MOVEMENT OF PHENOLIC COMPOUNDS IN GROUND WATER

By

ALI TORABIAN

Bachelor of Chemistry
Pars College
Tehran, Iran
1976

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1978

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Thesis Approved:

Don F Kincannon
Thesis Adviser

William F. McTernan

John N. Veenstra

Marcia Bates

Don Wagner

Norman N. Durham
Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Ground water is a valuable natural resource. Its volume is estimated at about fifty times the annual flow of surface water, according to Swep (1). Ground water supplies twenty-five percent of the fresh water and for all purposes in the U. S. A., as stated by James, et al. (2). Approximately thirty trillion gallons of fresh ground water was withdrawn for all uses in 1975. In the years from 1950 to 1975, the use of fresh ground water increased more than 140 percent. Increasing ground water use shows the importance of this vast resource. Ground water is vulnerable to contamination; the degree of threat to ground water depends on the material underlying the surface site and the particular geologic and hydrologic conditions. Contamination of ground water from human activities may come from impoundments, landfills, agriculture, leaks and spills, land disposal of waste waters, septic tanks, mining, petroleum production, underground injection, wells, and other sources.

EPA's 1977 Report to Congress (3) on waste disposal practices and their effect on ground water identified the disposal of industrial wastes at industrial impoundments and solid waste disposal sites as the most important source of ground water contamination. EPA estimated that approximately 57 million of the 378 million tons of liquid and solid industrial wastes generated in 1978 were hazardous. Most hazardous wastes are disposed of in landfills or lagoons in ways that do not meet new federal standards, according to a Report of the Council on Environmental Quality (4), and thus are a threat to ground water quality.

In addition to industrial waste, the 1977 Report identified the secondary source of national importance: septic tanks, municipal wastewater, mining and petroleum exploration and production, although concentration of toxic material for these sources are lower than for industrial waste disposal; however, they can be significant regionally. This Report indicates that 30,000 to 50,000 disposal sites in the USA contain hazardous waste, but the extent of contamination is unknown. Ground water systems close to these sites are in danger. Existing technology cannot guarantee that soil attenuation alone will be sufficient to prevent ground water contamination from a waste disposal source. Once ground water has been contaminated, one of the options that can be tried to reverse the danger is extensive pumping. This, however is sometimes impractical. In order to minimize man's activity on ground water quality, factors relating to prevention and containment of ground water contamination need to be understood. Much interest has been shown in developing a transport model to predict the movement of chemical contaminates in saturated and unsaturated zones. One of the factors or processes incorporated in the contaminant transport model is the factor of adsorption. It has been recognized as one of the major abiatic processes influencing movement of solutes relative to the bulk movement of water.

Some methods used to determine the extent of adsorption of organic compounds by the soil include batch technique, soil columns, and soil thin-layer chromatography.

Batch techniques have gained wide acceptance because of its relatively low cost, fewer labor requirements and uncomplicated procedure, according to EPA's Report on Pesticide Progams (5). A disadvantage of this method is over-prediction of the amount adsorbed. Soil columns are used to determine the breakthrough curve, which is important in describing adsorption and desorption of organic chemicals in the soil water system. The breakthrough curve can also be used for describing models which have been prepared and evaluated for defining the chemical adsorption and desorption process. These models have had varying degrees of success. Many of them predict a symmetrical breakthrough curve, while experimental BTC is different than predicted BTC.

In terms of quantity produced, phenol ranks near the top of the list of synthetic aromatic compounds manufactured. Annual production of phenol is approximately 1.25 billion Kg, according to Chemical Engineering News (6), and it is the basic structural unit for a variety of synthetic organics such as adhesives, fabricated plastics, antimicrobial agents for disinfection in hospitals, cosmetics, and many agricultural chemicals. Scott, et al. (7) found that phenol and substituted phenols are degradation products of several pesticides and herbicides. Thus, the appearance of phenol and its compounds in groundwater may result from the intentional application of pesticides and from unintentional releases associated with manufacturing processes and waste disposal.

The major aim of this study was to understand the role of adsorption in the movement of phenolic compounds in the saturated soil columns and provision of experimental breakthrough curve and data that can be used by those developing the model.

Soil properties such as organic content, clay content, and the effect of missible solvent on adsorption for the near source contamination were studied.

CHAPTER II

LITERATURE REVIEW

Adsorption is important in determining the fate of organic chamicals in the subsurface and natural water systems. The fate of organic pollutants in the subsurface environment depends on understanding the adsorption process. This process can be described as either physical adsorption or chemical adsorption. Physical adsorption results when the adsorbate adheres to the adsorbent surface by Vanderwall's forces. Chemical adsorption occurs when adsorbate and adsorbent share electrons and form a chemical bond. During the process of adsorption heat, described as the heat of adsorption, is released. The quantity of heat released during physical adsorption is about equal to the heat of condensation, but the heat released during the chemisorption is equal to the heat of reaction. Chemisorption is characterized by the formation of a monolayer on the surface of the adsorbent, while physical adsorption can be characterized by the formation of multiple layers on the surface of the adsorbent.

Adsorption Equilibrium Isotherms

Adsorption equilibrium studies have been used to describe the sorption of organic compounds by soil and determine the relationships between the amount of adsorbed and the equilibrium solution concentration. Several mathematical expressions with theoretical and empirical bases have been employed to describe the adsorption process. The most widely used models are the Langmuir adsorption isotherm (8) and Freundlich adsorption isotherm (10).

The Langmuir equation was originally developed to describe the adsorption of gas by a clean solid surface. It has been used by several investigators to describe adsorption at a solid-liquid interface. Veith and Sposito (9) used it to interpret adsorption in soil systems, given as:

$$\frac{X}{m} = \frac{KbC}{1 + KC}$$

where

$\frac{X}{m}$ = amount of adsorbate adsorbed per unit mass of adsorbent

C = equilibrium concentration of the adsorbate in solution

K = a constant related to bonding energy of the adsorbate to adsorbent

b = maximum adsorption or capacity factor

In order to test the equilibrium data, the Longmuir isotherm is generally used in the linear form:

$$\frac{1}{\frac{X}{m}} = \frac{1}{b} + \frac{1}{KbC}$$

A plot of $\frac{1}{\frac{X}{m}}$ against $\frac{1}{C}$ yields a slope of $\frac{1}{Kb}$ and an intercept at $\frac{1}{b}$.

The Freundlich isotherm equation (10) is a semi-empirical equation which is widely used in the low to intermediate concentration range. The Freundlich equation ((10) is expressed as:

$$\frac{X}{m} = KC^{1/n}$$

where

C = the equilibrium concentration in the solution after adsorption

$\frac{X}{m}$ = the adsorption value

K and $\frac{1}{m}$ are constants

The Freundlich equation normally fits the adsorption data in its linear form:

$$\log \frac{X}{m} = \log K + \frac{1}{n} \log C$$

A plot of $\log \frac{X}{m}$ against $\log C$ will give a straight line with a slope of $\frac{1}{m}$ and intercept equal to log K. When $\frac{1}{m} = 1$, The Freundlich equation isotherm reduces to a partition equation:

$$K = \frac{\frac{X}{m}}{C} = \frac{C_s}{C_w}$$

where

C_s = concentration of solute in solid phase

C_w = concentration of solute in liquid phase.

In general, it varies inversely with the solubility of the adsorbate and directly with organic and clay fraction of the solids.

Continuous Flow Adsorption Process

In the continuous flow adsorption process, adsorbents are placed in a column in which a liquid containing the absorbate is passed through the adsorbent particles.

For fresh absorbent, the adsorbate is readily removed in the region of the bed closest to the influent. Adsorbate not removed immediately has a chance to be absorbed as it passes through the bed, depending on the characteristic of the adsorbate and absorbent as well as the physical and hydraulic nature of the system. The region of the bed where adsorption and removal of the adsorbate takes place is referred to as the mass transfer zone or as the adsorption zone. When the adsorbent is exhausted, the adsorption zone approaches the end of the bed and effluent concentration of adsorbate becomes equal to its influent concentration, and no removal occurs. This phenomenon is called breakthrough. Time required to reach the maximum allowable concentration is called the breakthrough time. The effluent concentration-time curve is referred to as the breakthrough curve, and is used for analysis of the packed-bed absorbers. This curve is a function of the adsorber characteristic, operating condition and equilibrium adsorption data, according to Hines, et al. (11). The area behind the breakthrough curve represents the quantity of adsorbate adsorbed in the column.

Mass balance equation for the loss of solute by the solution passing through the adsorption column can be written as:

$$- \frac{\varepsilon V_z}{\rho_b} \left(\frac{\delta C_A}{\delta z}\right)_T - \frac{\varepsilon}{\rho_b} \left(\frac{\delta C_A}{\delta T}\right)_z = \left(\frac{\delta q_A}{\delta T}\right)_z$$

where

ε = void fraction in bed

ρ_b = density of adsorption bed

v_z = velocity

q_A = uptake by adsorbent

C_A = concentration of A in the fluid phase

The mass balance equation is based on the following assumption:

1. The axial diffusion is neglected compared to bulk flow and radial concentration gradian does not exist.
2. Velocity is constant.

A solution to the mass balance equation requires information regarding the transfer of solutes from the fluid to the adsorbent. The rate of transfer may be limited by one or a combination of the following mechanisms, according to Hines, et al. (11): 1) external mass transfer, 2) adsorption onto the surface of the adsorbent, 3) internal mass transfer through the fluid phase which occupies the pores of the adsorbent, and 4) internal transfer along the solid surfaces of the pores of the adsorbent.

The effective rate of adsorption will be controlled by the step exerting the greatest resistance to transfer; that is, the slowest step. Two alternative techniques have been used to solve the mass transfer equation. One approach involves the solution of the differential equation with considering the diffusion equation from the mass transfer. This method is difficult, and numerical techniques are used to obtain the solution. The other technique assumes a model to describe the rate of mass transfer of the solute from the liquid to the adsorbent. Using a model to represent one or more of the mechanisms and introducing equilibrium data for the adsorbate-adsorbent system, the differential equations can be integrated to produce the unsteady-state concentration profile in the packed bed. The uptake of adsorbate can then be predicted from the breakthrough curve.

If the second order kinetic is the rate-controlling step, the rate of adsorption can be expressed by the Thomas equation (12):

$$\left(\frac{\delta q}{\delta T}\right) = K_a \left[C_A \ (C - q) - \frac{1}{K} q\right]$$

where

Ka = rate constant for adsorption 1/mg hr

C = mass of one monomolecular layer of adsorbate mg/g

K = adsorption equilibrium constant 1/mg

q = concentration of adsorbed mg/g

The Thomas model for an adsorption column is given by Reynolds (13):

$$\frac{C}{Co} \cong \frac{1}{1 + e^{\frac{K_1}{Q} (q_o M - C_o v)}}$$

where

C = effluent solute concentration

C_o = influent solid concentration

K_1 = rate constant

q_o = maximum solid phase concentration of the sorbed solute gm/gm

M = mass of adsorbent gm

v = throughout volume (L)

Q = flowrate L/hour

Cross multiplying gives:

$$1 + e^{\frac{K_1}{q}(q_oM - C_ov)} = \frac{C_o}{C}$$

Rearranging and taking the natural logarithms of both sides, the equation can be written as:

$$\mathrm{Ln}\left(\frac{C_o}{C} - 1\right) = \frac{K_1q_oM}{Q} - \frac{KC_ov}{Q}$$

A plot of $L_n\left(\frac{C_o}{C} - 1\right)$ vs v yields a slope of $\frac{K_1C_o}{Q}$ and an intercept of $\frac{K_1q_oM}{Q}$ The rate of uptake for the case where the external mass transfer is the rate-controlling step is proposed by Hougen and Marshall (14), and can be expressed as:

$$\left(\frac{\delta q}{\delta T}\right)_z = \frac{K_f a}{\rho_b} \quad (C - C^*)$$

where C is the concentration of the fluid phase that is in equilibrium with the solid and a is the surface area of the solid per volume of bed. ρ_b bulk density of bed C^* equilibrium fluid phase concentration. K_f = mass transfer coefficient.

Rosen (15) proposed a model for the breakthrough curve for the case in which both film resistance and interparticle diffusion are rate-controlling, although the Rosen model, restricted to linear equilibrium isotherm and spherical adsorbent particles, it has been used successfully for many experimental systems by using an equivalent spherical radius and a linear approximation to the isotherm over the concentration region of interest. The Thomas model (12) is probably the most accurate method for describing adsorption in a packed bed, but it is more difficult to use than are the Rosen (15) and Hougen and Marshall (14) methods.

Kao (16) in a study with activated carbon, pointed out that external and internal film models cannot describe the experimental data for the entire concentration range; however, the Thomas model can describe the experimental data in any concentration, and pointed out that the Thomas model would predict the rate of solute uptake in a packed bed with reasonable accuracy.

Chemical Transport Through Porous Media

The following provides a review of current literature on the subject of chemical transport through porous media.

Darcy's Law

Darcy's Law can be written as $v = - K \frac{dh}{dL}$. It has been widely used to describe water transport through saturated soil. It is applied under many conditions; however, recent investigations have found under special flow conditions that there can exist a resistance to water flow which causes water to exhibit non-Darcian behavior, as stated by Brower (17). These special conditions include turbulent flow and chemical bonding between water and a clay surface, and adsorption of ions. However, turbulent flow does not exist in fine material under field conditions. It might occur in cracks, and has a great impact on transport of solute in these environments.

Hydrodynamic Dispersion

Transport of the pollutant at the ground water flow velocity is known as advection. Due to advection, nonreactive solutes are transported at an average velocity of the water. There is a tendency, however, for the solute to spread out from the usual path of flow direction. This spreading phenomenon is called hydrodynamic dispersion, as cited by Freeze and Cherry (18). It causes dilution of solute, and occurs because of mechanical mixing during fluid advection and molecular diffusion. Fick's Law is used to express the diffusion of substance passing through a given cross-section per unit time, and is given as

$$F = -D \frac{dC}{dX}$$

where

F = mass flux of solute per unit area per unit time

D = diffusion coefficient

C = solute concentration

$\frac{dC}{dX}$ = concentration gradient

Fick's second law is used to express diffusion of substance with time and space:

$$\frac{\delta C}{\delta T} = D \frac{\delta^2 C}{\delta X^2}$$

When the mass of solute transports by dispersion and advection in saturated media, according to Freeze and Cherry (18), it can be described as:

$$D \frac{\delta^2 C}{\delta X^2} - v \frac{\delta C}{\delta X} = \frac{\delta C}{\delta t} \qquad \text{(a)}$$

where

v = average ground water velocity

D = coefficient of hydrodynamic dispersion in direction of flow

Coefficient of dispersion is the function of dispersivity and molecular diffusion of solute in porous media. Equation (a) can be solved by using a boundary condition for a saturated homogeneous media. Breakthrough curve shapes can be predicted for tracer or contaminant migration through porous materials which are caused by dispersion.

Adsorption

One of the most important factors affecting the movement of organic chemicals is the factor of adsorption. Partitioning of solute between a soil particle and a liquid phase is a relatively complicated phenomenon. Adsorption generally occurs when the attractive forces between the solid surface and the sorbing species overcome the attractive forces between the sorbing species and solvent. Huang, et al. (19) and McCarty, et al. (20) indicate when organic compounds move through the soil, several phenomena will affect the movement of organic compounds in the system. Figure 1 shows the different phenomena that affect the breakthrough curve of chemicals undergoing transport. If there is no biological activity, it can be seen that adsorption and dispersion are controlling the movement of organic chemicals in subsurface environment.

Influence of Soil Properties on Adsorption

a) Organic Content. It has been known for some time that soil with a larger percentage of organic matter shows greater adsorption capacities for nonpolar organic compounds, according to Dzombak, et al. (21). Lambert (22, 23, 24) found that the adsorption of natural organic pesticide can be correlated with organic matter content of a given soil. Lambert defined a parameter known as effective organic matter that can be used for adsorptive differences between different types of soil. This parameter normalized adsorption of a particular compound on a given soil to a reference soil system. Lambert also concluded that the role of soil organic matter is similar to that of organic

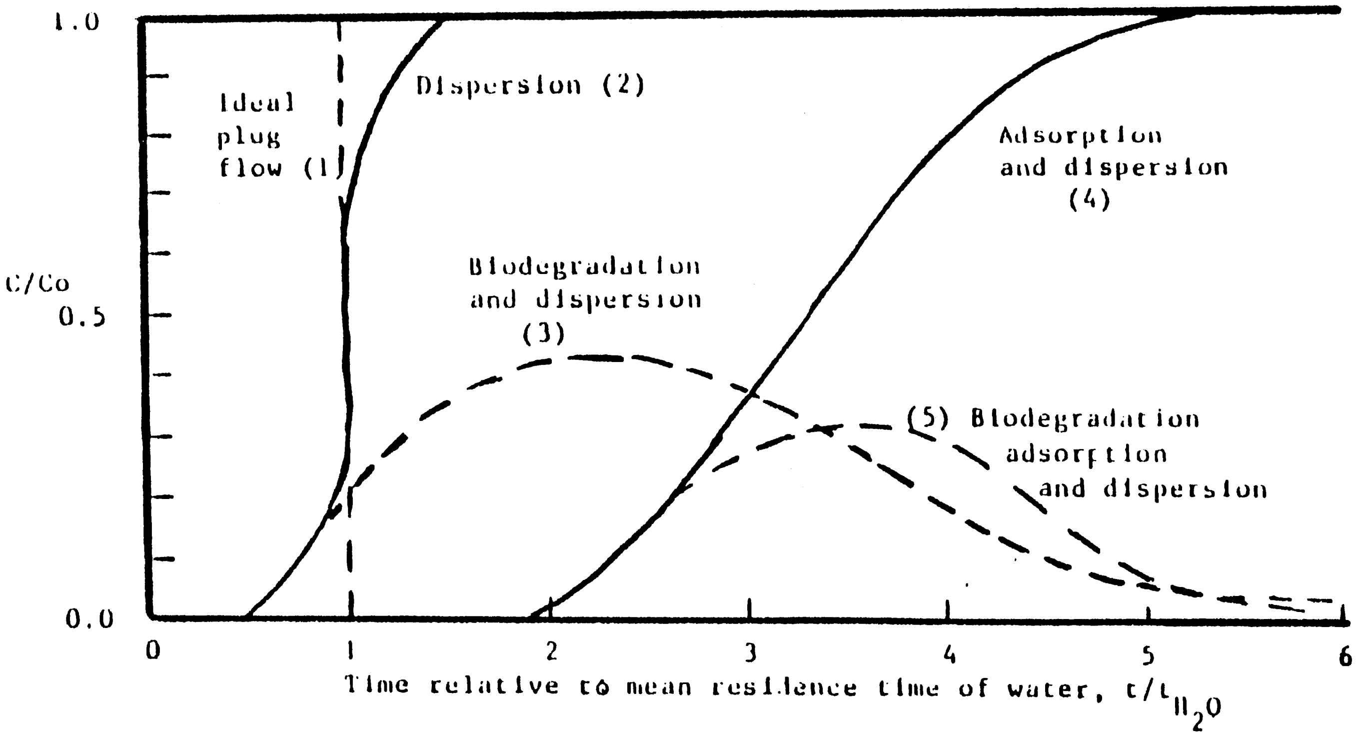


Figure 1. Organic Transport in Soil Environment (McCarty, et al., 1981)

solvent in extraction.

Weed and Weber (25) noted that hydrophobic surfaces in soil organic matter such as waxes, fats, resins, aliphatic side chain of humic and fulvic acids are responsible for accumulation of nonpolar molecules on soil sites. They pointed out that the process of accumulation of non-charged molecules at these sites which are called hydrophobic bonding is actually a partitioning between a solvent and soil organic matter rather than active adsorption.

Karickoff, et al. (26) studied the adsorption of hydrophobic compound on natural sediment and concluded that adsorption behavior of hydrophobic organic pollutants can be predicted from the knowledge of particle size distribution and associated organic carbon content of sediment of soils.

Schwarzenbach and Westal (27), Helling (28) and Karickoff (29) showed that the adsorption of organic material is highly correlated with soil organic content. They developed a mathematical relationship between equilibrium partition coefficient of the hydrophobic compound and its octonal/ water partition coefficient and fraction mass of organic matter in adsorbent.

$$K = f_{oC} \, K_{oC} = f_{oC}^{\,b} \, (K_{ow})^{a} \qquad \text{(b)}$$

where

K = equilibrium partition coefficient of the compound between the adsorbent and water

K_{oC} = partition coefficient of the compound between water and hypothetical natural sorbent of 100%

organic carbon representing the organic material present in the adsorbent

f_{oC} = fraction mass of organic carbon in adsorbent
a and b are constant

However, Means, et al. (30) found significant differences between adsorption predicted from hydrophobic equation (b) and experimental data for polycyclic aromatic amines.

Schellenberget et al. (31) showed that a hydrophobic model is applicable only to a limited degree to compounds which are fully or partially ionized at natural pH values. Such compounds include amines, phenols, carboxilic acids. They studied the sorption of chlorinated phenol by natural sediment and aquifer material, and pointed out that a distribution coefficient can be calculated by:

$$K = f_{oC}^{\ b} \ K_{ow}^{\ a} \ \left[1/(1 + Ka/(H)_{w} \right]$$

They concluded that if the pH of the water is not more than one unit above the PK_a of the compound, the hydrophobic model can be used for predicting adsorption of chlorinated phenol.

Chiou, et al. (32) believed that uptake of organics by soils is due to partitioning in soil organic matter and clays, but that organic matter is a more important factor. The importance of organic matter is supported by Hamaker and Thompson (33).

The work of Hague and Freed (34) agrees with the work of other researchers, but further states that sorption of organic compounds on soil is a function of solubility, molecular weight, functional groups, charge distribution, and polarity and molecular configuration.

Clay Content. O'Connor and Connolly (35) studied the effect of clay on adsorption, and noted that adsorption increases with increasing clay content of the soil due to increasing surface area and cation exchange capacity. They observed higher partitioning for Bentomite clay than for Kaolinite.

Hasset, et al. (36) indicated that the relative contribution of mineral fractions to total sorption becomes significant as the ratio of swelling clay to organic carbon increases. Means, et al. (30) observed significant adsorption for polynuclear aromatic hydrocarbons containing amino and carboxyl when the ratio of clay fraction of soil to organic content was decreased to less than thirty.

Pinaki (37) studied the sorption of organic compounds by low carbon soil and concluded that the clay content is an important predictor for adsorption of orthchlorotolume by low organic carbon soil.

Rogers, et al. (38) investigated the adsorption and desorption of benzene in two soils and a montmorillonited clay. One gram of soil and .5 grams of clay sample were used with a mixing ratio of 1:25 (adsorbent solution) and 1:50 for soil and clay, respectively. The solution concentrations were 10-100, 1000 ppb of C_{14} labeled benzene. They found that clay adsorption of benzene did not increase after a 16-hour equilibrium. This was also reported by Morrill, et al. for other organic pollutants. Soil adsorption of benzene, however, continued to increase for many hours. They speculated that adsorption of benzene by montmorillonated clay saturated with Al^{+3} was three times greater than montmorillonite clay saturated with Ca^{+2}. Once benzene sorbed, benzene tended to resist adsorption.

Helling (39) investigated the influence of soil cation exchange capacity and clay content on adsorption of pesticides and found adsorption of diuron and chlorproham was related to a total clay content; simazine was less closely related, but all three compounds' adsorptions were correlated with soil CEC.

Saltzman and Yarin (40) studied the sorption of phenol by montmorillonated saturated with different cations by IR and X-ray spectroscopy. They observed phenol would have very little affinity for clay, and it can be almost completely desorbed from a thin layer of montmorillonite that has been exposed for one week, but no nitrophenol desorbed under the same condition.

Aly and Faust (41) investigated the adsorption of 2,4-dichlorophenol by kaolinite, ilite, and bentonite clay. They conducted adsorption isotherm studies and found 2,4-dichlorophenol sorbed in the following decreasing order: bentonite, ilite, and kaolinite. In general, the sorbed amount of 2,4-dichlorophenon was not significant.

Effect of Missible Solvent on Adsorption

Adsorption results when the forces of attraction between solute and adsorbent overcome the forces of attraction between solute and solvent. There are two cases when the affinity of solute for adsorbent is greater than the affinity of solute for solvent.

In the first case, there is a strong interaction between the sorbate and sorbent due to coulumbic attraction or hydrogen bonding, reported by Hamaker and Thompson (33). The adsorption of polar organic molecules by clay is an example of this type of adsorption reported by Weber, et al. (42). In the second case, adsorption takes place not because of strong interaction between solute and sorbent, but due to weak solute-solvent interaction. In this case, even a small positive adsorbate-adsorbent interaction can overcome solute-solvent force and result in adsorption. This kind of adsorption has been called hydrophobic adsorption.

Factors which increase the affinity of solute for soil surfaces or decrease the affinity of adsorbate for solvent result in greater adsorption. Gustafson and Paleas (43) found that molecular properties such as chain length, molecular weight, carbon number and polarity have been shown to influence adsorption. It was demonstrated by Hasset, et al. (36) that chain length, molecular weight, and carbon number increases cause the water solubility to decrease and the solute-solvent interaction weakens, and hence influences adsorption.

Karickoff, et al. (29) and Means, et al. (30) show the adsorption of hydrophobic compound increases when water solubility of compound decreases. The adsorption of more polar compounds has also been shown to increase with decreasing water solubility, but only within a family of compounds, as reported by Bailey and White (44).

Fu and Luthy (45) investigated the solubility of various aromatic compounds in missible, polar solvent/water mixture, and observed the presence of appreciable organic solvent in the aqueous phase had a significant effect on solubility of the solute. In general, they found that there is a semi-logarithmic increase in solubility with increasing solvent volume fraction. The adsorption behavior of four aromatic solutes into three different soils with solvent-water mixture also was investigated by Fu and Luthy (46). They evaluated the effect of polar solvent in the aqueous phase on aromatic solute adsorption, and pointed out an increasing fraction of organic solvent decreases the adsorption of aromatic solute due to increasing water solubility.

Adsorption and Desorption of Phenolic Compounds by the Soil

Isaacrom and Frink (47) studied the sorption and desorption of phenol, 2,4-dichlorophenol, 2-chlorophenol by sediment. They performed sorption and desorption isotherms by using a thermostated continuous flow stirred cell apparatus.

Fine and coarse sediment was used as adsorbent. The same fine and coarse sediment treated with hydrogen peroxide to remove organic matter was used for sorption studies. They observed that linear isotherm models can describe data only in diluted solute concentration, and after that, sorption became a limiting process and the isotherm slopes decreased significantly, indicating that sediment has a limited sorption capacity for each phenol. They also concluded 1) the sorption mechanism involved hydrogen-bond interactions between sorbate and sorbent in addition to purely hydrophobic interactions; 2) the behavior of each solute was a function of its solubility and its hydrogen-bonding ability, and it was influenced by the amount and nature of the organic matter associated with the sediment fraction; 3) the organic matter exerted a major influence on the progress of sorption of compounds; 4) desorption was a slower process than was adsorption in all cases. A part of each sorbate was irreversibly held by each sediment fraction; and 5) magnitude of sorption for chlorophenol was greater than 2,4-dichlorophenol and phenol.

The adsorption of 3-methyl-4-nitrophenol and fenitrathion on soils and sediment was investigated by Baarschers and Ryan (48). Five-tenths gram soil was used with a series concentration of 10-350 mg/l of methylnitrophenol and 4-23 mg/l of fenitrathion. They found the adsorption of both compounds increasing with the percentage of organic matter in the adsorbents, and in all soils studied, methynitrophenol was more mobile than was fenetrathion. The adsorption of phenol by soils with different CEC were studied by Scott, et al. (49). They conducted adsorption isotherms for sterile and non-sterile soil by using 1:5 soil/solution ratio and found low mean adsorption coefficient value which indicated a low affinity of these soils for phenol. However, Ahlert and Uchrin (50) conducted a column study for phenol on two aquifer soils which contained different amounts of organic carbon, and reported that the aquifer soil with low organic carbon had no affinity for phenol but soil with high amounts of organic matter adsorbed some phenol and adsorption was quite reversible.

Sugiura, et al. (51) investigated the fate of 2,4,6-trichlorophenol, pentachlorophenol and PCB in an outdoor experimental pond, and found equilibrium coefficients by shaking the bulk sediment and solution containing TCP, PCP, and PCB. They also used stainless tubes with one open end packed with sediment for their study. The tubes were placed in water tanks in which the aqueous concentration of the compounds were maintained constant. They found adsorption and desorption processes in the sediment column can be explained by assuming that the compounds are transferred through the pore water by diffusion. Therefore it was concluded that the sorption and desorption process in columns can be explained by a first-order rate kinetic of one component system.

Fortuny and Fuller (52) studied leaching of phenols into 11 cm long and 5 cm diameter PVC cylinders which were packed with soils containing different kinds of clay. They observed phenols migrate through the soils rapidly, but fine-textured soils containing appreciable iron oxides are more likely to slow the migration of phenols more than soils without iron oxides. They also reported 2,4-dichlorophenol and dimethylphenol move slower than does phenol, and humic and fulvic acid can cause the disappearance of phenol in the leachate. It is interesting that Choi and Aomine (53) found in studying adsorption of pentachlorophenol by soil varies in the specious of clay minerals and organic matter indicated the adsorption depends on soil pH, and adsorption occurs to the greatest extent on the strong acid soil system compared to the moderate content, and there is no adsorption on the slightly acid or neutral soil system.

Boyd (54) developed equilibrium adsorption isothems for phenols, and concluded 1) the introduction of CH_3, OCH_3, and $C\ell$ groups to phenol resulted in increased adsorption due to decreased water solubility; 2) adsorption of phenols with the exception of o-nitro phenol was greater than predicted by hydrophobic model; and 3) increasing the degree of chlorination resulted in increasing adsorption.

CHAPTER III

MATERIALS AND METHODS

This chapter describes experimental procedures used during the adsorption study, including description of material, equipment, and analytical methods.

Soil Reactor

For acquiring the required data to evaluate the concept of adsorption, a soil reactor as shown in Figure 2 was used. The glass columns were three inches in diameter, and eighteen inches in length. A fine screen was placed between the column and its bottom bell to support the soil in the column and for drainage. The bottom bell contained gravel and had a volume of 55 ml. There were three sampling ports on the column which were 4.5 inches apart. PVC plastic tubing (clear) was used to deliver to and discharge from the column. The discharge tubes connected to a T fitting, and were placed in a position that acted as a weir, allowing the water level to stay on top of the soil. The system was saturated with water and a drop going in forced a drop to go out. Depth of soil in the column was 12.5 to 13 inches. A positive displacement pump (Mini Pump, Masterplex) connected to a timer was used ot provide continuous flow to the system.

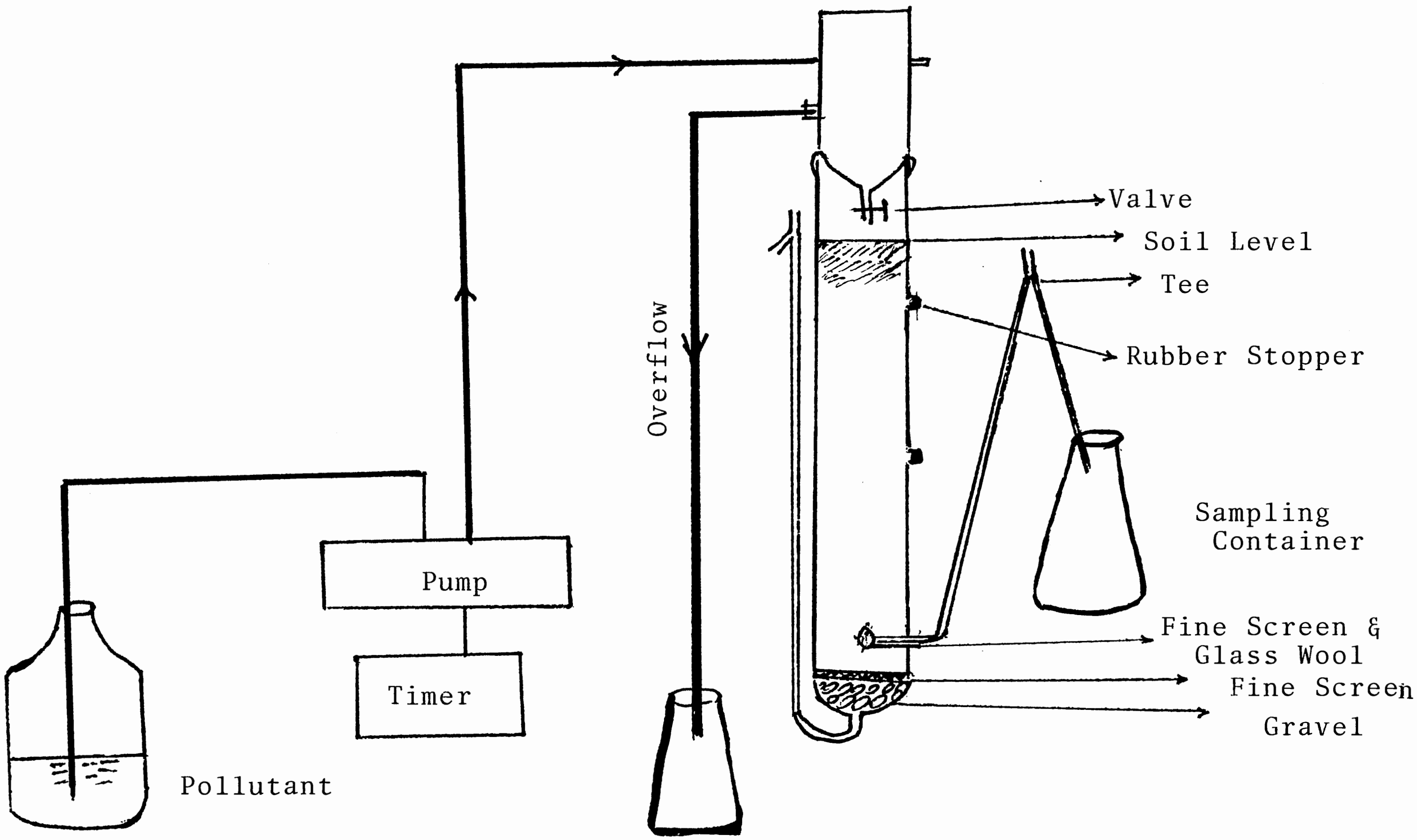


Figure 2. Schematic of Experimental Apparatus (Soil Reactor)

Characteristics of Adsorbent Media

Synthetic soils consisting of Ogallala sand and peat, Ogallala sand and clay, Ogallala sand and milorganite were used in this study. Description of each component is as follows:

Sand

The sand used in this study was Ogallala sand obtained from the Environmental Engineering Laboratory of Oklahoma State University. Particle size analysis for this sand was performed according to procedures described by Lambe (55), in which the soil was dried prior to sieving and a quantity (1000 gr) was passed through a series of sieves. The soil was shaken mechanically and sieved for ten minutes. Results of this sieve analysis for Ogallala sand are presented in Table I. The sieve analysis shows four percent of the particles passed through a No. 200 sieve; distribution of the curve is shown in Figure 3, indicating that the soil was a fine sand and there was no need for a hydrometer test.

Peat

Peat moss was used in this study as the source of natural organic for the soil. It was purchased from the agriculture store, and was a product of Fison Western Corporation, Vancouver, Canada. It was passed through a No. 20 sieve prior to use.

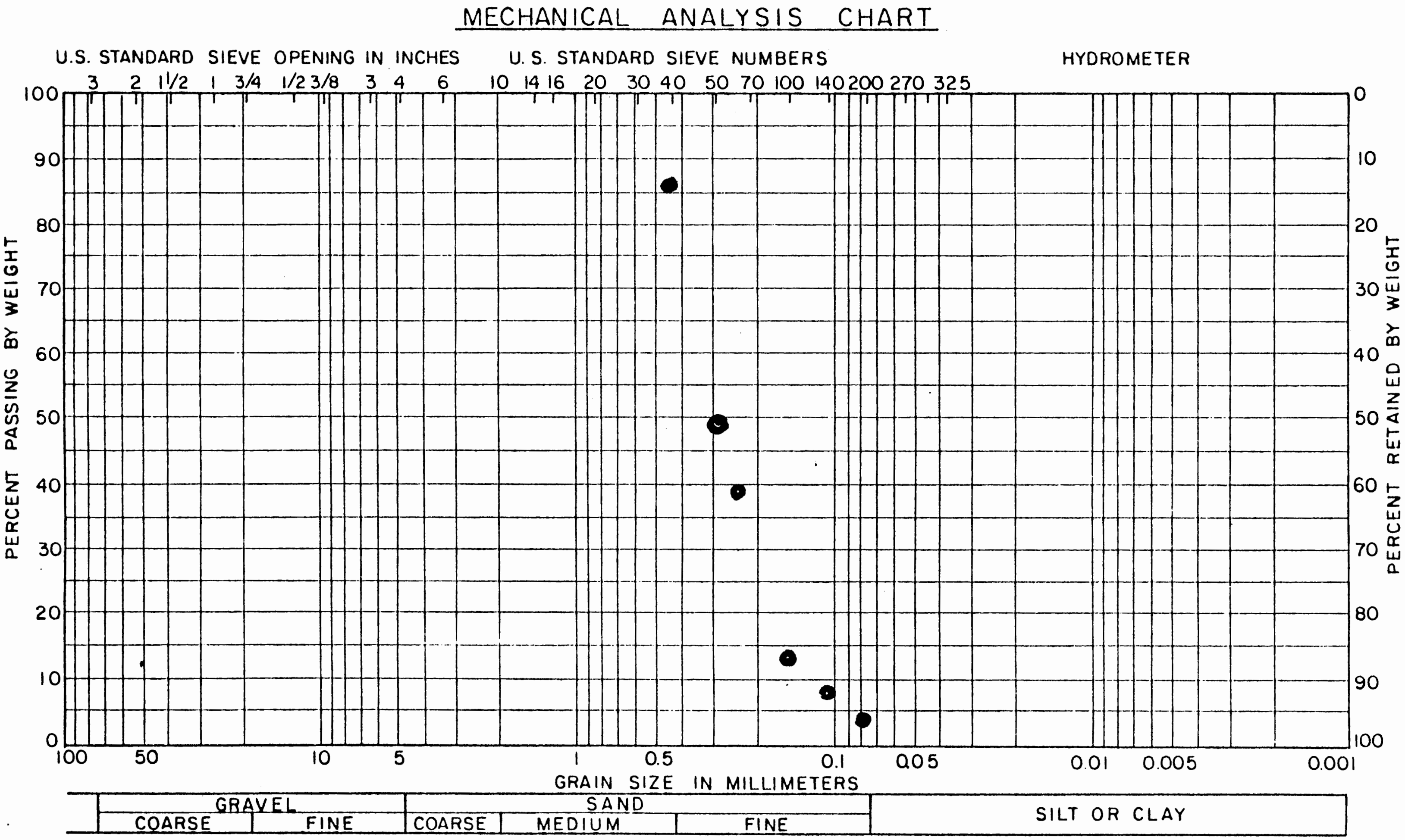


Figure 3. Ogallala Sand Grain Size Distribution

TABLE I

SIEVE ANALYSIS OF OGALLALA SAND

Sieve No.	Sieve Opening (microns)	Weight Retained (g)	Partially Retained (%)	Totally Retained (%)	Total Passing (%)
40	420	142.8	14.28	14.28	85.72
50	297	366.6	36.66	50.95	49.05
60	250	95.8	9.58	60.53	39.47
100	150	265.1	26.51	87.04	12.96
140	106	51.1	5.11	92.15	7.85
200	75	34.0	3.40	95.55	4.45
FAN		44.5	4.45	100.00	0

Kaolin Clay, Ca-montmorillonite

Kaolin, well crystalized, from Washington County, Georgia, and Ca-montmorillonite from Gonzales County, Texas, were used in this study. They were purchased from the Clay Minerals Society, University of Missouri at Columbia.

Milorganite

Milorganite is a digested sewage sludge which is produced by the City of Milwaukee, Wisconsin, and was obtained from the Department of Agronomy, Oklahoma State University.

Specific Gravity

The specific gravity of a soil is determined by comparing the weight of a given volume of soil in air to the weight in air of an equal volume of distilled water at a temperature of 4°C. A pyconometer was used for measurement. The test was performed by placing 150 gr of oven-dried soil in a 1000 ml volumetric flask. The flask was filled one-half full of distilled water, and then boiled gently for several minutes to remove the air which was entrapped in the soil. The flask was cooled to room temperature, filled with distilled water, and then weighed. Temperature was measured, the soil solution removed from the flask, and the flask was filled with distilled water at the same temperature, and weighed. The specific weight gravity of the soil calculated was as follows:

$$C_S = \frac{W_S \quad G_T}{W_S - W_1 + W_2}$$

where

W_S = dry weight of soil

W_1 = weight of flask, soil and water

W_2 = weight of flask and water

G_T = specific gravity of distilled water at temperature T

Porosity Determinatin

Porosity depends on how the soil is packed in the column. It is defined as the ratio of the volume of void to the total volume of soil. In this study, porosity was measured by measuring the volume of the column before placing the soil in the column by filling with distilled water to the level which was supposed to be the soil level (total volume). Then the column was filled with soil, and water was added until all of the soil became saturated. The volume of water was monitored (volume of void). The porosity was calculated by using the equation:

$$n = \frac{V(\text{void})}{V(\text{total})} \times 100$$

Hydraulic Conductivity (Permeability)

The rate of movement of water through the soil is very important in many aspects. Water moves through the soil because of gravitationl, adsorptive, and osmotic forces. The hydraulic conductivity of saturated soil can be determined by Darcy's Law:

$$K = \frac{Q}{A} \times \frac{\Delta h}{\Delta L}$$

where K is the hydraulic conductivity

Q = flow rate

A = surface area

$\frac{\Delta h}{\Delta L}$ = hydraulic gradient

Hydraulic conductivity was determined by placing soil in the column without compressing. Water was pumped to the column, as shown in Figure 4.

Water level in the column was held constat at about 2.5 cm above the top of the soil. After the discharge flow came to steady state, the head loss was measured by two monometers placed on two sampling ports. Since the area

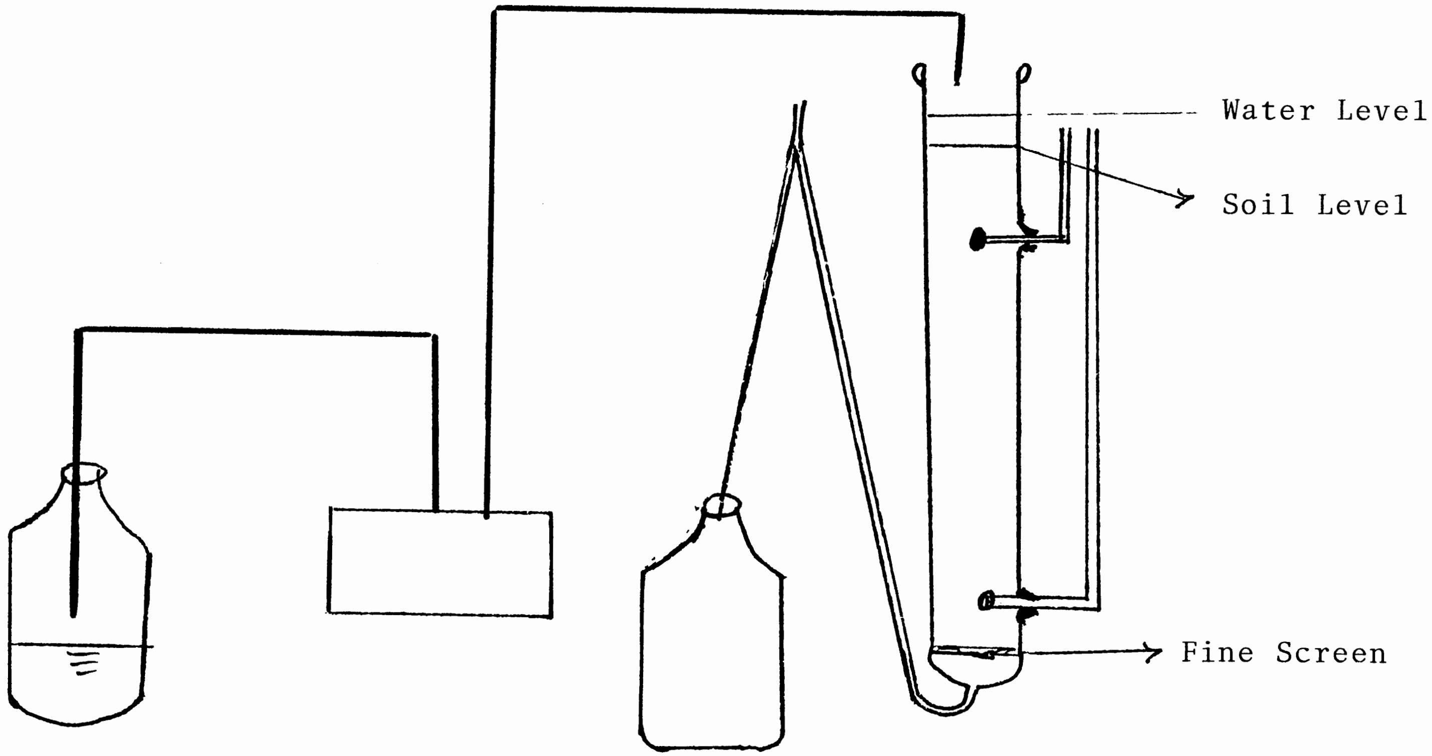


Figure 4. Schematic of Experimental Apparatus for Measurement of Hydraulic Conductivity

was 48 cm^2, the flow rate and H were monitored, and hydraulic conductivity (K) was obtained from the flormula.

Organic Carbon Content

Organic carbon was determined by two methods, the Walkley-Black method (56) and the Hach method (57). The results obtained from these two methods were almost identical. In the Walkley-Black method, a soil sample weighing 0.2 to 1 gr was added to a 500-ml wide-mouth Erlenmeyer flask. Ten ml of 1.0 $K^2cr^2O^7$ was added. and the flask was gently shaken to mix the soil in solution. Twenty ml concentrated H^2SO^4 was then added to the flask and mixed for one minute. After 30 minutes, 200 ml deionized water was added and the suspension was filtered. Three drops of phenanthroline indicator was added and titrated with 0.5 N $FeSO^4$. Titration resulted with a sharp end point, with the change of color from blue to red. The amount of H^2SO^4 was recorded.

The organic carbon can be calculated according to the Alison formula:

$$\text{organic carbon \%} = \frac{(\text{meq } K^2cr^{20^7} - \text{meq } SO^4Fe) \times .003 \times f}{\text{g of dry soil}}$$

f (correction factor) = 1.35.

In the Hach method, a soil sample weighing 1 gr was transferred to a 250-ml Erlenmeyer flask. Ten ml of 1-N potassium dichromate solution was added. Twenty ml of H^2SO^4 was then added to the flask and swirled gently to mix. The flask was placed on hot pads for ten minutes. After exactly ten minutes, 100 ml demineralized water was added to the flask and swirled to mix. Twenty-five ml of suspension filter was placed in the cell sample in a spectrometer. The organic matter scale was placed and adjusted to a wavelength of 610 nm, and the organic carbon from the scale was read.

Cation Exchange Capacity

The cation exchange capacity (CEC) was determined by the calcium saturation method according to Jackson (69). In this method cation exchange capacity of the soil was determined by placing 10 gm of oven-dried soil in a 200-ml Erlenmeyer flask. Fifty ml of 1. N $CaCl_2$ was added to the flask and shaken intermittently for 24 hours. The soil-salt medium was filtered on a 5.5 Buchner funnel fitted with a Whatman 42, 5.5 cm filter paper. The flask was rinsed with three rinses of 50 ml $CaCl_2$ and 50 ml deionized water. Leachate of water and $CaCl_2$ were discarded. The soil was washed thoroughly with 150 ml of 1.N $NaNO_3$. The leachate was removed and diluted to 200 ml with demineralized water. Ten ml of leachate was placed in a 200-ml flask and titrated with EDTA at pH 10 to find the milliequivalents of calcium per 100 gm of soil. An additional 10 ml leachate was titrated with silver nitrate to determine the milliquivalent of chloride per 100 grams of soil. The cation exchange capacity was calculated using the following formula with the result expressed as milliequivant per 100 grams of soil:

Cation exchange capacity/100 gr soil = meq
calcium/100 gr - meq chloride/100 gr

Soil Sterilization

Sterilization of the soil was achieved by incubating the soil under a temperature of 125^{o}C and 15 psi steam pressure for two hours. A standard plate count was performed before and after sterilization of the soil to ensure that biological activity was not taking place in the columns. A standard plate count test was performed by the Francis Clark method (58).

Gross Chemical Fractionation of Organic Matter

The amount of fats, waxes, oils, resins, water soluble polysaccharides, hemicellulose, cellulose in peat and milorganite was determined according to Stevenson (59).

Extraction of Soil Organic Matter

Extraction of soil humic substance was performed according to Stevenson (59). In this method to isolate the humic substance of peat and milorganite, 30 gr milorganite and peat sample were placed in a 500-ml Erlenmeyer flask. Two hundred ml of .5 NaOH solution were added to the flask, and the flask was stoppered with a rubber stopper. The mixture was shaken for twelve hours on a mechanical shaker. The mixture was centrifuged; the supernatant liquor was decanted and filtered through glass wool to remove suspended material. An additional 200 ml of 0.5 NaOH solution was added to the soil; the mixture was shaken for two hours, centrifuged, and the decanting procedure was repeated. The residues were dispersed with 200 ml distilled water. After centrifugation, the mixture supernatant liquor was added to the previous extracts. The peat sample extract was dried by using a lyophilizer located in the Biochemistry Department of Oklahoma State University. The milorganite sample was dried by using a rotary evaporator at about 38°C.

Determination of E_4/E_6 Ratios

In order to characterize the humic substance which was extracted from peat and milorganite, E_4/E_6 ratio was determined by the Schnitzer method (70). This method involves dissolving 50 mg of .05N $NaHCO^3$ solution. The resulting pH was near 8. Twenty-five ml $NaHCO^3$ 0.05 were placed in a reference cell in a Spectrometer 20, and the wavelength was adjusted. Absorbance was measured at 465 and 665 for peat and milorganite humic material. The ratio of two absorbance is a E_4/E_6 ratio.

Molecular Weight Analysis

The molecular weight distribution of humic material which was extracted from peat and milorganite was determined by the gel filtration technique. The dextrant gel (sephadex) G_{50} purchased from SIGMA Chemical Company was used in this study. In order to prepare the dried sephadex for packing, it was placed in an excess amount of buffer solution to swell. The swelling time for G_{50} was twenty hours. The buffer solution contained a .01M solution of K^2HPO^4 and KH^2PO^4 and 0.02 percent concentration of sodium azide to eliminate biological activity in the column. The solution provided buffering capacity and sufficient ionic strength to avoid ionic exclusion interactions with the sephadex. The pH of the buffer solution was 7.2. The column used in this study was made of glass, and was manufactured by Glenco Scientific, Houston, Texas. It was 1.5 cm in diameter and 100 cm in length with teflon plates, bed support and tubing. The column was packed as follows: 1) the column was aligned in a vertical position; 2) the outlet valve was checked. If the valve was closed, the buffer solution was placed in the column to a height of four to five inches. A part of the solution was drained to ensure removal of air pockets; 3) the reservoir was placed on top of the column; 4) the outlet valve to the column was opened. At the same time, the gel slurry was poured into the reservoir on top of the column. Care was taken to stir the gel slurry continuously while pouring it into the reservoir; 5) after the column was poured, the reservoir was removed and the top endplate was connected to the elevated reservoir with teflon tubing; 6) the column was washed with buffer until the bed became stable. The column operated in the downflow made with a constant head of 150 cm of H_2O. The flow rate was 40 ml/hr. The elutrant was collected in eighty 2.5 ml fractions in 3 x 100 mm test tubes by a Gibson F_c-80 microfractionator operating in a drop counting mode. The column was calibrated by use of known molecular weight compounds. Table II shows the compounds used and their molecular weight.

TABLE II

MOLECULAR WEIGHT MARKERS

Known Molecular Weight Compounds	Molecular Weight
Blue Dextron 2000	2,000,000
Cytochrome C	23,560
Inulin	7,000
Bacitracin	1,430

The void volume (Vo) of the column was determined by blue dextron 2000 which was completely excluded from the gel and was measured by Hitachi 100-80A ultraviolet spectrophotometer located in the Biochemistry Department of the Oklahoma State University. The wavelength was 620 mm. When two out of three consecutive void volume determinations agreed, the column was considered ready for calibration. The marker compound was dissolved in a buffer solution in sufficient concentration to assure detection by spectrophotometer at 280 mm. Before introducing all samples (1 ml in volume) into the top of the column, the column outlet valve was closed and the sample was injected by use of a syringe. Then the outlet valve was opened so that the sample could be transported down through the gel column in the buffer solution. The organic content in the elution volume of the markers was determined by a spectrophotometer. The calibration curve was obtained by plotting log MS versus elution volume. The relationship was linear.

The peat and milorganite humic material scanned by UV to obtain optimum wavelength for maximum absorbance and optimum wavelengths were 250, 220 for peat and milorganite, respectively.

Stock Solution of Phenols

The four phenols used--phenol and 2,4-dichlorophenol, 2,4-6 trichlorophenol, and 2,4-dinitrophenol, were purchased at purities of 99% from the Aldrich Chemical Company. To prepare stock solution, 500 ppm of each phenol (except for phenol which was 1000 ppm), weighed, and the amount of each phenol was diluted in deionized water. These stock solutions were determined by GC to have the desired level of phenols.

Table III lists the chemical properties, as given by U.S. EPA (60).

Soil Reactor Operation

The column was operated in the downward gravity flow mode. Interconnection and fittings were made of glass and

TABLE III

CHEMICAL AND PHYSICAL PROPERTIES OF PHENOLS

Name	MW	Boiling Point	Solubility in Water (mg/l)	P_{K_a}	$\mathrm{log}_{K_{ow}}$
Phenol	94.11	181.75	93,000	10.02	1.46
2,4-dichlorophenol	163	210	4,500	7.8	2.85
2,4-6 trichlorophenol	197.45	244.5	800	5.9	3.38
2,4-dinitrophenol	184.11	no data available	54,000	4.09	1.6

plastic. The sterilized soil was placed into the column and compressed slowly. Distilled water was pumped to the column in order to ensure saturation of the soil and prevention of channeling through the column. The discharge tube was held on the level to have a constant head of water on top of the soil. The water level was maintained at 1 to 2 cm above the soil level. Before introducing feed solution to the column, flow, porosity and hydraulic conductivity were measured. Samples were taken from the sampling port, which was located at the bottom of the column.

Sample Collection and Treatment

Samples were collected in a 250-ml Erlenmeyer flask at different times, and analyzed daily. The samples were collected very late at night, refrigerated, and analyzed during the day. The feed sample was analyzed before introducing the column, and was also checked daily in order to have a constant concentration of phenolic compound inflow. To determine the concentration of phenolic compounds in the sample, gas chromotagraph (GC) was used. The samples had to be extracted. The liquid extraction method used in this study and the procedure used for extraction were as follows: 1) A 90-ml sample was placed in a 150-ml Erlenmeyer flask and the pH was brought to two or less by adding a 50% concentration of phosphoric acid; 2) the sample was transferred to a 100-ml long-neck volumetric flask; 3) 30 grams of sodium chloride were added to the sample. This was shaken until most of the salt was dissolved; 4) one ml of isoprophyl ether then was added to the flask. The flask was closed tightly and shaken vigorously for three minutes and allowed to stand for one minute for the layers to separate. A 2-μl aliquot of the isoprophyl ether phase was withdrawn by using a syringe (Hamilton) and injected into the gas chromatograph.

The percent recoveries obtained from the above extraction were 61-58%, 96-94%, 97%, 37-40% for phenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and 2,4-dinitrophenol, respectively. The detection limit for the above extraction method was 100 μg/l for dichlorophenol, phenol, and trichlorophenol, and 1 mg/l for dinitrophenol. When ethyl alcohol was used as a solvent in this study, the sample concentrated to 1 ml; 2 μl was withdrawn by a syringe and injected to GC.

Perkin-Elmer Sigma 3B gas chromatograph equipped with flame ionization detector was used for the analysis of phenolic compounds. A glass column packed with 1% SP-1240 DA was used to perform the separation. A computerized integrator was employed to print out the detention time and the area corresponding to each compound. The carrier gas was nitrogen; the instrument condition for a gas chromatograph analysis is shown in Table IV.

Standard curves for each phenolic compound were obtained. Each compound was injected to GC at several concentrations, and areas for the corresponding concentrations were plotted. The standard curves were then used to determine the specific organic compound concentration in each sample.

TABLE IV

SPECIFIC CONDITIONS OF THE GC FOR PHENOL AND 2,4-DICHLOROPHENOL

Parameter	Value
Injection temperature	200°C
Detector temperature	200°C
Initial oven temperature	100°C
Initial time	0
Temperature rate	10°C/min
Final oven temperature	175°C
Final time	2 min
Hydrogen flow	20 lb/in
Airflow	20 lb/in
Nitrogen flow	40 lb/in
Conditions of the GC for dichlorophenol, dinitrophenol,2,4,6-trichlorophenol	
Injection temperature	200°C
Detector temperature	200°C
Initial oven temperature	165°C
Initial time	0
Temperature rate	10°C/min
Final oven temperature	175°C
Final time	15 min

Chloride Determination

Chloride was used as a nonadsorbing tracer. Chloride in the form of .01N $CaCl_2$ was chosen for this purpose. The chloride concentration was determined by the mercuric nitrate method according to Standard Methods (61).

Soil Extraction

After the column breakthrough curves were completed and no phenol or dichlorophenol was detected in the soil column's effluent, the soil was extruded from a different sampling port and analyzed for residual dichlorophenol and phenol. Soil extractions were performed according to EPA (71).

The materials and methods used in this study are discussed above. The data obtained using the cited materials and methods are discussed in the next chapter.

CHAPTER IV

RESULTS

The experimental results will be presented in three major sections.

1. The Effect of Cation Exchange Capacity and Hydraulic Conductivity of Soil on Adsorption of Phenol and 2,4-dichlorophenol

To evaluate the movement of phenol and 2,4-dichlorophenol through the soil columns, a fine Ogallala aquifer sand was mixed with different amounts of Kaolin clay or Ca-montmorillonite clay. A control column which contained only Ogallala sand was used. The soil properties and mixtures, flow rates, and weight of soil are given in Table V. It can be seen when 4%, 8% and 16% by weight of Kaolin clay and 5% Ca-montmorillonite clay were mixed with Ogallala sand, the porosity and specific gravity did not change significantly and remained almost constant. It also shows that the hydraulic conductivity of Ogallala sand decreased from 2.53 cm/hr to 0.4 cm/hr, and the cation exchange capacity increased from 0.95 meq/100 gr to 13.3 meq/100 gr by increasing the percentage of Kaolin clay. It is interesting

TABLE V

ADSORBENT MEDIA PROPERTIES FOR CATION EXCHANGE STUDY

Adsorbent	Weight (gr)	Flow Rate gpd/ft^2 (ml/hr)	Porosity (%)	Hydraulic Conductivity (cm/hr)	Specific Gravity	CEC (meg/100 gr)
a) Dichlorophenol						
Ogallala sand	1784	15.5 (135)	40	2.53	2.65	.95
Mixture of 4% Kaolin clay and 96% Ogallala sand	1700	9.2 (80)	42	1.40	2.59	2.90
Mixture of 8% Kaolin clay and 92% Ogallala sand	1700	6.2 (55)	45	1.0	2.52	4.20
Mixture of 16% Kaolin clay and 84% Ogallala sand	1800	2.3 (20)	47	.4	2.36	13.30
Mixture of 5% Ca-mont. clay and 95% Ogallala sand	1807	.58 (5)	45	.08	2.41	11.40
b) Phenol						
Ogallala sand	1885	17.31(150)	40	2.95	2.65	.95
Mixture of 4% Kaolin clay and 96% Ogallala sand	1703	8.1 (70)	43	1.3	2.59	2.9
Mixture of 16% Kaolin clay and 84% Ogallala sand	1704.3	2.1 (18)	46	.35	2.36	13.3
Mixture of 5% Ca-mont. clay and 95% Ogallala sand	1807	.58 (5)	45	.08	2.41	11.4

to note that when 5% Ca-montmorillonite clay was mixed with 95% Ogallala sand, the hydraulic conductivity decreased from 2.53 to .08 cm/hr, but the cation exchange capacity increased to 11.4 meq/100 gr. This shows that the type of clay had a significant effect on the hydraulic conductivity and cation exchange capacity of the mixture.

In order to observe the phenol or 2,4-dichlorophenol transport, feed solution concentration was maintained at 50 mg/l phenol or 2,4-dichlorophenol and .01N $CaCl_2$ throughout the study. The soil column's effluent chloride and phenol or 2,4-dichlorophenol concentrations were measured at various times. When the concentration of phenol in the effluent from the columns reached a level greater than 95% of its influent value, the feed solution was adjusted to contain no phenol or 2,4-dichlorophenol and chloride ion. The phenol, 2,4-dichlorophenol and chloride concentration in the column's effluent are given in Appendix A. The breakthrough curve (BTC) for dichlorophenol and phenol in Ogallala sand are shown in Figures 5 and 6. Figures 5 and 6 indicate that phenol and 2,4-dichlorophenol had no affinity for Ogallala sand. The data show that concentration of the tracer (Cl^-) in the effluent reached its maximum value, the phenol or dichlorophenol also reached breakthrough. The phenols moved as fast as the tracer moved through the column. In other words, the factor controlling this movement was dispersion, not adsorption. If there was no dispersion, the chloride ion would pass through the column as a plug and would exit from the column as a step function, but it can be seen it was a

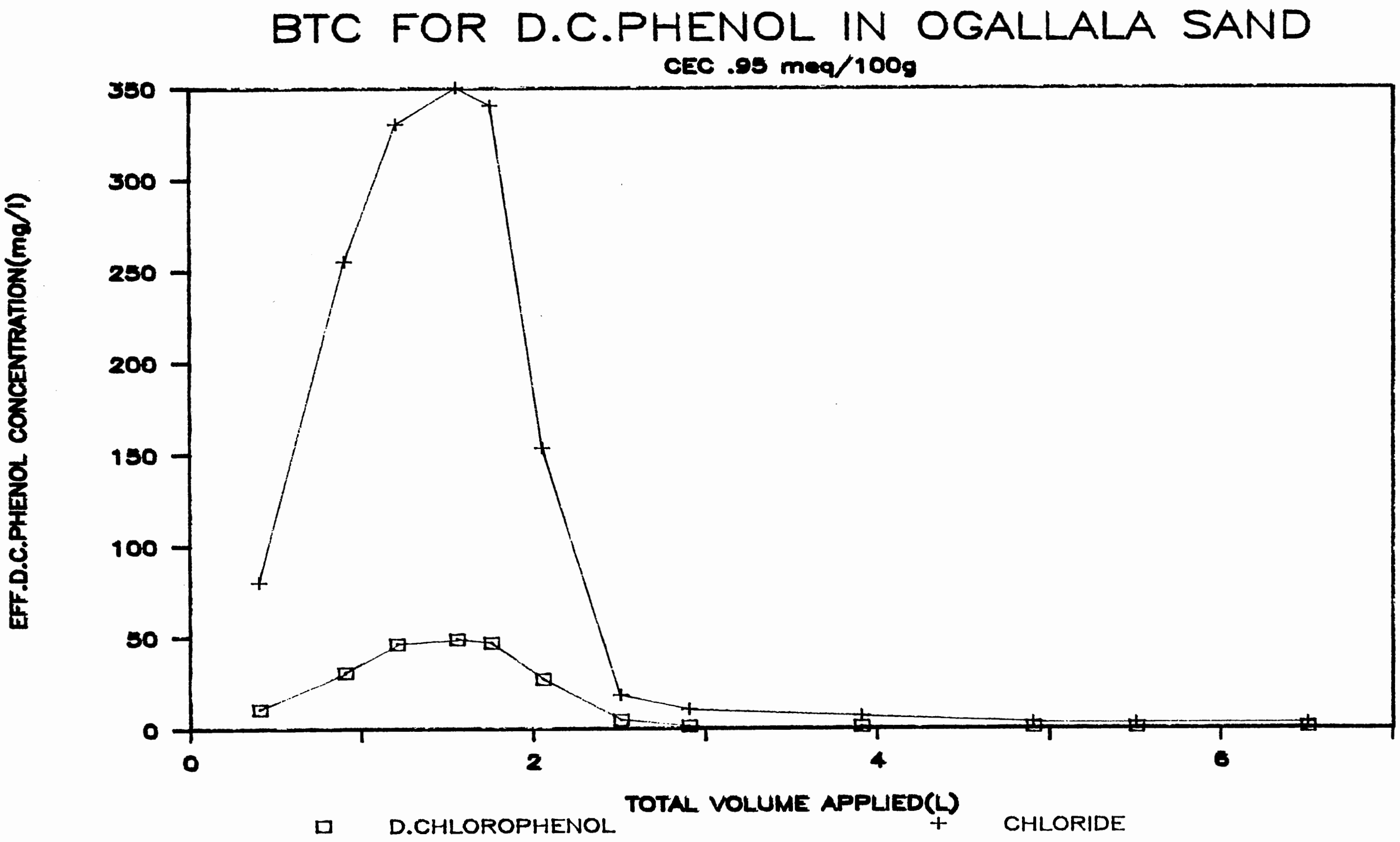


Figure 5. BTC for Dichlorophenol and Chloride in Ogallala Sand (CEC) of 0.95 meq/100 gr)

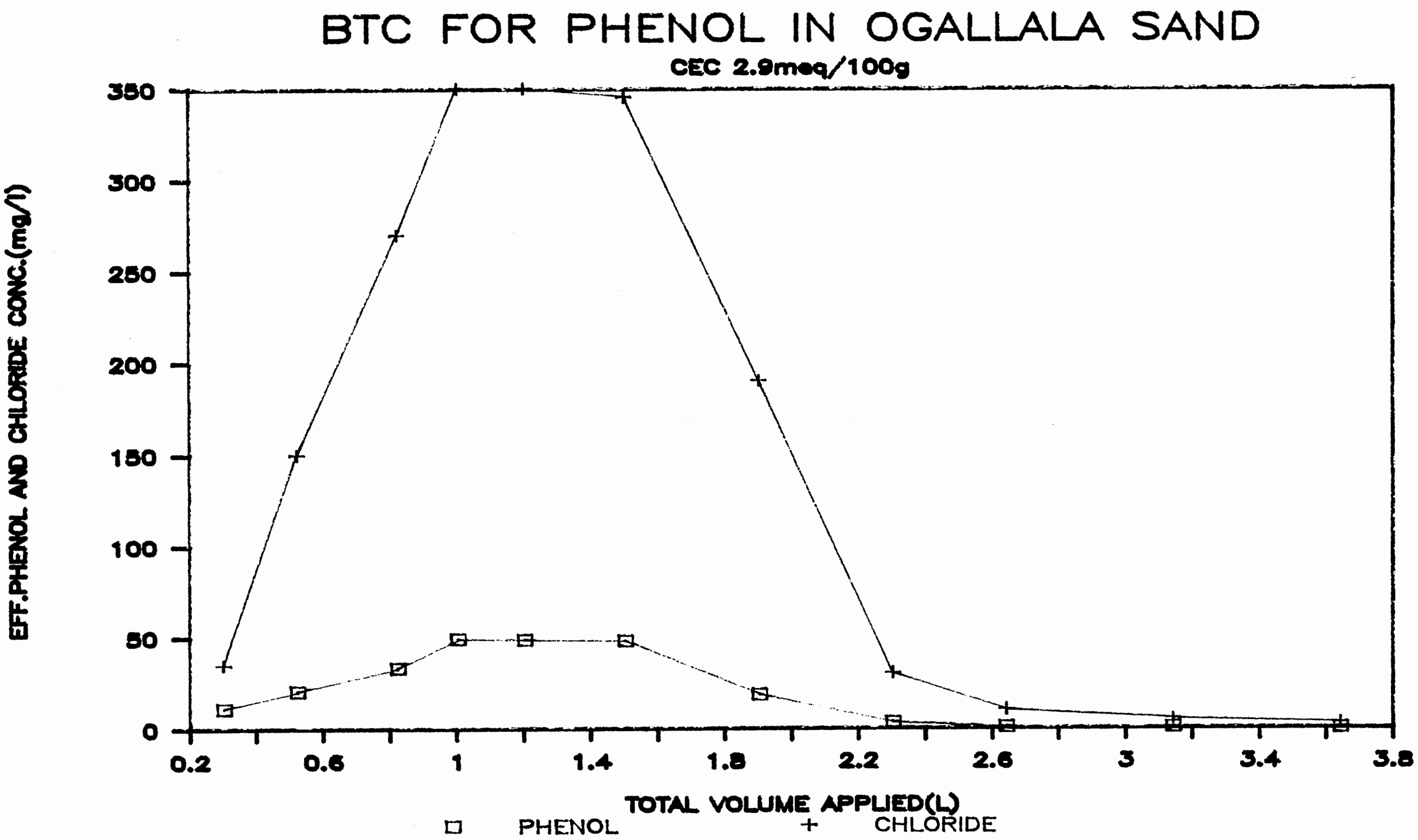


Figure 6. BTC for Phenol and Chloride in Ogallala Sand
(CEC 0.95 meq/100 gr)

function of time, and the concentration of chloride ion increased with time, and stayed constant. A dispersion model can be developed and calibrated to fit the data, but it is imperative to mention that the modeling or application of any models to fit the data are not the objective of this study. Figures 5 and 6 also indicate when the system was converted to distilled water, dichlorophenol and phenol diluted out the same as the chloride ion. When phenol and dichlorophenol could not be detected in the soil column's effluent, soil samples were taken and analyzed for phenol and dichlorophenol. There was no detection of phenol or dichlorophenol in the soil samples.

Figures 7 and 8 show the breakthrough curve of 2,4-dichlorophenol and phenol in a mixture of 4% Kaolin clay and 96% Ogallala sand. Figure 7 shows that the throughput volume (L) or time for the chloride ion to reach its maximum value in the effluent was smaller than the volume required for dichlorophenol to reach breakthrough. The volume for chloride was 1.75 liters, while the volume for dichlorophenol was about 2.2 liters. This indicates that dichlorophenol was moving slightly slower than the chloride ions. In Figure 8, the throughput volumes or time for phenol and chloride are identical. This means that phenol moved at the same rate as the chloride. Figures 7 and 8 also show that when distilled water was pumped to the column, dichlorophenol, phenol and chloride concentrations decreased rapidly. The volume of distilled water required to clean up dichlorophenol

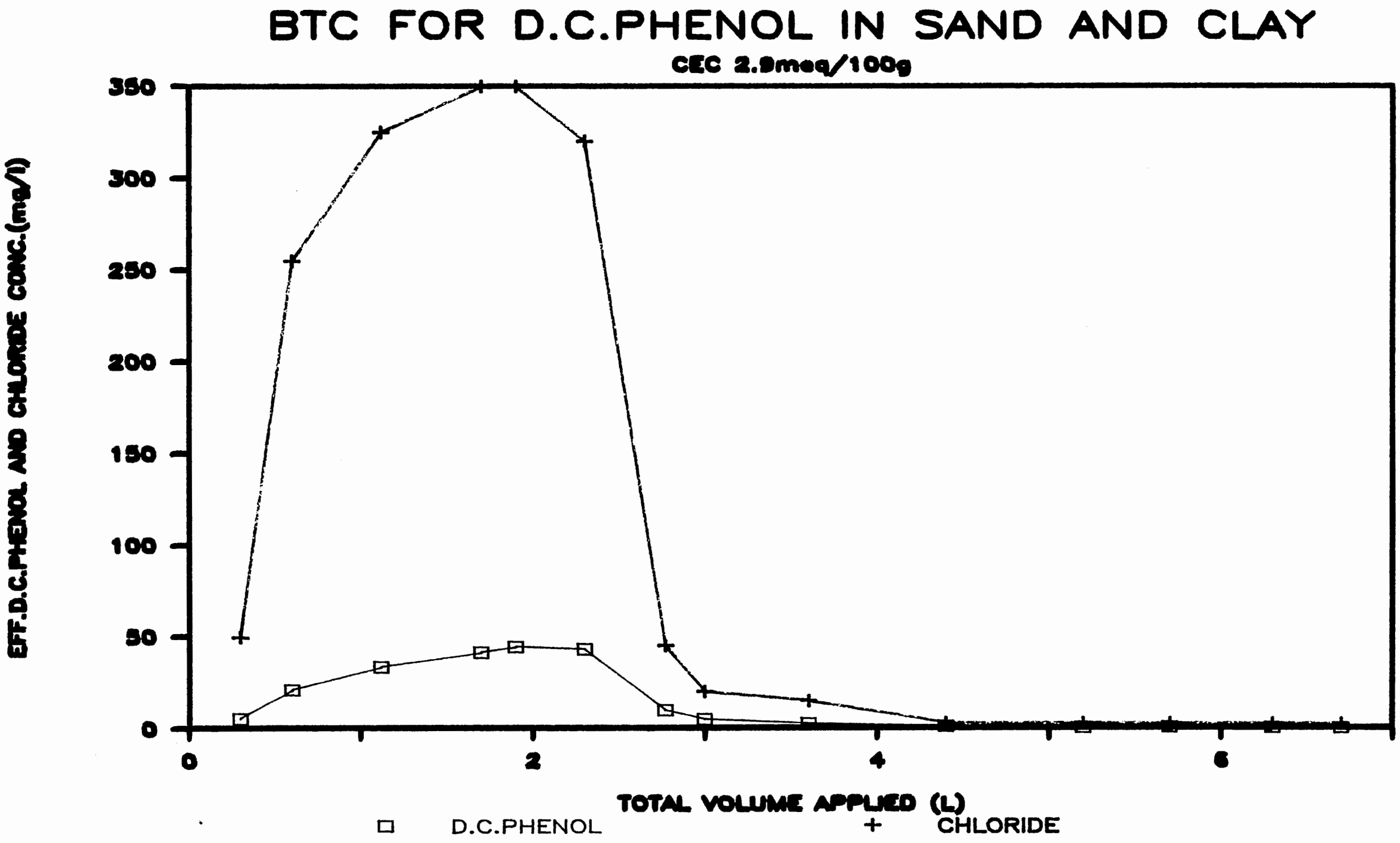


Figure 7. BTC for Dichlorophenol and Chloride in Sand With 4% Kaolin Clay (CEC 2.9 meqr/100 gr

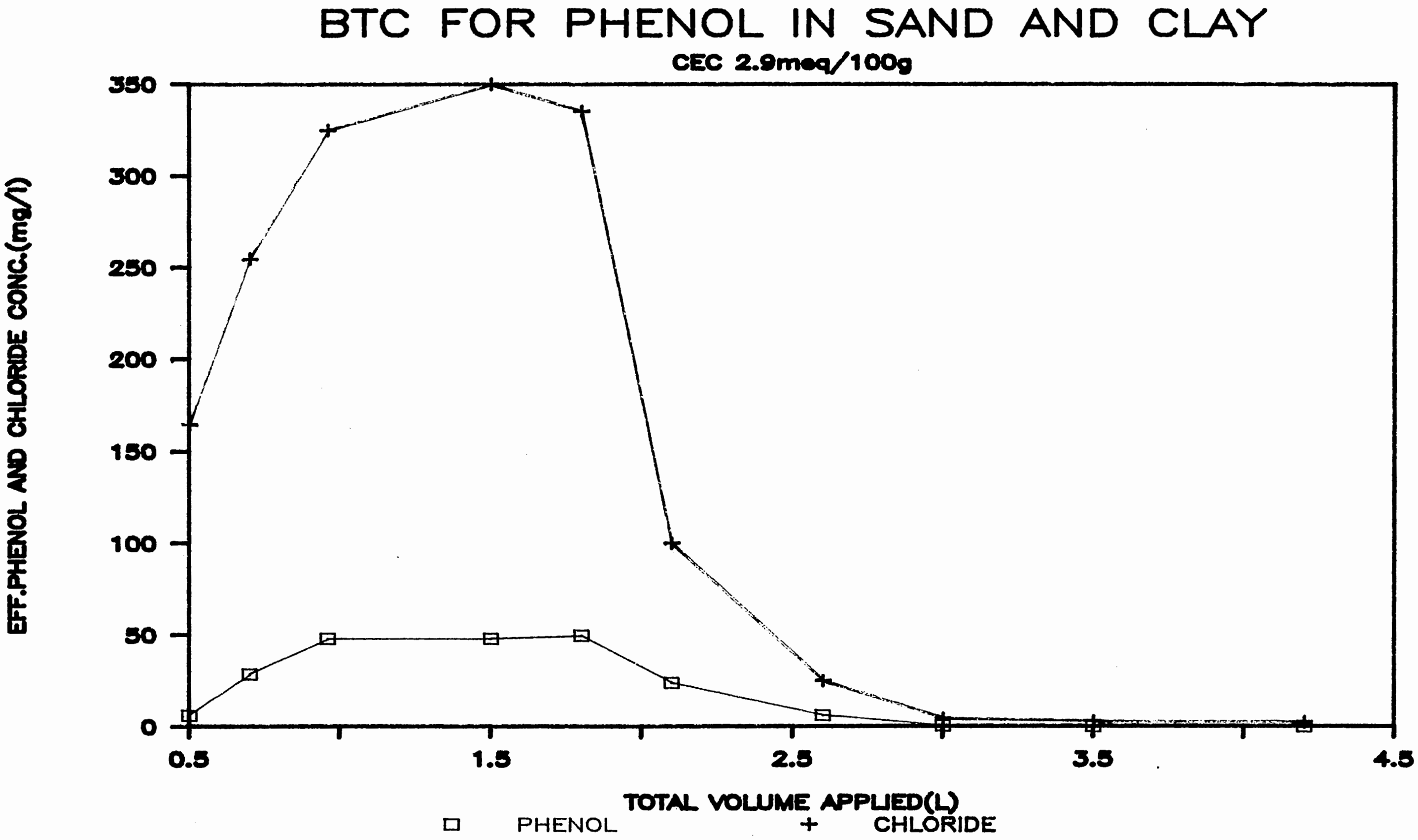


Figure 8. BTC for Phenol and Chloride in Sand With 4% Kaolin Clay (CEC 2.9 meq/100 gr)

was greater than the volume of water used to clean up the phenol. When there was no detection of these compounds in the soil column's effluent, soil samples were taken and analyzed for phenol and dichlorophenol. There was no detection of phenol, but the amount of dichlorophenol in the soil was 1.5 μg per gram of soil.

The breakthrough curve for dichlorophenol in the mixture of 8% Kaolin clay and 92% Ogallala sand is shown in Figure 9. This shows that the volume of sample required for the chloride to reach breakthrough was the same as in the mixture of 4% clay and 96% Ogallala sand, but the throughput volume used for dichlorophenol to reach breakthrough was increased to three liters. It also shows the volume of distilled water used to clean up the soil to the extent that no dichlorophenol was detected in the effluent was greater than the mixture of 4% clay and 96% sand. The amount of dichlorophenol left in the soil sample after no detection of dichlorophenol in the effleunt was 3.4 μg per gram of soil. Figures 10 and 11 show the breakthrough curve for phenol and dichlorophenol in the mixture of 16% Kaolin clay and 84% Ogallala sand, which had a CEC of 13.3 meq/100 gr.

Figure 10 shows, in spite of the increasing percent of clay, decreasing hydraulic conductivity of soil mixture and increasing cation exchange capacity of the mixture, phenol moved the same as chloride ion through the column. Figure 11 indicates the throughput volume for chloride was about 1.7 liters, while the throughput volume for dichlorophenol

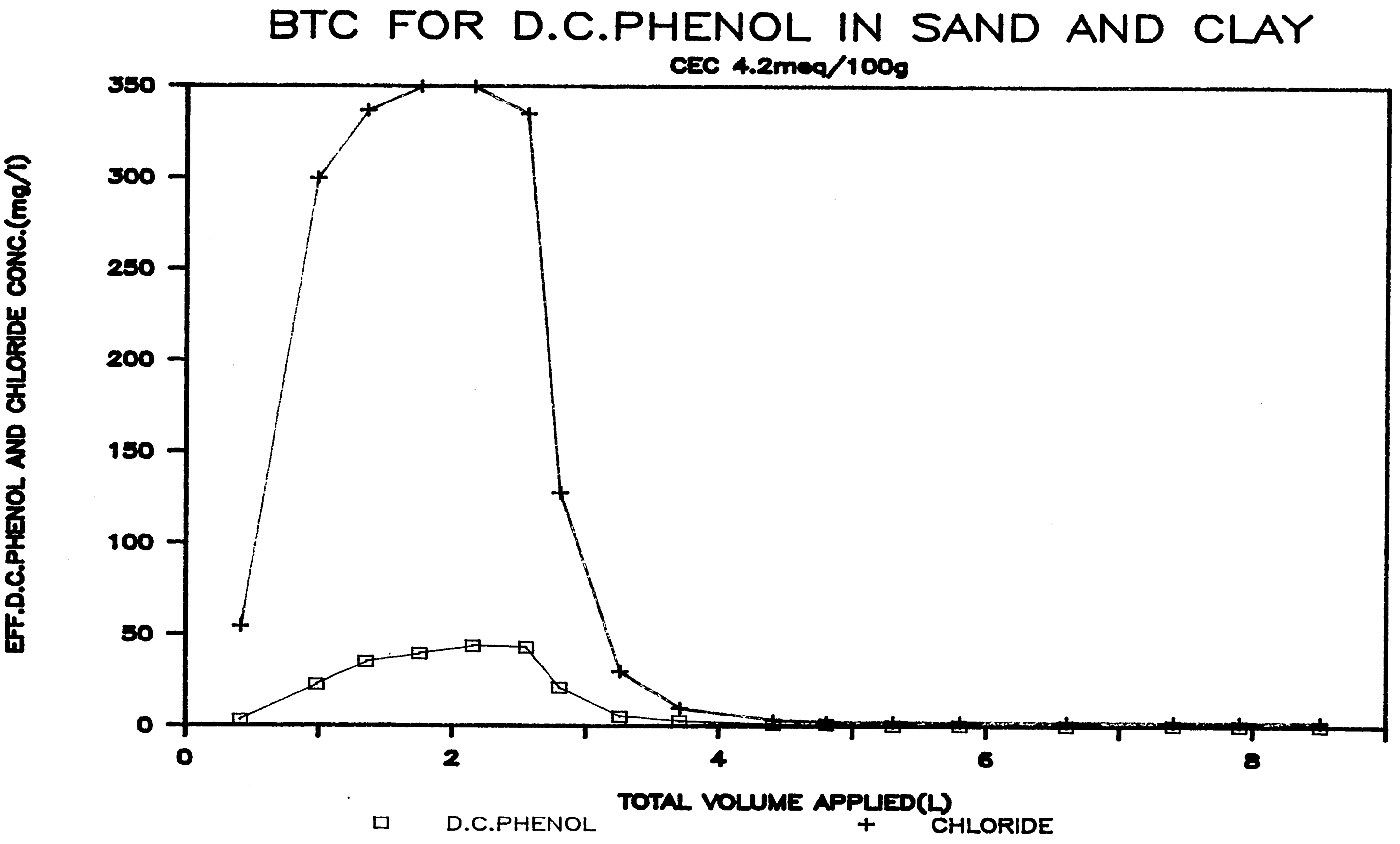


Figure 9 . BTC for Dichlorophenol and Chloride in Sand With 8% Kaolin Clay (CEC 4.2 meq/100 gr)

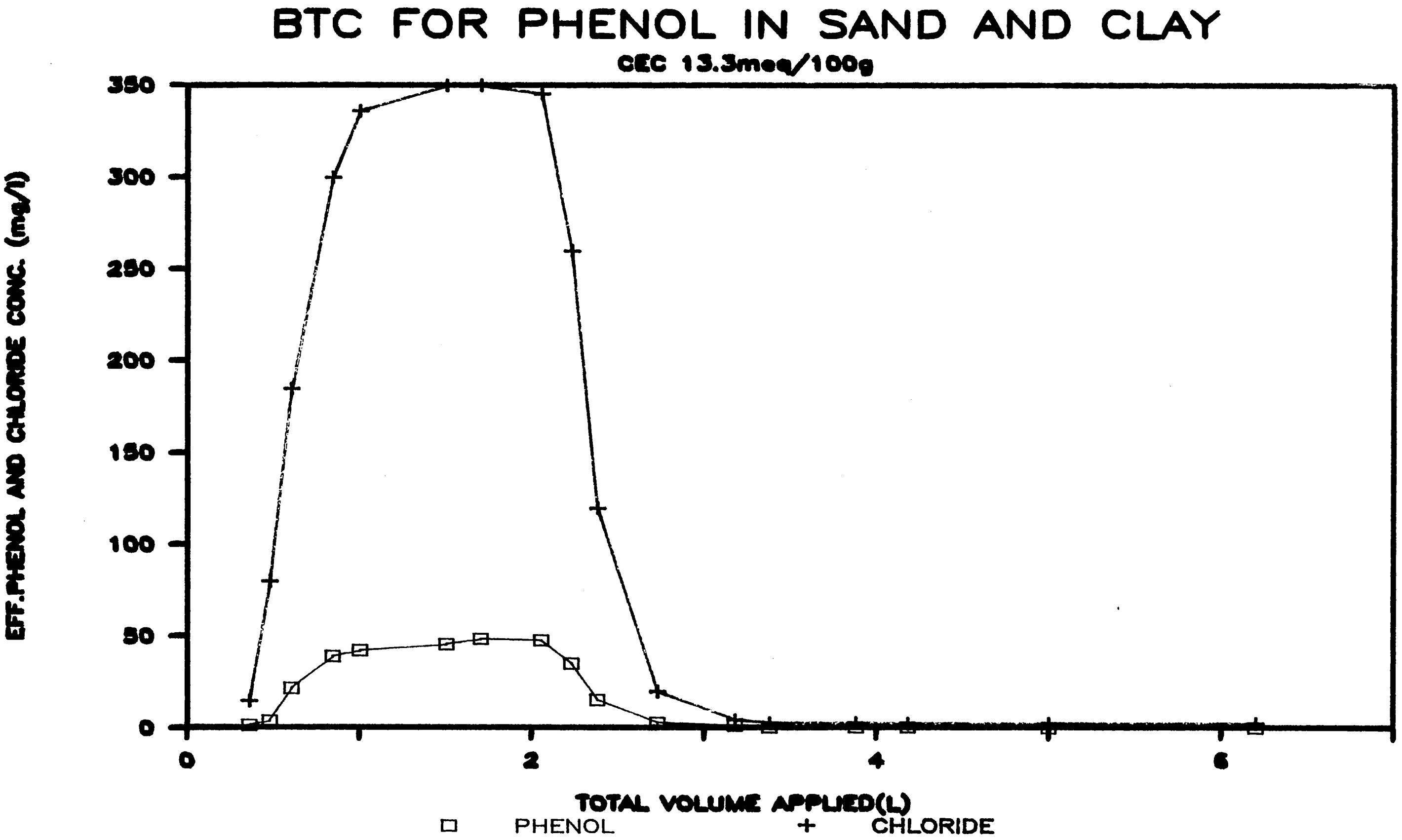


Figure 10. BTC for Phenol and Chloride in Sand With 16% Kaolin Clay (CEC 13.3 meq/100 gr)

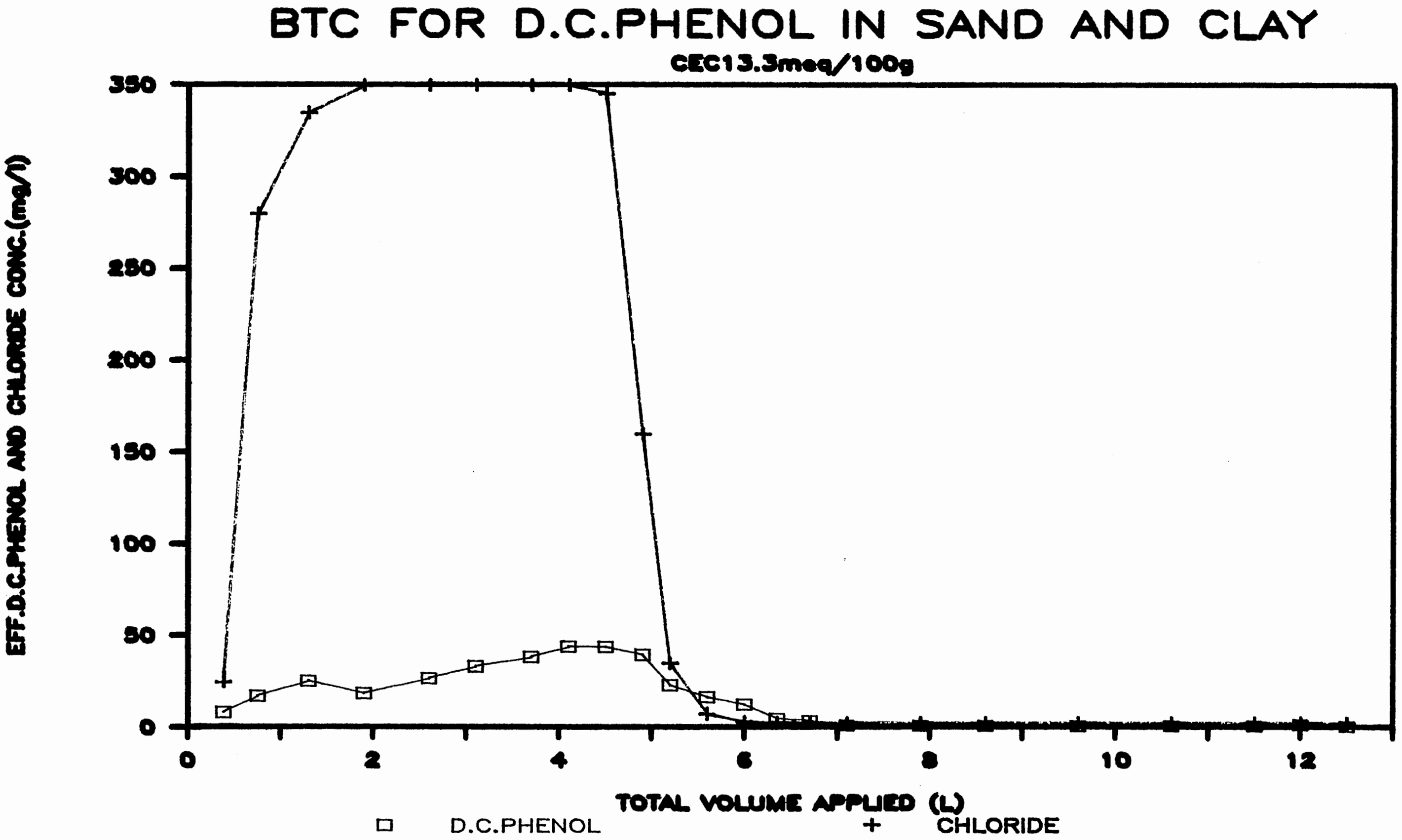


Figure 11. BTC for Dichlorophenol and Chloride in Sand With 16% Kaolin Clay (CEC 13.3 meq/100 gr)

to reach its maximum value in the effluent was about 4.8 liters. This means the increasing percent of Kaolin clay and increasing cation exchange capacity caused dichlorophenol to reach breakthrough at a longer time than before. Figure 11 also shows when distilled water was pumped to the system, the chloride concentration in the effluent decreased much more rapidly than did the dichlorophenol concentration, and the volume of distilled water required to observe no detection of dichlorophenol in the effluent was much greater than before. The amount of dichlorophenol left in the soil (residue) was 10 μg per gram of soil, and no phenol was detected in the soil sample. Figure 12 shows the breakthrough curve for phenol and 2,4-dichlorophenol in the mixture of 5% Ca-montmorillonite clay and 95% Ogallala sand. This indicates again that chloride and phenol were reaching breakthrough at the same time. Phenol moved the same as did chloride through the column. This means that the type of clay had no effect on the movement of phenol. It shows that dichlorophenol moved much more slowly than did chloride and phenol. The volume needed for dichlorophenol to reach the breakthrough was five liters, while the volume for phenol and chloride was 1.7 liters. Pumping distilled water to the system resulted in rapid dilution of chloride and phenol, but gradually decreasing concentration of dichlorophenol in the effluent. The soil samples were taken after no detection of phenol and dichlorophenol in the effluent were observed. These soil samples were analyzed for phenol

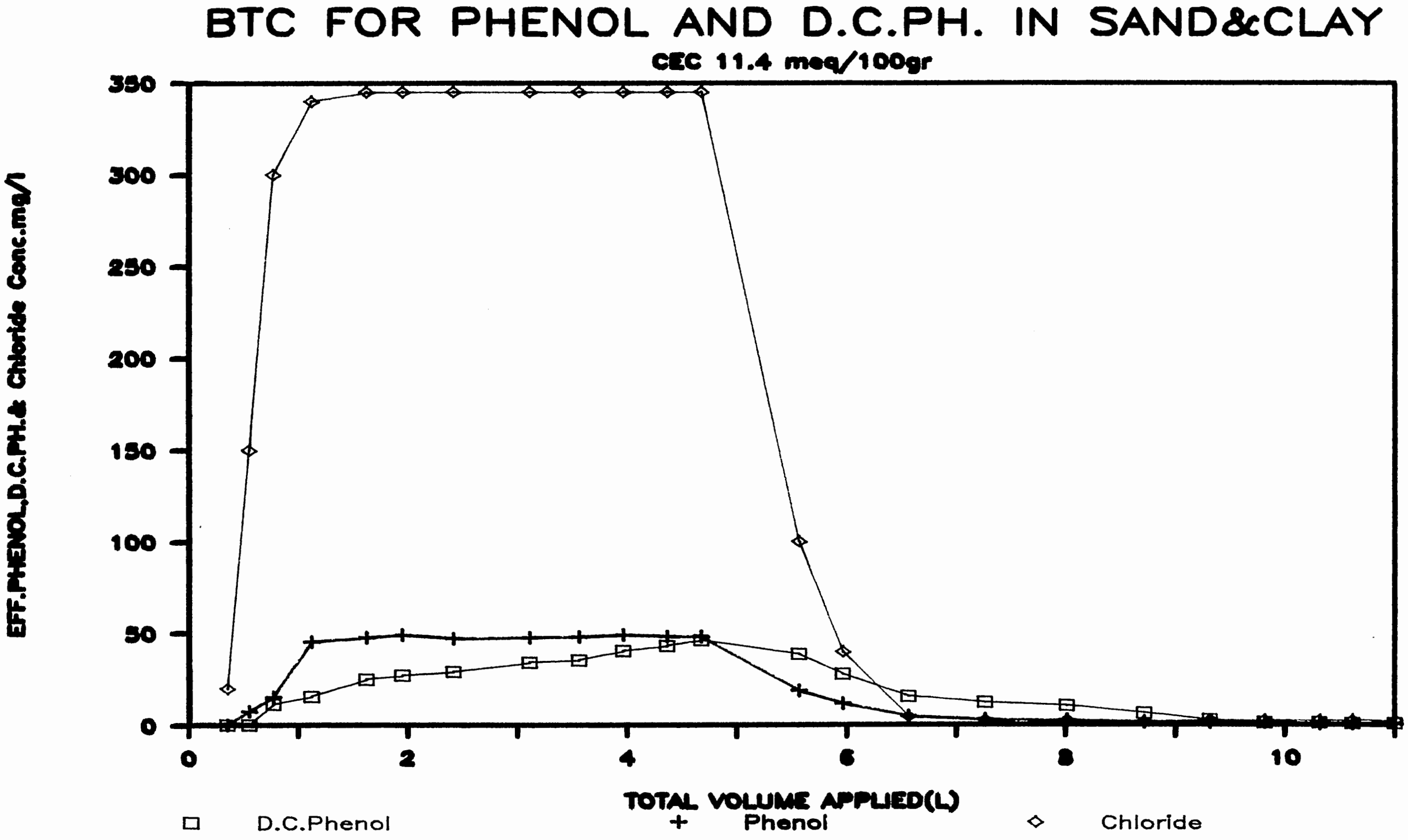


Figure 12. BTC for Phenol, Dichlorophenol, and Chloride for Sand With 5% Ca-montmorillonite (CEC 11.4 meq/100 gr)

and dichlorophenol. There was no phenol detected, but 12 μg dichlorophenol per gram of soil was found in the soil mixture. The amount of dichlorophenol adsorbed per gram of soil with different cation exchange capacity and hydraulic conductivity was computed from the breakthrough curve and is presented in Table VI. These were determined by subtracting the area behind the breakthrough curve of chloride (the amount of dilution) from the area behind the breakthrough curve for dichlorophenol (the amount of adsorption). Table VI indicates the increasing amount and type of clay or, in other words, decreasing hydraulic conductivity and increasing cation exchange capacity had no effect on the adsorption of phenol but had a significant effect on the adsorption of dichlorophenol. It shows the amount of dichlorophenol adsorbed per gram of soil increased from 8.45 μg/gr when the soil cation exchange capacity increased from 2.9 meq/100 gr to 13.3 meq/gr and hydraulic conductivity decreased from 2.53 cm/hr to .08 cm/hr.

The amount of dichlorophenol left in the soil after no detection of dichlorophenol was observed in the soil column's effluent is shown in Table VII. This indicates the amount of dichlorophenol residue increased with increasing percent of clay and cation exchange capacity. It is important to note the type of clay makes a difference in the mount of dichlorophenol residue in the soil.

TABLE VI

EFFECT OF SOIL CATION EXCHANGE CAPACITY AND HYDRAULIC CONDUCTIVITY ON ADSORPTION OF DICHLOROPHENOL AND PHENOL

Adsorbent	(C.E.C.) (meq/100 gr)	Hydraulic Conductivity (cm/hr)	Adsorbate	Amount Adsorbed
Ogallala Sand	.95	2.53	dichlorophenol	no adsorption
4% Kaolin Clay	2.9	1.40	dichlorophenol	8.45 μg/g
8% Kaolin Clay + 92% Ogallala Sand	4.2	1.0	dichlorophenol	14.4 μg/g
16% Kaolin Clay + 84% Ogallala Sand	13.3	.4	dichlorophenol	81.27 μg/g
5% Montmorillonite Clay + 95% O. Sand	11.4	.08	dichlorophenol	91.8 μg/g
Ogallala Sand	.95	2.95	phenol	no adsorption
4% Kaolin Clay + 96% Ogallala Sand	2.9	1.3	phenol	no adsorption
16% Kaolin Clay + 84% Ogallala Sand	13.3	.35	phenol	no adsorption
5% Montmorillonite Ca-Clay + 95% Ogallala Sand	11.4	.08	phenol	no adsorption

TABLE VII

AMOUNT OF DICHLOROPHENOL RESIDUE IN SOILS

Adsorbent	Residue
Ogallala sand	< DL
4% Kaolin clay	1.5 μg/g
8% Kaolin clay	3.4 μg/g
16% Kaolin clay	10.0 μg/g
5% Ca-montmorillonite clay	12.0 μg/g

2. The Effect of Organic Content of Soil on Adsorption of Phenol and 2,4-dichlorophenol

The results of this phase will be presented in three sections.

a. The Effect of Increasing the Soil Organic Content on Adsorption of Phenol and 2,4-dichlorophenol

In order to study the increasing effect of soil organic content on adsorption of phenol and 2,4-dichlorophenol, the same fine Ogallala sand was mixed with different amounts of peat in several columns. the soil properties, mixture, flow rate, and weight of soil in each column are shown in Table VIII. It can be seen that when 2%, 5%, and 8% by weight of peat was mixed with adequate portions of Ogallala sand, the hydraulic conductivity did not change significantly. The porosity of the mixture of sand and peat increased from

TABLE VIII

SOIL PROPERTIES FOR THE EFFECT OF INCREASING SOIL ORGANIC CONTENT STUDY

Adsorbent	Weight (gr)	Flow Rate gpd/ft^2 (ml/hr)	Porosity (%)	Hydraulic Conductivity (cm/hr)	Specific Gravity	Organic Carbon (%)
a) 2,4-dichlorophenol						
Mixture of 2% peat and 98% Ogallala sand	1860	15.0 (130)	45	2.9	2.32	1.45
Mixture of 5% peat and 95% Ogallala sand	1500	14.5 (126)	50	2.7	-	2.87
Mixture of 8% peat and 92% Ogallala sand	1208	17.31 (150)	53	2.5	1.95	5.12
b) Phenol						
Mixture of 2% peat and 98% Ogallala sand	1853	15.6 (135)	44	2.7	2.4	1.35
Mixture of 8% peat and 92% Ogallala sand	1250	13.5 (117)	49	2.6	1.95	4.9

2% to 8%. It is also seen that by increasing the percent of peat from 2% to 8% resulted in decreasing the specific gravity from 2.3 to 1.95. Table VIII indicates that the mixture of 2% by weight peat and 98% Ogallala sand contained 1.45% organic carbon after it was washed several days with distilled water, while the mixture of 8% peat and 92% Ogallala sand had 5% organic carbon.

The phenol, 2,4-dichlorophenol and chloride concentrations in the soil column's effluent are given in Appendix B. Figures 13 and 14 show the breakthrough curve for phenol and dichlorophenol in a mixture of peat and sand which had 1.3% and 1.45% organic carbon. Figure 13 indicates the throughput volume or time required for the tracer to reach breakthrough was the same as the time for phenol to reach its maximum value in the effluent. This means that phenol moved the same as did chloride ion through the column. The factor controlling their movement was dispersion, not adsorption. Adding distilled water to the column caused dilution of phenol and chloride; they behaved identically. There was no phenol found in the soil after no detection of phenol was observed in the soil column's effluent.

Figure 14 shows that the chloride ion moved more rapidly than the dichlorophenol. The volume required for the chloride to go to breakthrough was about 1.7 liters, while the volume needed for dichlorophenol to reach breakthrough was six liters. The volume for dichlorophenol was three times greater than the volume for chloride. This indicates that

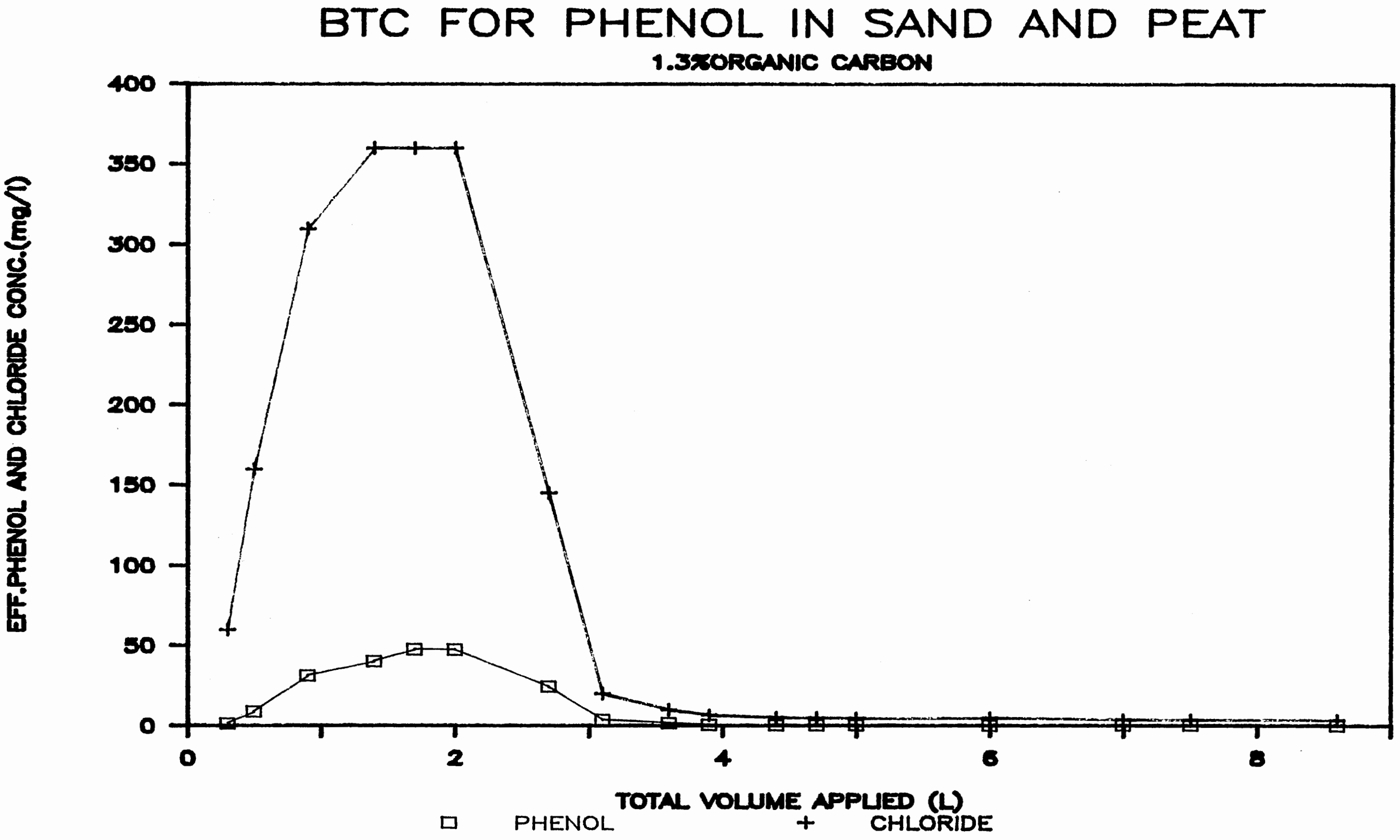


Figure 13. BTC for Phenol and Chloride in Sand With Peat (1.3% Organic Carbon)

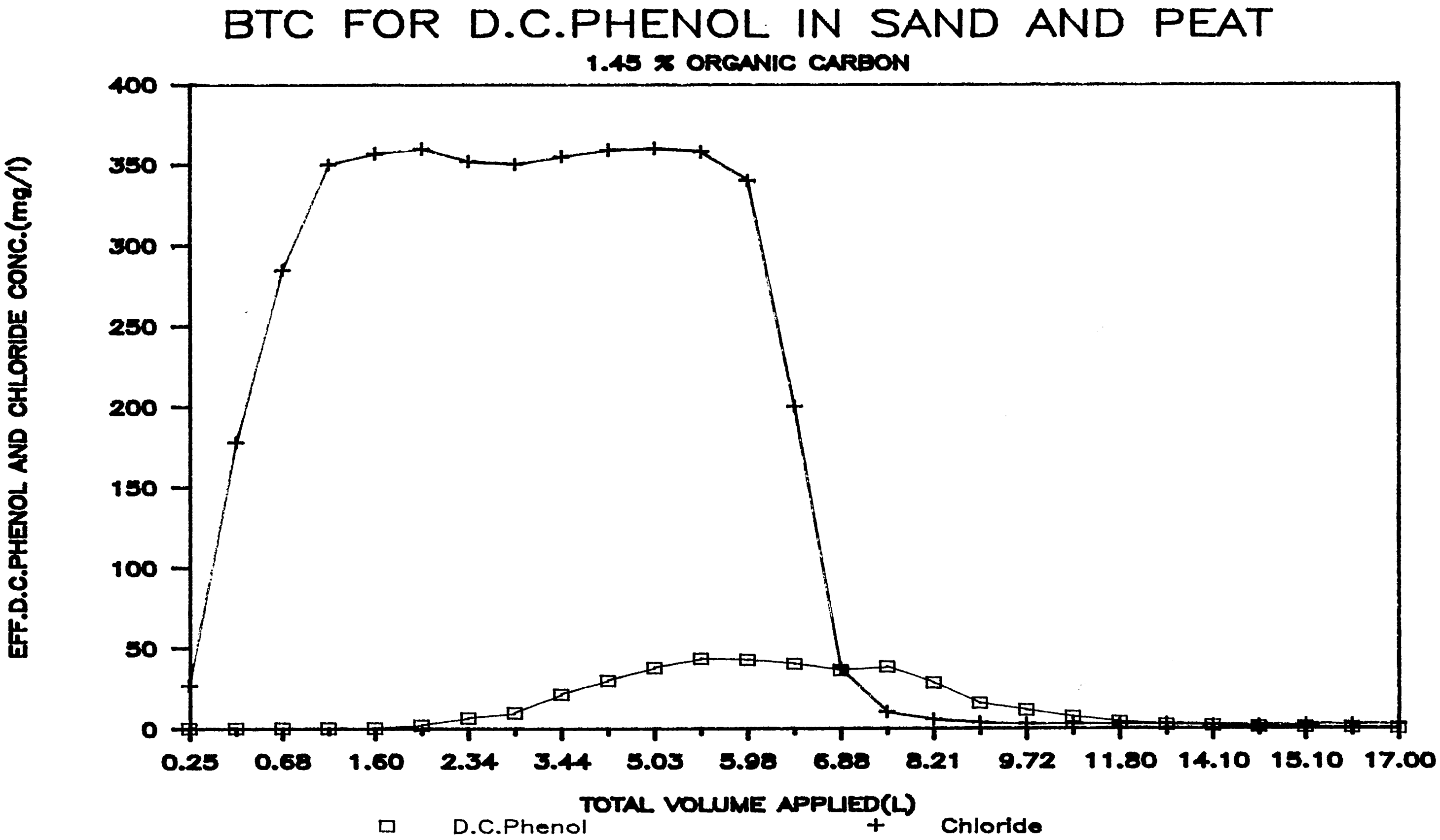


Figure 14. BTC for Dichlorophenol and Chloride in Sand With Peat (1.45% Organic Carbon)

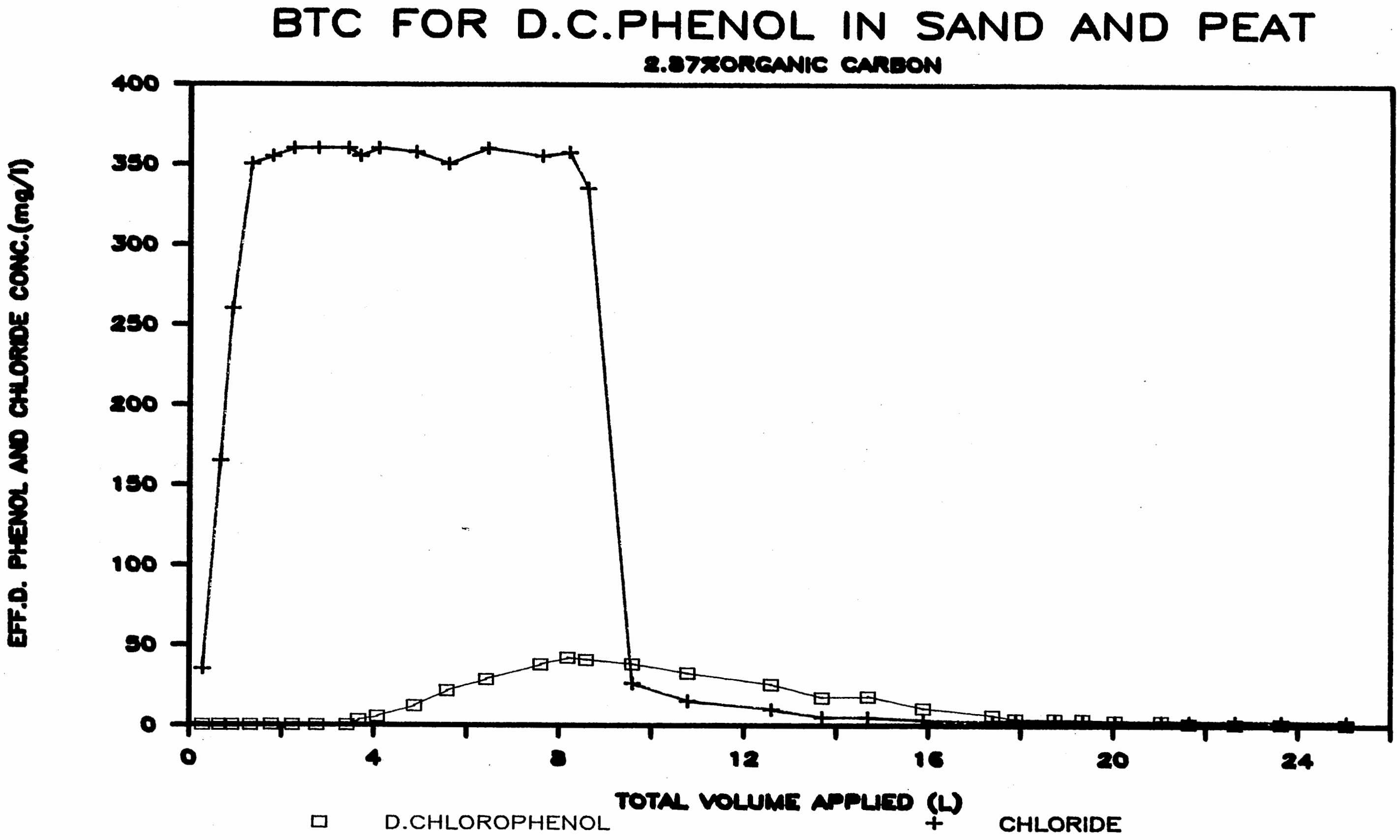


Figure 15. BTC for Dichlorophenl and Chloride in Sand With Peat (2.87% Organic Carbon)

the factor controlling the movement of dichlorophenol was not only dispersion, but was also adsorption. It also shows that when the system was converted to distilled water, the chloride ion diluted out very rapidly, but the dichlorophenol concentration decreased gradually. It can be shown that the volume required to wash this column to the extent that no detection of dichlorophenol was observed in the effluent was double the volume used to wash the phenol column. The amount of dichlorophenol in the soil was 16 μg per gram of soil.

Figure 15 shows the breakthrough curve for dichlorophenol in the mixture of sand and peat with 2.8% organic carbon. It can be seen that the volume required for dichlorophenol to go to breakthrough increased to nine liters, while the volume for chloride remained constant. This indicates that in this column the dichlorophenol moved slower than it did in the column that had a mixture with 1.45% organic carbon. It shows that when the system was converted to distilled water, the chloride concentration decreased rapidly but the dichlorophenol concentration in the effluent decreased gradually. About 25 liters of distilled water was required to have no detection of dichlorophenol in the effluent. This volume was much greater than the volume of water used to clean the column containing a mixture of peat and sand with 1.45% carbon. The amount of dichlorophenol left in the soil when there was no detection observed in the effluent was 43 μg per gram of soil.

The breakthrough curves for phenol and dichlorophenol in a mixture of peat and Ogallala sand with 4.9% and 5.12% organic carbon are presented in Figures 15 and 17. Figure 16 indicates the phenol and chloride reached breakthrough at the same time and diluted out in the same manner when the system was converted to distilled water. Figure 17 shows that the volume required for dichlorophenol to reach breakthrough was 15 liters, while the volume required for the chloride was 1.5 liters. It can be seen that the volume required for breakthrough for dichlorophenol was ten times greater than the volume required for chloride to reach breakthrough. It also indicates that in this column, dichlorophenol moved slower than the column containing a mixture of sand and peat with 2.87% organic carbon. It is seen that desorption of dichlorophenol occurred when the system was converted to distilled water. The amount of dichlorophenol in the soil when there was no dichlorophenol in the column effluent was 70 μg per gram of soil.

The effect of increasing the soil organic content on adsorption of phenol and 2,4-dichlorophenol is presented in Table IX. The amount of dichlorophenol sorbed per gram of soil was determined by measuring the area behind the breakthrough curve of chloride ion and the area behind the dichlorophenol breakthrough curve. This was computed by subtracting the area of dilution (chloride ion) from the area of dichlorophenol. Table IX shows that an increasing percent of organic carbon had no effect on adsorption of phenol but had a significant effect on the sorption of

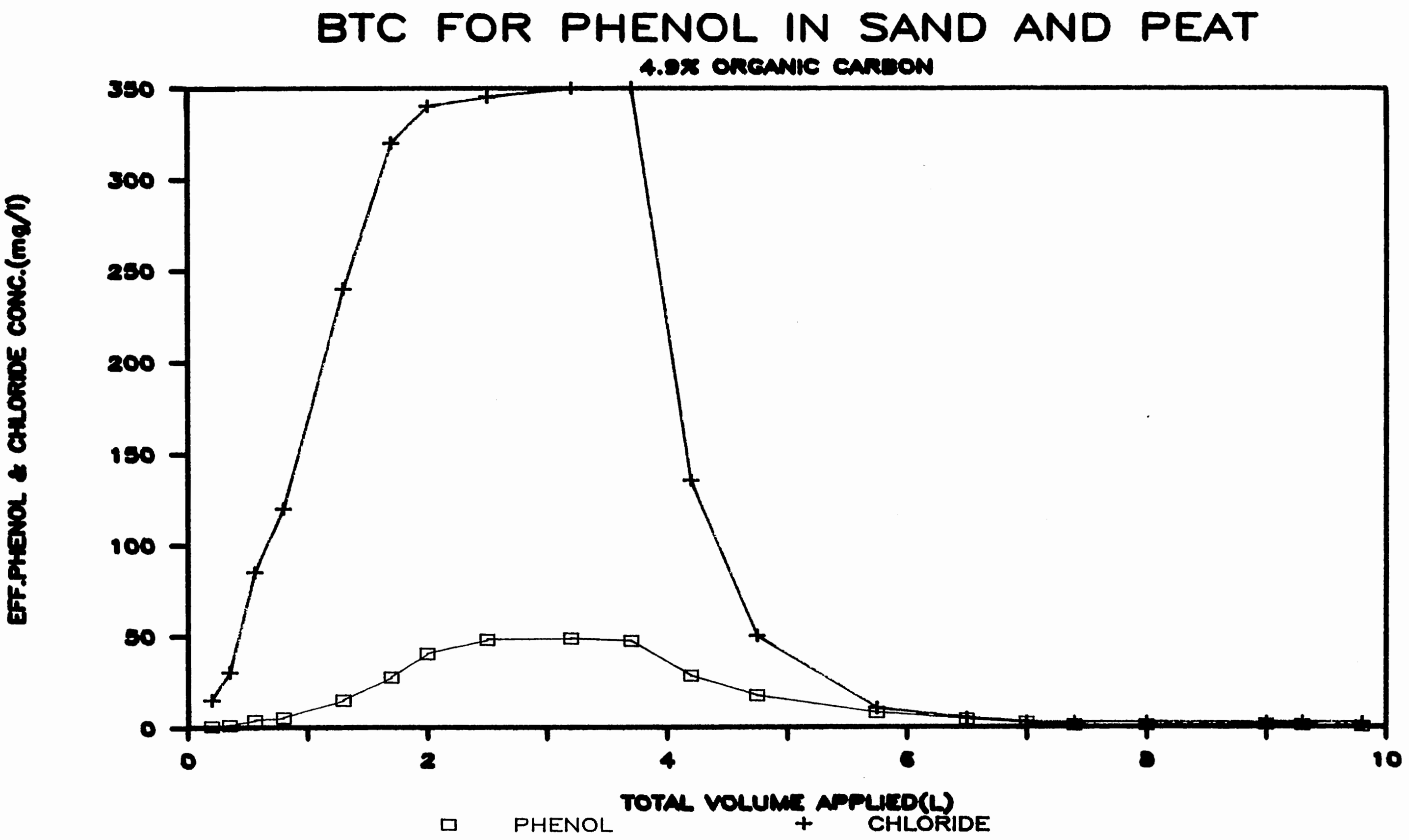


Figure 16. BTC for Phenol and Chloride in Sand With Peat (4.9% Organic Carbon)

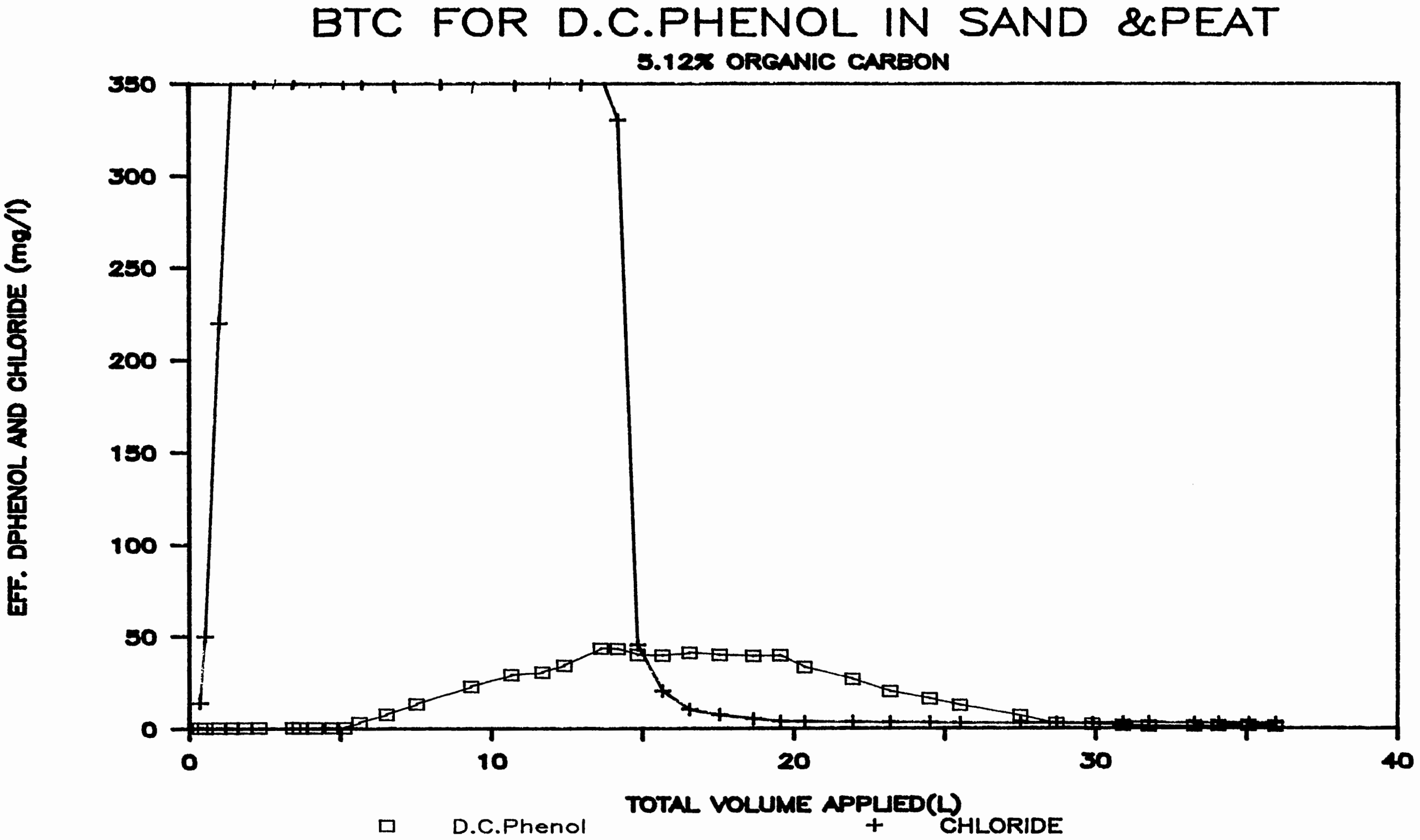


Figure 17. BTC for Dichlorophenol and Chloride in Sand With Peat (5.12% Organic Carbon)

dichlorophenol. It can be seen that the amount of dichlorophenol sorbed per gram of soil increased from 131.8 μg per gram of soil to 486 μg per gram when the percent of organic carbon in the soil had increased from 1.45% to 5,12%. The amount of dichlorophenol in the soil after washing the column with distilled water is shown in Table X. This indicates that the amount of dichlorophenol residue in the soil increased from 16 μg per gram of soil to 70 μg per gram of soil when the percent of organic carbon increased from 1.45% to 5.12%.

TABLE IX

EFFECT OF SOIL ORGANIC CONTENT ON ADSORPTION OF DICHLOROPHENOL AND PHENOL

Adsorbent	Organic Carbon (%)	Adsorbate	Amount Adsorbed
2% Peat and 98% Sand	1.45	Dichlor.	131.8 μg/g
2% Peat and 98% Sand	1.3	Phenol	none
5% Peat and 95% Sand	2.87	Dichlor.	230 μg/g
8% Peat and 92% Sand	5.12	Dichlor.	486 μg/g
8% Peat and 92% Sand	4.9	Phenol	none

TABLE X

AMOUNT OF DICHLOROPHENOL RESIDUE IN SOIL

Organic Carbon (%)	Residue (μg/g)
1.45	16
2.87	43
5.12	70

b. Adsorption of Phenol and 2,4-dichlorophenol

To determine whether or not 2,4-dichlorophenol behaves differently when present with phenol, a feed solution containing 50 mg/l phenol, 50 mg/l 2,4-dichlorophenol, and .01N $CaCl_2$ was passed through two soil columns. The soils consisted of Ogallala sand and peat. One column had 2% peat and 98% sand; the second column had 8% peat and 92% sand. The soil properties, weight of soil, and flow rate for these two columns are shown in Table XI. It can be seem that the two mixtures had almost the same hydraulic conductivity but different specific gravities. It can be seen that the mixture containing 2% peat and 98% sand had 1.7% organic carbon, while the mixture containing 8% peat and 92% sand had 5.15% organic carbon.

The effluent chloride, phenol and 2,4-dichlorophenol concentration are given in Appendix C. The breakthrough curve for phenol and dichlorophenol in the soil with 1.7% organic carbon is shown in Figure 18. It can be seen that the volume required for phenol and chloride to reach the breakthrough was about 1.8 liters, but the volume required for dichlorophenol to reach breakthrough was about 7.0 liters. This indicates again that phenol and chloride behaved similarly to when the dichlorophenol was not present in the feed solution. It is interesting to see that the presence of phenol had slight effect on the movement of

TABLE XI

SOIL PROPERTIES FOR A MIXTURE OF PHENOL AND 2,4-DICHLOROPHENOL ADSORPTION STUDY

Adsorbent	Weight (gr)	Flow Rate (gpd/ft^2)	Porosity (%)	Hydraulic Conductivity	Specific Gravity	Organic Carbon (%)
Mixture of 2% peat and 98% Ogallala sand	1850	16.8 (146)	44	2.6	2.32	1.7
Mixture of 8% peat and 92% Ogallala sand	1200	13.6 (117)	50	2.4	1.95	5.15

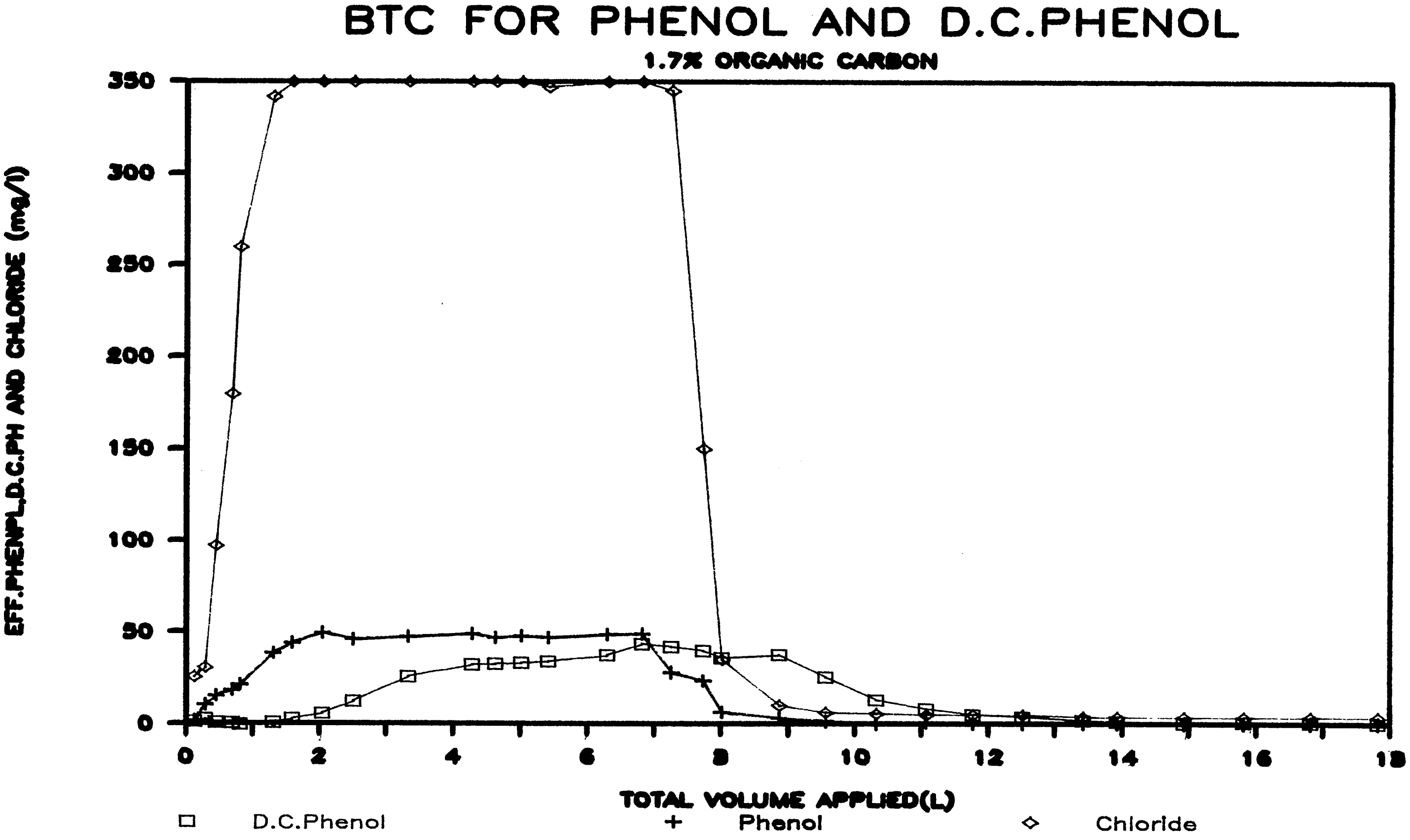


Figure 18. BTC for Phenol, Dichlorophenol and Chloride in Sand With Peat (1.7% Organic Carbon)

dichlorophenol. Since the phenol moved more rapidly than the dichlorophenol through the column, it caused leakage of dichlorophenol in the column effluent as opposed to when only dichlorophenol was in the solution. Figure 18 shows the desorption of dichlorophenol occurred much more slowly than the dilution of chloride and phenol. Soil samples were taken and analyzed for phenol and dichlorophenol when there was no phenol and dichlorophenol detected in the effluent. The amount of dichlorophenol in the soil was 18 μg per gram of soil, and there was no phenol found in the soil samples.

The breakthrough curve for phenol and dichlorophenol in the mixture of sand and soil with 5.1% organic carbon is presented in Figure 19. It can be seen that increasing the percent of organic carbon had no effect on the movement of phenol and chloride. The volume required for dichlorophenol to reach its maximum value in the effluent was 15 liters. This shows that the volume for dichlorophenol increased from seven liters to 15 liters. In other words, dichlorophenol in this column moved more slowly than it did in the column containing soil with 1.7% organic carbon, while phenol and chloride moved the same as before. This also indicates that the presence of phenol caused some slight leakage of dichlorophenol in the effluent. Figure 19 shows the amount of distilled water required to wash the column to be clear of phenol and dichlorophenol was almost twice that of the previous column. No phenol was found in the soil samples, but the amount of dichlorophenol in the soil was 61 μg per gram.

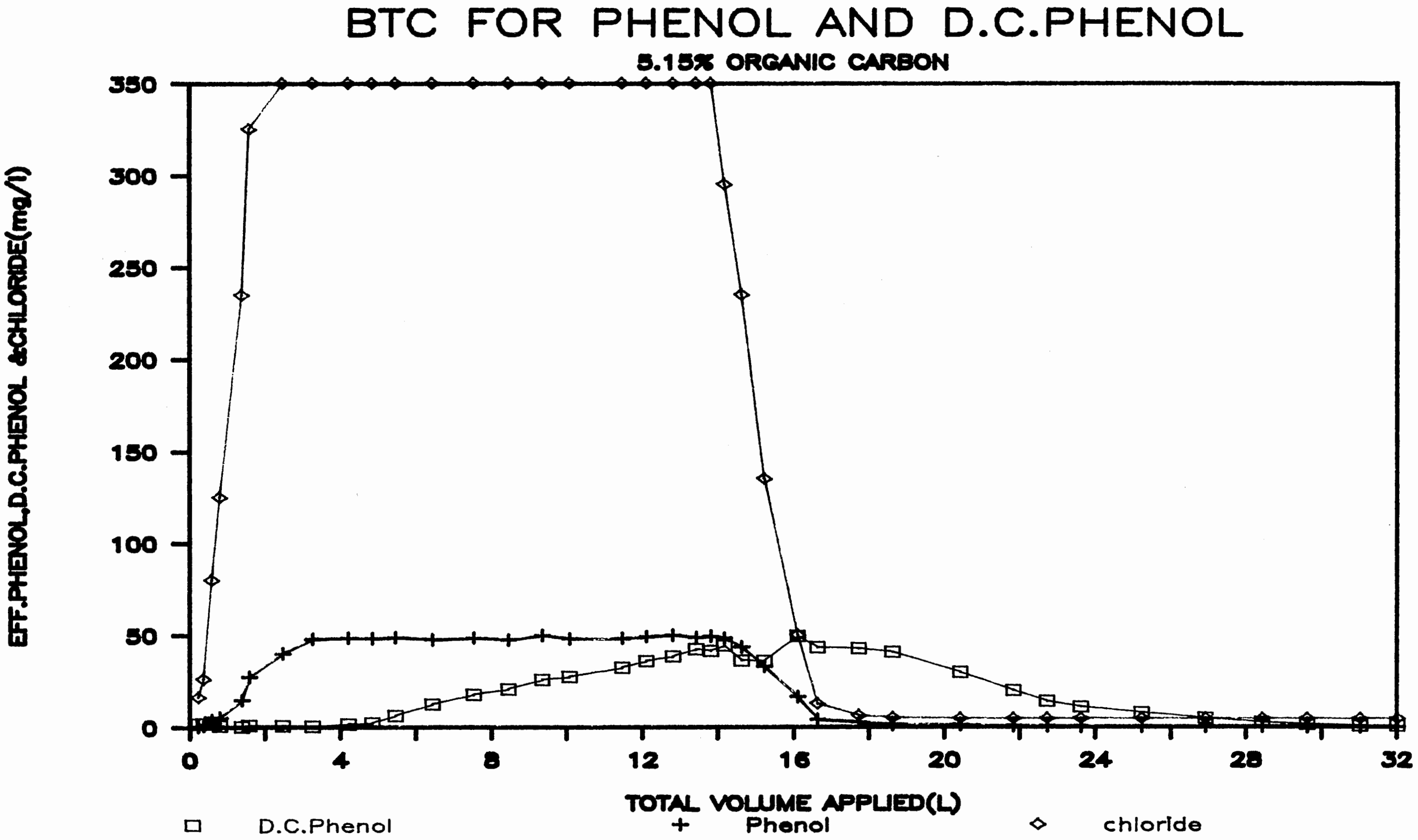


Figure 19. BTC for Phenol, Dichlorophenol and Chloride in Sand With Peat (5.15% Organic Carbon)

The amount of dichlorophenol sorbed per gram of soil determined from the breakthrough curve is presented in Table XII. This indicates again that increasing the percent of organic carbon increased the adsorption of dichloropenol but had no effect on adsorption of phenol. This also shows that there was no competition for phenol and dichlorophenol for the adsorption site. Phenol behavior was similar to previous behavior, and this confirms the results of the previous experiment with dichlorophenol. Table XII shows the amount of dichlorophenol in the soil increased with the amount of organic carbon in the soil.

TABLE XII

ADSORPTION OF DICHLOROPHENOL WHEN PRESENT WITH PHENOL

Adsorbent	Organic Carbon (%)	Adsorbate	Amount Adsorbed μg/g	Residue μg/g
2% Peat + 98% Sand	1.7	dichlorophenol	158.8	19
		phenol	-	none
8% Peat + 92% Sand	5.15	dichlorophenol	471.0	61
		phenol	-	none

C. The Effect of Different Kinds of Organic Content of Soil on Adsorption

To study the effect of different organic contents of soil on adsorption of phenol and 2,4-dichlorophenol, peat moss from Fison Western Company and milorganite (digested sewage sludge) from the City of Milwaukee were mixed with fine Ogallala sand and placed in columns. Soil properties, weight, and flow rate for these two columns are presented in Table XIII. It can be seen when nine percent by weight milorganite and eight percent peat were mixed with different amounts of Ogalalla sand, the mixture had almost the same amount of organic carbon and porosity but had different specific gravities. It shows the hydraulic conductivity in these two columns were slightly different. It is important to mention that the organic contents of these two soils were determined after washing the columns several times with distilled water. (Soil organic matter consists of two major groups of compounds, nonhumic substance and humic substance.) In order to determine that these two organic materials (peat and milorganite) were different in humic and nonhumic substance, several analyses were performed. The gross fractionation of peat and milorganite is shown in Table XIII. This table shows these two natural sources had almost the same organic matter. It also indicated that the milorganite contained more fats, resins and polysaccharides but peat had more hemicellulose.

To determine the difference between the humic substance of these two organic materials, two methods were used. The first method was E_4/E_6 ratio (the ratio of optical density or absorbance of dilute aqueous humic and fulvic acid solution at 465 and 665 nm). This ratio is widely used by soil

TABLE XIII

SOIL PROPERTIES FOR DIFFERENT KINDS OF ORGANIC MATTER STUDY

Adsorbent	Weight	Flow Rate (gpd/ft^2) (ml/hr)	Porosity (%)	Hydraulic Conductivity (cm/hr)	Specific Gravity	Organic Carbon
9% milorganite and 91% sand	1800	11.54 (100)	54	1.8	2.30	5.68
8% peat and 82% Ogallala sand	1200	13.6 (117)	50	2.4	1.95	5.75

TABLE XIV

GROSS CHEMICAL ANALYSIS FOR PEAT AND MILORGANITE

	Peat (%)	Milorganite (%)
Organic matter	54	50
E_4/E_6	3.1	6.6
Fats, waxes, oils	1.1	5.4
Resins	0.95	3.0
Water-soluble polysaccharides	1.8	5.0
Hemicellulose	3.7	3.0

scientists for the characterization of these materials. It has been suggested by several investigators (Chen, 62; Konova, 63) that E_4/E_6 is related to the degree of condensation of the aromatic carbon network, carbon content and molecular weight of humic substances. According to Konova (57) and Schnitzer (64), low ratio indicates a relatively high degree of condensation of aromatic humic constituents or high molecular weight. Conversely, a high E_4/E_6 ratio reflects a low degree of aromatic condensation and infers the presence of a large portion of alphatic structure (low molecular weight).

E_4/E_6 for peat and milorganite were determined and the results are shown in Table XIV. It can be seen that peat had a lower E_4/E_5 ratio than did milorganite. The ratio for milorganite was almost twice that of peat. This indicates that peat should have humic substance with a higher molecular weight when compared to milorganite.

Another method that was used in this research to characterize humic substance was "SEPHEDEX" gel filtration. The idea of utilizing this method was originated from the work of Veenstra (65) and Khan (66). In this method, humic compounds were fractionated, not on the basis of their varying solubilities, but according to their molecular weight, by passing through a column of Sephedex (G_{50}). This technique provided valuable information on the molecular size of the humic compound. The apparent molecular distribution for peat and milorganite humic substances are shown in Figures 20 and 21, respectively. It can be seen that milorganite

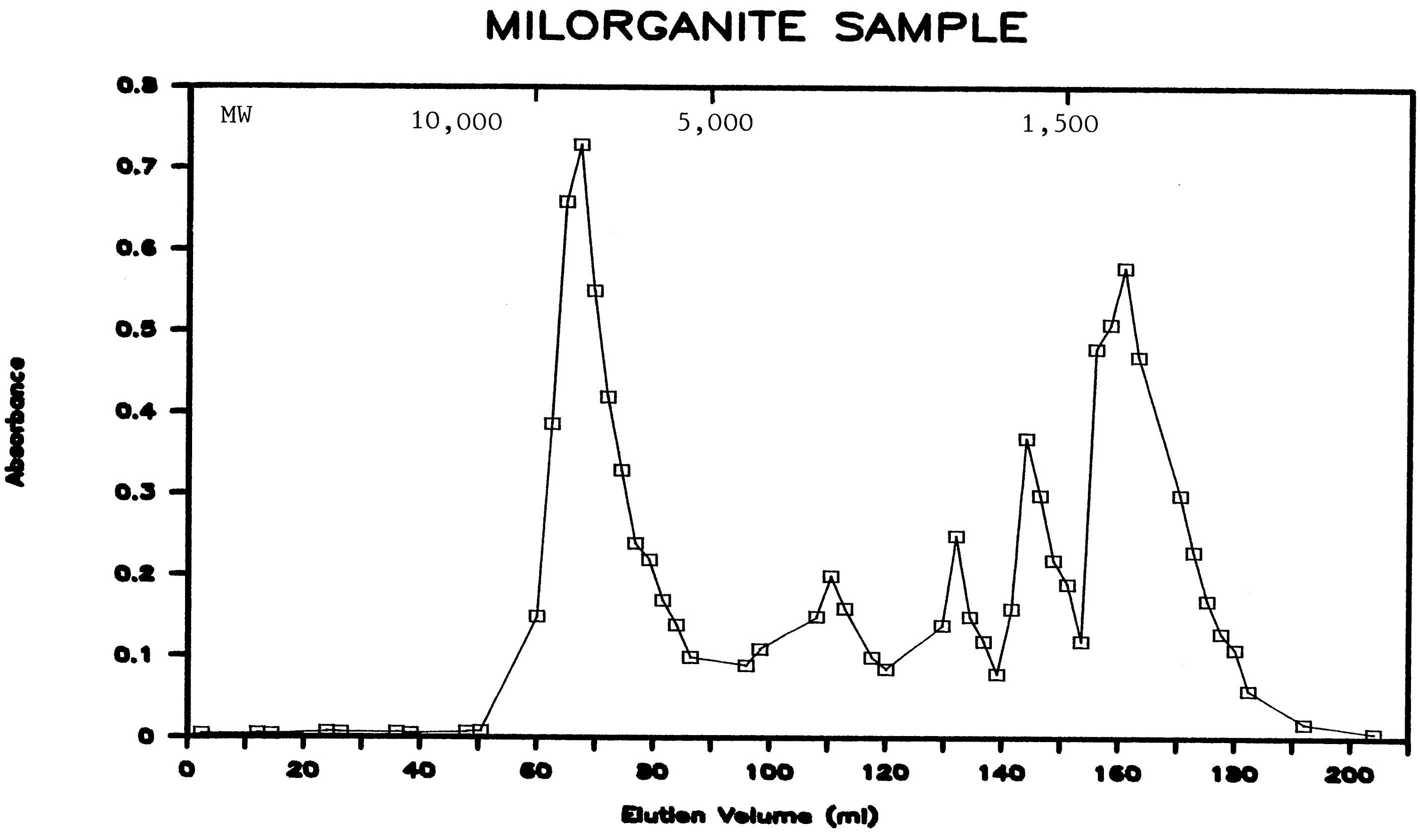


Figure 20. UV Absorbance Chromatogram to Find Apparent Molecular Weight for Milorganite Humic Substance (γ = 250)

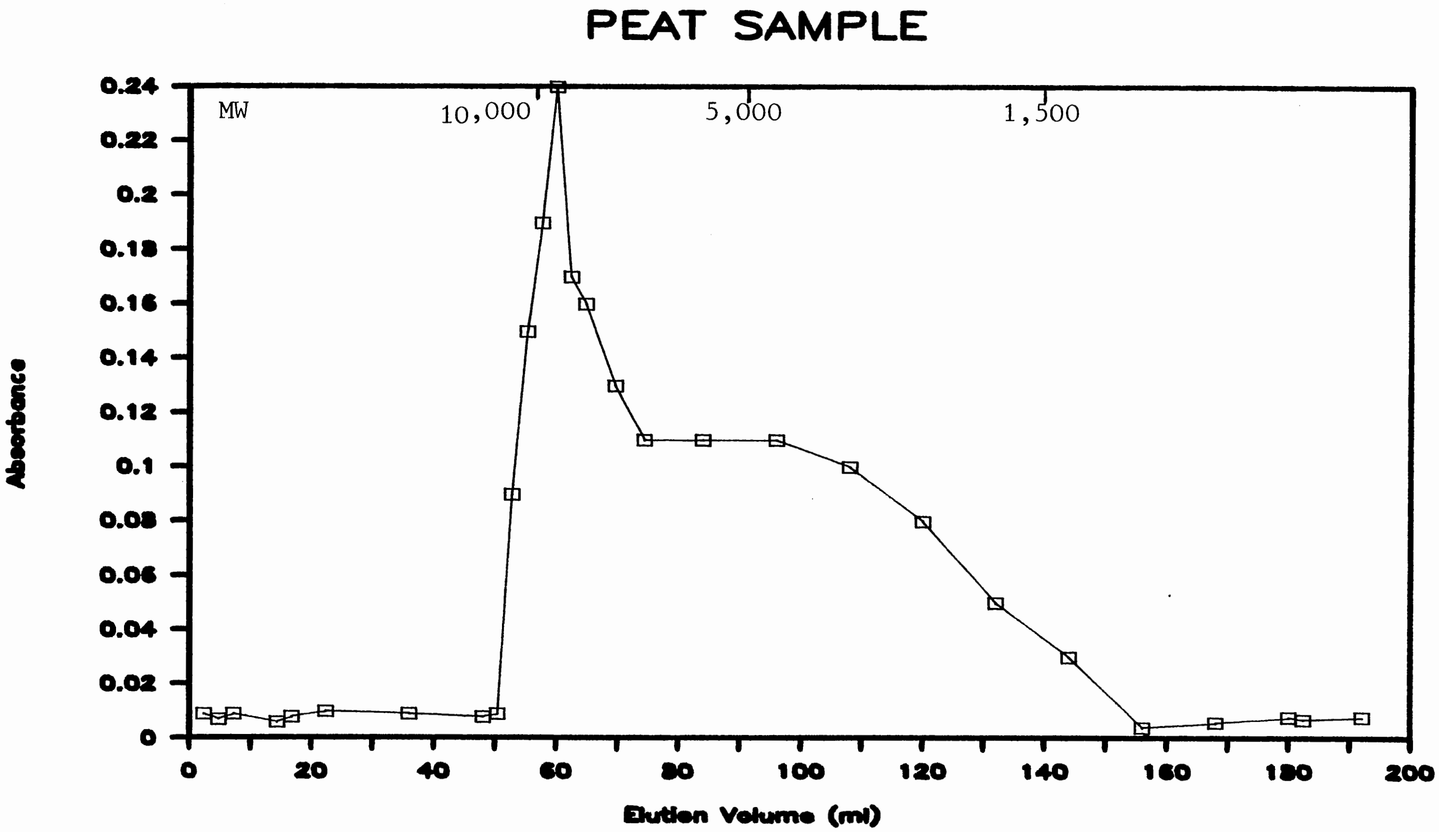


Figure 21. UV Absorbance Chromatogram to Find Apparent Molecular Weight for Peat Humic Substance (γ = 220)

humic substance had a variety of molecular-size fractions from 1000 to 10,000 MW; however, peat humic substance shows a peak in a range of 6000 to 10,000 MW. According to the apparent molecular size distribution, E_4/E_6 ratio and gross chemical analysis, the conclusion can be made that peat and milorganite organic matter are different.

The effluent chloride, phenol, and 2,4-dichlorophenol concentrations for these two columns are given in Appendix D. The breakthrough curve for phenol and 2,4-dichlorophenol transport in 9% milorganite by weight and 91% Ogallala sand is shown in Figure 22. It can be seen that phenol did not move through the column as rapidly as did chloride. In other words, the volume or time required for phenol to reach breakthrough was greater than the volume or time required for chloride to reach its effluent maximum value. This means that the factor controlling the movement of chloride was dispersion, while adsorption and dispersion controlled the movement of phenol. This also indicates that the type of organic material had a slight effect on the transport of phenol. Figure 22 also shows the throughput volume or time required for dichlorophenol to reach breakthrough was much greater than the volume or time required for phenol and chloride to go to breakthrough. The volume required for dichlorophenol to go to breakthrough was about 32 liters, while the volume required for phenol was about five liters. This means that dichlorophenol moved through the column much more slowly. When the system went back to distilled

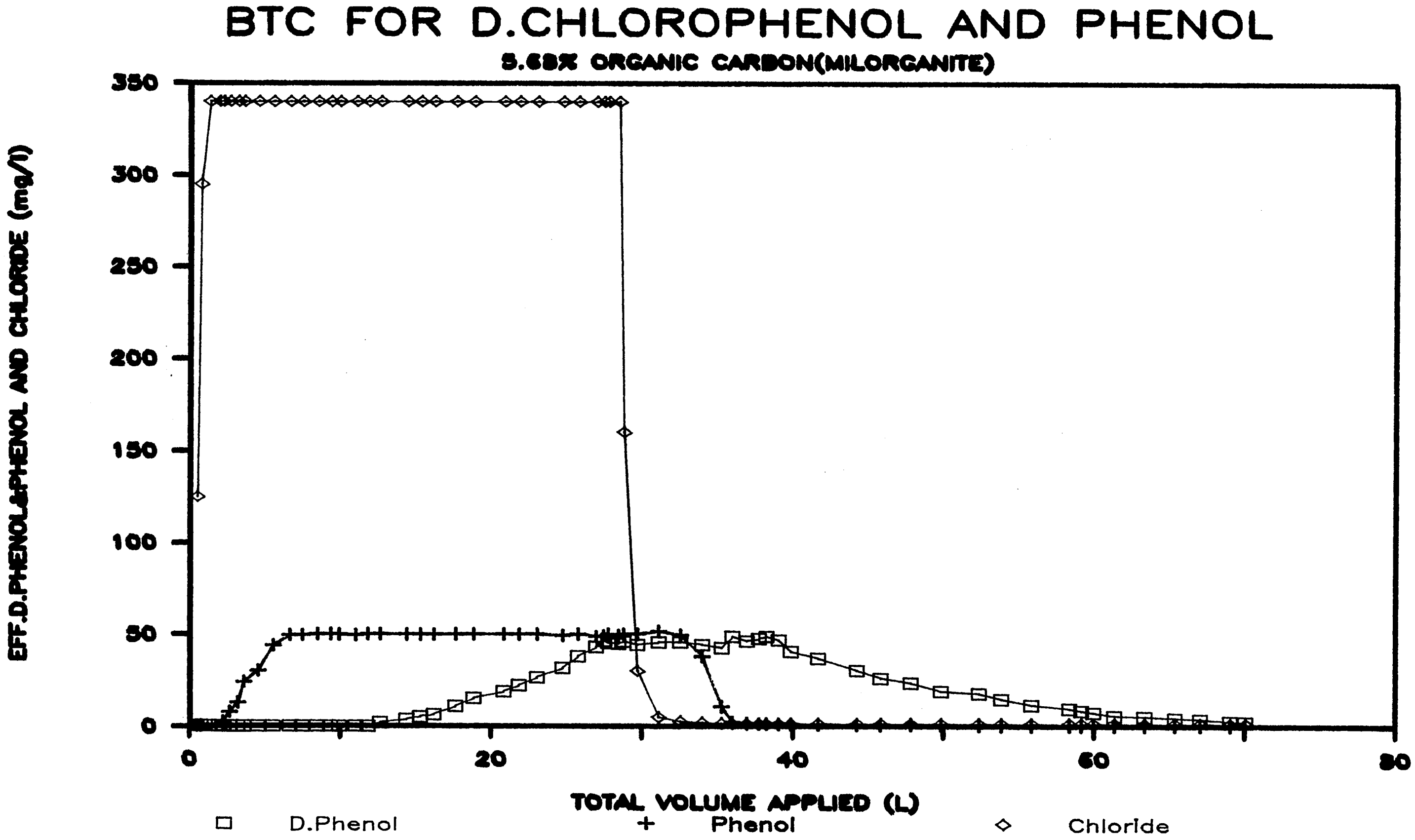


Figure 22. BTC for Dichlorophenol, Chloride and Phenol in Sand With Milorganite (5.68% Organic Carbon)

water, the chloride ion diluted out much more rapidly than did dichlorophenol. More than 40 liters of water were required before it was observed that no dichlorophenol was in the effluent. The amount of dichlorophenol detected in the soil after there was no detection of dichlorophenol was 96 μg per gram of soil.

The breakthrough curve for dichlorophenol and phenol in 8% peat by weight and 92% Ogallala sand which had the same amount of organic carbon as the mixture of milorganite and Ogallala sand is shown in Figure 23. It can be seen in this column that although the quantity of organic matter had not changed, phenol moved as rapidly as chloride moved through the column. Figure 23 indicates the volume required for dichlorophenol to reach breakthrough was about 15 liters, while the volume required for phenol was about 1.7 liters. When the system was converted to distilled water, phenol diluted out the same as the chloride. It took some time for the dichlorophenol to be diluted out of the effluent. The amount of dichlorophenol remaining in the soil was 61 μg per gram of soil. The effect of different types of organic material in soils on adsorption of phenol and dichlorophenol are shown in Table XV. This table shows the amount of phenol adsorbed per gram of mixture of milorganite and Ogallala sand was 55 μg, while there was no adsorption of phenol for the mixture of peat and Ogallala sand. The amount of dichlorophenol adsorbed per gram of milorganite and sand was almost twice the amount of dichlorophenol sorbed per gram of peat

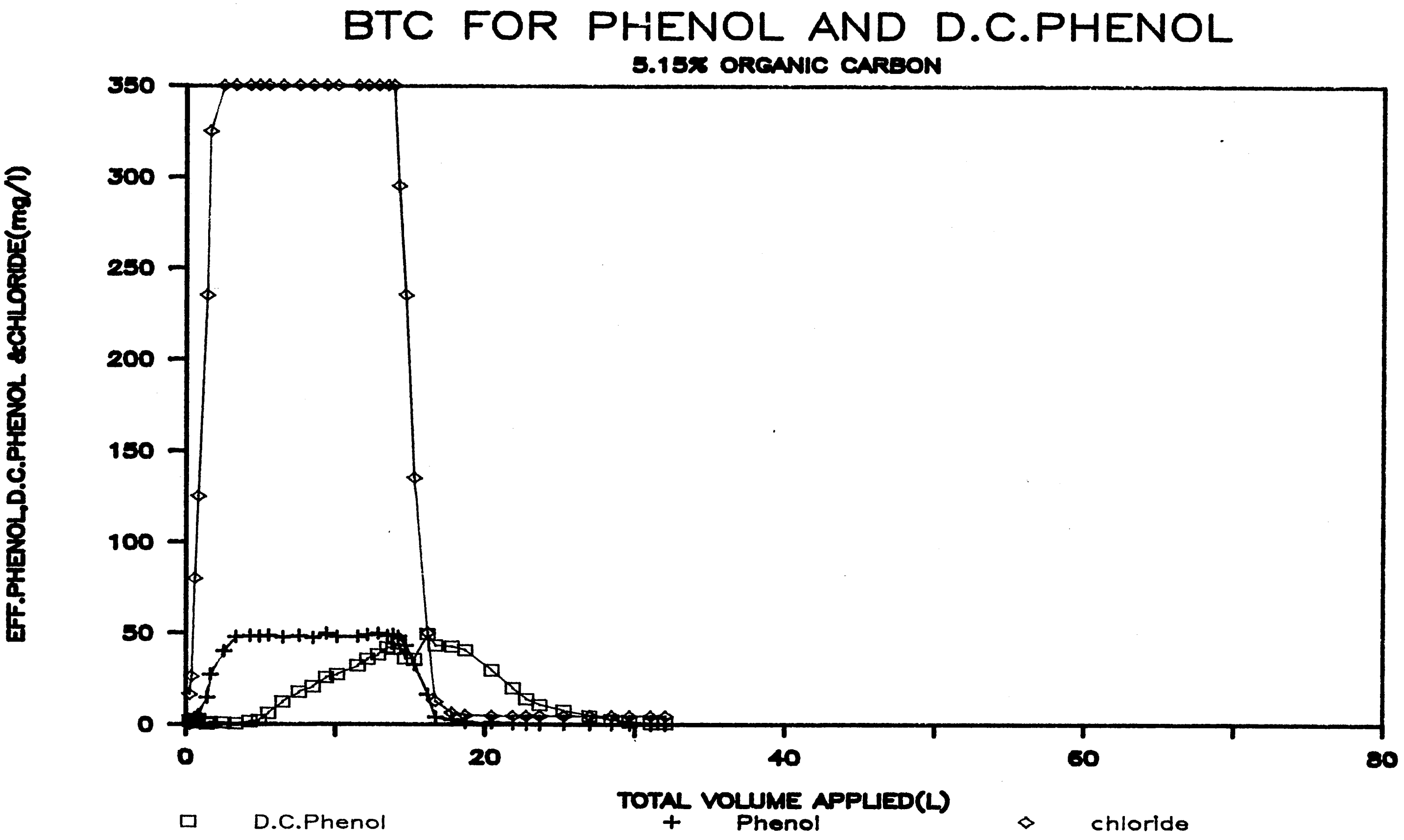


Figure 23. BTC for Phenol, Dichlorophenol and Chloride in Sand With Peat (5.15% Organic Carbon)

and Ogallala sand which contained the same percent or organic carbon as milorganite and sand. This indicates that the type of organic material in a soil has a significant effect on the adsorption of dichlorophenol, but only a slight effect on the adsorption of phenol. Table XV also shows the amount of dichlorophenol residue in sand and milorganite was greater than the dichlorophenol residue in peat and sand.

TABLE XV

EFFECT OF DIFFERENT TYPES OF ORGANIC MATERIAL IN SOIL ON ADSORPTION

Adsorbent	Organic Carbon (%)	Adsorbate	Amount of µg/g	Residue µg/g
9% Milorganite and 91% Sand	5.68	Phenol	55	<DL
		Dichlor.	708.6	96
8% Peat and 92% Sand	5.15	Phenol	no adsorp.	<DL
		Dichlor.	471.0	61

3. The Effect of Missible Solvent on the Adsorption of 2,4-dichlorophenol, 2,4-dinitrophenol and 2,4,6-trichlorophenol

It is also important to know the effect of missible solvent on contamination transport. This study was accomplished by pumping a 35% solution of ethyl alcohol with a 65% solution of distilled water and phenolic compound; a 100% solution of ethyl alcohol and phenolic compound; a solution of distilled water and phenolic compound into three columns, the soil mixture and properties of which are shown in Table XVI. It can be seen that the adsorbent contained 2% Kaolin clay, 3% milorganite and 95% Ogallala sand for all three columns. It is important to note that these columns had almost the same weight, porosity, hydraulic conductivity and organic carbon. The effluent chloride, 2,4-dichlorophenol, 2,4-dinitrophenol and 2,4,6-trichlorophenol concentrations are given in Appendix E. The breakthrough curves for the mixture of 2,4-dichlorophenol, 2,4-dinitrophenol and 2,4,6-trichlorophenol when present with water are shown in Figure 24. This figure shows that the volume required for chloride to reach its maximum value in the effluent was about 1.6 liters, but the volume required for dinitrophenol, 2,4,6-trichlorophenol and 2,4-dichlorophenol to reach breakthrough were 3, 10, and 12 liters, respectively. This means that dinitrophenol was not moving much more rapidly than chloride through the column, but

TABLE XVI

SOIL PROPERTIES FOR MISSIBLE SOLVENT STUDY

Adsorbent	Weight	Flow Rate (gpd/ft^2) (ml/hr)	Porosity (%)	Hydraulic Conductivity (cm/hr)	Specific Gravity	Organic Carbon (%)
2% Kaolin clay Milorganite 95% sand	1984.5	8.1 (70)	49	1.1	2.6	2.6
2% Kaolin clay 3% Milorganite 95% sand (35% alcohol) (65% water)	1984	7.73 (67)	51	1.2	2.6	2.42
2% Kaolin clay 3% Milorganite 95% sand 100% alcohol	1975.5	7.50 (65)	52	1.34	2.6	2.83

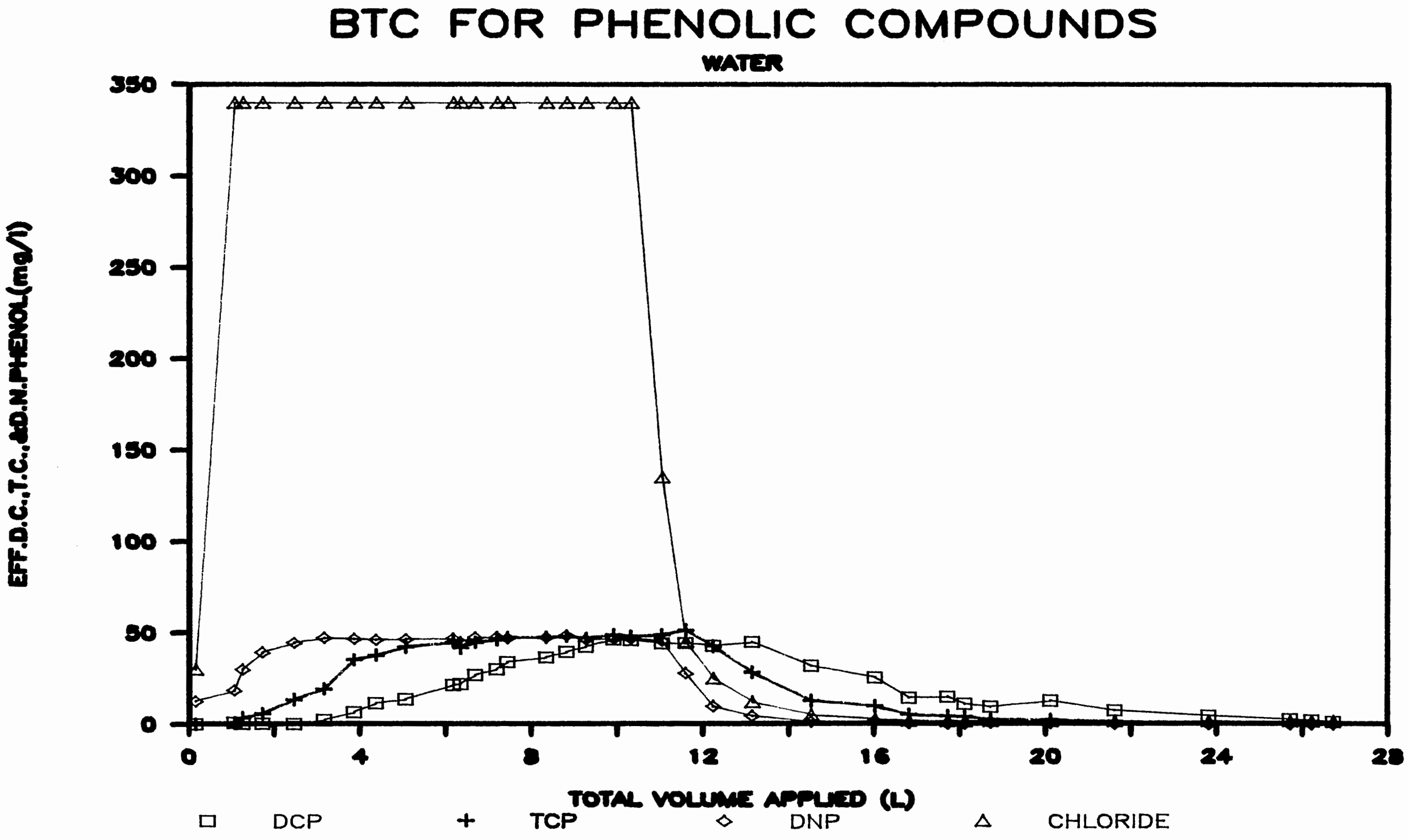


Figure 24. BTC for Phenolic Compounds and Chloride in Sand With 2% Kaolin Clay and 3% Milorganite (Water)

dichlorophenol and trichlorophenol were moving much slower than chloride and dinitrophenol. Figure 24 also indicates that when the system converted to distilled water, chloride and dinitrophenol were diluted out much more rapidly than trichlorophenol and dichlorophenol.

The breakthrough curve for dichlorophenol, dinitrophenol and trichlorophenol when present in a mixture of 35% ethyl alcohol and 65% distilled water, is shown in Figure 25. It is seen that the volume required for chloride and dinitrophenol to reach breakthrough was about two liters. In other words, in this column, dinitrophenol moved as rapidly as chloride moved through the column. The volumes needed for trichlorophenol and dichlorophenol to reach breakthrough were about five and six liters, respectively. This figure also shows that the volume of distilled water needed to wash out chloride and dinitrophenol were identical, but it takes longer to observe no detection of trichlorophenol and dichlorophenol in the effluent. The breakthrough for these compounds when the solvent was ethyl alcohol is shown in Figure 26. It is interesting to note that in this column dinitrophenol, trichlorophenol and dichlorophenol behaved similarly. They reached breakthrough at almost the same time. The effect of missible solvent (ethyl alcohol) in adsorption of phenolic compound is shown in Table XVII. This research shows that the adsorption expressed in μg per gram of soil decreased significantly with an increased volume fraction of solvent in the aqueous solution.

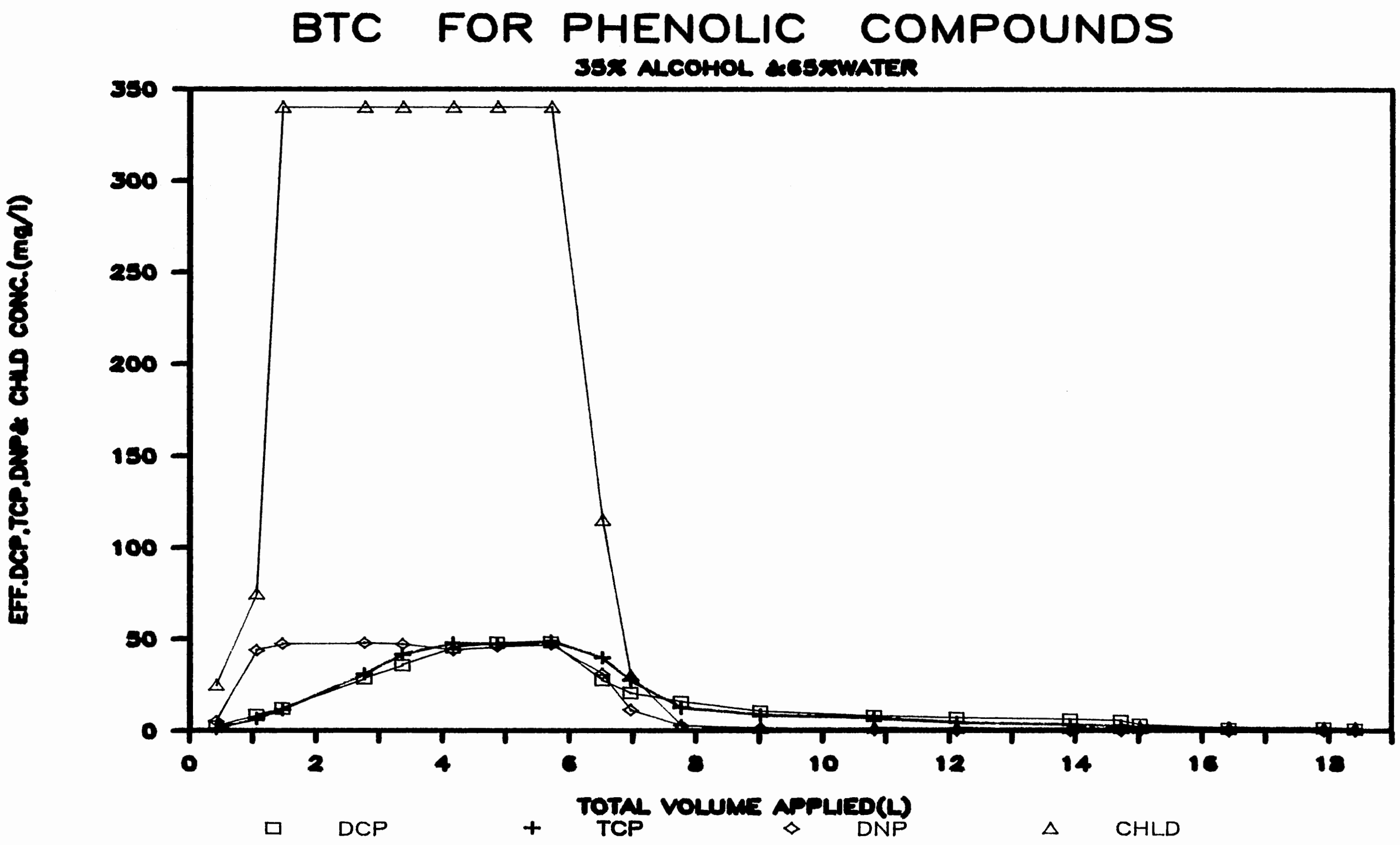


Figure 25. BTC for Phenolic Compounds in Alcohol/Water Mixture and Chloride in Sand With 2% Kaolin Clay and 3% Milorganite

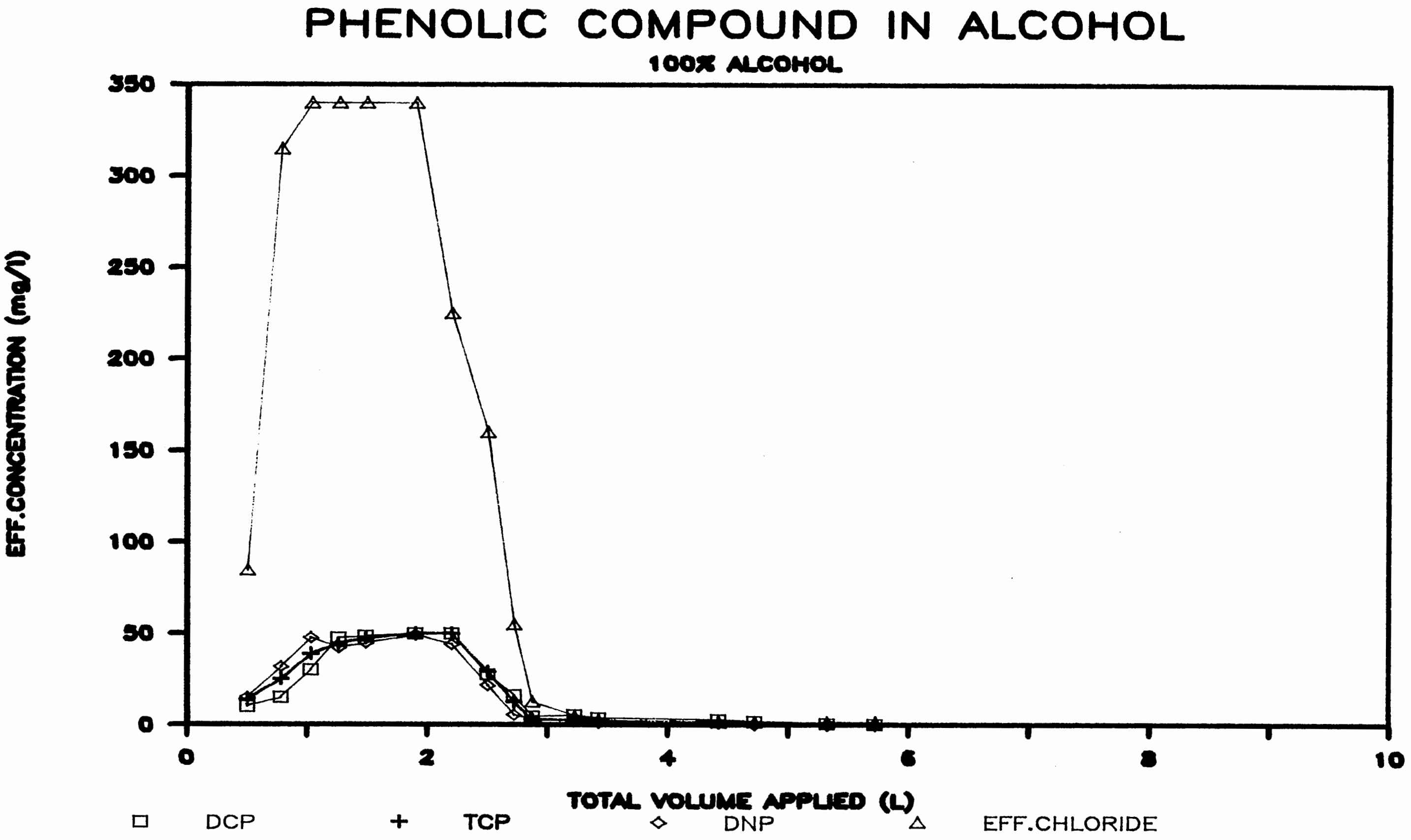


Figure 26. BTC for Phenolic Compounds in Alcohol and Chloride in Sand With 2% Kaolin Clay and 3% Milorganite

TABLE XVII

EFFECT OF MISSIBLE SOLVENT ON ADSORPTION

Adsorbent	Adsorbate	Solvent	Amt.sorb. (μg/g)
2% Clay, 95% Sand + 3% Milorganite	dichlorophenol		231.58
	trichlorophenol	water	191.4
	dinitrophenol		51.0
2% Clay, 95% Sand + 3% Milorganite	dichlorophenol	35% aclohol + 65% water	112.0
	trichlorophenol		91.77
	dinitrophenol		none
2% Clay, 95% Sand + 3% Milorganite	dichlorophenol		32.0
	trichlorophenol	alcohol	18.0
	dinitrophenol		none

CHAPTER V

DISCUSSION

The results previously presented indicate that soil organic content, soil clay content, and nature of the solvent are vitally important in the movement of phenolic compounds through a saturated soil. The results also indicate that a substituted phenol such as 2,4-dichlorophenol moved much slower through the soil columns than did phenol. This may be attributed to 1) water solubility of 2,4-dichlorophenol, or 2) H-bond formation of dichlorophenol with H-bonding sites on clay and organic matter.

1) Phenol has a water solubility of 93,000 mg/l, while 2,4-dichlorophenol has a water solubility of 4,000 mg/l. Introduction of Cl groups to phenol decreased the water solubility from 93,000 mg/l to 4,000 mg/l. Water solubility has an important role in solute-solvent interactions. Decrease of water solubility causes the solute-solvent relationship to weaken, and hence influence adsorption. 2) The H-bond formation between the phenolic hydroxyl and H-bonding sites on clay and organic matter surfaces can be effected by the addition of the (Cl) group to phenol. The (Cl) group has electron-donating ability if it is in a position of 2,4. These groups in a position of 2,4 increased the basicity of

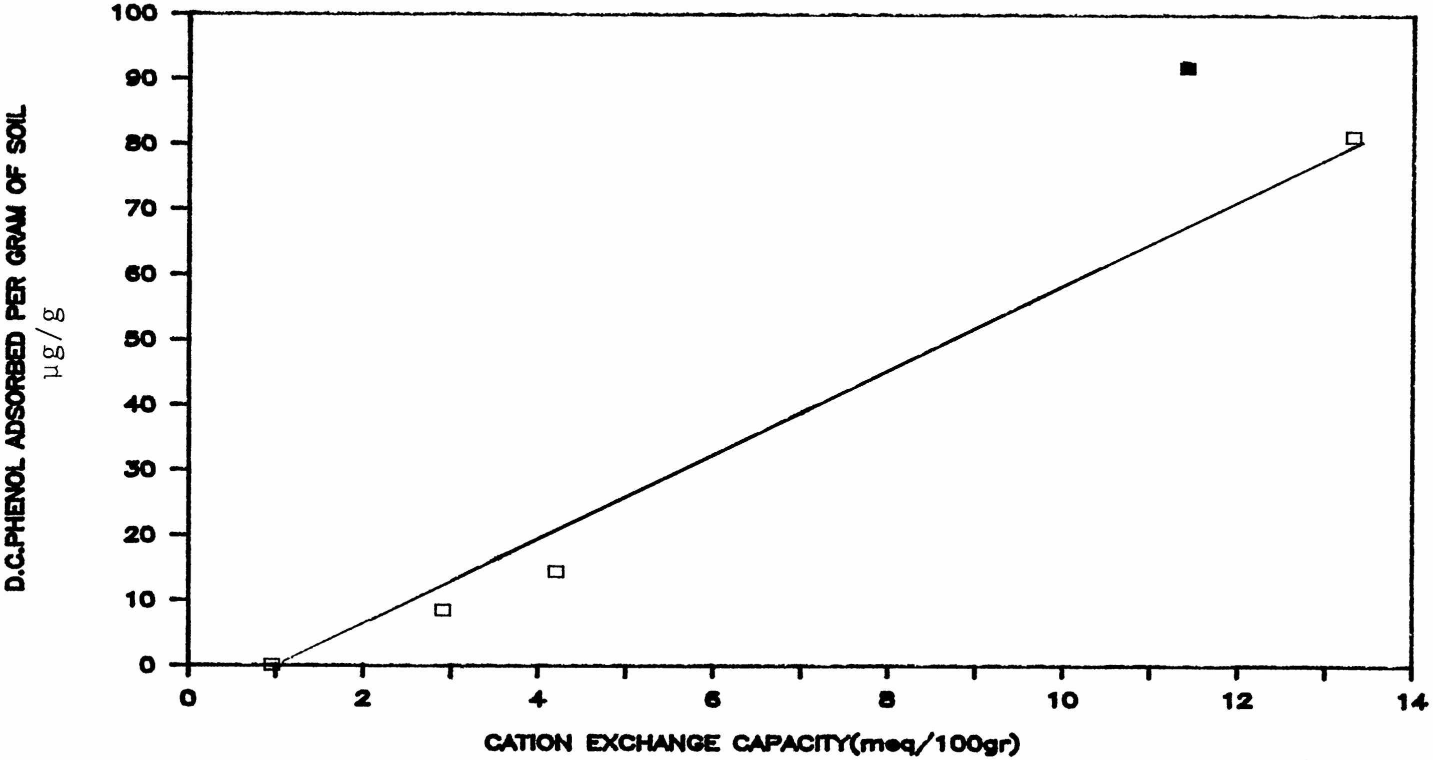
phenolic-OH and thereby enhanced its ability to H-bond by acting as a proton acceptor (electron donor). This can be another reason for the difference in adsorption behavior of phenol and dichlorophenol which was observed during the study. This agrees with the work reported by Boyd (54) who found that increasing the degree of chlorination resulted in increased adsorption.

The Effect of Soil Clay Content on Adsorption on Phenol and 2,4-dichlorophenol

The results presented in Table VI indicate that Ogallala sand had no affinity for phenol and dichlorophenol. They behaved the same as a tracer through the column. It also shows that the addition of Kaolin clay and Ca-montmorillonite clay increased the cation exchange capacity an decreased the hydraulic conductivity of the Ogallala sand. It is interesting to note that decreasing hydraulic conductivity and increasing cation exchange capacity provided by the addition of different percentages and types of clay to Ogallala sand had no effect on adsorption and desorption of phenol. In other words, the factor that was controlling the movement of phenol in Ogallala sand which contained different amounts and types of clay was dispersion, not adsorption. This result agrees with the laboratory column study done by Ahlert (50) for aquifer soil with low organic carbon and 6% clay, and indicated no adsorption for phenol by that particular soil.

The results shown in Table VI show that decreasing hydraulic conductivity and increasing cation exchange capacity of Ogallala sand by the addition of different amounts and types of clay influence the adsorption of 2,4-dichlorophenol. Figure 27 shows the amount of 2,4-dichlorophenol adsorbed per gram of soil containing Kaolin and Ca-montmorillonite clay was correlated with the cation exchange capacity of the soil with a correlation coefficient of .97. The correlation coefficient can be increased to .99 if we do not consider Ca-mortmorillonite data on regression analysis. This means the type of clay had an effect on the relation of cation exchange capacity on the soil and adsorption of 2,4-dichlorophenol. Table VI also shows the Ogallala sand containing 5% Ca-montmorillonite clay adsorbed more 2,4-dichlorophenol than did the Ogallala sand containing 8% Kaolin clay. This indicates that the type of clay had an effect on adsorption of 2,4-dichlorophenol because the type of clay influenced cation exchange capacity and hydraulic conductivity of the soil. This result, even though it agrees with the work of Helling (39) and Weber (67), who found that the adsorption of pesticides is highly correlated with soil cation exchange capacity and soil clay content, it also indicates that the type of clay needs to be considered in the movement of organic contaminants on the static soil water system.

Desorption of 2,4-dichlorophenol was not completely reversible, because when the input of dichlorophenol to the



☐ = Kaolin Clay ■ = Ca-montmorillonite

Figure 27. A Plot of Dichlorophenol Adsorbed per Gram of Soil vs Soil Cation Exchange Capacity

columns was discontinued and only distilled water was pumped to the system, dichlorophenol moved as a cloud or enclave through the system. This means that the dichlorophenol diluted out as time went on. If the partitioning reaction were completely reversible, all the dichlorophenol would be eventually desorbed from the system. However, data presented in Table VII shows that dichlorophenol residue (the amount of 2,4-dichlorophenol left in the soil after no detection of dichlorophenol in the soil's effluent was observed) increased with increasing clay content of the mixture. This makes cleaning the aquifer costly and difficult, because for a complete cleaning of the aquifer that is contaminated with dichlorophenol, hot water or another solvent would needs to be used. This means extra cost for the cleanup.

Effect of Organic Content of Soil on Adsorption of Phenol and 2,4-dichlorophenol

The role of soil organic matter in the adsorption of phenol and 2,4-dichlorophenol is shown in Table IX. Increasing the amount of organic content of the soil changed its adsorption capacity for dichlorophenol significantly, but had no effect on the adsorption of phenol. Phenol moved through the columns as rapidly as did chloride. This indicated mechanical dispersion or molecular diffusion controlled the movement of phenol through the saturated soil.

A plot of dichlorophenol adsorbed per gram of soil versus percentage of soil organic carbon in Figure 28 shows

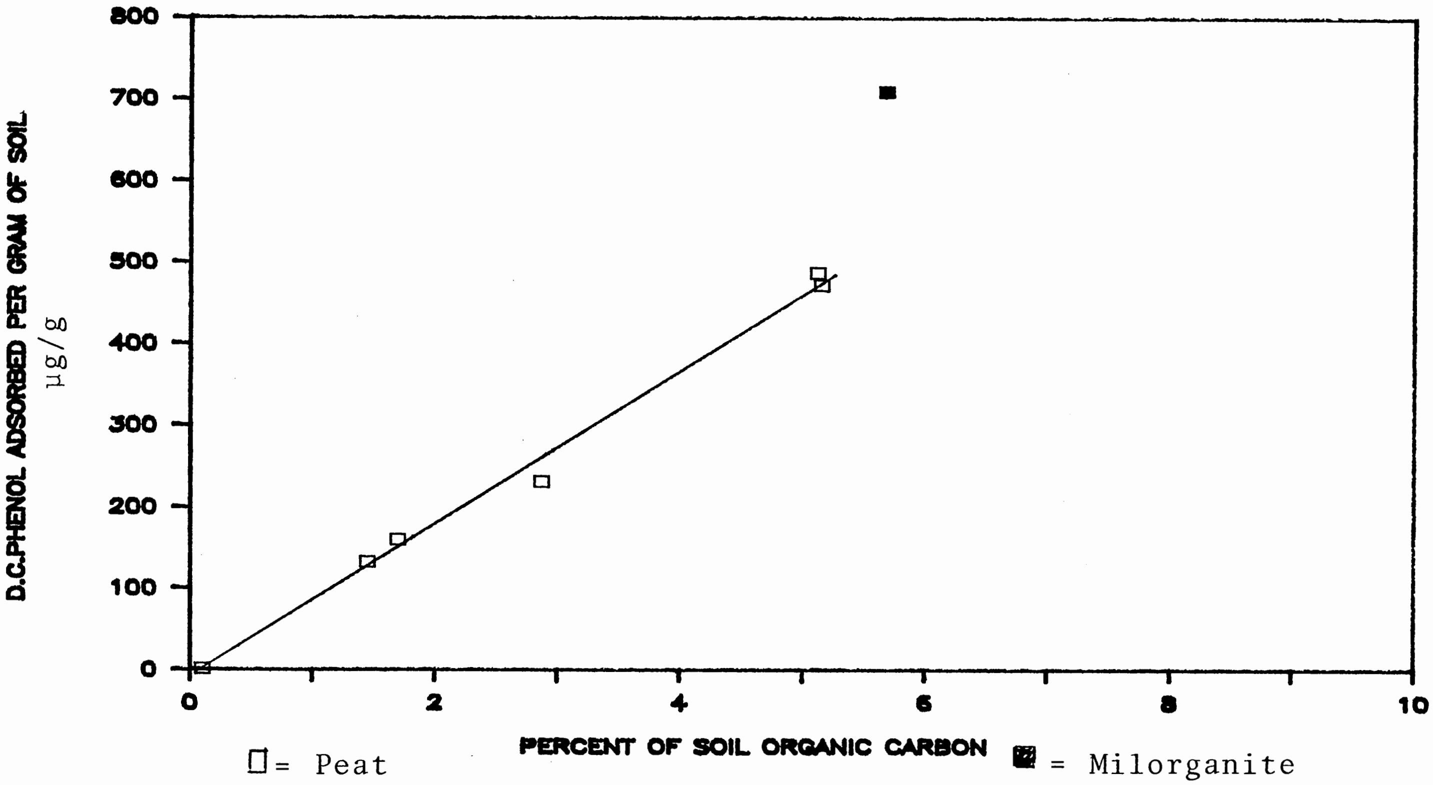


Figure 28. A Plot of Dichlorophenol Adsorbed per Gram of Soil versus Percent of Soil Organic Carbon

that the adsorption of 2,4-dichlorophenol was highly correlated with soil organic carbon with a correlation coefficient of 0.99. This would agree with work reported by Chiou (32), Means (30), and Karickoff (29), who found excellent relationships for adsorption of hydrophobic compounds with soil organic carbon and developed a semi-empirical method for estimating the adsorption of hydrophobic compounds. Using their method and having the percentage of soil organic carbon and organic compound octonal water/partition coefficient, the adsorption of organic compound can be predicted. However, the results presented in Table XV show that not the amount of organic carbon but the type of organic matter has an influence on adsorption. The results in Table XV show the mixture of milorganite (sewage sludge) and Ogallala sand adsorbed 2,4-dichlorophenol and phenol in a much greater capacity than did a mixture of sand and peat with almost the same amount of organic carbon. This difference is due to the nature of these two natural organic sources.

The apparent molecular distribution of peat and milorganite humic substance indicates that milorganite humic substance had a variety of molecular size fractions ranging from 1,000 to 10,000 MW, while peat humic substance consisted of molecules in the range of 5,000 to 10,000. The E_4/E_6ratio of milorganite indicates a low degree of aromatic condensation and a greater presence of aliphatic structure, while E_4/E_6 ratio of peat indicates a high degree of aromatic condensation and a small portion of aliphatic structure. Finally, the gross chemical analysis of peat and milorganite indicates that they are different in nature, so any prediction of adsorption based only on the percentage of soil organic carbon cannot set experimental data in dynamic soil-water systems. Based on the magnitude of soil organic carbon, there should have been the same amount of adsorption for dichlorophenol and phenol by these two solids (sand and milorganite, sand and peat), but the results show that milorganite and sand adsorbed almost twice as much dichlorophenol as did the mixture of peat and sand with the same amount of organic carbon. The mixture of sand and milorganite also adsorbed some phenol, while sand and peat had no affinity for phenol. It is important to consider not only the quantity of organic carbon, but also the quality of organic carbon such as molecular size, aliphatic portion and aromatic portion of each fraction of soil such as fats, polysaccharides, etc. which influence the adsorption of dichlorophenol and phenol. To assess the adsorptive behavior of organic contents and to appreciate the effect of each fraction of organic content such as fats, resins, and proteins on the adsorption of phenolic compounds, more study is needed. The difference in behavior on the movement of phenol and 2,4-dichlorophenol through milorganite and sand resulted in different molecular size and aliphatic portions of milorganite humic substance.

2,4-dichlorophenol and 2,4,6-trichlorophenol are important because they can be produced during the degradation of some pesticides such as 2,4-dichlorophenoxyacetic. Movement of 2,4-dichlorophenoxyacetic in a subsurface environment can be considered with its degradation to 2,4 dichlorophenol. If 2,4D degraded to 2,4-dichlorophenol in a soil, the type and amount of organic content of the soil needs to be considered for the movement of dichlorophenol. Influence of organic and clay content of the soil needs to be taken into account in modeling of organic contaminate movement in a subsurface environment. Prediction based only on soil organic carbon and compound octonal partition coefficient or compound water solubility sometimes cannot fit the field or experimental data.

Desorption of dichlorophenol took place when the input of dichlorophenol to the columns was discontinued and the columns were washed with distilled water. However, dichlorophenol diluted out as time went on and the volume of water needed for cleaning to the extent that there was no detection of chlorophenol in the effluent was observed to increase with increasing percent of soil organic carbon. The amount of dichlorophenol left in the soil (residue) versus the percent of soil organic carbon is shown in Figure 29. This figure shows the amount of 2,4-dichlorophenol left in the soil was correlated with the percentage of organic carbon in the soil. The correlation coefficient was .98. This is very important from the standpoint of cleaning the aquifer contaminated with dichlorophenol. The cleanup will be costly and difficult if the aquifer media has more organic carbon.

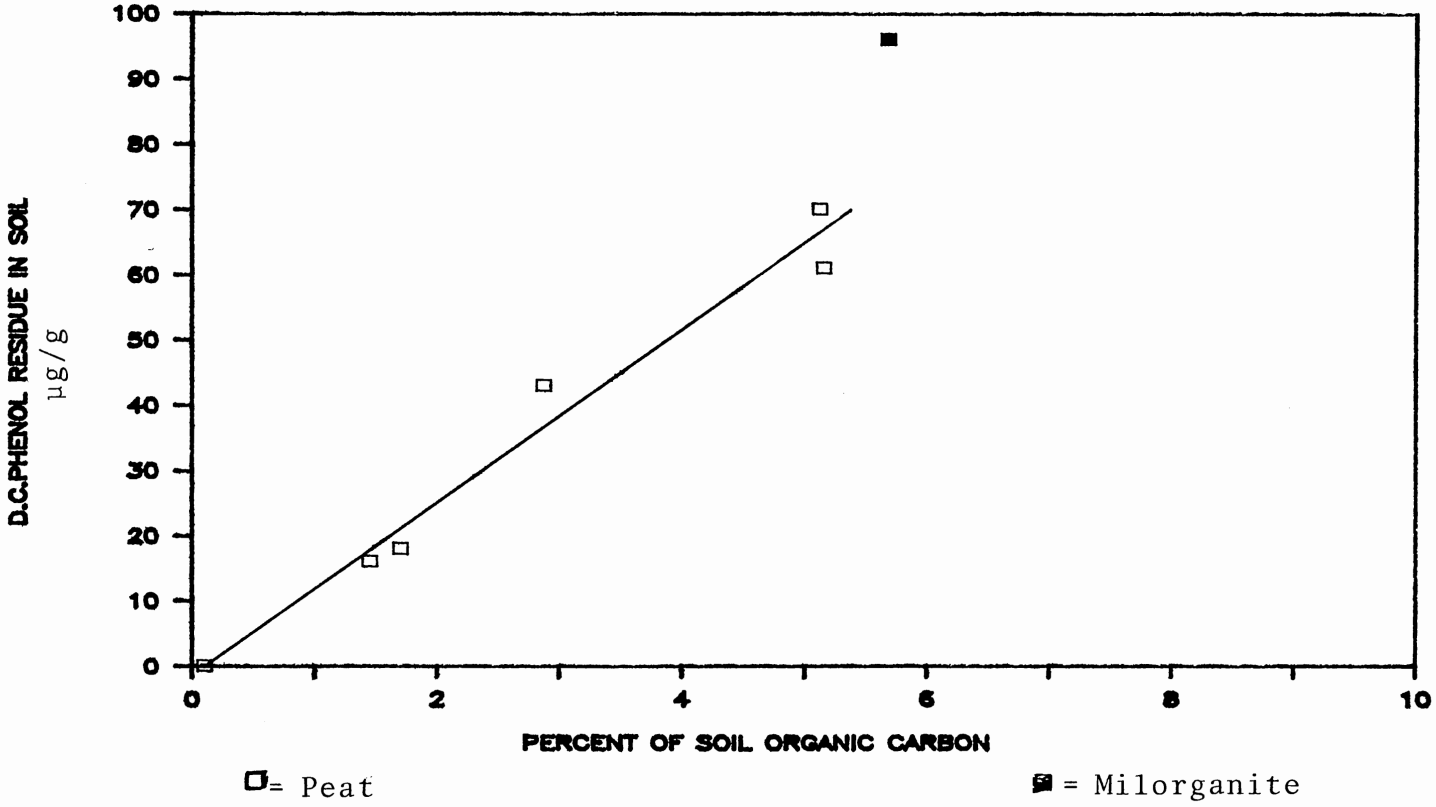


Figure 29. A Plot of Dichlorophenol Residue per Gram of Soil versus Percent of Soil Organic Carbon

Comparison of Soil Clay and Organic Content on Adsorption of 2,4-dichlorophenol and Phenol

The results presented in Table VI and Table IX indicate that increasing the clay content and organic content of Ogallala sand did not affect the adsorption of phenol. It also shows the amount of dichlorophenol adsorbed per gram of soil containing Ogallala sand and organic matter was much greater than was the amount of dichlorophenol adsorbed per gram of soil containing Ogallala sand and Kaolin or Ca-montmorillonite clay. Even though the hydraulic conductivity of the sand and clay mixture was much slower than was the hydraulic conductivity of a mixture of peat and sand, but it did not affect the adsorption of dichlorophenol as much as did the organic content. It is interesting to note that the amount of dichlorophenol adsorbed per gram of soil with 2% organic carbon was twice that of a soil with 16% Kaolin clay and 5% Ca-montmorillonite clay. The conclusion can be drawn that soil organic content played a more important role that did soil clay content on the adsorption of 2,4-dichlorophenol.

Effect of Missible Solvent on Adsorption of Phenolic Compound

The results presented in Table XVI are important in assessing a near source contaminant transport in soil in the event of spillage or discharge of phenolic compound waste containing water-soluble solvent. This provided important information regarding the sorption of solute into a soil system containing greater or lesser amounts of missible solvent. It was observed that adsorption decreased significantly with increasing fraction of organic solvent in the aqueous solution. This result can be explained because of increasing of solubility with an increasing volume fraction of solvent in water. Fu and Luthy (45) pointed out that the aromatic compound solubility in a solvent water system generally increases semi-logarithmically with an increase of volume fraction of solvent. This relationship can be shown in a semi-logarithmic plot for the amount of dichlorophenol and trichlorophenol adsorbed per gram of soil versus the volume fraction of solvent in Figure 30 . This shows that the adsorption of dichlorophenol and trichlorophenol decreases semi-logarithmically with an increasing volume fraction of organic solvent. This means increasing the fraction of organic solvent results in an exponential decrease in sorption which, in turn, leads to enhanced solute mobility. This result agrees with the work of Rao and Hornsby (68), who studied the influence of organic cosolvent in leaching of pesticides through soils, and indicates that increasing of methanol results in a significant decrease in sorption.

The influence of organic missible solvent is an important factor for application and developing of an adsorption model or contamination transport model. The modeler

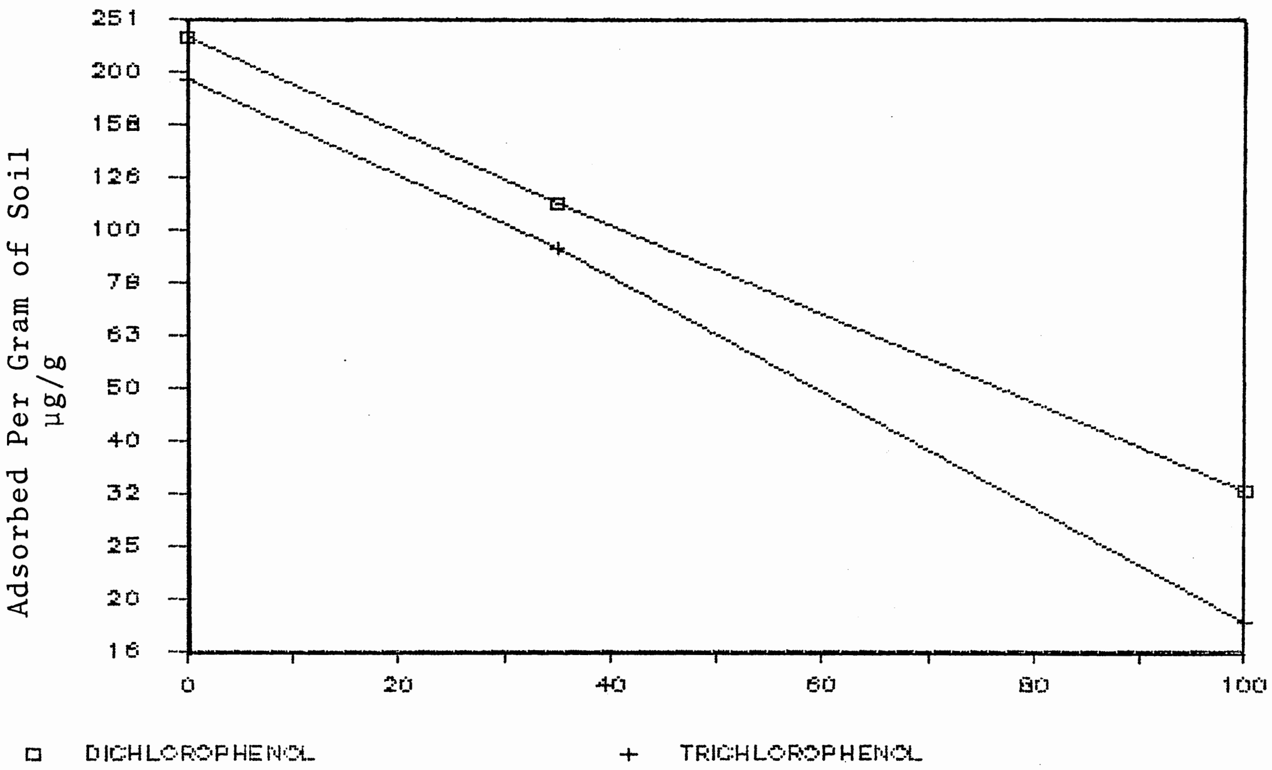


Figure 30. A Semilog Plot of Dichlorophenol and Trichlorophenol Adsorbed per Gram of Soil versus Volume Fraction of Solvent (Alcohol)

should be aware of all factors such as organic matter quality and quantity, characteristics of the liquid phase or solvent, clay content of the soil and finally, chemical and physical properties of the compound.

CHAPTER VI

CONCLUSION

Based on the experimental evidence presented, the following conclusions can be drawn:

1. From the study, it was found that the Ogallala aquifer sand had no affinity for phenol and 2,4-dichlorophenol. The factor controlling the movement of these compounds was dispersion, not adsorption.

2. Decreasing hydraulic conductivity or increasing cation exchange capacity of Ogallala sand, which is provided by the addition of different amounts and types of clay, had no influence on the adsorption of phenol. However, the clay content and type of clay was effective on the movement of 2,4-dichlorophenol.

3. The 2,4-dichlorophenol residue (dichlorophenol) left in the soil after cleaning the columns with distilled water, increased with increasing clay content of the soil.

4. Addition of natural organic matter (peat and milorganite) to the Ogallala sand resulted in increased organic content and porosity. The increasing organic content and porosity had no effect on the movement of phenol. Adsorption of 2,4-dichlorophenol was highly correlated with

the percentage of soil organic carbon.

5. The amount of 2,4-dichlorophenol residue in the soil was highly correlated with the amount of soil organic content.

6. The soil organic content played a more important role in the adsorption of 2,4-dichlorophenol than did soil clay content.

7. The quality and nature of organic matter such as the degree of condensation of the aromatic carbon network, portions of aliphatic structure and molecular distribution, were influential in the adsorption of phenol and dichlorophenol.

8. Adsorption of 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 2,4-dinitrophenol deceased significantly with an increase in the volume fraction of organic missible solvent in the aqueous solution.

CHAPTER VII

SUGGESTIONS FOR FURTHER STUDY

Based on the findings of this study, the following suggestions for future study are made:

1. Study the effect of soil properties such as clay content, organic content, and surface area similar to this study for aromatic hydrocarbons.

2. Study the effect of unsterilized soil properties similar to this study on adsorption of phenolic compounds.

3. The effect of soil organic content structure such as molecular weight, aliphatic and aromatic portions of organic matter on the adsorption of organic compounds need to be fully investigated.

4. The effect of soil cation exchange capacity and hydraulic conductivity on adsorption of phenol and dichlorophenol needs to be fully investigated.

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APPENDIX A

BTC DATA FOR PHENOL, DICHLOROPHENOL AND CHLORIDE IN SOIL WITH DIFFERENT CATION EXCHANGE CAPACITY

TABLE XVIII

BTC DATA FOR 2,4-DICHLOROPHENOL IN OGALLALA SAND
(CEC .95 meq/100 gr)

TOT.VOL. (L)	EFF.D.C.PHENOL mg/l	EFF.CHLORIDE mg/l
0.40	10.50	80.00
0.90	30.40	255.00
1.20	46.20	330.00
1.55	48.70	350.00
1.75	46.87	345.00
2.05	26.90	153.00
2.50	4.60	18.00
2.90	1.00	10.00
3.90	0.75	6.50
4.90	0.56	2.90
5.50	0.35	2.50
6.50	0.59	2.50
7.00	<DL	2.50

TABLE XIX

BTC DATA FOR PHENOL IN OGALLALA SAND
(CEC .95 meq/100 gr)

TOT.VOL. (L)	EFF.PHENOL mg/l	EFF.CHLORIDE mg/l
0.30	11.30	35.00
0.52	20.62	150.00
0.82	33.20	270.00
1.00	49.40	350.00
1.20	48.78	350.00
1.50	48.14	345.00
1.90	18.75	190.00
2.30	3.10	30.00
2.64	0.56	10.00
3.14	0.31	5.00
3.65	0.10	2.50
4.50	<DL	2.50

TABLE XX

BTC DATA FOR D. C. PHENOL IN SAND & CLAY (CEC 2.9 meq/ 100 gr)

TOT.VOL. (L)	EFF.D.C.PHENOL mg/l	EFF.CHLORIDE mg/l
0.30	5.50	50.00
0.60	21.30	255.00
1.12	33.70	325.00
1.70	41.50	350.00
1.90	44.70	350.00
2.30	43.30	320.00
2.77	10.00	45.00
3.00	5.20	20.00
3.60	2.66	15.00
4.40	1.30	3.00
5.20	0.66	2.70
5.70	0.76	2.50
6.30	0.50	2.50
6.70	0.18	2.50
7.50	<DL	2.50

TABLE XXI

BTC DATA FOR PHENOL IN SAND & CLAY (CEC 2.9 meq/100 gr)

TOT.VOL. (L)	EFF.PHENOL mg/l	EFF.CHLORIDE mg/l
0.50	6.25	160.00
0.70	28.75	255.00
0.96	48.12	325.00
1.50	48.26	350.00
1.80	50.00	340.00
2.10	24.00	100.00
2.60	6.33	25.00
3.00	0.61	4.50
3.50	0.16	3.00
4.00	0.10	2.50
4.50	<DL	2.50

TABLE XXII

BTC DATA FOR D. C. PHENOL IN SAND & CLAY (CEC 4.2 meq/100 gr)

TOT.VOL. (L)	EFF.D.C.PHENOL mg/l	EFF.CHLORIDE mg/l
0.41	3.57	55.00
0.98	23.00	300.00
1.35	35.30	337.00
1.75	40.00	350.00
2.15	44.00	350.00
2.55	43.30	335.00
2.80	21.20	128.00
3.25	5.50	30.00
3.70	3.00	10.00
4.40	1.33	3.50
4.80	1.30	2.50
5.30	0.66	2.50
5.80	0.57	2.50
6.60	0.48	2.50
7.40	0.50	2.50
7.90	0.34	2.50
8.50	0.17	2.50
9.20	<DL	2.50

TABLE XXIII

BTC DATA FOR D. C. PHENOL IN SAND & CLAY
(CEC 13.3 meq/100 gr)

TOT.VOL. (L)	EFF.D.C.PHENOL mg/l	EFF.CHLORIDE mg/l
0.38	8.50	25.00
0.75	16.30	280.00
1.30	25.60	335.00
1.90	18.60	350.00
2.60	27.00	350.00
3.10	33.40	350.00
3.70	38.50	350.00
4.10	44.30	350.00
4.50	44.00	345.00
4.90	39.80	160.00
5.20	23.20	35.00
5.60	16.70	7.50
6.00	12.50	3.00
6.35	5.00	2.50
6.70	3.75	2.50
7.10	1.33	2.50
7.90	1.12	2.50
8.60	1.11	2.50
9.60	1.00	2.50
10.60	0.95	2.50
11.50	0.90	2.50
12.00	1.85	2.50
13.50	<DL	2.50

TABLE XXIV

BTC FOR PHENOL IN SAND & CLAY (CEC 13.3 meq/100 gr)

TOT. VOL. (L)	EFF.PHENOL mg/l	EFF.CHLORIDE mg/l
0.36	1.80	15.00
0.48	4.06	80.00
0.61	21.88	185.00
0.85	39.37	300.00
1.01	42.50	336.00
1.51	45.80	350.00
1.71	48.70	345.00
2.06	47.90	260.00
2.23	35.45	120.00
2.38	15.62	20.00
2.73	3.12	4.50
3.18	1.60	2.75
3.38	0.62	3.00
3.88	0.57	2.50
4.18	0.50	2.50
5.00	0.20	2.70
6.20	0.10	2.50
7.20	<DL	2.50

TABLE XXV

BTC DATA FOR PHENOL AND D. C. PHENOL IN SOIL (CEC 11.4 meq/100 gr)

TOT.VOL. (L)	EFF.PHENOL mg/l	EFF.D.C.PHENOL mg/l	EFF.CHLORIDE mg/l
0.35	0.00	0.00	20.00
0.55	7.34	0.00	150.00
0.77	15.12	11.25	300.00
1.12	45.30	15.56	340.00
1.62	47.50	24.70	345.00
1.95	48.87	27.00	345.00
2.41	47.00	29.00	345.00
3.11	47.50	34.11	345.00
3.56	48.00	35.20	345.00
3.96	48.90	40.34	345.00
4.36	48.00	43.10	345.00
4.67	47.90	46.30	345.00
5.56	18.50	38.47	100.00
5.96	11.37	27.63	40.00
6.56	4.25	15.50	4.50
7.26	2.56	12.25	2.50
8.01	2.22	10.37	2.50
8.71	1.12	6.25	1.75
9.31	1.00	2.50	2.50
9.81	0.92	1.25	2.50
10.31	0.23	1.18	2.50
10.61	0.10	0.80	2.50
11.00	<DL	0.40	2.50
11.50	<DL	<DL	2.50

APPENDIX B

BTC DATA FOR PHENOL, DICHLOROPHENOL AND CHLORIDE IN SOIL WITH DIFFERENT PERCENT OF ORGANIC CARBON

TABLE XXVI

BTC DATA FOR D. C. PHENOL IN SAND WITH PEAT (1.45% ORGANIC CARBON)

TOT.VOL. (L)	EFF.D.C.PHENOL mg/l	EFF.CHLORIDE mg/l
0.25	0.00	27.00
0.50	0.00	178.00
0.68	0.00	185.00
1.37	0.00	350.00
1.60	0.00	357.00
1.94	1.87	360.00
2.34	6.25	352.00
2.64	9.37	35.00
3.44	21.09	355.00
4.19	29.68	359.00
5.03	37.50	360.00
5.68	43.18	358.00
5.98	42.50	340.00
6.48	40.10	200.00
6.98	35.93	37.00
7.58	38.20	10.00
8.21	28.30	5.90
8.96	15.60	3.50
9.72	11.30	2.50
11.10	7.03	2.50
13.30	2.10	3.00
14.10	1.50	2.00
14.70	0.80	2.00
15.10	0.71	2.50
15.65	0.55	2.50
17.00	<DL	2.50

TABLE XXVII

BTC DATA FOR PHENOL IN SAND WITH PEAT (1.3% ORGANIC CARBON)

TOT.VOL. (L)	EFF.PHENOL mg/l	EFF.CHLORIDE mg/l
0.30	1.25	60.00
0.50	8.71	160.00
0.90	31.19	310.00
1.40	40.20	360.00
1.70	47.56	360.00
2.00	47.34	145.00
2.70	24.30	20.00
3.10	3.65	10.00
3.60	1.52	6.50
3.90	0.55	5.00
4.40	0.12	5.00
4.70	0.13	6.10
5.00	0.21	4.50
6.00	0.10	3.50
7.00	0.15	3.50
7.50	0.08	3.50
8.60	<DL	3.50

TABLE XXVIII

BTC DATA FOR D. C. PHENOL IN SAND WITH PEAT (2.8% ORGANIC CARBON)

TOT.VOL. (L)	EFF.D.C.PHENOL mg/l	EFF.CHLORIDE mg/l
0.30	0.00	34.00
0.67	0.00	165.00
0.93	0.00	260.00
1.34	0.00	350.00
1.79	0.13	355.00
2.25	0.00	360.00
2.78	0.00	360.00
3.44	3.10	360.00
3.69	5.40	355.00
4.09	12.19	360.00
4.89	21.50	357.50
5.59	28.70	350.00
6.44	37.93	360.00
7.62	42.20	355.00
8.20	41.00	357.50
8.60	38.30	335.00
9.60	32.60	26.00
10.80	25.70	15.00
12.60	17.50	10.00
13.71	18.30	5.00
14.70	10.84	5.00
15.90	6.30	3.50
17.40	4.10	2.50
17.90	4.00	3.10
18.75	3.00	2.50
19.35	3.80	2.50
20.05	3.00	2.50
21.05	2.50	2.50
21.65	1.30	2.50
22.65	0.95	2.50
23.65	1.05	2.50
25.05	0.53	2.50
26.00	<DL	2.50

TABLE XXIX

BTC DATA FOR D. C. PHENOL IN SAND WITH PEAT (5.12% ORGANIC CARBON)

TOT.VOL. (L)	EFF.D.C.PHENOL mg/l	EFF.CHLRIDE mg/l
0.38	0.00	14.00
0.51	0.00	50.00
1.00	0.00	220.00
1.41	0.00	358.00
1.83	0.00	362.00
2.32	0.00	364.00
3.45	0.00	361.00
3.66	0.00	363.00
4.19	0.00	358.00
4.75	0.00	355.00
5.15	0.00	357.00
5.65	2.80	360.00
6.55	7.33	360.00
7.53	13.03	360.00
9.33	22.50	355.00
10.68	28.75	359.00
11.71	30.12	355.00
12.43	33.78	355.00
13.63	43.10	355.00
14.18	42.90	330.00
14.85	39.47	45.00
15.67	39.10	20.00
16.57	40.78	10.00
17.57	39.50	7.50
18.67	39.00	5.00
19.57	39.40	3.50
20.37	32.89	3.40
21.97	26.31	3.40
23.22	19.73	3.00
24.52	15.78	3.00
25.52	12.15	2.50
27.52	6.57	2.50
28.72	2.12	2.50
29.92	1.85	2.50
30.92	1.10	3.00
31.77	0.87	3.00
33.27	0.76	2.50
34.07	0.91	2.50
35.07	1.25	2.50
35.97	0.45	2.50
37.50	<DL	2.50

TABLE XXX

BTC DATA FOR PHENOL IN SAND WITH PEAT (4.9% ORGANIC CARBON)

TOT.VOL. (L)	EFF.PHENOL mg/l	EFF.CHLORIDE mg/l
0.20	0.52	15.00
0.35	1.25	30.00
0.56	4.00	85.00
0.80	5.30	120.00
1.30	15.00	240.00
1.70	27.50	320.00
2.00	40.60	340.00
2.50	48.10	345.00
3.20	48.75	350.00
3.70	47.30	350.00
4.20	28.41	135.00
4.75	17.50	50.00
5.75	8.10	10.50
6.50	4.50	5.00
7.00	2.50	2.50
7.40	1.25	2.50
8.00	1.12	2.50
9.00	1.54	2.50
9.30	1.15	2.50
9.80	0.54	2.50
10.50	0.23	2.50
11.60	<DL	2.50

APPENDIX C

BTC DATA FOR CHLORIDE AND MIXTURE OF PHENOL AND DICHLOROPHENOL IN SOIL WITH DIFFERENT PERCENT OF ORGANIC CARBON

TABLE XXXI

BTC DATA FOR D. C. PHENOL AND PHENOL IN SAND WITH PEAT (1.7% ORGANIC CARBON)

TOTAL VOLUME (L)	EFFLUENT D.C.PHEN mg/l	EFFLUENT PHENOL mg/l	EFFLUENT CHLORIDE mg/l
0.13	1.50	1.87	25.70
0.29	2.68	10.62	30.80
0.45	0.90	15.60	97.60
0.69	0.85	18.75	180.00
0.81	0.00	21.56	260.00
1.31	0.91	38.75	342.00
1.59	3.00	44.37	350.00
2.04	5.90	50.00	350.00
2.51	12.50	46.25	350.00
3.33	25.93	47.81	350.00
4.28	32.50	49.37	350.00
4.63	32.80	47.23	350.00
5.02	33.40	48.18	350.00
5.42	34.26	47.18	347.00
6.30	37.80	49.00	350.00
6.82	43.81	49.40	350.00
7.26	42.25	23.18	345.00
7.74	40.12	23.50	150.00
8.02	36.15	6.56	35.00
8.87	37.87	3.12	10.00
9.56	25.80	1.56	6.00
10.32	13.30	0.26	5.50
11.07	8.50	0.93	5.00
11.77	5.26	0.46	5.00
12.52	4.12	0.15	5.00
13.42	2.18	0.46	4.00
13.92	1.56	0.12	4.00
14.92	0.63	0.11	4.00
15.81	1.25	0.10	4.00
16.81	0.96	<DL	4.00
17.82	0.66	<DL	4.00
19.10	<DL	<DL	4.00

TABLE XXXII

BTC DATA FOR D. C. PHENOL AND PHENOL IN SAND WITH PEAT (5.15% ORGANIC CARBON)

TOTAL VOLUME (L)	EFFLUENT D.C.PHE mg/l	EFFLUENT PHENOL mg/l	EFFLUENT CHLORIDE mg/l
0.21	1.87	0.63	16.40
0.34	2.10	1.25	26.20
0.56	3.12	4.00	80.00
0.78	0.93	5.30	125.00
1.36	0.31	15.00	235.00
1.56	1.20	27.50	325.00
2.45	0.92	40.37	350.00
3.25	0.60	48.10	350.00
4.20	1.81	48.76	350.00
4.82	2.40	48.43	350.00
5.44	6.25	49.00	350.00
6.41	12.60	47.85	350.00
7.51	17.90	48.75	350.00
8.43	20.93	47.50	350.00
9.33	25.90	50.10	350.00
10.05	27.50	48.21	350.00
11.45	32.50	48.33	350.00
12.08	35.90	49.30	350.00
12.80	38.50	50.12	350.00
13.40	42.40	48.70	350.00
13.80	41.56	49.50	350.00
14.15	44.37	48.30	295.00
14.61	36.25	43.40	235.00
15.21	35.93	32.80	135.00
16.08	49.80	16.50	50.00
16.61	43.44	4.06	12.50
17.71	42.80	2.50	6.00
18.61	40.93	1.20	5.00
20.41	29.80	1.25	4.50
21.81	20.10	0.53	4.50
22.71	14.12	0.30	4.50
23.61	11.00	0.15	4.50
25.21	7.80	0.15	4.50
26.91	5.00	0.15	4.50
29.60	1.50	0.10	4.50
28.40	2.50	0.12	4.50
31.00	0.88	<DL	4.50
32.00	0.65	<DL	4.50
32.60	<DL	<DL	4.50

APPENDIX D

BTC DATA FOR PHENOL, DICHLOROPHENOL AND CHLORIDE IN SOIL WITH DIFFERENT TYPE OF ORGANIC CARBON

TABLE XXXIII

BTC DATA FOR D. C. PHENOL AND PHENOL IN SAND WITH PEAT (15.15% ORGANIC CARBON)

TOTAL VOLUME (L)	EFFLUENT D.C.PHE mg/l	EFFLUENT PHENOL mg/l	EFFLUENT CHLORIDE mg/l
0.21	1.87	0.63	16.40
0.34	2.10	1.25	26.20
0.56	3.12	4.00	80.00
0.78	0.93	5.30	125.00
1.36	0.31	15.00	235.00
1.56	1.20	27.50	325.00
2.45	0.92	40.37	350.00
3.25	0.60	48.10	350.00
4.20	1.81	48.76	350.00
4.82	2.40	48.43	350.00
5.44	6.25	49.00	350.00
6.41	12.60	47.85	350.00
7.51	17.90	48.75	350.00
8.43	20.93	47.50	350.00
9.33	25.90	50.10	350.00
10.05	27.50	48.21	350.00
11.45	32.50	48.33	350.00
12.08	35.90	49.30	350.00
12.80	38.50	50.12	350.00
13.40	42.40	48.70	350.00
13.80	41.56	49.50	350.00
14.15	44.37	48.30	295.00
14.61	36.25	43.40	235.00
15.21	35.93	32.80	135.00
16.08	49.80	16.50	50.00
16.61	43.44	4.06	12.50
17.71	42.80	2.50	6.00
18.61	40.93	1.20	5.00
20.41	29.80	1.25	4.50
21.81	20.10	0.53	4.50
22.71	14.12	0.30	4.50
23.61	11.00	0.15	4.50
25.21	7.80	0.15	4.50
26.91	5.00	0.15	4.50
29.60	1.50	0.10	4.50
28.40	2.50	0.12	4.50
31.00	0.88	<DL	4.50
32.00	0.65	<DL	4.50
32.60	<DL	<DL	4.50

TABLE XXXIV

BTC DATA FOR PHENOL AND D. C. PHENOL IN SAND WITH MILORGANITE (5.68% ORGANIC CARBON)

TOTAL VOLUME (L)	EFFLUENT D.C.PHEN mg/l	EFFLUENT PHENOL mg/l	EFFLUENT CHLORIDE mg/l
0.48	0.18	1.87	220.00
0.74	0.31	7.50	300.00
1.33	0.12	12.50	340.00
1.93	0.10	23.75	340.00
2.20	0.00	30.00	340.00
2.65	0.00	43.75	340.00
3.20	0.00	49.30	340.00
3.59	0.00	49.30	340.00
4.54	0.00	50.00	340.00
5.54	0.00	50.00	340.00
6.64	0.00	49.70	340.00
7.49	0.00	49.30	340.00
8.49	0.00	50.00	340.00
9.34	0.00	50.00	340.00
9.94	0.00	49.70	340.00
11.04	0.00	49.70	340.00
11.48	0.00	50.00	340.00
12.64	1.89	50.00	340.00
14.39	3.79	50.00	340.00
15.29	5.06	50.00	340.00
16.19	6.32	50.00	340.00
17.64	10.75	49.10	340.00
18.84	15.18	50.00	340.00
21.84	22.15	49.00	340.00
23.04	26.50	50.00	340.00
24.74	31.60	49.20	340.00
25.74	37.90	50.00	340.00
26.94	43.00	50.00	340.00
27.44	46.50	51.50	340.00
27.76	45.30	49.30	340.00
28.44	44.85	37.50	340.00
28.78	46.10	10.50	160.00
29.71	44.30	2.25	30.00
31.10	45.56	1.50	5.00
32.56	45.56	1.20	2.50
34.01	44.30	1.10	1.50
35.31	42.40	1.00	1.50
36.01	48.70	0.82	1.50

TABLE XXXIV (Continued)

TOTAL VOLUME (L)	EFFLUENT D.C.PHEN mg/l	EFFLUENT PHENOL mg/l	EFFLUENT CHLORIDE mg/l
36.96	46.20	0.78	1.50
37.76	47.50	0.51	1.50
38.26	48.80	0.41	1.50
39.06	46.80	0.52	1.50
39.86	40.50	0.41	1.50
41.65	36.70	0.17	1.50
44.25	30.37	0.10	1.50
45.86	25.90	0.10	1.50
47.86	23.40	0.10	1.50
49.86	18.90	<DL	1.50
52.36	17.72	<DL	1.50
53.86	14.55	<DL	1.50
58.36	9.40	<DL	1.50
59.15	8.22	<DL	1.50
59.95	7.20	<DL	1.50
61.35	5.60	<DL	1.50
63.35	5.10	<DL	1.50
65.35	4.40	<DL	1.50
67.00	3.70	<DL	1.50
69.05	2.50	<DL	1.50
70.05	2.40	<DL	1.50
71.00	0.76	<DL	1.50
72.00	<DL	<DL	1.50

APPENDIX E

BTC DATA FOR PHENOLIC COMPOUNDS AND CHLORIDE

TABLE XXXV

BTC DATA FOR PHENOLIC COMPOUNDS AND CHLORIDE (WATER)

TOTAL VOLUME (L)	EFFLUENT D.C.PHE mg/l	EFFLUENT T.C.PHE mg/l	EFFLUENT D.N.PHE mg/l	EFFLUENT CHLORIDE mg/l
0.15	0.00	0.00	12.76	30.00
1.05	0.75	0.57	18.75	340.00
1.25	0.19	3.34	30.12	340.00
1.71	0.10	5.76	39.50	340.00
2.46	0.00	13.46	44.80	340.00
3.16	2.25	19.20	47.50	340.00
3.86	6.50	35.20	47.00	340.00
4.36	11.50	37.80	46.40	340.00
5.06	13.50	42.30	46.80	340.00
6.16	21.50	44.87	47.20	340.00
6.33	22.00	41.60	45.30	340.00
6.68	27.00	44.90	47.80	340.00
7.18	30.10	46.15	47.90	340.00
7.47	34.00	47.50	47.30	340.00
8.33	36.50	47.50	47.75	340.00
8.81	39.50	48.20	48.75	340.00
9.26	42.50	47.00	46.60	340.00
9.91	46.40	48.90	46.98	340.00
10.31	46.00	48.00	47.00	340.00
11.04	44.30	49.00	45.90	135.00
11.59	44.50	51.50	27.85	45.00
12.24	42.80	42.50	9.80	25.00
13.14	45.00	28.15	4.50	12.00
14.51	31.87	12.50	1.30	5.00
16.01	25.60	9.70	1.76	2.50
16.81	14.40	5.00	0.65	1.80
17.71	15.00	4.10	0.21	1.50
18.11	11.00	3.75	0.25	1.50
18.71	9.40	2.10	0.87	1.50
20.11	12.70	2.18	0.56	1.50
21.61	7.50	1.18	0.10	1.50
23.81	4.50	0.50	0.00	1.50
25.71	2.50	0.40	0.00	1.50
26.21	2.00	0.25	0.00	1.50
26.71	1.20	0.42	0.00	1.50

TABLE XXXVI

BTC DATA FOR PHENOLIC COMPOUNDS AND CHLORINE (35% ALCOHOL AND 65% WATER)

TOTAL VOLUME (L)	EFFLUENT D.C.PHE. mg/l	EFFLUENT T.C.PHE. mg/l	EFFLUENT D.N.PHE. mg/l	EFFLUENT CHLORIDE mg/l
0.42	2.35	1.12	5.50	25.00
1.05	8.75	6.60	44.00	75.00
1.46	12.14	11.66	47.60	340.00
2.76	28.50	30.83	48.10	340.00
3.36	35.70	41.60	47.39	340.00
4.16	45.40	47.85	44.13	340.00
4.86	47.93	46.90	45.93	340.00
5.71	48.12	48.75	47.10	340.00
6.51	27.57	39.60	31.00	115.00
6.96	20.40	27.34	11.40	30.00
7.76	15.81	12.35	2.90	2.50
9.01	10.71	8.40	1.47	1.50
10.81	8.12	6.66	0.30	1.50
12.11	7.12	4.30	0.21	1.50
13.91	6.37	3.16	0.11	1.50
14.71	5.50	2.80	0.08	1.50
15.02	3.27	1.70	0.00	1.50
16.41	1.27	1.40	0.00	1.50
17.91	1.50	1.13	0.00	1.50
18.41	1.20	0.89	0.00	1.50

TABLE XXXVII

BTC DATA FOR PHENOLIC COMPOUNDS AND CHLORIDE (ALCOHOL)

TOTAL VOLUME (L)	EFFLUENT D.C.PHE. mg/l	EFFLUENT T.C.PHE. mg/l	EFFLUENT D.N.PHE. mg/l	EFFLUENT CHLORIDE mg/l
0.50	10.00	13.80	15.30	85.00
0.78	15.00	25.00	32.00	315.00
1.03	30.00	38.80	48.00	340.00
1.26	47.50	44.40	42.50	340.00
1.49	48.59	47.36	45.00	340.00
1.90	50.00	50.00	49.50	340.00
2.20	50.00	50.00	44.30	225.00
2.50	27.50	28.90	21.80	160.00
2.72	16.10	12.16	5.80	55.00
2.87	4.50	2.50	3.33	12.50
3.22	5.30	2.50	2.85	5.00
3.42	3.75	1.90	1.47	2.50
4.42	2.85	1.10	1.47	1.50
4.72	1.80	0.75	0.19	1.50
5.32	0.62	0.23	0.00	1.50
5.80	0.29	0.17	0.00	1.50

VITA

ALI TORABIAN

Candidate for the Degree of

Doctor of Philosophy

Thesis: MOVEMENT OF PHENOLIC COMPOUNDS IN GROUND WATER

Major Field: Civil Engineering

Biographical:

Personal Data: Born in Tehran, Iran, April 21, 1953, the son of Mohmad and Akram Torabian.

Education: Graduated from Hadaf High School, Tehran, Iran, in June, 1972; received the Bachelor of Chemistry degree from Pars College, Tehran, in February, 1976; received the Master of Science degree in Bioenvironmental Engineering from the Oklahoma State University, Stillwater, Oklahoma, in December, 1978; completed requirements for the Doctor of Philosophy degree at the Oklahoma State University in May, 1988.

Professional Experience: Worked as Environmental Engineer for consultant engineers in Tehran, Iran, from May, 1979, to August, 1984; Graduate Research and Teaching Assistant at the Oklahoma State University from June, 1985, to December, 1987.

Membership in Professional Societies: Member of Water Pollution Control Federation, American Waterworks Association, Chi Epsilon.