

Organic Groundwater Contamination Evaluation and Prediction

Principal Investigators: John T. O'Connor
Mriganka M. Ghosh
Shankha K. Banerji
University of Missouri
Columbia, Missouri

Student Assistants: Keith Piontek
Edgar Aguado
T.M. Prakash

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U.S. Geological Survey
U.S. Department of Interior

Missouri Water Resources Research Center
University of Missouri
Sinclair Road - Route 3
Columbia, Missouri
65203

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Abstract

Title: "Organic Groundwater Contamination Evaluation and Prediction"

Adsorption of two organic compounds, Trichloroethylene (TCE) and Pentachlorophenol (PCP), on several Missouri soils were determined. The soils used were of the Coppock, Parsons, Putnam, Grundy and Lebanon series. TCE concentrations were determined by gas chromatography, while PCP concentrations were measured by radio-assay technique. Batch adsorption experiments were conducted using a soil and various organic compound concentrations. It was found that adsorption data for both TCE and PCP fit a Freundlich relationship. TCE and PCP adsorption on Missouri soils decreased with increasing pH. Organic matter in soil was an important parameter in determining the extent of TCE and PCP adsorption. TCE was poorly adsorbed on the soils tested while PCP adsorption was more strongly adsorbed. This would indicate that TCE would migrate readily with the groundwater, while PCP migration would be somewhat retarded.

ORGANIC GROUNDWATER CONTAMINATION EVALUATION AND PREDICTION

1. INTRODUCTION

More than forty percent of the U.S. population depend upon groundwater for their water supply. Generally, these fresh groundwater supplies are of relatively good quality, and are used for drinking water supply, often with only minimal treatment, such as, disinfection. However, recent evidence indicates that some groundwater is contaminated with synthetic organic chemicals, especially in urban and industrial areas, which could render the supply unsuitable for beneficial use.

The potential threat of groundwater contamination by synthetic organic chemicals arises from the increased production, transport and consumption of these chemicals. The production of organic chemicals in the U.S. has increased steadily for the last four decades, currently producing over 40,000 compounds (1). The quantity of chemicals discharged from production and domestic transport is very difficult to evaluate. The discharges occur almost inevitably from loading and transfer operations and accidental spills which can result in groundwater contamination. The major source of organic pollutants results from consumptive use and the subsequent waste disposal on lands. Significant quantities of organic chemicals are released into the soil from authorized as well as unauthorized solid waste and chemical landfills in the form of leachates.

The organic pollutants, unlike the inorganic contaminants may not be contained within conventional barriers such as clay layers or plastic liners. Hence, they can enter an aquifer and be transported great distances. Also, contamination of groundwater occurs over a long period and is only slowly perceived owing to the slow rate of groundwater movement. Unlike surface waters,

decontamination of groundwater is extremely difficult because of the lack of natural cleansing mechanisms common in surface water (2). Monitoring to determine the location, extent and source of contamination is also far more difficult and expensive than with surface waters. Therefore, it is essential that groundwater contaminants be detected early and remedial actions be taken to minimize continuing contamination.

In establishing regulatory schemes to protect groundwater resources from organic contaminants, the fate, transport and transformation of contaminants in or on their way to groundwater must be studied. Questions of importance are: How effectively are organic pollutants removed during the transport through the unsaturated and saturated zone of the aquifer? What are the mechanisms and rate of removal or transformation? What are the end products of possible transformation? These questions on behavior of organic pollutants in subsurface environment are addressed in this study.

Two subsurface contaminants for study are trichloroethylene (TCE) and pentachlorophenol (PCP). TCE has been listed by U.S. Environmental Protection Agency (EPA) as priority toxic pollutant (3). TCE belongs to a group of aliphatic hydrocarbons that are commonly used as industrial solvents. They have been found to be groundwater contaminants in Missouri (4) and in other states (5, 6). PCP is used extensively as an antimicrobial and antifungal agent in the wood and construction industries. It is also used in petroleum industry as a bactericide in drilling muds, gypsum muds, packer fluids, and in secondary oil recovery injection water. It is quite a toxic compound and could be a precursor of chlorinated dibenzo-para-dioxins under high temperature conditions (7).

2. PROJECT OBJECTIVES

Fate and transport of contaminants such as TCE and PCP are thought to depend on the sorptive nature of the soils, the geochemical conditions that may control biological or chemical transformation and hydrodynamic characteristics of the aquifer. Where conditions do not favor transformation, sorption of the contaminant by the soil may become a dominant process in migration through unsaturated zone to the aquifer. Hence, the objectives for the present project were focused on sorption characteristics of Missouri soils under different environmental conditions for the organic compounds under study. Specifically, the objectives are:

- (1) To develop kinetic and isotherm data for sorption of these compounds on Missouri soils.
- (2) To determine the effect of pH, ionic strength and organic content of soils on sorption capacities of Missouri soils for selected compounds.
- (3) To predict the migration of TCE through Missouri soils by model calculations.

3. LITERATURE REVIEW

The literature review presented here summarizes some of key articles pertaining to TCE & PCP contamination of groundwater and their interactions with soils.

A. Trichloroethylene Literature:

Physical and Chemical Properties

Trichloroethylene (TCE) is a chlorinated hydrocarbon which is produced in major quantities in the U.S. and is used as degreasing solvent in many industries including metal industry, food processing, textile, polyvinyl chloride production and fungicide manufacturing (8). At normal temperatures, TCE is a colorless sweet-smelling, non-flammable in air, volatile liquid, and has poor solubility in water. Commercial grades of TCE contains stabilizers to prevent decomposition by oxygen.

Table 1 presents the physical and chemical properties of TCE available from literature. TCE is not expected to persist in the environment because of its rapid photooxidation in air, and its volatility (8). However, significant concentrations of TCE are detected in various environmental samples including industrial wastewaters and groundwater supplies.

Trichloroethylene in Groundwater Supplies

Improved detection methods and wider sampling have demonstrated the existence of TCE in locations as diverse as untreated surface and groundwaters, drinking water, industrial wastewaters and treated effluents (6). Tables 2 and 3 present a summary of TCE concentrations detected in industrial wastewaters, surface waters and groundwaters, respectively. TCE does not occur naturally in groundwater, and its presence has resulted in closing of public water supply wells in several states including California, Delaware, Massachusetts,

Table 1 Physical and Chemical Characteristics of Trichloroethylene

Characteristics		Reference
Alternate Names	Trichloroethene Ethylene trichloride 1,1,2-trichloroethylene	6
Formula	C_2HCl_3	14
Molecular Weight	131.4	9
Density	1.456 g/ml	6
Solubility in Water	1,100 mg/l	5,9
Specific Gravity	1.46	9
Boiling Point	87 °C	5,9
Melting Point	-87 °C	9
Color	Colorless	9
Odor	Chloroformlike	9
Threshold Odor	500 µg/l	5
Flammability	Nonflammable	9
Heat of Vaporization	63.2 cal/g	14
Henry's Law Constant	0.48 atm-m ³ /mol	5
Octanol/Water Partition Coefficient	195	14,6,8
Saturated Vapor Conc.	4.3×10^{-4} g/cm ³	14
Diffusion Coeff. in air	0.072 cm ² /s	14
Diffusion Coeff. of vapor through Soil	0.039 cm ² /s	14
Molar Refraction	30.42	5
Percent Chlorine by Weight	81	9

Maine, Missouri, New York and New Jersey (6). TCE concentrations as high as 35,000 µg/l have been measured in certain states. In most samples analyzed, TCE concentrations exceeded the suggested no adverse response level (SNARL) of 4.5 µg/l in drinking water recommended by EPA (9).

Environmental Significance and Health Effects of TCE

Even though EPA and other federal and state agencies have detected concentrations of TCE in groundwater at higher levels, as well as in samples of soils, air, surface water, industrial wastewater and treated effluents throughout the country, the environmental impact of TCE is not completely known and no adverse ecological effects have been reported yet.

TCE has been classified as a suspected human carcinogen, although no definitive data have confirmed such a linkage. Apart from the matter of carcinogenicity, TCE is intrinsically toxic and its action can be acute or chronic. The primary physiological response from exposure to TCE is depression of the central nervous system, resulting in impaired vision and changes in skin sensitivity. Also mental confusion, fatigue and sometimes nausea and vomiting are observed. When the vapor is inhaled it is diffused through the bloodstream from the lungs. Both the liver and kidneys can be severely damaged by chronic exposure. Ingestion of high concentrations of TCE have resulted in death through edema of the lungs and severe damage to the liver and kidneys.

Studies on Transport and Fate of TCE in Groundwater

Limited studies have been reported in the literature regarding the transport and fate to TCE in groundwaters. In general it has been observed that TCE and other relatively nonpolar organic compounds have low adsorption intensity and are relatively stable in the subsurface environment (10, 11).

Column studies reported by Wilson et al (1) indicated that TCE and other

Table 2 Trichloroethylene in Industrial Wastewaters*

	Untreated Wastewater ($\mu\text{g/l}$)		Treated Wastewater ($\mu\text{g/l}$)	
	mean	range	mean	range
Coal mining	<1.4	ND-<10	<1.1	ND-<10
Textile mills	47	NA-840	4.9	NA-87
Paint and Ink	960	ND-5000	78	ND-300
Rubber processing	--	--	550	NA-1600
Pulp, paper and paperboard	--	--	<3	<1-6
Auto and other laundries	90	ND-800	11	ND-300
Pharmaceutical	8	ND-62	0.8	ND-7
Foundries	109	ND-280	--	--
Coil Coating	<10	ND-310	--	--
Nonferrous metals	59	ND-900	18	ND-330

Note- ND = Not Detected
 NA = Not Available
 - = No data

Table 3 Trichloroethylene in surface and Groundwaters*

	Surface Water		Ground Water	
	Raw	Finished	Raw	Finished
Cities sampled	105	133	13	25
Positive samples (%)	11.4	32.3	38.5	36.0
Concentrations found ($\mu\text{g/l}$)				
mean	0.4	0.47	29.7	6.7
median	0.25	0.26	1.3	0.3
range	0.1-0.92	0.06-3.2	0.2-125	0.11-53

* Tables adapted from Loehr (1983) Ref. # 6.

chlorinated organic compounds were not degraded in a soil profile near Ada, Oklahoma. These compounds percolated rapidly through the soil and their retardation factors (velocity of tritiated water through soil divided by apparent velocity of pollutant through soil) were 2.5 or less. Richter, (2) evaluated the sorption intensity of TCE and other chlorinated compounds on soil constituents such as hydrous manganese oxide, bentonite clay, organic peat and the fine fraction of glacial till. The results confirmed the relationship between the adsorption intensity of an organic compound to the octanol/water partition coefficient and the water solubility of the compound.

Rogers and McFarlane (13) reported on sorption of TCE, carbon tetrachlorine and ethylene dibromide in two silty clay loam soils and aluminum or calcium-saturated montmorillonite clay. They reported very low (6% or less) sorption of each chemical except for a 17% sorption of TCE by Al-saturated clay. Data from this study supported the methods used to estimate soil sorption of neutral organic chemicals.

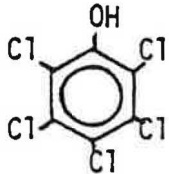
B. Pentachlorophenol Literature:

Physical and Chemical Properties

Pentachlorophenol is a fully chlorinated phenol. In a pure state at room temperature, PCP is a white, needle-like, crystalline solid. Some physical properties of PCP are listed in Table 4.

The molecular form of PCP has a relatively low solubility in water (14 ppm at 20 C). This solubility is however, strongly dependent on solution pH. The OH bond in water is polar and provides the dipole necessary to solvate ions. PCP is a weak acid, and the anionic form is readily soluble. Phenolic hydroxyl groups generally dissociate at a relatively high pH. PCP is an exception to this, for increasing chlorine substitution around an aromatic ring results in a decreased dissociation constant (pKa). Reports on

 Table 4. CHEMICAL AND PHYSICAL PROPERTIES OF PENTACHLOROPHENOL^a (16)

Structural Formula	
Molecular Formula.....	C_6HCl_5O
Molecular Weight.....	266.36
Melting Point.....	174 C, 190 C (18)
Boiling Point.....	293 C
Density.....	1.85
Vapor Pressure (20 - 100 C).....	0.00011 - 0.12 mm Hg
Henry's Constant.....	0.12 atm.
Dissociation Constant	$3.15 (10)^{-5} - 5.01(10)^{-6}$ (15)
Octanol/water Partition Coefficient ...	6400 (17)
Solubility (gm/100 gm solvent at 20 - 30 C)	
water	0.0014 - 0.0019
carbon tetrachloride.....	2 - 3
benzene	11 - 14
xylene	14 - 17
acetone	21 - 23
ethanol	47 - 52
diethyl ether	53 - 60
methanol	57 - 65

PCP's pKa vary from 4.5 to 5.3 (15).

PCP reacts with alkaline metals to form a phenate. Because it is readily soluble, the sodium salt of PCP, sodium pentachlorophenate (Na-PCP), is used in many practical applications. Because PCP has a relatively low solubility in water (14 ppm at 20 C) the readily soluble sodium salt of PCP, sodium pentachlorophenate (Na-PCP), is used in many practical applications.

Fate and Impact in the Environment

As discussed earlier, PCP is used widely and in a variety of applications. Its pattern of usage presents a serious potential for environmental contamination (16). PCP has been found in the atmosphere, in rain and snow, in rivers and lakes, in groundwaters, and in food (18). PCP was detected in 76% of some 600 human urine samples taken in a nation-wide study of pesticide exposure (19).

It is obvious that the past use of pentachlorophenol has resulted in widespread contamination of the environment and some degree of exposure in a large percentage of the human population. Various aspects of this contamination will be presented in the following discussion.

In Water

The most important point sources of PCP pollution of water are apparently facilities which manufacture PCP or use it in wood-treatment or slime control. Discharges of PCP from these sites can be continuous or intermittent.

Thompson and Dust (21) analyzed raw wastewater from a number of wood preserving plants and found PCP at levels ranging from 25-150 ppb.

Spills and other unintentional discharges of PCP into receiving waters also occur at these types of operations. In Mississippi, water contaminated with a PCP/fuel-oil mixture overflowed the banks of a wood treating company's wastewater holding pond. The fish kill which resulted in an adjacent 60 acre

lake was described as extensive to total. Other accidents of this nature will be discussed in a later section of this report.

Storm runoff can carry PCP to receiving waters from sites where PCP-treated lumber is stored. Following a heavy rain, Bevenue et.al. (21) detected 1.14 ppb PCP in a ditch which drained the grounds of a wood-treatment plant. The source of PCP found in the ditch was believed to be a large pile of treated lumber which had been drenched by rain.

Buhler and others (22) studies PCP levels found in municipal wastewater and its removal in wastewater treatment plants. PCP levels in composite samples of wastewater influent collected simultaneously from 3 Oregon cities ranged from 1 to 5 ppb. Analysis of effluent samples collected from the same plants reflected a PCP removal efficiency of 4 to 28%. These figures and data on the population served by wastewater treatment plants discharging into the Wilamette River upstream of the city of Corvallis were then used to estimate an expected level of PCP in the river. Actual levels (0.10 to 0.70 ppb) were much higher than estimated levels and indicated that paper and plywood mills and other industries along the river probably contributed to the PCP loading in the river.

The city of Corvallis obtains part of its drinking water from the Wilamette River. The concentration of PCP in this water was monitored at various stages of the water treatment process. It was reported that the PCP concentration in the raw water was 0.17 ppb; the finished water contained 0.06 ppb. Unfortunately, the report did not state whether the "finished water" was sampled prior to or following chlorination.

Persistence

PCP is quite stable. It does not decompose when heated at temperatures

up to its boiling point for extended periods. Pure pentachlorophenol is considered to be relatively chemically inert (23). Its chemical properties together with information on environmental monitoring would place the compound in the category of persistent compounds. The toxic activity of the chemical in the environment can be alleviated by biodegradation (under the proper conditions) and by sorption to soils and sediments.

Early studies on the transformation of PCP in the environment were done, not out of concern over the adverse effects of its persistence, but rather to assess the effects of biodegradation and sorption on the effectiveness of PCP as a biocide.

Adsorption by Soils and Sediments

Adsorption by soil was an important consideration in the use of PCP as a pre-emergence herbicide in Hawaiian sugar cane fields. PCP is severely phytotoxic when applied to sugar cane root systems. Protection for these root systems (the prevention of excessive PCP leaching) must be supplied by the soil cover. On the other hand, optimal pre-emergence weed control cannot be achieved in soils of extremely high adsorbtivity.

Hilton and Yuen (24) studied the adsorption of PCP and several substituted area and triazine herbicides on Hawaiian sugar cane soils. Adsorption of PCP was the highest of all the compounds studied. Increased rates of application (up to 500 pounds/acre) gave little better weed control than 50 pounds/acre. The researchers noted that the steep slope of the adsorption isotherms for PCP suggested that large increases in PCP application would be required for a significant increase in the percentage of the chemical in the soil solution.

Choi and Aomine have studied the interaction of PCP and soil extensively. The results of these studies are summarized below.

After citing earlier studies indicating the importance of the humus and clay fractions in the adsorption of PCP, Choi and Aomine (25) investigated PCP adsorption on a number of clay soils in an effort to elicit the effect of these parameters on the herbicidal effectiveness of PCP applied to soils.

Equilibrium adsorption experiments were performed using 10 different soils and 4 PCP solutions - 10, 20, 40 and 80 ppm. The concentration of PCP was obviously lower in the supernatant solution than in the suspension of every soil sample. All humus rich soils showed a greatly reduced PCP concentration in the supernatant. Soils with low humus contents showed a variation in adsorbability. The adsorption in some of these soils compared to the humus-rich soil, the adsorption in others was significantly less. No relation could be found between the concentration of PCP in the supernatant solution and the clay content, the species of the dominant clay minerals, or the cation exchange capacity of the soil. It was found, however, that the concentration of PCP in the supernatant was closely related to the pH of the soils.

The study also included bioassays conducted on wheat seedlings to measure the inhibitory rate of adsorbed PCP. It was determined that precipitated and/or adsorbed PCP retained some plant toxicity, but to a lesser extent than dissolved PCP.

Choi and Aomine (26) later studies adsorption behavior by using 13 soil samples which had various clay mineral species, organic matter content, and pH. Initial concentration of PCP was varied from 12.5 to 500 mg/l. They concluded that the major factor governing the magnitude of "apparent adsorption" is pH. "Apparent adsorption" was defined as the amount of PCP that disappeared from the liquid phase of the soil-PCP system. Apparent adsorption occurred to the greatest extent in the strong acid soil system compared to the moderate

acid soil system, regardless of the species of clay mineral and organic matter content. No adsorption occurred in the slightly acid or neutral soil system.

In acid clays, the mechanism of "apparent adsorption" seemed to include adsorption on colloids and precipitation in both the soil micelle and in the external liquid phase. Soils rich in organic matter exhibited a great adsorbance of PCP irrespective of pH. Comparisons of untreated soil and soils treated with hydrogen peroxide to remove organic matter showed a decrease in adsorption for every hydrogen peroxide-treated soil. The decrease in adsorption was greatest for soils containing the highest organic matter content. It was noted, however, that humic matter could make a close complex with allophanic colloids reducing the adsorptive capacity of each component. Despite this observation it was concluded that organic matter appeared to play an important role in the adsorption of PCP in soil.

Choi and Aomine (27) conducted further experimentation to elicit the mechanism of PCP adsorption in soils. An adsorption experiment was carried out with allophanic clay separated from soil to evaluate the effect of the amount and particle size of the clay on adsorption of PCP. The equilibrium concentration of PCP in the supernatant solution at pH 5.0 was essentially the same regardless of the amount of clay added. The concentration was in agreement with that expected from the solubility of PCP at pH 5.0, indicating the occurrence of precipitation. Above pH 5.4 the equilibrium concentration of PCP decrease as the amount of clay increased, indicating adsorption of PCP by the clay.

To further distinguish the precipitation from adsorption in allophanic clays, adsorption-washing experiments were conducted. Clay-PCP suspensions were prepared by adding PCP solution to a given amount of clay with or without HCl. After shaking, the supernatant was removed and de-ionized water was added

in 50 ml increments to the clay, shaken, centrifuged and analyzed for PCP. This washing procedure was repeated 6 times. The PCP concentration of the supernatant liquids obtained from the HCl-added suspensions by the first washing was about the same as that obtained by the second washing. This indicated considerable amounts of PCP were present as precipitates in the HCl-added suspensions, and that precipitated PCP was easily dissolved by washing with deionized water. On the other hand, the PCP concentration of the supernatant liquid gradually decreased in subsequent washings. The pattern of this decrease in PCP concentration was similar in all solutions regardless of HCl addition. This gradual reduction of PCP in the supernatant solution in successive washings indicates that allophanic clays adsorb PCP.

Choi and Aomine (27) also studied the effects of temperature on adsorption of PCP by soil. Four allophanic soils with pH adjusted to 5.6 by addition of NaOH or HCl were used to measure the adsorption of PCP at 4 C and 35 C. Three soils showed a significant increase in PCP adsorption at higher temperature, but the fourth soil showed a decrease. The authors explained this difference with the assumption that the andosols (all of which exhibited an increase in adsorption) chiefly adsorbed PCP as an anion while in soil showing a decrease in adsorption ratio of about (2) the major factor influencing adsorption was a van der Waal's force.

Adsorption experiments were also carried out on 3 soil samples in the presence of chloride or sulphate ions. Results indicated the occurrence of competition between the inorganic ions and PCP ions for adsorption sites on the soil colloid. Sulfate ions appeared to be more powerful competitors to PCP in adsorption on allophane than chloride ions. Choi and Aomine concluded that PCP is adsorbed by allophanic soils as ions.

It appears that adsorption of pentachlorophenol onto soils has been studied quite extensively, but this is true only for PCP concentrations greater than its solubility limit (greater than 10 ppm). These studies have focused on the effects of soil adsorption on the biocidal effectiveness of PCP, whether in fields where PCP is applied as a herbicide or in streams where it is used as a molluscicide. The contaminant concentrations that are of concern in groundwater pollution are in the part per billion range. The adsorptive behavior of PCP at these concentrations will be investigated in this study.

Effects of Environmental Contamination

The most easily assessed effects of PCP contamination of the environment are those occurring due to acute exposure to relatively high levels of PCP. Much harder to assess are the effects of chronic exposure to the levels of PCP commonly found in the environment. Aspects of both acute and chronic exposure will be addressed in the following discussion.

Aquatic Life

Some of the most severe environmental impacts of PCP contamination have been observed in aquatic ecosystems. A review of fish kills occurring in the state of Missouri in 1972 and 1973 provides insight into the ways PCP may be released into the environment and its possible effects in receiving waters.

A fish kill occurred over a 15 mile stretch of the Big Piney River in 1972 when a tank truck was filled to overflowing and the PCP/fuel-oil mixture drained into the river. Analysis of water and dead fish collected at the time of the kill revealed substantial quantities of PCP (28).

A large pile of PCP-treated poles was the cause of a fish kill in 1973. These poles were stacked after shipment by rail, and had been treated prior to shipment. Nonetheless, a heavy rain leached PCP from the poles and into

a pond approximately a quarter of a mile from the lumber stack. Analysis of some of the approximately 5000 fish killed revealed toxic levels of PCP.

In two other 1972 incidents, fish kills resulted after PCP discharges from wood-treating companies. Seepage of PCP from freshly treated lumber resulted in a fish kill along 5 miles of a creek near Cabool, Mo., and discharge of a PCP/oil mixture from treatment ponds at another plant killed much of the fish population in a nearby 10 acre lake.

The effects on aquatic ecosystems of chronic exposure to low levels of PCP are not as obvious. These effects could include impacts on specie reproduction and survival or community relationships. As sedimentation and sorption by bottom sediments are thought to be major mechanisms of removal of PCP from the water column, benthic communities may be particularly susceptible to chronic exposure. This topic has not been investigated thoroughly.

In a study of a PCP spill and resulting contamination of a freshwater lake, Pierce (16) found that leaf litter from the contaminated watershed area and lake sediment contained high concentrations of PCP throughout a 2 year study period. PCP released into the lake ecosystem was apparently not rapidly assimilated by photo or microbial degradation. The effects of chronic exposure resulting from leaching of PCP from the contaminated watershed and incorporation of PCP into the benthic food chain were not determined. Food chain studies did show, however, that all game fish depended upon benthic organisms as either a direct or indirect food source.

Pruitt et.al. (29) found that bluegill exposed to sublethal concentrations of PCP accumulated the chemical in various tissues at levels 10 to 350 times the ambient concentration. Ecological magnification is a function of the lipid/water partition coefficient and the stability of a chemical and its

metabolites in an animal. Lu et.al. (17) found that an effective approximation of ecological magnification can be obtained when it is plotted as a function of the log of water solubility. Practical experience has shown that most pesticides with water solubilities of less than 0.5 ppm demonstrate bioaccumulation following field use and that most with solubilities of greater than 50 ppm have not shown bioaccumulation. The large group of pesticides with water solubilities falling between these two values (this group includes PCP) represent those pesticides which may demonstrate some significant degree of bioaccumulation under certain conditions of use.

Residues in Humans

On the topic of chronic exposure to PCP, another matter that merits discussion is the widespread occurrence of PCP in human urine samples. The National Center for Health Statistics collaborated with the USEPA in a four year study to assess the exposure of the general population to selected pesticides through analysis of blood serum and urine specimens. The Second Health and Nutrition Examination Survey (NHANES II) utilized samples collected from persons 12 to 74 years of age at 64 locations across the United States (19). Detectable levels of PCP (greater than 5-30 ppb) were found in 79% of approximately 6000 specimens.

Dougherty (30) reviewed a number of studies on PCP levels in human biofluids and tissue and concluded that contamination of human populations with PCP at levels of 10-20 ppb is quite general in industrialized societies.

The possible sources of general human exposure to PCP have been studied. Despite suggestions that chlorination of phenol in water supplies is responsible for the widespread occurrence of PCP in water, available evidence indicates that it is quite unlikely that this route substantially contributes to

the human PCP burden.

It has also been suggested that a possible source of the PCP is as a metabolite of other chlorinated compounds, particularly hexachlorobenzene (HCB) (31). It has been fairly well established that PCP is a metabolite of HCB. Lu and others (17) reported that HCB slowly converts to PCP to model ecosystem experiments. Based on HCB to PCP conversion efficiency in the rat, the EPA calculated the HCB exposure required to result in observed PCP urinary concentrations and concluded it is very unlikely for the general population to be exposed to HCB at such high levels. HCB is apparently only a minor contributor to the human population's body burden of PCP.

The general contamination of water and foodstuffs is a more likely route of human exposure. In 1978, 5% of 600 water samples taken at 153 sampling locations in 43 states showed detectable PCP upon analysis (32). The overall average concentration was 0.13 ppb.

The same year, the USDA collected liver samples from beef, swine, and poultry throughout the U.S. A preliminary survey showed that in all instances the percentage of positive findings for PCP residues was higher than 86%. In the state of Michigan, herds of dairy cattle were contaminated with PCP after exposure of the cattle to PCP. Pentachlorophenol had been used to treat barns where the cattle were housed and grain bins used to store cattle feed. PCP levels in 18 cows ranged from 58 to 1136 micrograms per kilogram; PCP was later found in the blood of cattle from 8 different herds. One sample of milk contained 0.09 ppm PCP (18).

In a spot survey of selected items from the food chain Dougherty and Ptotrowska (33) found PCP residues in powdered dry milk, soft drinks, bread, candy bars, cereal, noodles, rice, sugar and wheat. They suggested a likely source of contamination was storage of grains and sugars in PCP-treated

storage containers.

The EPA (34) has developed a water quality standard for pentachlorophenol. Based on the no-observed-adverse-effect-level (NOAEL) of 3 mg/kg determined by Schwetz et.al. (35) and applying a safety factor of 100 for extrapolation from animal studies, the EPA calculated the upper limit for non-occupational daily exposure for a 70 kg person to be 2.10 mg. Using this upper limit, and the assumption of 2 liters of water consumed daily and daily consumption of 0.0065 kg of fish which bioaccumulate PCP by a factor of 11, a water quality criterion based on human health was established as being 1.01 mg PCP per liter of water. This concentration is generally well below observed levels. It should be noted, however, that the criteria was based on a NOAEL for a purified grade PCP containing only low amounts of nonphenolic impurities.

Transport and Fate of Organic Pollutants in Subsurface Environment

The principles of various processes leading to groundwater contamination by organic pollutants have been extensively discussed in literature (2, 10, 36, 37). A general overview of these fundamental processes is presented in this section.

The subsurface soil, through which the pollutant is transported, is an exceedingly complex system. Not only is it composed of a solid, liquid and gaseous phases, but each of these phases possesses organic and inorganic constituents as well as inert and active compounds (37). This heterogeneous character strongly influences the physical and chemical properties of soil, thereby having a direct effect on solute transport and sorption in soil.

Various processes affecting the movement of organic compounds in a subsurface system can be divided into two categories: (i) the advective-dispersive transport of solutes through soil and (ii) the physical or chemical transformations of the solute during transport. The advective-dispersive solute

transport involves two processes: (a) advection which is the transport of a solute at a velocity equivalent to that of groundwater and (b) dispersion resulting from spatial variation in aquifer permeability, fluid mixing and molecular diffusion. The processes of physical and chemical transformations include, but are not limited to, various forms of adsorption, precipitation, dissolution, chemical degradation (as in hydrolysis), biodegradation, volatilization, and oxidation-reduction processes.

McCarty et.al. (2) have illustrated how various phenomenon affect the movement of organic compounds in a subsurface system from a ground water injection system. For one-dimensional, horizontal, single phase flow in a saturated unconsolidated, homogenous medium, the transport equation describing the macroscopic mass balance of a solute under transient condition is (37)

$$\frac{\delta C}{\delta t} = -u \frac{\delta C}{\delta x} + D \frac{\delta^2 C}{\delta x^2} - \frac{\rho a}{\epsilon} \frac{\delta \gamma}{\delta t} + \frac{\delta C}{\delta T} \quad m \dots \dots \dots (1)$$

where,

- u = average fluid velocity (m/s)
- C = solute concentration in aqueous phase (g/cm³)
- x = distance in flow direction (m)
- D = dispersion coefficient (m²/s)
- ρ = bulk density of soil (g/cm³)
- ε = soil void fraction
- γ = mass of solute sorbed per unit dry mass (g/g)
- t = time
- m = refers to degradation

The first two terms in Eq. 1 refer to the advection and dispersion processes, respectively. The effect of sorption on the movement of the contaminant through the aquifer is given by the third term on the right side of the equation. Chemical and biological transformation of the organic contaminants is taken into account in the transport equation by the fourth term of Eq. 1.

Dispersion

Groundwater can be defined as water occupying the subsurface intergranular void spaces divided into two zones. Near the land surface, the void spaces are partially occupied by air where the water pressure is less than atmospheric; this region is called unsaturated zone. With depth, the proportion of water to air increases until the pore spaces is entirely saturated with water which is called the saturated zone. The elevation (h) of the water table, the depth at which atmospheric pressure is encountered, is a measure of fluid potential gradient which is used to calculate the groundwater velocity, u_p .

Although the average pore velocity, u_p , is necessary for the description of contaminant movement, it does not account for the irregular, tortuous pore-level behavior of the fluids which promotes spreading of the contaminant by diffusion as displacement proceeds (38, 39). For unsaturated soils and for most water-saturated soils, the contribution of diffusion cannot be ignored.

Sorption

The extent to which an organic chemical partitions itself between the solid and solution phases of a water-saturated or unsaturated soil is determined by several physical and chemical properties of both the chemical and the soil. The contaminant properties which could affect the sorption on soils include molecular weight, water solubility, Henry's law constant, and octanol/water partition coefficient. Inorganic and organic content of the soil are also known to affect the contaminant sorption process.

The rate at which the contaminant interacts or exchanges with the solid phase, assuming conditions of local equilibrium, is described by isotherms, which may be of linear, Freundlich, Langmuir and of many other functional

relations of the concentration of the contaminant (37, 39).

The simplest and most widely used expression to equilibrium sorption isotherms is given by the linear relationship (36, 37)

$$\frac{\gamma}{C} = K \dots\dots\dots(2)$$

where,

- γ = amount of solute adsorbed by soil matrix
- C = conc. of solute in soil solution
- K_d = distribution coefficient

The value of K is a measure of retention of solute for the soil phase, relative to its affinity for water, the more strongly the solute will sorb, and the greater the value of K_d . Further, the retardation of the solute in their movement through an aquifer can be described as function of K_d given by

$$R_f = \left(1 + \frac{\rho_b}{\epsilon} K_d \right) \dots\dots\dots(3)$$

where,

- R_f = retardation factor or relative retention time
- ρ_b = bulk density
- ϵ = porosity of soil matrix

The retardation factor describes the relative velocity of movement of a concentration front of sorbing solute to the velocity of movement of a front of a conservative tracer (36).

Another commonly used expression for a non-linear adsorption of solutes by soils is given by the Freundlich isotherm

$$\gamma = K_f C^{1/n} \dots\dots\dots(4)$$

where K_f and $1/n$ are constants. The parameter K_f , defined as Freundlich adsorption coefficient, is analogous to the distribution coefficient K_d of linear isotherm. The value of the constant $1/n$ describes the non-linearity of the

isotherm and are generally found to range from 0.7 to 1.1 (14).

Degradation

Transformations of organic compounds in the subsurface environment can occur through chemical reaction as well as through chemical reaction as well as the action of microorganisms attached to particles or contained within the void spaces. Chemical oxidation and hydrolysis are believed to influence significantly the fate of organic chemicals in the subsurface environment (40). Chemical oxidation rate constants can be determined by structure-reactivity relationships as discussed by Mill (40). However, prediction of hydrolysis rates of organic chemicals in soil systems is complicated.

Kinetics of biodegradation by attached microorganisms is discussed by Rittman et. al. (41). Callahan et. al. (42) compiled and assessed data for the chemical and biological transformations of 129 priority pollutants in the aqueous environment. These data can be used for evaluating the significance of the reaction term in the transport model (equation 1).

4. MATERIALS AND METHODS

SOILS

Soil samples used for this study were obtained from the Department of Agronomy at the University of Missouri, Columbia. The soil samples were taken from five different sites in Missouri which are located in Boone, Davis, Laclede, Vernon, and Knox counties. From each sample site, representative soil samples from two horizons were selected, which included a surface sample (0 to 30 cm depth) and subsurface sample (50 to 70 cm depth). Additionally, for the Coppock series soil (Boone county), seven samples were taken, ranging from 0 to 152 cm depth, in order to obtain a textural representation of the sample site.

Physical and chemical properties of the soil samples are presented in Table 5. The soil analyses were conducted by the Soil Testing Services at the University of Missouri, Columbia. In general, there was little variability of organic matter content (0.5 to 1.8%) among the soils except for the Grundy surface soil which contained 3.7% organic matter. All the soil samples contained high percentage of silt and fall into the category of silty clay loam.

The soil samples used in all the experiments, except the experiments with peroxide digested soils, were prepared by the Agronomy Department at the University of Missouri, Columbia. However, for experiments to study the effect of soil organic matter on TCE adsorption, the surface soils of the five sample sites were treated with hydrogen peroxide in order to remove the organic matter from the soils. The peroxide treatment procedure, as suggested by Blanchar (43) consisted of adding sufficient hydrogen peroxide (30% solution) to about 100 g soil and warming the suspension on a hot plate till the evolution of gas bubbles completely stopped. Then the sample was dried at 105°C overnight. The dried sample was then ground before use in the experiments.

Table 5. Physical and Chemical Properties of Missouri Soils used in this study

Soil	Horizon	Depth cm	Particle Size (%)			pH _w [*]	Organic Matter %	CEC ^e	Ca ⁺⁺	Mg ⁺⁺
			Sand	Silt	Clay					
Coppock	AP	0-18	2	74	24	6.2	1.52	15.55	14.49	1.82
	E	18-28	2	58	40	6.5	1.46	16.66	14.85	1.84
	BE	28-38				5.4	1.00	18.66	13.26	2.81
	B ₁ t	38-61				4.8	1.10	25.27	15.06	4.32
	B ₂ t	61-84				4.8	0.76	26.88	16.70	5.50
	B ₃ t	84-119				4.8	0.52	29.43	18.14	6.02
	C	119-152				5.3	0.47	21.99	18.32	6.25
Parsons	AP	0-25	4	76	20	6.1	1.8	12.93	9.30	0.98
	A	25-50	4	70	26	5.7	0.8	10.27	6.03	1.33
	B ₂ t	50-68	2	45	53	5.0	0.8	30.71	12.85	6.62
Putnam	AP	0-30	3	70	27	6.5	1.8	20.19	14.38	2.79
	B ₂ t	45-93	1	38	61	4.9	1.3	42.18	20.28	9.21

Continued....

Table 5. Physical and Chemical Properties of Missouri Soils
used in this study
Continued....

Soil	Horizon	Depth cm	Particle Size (%)			pH _w [*]	Organic Matter %	CEC [@]	Ca ⁺⁺	Mg ⁺⁺
			Sand	Silt	Clay					
Grundy	AP	0-15	3	64	33	6.7	3.7	33.91	26.12	4.12
	B	50-71	2	52	46	6.0	0.3	34.08	20.17	9.44
Lebanon	A		9	74	18	5.0	1.7	9.32	2.07	0.97
	B		7	50	43	4.4	0.7	23.98	1.45	4.38

* pH of 1:1 water-soil paste

@ Cation Exchange Capacity

A humic acid extract was obtained by a method suggested by Blanchar (43). Approximately one kilogram of the surface layer of a soil expected to be rich in soil organic matter was collected from a wooded tract in Columbia, Missouri. After this soil was shaken in a 5:1 0.5N NaOH/soil solution for 24 hours, the supernatant was retained. The pH of the supernatant was lowered to 1.0 by the dropwise addition of concentrated HCl. The precipitate observed at this point was an unpurified humic acid extract. The unpurified humic acid extract was repeatedly washed with 0.5 N NaOH to dissolve the humic acid and acidified with HCl to form the precipitate. This washing procedure was repeated until the supernatant was clear. The precipitate obtained by this procedure was then washed with 0.05N HCl to purify the sample, and with deionized water to rinse out excess acid. Approximately 100 grams of humic acid extract was obtained in this manner.

Chemicals

Trichloroethylene: ACS certified trichloroethylene (TCE) obtained from Fisher Scientific Company was used as the adsorbate in this study.

Cyclohexane: Pesticide grade cyclohexane obtained from Fisher Scientific Company was used for extracting TCE from water and to prepare standards for the TCE analysis.

Pentachlorophenol: 100 grams of purified grade (99+%) pentachlorophenol was obtained from Research Organics, Inc. of Cleveland, Ohio. This PCP was used in conjunction with 6.3 mg of carbon-14 labelled pentachlorophenol obtained from Pathfinder Laboratories, Inc. of St. Louis, Missouri. This PCP was certified at 98+% pure and a specific activity of 10.57 mili Curies/millimole.

BATCH ADSORPTION EXPERIMENTS:

All the experiments for determining kinetics as well as equilibrium isotherms were conducted using the batch procedure.

TCE EXPERIMENTS:

A fresh stock solution of TCE in distilled water was prepared by adding 10 μ l of TCE to 100 ml of distilled deionized water in a volumetric flask. The flask was shaken thoroughly until all the TCE was in solution, yielding a concentration of 145.6 mg/l. Then the desired concentration of TCE solution, for use in the experiments, was prepared by diluting the stock solution.

The batch studies were conducted in 150 ml Wheaton glass bottles provided with Teflon lined caps. The bottles were thoroughly cleaned in distilled water rinsed with acetone and hexane, and dried in oven at 110°C until ready for use. Ten grams of the soil sample were placed in a bottle to which the TCE solution of a known concentration was added until the bottle was filled to the rim. The bottle was then closed tightly with teflon lined caps and sealed with teflon tape. This resulted in a minimum air space in the bottle and minimized loss of TCE due to evaporation. About 150 ml of TCE solution was required to fill the bottles, giving a solids to solution ratio of approximately 1:15. This ratio was used for all experiments reported in this study. The bottles were then placed on a rotary shaker. The temperature for the study was 22 \pm 2°C.

After a desired period of time, the bottles were taken out from the shaker and the mixture transferred to a clean 150 ml Corex centrifuge bottle. The pH of the soil-water solution was then measured by a pH probe. The solution was then centrifuged at 7000 rpm (5000 Xg) at 30 in refrigerated centrifuge. One-hundred ml of the supernatant was then transferred to a 250 ml separatory funnel for extraction of TCE from the water phase. The extracted TCE was analysed by gas-chromatograph as discussed in the later section.

Determination of TCE Concentration in Water

The analytical method selected for determining TCE concentration in water phase was by extraction of TCE from the water phase into an organic solvent phase and analyzing the TCE in the solvent phase by gas chromatography using an electron capture detector.

Extraction of TCE from Water Phase: After consultation with several researchers [44,45,46], a procedure was developed to extract TCE from water phase into an organic solvent phase. The organic solvent chosen was cyclohexane based on the high TCE fractionation coefficient and low solubility of cyclohexane in water compared to other organic solvents.

A 100 ml sample was placed in a 250 ml separatory funnel, to which 10 ml of cyclohexane was added. The separatory funnel was then vigorously shaken for two minutes. Then the mixture was allowed to stand for 10 minutes to achieve phase separation. The water phase (lower phase) and the cyclohexane phase was then separately collected. The water phase was transferred back to the separatory funnel and the procedure repeated for three more times. The cyclohexane phase (composite of the four extractions) was then analyzed for TCE using a gas chromatograph. Hence, by this method, the TCE in water phase was concentrated 2.5 times in the cyclohexane phase. The analyses was performed immediately after extraction.

In order to determine the extraction efficiency of this procedure, standard TCE solution of 100, 250, 500, 750, and 1000 ppb were extracted. Table 6 presents the extraction efficiency for each initial TCE concentration.

ANALYSIS OF TCE

Instrumentation: A Tracor MT-220 gas chromatograph equipped with electron capture detector (Ni^{63}) was used for quantitative measurement of Trichloroethylene.

Table 6. Extraction of TCE from Water
With Cyclhexane

TCE Conc. in Water $\mu\text{g}/\text{l}$	Percent Efficiency of Extraction		
100	61.6	\pm 2.2	(5 extractions)
250	68.0	\pm 7.2	(4 extractions)
500	72.0	\pm 8.6	(4 extractions)
750	70.5	\pm 6.8	(4 extractions)
1000	67.0	\pm 4.8	(4 extractions)

The system used Argon/Methane (1:9) mixture as the carrier gas.

Column Selection for Gas Chromatograph: The packing material for the chromatographic column was selected in accordance with Method 601-Purgeable halocarbons recommended by EPA. The column material selected was Carbowax B 60/80 coated with 1% SP-1000 (Supeloc Cat. #1-1815) packed in a 6 ft x 1/8 in ID glass column.

Calibration: Initially the column was conditioned isothermally at 50°C for one hour and then raising the column temperature to 200°C conditioning for 15 hours (overnight). Standard Solutions of TCE in cyclohexane were prepared to obtain the calibration curve. The TCE standard was injected (1.1 µl) into the column using a 10 µl syringe. The optimal chromatograph conditions used for this analysis is given in Table 7. The chromatograph of TCE was recorded at an attenuation factor of 128×10^2 . The height of the TCE peak was used as quantitative measure of TCE concentration in the solution.

The calibration curve for TCE was prepared using 100, 250, 750 and 1000 µg/l in cyclohexane. A typical calibration curve is shown in Figure 1. Standard Curves were prepared prior to every experiment.

PCP EXPERIMENTS:

Batch adsorption experiments were used in determining adsorption kinetics, adsorption isotherms, and adsorption reversibility of PCP solution on Coppock series horizon AP and B3_t. These studies were conducted in 150 ml Wheaton glass bottles topped with Teflon-lined caps. These bottles were thoroughly cleaned with hot water and rinsed with concentrated acid and caustic prior to every use. The addition of 140 ml PCP solution of known concentration and 14 grams of soil to these bottles resulted in minimal remaining airspace in the bottles. This 10:1 solution/soil ratio was employed in most of the batch experiments.

In most of the batch adsorption experiments, 10 sample bottles were prepared and used. PCP solutions of 7 different initial concentrations, ranging from

**Table 7. Instrumental Conditions Used for TCE
Analysis with Tracor MT220 GC/EC**

Column: 6 ft X 1/8 in. glass packed with
Carbopak B 60/80 coated with 1%
SP-1000 (Supelco Cat. # 1-1815)

Temperature: Column 190°C
Inlet 215°C
Detector 300°C

Gas Flows: Argon/Methane Carrier - 70cc/min
Argon/Methane EC Purge- 40cc/min

Electrometer: Attenuation - 128×10^2

Recorder: Voltage - 1 mV
Chart Speed - 0.5 in./min

approximately 100 micrograms/liter to nearly 10 milligrams/liter, were added to soil in 8 bottles (one being a duplicate). To one bottle containing no soil, a PCP solution of known concentration was added to monitor adsorption of PCP by the various containers used in the experimental protocol. One bottle containing soil and a PCP solution lacking any labelled compound was monitored to determine background activity and possible glassware contamination.

These bottles were then placed on a rotary shaker and shaken for the time required for equilibrium (as determined in the kinetic studies). The temperature for the study was $22 \pm 2^{\circ}\text{C}$. After mixing was completed supernatant samples were obtained by transferring 10 ml of the soil/water solution to a 16-ml centrifuge tube and centrifuging at 15,000 rpm for 5 minutes in a refrigerated centrifuge. One ml of the supernatant was transferred to a 20 ml glass vial containing 10 ml of Aquasol-2 scintillation cocktail. This vial was shaken vigorously and placed in a refrigerator to await counting.

The remaining contents of the sample bottle were then transferred to a 300 ml flask. The soil/water solution was mixed using a magnetic mixer and stirring bar. The pH of the soil/water solution was determined by immersing a pH probe in the mixture.

DETERMINATION OF THE PCP CONCENTRATION OF THE SUPERNATANT

With the use of carbon-14 labelled PCP, the determination of the equilibrium aqueous phase PCP concentration was made quite easy. Given an initial PCP concentration, the concentration remaining in the aqueous phase was determined by comparing the number of radioactive decays per second (the activity) in the initial solution with the activity of the final supernatant.

Carbon-14 is a beta-particle emitter. Beta-emissions are of low energy and are difficult to count due to self-absorption of the beta-particle and their absorption within the counter window. These problems are overcome in the liquid scintillation counting (LSC) method. In this method, the sample is mixed in a

solvent containing scintillator material. The beta-emissions electronically excite the solvent molecule which transfer their energy to the scintillator molecules, which in turn release the energy by emitting photons. These flashes of visible light can be detected and counted.

The counting method must account for quenching - reduced photon output for a given radioactive decay energy due to energy lost in the sample. The sample channel ratio (SCR) counting method does so by monitoring the shift in the beta-spectrum to the left (lower energy) as quenching increases. Two "windows", or counting channels, are employed. One channel (A) is set to monitor the whole beta spectrum; the second (B) monitors only a portion of the unquenched beta spectrum. As quenching increases, the ratio of counts in the B channel to counts in the A channel increases. With severe quenching, a portion of the pulse height distribution curve may exit the spectrum scanned by the A window. This would result in a count corresponding to a lower carbon-14 concentration.

In this study, it was suspected that significant quenching could result from the absorption of emitted photons by suspended colloidal particles in the supernatant. A quench curve was constructed by counting as a series of variably quenched standards formulated from the same counting solution used in the experimental samples. This curve is a plot of the counting efficiency as a function of the channels ratio (See Figure 2). The activity, and thus the concentration, of all experimental samples exhibiting a channels ratio higher than 0.54 was corrected using this calibration curve. The vast majority of samples, however, exhibited a channels ratio between 0.44 and 0.54.

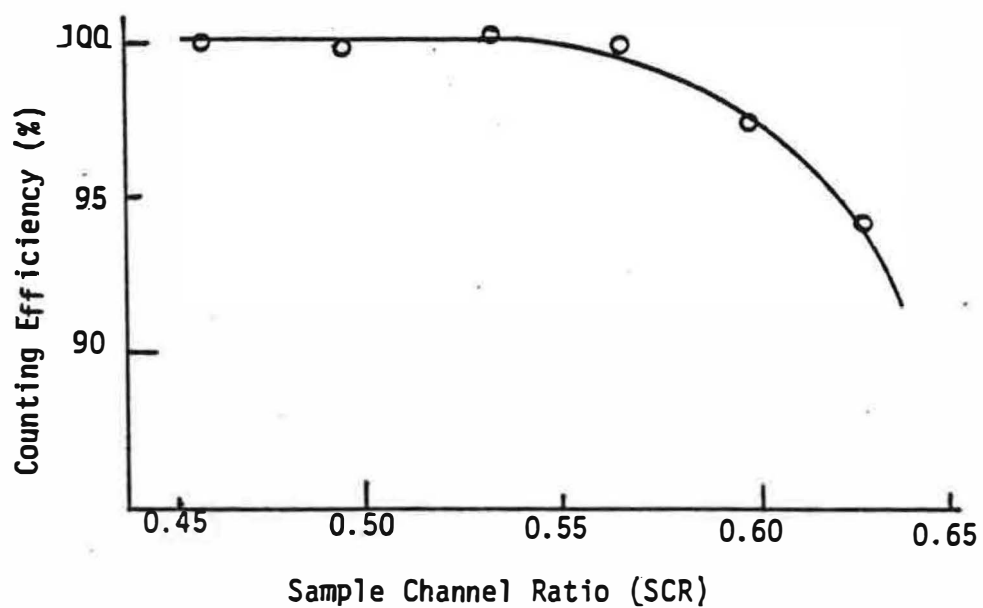
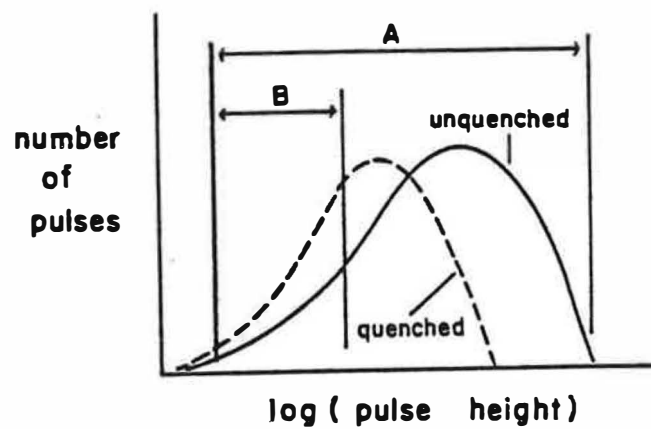


Figure 2. Counting Efficiency at Different Channel Ratios.

5. RESULTS AND DISCUSSIONS

TCE EXPERIMENTS

Sorption Behavior of TCE on Missouri Soils

Kinetics studies of TCE adsorption on Missouri soils were carried out in order to determine the time taken to reach equilibrium. The equilibration time was determined for at least one soil sample from each site using an initial TCE concentration of either 100 ppb or 500 ppb. A typical kinetic data for adsorption of TCE on Missouri soils is shown in Figure 3. In general, adsorption of TCE on the soils tested was observed to reach equilibrium after a period of about 48 hours. Similar equilibration time was assumed for the rest of the soil samples.

Based on the kinetic data, a period of 72 to 96 hours of shaking was chosen to obtain equilibrium adsorption isotherms. For each soil sample, isotherms were obtained by using five TCE concentration of 100, 250, 500, 750, and 1000 ppb (W/V).

The data collected for each sample was fitted to Freundlich's isotherm. The Freundlich sorption constants, k_p and $1/n$, were determined by linear regression. Typical Freundlich plot for selected soil samples are presented in Figure 4. The results of data analyses for all the soil samples tested are presented in Table 8.

The reported Freundlich isotherm coefficients for TCE adsorption (Table 8) indicate that only a minimal sorption would occur in any of the Missouri soils tested. It is observed that the Putnam AP soil adsorbed the highest amount of TCE, where as Grundy B soil adsorbed the least. In general, the surface soil samples from each site had higher partition coefficient (K_f) and the K_f value decreased with increasing depth of the sample. Because the soil organic carbon content has been observed to correlate well with adsorption of several organic

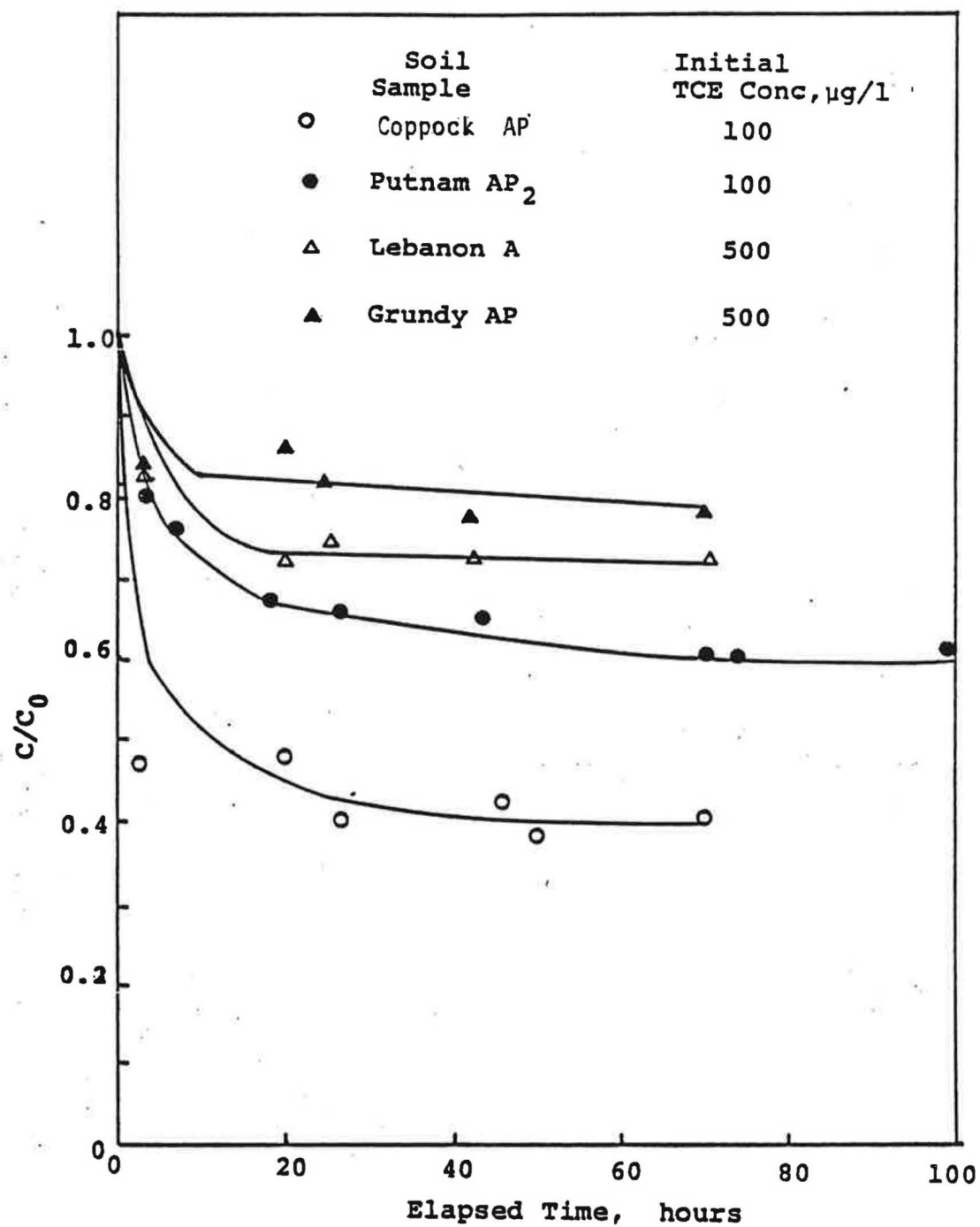


FIGURE 3. TYPICAL TCE SORPTION KINETICS ON MISSOURI SOILS

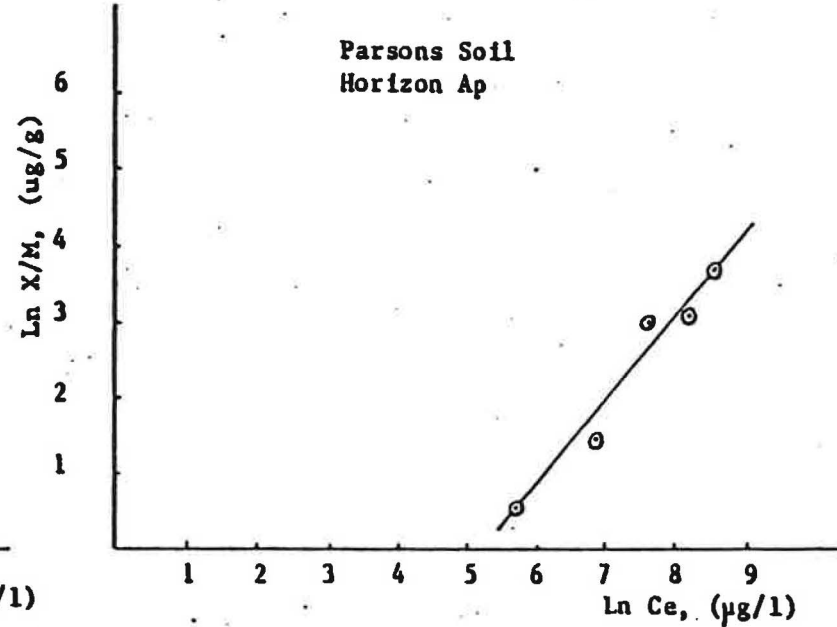
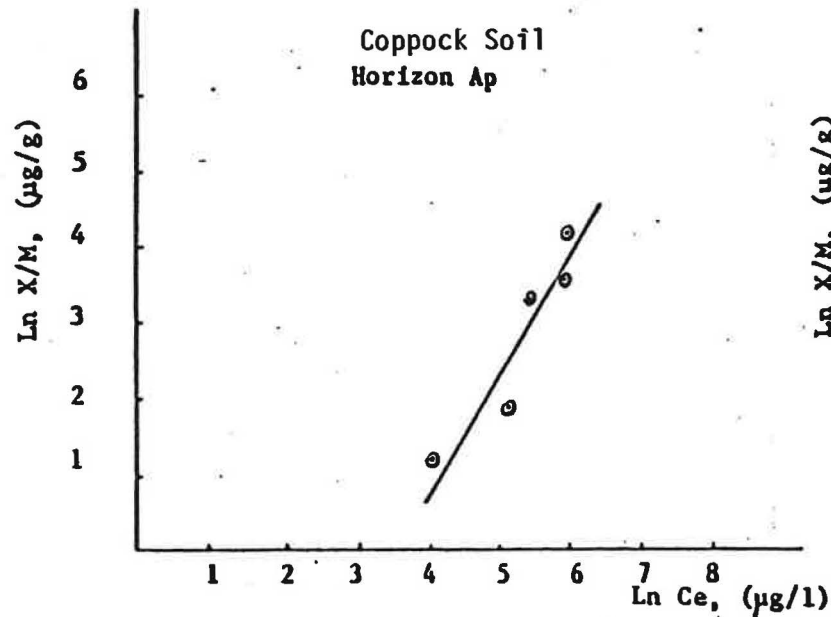
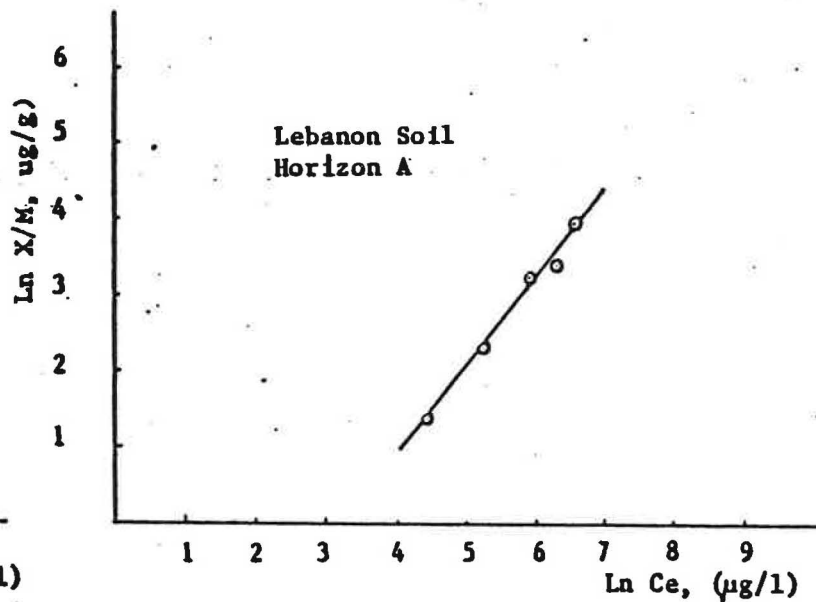
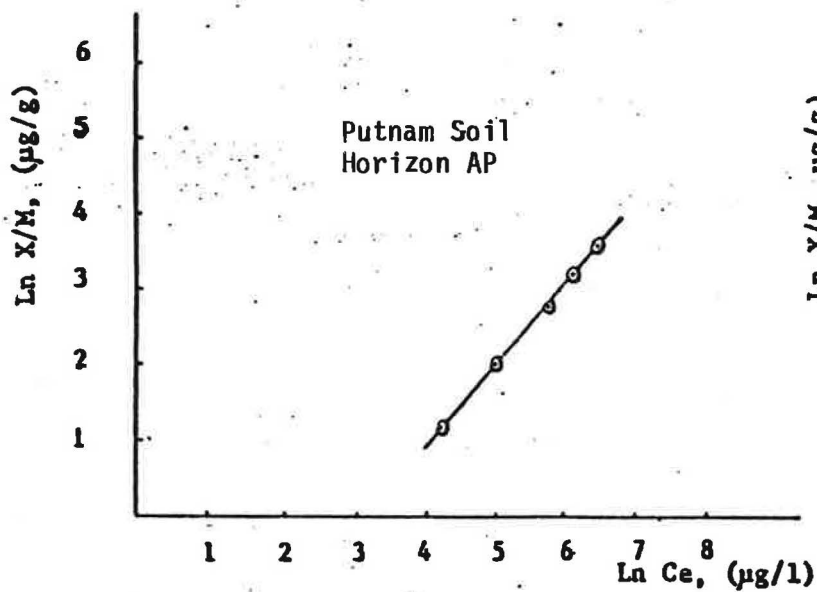


FIGURE 5. TYPICAL TCE ADSORPTION ISOTHERMS FOR MISSOURI SOILS

Table 8. Freundlich Isotherm Constants for TCE Adsorption on Missouri Soils

Soil	Horizon	K_p $\times 10^3$	1/n	Average* Isotherm $q = K_p C_e^{1/n}$
Coppock	AP	15.1	1.31	$q = 0.004 C_e^{1.44}$
	E	4.1	1.36	
	BE	1.1	1.47	
	B ₁ t	2.5	1.56	
	B ₂ t	1.8	1.39	
	B ₃ t	2.5	1.53	
	C	4.5	1.46	
Parsons	AP	8.7	1.15	$q = 0.007 C_e^{1.35}$
	A ₂	6.1	1.27	
	B ₂ t	6.0	1.64	
Putnam	AP	52.4	0.98	$q = 0.027 C_e^{1.15}$
	B ₂ t	7.8	1.31	
Lebanon	A	22.5	1.10	$q = 0.029 C_e^{1.05}$
	B	36.9	0.99	
Grundy	AP	1.7	1.42	$q = 0.001 C_e^{1.55}$
	B	0.4	1.68	

* q = Adsorbed TCE on soil, $\mu\text{g/g}$

C_e = Equilibrium TCE conc. in water phase, $\mu\text{g/l}$

compounds (47, 48, 13), the adsorption coefficient on the basis of organic carbon content rather than the total soil mass is generally reported. The organic carbon partition coefficient (K_{OC}) for the soil samples are calculated by the equation

$$K_{OC} = \frac{K_f}{\%OC} \times 100 \dots \dots \dots (5)$$

Since, in the present study, the soils were analyzed for organic matter content instead of organic carbon a conversion factor of 1.742 (generally reported in literature, (14)) was used. Hence, the K_{OC} was calculated by the equation

$$K_{OC} = \frac{K_f}{\%OM} \times 100 \times 1.742 \dots \dots \dots (6)$$

The K_{OC} values for the Missouri soils are summarized in Table 9. The results in Tables 8 and 9 indicate less variation in the K_{OC} values for TCE adsorption among the soil samples compared to the K_f values. Hamaker (49) and Rao and Davidson (50) have reported similar results where the K_{OC} values for a given pesticide were nearly independent of soil type. However, it should be recognized that soil pH, clay content, cation exchange capacity, play a significant role determining the adsorption of organics on soils.

Effect of Soil Properties on TCE sorption

Sorption mechanisms of an organic compound on soil could be influenced by the physical and chemical properties of the soil which ultimately govern the extent of retention in the soil phase. Among the several physical and chemical characteristics of the soil, organic carbon content is thought to affect significantly the sorption behavior of relatively non-ionic and hydrophobic organic compounds such as TCE. Most reported studies on the effect of soil organic matter on sorption of organic compounds have attempted to develop empirical relations to predict the sorption capacities of various soils and sediments.

Table 9. Freundlich Partition Coefficient (K_{oc})
Based on Organic Carbon Content

Soil	Horizon	Organic Matter %	K_{oc}	Average K_{oc}
Coppock	AP	1.52	1.71	
	E	1.46	0.49	
	BE	1.00	0.19	
	B ₁ t	1.10	0.39	0.85
	B ₂ t	0.76	0.41	
	B ₃ t	0.52	0.83	
	C	0.47	1.65	
Parsons	AP	1.8	0.83	
	A ₂	0.8	1.31	1.15
	B ₂ t	0.8	1.30	
Putnam	AP	1.8	5.02	
	B ₂ t	1.3	1.04	3.03
Lebanon	A	1.7	2.28	
	B	0.7	9.09	5.70
Grundy	AP	3.7	0.08	
	B	0.3	0.03	0.06

Effect of Organic Matter

Experimental results for TCE adsorption on Missouri soils were analyzed to determine the effect of soil organic matter on TCE adsorption. In general, the Freundlich sorption coefficient of TEC (K_f) decreased with decreasing soil organic matter among the soils tested (Tables 8 and 9). However, the K_f values varied significantly in different soils and no effect of organic matter was apparent. Grundy AP soil which contained highest organic matter (3.7%) among the soils tested, had the lowest partition coefficient (K_f or K_{OC}). Further analysis of the data suggested that there was no apparent correlation between the soil organic matter and TCE sorption coefficient.

Chiou et. al. (51) stated that sorption of nonionic organic compounds on soils from water solution occurs by equilibrium partitioning into a soil organic phase. Although there is a correlation between organic content and sorption, the partition coefficients of a compound in different soils can vary since the composition of humic component are not constant. Although the characterization of organic matter in the soils was not attempted, the variation of K_{OC} values among Missouri soils is evident from Table 9. Another important factor affecting the calculation of partition coefficients is the effect of soil organic matter dispersion into water, either in dissolved state or in association with colloidal soil particulates, which may not be effectively separated by centrifugation. In case of Grundy soils, significant coloration of centrifuged supernatant water was observed indicating soil organic matter released into the water phase. The TCE concentration associated with the organic matter in water phase was thus measured as unadsorbed TCE in the water phase. Hence, the K_f values calculated from the isotherms were very low compared to other soils with lower organic matter content.

Selecting only the surface samples of each soil, TCE sorption experiments were conducted after removing the soil organic matter by peroxide digestion.

Table 10 compares the effect of peroxide treatment on TCE sorption. There was no significant effect observed for the Parson and Lebanon soils. Sorption capacities for Coppock and Putnam soils significantly decreased and a dramatic increase of k_p value for Grundy soil was apparent.

A decrease in the sorption capacity in the absence of soil organic matter is generally expected. However, as observed by MacIntyre and Smith (52) a significant adsorption of nonionic compounds by soil minerals can be expected. Also, partial removal of organic matter, as might have happened in Grundy soils, could apparently increase the sorption coefficient.

McCarty et. al. (2) stated that there must be a critical level of organic matter in inorganic matrices at which sorption to organic and inorganic materials is the same, and below which the organic phase is not dominant. This critical level (f_{oc*}) is dependent on the silica-specific area, S , and octanol/water coefficient, K_{OW} , of the solute given by the equation

$$f_{oc*} = \frac{S}{200} \frac{1}{(K_{OW})^{1.84}} \dots \dots \dots (7)$$

For a typical soil, assuming $S = 13 \text{ m}^2/\text{g}$, the critical organic fraction of TCE was calculated to be about 0.1 percent (2). Most Missouri soils tested contained over 0.1 percent organic matter and hence according to this theory, soils organic phase would be most significant in TCE retention.

Effect of soil-water pH on TCE sorption

Unlike the surface acidity of soils, the pH of soil-water solution influences the properties of both adsorbent and adsorbate. The pH of the soil solution will determine the speciation of the adsorbate, which is a function of the pK_a of the organic compound. Therefore, whether a compound is present in the molecular, the cationic, or anionic form can affect the extent and magnitude of adsorption and the strength by which it is held, since the energy of adsorp-

Table 10. Effect of Soil Organic Matter Removal by Peroxide Digestion on TCE Adsorption of Missouri Soils

Soil	Horizon	Organic Matter %	CEC meq./100g	Freundlich Isotherm	
				Digested Soil	Undigested Soil
Coppock	AP	1.5	15.55	$q = 0.0001C_e^{1.85}$	$q = 0.015C_e^{1.31}$
Putnam	AP	1.8	20.19	$q = 0.008C_e^{1.27}$	$q = 0.052C_e^{0.98}$
Parsons	AP	1.8	12.93	$q = 0.007C_e^{1.34}$	$q = 0.009C_e^{1.15}$
Lebanon	A	1.7	9.32	$q = 0.030C_e^{1.24}$	$q = 0.022C_e^{1.10}$
Grundy	AP	3.7	33.91	$q = 0.036C_e^{0.98}$	$q = 0.002C_e^{1.42}$

Freundlich Isotherm: $q = K_f C_e^{1/n}$, where, q = sorbate conc. on soil, $\mu\text{g/g}$
 C_e = equilibrium solution sorbate concentration, $\mu\text{g/l}$
 $K_f, 1/n$ = Freundlich isotherm constants

tion may be vastly different between dissociated and associated forms (53). Frissel and Bolt (54) reported that the adsorption of acidic-type herbicides was dependent upon the pH of the suspension, while the adsorption of a basic compound was dependent upon the surface acidity.

The effect of the change in the soil-water solution pH on TCE adsorption behavior was studied for Coppock and Putnam soils. The experimental procedure remained same except that the soil-water pH was changed by using 1 N sodium hydroxide. The results of the experiments are presented in Table 11. Since TCE is relatively nonionic the adsorption of TCE on soils may not be affected by the soil-water pH changes. However, the results showed that an increase in soil-water pH decreased the sorption capacity of the soil as reflected by lower k_f values. It should be noted that the increased in pH could affect the surface properties, including release of organic matter into the water phase resulting in an apparent decrease of calculated k_f values.

Prediction of TCE Transport in Soils

An analysis of contaminant transport in soil requires an extensive knowledge of the geochemical characteristics and the groundwater flow patterns. Such an analysis is usually expensive, time consuming, and involves field observations.

However, a rough estimate of the retention behavior of a given hydrophobic organic compounds, such as TCE, may be obtained by treating transport through the subsurface system as a one-dimensional process with constant flow in a homogeneous porous medium. An average retardation factor (ratio of the residence time of the solute to the residence time of the water) can then be calculated for a given segment of the subsurface system, assuming a linear sorption isotherm, by the equation:

$$R_f = 1 + \frac{P_B}{E} K_f \dots \dots \dots (3)$$

Table 11. Effect of Soil-Water Solution pH Changes on TCE Adsorption of Missouri Soils

Soil	Horizon	Soil-Water Solution pH	Freundlich Adsorption Isotherm
Coppock	AP	6.80 (natural)	$q = 0.015 C_e^{1.31}$
	AP	9.57	$q = 0.001 C_e^{1.43}$
	C	5.98 (natural)	$q = 0.047 C_e^{1.06}$
	C	9.92	$q = 0.002 C_e^{1.43}$
Putnam	AP	6.43 (natural)	$q = 0.052 C_e^{0.98}$
	AP	7.49	NS*
	AP	8.96	$q = 0.006 C_e^{1.27}$
	B ₂ t	5.61 (natural)	$q = 0.008 C_e^{1.31}$
	B ₂ t	6.66	NS
	B ₂ t	9.44	$q = 0.019 C_e^{1.04}$

*NS = No apparent sorption

where,

R_f = retardation factor

K_f = soil-water TCE partition coefficient

P_b = bulk density of soil, (g/cm³)

E = porosity of soil matrix.

The retardation factor allows an estimation of the maximum quantity of contaminant that can be accumulated in the subsurface system when contaminated water flows through it. This can be important in estimating the time required to flush out an adsorbed contaminant (2).

Table 12 presents the retardation factors calculated from the adsorption isotherms for the various Missouri soils. The values for P_b and E of Columbia soils were measured at the site for various horizons (55). For the rest of the soil the values for P_b and E were estimated (55). Table 12 also presents the predicted retardation factors for the various soils assuming that retention is solely due to the organic phase. Using the relationship given by Karickhoff et. al. (47) the predicted retention factor for a soil is calculated by

$$R_f = 1 + 0.63 f_{oc} (K_{ow}) \frac{P}{E} \dots \dots \dots (8)$$

where,

f_{oc} = fraction of organic carbon in the soil

K_{ow} = octanol/water partition coefficient.

A comparison of the predicted and the observed retardation factors suggests that for most soils the organic phase is a dominant stationary phase of significance retaining and accumulating TCE in Missouri soils. However, Putnam AP soil shows a clearly higher sorption capacity for TCE compared to the predicted adsorption solely due to the organic phase.

As discussed earlier, inorganic components of the soils may also significantly influence the sorption capacity of the soils.

Table 12. Retention of TCE in Missouri Soils

Soil	Horizon	Porosity	Density g/cm ³	Retardation Factor	
				Observed	Predicted
Coppock	AP	0.50	1.32	41	3.9
	E	0.44	1.49	15	4.5
	BE	0.42	1.53	5	3.6
	B ₁ t	0.43	1.50	9	2.7
	B ₂ t	0.43	1.51	7	2.9
	B ₃ t	0.41	1.56	10	2.4
	C	0.40	1.58	19	1.3
Putnam	AP	0.51	1.30	134	4.3
	B ₂ t	0.54	1.25	19	3.2
Parsons	AP	0.51	1.30	23	4.3
	A ₂	0.51	1.30	17	2.5
	B ₂ t	0.54	1.25	15	2.3
Lebanon	A	0.54	1.25	53	3.8
	B	0.51	1.30	95	2.3
Grundy	AP	0.51	1.30	5	7.7
	B	0.54	1.23	2	1.5

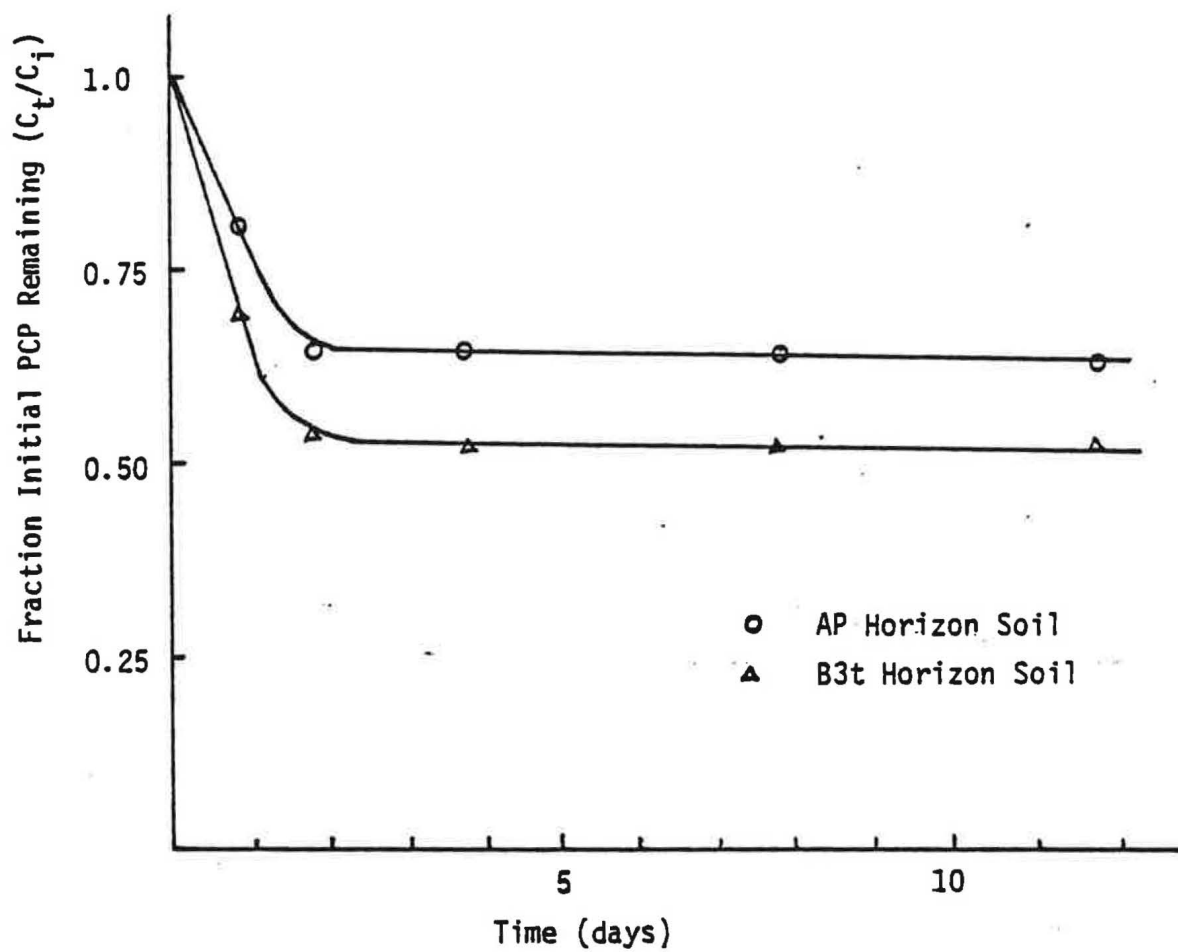


Figure 5. PCP Sorption Kinetics on Coppock Series Soils.

PCP EXPERIMENTS:Kinetic Studies

A kinetic study was done on both soils to determine the time required for equilibrium to be reached. The initial pentachlorophenol concentration used in both cases was 1 mg/l. As illustrated in Figure 5, nearly 100% of the adsorption that occurred over the course of the 12 day subsequent adsorption experiments, a mixing time of 72 hours was employed. It was assumed that this 50% increase in mixing time would cover any changes in sorption kinetics which could occur as a result of changing pH, ionic strength and other parameters.

Freundlich plot of the data of PCP adsorption on Coppock soil gave the best fit. Figure 6 shows the Freundlich plots for PCP adsorption on Coppock soils.

The Freundlich constants n and K_f for these two batch experiments, along with the constants obtained in all succeeding batch experiments, are presented in Table 13. Because adsorption coefficients are often calculated on an organic carbon basis (K_{OC}), the Freundlich constants in Table 13 are also presented in this manner. The K_f constants were converted to the organic carbon basis using the following relationship:

$$K_{OC} = K_f / f_{om} \times 1.724 \dots \dots \dots (9)$$

where,

f_{om} - the fraction of organic matter in the soil

1.724 = conversion factor for organic matter to organic carbon (14).

The data in Figure 6 and Table 13 show that the B3t soils adsorbed more PCP than the AP soil. This was a bit surprising in light of the fact that the AP soil contained approximately 3 times as much organic matter as the B3t soil. As discussed earlier, organic matter content is the soil parameter most often linked to adsorption of organics. The B3t soil does have a greater CEC than the AP soil, but this would not be expected to greatly influence the adsorption of pentachlorophenol, an acidic organic.

The pH of the B3t soil/PCP solution suspension was measured as 5.7, compared to a suspension pH of 6.7 for the AP horizon. The pH of the soil suspension will determine the degree of dissociation of a weak acid like PCP. Whether a compound is present in the molecular or ionized form can affect the extent and magnitude of adsorption of an organic, and the strength by which it is held, since the energy of adsorption may be vastly different between the dissociated and molecular form (56).

Effect of Suspension pH

An investigation of the effects of suspension pH on the adsorption of PCP was then conducted. For both the AP and B3t horizons, the suspensions pH was adjusted by the addition of NaOH or HCl. Freundlich adsorption isotherms were obtained by the batch method.

Pentachlorophenol adsorption by both the B3t and AP clearly increased with decreasing pH, as illustrated in Figure 7. The Freundlich constants of maximum and minimum adsorption for each soil (corresponding to the lowest and highest adjusted pH values) are presented in this figure. Another description of this trend toward increased adsorption with decreasing pH is presented in Figure 8. In this figure, % removal was calculated by determining the amount of PCP which would be adsorbed by 14 grams of soil from 140 mls. of a 1 ppm PCP/water solution as predicted by the Freundlich equation. Freundlich constants used in the calculation were obtained from the appropriate isotherm.

Hamaker and Thompson (57) reviewed several studies concerning the adsorption of weakly acidic organics by soils and concluded that weak acids are very much more highly adsorbed when in the free acid as compared to the anion. Anions tend to be repelled from the negatively charged clay surfaces, inhibiting adsorption at these sites. Repulsion of the anion by the predominantly negatively charged surface of organic matter can also reduce adsorption. The dissociation constant of acidic groups in humic acids (COOH plus phenolic- and enolic- OH) is

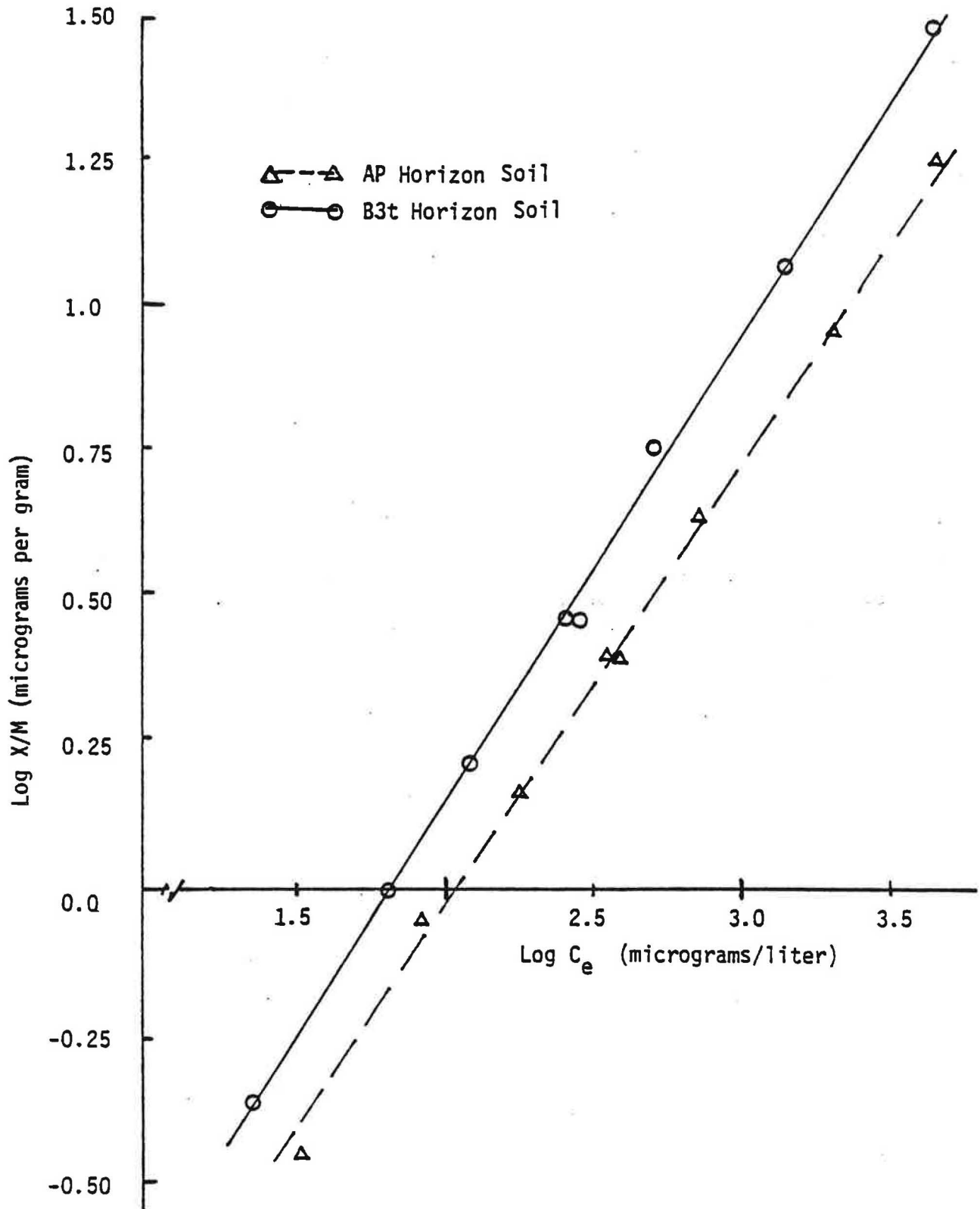


Figure 6. Freundlich Adsorption Isotherm for PCP on Coppock Soils.

Table 13. PCP Freundlich Adsorption Isotherm Data on Coppock Soil Services

Treatment	pH	Freundlich Constants			
		n	K_f	K_{oc}	r^2
AP Horizon					
----	6.8	1.33	0.029	32.2	0.999
HCl	5.8	1.40	0.060	66.7	0.987
HCl	6.1	1.45	0.042	46.7	0.998
NaOH	7.1	1.30	0.016	17.8	1.000
NaOH	7.5	1.22	0.007	7.8	0.996
NaOH	7.9	1.07	0.002	2.2	0.991
NaCl	6.5	1.26	0.025	27.8	0.994
NaCl	6.6	1.26	0.026	28.9	0.999
NaCl	6.7	1.29	0.031	34.4	0.997
B3t Horizon					
----	5.6	1.26	0.035	117	0.998
HCl	4.2	1.20	0.058	193	0.998
HCl	4.8	1.79	0.154	513	0.995
NaOH	5.7	1.22	0.017	56.7	0.996
NaOH	6.1	1.30	0.012	40	0.996
NaOH	6.6	1.25	0.005	16.7	0.993
NaCl	5.2	1.22	0.048	160	0.997
NaCl	5.2	1.27	0.062	207	0.994
NaCl	5.1	1.24	0.066	220	0.993
Humic Acid Extract Experiments					
*	4.1	1.08	0.219	0.38	1.000
**	4.9	1.14	0.054	0.33	1.000

* 3.95 grams purified humic acid extract and 140 mls PCP/water solution

** " " " " mixed with 14 grams B3t soil " "

in approximately the same range as that of PCP, 4.5 to 5.5. As this pH range is approached, increased adsorption of PCP by organic matter could be attributed to the hydrogen-bonding of molecular PCP with the COOH, C=O, and NH₂ groups of organic matter (58). Adsorption of pentachlorophenol onto organic matter through hydrophobic bonding would also increase as both the PCP and organic colloids become less polar (un-ionized).

It can be seen in Figure 8, for adsorption at the same suspension pH, the surface soil (AP) adsorbed more PCP than the subsurface soil (B3t). This may be due to the higher organic matter content of the surface soil. Figure 9 is a plot of the removal of PCP on an organic carbon basis as a function of pH. In this figure, removal is represented by X/M, the amount of PCP adsorbed per unit weight organic carbon. X/M values were computed using the appropriate Freundlich constants and assuming an initial PCP concentration of 1 ppm. This figure illustrates, that for the same suspension pH, the sorptive capacities of the two soils are quite similar when viewed on an organic carbon basis. The B3t soil, in fact, exhibits a higher PCP adsorption per gram organic carbon than the AP soil. This contrasts with the trend illustrated in Figure 8, where adsorption is presented on a "total soil" basis.

To further elicit the role of organic matter content in the adsorption of PCP by these soils, additional batch adsorption experiments were conducted.

Influence of Soil Organic Matter

140 mls of PCP/water solution were placed in two sets of sample bottles. Approximately 4 grams of purified humic acid extract were added to one set of bottles, to the other set of bottles a mixture of approximately 18 grams of an equilibrated mixture of approximately 4 grams of purified humic acid extract and 14 grams of B3t horizon soil were added. After mixing, equilibrium pH values were measured and Freundlich isotherms were constructed from the resulting data.

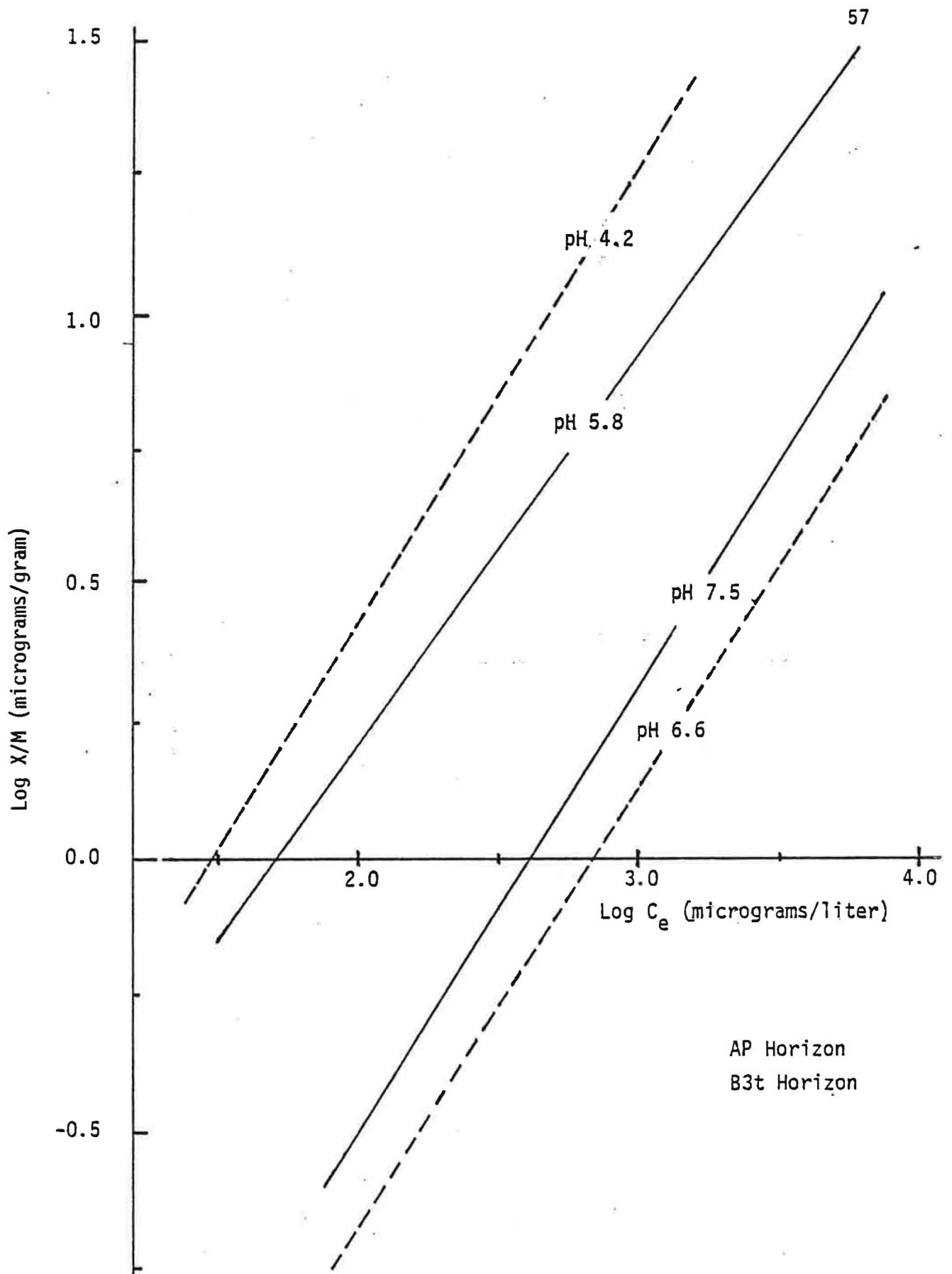
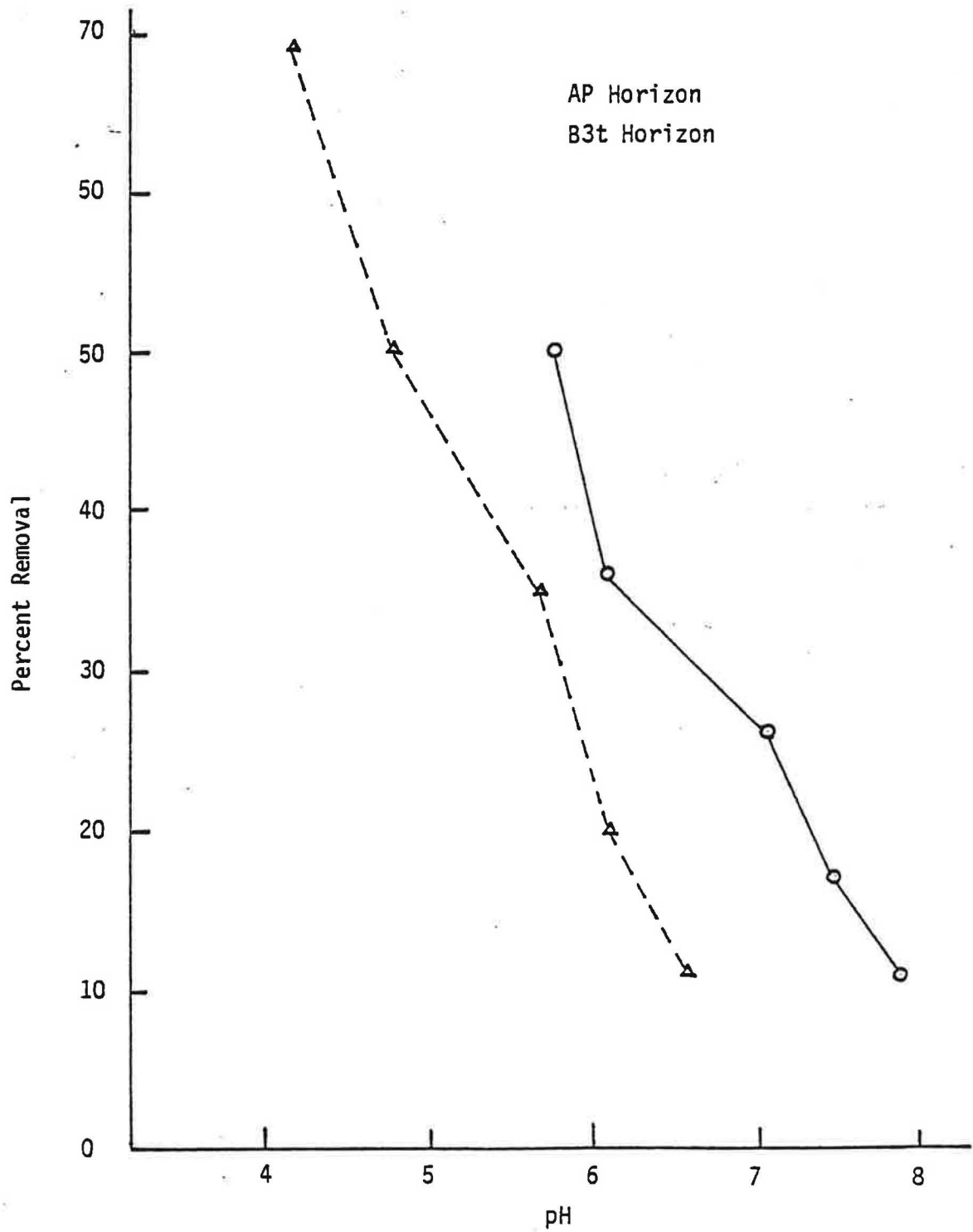


Figure 7. Effect of pH on PCP Adsorption Coppock Soils

Figure 8. PCP Removal as a Function of pH.



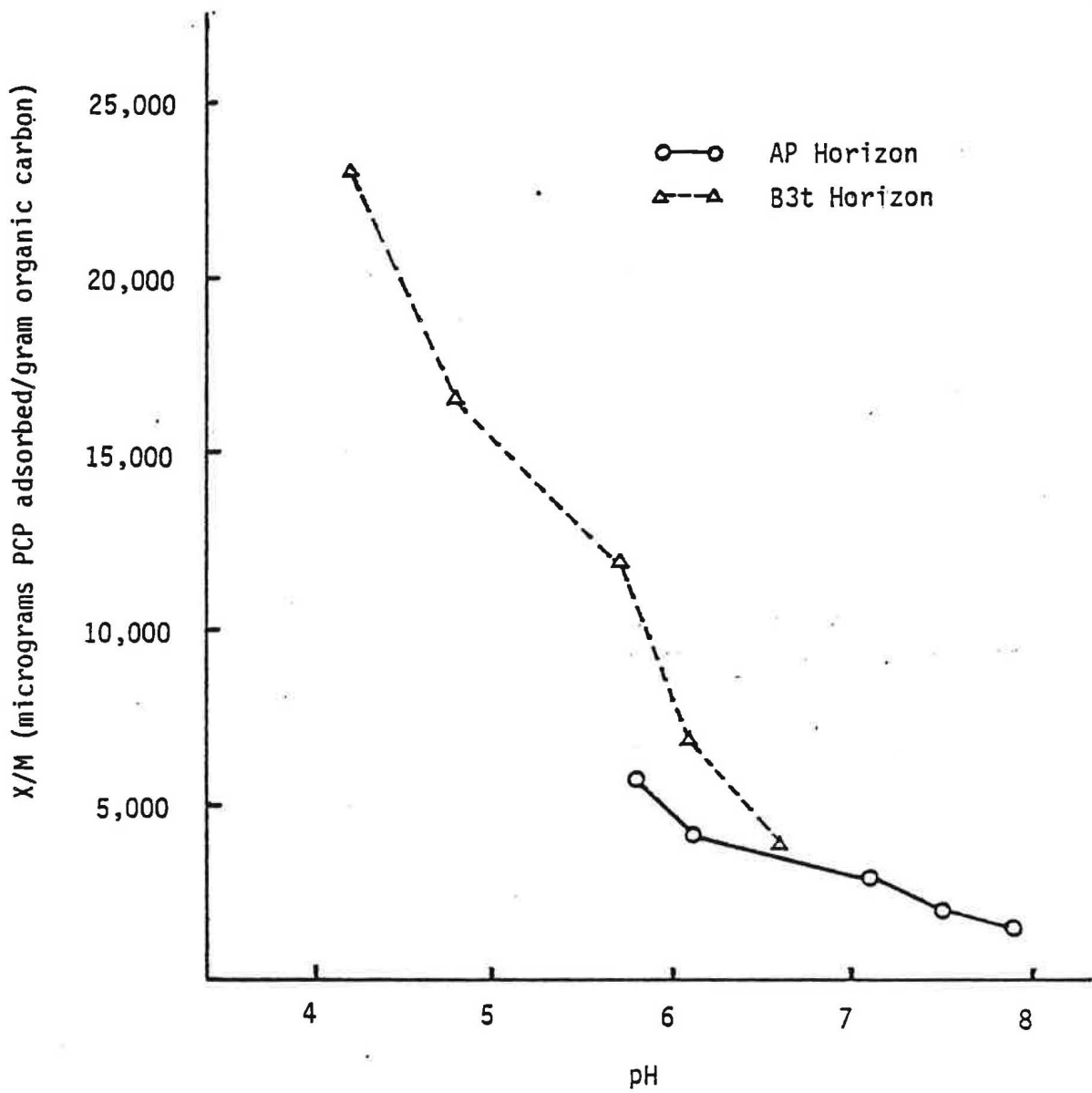


Figure 9. PCP Adsorption as a Function of pH.

γ values were then computed on a total soil and an organic carbon basis. An initial PCP concentration of 1 ppm was assumed. The results of these computations are presented in Table 14. On a total soil basis, the γ values of the humic acid extract and the humic acid extract/B3t soil mixture were higher than the γ values of the B3t soil at a similar pH. This indicated the importance of organic matter in adsorption. When computed on an organic carbon basis, however, the γ values of the humic acid extract and extract/soil mixture were dramatically lower than the corresponding γ values of the B3t soil.

Table 14. The Effect of Increased Organic Matter on γ

Sorbent	pH	$\gamma(X/M)$	X/Moc
Humic acid extract	4.1	28.6	49.3
B3t horizon soil	4.2	6.6	22,000
B3t horizon soil	4.8	4.9	16,300
extract/soil mixture	4.9	7.0	42.2

Hamaker and Thompson (59) noted that whereas adsorption coefficient values for soils high in organic matter content are much higher than those of "normal" soils, the values of the adsorption coefficient on an organic carbon basis (K_{oc}) are usually much lower than the corresponding K_{oc} values of normal soils. This may be due to a "piling up" of the organic matter, which limits the adsorbing surface per unit weight of organic matter (57) of soil.

ADSORPTION REVERSIBILITY

The reversibility of PCP adsorption by the surface soil was examined by conducting the standard batch adsorption experiment (140 mls of PCP/water solution and 14 grams of soil), centrifuging the entire sample bottle to retain the soil,

sampling and discarding the supernatant, adding 140 mls of "clean" deionized water, and then mixing for the 72 hour equilibration time. Two desorption isotherms were obtained in this manner. A final desorption was done using an organic solvent (2-propanol) instead of water. The results of these desorption experiments are presented in Table 15.

The percentage of PCP initially adsorbed that was desorbed during the three washings averaged 84%. The bulk of the total PCP desorbed in the three washings was desorbed in the first washing. The amount of PCP not recovered in the three washings varied from 0.20 micrograms/gram soil to 1.39 micrograms/gram soil.

Breakdown of PCP to carbon dioxide would have been required for the labelled ring carbon atom of PCP to escape detection. The relatively short time involved in the experiment and the absence of an acclimated microbial population makes it unlikely that microbial degradation contributed significantly to the amount of PCP not recovered. Rather, it appears that a fraction of the PCP initially adsorbed was adsorbed irreversibly. Other investigations of adsorption of organics onto soil have confirmed that desorption appears to differ from adsorption in being slower and also in that a portion of the adsorbed material is very difficult to remove. The desorption isotherm reflects the higher retention of the chemical in the solid (59).

By examining the Freundlich constants in Table 15, one can see that the adsorption/desorption isotherms are not single valued. This indicates that a contaminant transport model cannot exactly describe contaminant retardation (adsorption) using a single adsorption coefficient to describe both adsorption and desorption.

Table 15. Desorption of PCP from Coppock Soil.

C_e^*	$\gamma = X/M$ (micrograms PCP/gram soil)					% recovered
	Adsorbed	Desorbed			Remaining	
		#1	#2	#3		
6040	15.73	10.87	2.08	2.29	0.49	96.9
6290	13.21	8.14	1.83	1.88	1.36	89.7
3020	9.06	5.14	1.23	1.47	1.22	86.5
3120	8.13	5.01	1.21	1.45	0.46	94.3
1260	4.65	2.38	0.64	0.80	0.83	82.1
1280	4.44	2.37	0.62	0.86	0.60	86.6
700	2.89	1.33	0.38	0.59	0.59	79.6
420	1.95	0.81	0.24	0.45	0.45	77.0
430	1.88	0.86	0.24	0.40	0.39	79.5
165	0.85	0.33	0.10	0.21	0.21	75.0
165	0.85	0.33	0.10	0.22	0.20	76.7
Freundlich Constants**						
n	1.29	1.02	1.03	1.00		
K	0.017	0.009	0.009	0.007		
K_{oc}	18.9	10.0	10.0	7.8		
r^2	1.00	1.00	1.00	1.00		

* Equilibrium PCP concentration in initial adsorption experiment (micrograms per liter)

** Constants for Freundlich Equation

$$X/M = K (C_e)^{1/n}$$

$$X/M_{oc} = K_{oc} \times (C_e)^{1/n}$$

6. CONCLUSIONS

TCE EXPERIMENTS:

The following conclusions can be made from the experiments on TCE adsorption on selected Missouri soils:

1. Measured equilibrium adsorption isotherms for nearly all soils were of nonlinear Freundlich type.
2. The Freundlich adsorption constant (K_{oc}) based on soil organic matter was much less variable among the soils than was the K_f based on total soil mass.
3. Removal of organic matter from soils by peroxide digestion decreased the K_f values for Coppock and Putnam soil, did not affect Parson and Lebanon soils, and significantly increased for Grundy soils. The apparent increase of K_f value for Grundy soil may be due to incomplete removal of organic matter by the peroxide digestion.
4. Increase of soil-water solution pH, generally decreased the TCE adsorption coefficient. The observed effect may be due to release of soil organic matter at high pH into the water phase.
5. Retardation factors (ratio of the residence time of the solute to the residence time of the water) calculated for most Missouri soils were low, indicating that TCE can be readily transported through these soils.
6. Comparison of predicted and observed retardation factors suggest that for most soils, the organic phase is a dominant stationary phase of significance, retaining and accumulating TCE in the Missouri soils.

PCP EXPERIMENTS:

The following conclusions can be made from the experiments of PCP adsorption on selected Coppock soils:

1. Adsorption of PCP to soils can be accurately described by the Freundlich relationship.
2. While the organic matter content of a soil is important in determining the extent of adsorption, an even more important soil property is pH.
3. Adsorption of PCP to soils significantly increases with decreasing pH.
4. Adsorption coefficients obtained in batch adsorption experiments indicate significant retardation of a PCP contaminant plume will occur during groundwater flow through the soil column.
5. Adsorption of PCP to soils is, to a large extent, a reversible process.

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