Acid Treatment

When the study was initially undertaken, it was hypothesized that a metal complex (chelate) could be formed, or ion exchange could occur between the surfactant and the modified peat, which would increase metolachlor removal by association of the herbicide with the bound surfactant. Khan (1969) showed that metallic cations form complexes with the humic acid fraction of peat. Kadlec and Keoleian (1986) state that the carboxlic acid and phenolic hydroxyl groups of humic and fulvic acids act as chelating agents to complex metals. Wolf et al. (1977) found that Ca^{2+} is not tightly bound to peat and can easily be replaced by heavy metals. In view of these findings, it was reasonable to assume that the sorption capacity could be enhanced by modifying peat with alkaline earth metals.

Following this experiment an ICAP analysis of formulated metolachlor was conducted. The results were previously stated (5.12). Alkaline earth metals present were Na^{+} and K^{+}. In general, ion exchange on peat is driven by a counter ion of higher valence (Kadleac and Keoleian, 1986). Therefore, displacement of Na^{+} and Ca^{2+} from the peat was not favored in this experiment. However, the $CaCl_2$ treated peat would theoretically have the ability to form a chelate between the salt forms of sulfated esters of fatty acids or

alkylbenzensulfonates and humic acids. This interaction between the surfactant and modified peat cannot be precluded. However, it has been found that Ca^{2+} is the resident ion in most soils (Baes and Bloom, 1988). Chelation may have been equally likely to occur in the $CaCl_2$ treated as the untreated peat. The poor performance of the $Ca(OH)_2$ treated peat can be explained by the pH of the solution phase. Above a pH of 8, Humic and fulvic acids begin to solubilize. This has a two-fold effect on peat's sorption capacity. It decreases its absorptivity by reducing the organic matter fraction; and, the soluble humic and fulvic acid colloids can sorb the pesticide and hold it in solution.

Peat's sorptive capacity was slightly increased by HCL treatment. MacCarthy and Djebber (1986) report an increase in the removal of paraquat, diquat and amitrole with sulfuric acid treated peat. Smith et al. (1986) showed that peat treated with sulfuric acid has an increased ability to complex with Na^{+}. There are several possible explanations for the increase in sorptive capacity. The acid treatment improves wettability of the material. Increased permeability could have exposed the pesticide to more binding sites; or, The sodium and potassium surfactants could have complexed with the peat. The later is supported by the reduction in solution pH following contact with the

pesticide, indicating that H^+ ions were being displaced from the peat's surface. Finally, the number of H-bonds could have been increased.

5.3.2 Particle Size

Sorption of chemicals to a solid surface is greatly affected by the available surface area. Surface area of a nonporous material is greatly increased with decreased particle size. Therefore, it was expected that an increased sorption rate would result with a decrease in particle size. This study did not show an increase in the percent of metolachlor removed from solution with a decrease in particle size. It is possible that the size differential was not significant enough to produce a the expected results.

Karickhoff and Brown (1979) studied paraquat sorption to natural sediments as a function of particle size. Their findings indicate that paraquat is preferentially sorbed to particles ranging between 0.065-0.44 um in size. Sorption decreased exponentially above and below this size range. It is possible that some mechanism of interaction with the sorbent was disrupted that negated the possible benefits of an increased surface area.

5.3.3 Wet and Dry Sorbents

Although acid treatment improves sorptivity, it is questionable whether this procedure is more economically feasible than hydrating the peat with distilled water. Peat showed increased removal of formulated metolachlor when it was hydrated prior to contact. Drying of peat to 8-10% moisture causes loss of wettability (Fuchsman, 1986). Some speculate that it may change the physical structure of the material. By pre-wetting the surface of peat, the number of sorptive sites is increased which is reflected in the increased removal of metolachlor. This same effect was not seen with the steam-exploded wood fibers. There is no ready explanation for this.

Treatment of rubber to wet the surface of the material did not improve removal efficiency. During the treatment process, the rubber was contacted with methanol, and the liquid subsequently removed by vacuum. The material was then rinsed with ultra-pure water. When the water came in contact with the methanol rinse, a cloudy, white solution resulted. This is not seen when regular methanol is contacted with water. The formation of a cloudy solution indicates that something was extracted from the rubber during the treatment process. This is likely the cause of the decreased performance of the methanol treated rubber.

5.4 OTHER EXPERIMENTS

5.4.1 Demulsification

Mullins et al. (1991) reported increased removal of several pesticides when $Ca(OH)_2$ was added as a demulsification agent to the pesticide sorbent mixture. Using a demulsification, sorption and filtration apparatus, Mullins et al. (1991) reported that only 9.9 $\pm$ 2.8% of the initial solution concentration of metolachlor remained in solution after contact with steam-exploded wood fibers, 5.9 $\pm$ 1.1% with activated carbon, and 39.6 $\pm$ 8.7% with peat. Because Mullins et al. (1991) did not report the percent of metolachlor remaining in solution without the demulsification step, it is difficult to assess whether an enhanced removal of the pesticide was seen. However, using the reported values for the percent remaining in solution, it appears that Mullins et al demulsification method is not as effective as a one-step sorption process when peat and activated carbon are used to remove formulated metolachlor from the aqueous phase. This correlates with the results of this demulsification study. Addition of $Ca(OH)_2$ as a demulsifying agent hindered removal of metolachlor when contacted with peat. This is probably due to the solubilization of humic and fulvic acids, which sorbed the pesticide and held it in solution.

Mullins et al. (1991) report an unusually high removal efficiency of metolachlor when $Ca(OH)_2$ is used with steam-exploded wood fibers. This conflicts with the results of this study. There are several possible explanations for this phenomena. Mullins et al. (1991) reported using concentrations of 5000 mg/L formulated metolachlor. This is well above the 450 mg/L surfactant stability level of the formulation as defined in this research project. When a solution becomes saturated, the surfactants separate to a liquid-crystal phase in either a hexagonal or lamellar phase formation (Hall and Tiddy, 1981). In the hexagonal phase, the surfactants associate in a cylindrical fashion. In the lamellar phase, there are alternating surfactant and water layers. Regardless of the phase formation, the mixture is no longer a colloidally-stable dispersion, but a suspension (Tadros, 1989). Sedimentation forces overcome those of Brownian diffusion and a portion of the surfactants settles to the bottom of the container. Interaction of surfactants in a saturated solution can also cause coagulation or flocculation. The net result is that there are larger and heavier particles that will tend to settle. In the Mullins et al. (1991) experiment, their high rate of removal is likely due to sedimentation or filtration of the larger particles, which would occur regardless of the addition of the demulsifier. It is also possible that the unsolubilized

crystalline $Ca(OH)_2$ provided additional surface area for the surfactants, causing increased flocculation and sedimentation. Neither of these effects would be seen at the concentration of formulated metolachlor investigated here.

The inability of $Ca(OH)_2$ to demulsify is further confirmed with the measurements of surface tension following contact with rubber, with and without the addition of $Ca(OH)_2$. Treated samples had a lower surface tension than the untreated samples. This indicates that there was more surfactant remaining in solution with the treated than the untreated samples.

Lissant (1983) indicated that an emulsion can be broken by the addition of an acid or base to the dispersion. In addition, some salts such as alum or ferric hydroxide act as demulsifying agents. Experimentation with the various chemicals failed to identify an effective demulsifying agent. Implications are that below 400 mg/L, formulated metolachlor is a stable emulsifiable concentrate. The addition of chemical agents to the formulation will not enhance the sorption capacity of the sorbents.

5.4.2 Phosphatase Treatment

Phosphate ester and water react in the presence of phosphatase to form an alcohol and phosphate ion. Because the ICAP analysis confirmed the presences of phosphorous in formulated metolachlor, an experiment was conducted to determine if phosphatase could degrade the phosphorus containing surfactants. This could allow an increased removal of metolachlor from solution by breaking the micelle structure, and eliminating competition between the pesticide and surfactant for binding sites on the sorbent.

Three conditions were tested; pH-adjusted phosphatase amendments, no-pH-adjusted phosphatase amendments, and no-enzyme treatment. Two separate contacts with formulated metolachlor were made. The first contact was with fresh unused sorbent. The samples were then dehydrated and retested for a second contact with formulated metolachlor.

Because no difference in surface tension of the samples was seen on either contact, it is likely that phosphatase with and without pH adjustment did not affect the concentration of the surfactant, nor did it enhance metolachlor sorption. There are several possible reasons for this finding including the possibility that the concentration of phosphatase added to each sample may have been insufficient to produce the desired effect, or the acidic nature of peat could have neutralized the pH in the pH-adjusted samples providing suboptimal performance of the

enzyme. The need to adjust the solution to a basic pH could have been avoided by using an acid phosphatase, however a bacterial source for the acid enzyme could not be located. If the peat did act to neutralize the adjusted pH, there should have been a treatment effect for the wood fibers and rubber samples. This was not observed, suggesting that pH neutralization was not a factor. It is also possible that the surfactant may not have been available to the enzyme if it immediately sorbed to the surface of the sorbent,or that the phosphatase sorbed to the matrices and became inactivated. The results of the recontact of formulated metolachlor with the used sorbents tends to support this interpretation. Less metolachlor was removed from solution for all three sorbents on second contact for both enzyme treatments than for the no-enzyme treatment. If the phosphatase occupied sites on the initial sorption layer, the multilayering affect with the surfactant and pesticide could have been reduced, due to a decreased number of binding sites.

There was a notable loss of metolachlor from the experimental controls. It is not likely that the phosphatase could act directly on the metolachlor. The phosphatase probably effectively demulsified the formulation causing the remaining surfactant to bind to the glassware. The loss of metolachlor was probably due to an association

with the glass-bound surfactant. The increase in surface tension of the phosphatase amended controls supports this hypothesis. This also provides further evidence that the phosphatase was inactivated with the sorbent samples. Because the glassware on the controls was not extracted, no definite conclusions about this experiment can be made.

5.4.3 Recontact and Reuse

Additional metolachlor was removed from a fresh dispersion of formulated metolachlor when contacted with the used sorbent. This confirms that sorption of metolachlor to the sorbents was mediated by the herbicide's solubility or polarity. The amount of metolachlor removed from solution upon contact of formulated metolachlor with used sorbent was only slightly less than the amount removed on initial contact. This suggests that a portion of the formulation was readily removed from solution, while another portion was hydrophillic.

The experiment further indicates multilayering of the surfactant and pesticide on the sorbents. If this is the case, the sorbent may have an unlimited number of sorption sites and reusability of the sorbents is feasible. Surface tensions of the peat and rubber samples were slightly lower on recontact. This could indicate that the multilayers are less efficient than the initial layers in removing the

surfactant and pesticide. This also indicates that the layers may not be purely surfactant or purely pesticide, but a mixture of the two components.

When the supernatant from the first contact was recontacted with fresh sorbent, additional metolachlor was removed. This suggests that there are sites on the surface of the sorbents that the herbicide was more strongly attracted to sites on the sorbent's surface than the subsequent multi-layers. Implications to the treatment process are that complete removal of metolachlor is only possible with continue recontact with fresh sorbent, perhaps in a column-type of reactor.

5.5 RUBBER PACKED COLUMN

An increased efficiency of metolachlor removal was seen with a column reactor. However, it appears that an equilibrium between sorption and desorption was reached within the column. This is evident because no additional metolachlor was removed when it was recirculated through the rubber column. This suggests that a column may not be able to reduce the dispersion concentration to trace levels of metolachlor. An additional column might be necessary to achieve optimal removal.

An activated carbon column was able to reduce the concentration of metolachlor in solution only slightly. Several factors may have decreased the carbon's efficiency. The construction of this treatment system should be reevaluated. Because the pesticide was circulated in an upflow direction, tubing was necessary to direct the effluent into a holding reservoir. To eliminate metolachlor loss to the tubing, pesticide saturated tubing was used on the outlet port. The concentration of metolachlor in the analyzed sample may be the result of desorption from this tubing; and, the carbon may have been much more efficient in removing the pesticide from the aqueous phase than this study indicates. To alleviate the problem in future experimentation, it is suggested that two outlet ports be used. One port will dispense the pesticide to the holding

reservoir, while the other can be constructed with glass tubing and used for sampling purposes only.

The efficiency of the carbon may be enhanced by decreasing the flow rate through the column. Another problem associated with this column was, that despite all efforts, saturated conditions were not obtained. The effect of this was a decreased surface area. More effective removal may be achieved through a batch system.

Results of the batch studies indicate that activated carbon is very efficient in removing formulated metolachlor from solution. However, final solution concentrations of unformulated metolachlor remained at around 2 mg/L. A similar level of removal was obtained with this column system. If all of the surfactant was removed through the initial column treatment, the remaining pesticide was essentially unformulated. If this was the case, activated carbon may not be an efficient means to remove metolachlor to trace levels after previous contact with another sorbent.

CHAPTER 6

6.0 CONCLUSIONS

6.1 Specific Conclusions

1. Rubber is the most effective sorbent followed by peat and then wood fibers. However, there was little difference between the sorptive capacities of the three materials.
2. The presence of surfactants did not affect the sorption of metolachlor within the concentration range investigated.
3. Enhanced sorption was achieved with hydrated peat, and HCl treated peat.
4. Continuous flow of formulated metolachlor through a rubber-packed column showed the greatest removal efficiency.
5. Trace concentrations of metolachlor were not obtained through any of the investigated treatment methods.

6.2 Future Developments

Based on the findings of this research project, peat, rubber and steam-exploded wood are all acceptable sorbent materials, and can be successfully incorporated into a two-phase pesticide waste disposal system. These phases would be sorption and biodegradation. It is likely that

the greatest removal efficiency will be obtained through a column type of reactor. Enhanced sorption may be possible by affixing functional groups on the sorbent which allows chemical sorption to occur. This possibility should be further investigated. Additional experimentation should be conducted to determine if a one-sorbent column system is sufficient, or if a multi-media column or multi-column system can improve pesticide removal. Experiments should also be conducted to optimize the flow rate through the column(s). A demulsification step is probably not cost effective, and should not be further investigated.

Through the sorption isotherm experiments, rubber was indentified as the best sorbent material. Use of this media in the treatment system may cause some functional problems. Phase two of the disposal process involves placing the spent sorbent into a bioreactor, where the pesticide can be biodegraded by a microbiological consortium. Experiments should be conducted to assess the bioavailability of rubber-sorbed pesticides. Ideally, the pesticide will desorb from the surface of the rubber and be biologically degraded. Then, the rubber can be recycled in the treatment process. Alternately, the rubber can be used until saturation is reached. The material could then be incinerated or sent to a certified landfill. This is a costly alternative and should only be

considered if the other sorbents are not able to achieve an acceptable level of purification.

Use of both peat moss and steam-exploded wood may provide a better medium for biodegradation. Acceptable residual levels of pesticide may be obtained by increasing the amount of sorbent used in the treatment process. Use of a small activated carbon column may be necessary to properly treat the wastewater. Experimentation should be conducted to determine if pesticide removal efficiencies are increased by using the same activated carbon column for the initial and final treatment steps.

Ultimately, the development of a pesticide waste disposal system will involve an economical balance between the sorption and biodegradation phases. A high-affinity sorbent should be utilized in the first phase; however, a less effective sorbent may be the appropriate choice so that the biodegradability of the pesticide will not be compromised.

LITERATURE CITED

Al-Bahrani; Martin, R.T. 1976. Adsorption Studies Using Gas-Liquid Chromatography: Effect of Molecular Structure. Water Research, 10, 731-736.

Auerbach, A.L. 1988. EPA Pesticide Registration Program. In: Pesticides: Risks, Management, Alternatives. Proceedings of a Symposium. Richmond, VA, Weigmann, D.L., ed., 51-57.

Baes,A.U.; Bloom, P.R. 1988. Exchange of Alkaline Earth Cations in Soil Organic Matter, Soil Science, 146(7), 6-14.

Bailey, G.W.; White, J.L. 1970. Factors Influencing the Adsorption/Desorption and Movement of Pesticides in Soil. Residue Reviews, 32, 29-80.

Baker, D.B. 1991. Herbicide Concentrations in Ohio's Drinking Water Supplies: A Quantitative Assessment. In Abstracts for: Pesticides in the Next Decade: The Challenges Ahead. Proceedings of 3rd National Research Conference on Pesticides, Richmond Va, Weigmann, D.L. ed., 2-3.

Boesten, J.J; Van der Pas, L.J. 1988. Modeling Adsorption/Desorption Kinetics of Pesticides in a Soil Suspension. Soil Science, 146(4), 221-230.

Bernardin, F.E. 1985. Experimental Design and Testing of Adsorption and Adsorbates. In: Adsorption Technology. Marcel Dekker, Inc., New York, Slejko, F.L. ed., 37-91.

Bridges, J.S.; Dempsey, C.R., eds. 1988. Pesticide Waste Disposal Technology. Noyes Data Corporation, Park Ridge, New Jersey.

Cancela, G.D.; Taboada, E.R.; Sanchez-Rasero, F. 1990. Adsorption of Cyanazine on Peat and Montmorillonite Clay Surfaces. Soil Science, 150(6), 836-843.

Chasin, D.G.; Zaucha, T.J. 1984. Surfactant Compositions for Pesticides. In: Emulsions and Emulsifier Applications, Noyes Data Corporation, NJ, 200-201.

Chesters, G; Simsiman, G.V.; Levy, J.; Alhajjar, B.J.; Fathulla, R.N.; Harkin, J.M. 1989. Environmental Fate of Alachlor and Metolachlor. In: Reviews of Environmental Contamination and Toxicology. Spring-Verlog, New York, N.Y.. Gunther, F.A. ed., 110, 2-67.

Clark, R.M.; Lykins, B.W., eds. 1989. Granular Activated Carbon: Design, Operation and Cost. Lewis Publishers, Chelsea, Michigan, 125-129.

Cloutier, J.N.; Leduy, A.; Ramalho, R.S. 1985. Peat Adsorption of Herbicide 2,4-D from Wastewaters. Canadian Journal of Chemical Engineering, 63, 250-257.

Coupal, B.; Lalancette,J.M. 1976. Treatment of Wastewaters with Peat Moss. Water Research, 10, 1071-1076.

Dennis,W.H.; Kobylinski, E.A. 1983. Pesticide-Laden Wastewater Treatment for Small Generators. Journal of Environmental Science and Health, B18(3), 317-331.

Dempsey, B.A.; O'Melia, C.R. 1983. Proton and Calcium Complexation of Four Fulvic Acid Fractions. In: Aquatic and Terrestrial Humic Material. Ann Arbor Science, Ann Arbor, MI, 239-269.

Dillaha, T. 1990. personal communication, Professor of Agricultural Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Va.

Edwards, D.; Luthy R.; Zhongbao L. 1991. Solubilization of Polycyclic Aromatic Hydrocarbons in Micellar Nonionic Surfactant Solutions. Environmental Science and Technology, 25, 127-133.

Faust, S.d.; Aly, O.M. 1983. Chemistry of Water Treatment. Butterworth Publishers: Boston, MS, 199-223.

Felsot, A.S.; Dzantor, E.K. 1990. Enhancing Biodegradation for Detoxification of Herbicide Waste in Soil. In: Enhanced Biodegradation of Pesticides in the Environment. American Chemical Society. Racke, K.D. and Coats, J.R. eds., 249-268.

Fuchsman, C.H. ed. 1986. Peat and Water: Aspects of Water Retention and Dewatering in Peat, Elsevier Applied Science Publishers: New York, NY., 1-15.

Gamble, D.S; Kahn, S.U., Tee, O.S. 1983. Atrazine Hydrolysis. Part I: Proton Catalysis at 25^{o}C. Pesticide Science, 14, 537-545.

Gillard, G. 1987. Enhancement of Pest Control by Use of Surfactant/Oil Blends, Pesticide Science, 19, 323-332.

Hales, D.R., Williams, B.K. 1986. An Invitation to Health.... Your Personal Responsibility. Benjamin Cummings Publishing Co., Menlo Park, California, 254.

Hall, D.G.; Tiddy, G.J.T. 1981. Surfactant Solutions: Dilute and Concentrated. In: Anionic Surfactants. Marcel Dekker, Inc., New York, Lucassen-Reynders, E.H., ed., 55-103.

Hall, D.W.; Lietman, P.L. 1991. Herbicides in Surface and Ground Water of Agricultural, Carbonate Valleys, Lancaster County, Pennsylvania. In: Abstracts for Pesticides in the Next Decade: The Challenges Ahead. Proceeding 3rd National Research Conference on Pesticides. Richmond Va, Weigmann, D.L. ed., 8-9.

Hartley, D.B.; Kidd, H.B.. 1987. The Agrochemicals Handbook: Second Edition. The Royal Society of Chemistry, Nottingam, England, 327.

Hermosin, M.C.; Cornejo, J. 1989. Assessing Factors Related to Pesticide Adsorption by Soils. Toxicology and Environmental Chemistry, 23, 45-55.

Hermosin, M.C.; Cornejo, J. 1987. Maleic Hydrazide Adsorption by Soils and the Use of the Mole Fraction Form of the Freundlich Equation. Soil Science, 144(6), 453-456.

Hetzel,G.H.; Mullins D.E.; Young,R.W.; Simonds,J.M. 1989. Disposal of Dilute and Concentrated Agricultural Pesticides using Absorption and Chemical Microbial Degradation. In: Pesticides in Terrestrial and Aquatic Environments. Proceedings National Research Conference, Richmond, Va. Weigmann, D.L. ed., 239-248.

Himmel, C.M.; Loats, H.; Bailey, G. 1990. Pesticides: Sources to the Soil and Principles of Spray Physics. In: Pesticides in the Soil Environment: Processes, Impacts and Modeling. Soil Science Society of America Book Series. Madison WI, 2, 7-46.

Judge, D.N.; Mullins, D.E.; Hetzel, G.H.; Young, R.W. 1990. Studies on Demulsification and Sorption of Several Pesticides onto Lignocellulosic Substrates using Fluorometric and Gas Chromatographic Techniques. In: Pesticides in the Next Decade: The Challenges Ahead. Proceeding 3rd National Research Conference on Pesticides. Richmond Va, Weigmann, D.L .ed., 145-158.

Kadlec, R.H.; Keoleian G.A. 1986. Metal Ion Exchange on Peat. In: Peat and Water. Elsevier Applied Science Publishers, New York, Fuchsman, C.H., ed., 61-94.

Karickhoff, S.W.; Brown, D.S.; Scott, T.A. 1979. Sorption of hydrophobic Pollutants on Natural Sediments. Water Research, 13, 241-248.

Khan, S.U. 1969. Interaction Between the Humic Acid Fractions of Soils and Certain Metallic Cations. Soil Science American Proceedings, 33, 851-854.

Kile, D.E.; Chiou, C.T. 1989. Water Solubility Enhancements of DDT and Trichlorobenzene by some Surfactants Below and above Critical Micelle Concentration. Environmental Science and Technology, 23, 832-838.

Kile, D.E.; Chiou C.T.; Helburn, R.S. 1990. Effect of Some Petroleum Sulfonate Surfactants in the Apparent Water Solubility of Organic Compounds, Environment Science and Technology, 24, 205-208.

Kissel, D.E. ed, Himmel, C.M.; Loats H., Bailey G. 1990. Pest Sources to Soil and Principles of Spray Physics. In: Pesticides in the Soil Environment: Processes, Impacts and Modeling, Soil Science Society of America, Book Series #2: Madison, WI, 7-46.

Knowles, C.O. 1988.The Pesticide Revolution, In: Pesticides: Risks, Management, Alternatives. Proc of Symposium. Richmond, VA, Weigmann, D.L., ed., 1-8.

Krause, A.; Hancock G.; Minard R.; Freyer, A.J.; Honeycutt, R.C. Lebaron, H.M.; Paulson, D.L.; Liu, S.Y.; Bollag, J.M. 1985. Microbial Transformation of the Herbicide Metolachlor by a Soil Actinomycete. Journal of Agricultural Food, 33.

Kruegar, R. 1988. Pesticide Disposal Regulations. In: Pesticides: Risks, Management, Alternatives. Proceedings of a Symposium. Richmond, VA, Weigmann, D.L., ed., 63-66.

Lebaron: McFarland; Simoneauz; Ebert. 1988. Metolachlor. In: Herbicides: Chemistry, Degradation and Mode of Action, Marcel Dekker, Inc., Kearney, P.C. and Kaufman, D.D. ed., 3, 336-379.

Lee J.F.; Crum, J.R., Boyd, S.A. 1989. Enhanced Retention of Organic Contaminants by Soils Exchanged with Organic Cations. Environmental Science and Technology, 23(11), 135-172.

Lissant, K.J., ed. 1983. Demulsification. Marcel Dekker Inc. New York, 63-89.

Lissant, K.J. ed. 1974. Emulsions and Emulsion Technology, Part I, Marcel Dekker Inc., NY, 60-78.

Liu, S.Y.; Zheng, Z.; Zhang, R.; Bollag, J.M. 1988. Biodegradation of Metolachlor in a Soil Perfusion Experiment. Biology and Fertility of Soils, 5, 276-278.

Liu, S.Y.; Zheng, Z.; Zhang, R.; Bollag, J.M. 1989. Sorption and Metabolism of Metolachlor by a Bacterial Community, Applied Environmental Microbiology, 3, 733-740.

Lucassen-Reynders, E.H., ed. 1981. Anionic Surfactants, Marcel Dekker, Inc., NY, 1-10.

MacCarthy, P.; Djebbar, K.E. 1976. Removal of Paraquat, Diquat and Amitrole from Aqueous Solution using Chemical Modified Peat. Journal of Environmental Quality, 15(2):103-107.

Mathan, G.N.; Viraraghavan, T. 1989. Use of Peat in the Treatment of Oily Waters. Water, Air and Soil Pollution, 45, 17-26.

McDermott, J.B.; Unterman, R.; Brennan, M.J.; Brooks, R.E.; Mobley, D.P. Schwartz, C.C.; Dietrich, D.K. 1989. Two Strategies for PCB: Soil Remediation Biodegradation and Surfactant Extraction. Environmental Progress, 8(1), 46-51.

McIntire, G.L. 1990. Micelles in Analytical Chemistry. Analytical Review in Analytical Chemistry, 21(4), 245-290.

McKay, G.; Allen, S.J. 1980. Surface Mass Tranfer Processes Using Peat as an Adsorbent for Dyestuff, Canadian Journal of Chemical Engineering 58, 521-526.

McKay, G.; Allen, S.J. 1983. A Mathematical Model for the Fixed Bed Adsorption of Telon Blue Dye on Peat. Journal of Separation Procedures Technology, 4(3), 8-15.

McKay, G.; Allen, S.J. 1984. Pore Diffusion Model for Dye Adsorption onto Peat in Batch Adsorbers, Canadian Journal of Chemical Engineering, 62, 340-345.

McKay, G.; Otterburn, M.S.; Sweeney, A.G. 1978. The Removal of Colour from Effluent using various Adsorbents: Some Preliminary Economic Considerations. JSDC, 357-372.

Moore. J. 1989. Effects of Surfactants on the Biodegradation of Toluene in Soil. Master of Science Thesis, Environmental Engineering, Virginia Polytechnic Institute and State University. Blacksburg, VA. 50-70.

Mullins, D.E.; Young, R.W.; Hetzel, R.W.; Berry, D.F. expected publication July, 1991. Pesticides Disposal Using a Demulsification, Sorption, Filtration, and Chemical and Biological Degradation Strategy. In: Proceedings Research Workshop on the Treatment/Disposal of Pesticide Wastewater, USEPA Cincinnati.

Mullins, D.E.; Young, R.W.; Palmer, C.P.; Hamilton, R.L.; Sherertz, P.C. 1989. Disposal of Concentrated Solutions of Diazinon using Organic Absorption and Chemical and Microbial Degradation. Pestide Science, 25, 241-254.

Munnecke, D.M. 1980. Enzymatic Detoxification of Waste Organophosphate Pesticides, Journal Agricultural Food Chemistry, 28, 109-117.

Myrik, C. 1990. AgriChemical Dealership Site Assessment and Remediation. Proceedings of Information Exchange Meeting, Memphis, TN. National AgriChem Retail Assocation, 1-60.

Norwood, V.M. 1990. A Literature Review of Waste Treatment Technologies which may be Applicable to Wastes Generated at Fertilizer/Agrichemical Dealers Sites. Tennessee Valley Authority Bulletin y-214, 1990, 1-40.

Overend, R. P.; Chornet, E. 1987. Fractionation of Lignocellulosics by Steam-Aqueous Pretreatments. Phil. Trans. R. Soc. Lond. A., 321, 523-536.

Perdue, E.M.; Wolfe, N.L. 1982. Modification of Pollutant Hydrolysis Kinetics in the Presence of Humic Substances. Environmental Science and Technology, 16, 847-852.

Petruska, J.A.; Mullins, D.E; Young, R.W.; Collins, E.R. 1985. A Benchtop System for Evaluation of Pesticide Disposal by Composting, Nuclear and Chemical Waste Management, 5, 177-182.

Poots, V.J.P.; McKay G.; Healy, J.J. 1976. The Removal of Acid Dye From Effluent Using Natural Adsorbents - I Peat. Water Research, 10, 1061-1066.

Rosen, M.J. 1978. Degradation of Aliphatic Hydrocarbons, In: Developments in Biodegradation of Hydrocarbons; Applied Science Publishers Ltd.: London, 178.

Reynold, T.D., ed. 1982. Unit Operations and Processes in Environmental Engineering. B/C Engineering Division, Boston, Massachusetts, 187-212.

Seaman, D. 1990. Trend in the Formulation of Pesticides--An Overview, Pesticide Science, 29, 437-449.

Schweitzer, P.A. ed. 1979. Handbook of Separation Techniques for Chemical Engineers. McGraw Hill Publishers, New York, NY, 199-254.

Smith, A.l. ed.; Smith, A.L.; Mitchel, D.P. 1976. The Centrifuge Technique in the Study of Emulsion Stability. In: Theory and Practice of Emulsion Technology; Proceedings of a Symposium, Society of Chemical Industry, 1974; Academic Press: London, 196-204.

Smith E.F.; MacCarthy, P., Yu, T.C.C; Mark, H.B. 1977. Sulfuric Acid Treatment of Peat for Cation Exchange. Journal of Water Pollution Control Federation, 633-637.

Stevenson, F.J. 1982. Humus Chemistry: Genesis, Composition Reactions. Wiley Interscience Publications: NY, 390-420.

Stiles, W.A. 1988. FIFRA and FIFRA Reauthorization. In: Pesticides: Risks, Mangement, Alternatives. Proc of Nat. Pest. Conf. Richmond, VA, Weigmann, D.L., ed., 58-62.

Stroebel, P. 1991. personal communication. Environmental Engineer, USEPA, Chicago, IL.

Tadros, T.F. 1989. Colloidal Aspects of Pesticidal and Pharmaceutical Formulation- an Overview. Pesticide Science, 26, 51-77.

Thomas, B. 1990. Regulatory Pressures on Pesticide Formulations, Pesticide Science 29, 475-479.

Vigon, B.W.; Rubin, A. 1989. Practical Considerations in Surfactant-Aided Mobilization of Contaminants in Aquifers. Journal of Water Pollution Control Federation, 61(7), 1233-1240.

Wauchope R.D.; Myers R.S. 1985. Adsorption-Desorption Kinetics of Atrazine and Linurin in Freshwater-Sediment Aqueous Slurries. Journal of Environmental Quality, 14,132-136.

Weber, J.B.; Peter, J.C. 1982. Adsorption, Bioactivity and Evaluation of Soil Tests for Alachlor, Acetochlor, Metolahclor. Weed Science, 30, 14-20.

Weber, W.J. 1985. Adsorption Theory, Concepts, and Models. In: Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application, Marcel Dekker, Inc., NY, 1-45.

Weber, W.J.; Morris, J.C. 1963. Kinetics of Adsorption on Carbon from Solution, Journal of Sanitary Engineering Division, Proceedings of American Society of Civil Engineers, SA2, 31-59.

Weber, J.B.; Peter, J.C. 1982. Adsorption, Bioactivity, an Evaluation of Soil Tesets for Alachlor, Acetochlor, Metolachlor. Weed Science, 30, 14-20.

Wilkins, R.M.Pesticide Group Symposium: Recent Developments in Controlled Release Formulations for Pest Control, Pesticide Science, 15, 258-267.

Weigmann, D.L. 1988. Prologue. In: Pesticides: Risks, Mangement, Alternatives. Proceedings of a National Pesticide Conference, Richmond, VA, Weigmann, D.L., ed., xiii.

Wolf, A.; Bunzl, K.; Dietl F.; Schmidt, W.F. 1977. Effects of Ca^{2+} - Ions on the Absorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} by Humic Substances. Chemospere, 5, 207-213.

Woodburn K.B., Lee, L.S.; Surech C.R.; Delfino, J.J. 1989. Comparison of Sorption Energics for Hydrophobic Organic Chemicals by Synthetic and Natural Sorbents from Methanol/Water Solvent Mixtures. Environmental Science and Technology, 23, 407-413.

Table 1. Kinetic Study for Unformulated Metolachlor

Time and Sample	Peat Moss	Rubber	Wood Fibers	Control
10 minutes				
A	144.97	85.45	118.18	200.00
B	141.03	85.45	123.64	
C	141.03	80.00	122.73	
Average	142.34	83.64	121.52	200.00
Std. Dev.	2.28	3.15	2.92	
30 minutes				
A	125.25	56.36	120.91	196.55
B	115.38	60.91	121.82	
C	114.40	* * * *	120.91	
Average	118.34	58.64	121.21	196.55
Std. Dev.	6.00	3.21	0.52	
1 hour				
A	113.41	42.44	87.19	193.10
B	104.54	41.67	90.66	
C	* * * *	41.67	93.75	
Average	108.97	41.92	90.53	193.10
Std. Dev.	6.28	0.45	3.28	
3 hours				
A	70.52	40.90	79.48	213.38
B	69.62	40.12	84.10	
C	74.14	* * * *	78.32	
Average	71.43	40.51	80.63	213.38
Std. Dev.	2.39	0.55	3.06	
6 hours				
A	73.24	36.65	83.33	198.92
B	84.09	38.58	84.88	
C	84.99	38.19	84.88	
Average	80.77	37.81	84.36	198.92
Std. Dev.	6.54	1.02	0.89	
12 hours				
A	* * * *	33.18	70.22	211.57
B	96.75	32.79	68.67	
C	72.33	35.88	69.83	
Average	84.54	33.95	69.57	211.57
Std. Dev.	17.26	1.68	0.80	
24 hours				
A	73.24	51.31	73.24	198.92
B	71.43	50.15	71.43	
C	65.10	* * * *	65.10	
Average	69.92	50.73	69.92	198.92
Std. Dev.	4.27	0.82	1.28	

* indentified as outliers Starting Conc. = 200mg/Lmetolachlor

Table 2. Kinetic Study for Formulated Metolachlor

Time and Sample	Peat Moss	Rubber	Wood Fibers	Control	Activated Carbon
10 minutes					
A	148.04	101.12	110.82	192.59	123.62
B	143.14	94.38	120.27		121.41
C	148.04	103.37	121.99		121.41
Average	146.41	99.63	117.70	192.59	122.15
Std. Dev.	2.83	4.68	6.01		1.27
30 minutes					
A	133.33	85.39	91.92	207.41	41.94
B	131.37	85.39	106.53		26.49
C	134.31	83.15	108.25		61.81
Average	133.01	84.64	102.23	207.41	43.41
Std. Dev.	62.82	41.26	49.38		
1 hour					
A	96.08	82.02	87.63	207.41	
B	105.88	75.28	109.11		
C	104.90	79.78	108.25		
Average	102.29	79.03	101.66	207.41	
Std. Dev.	5.40	3.43	12.16		
3 hours					
A	83.18	56.18	83.33	218.81	
B	83.18	44.94	94.50		
C	78.66	47.19	97.94		
Average	81.68	49.44	91.92	218.81	
Std. Dev.	2.61	5.95	7.64		
6 hours					
A	76.85	44.94	71.31	221.52	
B	76.85	41.57	79.90		
C	75.05	42.70	79.04		
Average	76.25	43.07	76.75	221.52	
Std. Dev.	1.04	1.72	4.73		
12 hours					
A	72.33	62.92	85.91	214.29	
B	63.29	62.92	85.91		
C	66.91	51.69	96.22		
Average	67.51	59.18	89.35		
Std. Dev.					
24 hours	72.33	58.43	84.19	217.00	
A	66.91	53.93	90.21		
B	63.29	44.94	81.62		
C	67.51	52.43	85.34	217.00	
Average	4.55	6.87	4.41		
Std. Dev.					

* activated carbon below detection limts after 30 min.

Table 3. Formulated Metolachlor Sorption to Peat Moss

Starting Conc. & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
50 mg/L					
A	10.39	0.26	0.85	0.75	1.13
B	9.14	0.23	0.88	0.75	1.18
C	11.64	0.29	0.82	0.75	1.09
Average	10.39	0.26	0.85	0.75	1.13
Std. Dev.	1.25	0.03	0.03		0.04
100 mg/L					
A	22.03	0.55	1.80	0.75	2.40
B	24.11	0.60	1.75	0.75	2.33
C	22.44	0.56	1.79	0.75	2.39
Average	22.86	0.57	1.78	0.75	2.37
Std. Dev.	1.10	0.03	0.03		0.04
200 mg/L					
A	43.23	1.08	3.25	0.75	4.33
B	46.55	1.16	3.17	0.75	4.22
C	42.81	1.07	3.26	0.75	4.35
Average	44.20	1.10	3.23	0.75	4.30
Std. Dev.	2.05	0.05	0.05		0.07
300 mg/L					
A	74.81	1.87	4.44	0.75	5.92
B	73.98	1.85	4.46	0.75	5.95
C	70.66	1.77	4.54	0.75	6.06
Average	73.15	1.83	4.48	0.75	5.97
Std. Dev.	2.20	0.05	0.05		0.07
400 mg/L					8.24
A	99.33	2.48	6.18	0.75	8.25
B	98.92	2.47	6.19	0.75	8.19
C	100.58	2.51	6.15	0.75	8.23
Average	99.61	2.49	6.17	0.75	8.22
Std. Dev.	0.87	0.02	0.02		0.03

Table 4. Formulated Metolachlor Sorption to Rubber

Starting Conc. & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
50 mg/L					
A	7.48	0.19	0.92	0.75	1.23
B	7.48	0.19	0.92	0.75	1.23
C	6.23	0.16	0.95	0.75	1.27
Average	7.07	0.18	0.93	0.75	1.24
Std. Dev.	0.72	0.02	0.02		0.02
100 mg/L					
A	13.72	0.34	2.01	0.75	2.68
B	14.13	0.35	2.00	0.75	2.66
C	14.55	0.36	1.99	0.75	2.65
Average	14.13	0.35	2.00	0.75	2.66
Std. Dev.	0.42	0.01	0.01		0.01
200 mg/L					
A	26.60	0.67	3.66	0.75	4.89
B	28.26	0.71	3.62	0.75	4.83
C	26.60	0.67	3.66	0.75	4.89
Average	27.15	0.68	3.65	0.75	4.87
Std. Dev.	0.96	0.02	0.02		0.03
300 mg/L					
A	37.41	0.94	5.37	0.75	7.17
B	46.55	1.16	5.15	0.75	6.86
C	42.39	1.06	5.25	0.75	7.00
Average	42.12	1.05	5.26	0.75	7.01
Std. Dev.	4.58	0.11	0.11		0.15
400 mg/L					
A	55.28	1.38	7.28	0.75	9.70
B	52.78	1.32	7.34	0.75	9.79
C	49.88	1.25	7.41	0.75	9.88
Average	52.65	1.32	7.34	0.75	9.79
Std. Dev.	2.70	0.07	0.07		0.09

Table 5. Formulated Metolachlor Sorption to Wood Fibers

Starting Conc. & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
50 mg/L					
A	15.13	0.38	0.73	0.75	0.98
B	15.97	0.40	0.71	0.75	0.95
C	5.88	0.15	0.96	0.75	1.28
Average	12.32	0.31	0.80	0.75	1.07
Std. Dev.	5.60	0.14	0.14		0.19
100 mg/L					
A	38.66	0.97	1.38	0.75	1.84
B	37.82	0.95	1.40	0.75	1.87
C	37.82	0.95	1.40	0.75	1.87
Average	38.10	0.95	1.40	0.75	1.86
Std. Dev.	0.49	0.01	0.01		0.02
200 mg/L					
A	74.79	1.87	2.46	0.75	3.28
B	81.51	2.04	2.29	0.75	3.06
C	74.79	1.87	2.46	0.75	3.28
Average	77.03	1.93	2.40	0.75	3.21
Std. Dev.	3.88	0.10	0.10		0.13
300 mg/L					
A	99.16	2.48	3.83	0.75	5.11
B	110.08	2.75	3.56	0.75	4.74
C	106.72	2.67	3.64	0.75	4.86
Average	105.32	2.63	3.68	0.75	4.90
Std. Dev.	5.60	0.14	0.14		0.19
400 mg/L					
A	156.30	3.91	4.75	0.75	6.34
B	149.58	3.74	4.92	0.75	6.56
C	161.34	4.03	4.63	0.75	6.17
Average	155.74	3.89	4.77	0.75	6.36
Std. Dev.	5.90	0.15	0.15		0.20

Table 6. Unformulated Metolachlor Sorption to Peat Moss

Starting Conc. & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
50 mg/L					
A	8.55	0.21	0.86	0.75	1.14
B	8.55	0.21	0.86	0.75	1.14
C	8.55	0.21	0.86	0.75	1.14
Average	8.55	0.21	0.86	0.75	1.14
Std. Dev.					
100 mg/L					
A	28.93	0.72	1.65	0.75	2.20
B	24.41	0.61	1.76	0.75	2.35
C	20.51	0.51	1.86	0.75	2.48
Average	23.65	0.59	1.78	0.75	2.38
Std. Dev.	4.21	0.11	0.11		0.14
200 mg/L					
A	52.14	1.30	3.95	0.75	5.27
B	51.28	1.28	3.72	0.75	4.96
C	51.28	1.28	3.72	0.75	4.96
Average	51.57	1.29	3.71	0.75	4.95
Std. Dev.	0.49	0.01	0.13		0.18
300 mg/L					
A	81.20	2.03	5.49	0.75	7.32
B	82.05	2.05	5.47	0.75	7.29
C	80.34	2.01	5.51	0.75	7.35
Average	81.20	2.03	5.49	0.75	7.32
Std. Dev.	0.85	0.02	0.02		0.03
400 mg/L					
A	100.00	2.50	7.02	0.75	9.36
B	100.85	2.52	7.00	0.75	9.33
C	84.62	2.12	7.40	0.75	9.87
Average	95.16	2.38	7.14	0.75	9.52
Std. Dev.	9.14	0.23	0.23		0.30

Table 7. Unformulated Metolachlor Sorption to Rubber

Starting Conc. & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
50 mg/L					
A	11.75	0.29	0.82	0.75	1.09
B	8.14	0.20	0.91	0.75	1.21
C	6.33	0.16	0.95	0.75	1.27
Average	8.74	0.22	0.89	0.75	1.19
Std. Dev.	2.76	0.07	0.07		0.09
100 mg/L					
A	12.66	0.32	2.03	0.75	2.71
B	16.27	0.41	1.94	0.75	2.59
C	17.09	0.43	1.92	0.75	2.56
Average	15.34	0.38	1.97	0.75	2.62
Std. Dev.	2.36	0.06	0.06		0.08
200 mg/L					
A	32.48	0.81	2.69	0.75	3.58
B	35.04	0.88	2.62	0.75	3.50
C	34.19	0.85	2.65	0.75	3.53
Average	33.90	0.85	2.65	0.75	3.54
Std. Dev.	1.31	0.03	0.03		0.04
300 mg/L					
A					
B	47.86	1.20	5.73	0.75	7.64
C	45.30	1.13	5.80	0.75	7.73
Average	46.58	1.16	5.77	0.75	7.69
Std. Dev.	1.81	0.05	0.05		0.06
400 mg/L					
A	54.70	1.37	8.41	0.75	11.22
B	55.56	1.39	8.39	0.75	11.19
C	53.85	1.35	8.43	0.75	11.25
Average	54.70	1.37	8.41	0.75	11.22
Std. Dev.	0.85	0.02	0.02		0.03

Table 8. Unformulated Metolachlor Sorption to Wood Fibers

Starting Conc. & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
50 mg/L					
A	22.30	0.56	0.51	0.75	0.69
B	18.87	0.47	0.60	0.75	0.80
C	17.15	0.43	0.64	0.75	0.86
Average	19.44	0.49	0.59	0.75	0.78
Std. Dev.	2.62	0.07	0.07		0.09
100 mg/L					
A	36.02	0.90	1.47	0.75	1.96
B	39.45	0.99	1.39	0.75	1.85
C	39.45	0.99	1.39	0.75	1.85
Average	38.31	0.96	1.42	0.75	1.89
Std. Dev.	1.98	0.05	0.05		0.07
200 mg/L					
A	93.48	2.34	2.92	0.75	3.89
B	99.49	2.49	2.51	0.75	3.35
C	102.06	2.55	2.45	0.75	3.26
Average	98.34	2.46	2.54	0.75	3.39
Std. Dev.	4.40	0.11	0.25		0.34
300 mg/L					
A	150.94	3.77	3.74	0.75	4.99
B	137.22	3.43	4.09	0.75	5.45
C	133.79	3.34	4.17	0.75	5.56
Average	135.51	3.39	4.13	0.75	5.51
Std. Dev.	9.08	0.23	0.23		0.30
400 mg/L					
A	174.96	4.37	5.14	0.75	6.86
B	150.94	3.77	5.74	0.75	7.66
C	166.38	4.16	5.36	0.75	7.14
Average	164.09	4.10	5.41	0.75	7.22
Std. Dev.	12.17	0.30	0.30		0.41

Table 9. Unformulated Metolachlor Sorption to Activated Carbon

Starting Conc. & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
50 mg/L					
A	2.36	0.06	1.05	0.75	1.40
B	2.36	0.06	1.05	0.75	1.40
C	2.36	0.06	1.05	0.75	1.40
Average	2.36	0.06	1.05	0.75	1.40
Std. Dev.	0.00	0.00	0.00		0.00
100 mg/L					
A	1.97	0.05	2.30	0.75	3.07
B	2.36	0.06	2.29	0.75	3.05
C	3.15	0.08	2.27	0.75	3.03
Average	2.49	0.06	2.29	0.75	3.05
Std. Dev.	0.60	0.02	0.02		0.02
200 mg/L					
A	22.05	0.55	2.95	0.75	3.93
B	22.83	0.57	2.93	0.75	3.91
C	24.41	0.61	2.89	0.75	3.85
Average	23.10	0.58	2.92	0.75	3.90
Std. Dev.	1.20	0.03	0.03		0.04
300 mg/L					
A	25.20	0.63	6.30	0.75	8.40
B	26.38	0.66	6.27	0.75	8.36
C	25.20	0.63	6.30	0.75	8.40
Average	25.59	0.64	6.29	0.75	8.38
Std. Dev.	0.68	0.02	0.02		0.02
400 mg/L					
A	24.41	0.61	9.17	0.75	12.23
B	23.62	0.59	9.19	0.75	12.25
C	24.41	0.61	9.17	0.75	12.23
Average	24.15	0.60	9.18	0.75	12.24
Std. Dev.	0.45	0.01	0.01		0.02

Table 10. Formulated Metolachlor Sorption to Different Weights of Peat Moss

Weight (g) & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
0.25g					
A	180.00	4.50	5.40	0.25	21.60
B	176.00	4.40	5.50	0.25	22.00
C	220.00	5.50	4.40	0.25	17.60
Average	192.00	4.80	5.84	0.25	23.36
Std. Dev.	24.33	0.61	0.61		2.43
0.50g					
A	143.82	3.60	6.30	0.50	12.61
B	143.82	3.60	7.04	0.50	14.09
C	141.58	3.54	7.10	0.50	14.20
Average	143.07	3.58	7.06	0.50	14.13
Std. Dev.	1.29	0.03	0.44		0.89
0.75g					
A	108.05	2.70	7.20	0.75	9.60
B	110.28	2.76	7.14	0.75	9.52
C	* * *	* * *	* * *	* * *	* * *
Average	109.17	2.73	7.91	0.75	10.55
Std. Dev.	1.58	0.04	0.04		0.05
1.00g					
A	84.20	2.11	7.79	1.00	7.79
B	79.73	1.99	7.91	1.00	7.91
C	83.46	2.09	7.81	1.00	7.81
Average	82.46	2.06	8.58	1.00	8.58
Std. Dev.	2.40	0.06	0.06		0.06
1.25g					
A	68.55	1.71	8.93	1.25	7.14
B	67.81	1.70	8.94	1.25	7.16
C	64.08	1.60	9.04	1.25	7.23
Average	66.82	1.67	8.97	1.25	7.18
Std. Dev.	2.40	0.06	0.06		0.05

*** indentified as an outlier

Table 11. Formulated Metolachlor Sorption to Different Weights of Rubber

Weight (g) & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
0.25g					
A	120.19	3.00	6.90	0.25	27.58
B	117.31	2.93	6.97	0.25	27.87
C	122.12	3.05	6.85	0.25	27.39
Average	119.87	3.00	6.90	0.25	27.61
Std. Dev.	2.42	0.06	0.06		0.24
0.50g					
A	82.69	2.07	7.83	0.50	15.67
B	76.92	1.92	7.98	0.50	15.95
C	81.73	2.04	7.86	0.50	15.71
Average	80.45	2.01	7.89	0.50	15.78
Std. Dev.	3.09	0.08	0.08		0.15
0.75g					
A	61.54	1.54	8.36	0.75	11.15
B	64.42	1.61	8.29	0.75	11.05
C	61.54	1.56	8.34	0.75	11.12
Average	62.50	1.57	8.33	0.75	11.11
Std. Dev.	1.67	0.05	0.05		0.07
1.00g					
A	50.96	1.27	8.63	1.00	8.63
B	51.92	1.30	8.60	1.00	8.60
C	55.77	1.39	8.51	1.00	8.51
Average	52.88	1.32	8.58	1.00	8.58
Std. Dev.	2.54	0.06	0.06		0.06
1.25g					
A	43.27	1.08	8.82	1.25	7.05
B	43.27	1.08	8.08	1.25	6.46
C	45.19	1.13	8.03	1.25	6.42
Average	43.91	1.10	8.31	1.25	6.65
Std. Dev.	1.11	0.03	0.44		0.35

Table 12. Formulated Metolachlor Sorption to Different Weights of Wood Fibers

Weight (g) & Sample #	Equilibrium Conc. Ce (mg/L)	Amount in Solution (mg)	Amount on Sorbent (mg)	Weight of Sorbent (g)	Amount Sorbed Se (mg/g)
0.25g					
A	313.89	7.85	2.05	0.25	8.21
B	209.00	5.23	4.68	0.25	18.70
C	166.67	4.17	5.73	0.25	22.93
Average	229.85	5.75	4.15	0.25	16.61
Std. Dev.	75.79	1.89	1.89		7.58
0.50g					
A	173.62	4.34	5.56	0.50	11.12
B	115.07	2.88	7.02	0.50	14.05
C	129.21	3.23	6.67	0.50	13.34
Average	139.30	3.48	6.42	0.50	12.83
Std. Dev.	30.55	0.76	0.76		1.53
0.75g					
A	136.61	3.42	6.48	0.75	8.65
B	135.26	3.38	6.52	0.75	8.69
C	96.23	2.41	7.49	0.75	9.99
Average	122.70	3.07	6.83	0.75	9.11
Std. Dev.	22.93	0.57	0.57		0.76
1.00g					
A	87.48	2.19	7.71	1.00	7.71
B	90.17	2.25	7.65	1.00	7.65
C	88.83	2.22	7.68	1.00	7.68
Average	88.83	2.22	7.68	1.00	7.68
Std. Dev.		0.03	0.03		0.03
1.25g					
A	88.83	2.22	7.68	1.25	6.14
B	109.69	2.74	7.16	1.25	5.73
C	107.67	2.69	7.21	1.25	5.77
Average	102.06	2.55	7.35	1.25	5.88
Std. Dev.	11.51	0.29	0.29		0.23

Table 13. Emulsion Concentration (mg/L) Following Contact with Chemically Modified Peat Moss

Chemical Treatment	Sample A	Sample B	Sample C	Average	Standard Deviation
Calcium Hydroxide	122.55	129.08	120.10	123.91	4.64
Calcium Chloride	52.29	66.99	57.19	58.82	7.48
Sodium Chloride	58.01	58.01	62.91	59.64	2.83
Hydrochloric Acid	46.57	47.39	50.65	48.20	2.16
No Treatment	61.27	66.18	62.91	63.45	2.50
Control	350.00	355.00	345.00	350.00	5.00

Table 14. Dispersion Concentration (mg/L) with and without Treatment of Emulsion with Calcium Hydroxide

Sorbent	Sample A	Sample B	Sample C	Average	Standard Deviation
Calcium Hydroxide					
Peat Moss	210.91	214.55	205.45	210.30	4.58
Rubber	43.27	54.81	42.31	46.79	6.96
Wood Fibers	196.36	200.00	210..91	202.42	2.57
Control	367.27	367.27	367.27	367.27	0.00
No Treatment					
Peat Moss	107.27	94.55	100.00	100.61	6.38
Rubber	63.46	64.42	65.38	64.42	0.96
Wood Fibers	135.45	139.09	138.18	137.58	1.89
Control	403.57	385.71	421.43	403.57	17.86

* Initial Solution Concentration = 375mg/L for all samples, . except rubber which was 370mg/L.

Table 15. Total Amount (mg) of Metolachlor Sorbed to Different Materials following Recontact of Used Sorbent with Dual

	Peat Moss	Rubber	Wood Fibers	Control
adjusted pH				
A	12.21	15.17	9.27	0.93
B	12.53	15.40	10.19	4.26
C	12.95	15.36	9.22	3.70
Average	12.56	15.31	9.56	2.96
Std. Dev.	0.37	0.12	0.55	1.78
no pH adjustment				
A	13.18	16.00	10.15	1.76
B	13.32	15.36	9.97	0.37
C	13.04	15.21	9.69	2.04
Average	13.18	15.52	9.94	1.39
Std. Dev.	0.14	0.42	0.23	0.89
no enzyme				
A	13.69	14.46	11.05	-0.28
B	13.55	14.45	11.28	-0.28
C	13.69	13.94	10.91	0.28
Average	13.64	14.28	11.08	-0.09
Std. Dev.	0.08	0.30	0.19	0.32

Vita

Lynn E. Hutchinson was born on May 23, 1966 in a suburb of Philadephia, Pennsylvania. In May 1988, she received a Bachelor of Science degree from the University of Richmond with a dual major in Biology and Health. In September, 1989, after working for Cigna Insurance Companies as a Claims Analyst, she entered the Master of Science program in Environmental Science and Engineering at Virginia Polytechnic Institute and State University. She completed this degree in July, 1991.