Investigation of Multicomponent Sorption and Desorption Rates in Saturated Groundwater Systems

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Abstract

Laboratory experiments were performed and mathematical models were developed and used to analyze sorption and desorption processes of hydrophobic organic solutes to subsurface materials. The work included consideration of both single and multisolute systems, while experiments were performed in both batch and one-dimensional column reactor systems. The solutes used covered a range of hydrophobicity, which fell within a log octanol-water partition coefficient range of 2.18 to 4.30. One of the solutes, γ-hexachlorocyclohexane (lindane), was observed to degrade by an E2 elimination process, which occurred at a rate that was dependent upon the pH of the system. Two sandy subsurface materials were used in the experimental work, which had organic carbon contents that covered a relatively wide range, 0.026 to 1.200%.

Mathematical model development included a variety of batch, one-dimensional, and two-dimensional models for simulating single and multicomponent sorption processes described by nonlinear equilibrium expressions and diffusional rate models. Petrov-Galerkin finite element methods were used to accommodate sharp-front problems, while sorption rates were simulated using a method of lines solution procedure. Numerical procedures used also included operator splitting methods and consideration of parallel processing.

A set of experiments was performed to analyze desorption equilibrium and rate behavior for lindane on the high total organic carbon subsurface material. The results indicated that rates of sorption and desorption are important factors contributing to apparent desorption hysteresis. Rate modeling of experimental data showed that a substantial fraction of the hysteresis could be explained by non-attainment of equilibrium in pseudo-equilibrium batch experiments. This result is especially important in view of the finding that time scales on the order of a few months to a year are needed to approach equilibrium in the systems investigated. This time far exceeds the period over which most experimental sorption work is performed.

A complete and consistent set of multicomponent sorption rate and equilibrium experiments was performed for both solid materials using the solute lindane and 1,2,4-trichlorobenzene. These experiments reinforced the findings that time scales for equilibration are on the order of months, and sorption equilibrium relationships are nonlinear. Competition was not observed in batch experiments, either with regard to sorption equilibrium or with regard to the rate of sorption. This lack of competition did not agree well with predictions made using ideal adsorbed solution theory. However, significant competition was observed in a set of column experiments. It is concluded that column experiments provide a more sensitive indicator of competitive sorption than batch experiments.
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Summary and Conclusions

An investigation was undertaken to evaluate sorption and desorption processes in single and multicomponent solute systems, which included subsurface sand materials of varying total organic carbon content, and neutral organic solutes of varying lipophilicity. The experimental work was reinforced by mathematical modeling work, which was used to interpret laboratory data and to evaluate the significance of the findings with regard to length and time scales other than those investigated.

The specific objectives of the project were (1) an evaluation of multicomponent solute effects on sorption rates and equilibria, (2) an evaluation of sorption and desorption rate effects as an explanation for apparent desorption hysteresis, and (3) the development of improved numerical schemes for simulating nonlinear and rate controlled sorption and desorption processes in batch, one-dimensional, and two-dimensional systems. The conclusions from this work are as follows:

1. Sorption and desorption rates were found to be slow compared to the typical time allowed for equilibration in most other experimental work published to date—on the order of a few to several months was required for equilibrium to be approached.

2. A variety of numerical models was developed to simulate sorption and desorption processes for single and multisolute systems in batch, one-dimensional, and two-dimensional systems. These models simulated nonlinear sorption equilibria using the single-solute Freundlich equilibrium model and ideal adsorbed solution theory. Rate effects were simulated as diffusional processes, assuming spherical symmetry.

3. Experimental work and surface diffusion modeling were used to show that the majority of apparent desorption hysteresis may be explained as an artifact of sorption and desorption rate effects. That is, slow sorption and desorption processes can be the cause of apparent hysteresis in laboratory desorption experiments, which do not allow sufficient time for attainment of equilibrium.

4. Bisolute batch experiments performed for both of the subsurface materials showed no evidence for competitive effects on either sorption equilibria or sorption rates.

5. Column experiments did, however, show evidence of competitive sorption effects—suggesting that column experiments are more sensitive experiments for observing such phenomena.
Recommendations

The work summarized in this document suggests several recommendations—some that are immediately applicable, and some that require additional research. These recommendations may be summarized by:

1. Nonlinear sorption equilibrium should be considered when assessing solute transport at the field scale, especially when estimating aquifer restoration times.

2. Sorption rate effects are likely to cause deviations from local equilibrium for a significant fraction of field-scale problems, and inclusion of these effects in simulation models should be used to provide more accurate simulations.

3. Additional work is needed to determine the extent of multisolute competitive effects on sorption equilibria and rates. Important issues to be resolved include competition in systems with more than two solutes, and the development of models to predict competitive effects.

4. Development work should continue on numerical algorithms that can be efficiently used for multidimensional, field-scale problems.
1 Introduction

1.1 Motivation

The groundwater resources of the United States have been extensively contaminated by a wide variety of organic pollutants. This widespread contamination has led to a need for a better understanding of the processes that influence the transport and eventual fate of such contaminants. A better understanding of these fundamental processes is necessary to more accurately assess health risks, and to more economically and effectively design aquifer renovation measures.

The sorption-desorption process is one of the most important processes influencing contaminant movement in groundwater systems. Sorption is the interphase mass transfer of a solute from the groundwater phase to the solid phase; desorption is the interphase mass transfer of a solute from the solid phase to the groundwater phase. Similar to all inter-phase, mass-transfer processes, the sorption-desorption process can be defined by the final phase equilibrium of the solute between the two respective phases and the time required to approach that final equilibrium.

While the importance of the sorption-desorption process in subsurface environments has been recognized for some time, many important gaps presently exist in knowledge of the fundamentals of this process and in understanding of the relative importance of non-ideal conditions (i.e., nonlinear or hysteretic equilibrium, and non-instantaneous rates). These gaps include:

- a mechanistic explanation of sorption rate phenomena;
- an understanding of the cause(s) of desorption hysteresis;
- an understanding of sorption-desorption phenomena to low organic carbon solids;
- an understanding of the effects of multiple solute components on the rate and equilibrium of sorption-desorption;
- an appreciation of the effects of sorption rates and nonlinearity on contaminant transport at the field scale as a function of solute source condition; and
- a better understanding of the effects of sorption rates and nonlinearity on solute transport at the field scale compared to subsurface heterogeneity.
1.2 Objectives

The overall objective of this project was to determine the influence of sorption-desorption rates and equilibrium on the movement of multicomponent, hydrophobic, organic constituents in saturated groundwater systems. This overall objective can be divided into sub-objectives:

1. to investigate the equilibrium and rate of sorption-desorption for single, and multicomponent hydrophobic organic solutes to aquifer materials;

2. to evaluate the relationship between sorption-desorption rates and equilibria for a variety of solute-aquifer material systems;

3. to develop and apply mathematical models to describe sorption-desorption processes;

4. to evaluate the significance of the sorption-desorption rates determined as a function of contaminant source relationship;

5. to investigate the significance of sorption-desorption rates for typical heterogeneous aquifer conditions.
2 Previous Research

2.1 Sorption Equilibrium

A large body of literature exists describing experimental observations of sorption equilibria between soils and sediments for a wide variety of organic and inorganic compounds (Bailey and White, 1970; Pierce et al., 1971; Browman and Chesters, 1975; Karickhoff et al., 1979; Kenaga and Goring, 1980; Morrill et al., 1982; Murali and Aylmore, 1983a, 1983b; Voice and Weber, 1983; Karickhoff, 1984; Chiou, 1989). This work has led to a maturing of the current level of understanding of the sorption-desorption process, from both a predictive and a mechanistic perspective. It is well understood that sorption to soils (or sediments) is a function of several variables: ionic nature of the solute; polarity of the solute; solvency of the solute with respect to the solvent; presence of competing solutes; organic carbon content of the soil; mineral content of the soil; system pH; temperature; and ionic strength of the solvent.

Much of the recent research has dealt with the sorption and desorption of neutral, hydrophobic organic compounds to soils and sediments (Karickhoff et al., 1979; Chiou et al., 1983; Karickhoff, 1984; Gschwend and Wu, 1985; Miller and Weber, 1986; Woodburn et al., 1986). It is currently understood that the fraction of organic matter of a soil or sediment is the dominant characteristic that influences the sorption of a given neutral, low polarity, hydrophobic, organic compound from an aqueous solution. Further, there is significant evidence present to suggest that sorption for such systems is a partitioning like phenomenon—or an absorption of the organic solute into the organic matter of the soil or sediment.

Unfortunately, less work has been done on typical aquifer soils that have very low (less than 0.1 percent) total organic carbon content. The low organic carbon work that has been done suggests that mineral surface sorption may be important for typical aquifer soils systems (Means et al., 1980, and 1982; Mingelgrin and Gerstl, 1983; Banerjee et al., 1980; Goltz and Roberts, 1986; Mackay et al., 1986; Stauffer and MacIntyre, 1986).

2.2 Sorption Rates

Definition of the sorption-desorption, mass-transfer process also requires a determination of the rate at which equilibrium is approached. Many investigations have assumed that the sorption-desorption process may be accurately characterized by an instantaneous, local equilibrium between the solid and the aqueous phase (Back and Cherry, 1976; Anderson, 1979; Freeze and Cherry, 1979; Faust and Mercer, 1980; Prickett et al., 1981; Roberts et al., 1982). However, the literature substantiates that rates of sorption-desorption are important for many organic solute/soil systems (Kay and Elrick, 1967; Leenheer and Ahlrichs, 1971; Boucher and Lee, 1972; Karickhoff, 1980; Hutzler et al., 1986; Karickhoff, 1984;
Miller, 1984; Miller and Weber, 1984a, 1984b, 1986, and 1988; Coates and Elzerman, 1986; Crittenden et al., 1986; Wu and Gschwend, 1986; Weber and Miller, 1988). Recent work has described the relationship among sorption-desorption rates, solute source function, and system hydrodynamics (Valocchi, 1985, and 1986; Parker and Valocchi, 1986). It is now understood that the sorption-desorption process may require months to years to achieve "true equilibrium" in some hydrophobic solute-soil systems (Coates and Elzerman, 1986; Miller and Weber, 1986, and 1988; Weber and Miller, 1988).

2.3 Multicomponent Sorption

Of additional concern, for the description of the sorption-desorption process, is the influence that multiple solute components (multi-component) have on both system equilibrium and the rate of sorption-desorption. The behavior of multi-component systems is important to understand because most cases of groundwater contamination include more than one solute constituent. However, relatively few studies have investigated multi-component sorption-desorption (Boyd, 1982; Chiou et al., 1983; Coates and Elzerman, 1986; Weber et al., 1986). The small amount of work that has been done suggests that competition exists between solutes at equilibrium with the solid phase, especially for high solute concentrations—typical of regions of many groundwater contamination sites (Boyd, 1982; Coates and Elzerman, 1986; Weber et al., 1986). Of additional interest is the recent finding that multi-component systems of PCBs and river sediments desorbed at a rate which was 60% slower than a similar single component system (Coates and Elzerman, 1986).
3 Materials and Methods

3.1 Overview

The discussion included in this chapter is (1) a summary of the physical and chemical properties of the solute and solid materials used, (2) a discussion of the experimental methods used to perform the various types of experiments used in this investigation, and (3) details on the analytical procedures used to measure solute concentrations in samples collected from the experiments.

3.2 Materials

3.2.1 Chemicals

Water used throughout the experiments was distilled and deionized by a Corning AG-11 Still and Corning Mega-Pure System D1 deionizer. Chemicals added to distilled and deionized water to make a buffered solution for the experiments included sodium azide (0.005M), sodium borate (0.005M), and calcium chloride (0.005M). Azide was added to inhibit biological activity, thus reducing the potential for biodegradation of the target compounds. Hydrochloric acid was used to adjust the borate buffer to a pH=8.4±0.02; buffering was employed to eliminate potential effects of pH on sorption. Calcium aided in the separation of particles from solution during centrifugation. All inorganic chemicals were purchased from Fisher Scientific.

Four nonionic organic chemicals served as solutes for the sorption and desorption experiments: biphenyl, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron), γ-1,2,3,4,5,6-hexachlorocyclohexane (lindane), and 1,2,4-trichlorobenzene (TCB). The physical and chemical properties of these solutes are summarized in Table 1. The solutes may be characterized as slightly (diuron) to moderately (TCB) lipophilic—based upon the octanol-water partition coefficient (K_{ow}), non-volatile (diuron) to semi-volatile (TCB)—based upon the Henry’s constants (H_c), and of varying reactivity—chemical and biological. Assuming a direct correlation between the K_{ow} and tendency to sorb, the expected order of sorption is diuron< biphenyl~<lindane< TCB. Note that a different order of sorption tendency would be predicted based upon aqueous solubility, or hydrophobicity.

Spiked solutions were prepared in the buffer solution previously described. Biphenyl, lindane and TCB were introduced into the buffer using a methanol carrier solvent. The methanol solutions of lindane and TCB ranged in concentration from 40 to 100 g/ℓ, thus spiking volumes were at the μℓ level to obtain the desired initial concentration values. Methanol has been found to have no effect on sorption at such low concentrations (Nkedi-Kizza et al., 1985). Diuron solutions were prepared by dissolving solid diuron directly into
Table 1. Solute Properties

<table>
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<tr>
<th>Property</th>
<th>Biphenyl</th>
<th>Diuron</th>
<th>Lindane</th>
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<td>—</td>
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<td>C9 H10 C12 N2 O</td>
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<td>Density (g/cm$^3$)$^a$</td>
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<tr>
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<td>—</td>
<td>—</td>
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<td>158</td>
<td>112</td>
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<td>Aqueous Solubility (mg/l)$^a$</td>
<td>7.5$^a$</td>
<td>42$^a$</td>
<td>7.8$^b$</td>
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<tr>
<td>Vapor Pressure (atm)$^b$</td>
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<td>2.1 x 10$^{-7}$</td>
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<td>$H_c$ (atm-m$^3$/mol)$^c$</td>
<td>1.5 x 10$^{-3}$</td>
<td>—</td>
<td>7.85 x 10$^{-6}$</td>
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<td>Log $K_{ow}$$^d$</td>
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<td>b.</td>
<td>From Mercer et al., 1990.</td>
</tr>
<tr>
<td>c.</td>
<td>Henry's Constant From Mercer et al., 1990.</td>
</tr>
<tr>
<td>d.</td>
<td>Log Octanol-Water Partition Coefficient From Mercer et al., 1990.</td>
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the buffer solution and filtering through a 0.45-μm filter to remove any remaining solid particles.

3.2.2 Solids

Two subsurface materials with differing properties were used for the sorption experiments. Both solid samples were collected in Michigan in October of 1988. The Wagner material was collected from a gravel pit, from a depth of about 25-m below ground surface. At a separate location, Traverse City material was collected at a depth of approximately 1-m below ground surface.

The solid samples were air dried and then sieved to remove grains ≥ 2-mm diameter. Using buffered water, the subsurface materials were “preleached” of natural organic material to aid in pH control during the sorption experiments, and to prevent hysteresis during desorption due to non-settleable particles (Gschwend and Wu, 1985). The Wagner material received 12 consecutive leaching treatments. The treatments were performed as follows: 1-ℓ containers were half filled with solid material, and the remaining volume filled with buffer solution without azide (pH=8.4). The slurry was tumbled continuously for one week and then settled overnight to separate the phases. The supernatant was siphoned and the bottle was refilled with buffer for another round of leaching.

Since humics are comprised mainly of aromatic organic compounds, ultra-violet (UV) absorbance was used to indirectly monitor changes in the condition of the subsurface materials during the preleaching treatments. Absorbance was measured at 250 nm in each supernatant fraction removed. In addition, pH and turbidity were monitored. The Wagner material showed no significant change in supernatant pH from 8.6 over the 12 weeks. Turbidity showed no trend. The change in absorption over time indicated a greater leaching of humics initially, followed by a steady, slower leaching.

The Traverse City material was treated with a similar procedure; however, the pH of the buffer was 9.1. Again pH, turbidity, and UV absorption were monitored in the supernatant after each washing. The pH increased from 8.5 to approximately 9.0. Turbidity showed no trend while UV absorbance values showed a decreasing trend of much larger magnitude than the Wagner material.

Solid materials were characterized by grain-size distribution, uniformity, pH, density, and organic carbon content. The methods used for particle density, pH, and grain distribution are found in Black (1965). Organic carbon analyses were performed using a persulfate oxidation technique, and an O.I. Corporation Model 700 TOC analyzer. The results of these characterizations are summarized in Table 2. The results of these analyses show that the Traverse City material is fine and more uniform than the Wagner material, but both materials are considered sands. A significant contrast exists in the organic carbon content, with the expectation that the Wagner material would tend to sorb hydrophobic organic solutes to a greater extent than the Traverse City material. This wide contrast in organic
carbon content provides a basis of comparison for the relative importance of the mineral fraction of the solid phase on sorption of hydrophobic solutes.

3.3 Experimental Methods

3.3.1 Method Overview

Two types of laboratory experiments were performed in this investigation: bottle-point experiments, and column experiments. Bottle-point experiments were performed to isolate the sorption-desorption process from the bulk transport processes (advection and hydrodynamic dispersion), which occur in column studies. Column studies were performed to ensure that bottle studies adequately represented the sorption-desorption process and provided good indicators of the sorption-desorption process reactions that occurred in the column studies. Column studies are hypothesized as being representative of conditions existing in a homogeneous and isotropic aquifer consisting of the solid material used in the studies. The effects of heterogeneity on solute transport and fate are approximated using mathematical modeling, which is discussed in the following chapter.

The rate investigations and equilibrium isotherm studies were conducted as completely mixed batch reactor (CMBR) experiments. Individual reactors were used for each data point. For the rate studies, 24 to 60 identical bottle reactors were prepared containing solids and buffer solution with dissolved target compound(s). The reactors were tumbled to maintain constant mixing. Two bottles were removed at a time over a period of hours, days, and weeks subsequent to initiation of the experiment. The target compound was then extracted from the aqueous phase to determine residual contaminant concentration in the solution phase. Diuron was measured directly in the aqueous phase using UV methods.
Bottle point equilibrium studies were performed by placing equal masses of solid material in each of 18 to 27 bottle reactors, and adding equal volumes of buffer solution containing a known, concentration of solute. Bottle reactors were tumbled for a length of time determined by rate studies to show apparent sorption equilibrium. The solid and solution phases were then separated and the solute concentration in the solution phase was determined after extraction into hexane, except for diuron which was measured directly in the aqueous phase.

3.3.2 Rate Studies

The following procedure was used for preparation of the bottle point rate studies for each solute:

1. Predetermined masses of subsurface material were placed into 40-mл Kimax glass centrifuge bottles, correct to ±1 mg.

2. The solid material in the bottles was prewetted with the buffer solution described in the previous section (pH 8.4) and allowed to hydrate overnight. The volume of prewetting solution was dependent upon solid quantity and solid to solution ratio for the experiment. The actual volume delivered was determined by measuring mass and converting to volume, assuming the density of water to be 0.9976 g/cm$^3$ at 23°C.

3. Buffer solution spiked with solute(s) was added to the bottles the following day. The spiked buffer was delivered in a volume that gave the correct solids ratio, and a concentration that gave the desired initial solute concentration. The bottles were sealed with Teflon-lined septa caps.

An experimental solids ratio refers to the ratio of solid mass (g) to solution volume (ml) used in the CMBR's. Solids ratios were chosen based on the sorptive capacity of the two subsurface materials. Preliminary studies indicated the solids ratios necessary to allow 50±20% relative fluid-phase concentration to be sorbed at apparent equilibrium. A ratio of 1:10 was chosen for the Wagner material for all solutes except diuron, which was 1:5, and 2:1 was selected for the Traverse City material, reflecting the fact that the Traverse City material sorbed less than the Wagner material due to a lower fraction of organic carbon content, $f_{oc}$.

The initial solute concentration in the bottle reactors ($C_o$) was found by measuring concentration of the spiked buffer, and correcting for dilution by the prewetting. A known volume of the spiked solution was extracted with hexane, which contained an internal standard. The internal standard used depended upon the experiment being performed. The internal standards used included TCB, 1,2-dichlorobenzene, and heptachlor. Gas chromatographic analysis was used to determine the analyte concentration. Because quantifying $C_o$ was so important to the studies, at least six $C_o$ samples were collected and analyzed for each bottle-point rate study.
4. The bottle-point reactors were constantly mixed at $23^\circ C \pm 2^\circ C$ on a tumbler. Because solute volatilization was a concern with TCB, the total volume of solid plus solution was adjusted to minimize the headspace in the centrifuge bottles for TCB studies. There was no evidence of loss of TCB during set-up, and no decrease in TCB $C_0$ between the first and last bottles was detected. Control studies conducted with no solids were also routinely performed as experiment blanks to observe losses due to sorption to bottles or tops, or losses to volatilization during the experiments. Bisolute rate studies were set up using the same procedure.

Studies extended at least eight weeks for the Traverse material and at least 12 weeks for the Wagner material. Two bottle reactors were removed at a time with sampling occurring most frequently in the first two weeks. All bottles were removed simultaneously for the equilibrium isotherm experiments. The bottles were centrifuged at approximately 1500 relative centrifugal force (RCF) for 30 min. A volume of water was removed by pipette and placed in a vial containing hexane spiked with an internal standard for liquid-liquid extraction of the analyte.

3.3.3 Equilibrium Studies

The procedure for preparing equilibrium studies was nearly identical to that for rate studies. Solids were weighed into centrifuge bottles, hydrated with buffer overnight, and filled with the appropriate volume of spiked solution the following day. Bottles were sealed and tumbled constantly at $23^\circ C \pm 2^\circ C$; all bottles were removed simultaneously for analysis.

Solids ratios were consistent with rate studies. Equilibrium studies covered an initial concentration range of more than an order of magnitude with at least two replicate bottles at each concentration. The range was chosen such that the lower concentrations gave equilibrium concentrations, $C_e$, close to 100 \( \mu g/\ell \) or less.

3.3.4 Desorption Studies

Desorption studies were performed using similar procedures as detailed for the bottle-point rate and equilibrium studies in the previous two subsections. For desorption equilibrium studies:

1. sorption was allowed to proceed for a period of time sufficient to approach equilibrium conditions;

2. phase separation was performed by centrifugation;

3. a portion of the solution phase was removed and replaced with solute-free solution;

4. the solute concentration in the solution phase removed was measured;
5. the bottles were allowed to re-equilibrate, which resulted in solute desorbing from the solid phase; and

6. steps 2 to 5 were repeated two to three additional times.

Desorption rate studies were performed using a procedure similar to the procedure used to perform desorption equilibrium experiments. The main differences were that identical initial solids and solute concentrations were used for all bottles, and following the sorption equilibration step sets of bottles (two replicate samples) were removed after varying lengths of desorption time.

3.3.5 Solid-Phase Extraction

Extraction of the solid phase was performed periodically during rate and equilibrium studies to investigate mass balance in the systems. After the fluid-phase sample was removed from the centrifuge bottle, additional fluid phase was quantitatively removed, leaving a known, small volume of fluid in the bottle with the solid material. One drop of hydrochloric acid was added to the bottle to reduce pH. Acetone (5 ml) was then added to reduce the partition coefficient relative to the pure water system. Studies by Nkedi-Kizza and coworkers (1985) showed use of acetone as a cosolvent reduced partitioning to the solid phase by as much as three orders of magnitude in their systems. The slurry was tumbled for at least 12 hours. Hexane was then added to the slurry, which was again tumbled for at least 12 hours. After centrifugation, the hexane fraction was removed carefully by pipette (as completely as possible), and fresh hexane was added. This hexane addition, centrifugation, and removal were repeated at least three times. The hexane fractions were combined and brought to a known volume. A portion of the hexane was analyzed for solute concentration.

3.3.6 Column Studies

Two column apparatuses were constructed due to the labor intensive nature of column studies. This allowed two experiments to be run simultaneously. A schematic representation of the column design is shown by Figure 1.

Two reservoirs were needed; one to contain buffer solution, and the second to contain buffer solution with organic solute. A 4-ℓ KIMAX or PYREX brand erlenmeyer flask was used to contain buffer solution. A 6-ℓ KIMAX or PYREX brand erlenmeyer flask was used to contain buffer solution with organic solute. Both reservoir flasks were modified by construction of a threaded outlet near the bottom of the vessel. A threaded cap was added to the top of the organic solute reservoir. This allowed the reservoir to be sealed to minimize loss of volatile organic solutes. A small threaded opening was constructed near the top of the reservoir. Narrow stainless steel tubing was inserted into this opening to prevent a vacuum from forming as solution was being drawn from the reservoir.
A MiniPump metering pump (Milton Roy, Riviera Beach, Florida) was used to deliver solution to the column. The pump provided accurate delivery of solution at flow rates between 1.9 to 19 ml/hr.

All tubing from the reservoirs to the pump, from the pump to the column, and from the column to the effluent sample vial was made of regular grade 304 stainless steel supplied by Supelco, Inc. (Bellefonte, Pennsylvania). The tubing had the outside/inside diameters: 0.635/0.530, 0.318/0.210, and 0.159/0.076 cm.
Glass columns of varying lengths with threaded Teflon end pieces were provided by University Research Glassware Corp. (Carrboro, North Carolina). The glass columns had an inner diameter of 2.4 cm.

Each column was packed wet. Buffer solution was pumped in an up-flow manner through the column. A small piece of silane treated glass wool (Supelco, Inc., Bellefonte, Pennsylvania) was placed at the entrance of the column to prevent migration of glass beads. A weighed amount of glass beads (McMaster-Carr Supply Company, Dayton, New Jersey) was added. The column was gently tapped on the outside to aid in compacting the glass beads. A weighed amount of subsurface material was added. The column was again gently tapped on the outside to aid in compacting the subsurface material. Glass beads were then added until the column was completely filled. A small piece of glass wool was placed on top of the beads to prevent migration of material from the bed. A threaded Teflon end piece was then put in place.

Buffer solution was pumped through the column overnight. During this period the pump was adjusted until the desired flow rate was achieved. The sorption part of the experiment was started by switching the feed to the pump to the reservoir containing the buffer solution with organic solute. After the desired sorption period the feed to the pump was switched to the buffer solution reservoir. This switch marked the start of the desorption part of the experiment.

Effluent samples from the column were collected in 25 ml sample vials that had been weighed. The sample vials were reweighed to determine the mass of the samples collected. Sample masses were converted to sample volumes by density considerations. The samples were assumed to be at room temperature (23°C) and have a density of 0.9976 g/ml.

Influent samples from the reservoir containing buffer with organic solute were obtained from a line tapped into the feed line. These samples were collected in a manner similar to that for the effluent samples.

### 3.4 Analytical Methods

#### 3.4.1 Gas Chromatography Methods

Gas chromatographic (GC) analysis was performed on a portion of the hexane fraction using a Hewlett-Packard 5890A GC equipped with an electron capture detector (ECD) and a flame ionization detector (FID), a HP 3396A integrator, and an automatic injector. For analysis of the TCB and lindane individually, as well as for bisolute samples, a 10-m HP-1 megabore column (Hewlett-Packard, Avondale, Pennsylvania) was used, which had a 0.53-mm inner diameter, and a 2.65-µm cross-linked methyl silicone gum phase. The packed column injector was 250°C; analysis was isothermal with an oven temperature of 220°C and detector temperature of 300°C. Makeup gas flow was approximately 60 ml/min, and carrier flow was 5 ml/min. Individual sample runs were about 5 minutes long.
Biphenyl was measured using a 30-m DB-5 column (J&W Scientific, Folsom, California), which had 0.25-mm inner diameter, for both split (30 to 1 split ratio) and splitless operation. A FID detector was used with a carrier gas flow rate of 1 ml/min, while the detector temperature was 300°C. The injector and oven temperature varied between split and splitless methods.

Each sample and standard was injected twice, and the ratio of analyte peak area to internal standard peak area was calculated. A multi-point calibration was used, fit with a second order polynomial.

3.4.2 UV Spectroscopy Methods

This work involved three basic types of experiments: batch kinetic, batch isotherms, and soil column experiments. The two batch experiments can be grouped under the title bottle point experiments. The Perkin Elmer Lambda 3 UV/VIS Spectrophotometer was used in all three types of experiments, while the Guided Wave Model 200 Optical Waveguide Spectrum Analyzer was used for a batch kinetic study and several soil column studies.

UV absorbance spectroscopy was chosen as the appropriate technique for the analyses of diuron in the aqueous phase because of the pesticide's relatively strong absorbance peak at approximately 248 nm. Preliminary studies were performed to confirm that this peak occurred at approximately 248 nm with several different molar concentrations of diuron.

A Perkin Elmer Lambda 3 UV/VIS spectrophotometer was used to measure the UV absorbance of diuron. This instrument is a dual beam UV/VIS spectrophotometer that utilizes a constant reference cell holding a cuvette that can contain a reference liquid of choice. For all experiments that were conducted here, DDI water was used in the reference cell. The Lambda 3 has two available light sources: a tungsten bulb for visible and near infrared, and a Deuterium lamp for UV. The UV source was used for all the experiments that were performed, the visible light source was used to align the cell holders in this experiment. The Lambda 3 performs a series of self-diagnostic checks on startup and constantly corrects for probe light variations by monitoring the output of the source lamp through the reference cell. The instrument has a zeroing function which along with the previously mentioned features sets the dynamic range of the instrument for a particular experiment. The sample cuvette was filled with DDI water and the wavelength set for 248 nm in order to zero the instrument for all of the experiments. The Lambda 3 had a very stable and repeatable baseline for all of the experiments performed.

Two cell holders were custom designed by the UNC shop in addition to the standard 1-cm path-length cuvette holders that came with the instrument. These cell holders were designed to hold the 24-mm path-length Suprasil tubes used in some batch rate experiments. Because the tubes had slight variations in their diameter, the cell holders had a set screw to maintain the angular position of the tubes from one measurement to the next.
The spectrophotometer was turned on approximately 1 hour before any measurements were taken in order to give the machine a chance to perform self-diagnostic checks and stabilize. The UV source was turned on approximately 10 seconds after the spectrophotometer.

Two 1-cm path length quartz cuvettes were used. These cuvettes were frosted on two sides. The cuvettes were rinsed several times with DDI water, then filled with DDI water and placed in the reference and sample cell holders. The cuvettes were always held by the frosted sides and were wiped with a clean, dry wipe if wet. Care was taken not to let the cuvette windows get any dirt or grease on them. After the two cuvettes filled with DDI water were placed in the cell holders, the instrument was zeroed at 248 nm and left to stabilize.

After the machine had settled, the sample cuvette was rinsed and drained 2 to 3 times with DDI water, then rinsed once with the sample to be measured, and finally refilled with the rest of the sample to be measured. The sample cuvette was then wiped and placed in the cell holder. The spectrophotometer was allowed to settle for 5 to 10 seconds before a measurement was recorded. This procedure was repeated beginning with the DDI water rinses for all samples. The only deviation from this procedure occurred when the samples were too small to allow for the single sample pre-rinse. In this case, the sample cuvette was vigorously shaken empty after the DDI rinses and simply filled with the sample to be measured. Procedures were kept constant throughout a given experiment.

Each set of measurements began and ended with a set of standard measurements. The set of standards consisted of 6 to 8 standard concentrations of diuron in buffer, beginning with pure buffer and ending with the stock concentration of diuron in buffer. After a set of standards had been measured, approximately 16 to 20 samples were measured and the standard measurements were repeated. Several sets of standard measurements were taken to account for any instrument variations that might have been missed by the self-diagnostics of the Lambda 3. When the data were analyzed, the standards were fitted to a second order polynomial and the data interpreted by the fit. Each sample was weighted depending on its proximity to the two standard curves it fell between. The closer a data point was to a standard curve, the more it was weighted to that curve in the interpolation of its concentration.

For each time period, there were four data points. They consisted of two diuron solution with subsurface samples (replicates), and two buffer solution with subsurface solid samples (replicates). Solid to solution ratios were kept constant for a given experiment. Four bottles were removed from the tumbling set at their prescribed measurement time and centrifuged at 2000 rpm for 30 minutes. Approximately 10 ml of the supernatant were pipetted from the sample bottles (standard borosilicate centrifuge tubes with Teflon-lined caps) into four clean sample vials which were sealed with Teflon-lined caps and stored in a refrigerator. The samples were individually analyzed on the Lambda 3 after several measurement times had accumulated. The samples were discarded after measurement, a destructive-type procedure. The two buffer solution replicates were averaged and this
average was subtracted from the two diuron samples. The result was then used in conjunction with the standard curves to determine the concentration of each of the two replicate samples.
4 Mathematical Modeling

4.1 Overview

Mathematical modeling can be used to simulate experimental data, to predict experimental results, to aid in evaluating mechanisms, and to assess the effects of source conditions and scale on solute distributions at scale different than those investigated—e.g., field scale. Modeling was used for all of these purposes in this work. The types of models considered are equilibrium sorption-desorption models, batch reactor sorption rate models, and transport and reaction models. A variety of models was developed to simulate single and multicomponent systems, and systems in which transport occurs in one or two dimensions. A summary of these models follows in subsequent sections.

4.2 Sorption-Desorption Equilibrium

4.2.1 Single-Component Systems

Much of the sorption work accomplished to date has relied upon a simple linear equilibrium model of the form

\[ q_e = K_p C_e \]  

(1)

where \( q_e \) is the solid-phase solute concentration at equilibrium \([\text{M}/\text{M}]\), \( K_p \) is a linear partition coefficient \([\text{L}^3/\text{M}]\), and \( C_e \) is the fluid-phase solute concentration at equilibrium \([\text{M}/\text{L}^3]\).

While appealing in concept and application, the linear equilibrium model has been found to be a poor predictor of much experimental data for hydrophobic organic solute sorption to natural solid materials (e.g., Miller and Weber, 1984a; Weber and Miller, 1989). The Freundlich equilibrium model has provided a better descriptor of hydrophobic solute sorption data, especially when the equilibrium sorption concentrations cover more than an order of magnitude. The Freundlich equilibrium model is a standard power-law relationship

\[ q_e = K_f C_e^{n_f} \]  

(2)

where \( K_f \) is a sorption capacity constant \(([\text{M}/\text{M}] (\text{L}^3/\text{M})^{n_f}]\), and \( n_f \) is a sorption intensity constant. For \( n_f < 1 \) the sorption equilibrium relationship is termed favorable, while for \( n_f > 1 \), the sorption equilibrium relationship is termed unfavorable (Weber, 1972).
Typically many natural-solid/hydrophobic solute systems investigated have $0.65 \leq n_f \leq 1.00$ (Weber and Miller, 1989).

4.2.2 Multicomponent Systems

When more than one solute is present, solutes may compete for sorption sites within the solid phase, thus altering the final distribution of each solute between the fluid and solid phases. The ideal adsorbed solution theory (IAST) can be used to predict the degree to which competition alters the distribution of each solute (Radke and Prausnitz, 1972). If the Freundlich isotherm equation is used to describe single-solute behavior in the IAST, then the fluid-phase solute concentration at equilibrium with the solid-phase solute concentrations is

$$C_{el} = \frac{q_{el}}{\sum_{k=1}^{n_c} q_{ek}/K_{f,k}/n_i} \left( \sum_{k=1}^{n_c} q_{rk}/n_k \right)^{1/n_i}$$

where $i$ is the species index, and $n_c$ is the number of solutes (Crittenden et al., 1985).

It should be noted that violation of the assumptions implicit in the IAST model certainly occurs in most engineered and natural systems. As noted in a previous chapter, much remains to be learned about multicomponent effects in groundwater systems. A comparison of experimental and IAST model predictions is presented in a subsequent chapter, to evaluate the applicability of the IAST model for natural systems.

4.3 Batch Reactor Systems

4.3.1 Material Balance

For the general case of a batch reactor a material balance expression may be expressed as

$$\frac{dC}{dt} = -\left( \frac{dq}{dt} \right)_{srp} + \left( \frac{dC}{dt} \right)_{rzn} + \Gamma(C)$$

where the subscript $srp$ indicates sorption and $rzn$ indicates solute reaction from the fluid phase, and $\Gamma(C)$ is a general solute source function. For the case of a first-order degradation reaction from the fluid phase and no solute source other than the initial condition, Equation (4) becomes
where $k_a$ is a first-order solute degradation rate for solute loss from the fluid phase.

For the case of multiple solutes, Equation (6) may be generalized to

$$\frac{dC}{dt} = -\left(\frac{dq}{dt}\right)_{s_{rp}} - k_a C$$

where $k_a$ is the species index.

As is noted from the above formulations and fundamental considerations of the nature of a batch reactor, fluid-phase concentrations in a closed system are only affected by sorption-desorption reactions and solute degradation or transformation reactions. Substitution for the general sorption rate expression is required for a complete model specification; the following sections outline formulations of surface-diffusion and pore-diffusion dual-resistance sorption rate models.

4.3.2 Surface-Diffusion Model

Sorption rates are often considered to be a result of a diffusive transport process (Karickhoff, 1984; Miller and Weber, 1986; Brusseau and Rao, 1989). Several types of diffusive transport processes are possible. One common type of diffusive model is a surface-diffusion, dual-resistance model (Weber and Miller, 1988) in which sorption rates are represented as the result of a resistance due to diffusion through a boundary layer film and surface diffusion within a spherical particle. For this model Equation (7) may be written as

$$\frac{dC}{dt} = -\left(\frac{dq}{dt}\right)_{s_{rp}} - k_{as} C$$

and the companion solid-phase equation is

$$\frac{\partial q_r}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_r}{\partial r} \right) - k_s q_r,$$
which may also be written as

\[ \frac{\partial q_r}{\partial t} = D_s \left( \frac{\partial^2 q_r}{\partial r^2} + \frac{2}{r} \frac{\partial q_r}{\partial r} \right) - k_s q_r \]  

(11)

subject to

\[ \frac{\partial q_r}{\partial r} \bigg|_{r=R} = \frac{k_f}{D_s \rho} (C - C_s) \]  

(12)

\[ \frac{\partial q_r}{\partial r} \bigg|_{r=0} = 0 \]  

(13)

\[ q_r(0 \leq r \leq R, t = 0) = 0 \]  

(14)

\[ C(t = 0) = C_0 \]  

(15)

where \( k_f \) is a boundary layer film mass transfer coefficient \([L/T]\), \( M \) is the mass of the solid phase in the batch reactor \([M]\), \( R \) is the radius of the spherical solid particles—assumed constant \([L]\), \( V \) is the volume of the fluid phase \([L^3]\), \( \rho \) is the macroscopic particle density of the solid phase \([M/L^3]\), \( C_s \) is the fluid-phase solute concentration corresponding to an equilibrium with the solid-phase solute concentration at the exterior of particle (i.e., \( q_r(r = R) \)) \([M/L^3]\), \( q_r \) is the solid-phase solute concentration \([M/M]\) as a function of radial position \( r \) \([L]\), \( R \) is the radius of the solid particle, \( D_s \) is a surface diffusion coefficient \([L^2/T]\), and \( k_s \) is a first-order solute decay coefficient for solute in the solid phase.

A method of lines solution was used to solve the surface diffusion model in a batch reactor by first converting Equation (10) to (15) to a set of ordinary differential equations in time using the Galerkin finite element method (Pedit and Miller, 1988). The resulting set of ordinary differential equations was solved using an algorithm for stiff equations (Gear, 1971).

The Galerkin finite element method may be used to approximate the spatial derivative in Equation (11) by first defining a trial function

\[ \tilde{q}_r(r) = \sum_{j=1}^{n_s} N_j(r) q_{rj} \]  

(16)

where \( N_j \) are the Lagrange polynomial basis functions given by
where: \( j \) is a node index; \( r_j \) and \( r_k \) are the locations of node \( j \) and node \( k \); \( n_n \) is the total number of nodes; and \( n_e \) is the number of nodes in an element. The number of nodes in an element determines the order of the Lagrange polynomial basis function. A general computer code was developed that can use any order of element. Pedit and Miller (1988) demonstrated the advantage of using higher order schemes.

The weighted residual method requires that a system of equations—one equation for each node in the discretized domain—when formed with respect to the governing partial differential equation and integrated over the domain vanish, which gives for the solid-phase equation

\[
\int_0^R \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \hat{q}_r}{\partial r} \right) - k_s \hat{q}_r - \frac{\partial \hat{q}_r}{\partial t} \, r^2 \, dr = 0
\]

for \( i = 1, ..., n_n \)

where \( W_i \) is a weighting function. The Galerkin finite element method requires that the weighting function be equivalent to the basis function, which gives

\[
\int_0^R N_i \left[ \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \hat{q}_r}{\partial r} \right) - k_s \hat{q}_r - \frac{\partial \hat{q}_r}{\partial t} \right] r^2 \, dr = 0.
\]

for \( i = 1, ..., n_n \)

Accuracy and stability of the Galerkin finite element method require completeness and consistency of the trial solution (Huyakorn and Pinder, 1983). Lagrange polynomials are \( C^0 \) continuous—interpolation of the dependent variable is continuous at element boundaries, but interpolation of any derivative of the dependent variable is not continuous. Therefore, it is necessary to reduce the second-order partial derivative in Equation (19) by integrating by parts

\[
\int_0^R N_i \frac{\partial \hat{q}_r}{\partial t} r^2 \, dr = -D_s \int_0^R \frac{d}{dr} N_i \frac{\partial \hat{q}_r}{\partial r} r^2 \, dr - \int_0^R k_s d N_i \hat{q}_r r^2 \, dr + D_s N_i r^2 \frac{\partial \hat{q}_r}{\partial r} \bigg|_{r=0}^{r=R} = 0
\]

for \( i = 1, ..., n_n \)
which may be written in matrix-vector notation as

\[
[A]\{q'\} = \{b\}
\]

(21)

where; \([A]\) is a coefficient matrix resulting from solution of the left-hand-side of Equation (20); \(\{q'\}\) is vector of \(dq_r/dt\) terms corresponding to each radial node; and \(\{b\}\) is a vector resulting from evaluation of the right-hand-side of Equation (20) for a given vector \(\{q_r\}\).

Equation (20) was combined with Equation (10), subject to the boundary and initial conditions—yielding a system of \(n_n + 1\) ordinary differential equations in time. The system of equations was solved using Gear's method for stiff equations (Gear, 1971).

4.3.3 Pore-Diffusion Model

For a pore diffusion model, resistance to mass transfer within the particle is attributed to diffusion in the aqueous-phase fraction of the particle, i.e., within the micro porosity of a solid particle. The formulation for a pore-diffusion model may also include resistance through a boundary layer film surrounding the solid particle. This model too is a dual-resistance model, and the formulation is similar to the surface-diffusion model previously presented.

\[
\frac{dC}{dt} = -\frac{3k_fM}{RV\rho}(C - C_p) - k_a C,
\]

(22)

and the companion solid-phase equation is

\[
R_p \frac{\partial C_p}{\partial t} = \frac{D_p}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_p}{\partial r} \right) - k_s R_p C_p,
\]

(23)

which may be written as

\[
R_p \frac{\partial C_p}{\partial t} = D_p \left( \frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right) - k_s R_p C_p
\]

(24)

where

\[
R_p = 1 + \frac{\rho n_f K_f}{\epsilon} C_p^{n_f - 1}
\]

(25)
subject to

$$\frac{\partial C_p}{\partial r} \bigg|_{r=R} = \frac{k_f}{\epsilon D_p \rho} (C - C_p) \quad (26)$$
$$\frac{\partial C_p}{\partial r} \bigg|_{r=0} = 0 \quad (27)$$
$$C_p(0 \leq r \leq R, t = 0) = 0 \quad (28)$$
$$C(t = 0) = C_o \quad (29)$$

where $C_p$ is the fluid-phase solute concentration in the solid phase pore [M/L³] as a function of radial position, $\epsilon$ is the void fraction within the solid particle, and $D_p$ is the pore diffusion coefficient of the solute within the solid phase [L²/T], which includes the effect of the tortuosity of the travel path.

### 4.3.4 Multicomponent Rate Models

The extension of either of the dual-resistance models—surface diffusion or pore diffusion—to simulate multicomponent systems is straightforward in concept. The extension requires incorporation of an appropriate multicomponent equilibrium model—IAST along with the Freundlich equilibrium model was used in this work—and simultaneous nonlinear solution of the resultant fluid-solid equilibria equations. For the surface-diffusion model, equilibria calculations are performed only at the exterior surface of the particle. For the pore-diffusion model, the derivative of the equilibria conditions is required at each spatial node, as expressed by $R_p$. A method of lines solution for a multicomponent surface diffusion model has been developed previously by the principal investigator and a co-worker (Pedit and Miller, 1988); this model was generalized to arbitrary order basis functions and used in this work.

### 4.4 Transport and Reaction Systems

#### 4.4.1 Governing Equations

It is widely accepted that the governing equation for contaminant transport in porous media systems is the advective-dispersive-reactive (ADR) equation

$$\frac{\partial C}{\partial t} = \nabla \cdot (D_k \cdot \nabla C) - \bar{v} \cdot \nabla C + \left( \frac{\partial C}{\partial t} \right)_{rzn} + \Gamma(C) \quad (30)$$
where $D_h$ is a second-rank symmetric hydrodynamic dispersion tensor, and $\bar{v}$ is an average macroscopic pore velocity vector (Bear, 1979). Saturated flow and a constant porosity have been assumed. It is obvious that solution of Equation (30) requires knowledge of the flow field, which in-turn requires solution of a flow equation, or explicit knowledge of $\bar{v}$ as a function of time.

For the case of a first-order degradation from the fluid phase and sorption, Equation (30) becomes

$$\frac{\partial C}{\partial t} = \nabla \cdot (D_h \cdot \nabla C) - \bar{v} \cdot \nabla C - \left( \frac{\partial C}{\partial t} \right)_{srp} - k_a C + \Gamma(C)$$  \hspace{0.5cm} (31)

where $k_a$ is a first-order degradation rate for solute loss from the fluid phase.

For laboratory column systems, and some field situations, a one-dimensional transport equation is a realistic statement of the problem. A one-dimensional velocity field and lack of hydrodynamic dispersion in directions transverse to the mean velocity field (i.e., no concentration gradients in the transverse directions) are required to reduce the ADR equation to one dimension. For cases in which such assumptions are applicable a common form of the ADR equation is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_{hz} \frac{\partial C}{\partial x} \right) - v_x \frac{\partial C}{\partial x} - \left( \frac{\partial C}{\partial t} \right)_{srp} - k_a C + \Gamma(C)$$  \hspace{0.5cm} (32)

for the case of steady flow this becomes

$$\frac{\partial C}{\partial t} = D_{hz} \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \left( \frac{\partial C}{\partial t} \right)_{srp} - k_a C + \Gamma(C)$$  \hspace{0.5cm} (33)

where $D_{hz}$ is the dispersion coefficient in the $x$ direction $[L^2/T]$, and $v_x$ is the average macroscopic velocity in the $x$ direction.

For steady-flow in a two-dimensional domain the general ADR equation may be written as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_{hzz} \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial z} \left( D_{hzz} \frac{\partial C}{\partial z} \right) + 2D_{hzz} \frac{\partial^2 C}{\partial x \partial z} - v_x \frac{\partial C}{\partial x} - v_z \frac{\partial C}{\partial z} - \left( \frac{\partial C}{\partial t} \right)_{srp} - k_a C + \Gamma(C)$$  \hspace{0.5cm} (34)
where

\[ D_{hzz} \frac{\partial^2 C}{\partial x \partial z} = D_{hzx} \frac{\partial^2 C}{\partial z \partial x} \]  

(35)

is used to combine hydrodynamic dispersion, cross-derivative terms.

The three-dimensional form of the ADR is a simple extension to the above forms, but it will not be written here since only two-dimensional systems were considered. However, it should be noted that the two-dimensional form used does not assume vertical-averaging in the z direction. The vertical dimension is explicitly included. This will allow for a realistic evaluation of sorption effects at the field scale for heterogeneous sorption and hydraulic properties, both of which often vary markedly with respect to the vertical dimension. The expense for this approach is a somewhat restrictive assumption of no concentration gradient in the y direction. This would require a source condition that is transverse to the x-z plane and long with respect to the length scales of concern in the x and z directions.

For a well posed problem, it is necessary to assign an appropriate set of auxiliary conditions. These conditions often are Dirichlet conditions (assigned conditions for the dependent variable) along portions of the domain where fluid is entering, and Neumann (assigned conditions for the derivative of the dependent variable) along portions of the domain where fluid is leaving.

4.4.2 Single-Component Solution

For the case of surface diffusion, the governing ADR equation is

\[ \frac{\partial C}{\partial t} = D_{hx} \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{3(1-n)k_f}{nR} (C - C_s) - k_d C. \]  

(36)

The ADR equation is coupled to a separate solid-phase equation at each spatial location in the surface diffusion model by the presence of \( C_s \) in the ADR equation. \( C_s \) is solved from a solid-phase surface diffusion equation of the form

\[ \frac{\partial q_r}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_r}{\partial r} \right) - k_s q_r; \]  

(37)

the external solid-phase equilibrium condition
and the boundary conditions

\[ \frac{\partial q_r}{\partial r} \Bigg|_{r=R} = \frac{k_f}{D_s \rho} (C - C_s), \]  

and

\[ \frac{\partial q_r}{\partial r} \Bigg|_{r=0} = 0, \]  

where the initial conditions are

\[ C(t = 0, x) = C_0 \]  

\[ q_r(t = 0, 0 \leq r \leq R) = 0 \quad \forall x. \]

Conventional methods of solution for the above system of nonlinear equations rely upon solving a fully-coupled system of equation iteratively at each time step (e.g., Miller and Weber, 1988). Such solutions have been accomplished using both conventional Eulerian methods (Miller and Weber, 1986) and method of lines solution procedures using conventional Eulerian methods to resolve the space derivatives in the ADR and solid-phase equations (e.g., Miller and Weber, 1988). Either of the above approaches leads to a large system of equations that requires simultaneous solution. The number of equations requiring solution is

\[ n_t = n_n (n_r + 1) \]

where \( n_t \) is the total number of equations, \( n_n \) is the number of macroscopic spatial nodes in the \( x \) dimension, and \( n_r \) is the number of radial nodes for the spherical particles. If a linear interpolating function is used in a standard Eulerian method—finite element or finite difference—to approximate the ADR equation, a banded coefficient matrix results. In an optimal nodal numbering scheme, the band-width of the resulting coefficient matrix is dependent upon the number of radial nodes, but is not dependent upon the order of the interpolation function within the spherical particle. The band-width of the coefficient
matrix—or Jacobian matrix for a Newton-Raphson nonlinear solution method—for a linear interpolation function in the ADR equation is

\[ n_b = 2n_r + 3. \]  \hspace{1cm} (44)

If a direct solver is used, fill-in of non-zero entries within the banded structure occurs. Thus for a direct solution method, no advantage can be taken from the sparse nature of the coefficient matrix within the banded structure. Coupling this observation with the advantage of high-order elements demonstrated by Pedit and Miller (1988), it follows that high-order interpolation of the spherical nodes should be used for an economical solution, when direct solvers are used. However, the cost of using interpolation functions of a higher order than linear for the macroscopic ADR equation is prohibitive, when the solid-phase is fully coupled and solved simultaneously.

Two additional problems exist when solving the ADR equation for the case of spherical diffusion. Large systems of equations may result because of the need to meet the normal spatial and temporal discretization limits summarized by

\[ Pe = \frac{v_x \Delta x}{D_{hx}} \leq 2.0 \]  \hspace{1cm} (45)

\[ Cr = \frac{v_x \Delta t}{\Delta x} \leq 1.0 \]  \hspace{1cm} (46)

where \( Pe \) is the Peclet number, \( \Delta x \) is the spatial discretization size, \( Cr \) the Courant number, and \( \Delta t \) is the temporal discretization size. It may be noted that small values of \( D_{hx} \) lead to both fine spatial and temporal discretization, which translates to increased computational cost.

A problem may also result from the time scales of the transport and reaction steps. Depending upon the values of the reaction parameters, \( k_f, D_s, k_a, \) and \( k_s, \) much smaller time steps than those dictated by the \( Cr \) criteria may be required to solve accurately the overall transport and reaction problem.

An approach to resolving these problems has been to use a method of lines solution along with high-order global collocation methods to resolve spatial derivatives (Crittenden et al., 1986). While giving accurate results, the coupled method of lines solution procedure has disadvantages as well: a relatively large coupled system of equations results, sharp-front problems are still difficult to resolve economically, and generalization to more than one spatial dimension is economically prohibitive. The method of lines collocation method has enjoyed popularity in the chemical engineering field, where it was applied to similar
problems more than a decade ago, because the chemical engineering systems of concern are typically one-dimensional.

In this work, an alternative approach was taken to solve the transport and reaction problem: (1) a Petrov-Galerkin finite element method (Cornew and Miller, 1990, Cornew et al., 1990) was used to solve the advective and dispersive components of the ADR equation, and (2) an operator splitting approach was used to decouple the reaction component at each spatial location. This approach offers the advantages of accurately resolving sharp-front problems, while solving a series of relatively small problems with narrow band-widths. The method can also be readily extended to two- and three-dimensional systems (Nelson et al., 1990; Rabideau and Miller, 1990a, 1990b).
5 Desorption Hysteresis

5.1 Overview

An integrated set of experiments was performed to investigate the long-term sorption and desorption characteristics of lindane to the Wagner solid material. The objective of these experiments was to determine the relationship between the rate at which sorption and desorption occurs and apparent hysteresis. Desorption hysteresis is manifest as a history dependent desorption relationship. Typical functional representations show that the desorption path is a function of the maximum sorption equilibrium concentration achieved. Desorption hysteresis has been noted frequently in the literature, and a variety of potential explanations has been advanced as explanations for the observations.

The majority of sorption and desorption experiments that have been performed have allowed relatively short periods of time for equilibration—typically a few hours to a day—relative to recent evidence that suggests that much longer times may be required to approach true equilibrium (Coates and Elzerman, 1986; Miller and Weber, 1986; Brusseau and Rao, 1989). Deviations from sorption equilibrium are consistent with typical hysteresis observations in which more solute is associated with the solid phase than would be expected based upon a singular equilibrium relationship. The extent to which rate effects can explain observed desorption hysteresis is unknown. The experiments and modeling discussed in this chapter provide an analysis of this issue.

The investigation of the long-term sorption-desorption phenomenon of lindane to the Wagner material was complicated by the slow nature of the sorption and desorption reactions, and by the degradation of lindane that occurred from the fluid and solid phases at different rates. With respect to the surface diffusion modeling framework previously presented, the behavior of lindane in batch reactor systems is a function of six unknown model parameters for a singular sorption-desorption relationship and eight unknown model parameters for a hysteretic sorption-desorption relationship. The unknown parameters for the singular equilibrium case are: \( k_a, k_s, K_f, n_f, k_f, D_s \). These parameters correspond to solute degradation parameters, sorption equilibrium parameters, and sorption rate parameters. For hysteretic desorption, two additional desorption parameters are needed. Only the singular case is analyzed here. The approach taken in this work is to isolate subsets of these parameters in single types of experiments and to test the adequacy of the independently determined parameters through the prediction of results from desorption rate experiments. Finally, after calibration and experimental validation, the model is used to evaluate the central issue: the importance of sorption nonequilibrium as a cause of apparent desorption hysteresis.
5.2 Background

Lindane has been shown to sorb to natural solids, degrade abiotically, biodegrade aerobically, and biodegrade anaerobically. Factors affecting the sorption and desorption of lindane in aqueous-solid systems have been investigated for more than 30 years (Swanson et al., 1954; Kay and Elrick, 1967; Lotse et al., 1968; Mills and Biggar, 1969; Adams and Li, 1971; Boucher and Lee, 1972), and vapor-phase diffusion and sorption of lindane to natural solid materials have been investigated for about 20 years (Ehlers et al., 1969a, 1969b; Guenzi and Beard, 1970; Spencer and Cliath, 1970). These results show that: the organic carbon content of the solid phase is an important consideration affecting the extent of sorption to the solid phase (Kay and Elrick, 1967; Lotse et al., 1968; Adams and Li, 1971) and system pH and cation exchange capacity are relatively unimportant variables (Swanson et al., 1954; Adams and Li, 1971; Boucher and Lee, 1972).

The thermodynamics of the sorption-desorption process have been investigated by varying system temperature (Mills and Biggar, 1969; Ehlers et al., 1969b; Spencer and Cliath, 1970; Boucher and Lee, 1972) with results that appear to be a function of the solid phase investigated. Sorption of lindane to natural solid materials has been found to be nonlinear at equilibrium and describable with the Freundlich model (Lotse et al., 1968; Mills and Biggar, 1969; Boucher and Lee, 1972). Sorption rate investigations have shown a direct relationship between the fraction of organic carbon and the time required to approach equilibrium (Kay and Elrick, 1967), and lindane sorption has been found to persist for more than 100 hours (Boucher and Lee, 1972).

The abiotic dehydrochlorination of lindane, an E2 elimination reaction, has been known to occur for more than 40 years (Cristol, 1947; Nakazima et al., 1949). The rate of E2 elimination reactions is first order with respect to the hydroxide ion concentration and first order with respect to the parent molecule being degraded, or second-order overall. These early studies showed that lindane is converted first to γ-pentachlorocyclohexene (γ-PCCH) and ultimately to primarily 1,2,4-trichlorobenzene. Cristol (1947) assumed that the rate-limiting step in the sequential elimination reactions was the first step: the conversion of γ-hexachlorocyclohexane to γ-PCCH. Nakazima et al. (1949) found using a polarographic method that the rate constant for conversion of γ-PCCH to γ-tetrachlorocyclohexene was approximately the same as the rate constant of the first elimination step—the conversion of γ-hexachlorocyclohexane to γ-PCCH.

In a study of sorption and desorption of lindane, loss of lindane was observed with calcareous soil systems (Adams and Li, 1971). The degradation of lindane to γ-pentachlorocyclohexene (γ-PCCH) was found to occur in soils and buffered water solutions, with rates that increased with pH (Yule et al., 1967) The γ-PCCH degradation product was also found in a study that investigated the volatilization of lindane as a function of drying cycles for four soil systems (Guenzi and Beard, 1970). Not more than 0.2% of the lindane added to an agricultural loam soil was recovered 15 years after a single application, and 45 to 57% was not recovered after the first growing season (Lichtenstein et al., 1971). Gas-liquid chromatography of isolates obtained from thin-layer chromatography, from test
plots treated with lindane, showed compounds with retention times that matched the retention times of $\gamma$-PCCH and 1,2,3,4-tetrachlorobenzene, as well as four other peaks with unmatched retention times.

Aerobic degradation using lindane as a sole carbon source was found to occur readily in the individual presence of eight bacteria and three fungi species (Tu, 1976). These enzyme-producing degraders included five species of *Pseudomonas*, two species of *Bacillus*, and two fungi species from the genus *Penicillium*. Degradation products of lindane were found to include $\gamma$-PCCH, $\alpha$-, $\beta$-, and $\gamma$-3,4,5,6-tetrachloro-1-cyclohexene (TCCH), and pentachlorobenzene.

Anaerobic and facultative microorganisms were found to readily degrade lindane (Jagnow et al., 1977). The primary degradation product found under anaerobic conditions was $\gamma$-TCCH. A similar rapid degradation of lindane to $\gamma$-TCCH was observed under anaerobic incubation with *Clostridium sphenoides* (Heritage and MacRae, 1979), although under alkaline conditions dehydrochlorination of lindane to $\gamma$-PCCH was also observed.

### 5.3 Fluid-Phase Degradation

It is clear from the above discussion that lindane degrades chemically by a dehydrochlorination ($E_2$ elimination) reaction, and microbially—under both aerobic and anaerobic conditions. Based upon this information, sodium azide was included in the buffered aqueous solution in which all experiments were performed. This accomplished two objectives: sodium azide poisoned potential biodegradation reactions, and the buffer solution maintained a steady pH, which in turn led to a predictable rate of abiotic degradation.

Conventional bottle-point methods were used to quantify the rate of abiotic degradation in the aqueous phase. This was accomplished by observing the disappearance of lindane as a function of time in a buffered solution that was devoid of solids. Buffering was useful since the rate of dehydrochlorination in an $E_2$ elimination reaction is a function of both the parent compound and the hydroxide ion concentration. The reaction rate may be described for a batch reactor by

\[
\frac{dC}{dt} = -k_2 C \cdot C_h \tag{47}
\]

where $k_2$ is a second-order abiotic degradation rate constant $[L^3/M \cdot T]$, and $C_h$ is the hydroxide ion concentration $[M/L^3]$. For a buffered system, the general second-order relationship reduces to the pseudo-first-order model

\[
\frac{dC}{dt} = -k_a C \tag{48}
\]
where the aqueous-phase degradation rate is the product of $k_2$ and $C_h$.

Figure 2 shows the experimental data for the dehydrohalogenation of lindane in a buffered system (pH 8.4) as a function of time and the pseudo-first-order model fit for $k_a$. The model was fit by

$$\min_k \sum_{n=1}^{n_d} \left( \frac{(C_{d,n} - C_{m,n})}{C_{m,n}} \right)^2$$

(49)

where $C_{d,n}$ is the experimental solute concentration [M/L$^3$] and $C_{m,n}$ is the model solute concentration [M/L$^3$] corresponding to data point $n$, and $n_d$ is the total number of experimental points. The minimization process resulted in the estimate: $k_a = 1.23 \times 10^{-4}$ hr$^{-1}$.

5.4 Solid-Phase Degradation

It is well known that the rate of abiotic degradation may vary as a function of whether a solute is present in the aqueous phase or sorbed to the solid phase. Experimental determination of the solid-phase solute degradation rate is complicated because sorption, fluid-phase degradation, and solid-phase degradation occur simultaneously; and because of the slow nature of the sorption and desorption process. While it is possible to fit a model simultaneously for several parameters, the significance of the resultant parameter values and model is difficult to assess. For this reason, a method was devised to solve for the solid-phase degradation rate independently of all other parameters in the reactive surface diffusion model.

The experimental data used to determine the solid-phase degradation rate, $k_s$, was a bottle-point rate study that was performed over a period of 2114 hours (kin88-04). Extraction measurements of the mass of solute on the solid phase as a function of time were made during this experiment. The data allowed experimental calculation of the fluid-phase solute mass, the solid-phase solute mass, and the total system mass as a function of time. These data are shown on Figure 3 for experimental conditions that are summarized in Table 3. Model parameters are summarized in Table 4.

The procedure used to determine $k_s$ was (1) fit an empirical model to the fluid-phase solute mass data as a function of time; (2) derive an expression for total system mass as a function of time using the empirical model from step 1; and (3) use the solid-phase solute extractions and the results from step 2 to determine $k_s$ by regression analysis.

The empirical model used to describe the aqueous-phase solute concentration as a function of time was
Figure 2. Fluid-phase lindane dehydrohalogenation as a function of time.

\[ C_m = \alpha_0 + \alpha_1 \exp(-\beta_1 t) + \alpha_2 \exp(-\beta_2 t) \]  

(50)

which was restricted to require a match of the initial starting concentration by

\[ \alpha_0 = C_0 - \alpha_1 - \alpha_2 \]  

(51)
Figure 3. Solute mass normalized by initial system mass as a function of time for experiment kin88-04.

where $C_m$ is the model-predicted solute concentration $[M/L^3]$, and $\alpha_1$, $\alpha_2$, $\beta_1$, and $\beta_2$ are empirical constants $[M/L^3]$. A four-parameter fit was accomplished for the objective function

$$
\min_{\alpha_1, \alpha_2, \beta_1, \beta_2} \sum_{n=1}^{n_d} \left( \frac{M_{am,n} - M_{ad,n}}{M_o} \right)^2
$$

(52)
Table 3. Lindane-Wagner Experimental Conditions

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<th>Type</th>
<th>Mass of Solids (g)</th>
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<th>Desorption Time (hr)</th>
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Table 4. Lindane-Wagner Model Parameter Estimates

<table>
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</table>

where $M_{aq,n}$ is the solute mass in the aqueous phase predicted by the empirical model $[M]$, $M_{ad,n}$ is the solute mass in the aqueous phase calculated from the experimental data $[M]$, and $M_0$ is the initial solute mass added to the system $[M]$. As may be noted from Figure 3 an accurate description of the aqueous-phase solute mass data was obtained using this method, while the values of the coefficients used to fit the aqueous-phase data are summarized in Table 5.

An analytical solution for the total mass of solute in the system as a function of time may be derived by first noting
where $M$ is the mass of solute in the system [M], $V$ is the aqueous-phase volume in the system [L$^3$], $M_s$ is the mass of the solid phase in the system [M], and $q$ is the solid-phase solute concentration [M/M]. If solute mass is lost from the system as a result of pseudo-first-order kinetics from both the fluid and solid phases, the system solute mass loss rate may be expressed as

$$\frac{dM}{dt} = -k_a V C - k_s M_s q.$$  \hspace{1cm} (54)

Combining Equations (53) and (54) yields

$$\frac{dM}{dt} = (k_s - k_a) V C - k_s M.$$ \hspace{1cm} (55)

Combining Equations (50) and (55) gives

$$\frac{dM}{dt} = (k_s - k_a) V [\alpha_0 + \alpha_1 \exp(-\beta_1 t) + \alpha_2 \exp(-\beta_2 t)] - k_s M,$$ \hspace{1cm} (56)

which may be solved, giving

$$M_m = M_0 \exp(-k_s t) + V (k_s - k_a) \left( [1 - \exp(-k_s t)] \frac{\alpha_0}{k_s} + \exp(-\beta_1 t) \right)$$

$$- \exp(-k_s t) \frac{\alpha_1}{k_s - \beta_1} + [\exp(-\beta_2 t) - \exp(-k_s t)] \frac{\alpha_2}{k_s - \beta_2}.$$ \hspace{1cm} (57)

where $M_m$ is the total solute mass predicted by the model [M].

Experimental data on total solute mass, $M_d$, were used along with the empirical model given by Equation (57) to satisfy the objective function

$$\min_{k_s} \sum_{n=1}^{n_k} \left( \frac{M_{m,n} - M_{d,n}}{M_c} \right)^2$$ \hspace{1cm} (58)
where $M_{m,n}$ and $M_{a,n}$ are the solute mass predicted by the model (Equation (58)) and calculated from the experimental data for an arbitrary point $n$ [M]. The minimization procedure yielded a best-fit value for $k_s$ of $7.48 \times 10^{-5}$ hr$^{-1}$, which is about 39% less than the fluid-phase degradation rate.

### 5.5 Pseudo-Sorption-Desorption Equilibrium

A pseudo-sorption-desorption equilibrium experiment was performed by using methods previously described. The sorption step was performed for 732 hr, followed by three consecutive desorption steps in which approximately 384 hours were allowed for equilibration during each step. The data collected from this experiment are posted on Figure 4, where three subsets of data are identified based upon similar initial solute concentrations. These data are referred to as pseudo-equilibrium data since 732 hours were not adequate to reach equilibrium based upon the rate data shown in Figure 3. The sorption-desorption data shown in Figure 4 are markedly hysteretic.

Clearly equilibrium parameters $K_f$ and $n_f$ determined from a data set not indicative of equilibrium conditions would be in error. Preliminary numerical experimentation with the reactive surface diffusion model was used as a basis for the hypothesis that an estimate of $K_f$ would be much more sensitive to nonequilibrium conditions than $n_f$. For this reason, sorption data were regressed in log space to minimize the relative error—yielding the estimate $n_f \approx 0.742$.

### 5.6 Sorption Rates

The previously described steps yielded independent estimates for three of the six parameters needed in the reactive surface diffusion model: $k_a$, $k_s$, and $n_f$. The remaining model parameters are: $K_f$, $k_f$, and $D_s$—the sorption capacity constant, and both sorption rate parameters. No physical or mechanistic significance was ascribed to the empirical fits of the sorption rate data used to determine the solid-phase degradation rate.

Previous experimental work with similar materials (Miller and Weber, 1988; Weber and Miller, 1988) found that film mass transfer resistance was a relatively unimportant factor in determining the rate of sorption. That is, $D_s$ was sufficiently small that internal particle diffusion was the rate-determining step. A typical measure of the relative rate of intraparticle diffusion to film transport resistance is given by a Biot number (Hand et al., 1983)

\[
Bi = \frac{k_f R \theta_s}{D_s D_s \theta_a \phi_s} \left(1 - \frac{C_e}{C_o}\right)
\]  

(59)
Figure 4. Pseudo-sorption-desorption equilibrium data for experiment iso89-01.
where $D_g$ is the solute distribution parameter defined as

$$D_g = \frac{M_s q_{co}}{V \theta_a C_o}$$  \hspace{1cm} (60)

and $\theta_s$ is the volume fraction of the solid phase, $\theta_a$ is the volume fraction of the aqueous phase, $\phi_s$ is the ratio of the surface area of an equivalent volume sphere to the actual surface area of a typical particle, and $q_{co}$ is the solid-phase solute concentration in equilibrium with the initial fluid-phase solute concentration.

$Bi$ is directly related to the relative resistance due to intraparticle diffusion. In other words at large values of $Bi$, the rate of sorption is sensitive to $D_s$ and insensitive to $k_f$, since the surface diffusion resistance is dominant. Based upon the previously-published evidence (Weber and Miller, 1988), film mass-transfer resistance was assumed negligible for the Wagner-lindane solid-solute pair. All simulations were performed by setting $k_f = 10^3$ cm/hr, which yielded a corresponding $Bi$ number that was in the surface-diffusion dominant region.

The remaining two parameters needed to specify the reactive surface diffusion model, $K_f$ and $D_s$, were estimated simultaneously using two experimental sorption rate data sets (kin88-04 and kin89-01). The kin88-04 data set was used previously to determine the solid-phase decay rate. The parameter estimation performed can be summarized by

$$\min_{k_f, D_s} \sum_{ne=1}^{2} \sum_{n=1}^{n_{ne,d}} \left( \frac{C_{d,ne,n} - C_{m,ne,n}}{C_{0,ne}} \right)^2$$  \hspace{1cm} (61)

where $ne$ is the number of the experiment, $n_{ne,d}$ is the number of data points in experiment number $ne$, $C_{d,ne,n}$ is the experimental aqueous-phase solute concentration corresponding to the $ne$ experiment and the $n$ point [M/L^3], $C_{m,ne,n}$ is the modeled aqueous-phase solute concentration corresponding to the $ne$ experiment and the $n$ point [M/L^3].

Model predictions, using results from the two-parameter minimization, are shown along with the experimental data on Figures 7 and 8, where experimental conditions are summarized in Table 3 and model parameter values in Table 4. Examination of Figures 7 and 8 shows excellent agreement between model predictions and experimental data throughout the entire range of the data collected. Two features of the parameter estimates should be noted: the derivative of the error, as defined by Equation (61), was small with respect to the model parameters fit in the vicinity of optimal parameters; and the optimal parameter values are highly correlated. These features of the parameter estimation procedure suggest that model fits of a similar quality could be achieved with a different set of parameters, and the optimal values of the parameters are inversely related. It should be noted that
Figure 5. Experimental data and model fit for sorption rate experiment kin88-04.

the parameter values reported are global minimum—as confirmed by an exhaustive grid search in addition to the normal parameter estimation.
5.7 Desorption Rates

The previous sections described a systematic experimental and modeling procedure used to establish estimates of unknown parameters present in the reactive surface-diffusion model. These estimates yielded accurate descriptions of the data sets used to estimate the parameters. This is a necessary but not a sufficient condition for model accuracy. To assess the adequacy of the model and the reasonableness of the parameters, desorption rate experiments were performed and model predictions were made based upon the independently determined parameters in the reactive surface diffusion model. The results of
two desorption rate experiments and simulation predictions are shown by Figures 7 and 8, for experimental conditions that are summarized by Table 3. The difference between the two desorption simulations is that kin89-04 were allowed to sorb for about 2 days before desorption was initiated and 30 days was allowed for the sorption period in kin89-05.

Figure 7. Experimental data and model prediction for desorption rate experiment kin89-04.
Figure 8. Experimental data and model prediction for desorption rate experiment kin89-05.

Results from the prediction of both desorption experiments were similar: simulation results were typically within 2% of the experimental data, with predicted aqueous-phase concentrations slightly higher than observed concentrations. The accuracy of these simulations suggests that the reactive surface diffusion model is a reasonable predictor of the dynamics of solute reaction, and sorption and desorption for the system investigated.
5.8 Discussion

For a reactive solute in a batch reactor, an equilibrium condition is never achieved. To demonstrate the predicted dynamics of the system, a long-term simulation was performed using input conditions consistent with rate experiment kin88-04 and the model parameters estimated and previously described. The results of this simulation, shown in Figure 9, are a prediction of a monotonic decrease with time in the total system mass and fluid-phase solute mass. The solid-phase solute mass is predicted to increase rapidly initially, reach a maximum value after about 42 days, and to decrease with time thereafter. Although not shown, the simulation model predicts all solute would decay from both the fluid and solid phases as time tends to infinity.

An important assumption made in estimating the reactive surface diffusion model parameters was that $n_f$ could be determined accurately from a pseudo-equilibrium experimental data set that was allowed to sorb for only 30 days. To test this assumption, simulations were performed using model conditions similar to those that existed in the pseudo-equilibrium experiment (iso89-01). Model parameters used in the simulations were the final set of estimated reaction and surface diffusion model parameters. The procedure used involved (1) performing sorption rate simulations for each of the initial conditions used in iso89-01; (2) using rate model simulation results at varying times as input to a log-space Freundlich regression model to extract estimates of $K_f$ and $n_f$; and (3) noting the trends in predicted values of $K_f$ and $n_f$ relative to the assumed true values as a function of time. The results of this procedure are summarized by Figure 10.

Three interesting features are evident from this analysis. First, the assumption of $n_f$ being relatively insensitive and $K_f$ being relatively sensitive to time was accurate. Second, the use of pseudo-equilibrium data collected after 30 days was adequate to predict accurately the true value of $n_f$. Third, $K_f$ increases as a function of time up to about 6000 hr, at which time the regressed value exceeds the true value of $K_f$. This is so because degradation from the fluid phase is faster than the solid phase degradation rate, and at long times desorption is occurring from the solid phase because of the difference in degradation rates between the fluid and solid phases.

The predicted true equilibrium relationship based upon the estimates of $n_f$ and $K_f$ is shown by Figure 11 along with the pseudo-equilibrium data and a regression line based upon the 30-day equilibration time data. The estimated equilibrium line is parallel but lies substantially (since the results are shown in log format) above the 732 hours data and regression line. This is consistent with the use of a constant $n_f$.

The final test of the model, and the major objective of this investigation, was to evaluate the effect of slow sorption rates as an explanation for perceived desorption hysteresis. To accomplish this objective, rate model simulations were performed using conditions that mimicked the experimental conditions of the pseudo-equilibrium sorption-desorption experiment (iso89-01). Results of these simulations, Figure 12, show that a substantial fraction of the apparent desorption hysteresis is explained by the rate model. That is,
rate effects are an important contributor to apparent desorption hysteresis for the lindane-Wagner system investigated in this work.

Even accounting for rate effects, some apparent desorption hysteresis remains. This observation is also consistent with the desorption rate experiments and simulations in which a lower-than-predicted aqueous-phase solute concentration was observed. Many possible explanations for this observation are possible. One notion is that the reactive surface diffusion model is not the appropriate rate model. A reactive pore-diffusion model is typically
formulated in terms of an equilibrium condition at all locations of contact between the fluid and solid phases within a particle. Due to the favorable nature of the equilibrium model, this would translate to a slower rate of desorption, thus more apparent desorption hysteresis. The relatively good prediction offered by the reactive surface diffusion model would be consistent with a pore-diffusion explanation, since equivalent predictions are possible from both models for the case of a linear equilibrium relationship. Future work should investigate this explanation using both experimental and modeling approaches.
Figure 11. Comparison of predicted equilibrium relationship and 30-day pseudo-equilibrium data from experiment iso89-01.
Figure 12. Rate model simulation of pseudo-equilibrium sorption-desorption data from experiment iso89-01.
6 Multicomponent Systems

6.1 Overview

Experiments were conducted to investigate the nature of multicomponent sorption effects. Experiments were planned and data were evaluated to investigate two specific potential effects: the effect of a second solute on the rate of sorption, and the effect of a background solute of constant concentration on the equilibrium solute distribution between the fluid and solid phases for a second solute of varying concentration. Most experiments were conducted using the bottle-point method; however, studies were also performed for a set of single and binary solute columns. Bisolute experiments were conducted to parallel single-solute experiments as closely as possible to allow direct comparison by maintaining similar solid to solution ratios and initial solute concentrations for studies done in single and multicomponent systems.

6.2 Single-Solute Rate Studies

Studies were conducted to identify the rate of uptake of a solute for single and bisolute conditions on two subsurface materials: Wagner and Traverse City. The initial conditions for 12 studies are described in Table 5. In general, two single-solute studies and two bisolute studies were conducted with each subsurface material for TCB and for lindane. A relatively low and high initial concentration was used for the single-solute studies, and approximately those same concentrations were used when the solutes were combined for bisolute studies.

The solids ratios (mass of solids to mass of solution) were about 1:10 and 2:1 for Wagner and Traverse City subsurface materials, respectively. Fluid-phase concentrations were monitored for at least 84 days.

Results of the single-solute rate studies, after correction for outliers are presented in Figures 13 and 14 for the Wagner subsurface material, and Figures 15 and 16 for the Traverse City material. TCB results are shown first followed by lindane, and the plots show both the high and low \( C_0 \) studies in the same figure (studies conducted independently). The rate profiles show relative fluid-phase concentration \( (C/C_0) \) as a function of time. For both TCB and lindane, a two-phase behavior is evident: the sorption process follows a trend of rapid initial uptake, followed by a slower sustained rate.

It is evident from the non-degrading solute TCB that at least 75% of the total uptake observed was achieved in the first 10 days. Visual inspection of the TCB results suggests that the systems neared equilibrium after approximately 1200 hr, or 50 days. In contrast, the sloping tail in the lindane plots indicates no apparent equilibrium was achieved for those systems. As discussed at length in the previous chapter, lindane undergoes an E2
elimination, which confounds the determination of the time required to approach equilibrium by visual inspection. Some additional work on the abiotic degradation of lindane is discussed in later sections, as it bears upon interpretation of bisolute effects.

Visual inspection is the method used by many investigators to determine time required to reach equilibrium. When the scatter in the data exceeds the change in the fluid-phase concentration between subsequent samples, the system is assumed to be at equilibrium. Using this criterion, the TCB systems were considered to have reached apparent equilibrium within the experimental time frame, and equilibrium experiments were conducted within this time. However, a very small negative slope was still evident in the tail of the rate profile, suggesting that some uptake was still occurring after 2500 hours (if loss of analyte from the system was not significant). This long term sorption is a significant result. Again, this effect is difficult to identify in the lindane figures because no apparent equilibrium is reached for a degrading solute. The duration of this sustained long-term sorption effect is not known. It was not possible with the objectives of this project to conduct experiments of a longer duration than attempted here. It should be noted that very few studies have been performed using equilibration times of the order used in this work 50–90 days.

The results in Figures 13 through 16 also show that for the same solute-sorbent combination, the relative concentration approached at long times increased with increasing $C_o$. This result is consistent with a nonlinear equilibrium distribution, which is concave with respect to the fluid-phase concentration axis (i.e., $n_f < 1$).
Figure 13. Bottle-point rate study results for single-solute TCB sorption to Wagner material.

- ○○○○○ TCB \( C_0 = 1020 \mu g/L \)
- ▲▲▲▲▲ TCB \( C_0 = 6470 \mu g/L \)

Relative Fluid-Phase Concentration

Sorption Time (hours)
Figure 14. Bottle-point rate study results for single-solute lindane sorption to Wagner material.

The graph shows the relative fluid-phase concentration over sorption time for two different initial concentrations of lindane: 1947 µg/L and 5678 µg/L. The data points indicate a decrease in concentration over time, typical of sorption processes.
Figure 15. Bottle-point rate study results for single-solute TCB sorption to Traverse City material.

- ○○○○ ○ TCB $C_0 = 441 \, \mu g/L$
- ▲▲▲▲▲ TCB $C_0 = 2609 \, \mu g/L$
Figure 16. Bottle-point rate study results for single-solute lindane sorption to Traverse City material.

- ○○○○ TCB $C_0 = 1020 \ \mu g/L$
- ▲▲▲▲ TCB $C_0 = 6470 \ \mu g/L$
For the case of a linear equilibrium relationship in a batch system

\[ q_e = K_p C_e = (C_o - C_e) \frac{V}{M_s} \]  

(62)

where all variables have been defined previously. Rearranging Equation (62) gives

\[ \frac{C_e}{C_o} = \left( \frac{K_p M_s}{V} + 1 \right)^{-1}. \]  

(63)

Therefore if \( K_p, M_s, \) and \( V \) are constant, the ratio \( C_e/C_o \) would be constant as well. Since this was not the case, the linear equilibrium model was not an appropriate choice. The results observed in the rate experiments suggest that a concave equilibrium model would describe the system more accurately than a linear model. This was found to be the case, as the next section shows.

6.3 Single-Solute Equilibrium Studies

Single-solute equilibrium experiments were conducted to define the distribution relationship for the solid-phase solute concentration as a function of the fluid-phase solute concentration. The conditions for the eight equilibrium experiments are described in Table 6 (both single and multisolute experimental conditions are included). Three conditions were considered for each of the two subsurface materials in separate equilibrium experiments: (a) a single-solute TCB system, (b) a bisolute system with a relatively low lindane concentration, and (c) a bisolute system with a relatively high lindane concentration. This focused on the effect that adding lindane to the system had on the TCB equilibrium distribution.

TCB initial concentrations ranged from 504 to 5816 \( \mu g/\ell \) for experiments with the Wagner material, and from 130 to 1363 \( \mu g/\ell \) with the Traverse City material. The solids ratios in the reactors were consistent with rate studies, at about 1:10 and 2:1 for Wagner and Traverse City materials, respectively.

In addition a second solids ratio was used with the Wagner material in order to cover a wider range of equilibrium concentrations, keeping in mind the possibility of the so-called solids effect. Data have been presented in the literature showing that linear partition coefficients are dependent not only on the octanol-water partition coefficient of the chemical and on \( f_{oc} \) of the sediment, but also inversely upon the solids concentration in the system (O'Connor and Connolly, 1980). Several mechanisms have been proposed (Voice and Weber, 1983, 1985; DiToro, 1985; Mackay and Powers, 1987). Two TCB equilibrium experiments were performed at a 1:30 ratio with zero and high lindane background concentrations.
Table 6. Equilibrium Study Experimental Conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Subsurface Material</th>
<th>Solids Ratio (g/ml)</th>
<th>Initial TCB Concentration (µg/ℓ)</th>
<th>Initial Lindane Concentration (µg/ℓ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso89-05a</td>
<td>Wagner</td>
<td>3.6/35.9</td>
<td>504–5808</td>
<td>0</td>
</tr>
<tr>
<td>iso89-05b</td>
<td>Wagner</td>
<td>3.6/35.9</td>
<td>505–5816</td>
<td>818</td>
</tr>
<tr>
<td>iso89-05c</td>
<td>Wagner</td>
<td>3.6/35.9</td>
<td>1018–5801</td>
<td>2892</td>
</tr>
<tr>
<td>iso89-05d</td>
<td>Wagner</td>
<td>1.2/35.9</td>
<td>504–5808</td>
<td>0</td>
</tr>
<tr>
<td>iso89-05e</td>
<td>Wagner</td>
<td>1.2/35.9</td>
<td>505–5814</td>
<td>2856</td>
</tr>
<tr>
<td>iso89-06a</td>
<td>Traverse City</td>
<td>44.0/21.9</td>
<td>132–1387</td>
<td>0</td>
</tr>
<tr>
<td>iso89-06b</td>
<td>Traverse City</td>
<td>44.0/22.3</td>
<td>130–1363</td>
<td>485</td>
</tr>
<tr>
<td>iso89-06c</td>
<td>Traverse City</td>
<td>44.0/22.3</td>
<td>130–1363</td>
<td>1663</td>
</tr>
</tbody>
</table>

Equilibration times were 60 and 84 days for the Traverse City and Wagner subsurface materials, respectively. These are relatively long equilibration times when compared to similar studies discussed in the literature, as was previously noted. In most cases cited in the literature, sorption equilibrium studies are not accompanied by sorption rate studies, and an assumption of 24 to 48 hours equilibration times is often employed. Several investigators have cited much longer equilibration times for compounds and systems similar to those used in this study (Miller, 1984; Miller and Weber, 1984a; Coates and Elzerman, 1986; Brusseau and Rao, 1989a).

The equilibration times employed in these equilibrium experiments were determined from sorption rate experiments. The plateau region of TCB rate experiments indicated the required time for TCB systems. Solid-phase extractions of the lindane systems suggested this time was reasonable for the lindane systems as well. An additional consideration for lindane was the desire to minimize incubation time after approaching an apparent equilibrium to prevent further abiotic degradation of lindane.

Results of the equilibrium experiments, after correction for outliers were plotted in the conventional form of $q_e$ v. $C_e$. Assuming the following mass balance, the sorbed-phase concentration at apparent equilibrium was found by difference:

$$C + \frac{M_s q}{V} = C_o$$  \hspace{1cm} (64)

where $C$ and $q$ are fluid and solid-phase concentrations as a function of time, $t$; $M_s$ is the mass of solid phase and $V$ is volume of solution in the batch system. This relation is dependent upon the assumption of no loss of solute from the system or to the container walls. Further analysis of this assumption is given later. Figure 17 shows the TCB equilibrium results from the single-solute experiments with Wagner subsurface material at the
1:10 solids ratio; Figure 18 shows results for the 1:30 ratio. Traverse City material results are presented in Figure 19.

Inspection of the single-solute equilibrium plots indicates increased scatter in the data at higher fluid-phase concentrations. This phenomenon is consistent with the use of minimization of relative error for the purpose of model parameter estimation. Model parameter estimation is described in sections that follow.

6.4 Bisolute Equilibria Studies

6.4.1 Experimental Results

Results of bisolute equilibrium studies are plotted with single-solute results to allow comparison. Figure 20 shows results for the Wagner material at 1:10 solids ratio. Figure 21 shows results for the Wagner material at a 1:30 solids ratio, and Figure 22 shows results for the Traverse City material.

For clarity, a fitted Freundlich equilibrium model is used to represent the single-solute condition. In each plot, visual comparison of the data shows that very similar results were obtained for the single and bisolute studies. Within the scatter of the data, there is significant overlap. This suggests that the TCB equilibrium distribution was changed very little, if at all, by the presence of lindane in the system. It was essential to the goal of this study to determine if the TCB equilibrium isotherm results differ significantly under the conditions of zero, low, and high lindane background concentrations. If no difference can be shown, then all data represent the same TCB isotherm, unaffected by the presence of a second solute. Statistical analyses were used to establish the existence and degree of competition.

6.4.2 Equilibrium Modeling

6.4.2.1 Equilibrium Model Comparisons

All eight isotherm data sets were fit with Freundlich, Langmuir, and linear models by minimizing the sums of the squares of relative error

$$
\min \epsilon_r = \sum_{n=1}^{n_p} \left( \frac{q_e - q_m}{q_m} \right)^2
$$

(65)

where $q_m$ is a model-predicted sorbed concentration, and $n_p$ is the number of observations. The two nonlinear models provided a better description of the data sets, though the sorption data for the Traverse City material were notably more linear than for the Wagner.
Figure 17. Bottle-point equilibrium study results for single-solute TCB sorption to Wagner material for a 1:10 solid ratio.
Figure 18. Bottle-point equilibrium study results for single-solute TCB sorption to Wagner material for a 1:30 solid ratio.
Figure 19. Bottle-point equilibrium study results for single-solute TCB sorption to Traverse City material.
Figure 20. Comparison of single and bisolute sorption equilibrium results for TCB sorption to Wagner material for a 1:10 solids ratio.
Figure 21. Comparison of single and bisolute sorption equilibrium results for TCB sorption to Wagner material for a 1:30 solids ratio.
Figure 22. Comparison of single and bisolute sorption equilibrium results for TCB sorption to Traverse City material.
material. The parameters for the best model fits are listed in Table 7, and the mean squared relative errors are indicated as a measure of degree of fit. A visual inspection of the relative residuals versus \( C_e \) showed no apparent heteroscedasticity or autocorrelation for the nonlinear models. Figure 23 shows data for the TCB-Wagner system with the low background lindane concentration and an example of the fits. All residuals which follow in this work, relative or absolute, were consistently calculated as: observed value - model estimate.

The Freundlich and Langmuir models described the data equally well. Working with the Freundlich model offered some distinct advantages given the purpose of this study. The Freundlich model equation can be linearized by taking the logs of both sides of the equation to yield

\[
\log q_e = \log K_f + n_f \log C_e
\]  

(66)

or

\[
q_e^* = K_f^* + n_f C_e^*
\]  

(67)

which is a linear function in the log transformed variables \( q_e^* \) and \( C_e^* \). The linear regression of the log transformed data assumes a multiplicative error, that is, increasing residuals with increasing concentration, which was appropriate for these systems. In addition, confidence intervals can be conveniently constructed about a least squares best fit line of the log transformed data. The Freundlich model was used in this linearized form for all subsequent analysis. Table 8 shows the best fit parameter values, the 95% confidence intervals about the values, and the mean squared absolute errors. Again, a visual inspection of the residuals (log space) versus \( C_e^* \) showed no heteroscedasticity or autocorrelation (see Figure 24, for example). The \( r^2 \) values were generally greater than 0.9, indicating that the model described the data well.

Before performing quantitative regression comparisons between single and bisolute data sets, the single-solute TCB experimental results for the 1:10 and 1:30 solids ratios for the Wagner aquifer material were combined. A plot of the data showed significant overlap, and model fits of the data showed Freundlich parameters that were not statistically different at the 5% level (see Table 8). This provided a final single-solute equilibrium data set covering a wider sorbate concentration range. Figure 25 shows the combined isotherm and the least squares best fit line.

The fact that the solids effect was not evident in this system is due likely to the small range in difference in the solids ratios used. The effect has been documented in the concentration range 10 to 22,000 mg/\( \ell \). The concentrations employed in this study were relatively high, at 33,000 to 2,000,000 mg/\( \ell \).
Table 7. TCB Equilibrium Model Parameters

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Freundlich Model</th>
<th>Langmuir Model</th>
<th>Linear Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$ $(\mu g/g)(\ell/\mu g)^{n_f}$</td>
<td>$Q^0$ $(\mu g/g)$</td>
<td>$K_p$ $(\ell/g)$</td>
</tr>
<tr>
<td>iso89-05a</td>
<td>0.137 0.893 0.043</td>
<td>159.9 5.6 x 10^{-4}</td>
<td>0.074 0.044</td>
</tr>
<tr>
<td>iso89-05b</td>
<td>0.343 0.760 0.017</td>
<td>83.2 1.7 x 10^{-3}</td>
<td>0.102 0.077</td>
</tr>
<tr>
<td>iso89-05c</td>
<td>0.387 0.719 0.023</td>
<td>90.3 1.2 x 10^{-3}</td>
<td>0.077 0.058</td>
</tr>
<tr>
<td>iso89-05d</td>
<td>0.547 0.706 0.045</td>
<td>155.0 9.3 x 10^{-3}</td>
<td>0.094 0.140</td>
</tr>
<tr>
<td>iso89-05e</td>
<td>0.632 0.693 0.053</td>
<td>190.4 6.9 x 10^{-4}</td>
<td>0.090 0.091</td>
</tr>
<tr>
<td>iso89-06a</td>
<td>0.002 0.934 0.026</td>
<td>2.4 7.8 x 10^{-4}</td>
<td>0.002 0.027</td>
</tr>
<tr>
<td>iso89-06b</td>
<td>0.002 0.939 0.023</td>
<td>3.0 5.3 x 10^{-4}</td>
<td>0.001 0.023</td>
</tr>
<tr>
<td>iso89-06c</td>
<td>0.003 0.880 0.026</td>
<td>1.6 1.5 x 10^{-4}</td>
<td>0.002 0.033</td>
</tr>
</tbody>
</table>

MSR Error—Mean Square Relative Error
Figure 23. Equilibrium model fit comparison for iso89-05b.
Table 8. Confidence Intervals for Linearized Freundlich Model

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Model Estimates</th>
<th>Confidence Intervals</th>
<th>Mean Square Error</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$ (μg/g)(ℓ/μg)$^{n_f}$</td>
<td>$K_f$ (μg/g)(ℓ/μg)$^{n_f}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iso89-05a</td>
<td>0.115 0.914</td>
<td>[4.63,28.5] x 10^{-2} [0.759, 1.07]</td>
<td>7.30 x 10^{-3}</td>
<td>0.932</td>
</tr>
<tr>
<td>iso89-05b</td>
<td>0.353 0.751</td>
<td>[2.39,5.21] x 10^{-1} [0.680, 0.821]</td>
<td>3.34 x 10^{-3}</td>
<td>0.972</td>
</tr>
<tr>
<td>iso89-05c</td>
<td>0.426 0.698</td>
<td>[1.88,9.61] x 10^{-1} [0.561, 0.835]</td>
<td>4.38 x 10^{-3}</td>
<td>0.911</td>
</tr>
<tr>
<td>iso89-05d</td>
<td>0.522 0.704</td>
<td>[2.35,11.6] x 10^{-1} [0.582, 0.825]</td>
<td>9.39 x 10^{-3}</td>
<td>0.910</td>
</tr>
<tr>
<td>iso89-05e</td>
<td>0.442 0.736</td>
<td>[1.56,12.5] x 10^{-1} [0.579, 0.894]</td>
<td>1.01 x 10^{-2}</td>
<td>0.887</td>
</tr>
<tr>
<td>iso89-06a</td>
<td>0.002 0.934</td>
<td>[1.45,3.44] x 10^{-3} [0.848, 1.02]</td>
<td>5.03 x 10^{-3}</td>
<td>0.956</td>
</tr>
<tr>
<td>iso89-06b</td>
<td>0.002 0.960</td>
<td>[1.04,2.82] x 10^{-3} [0.863, 1.06]</td>
<td>3.98 x 10^{-3}</td>
<td>0.968</td>
</tr>
<tr>
<td>iso89-06c</td>
<td>0.003 0.870</td>
<td>[1.87,5.81] x 10^{-3} [0.760, 0.980]</td>
<td>4.68 x 10^{-3}</td>
<td>0.965</td>
</tr>
<tr>
<td>iso89-05a,d</td>
<td>0.221 0.822</td>
<td>[1.18,4.12] x 10^{-1} [0.722, 0.921]</td>
<td>1.19 x 10^{-2}</td>
<td>0.907</td>
</tr>
<tr>
<td>iso89-05a-e</td>
<td>0.281 0.787</td>
<td>[2.04,3.88] x 10^{-1} [0.734, 0.839]</td>
<td>9.12 x 10^{-3}</td>
<td>0.922</td>
</tr>
<tr>
<td>iso89-06a-c</td>
<td>0.002 0.921</td>
<td>[1.74,3.12] x 10^{-3} [0.863, 0.978]</td>
<td>5.55 x 10^{-3}</td>
<td>0.951</td>
</tr>
</tbody>
</table>

$r^2$ — correlation coefficient in log space.
Figure 24. Residuals of Freundlich equilibrium model fits in log space for TCB sorption to Wagner material.

![Graph showing residuals of Freundlich equilibrium model fits in log space for TCB sorption to Wagner material.](image)
Figure 25. Single solute data and Freundlich model fit for TCB sorption to Wagner material for both high and low solids concentrations (iso89-05a and iso89-05d).
6.4.2.2 Single and Bisolute TCB Comparisons

As a means of comparing single and bisolute equilibrium data, the previously determined single-solute model parameters \( (K_f, n_f) \) were used to construct a model estimate for each bisolute data set in log space. Residuals, therefore, represent the difference between the single-solute equilibrium model and bisolute data at a given \( C_e^* \). Plots were made of residuals versus \( C_e^* \) and inspected for trends with increasing concentration. Trends in the residuals were approximated by a line, and the resulting slopes and confidence intervals for all systems are listed in Table 9. Results are shown in Figures 26 and 27 for the Wagner and Traverse City materials, respectively. Residuals showed a negative trend in most cases, indicating decreasing residuals with increasing \( C_e^* \). However, 95% confidence intervals about the slopes included zero in all cases except one.

Table 9. Bisolute Residuals Regression Summary

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( n_p )</th>
<th>Slope log (( L/\mu g ))</th>
<th>Upper 95%</th>
<th>Lower 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso89-05b</td>
<td>13</td>
<td>-8.5 \times 10^{-2}</td>
<td>-2.4 \times 10^{-1}</td>
<td>7.3 \times 10^{-2}</td>
</tr>
<tr>
<td>iso89-05c</td>
<td>15</td>
<td>-7.1 \times 10^{-2}</td>
<td>-1.4 \times 10^{-1}</td>
<td>2.0 \times 10^{-4}</td>
</tr>
<tr>
<td>iso89-05e</td>
<td>14</td>
<td>-1.2 \times 10^{-1}</td>
<td>-2.6 \times 10^{-1}</td>
<td>1.4 \times 10^{-2}</td>
</tr>
<tr>
<td>iso89-06b</td>
<td>15</td>
<td>2.6 \times 10^{-2}</td>
<td>-7.0 \times 10^{-2}</td>
<td>1.2 \times 10^{-1}</td>
</tr>
<tr>
<td>iso89-06c</td>
<td>11</td>
<td>-6.4 \times 10^{-2}</td>
<td>-1.7 \times 10^{-1}</td>
<td>4.6 \times 10^{-2}</td>
</tr>
</tbody>
</table>

A second means of comparing the data sets was construction of confidence intervals about equilibrium model fits for single and bisolute experiments. The bisolute equilibrium data sets were described with the log-linearized Freundlich equilibrium model as were the single-solute data (see Table 7). Using the tabulated parameters to construct the equilibrium model lines, 95% confidence intervals for the mean \( q_e^* \) at a given \( C_e^* \) were calculated for the entire equilibrium fluid-phase concentration range for each study. Working in log-log space, this procedure generated confidence intervals around the model lines which, by nature of the analysis, are narrower in the center than at the extreme values. Figure 28 shows a plot of overlapping confidence intervals for the three background lindane concentrations for the TCB-Wagner system (1:10 solids ratio). Figure 29 shows the same information for only the high background lindane concentrations (1:10 and 1:30 ratios). Figure 30 shows the TCB-Traverse City results. All bisolute intervals overlap single-solute intervals and overlap each other for both subsurface materials.

Important assumptions in the analysis include that \( C_e^* \) is an observable constant, distribution of \( q_e^* \) is normal for a given \( C_e^* \), population variances for \( q_e^* \) are equal, and population variances of \( q_e \) are a linear function of \( C_e \). In addition, the Freundlich model is assumed to correctly describe the data.
Figure 26. Residuals of TCB bisolute data minus single-solute model prediction for Wagner material.
Figure 27. Residuals of TCB bisolute data minus single-solute model prediction for Traverse City material.
Figure 28. Comparison of Freundlich equilibrium model confidence intervals for TCB sorption to Wagner material at a 1:10 solids ratio.

- - - 1:10, Lindane $C_0 = 0 \mu g/L$
- - - 1:10, Lindane $C_0 = 818 \mu g/L$
- - - 1:10, Lindane $C_0 = 2892 \mu g/L$
Figure 29. Comparison of Freundlich equilibrium model confidence intervals for TCB sorption to Wagner material for single solute model fit and high background lindane concentration bisolute model fits.
Figure 30. Comparison of Freundlich equilibrium model confidence intervals for TCB sorption to Traverse City material.

![Figure 30](image-url)
6.4.2.3 Lindane Comparisons

Though equilibrium studies focused on the TCB portion of the experiments, the question of competition in the system studied can be considered from a second point of view: is the lindane equilibrium distribution affected by the presence of TCB? The lindane equilibrium data were analyzed to identify such an effect.

A complicating factor in these systems is that lindane is known to undergo abiotic degradation (Cristol, 1947; Nakazima et al., 1949), as was discussed at length in the previous chapter. Because experiments were conducted in buffered aqueous solution initially at pH 8.4, the abiotic degradation of lindane was a significant concern. A profile of pH in the CMBR's through the equilibration time showed no change in the Wagner system, and a decrease to approximately 8.0 for the Traverse City systems, as shown in Figure 31. Describing the equilibrium solute distribution between the fluid and solid phases for lindane required first quantifying the loss from the system as a function of time.

The sorbed solid-phase concentration of lindane \( q_s \) cannot be calculated accurately using the simple mass balance approach previously defined for TCB. The mass of lindane in the system after \( t = 0 \) is diminished. At any time, \( C \) represents a fluid-phase concentration that has been reduced by degradation in addition to sorption. In order to construct a true equilibrium model from the experimentally measured data for lindane \( (C_e) \), the rate of degradation was quantified and used in the sorbed-phase concentration calculations.

Although the plot in Figure 31 shows a time dependency in the pH of the Traverse City system, a fixed pH was assumed for both systems to simplify calculations to a pseudo-first order relationship (a mean pH of 8.2 was assumed for Traverse City systems). The following degradation rate model was used

\[
\frac{dC}{dt} = -k_a C
\]

where \( k_a \) is a fluid-phase degradation rate. In addition, the following relation was assumed

\[
k_a = k_s = k_o
\]

where the true fluid and solid-phase lindane degradation rates are \( k_a \) and \( k_s \), and \( k_o \) is a fluid-phase degradation rate estimated from the independent experiments. Assuming the fluid and solid-phase degradation rates to be equal allows the experimentally observed degradation rate to describe the overall loss from the system, both phases inclusive. Under this condition, the mass balance of lindane in a CMBR at any time can be described as

\[
C + \frac{M_a}{V} q = C_o \exp(-k_o t).
\]
Figure 31. Solution phase pH as a function of time in Traverse City bottle reactors.
Although, there is no apparent equilibrium in a CMBR containing a degrading solute, the solid-phase concentration of lindane at the chosen equilibration time is denoted $q_e$ for consistency and is given as

$$q_e = \left[ C_0 \exp(-k_v t) - C_e \right] \frac{V}{M_s}. \quad (71)$$

All lindane sorbed phase concentrations were calculated in this manner for the analyses that follow. The observed pseudo-first order fluid-phase degradation rates ($k_o$) were $1.28 \times 10^{-4}$ and $8.40 \times 10^{-4} \text{ hr}^{-1}$ for the Wagner and Traverse City systems, respectively, reflecting the fact that the lindane degradation rate depends upon the system pH.

The initial concentration of lindane was held constant in the bisolute equilibrium studies. If the bottle reactors had contained only lindane, a relatively constant $q_e$ would be expected among the bottles. A plot of lindane solid-phase concentration as a function of TCB solid-phase concentration indicates the effect of increased loading of TCB on lindane sorption. Figures 32 and 33 show such plots for the Wagner and Traverse City materials. Working in log space, linear regression was performed for each bisolute data set and showed no significant trend in lindane sorbed concentration at the 5% level. Table 10 shows slopes and the 95% confidence intervals, all of which include zero.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$n_p$</th>
<th>Slope log (g/g)</th>
<th>Lower 95% Interval</th>
<th>Upper 95% Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso89-05b</td>
<td>15</td>
<td>-1.6 x 10^{-2}</td>
<td>-2.02 x 10^{-1}</td>
<td>1.70 x 10^{-1}</td>
</tr>
<tr>
<td>iso89-05c</td>
<td>17</td>
<td>-4.9 x 10^{-3}</td>
<td>-3.10 x 10^{-2}</td>
<td>2.20 x 10^{-2}</td>
</tr>
<tr>
<td>iso89-05e</td>
<td>14</td>
<td>-1.4 x 10^{-3}</td>
<td>-7.60 x 10^{-2}</td>
<td>7.30 x 10^{-2}</td>
</tr>
<tr>
<td>iso89-06b</td>
<td>17</td>
<td>6.8 x 10^{-3}</td>
<td>-3.20 x 10^{-2}</td>
<td>4.50 x 10^{-2}</td>
</tr>
<tr>
<td>iso89-06c</td>
<td>13</td>
<td>8.3 x 10^{-3}</td>
<td>-5.60 x 10^{-2}</td>
<td>7.30 x 10^{-2}</td>
</tr>
</tbody>
</table>

As another basis of comparison, single-solute equilibrium models may be compared to bisolute experimental data. Figure 34 shows such a comparison for lindane sorption to the Wagner and Traverse City solid materials. The single-solute model fits were based upon complete single-solute equilibrium experiments—the results of which were regressed in log-log space.

For both subsurface materials, single and bisolute data sets overlap, and the Freundlich parameters in Table 11 are not significantly different. The equilibrium relationship constructed from the Traverse City bisolute study appears slightly higher than the single-solute study, however, confidence intervals for isotherm parameters suggest no difference.
Figure 32. Sorbed lindane concentration as a function of sorbed TCB concentration for the Wagner material.

Solids ratio, $C_0$:
- $1:30$, Lindane $C_0 = 2856 \mu g/L$
- $1:10$, Lindane $C_0 = 818 \mu g/L$
- $1:10$, Lindane $C_0 = 2892 \mu g/L$
Figure 33. Sorbed lindane concentration as a function of sorbed TCB concentration for the Traverse City material.

- Lindane $C_o = 485 \, \mu g/L$
- Lindane $C_o = 1663 \, \mu g/L$
Figure 34. Comparison of single-solute Freundlich equilibrium model with bisolute experimental data for lindane sorption.
Table 11. Freundlich Equilibrium Model Parameter Summary for Lindane Sorption

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Model Estimates</th>
<th>Confidence Intervals</th>
<th>Mean Square Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$ (µg/g)(ℓ/µg)$^{n_f}$</td>
<td>$K_f$ (µg/g)(ℓ/µg)$^{n_f}$</td>
<td></td>
</tr>
<tr>
<td>iso89-05b,c,e</td>
<td>1.00 x 10^{-1}</td>
<td>0.747</td>
<td>[6.81,14.8] x 10^{-2}</td>
</tr>
<tr>
<td>iso89-03</td>
<td>8.40 x 10^{-2}</td>
<td>0.759</td>
<td>[7.25,9.64] x 10^{-2}</td>
</tr>
<tr>
<td>iso89-06b,c</td>
<td>5.12 x 10^{-4}</td>
<td>1.05</td>
<td>[2.76,9.51] x 10^{-4}</td>
</tr>
<tr>
<td>iso89-04</td>
<td>7.11 x 10^{-4}</td>
<td>0.929</td>
<td>[6.06,8.33] x 10^{-4}</td>
</tr>
</tbody>
</table>

6.5 Bisolute Rate Studies

Results of bisolute sorption rate studies are plotted with single-solute results to allow comparison. The studies plotted together are essentially replicate studies with very similar initial concentrations. Figures 35 through 38 show results for the Wagner material with TCB first, followed by lindane. Figures 39 through 42 show the Traverse City material results in the same order. The overlap of the single and bisolute data is striking for both solutes. Within the variance in the data, the shapes of the bisolute rate curves appear nearly identical to the analogous single-solute curves for both subsurface materials.

To investigate consistency between experiment types, points from the rate studies were projected onto the experimentally determined equilibrium relationships. The two sets of experiments should coincide to indicate no serious inconsistencies in the experimental planning and set-up. To determine the concentration from the rate curve at the equilibrium experiment time, the slope of the plateau region was determined (approximately 1000 hours through the final t). $C$ was calculated at 2016 and 1440 hours for the appropriate rate studies, and the corresponding $q_e$ was calculated.

Figure 43 shows points from the TCB single and bisolute rate studies projected onto a single-solute equilibrium plot for both subsurface materials (the confidence intervals for the equilibrium models are used for comparative purposes). Figure 44 shows the analogous result for lindane, corrected for degradation. For the TCB systems falling in the isotherm concentration range, some of the rate studies show an equilibrium condition that falls just below the isotherm, suggesting slightly less sorption has occurred. The lindane systems, in contrast, fall just above the isotherms. The cause of the deviations is difficult to identify, but may be due to any of several factors: measurement error (method inherent variation), inability to estimate the precise relative concentration at equilibrium time from the rate profile, inconsistent loss between rate and isotherm studies of solute from the systems, or inaccurate estimate of the equilibrium model parameters because of sensitivity to outliers.
Figure 35. Comparison of single and bisolute TCB sorption rate profiles for Wagner material and low initial TCB concentrations.
Figure 36. Comparison of single and bisolute TCB sorption rate profiles for Wagner material and high initial TCB concentrations.
Figure 37. Comparison of single and bisolute lindane sorption rate profiles for Wagner material and low initial lindane concentrations.
Figure 38. Comparison of single and bisolute lindane sorption rate profiles for Wagner material and high initial lindane concentrations.
Figure 39. Comparison of single and bisolute TCB sorption rate profiles for Traverse City material and low initial TCB concentrations.

<table>
<thead>
<tr>
<th></th>
<th>TCB $C_0$:</th>
<th>Lind. $C_0$:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Solute</td>
<td>441</td>
<td>0</td>
</tr>
<tr>
<td>Bisolute</td>
<td>453</td>
<td>655</td>
</tr>
</tbody>
</table>

Relative Fluid-Phase Concentration vs. Sorption Time (hours)
Figure 40. Comparison of single and bisolute TCB sorption rate profiles for Traverse City material and high initial TCB concentrations.
Figure 41. Comparison of single and bisolute lindane sorption rate profiles for Traverse City material and low initial lindane concentrations.
Figure 42. Comparison of single and bisolute lindane sorption rate profiles for Traverse City material and high initial lindane concentrations.

TCB $C_0$: Lind. $C_0$:

- O O O O Single Solute 0 3494
- ▲ ▲ ▲ ▲ Bisolute 2202 3079

Relative Fluid-Phase Concentration vs. Sorption Time (hours)
Figure 43. TCB bisolute equilibrium values observed in bottle-point rate studies compared to equilibrium model confidence intervals.
Figure 44. Lindane bisolute equilibrium values observed in bottle-point rate studies compared to equilibrium model confidence intervals.
6.6 Control Studies

6.6.1 TCB Control Studies

The mass balance of TCB in the bottle-point studies was investigated. Blank studies were conducted with reactors containing only a TCB buffer solution. Liquid-liquid extraction of the fluid phase over time gave the result shown in Figure 45. Considering that the low points may represent outliers, approximately 30% of the total mass was lost from the solution phase after 800 hours. Because no degradation was suspected or documented for TCB, sorption to the container walls was investigated. Hexane extraction of the container brought the mass recovery to greater than 90% of the total. Approximately 1% loss was attributed to volatilization when the bottles were opened for sampling (this agrees with calculations using the Henry’s Law constant of $2.31 \times 10^{-3}$ atm-m$^3$/mole). Thus a small amount of the TCB mass ($<10\%$) was not accounted for in the analysis. It is assumed the mass was lost by sorption to the Teflon cap liners (small quantity because of small surface area) or by volatilization through the seal of the capped bottles.

The glass and Teflon cap liners can be considered sorbents that equilibrate with the fluid phase solute concentration. When the bottles contain solids, sorption onto the solid phase reduces the fluid-phase TCB concentration with which the container walls equilibrate. At long equilibration times, the mass of TCB sorbed to the glassware is a small fraction of the mass of TCB on the solid phase. Therefore, the sorption to the container was not included in solid-phase concentration calculations.

6.6.2 Lindane Control Studies

The mass balance of lindane was investigated to ensure that no loss from the system (aside from degradation) was occurring. Blank studies were conducted with CMBR’s containing no solid material and a lindane solution buffered to pH 6.5 to prevent abiotic degradation. Liquid-liquid extraction of the solution phase over 12 weeks showed between 98 and 100% recovery at all times with no increased loss over time. Thus no significant loss to glassware or by volatilization was evident.

Mass balance in the experimental systems was checked periodically by solid-phase extractions, and no significant loss occurred. Extraction of bottles from rate studies even at long equilibration times (when lindane was most degraded) gave total lindane masses that agreed well with those predicted by the degradation rates ($<5\%$ difference between actual and predicted total masses remaining, extraction efficiency considered).

Solid-phase extraction recovery was quantified by a study in which bottles contained solid material and a lindane solution buffered to a pH of 6.5 initially to reduce abiotic degradation. Over a period of 12 weeks, total recovery of mass from the Wagner system after the previously described triple solvent-extraction procedure was between 94 and 101% at
Figure 45. TCB concentration in blank control as a function of time.
all times. No significant decrease in recovery was observed over time. Single round solid-phase extraction was found to be greater than 95% efficient. These studies confirm that quantification of sorbed-phase lindane concentration by mass balance using the determined degradation rates was a reasonable method.

6.6.3 Lindane Degradation

Studies were conducted to quantify the rate of abiotic degradation of lindane in the experimental systems. The alkaline dechlorination mechanism was discussed in the previous chapter and is well-characterized in the literature (Cristol, 1947; Nakazima et al., 1949). An increasing byproduct peak was observed over time in the GC analysis of liquid-phase samples for the experimental CMBR's. Degradation rates were quantified for the two subsurface material systems separately because the pH differed for the two systems and the rate of degradation was known to be pH dependent.

The rate of disappearance of lindane was represented as

\[ \frac{dC}{dt} = -k_2 C + C = -k_o C \]  

(72)

where \( k_2 \) is the degradation rate constant, and \( k_o \) represents a pseudo first-order rate constant, valid at a fixed pH. If the pH of the experimental system was assumed to be constant throughout equilibration time, then integrating and rearranging give the rate model in the following form

\[ C = C_o \exp(-k_o t). \]  

(73)

An experimentally observed concentration profile of \( C \) as a function of time can be fit with the rate model in this form, and the degradation rate estimated for a fixed pH by a nonlinear least squares method. The Traverse City systems actually showed a time dependent pH change presented previously in Figure 31; the simplifying assumption of a mean pH of 8.2 was used because the degradation rate was quantified in a solution of natural organic matter obtained from the Traverse City material at half the equilibration time, which exhibited this pH.

Blank bottle studies accompanied sorption rate studies, in which blanks contained the identical lindane buffer solution (described in methods chapter) at pH 8.4 and no solids. The concentration of lindane was measured over time by fluid-phase sampling and GC analysis.
Because the bottles used for the rate and equilibrium sorption studies contained aquifer materials that leached natural organic matter (NOM) into solution, degradation rates were also studied in NOM solutions. The NOM solutions were prepared by tumbling each subsurface material with unspiked buffer solution for half the experimental equilibration times at the proper solids ratios (Wagner: 42 days, 1:10 and Traverse: 30 days, 2:1). The slurries were centrifuged and the supernatant collected. The resulting two solutions were considered models of the fluid-phase conditions in the true experimental bottles. The pH was considered representative of the mean pH of the full term experiments; pH values were 8.4 for Wagner humic solution and 8.2 for Traverse City material.

The two NOM solutions were spiked with lindane, placed in reactors, and tumbled. Fluid-phase lindane concentration was measured over time, sacrificing a CMBR for each measurement. The lindane concentration profiles in the blank, Wagner NOM, and Traverse City NOM solutions are shown in Figure 46.

The pseudo first-order rate model was fit to the concentration profiles for the blank and the two NOM solution systems. The lindane degradation rate at fixed pH ($k_o$) was estimated; the values are listed in Table 12. Good fits allowed high confidence in the estimated rates. It is notable that rates found in the blank and Wagner NOM solutions were nearly identical, indicating no confounding effect on degradation rates by the leached organic material in the solution. The degradation rate found in the Traverse City NOM solution is also nearly equal to the blank solution when the pH of Traverse City solution is taken into consideration using

$$\frac{k_{o,1}}{k_{o,2}} = \frac{C_{h,1}}{C_{h,2}}$$

(74)

The ratios of $k_o$ and $C_h$ for the blank and Traverse City NOM solutions are 1.5 and 1.6, indicating nearly equivalent degradation rates with no effect due to additional organic material in solution.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$n_p$</th>
<th>pH</th>
<th>$k_o$ (1/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>56</td>
<td>8.4</td>
<td>$1.23 \times 10^{-4}$</td>
</tr>
<tr>
<td>Wagner-NOM</td>
<td>8</td>
<td>8.4</td>
<td>$1.28 \times 10^{-4}$</td>
</tr>
<tr>
<td>Traverse City-NOM</td>
<td>8</td>
<td>8.2</td>
<td>$8.40 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Figure 46. Lindane degradation rates in NOM solutions.
The lindane degradation values determined in the NOM solution studies and listed in Table 12 were used throughout the experimental data analysis. As described previously, this degradation rate compared favorably with mass balances performed on experimental bottle reactors (using solid-phase extraction).

1,2,4-TCB is a by-product of lindane degradation (Cristol, 1947), and the possibility of significant formation of TCB was considered. Mass spectral identification of the by-products of a lindane sample 1750 hours old identified TCB and \( \gamma \)-pentachlorocyclohexane (\( \gamma \)-PCCH) by-products. Estimation from the GC chromatograph of relative mass quantities shows that greater than 16% of the 19% conversion to by-product was \( \gamma \)-PCCH, and approximately 1% was TCB. Thus TCB by-product was considered negligible.

6.7 Column Studies

Single and bisolute column studies conducted for the TCB-lindane pair were also performed using methods described in the methods chapter. The results from this study are summarized on Figure 47. The breakthrough curve of the more strongly sorbed compound, TCB, appeared unaffected by the presence of lindane. The less strongly sorbed lindane, however, showed earlier breakthrough of concentration through the bisolute column, indicating suppressed sorption capacity in the presence of TCB relative to the single-solute case. Breakthrough of low relative lindane concentrations (e.g., \( C/C_0 = 0.1 \)) occurred in approximately half as many bed volumes for the bisolute condition than the single-solute condition.

This indication of a competitive sorption is in contrast to the batch experimental data which showed little or no competition. Based upon this result, it is suggested that flow-through systems may be more sensitive experiments for studying competitive sorptive effects than bottle-point systems. The results also suggest that competitive sorption may have a significant impact on the first arrival time of contaminants during transport of hydrophobic organic compounds in the subsurface.

6.8 Discussion

6.8.1 Competitive Sorption Equilibria

The motivation for investigating competitive sorption stems from the fact that competition may lead to inaccurate estimation of equilibrium sorption behavior in multicomponent subsurface systems. This has specific implications for aquifer remediation efforts in typical conditions of aquifer contamination. This portion of the study focused on a particular system of contaminants and subsurface materials. The results must be viewed in that light. In addition, these results must be considered for implications to more general applications and for their relation to previous findings in the literature.
Figure 47. Comparison of single and bisolute concentration breakthrough profiles for the Wagner material.
Bisolute model simulations predict a reduction in sorbed-phase concentrations compared to the single-solute equilibrium distributions due to competition for sorption sites (Murali and Aylmore, 1983a, 1983b). Both $K_f$ and $n_f$ were affected by competition: $K_f$ decreased while $n_f$ increased. The higher the concentration of the second solute (held constant throughout the equilibrium experiment), the more depressed the isotherm relative to the single-solute case. The experimental results of McGinley and coworkers (1989) confirm this predicted result, for experiments performed with single-solute tetrachloroethylene (PCE) and bisolute PCE with a background concentration of p-dichlorobenzene (p-DCB).

Pignatello (1990) observed a similar result for binary competition between 1,2-dibromoethane (EDB) and two cosolutes on two soils. Diminished $K_f$ and increased $n_f$ values were reported: the higher the concentration of background solute, the greater the increase in $n_f$ value (e.g., $n_f$ increased from 0.88 to >0.97 as background sorbed concentration increased as little as one order of magnitude). The TCB experimental results were tested for a similar result. If competitive effects were operative and detectable, the bisolute isotherm is expected to be unique relative to the single-solute isotherm, with increased Freundlich $n_f$ and decreased $K_f$.

In this work, when the experimentally determined single-solute isotherms were fit to the corresponding bisolute data in log space, residuals were inspected for a trend (see Figures 26 and 27). The expected result for competitive sorption would appear as follows: (1) residual points (data minus model) would be negative because experimental bisolute $q_e$ would fall below the single-solute isotherm, and (2) residuals would show a negative trend due to increased $n_f$. Linear regression of residuals versus $C^*_e$ did not show the expected result. Residuals were scattered about zero rather than all negative. Slopes, however, were generally negative but did not differ from zero at the 5% significance level except for the Wagner system with a low background concentration of lindane. This was not sufficient evidence of a competitive effect.

The isotherm confidence interval plots illustrate the same result (see Figures 28 to 30). Overlap of the isotherms, single and bisolute, showed TCB equilibrium distribution appeared unaffected by the presence of lindane in the systems studied.

Given the absence of observable competitive sorption, all data were interpreted to represent a single equilibrium data set. Therefore, all data were pooled and fitted with the Freundlich model to provide an overall TCB equilibrium model for both subsurface materials (Figure 48). Table 7 lists the parameters found in these fits.

The potential for competitive sorption was considered from the point of view of lindane as well. Single-solute equilibrium models for TCB and lindane showed lindane to be the lesser sorbing compound of the two under the experimental conditions. For both the Wagner and Traverse City subsurface materials, Freundlich $K_f$ values for TCB were approximately two times the corresponding values for lindane. This parameter can be considered an indication of affinity between the sorbate and the solid, and bisolute models predict that sorption of the more weakly sorbing species is depleted in the presence of competition (Murali and
Figure 48. Pooled TCB equilibrium models using single and bisolute data.

Wagner
\[ K_f = 0.281 \]
\[ n = 0.787 \]

Traverse
\[ K_f = 0.002 \]
\[ n = 0.921 \]
Aylmore, 1983b). Therefore, if a competitive effect was operative in this system, it would be most evident in the lindane equilibrium data.

Equilibrium bisolute studies contained a constant background lindane concentration. If the reactors had contained only lindane, the expected result would be a relatively constant sorbed equilibrium concentration for all the bottles, with variance due only to bottle to bottle variation in \( C_0 \), solids concentration, and equilibrium concentration measurement. The expected result for competitive sorption is a decreasing lindane sorbed concentration with increasing TCB solid loading due to TCB's relative competitive advantage with increasing concentration. Figures 32 and 33 indicate no trend in lindane \( q^* \) was observed. The absence of a competitive effect was confirmed by the overlap of bisolute data and complete single-solute lindane equilibrium model fits.

The absence of an observable competitive effect requires evaluation, especially given that equilibrium models were nonlinear. This seems inconsistent with reports in the literature. In all cases of no competition for binary systems, linear single-solute isotherms were observed. In addition, McGinley and coworkers (1989) reported that competitive effects were manifest for all systems in which nonlinearity was observed. Linear equilibrium relationships are indicative of non-site-specific partitioning, while nonlinearity arises from either adsorption or non-ideal hydrophobic partitioning. Competition for sorption is likely for systems showing nonideal partitioning. Possible explanations for the absence of a competitive effect in these systems are as follows:

1. Sorptive strength of the cosorbate lindane was not sufficient to cause observable competition.

2. Scatter in the data masked a true competitive effect (i.e., method sensitivity was too low).

3. The two solutes do not sorb to the same sites, so competition was not important.

The ability of the cosolute to suppress the sorption of a particular compound has been found to depend upon the relative hydrophobicity of the compounds (McGinley et al., 1989), upon relative sorptive strength, and slightly upon compound structure or size (Pignatello, 1990). That is, an effect on the equilibrium distribution of a solute is expected when the sorption equilibrium relationships for single solute systems are nonlinear and when the background solute is a more strongly sorbing solute than the solute of varying concentration. It is notable that these were the only works to find competitive sorption for hydrophobic organic contaminants on natural solids other than PCB's, and neither complete work is published yet.

Since TCB is more strongly sorbing than lindane, little competition would be expected from lindane on the sorption of TCB. To further investigate this result, the bisolute sorption equilibrium for the experimental system was predicted using a model based on the Ideal Adsorbed Solution (IAS) theory, which was previously presented in the mathematical modeling chapter. Figure 49 shows the predicted effect of lindane on the TCB-Wagner equilibrium distribution at the concentrations used in this study. The data are plotted
for the high (squares) and low (circles) background lindane concentrations in the figure. Figure 50 shows the same for the Traverse City subsurface material. It is evident that the suppression of sorption predicted by the model is very small relative to the scatter in the data. Method sensitivity was not sufficient to detect such a small effect, if it truly existed. Additionally, it is significant to note that IAS will not predict much competitive effect if isotherms are nearly linear, as with the Traverse City material.

Figures 51 and 52 show the model prediction of the lindane sorbed concentration as a function of TCB solid-phase loading (analogous to Figures 32 and 33). The model predicts a decreasing trend that the data do not show, though sensitivity appears sufficient. The studies conducted by Pignatello gave considerable attention to a similar analysis in his systems. The $K_{oc}$ of the background solute was observed to decrease to a plateau as the principal solute concentration increased. This was attributed to either a small amount of sorption occurring on mineral or unidentified sites, or to the soil organic matter behaving as a nonideal hydrophobic partitioning medium containing internal sites that have a higher sorption potential than the bulk organic phase. The sites may be of molecular dimensions and restrictive of the number and size of sorbate molecules, fostering competition between solutes of similar size.

The system herein was considered in light of the second possibility. An estimate of molecular size of the compounds was found and compared to 12 binary solute pairs that exhibited competitive sorption. As a rough measure of molecular size, the molecular free surface areas ($S_m$, in squared angstroms, $A^2$) for TCB and lindane were calculated by the method of Gavezzotti (1985). This method considers the sum of atomic surface areas calculated from van der Waal’s radii minus the surface between the atoms that are unavailable due to bonding. The relative $S_m$ was calculated as $|\Delta S_m|$ and was compared to the reported relative $S_m$'s for the competing binary pairs. The $|\Delta S_m|$ value for TCB-lindane was approximately 60 $A^2$. Similar $|\Delta S_m|$ values in the binary pairs corresponded to 20% reductions in $K_{oc}$ for the background solute. The lindane equilibrium data did not agree with these results.

It is possible that the absence of a competitive effect indicates that any site sorption or selective partitioning occurs on different types of sites for the two solutes. These experiments do not provide mechanistic information to support or refute this idea.

6.8.2 Competitive Sorption Rates

A relatively small body of literature exists concerning the study of sorption rates. Further, the only reports of a competitive sorptive effect on rates concern desorption (Coates and Elzerman, 1986; Pignatello, 1990). In both reported cases, the multisolute system desorbed slower. The importance of such studies is evidenced by the work of van Genuchten and coworkers (1977) who reported that physical nonequilibrium was the most important cause of transport nonideality in their study systems. Competitive effects that decrease the rate of sorption and desorption can lead to early breakthrough and slower rates of desorption, compared to single-solute systems. Competitive sorption between a mixture of
Figure 49. IAS model prediction for expected TCB sorption competition for Wagner material studies.
Figure 50. IAS model prediction for expected TCB sorption competition for Traverse City material studies.
Figure 51. IAS model prediction for expected lindane sorption competition for Wagner City material studies.
Figure 52. IAS model prediction for expected lindane sorption competition for Traverse City material studies.
solute may complicate the estimate of transport parameters, and may affect groundwater contamination and cleanup.

Interpretation of the sorption rate results with regard to competitive sorption is straightforward. Experiments were designed to determine whether the presence of a second solute affected sorption characteristics. Three characteristics were endpoints of focus: the rate of sorption, the concentration at apparent equilibrium, and the time required to reach equilibrium. Figures 35 through 42 show overlapping single and bisolute concentration profiles over time. Qualitatively, it is evident from the plots that for each solute-sorbent combination, the shape of the rate curve was unchanged by the presence of the second solute. The coincident approach to $C_e$ suggests also that the ultimate equilibrium distribution was unaffected.

Quantitatively, the rate of sorption and $C_e$ can be determined by describing the rate data with an appropriate model. For the observed results, it was not deemed fruitful to model both single and bisolute results due to the absence of an observable competitive effect. Sorption rates were determined for single-solute studies, therefore, with the purpose of gaining mechanistic information and elucidating the meaning of these results in the context of the sorption rate literature. Results of modeling efforts are presented later in this section.

The third sorption characteristic of focus in the experiments was time required for equilibration of the system ($t_{eq}$). Accurate determination of $t_{eq}$ is complicated by potential losses of a chemical from a system by volatilization, sorption to glassware, or transformation (as with lindane) in long-term batch experiments. Quantitation is also complicated because the magnitude of the change observed at long times becomes smaller than the sensitivity of replicate measurements. For these reasons, incomplete and conflicting information has led to confusion in the sorption literature concerning the rate of attainment of sorption equilibrium (Karickhoff, 1984).

The small negative slope in the tail of the rate curves for the non-degrading solute TCB even at 84 days for each sediment suggests continued sorption. Although extrapolation beyond the time frame of the data set leads to uncertainty, it is reasonable to conclude that the bisolute and single-solute systems sorbing at the same rate exhibit the same $t_{eq}$. Quantifying $t_{eq}$ is not necessary for that purpose. However, the slope in the TCB long term rate data suggests that equilibrium experiments taken at 84 and 60 days are not correct descriptions of the ultimate equilibrium condition. Rather, they represent a snapshot in time of a changing distribution. Estimating $t_{eq}$ is valuable to an understanding of the degree of nonequilibrium of the isotherm studies and bias of the experimentally determined equilibrium model parameters. The $t_{eq}$ can be estimated from sorption rate coefficients determined by fitting the data with an appropriate model.

A physical diffusion controlled rate model was used to describe the data. The nature of the solutes, the shape of the rate curves, and corroborative evidence from the literature suggest that sorption in this system may be diffusion controlled (Miller and Weber, 1986, 1988; Weber and Miller, 1988; Brusseau and Rao, 1989a, 1989b). The two resistance model used includes diffusion through an external film, and subsequent surface diffusion as
the intra-particle mass transfer mechanism. Film diffusion was assumed to be very rapid due to sufficient agitation of the bottles. This allowed single parameter estimation of the intraparticle diffusion coefficient \( D_s \). The Freundlich equilibrium model and experimentally determined parameters were used to define the equilibrium distribution between solute and sorbent.

Single-solute TCB and lindane rate studies (low initial concentrations only) were fit with the model. Degradation rates were taken into account for the lindane model, and no system loss was assumed for the TCB. The resulting sorption rate coefficients, \( D_s \), are listed in Table 13 with mean squared errors. Figures 53 to 56 show the model fits to the experimental data as a solid line. The rate model and data disagreement, especially for each solute with the Traverse City material, is significant. It reflects the result shown in Figures 39 and 40, where projected rate study points did not coincide with the equilibrium experiments. Because the experimental Freundlich equilibrium model was assumed, the \( D_s \) estimate is influenced by the equilibrium model and the model prediction is biased in that direction (e.g., TCB-Traverse City rate projection falls below the isotherm, and the model predicts a fast \( D_s \) resulting in too much sorption).

Table 13. Intraparticle Diffusion Model Parameter Summary

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Estimate Basis</th>
<th>( K_f ) (( \mu g/g ))/(( \ell/\mu g ))^n_f</th>
<th>( D_s ) (cm^2/hr)</th>
<th>Mean Square Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>kin89-06</td>
<td>Equilibrium</td>
<td>8.40 \times 10^{-2}</td>
<td>7.89 \times 10^{-8}</td>
<td>8.08 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>Rate Model</td>
<td>1.27 \times 10^{-1}</td>
<td>2.53 \times 10^{-8}</td>
<td>1.53 \times 10^{-3}</td>
</tr>
<tr>
<td>kin89-10</td>
<td>Equilibrium</td>
<td>2.21 \times 10^{-1}</td>
<td>4.43 \times 10^{-8}</td>
<td>1.41 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>Rate Model</td>
<td>1.92 \times 10^{-1}</td>
<td>6.03 \times 10^{-8}</td>
<td>1.25 \times 10^{-3}</td>
</tr>
<tr>
<td>kin89-16</td>
<td>Equilibrium</td>
<td>2.23 \times 10^{-3}</td>
<td>6.99 \times 10^{-8}</td>
<td>6.07 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>Rate Model</td>
<td>1.72 \times 10^{-3}</td>
<td>1.70 \times 10^{-7}</td>
<td>2.99 \times 10^{-3}</td>
</tr>
<tr>
<td>kin89-23</td>
<td>Equilibrium</td>
<td>7.11 \times 10^{-4}</td>
<td>3.70 \times 10^{-7}</td>
<td>2.36 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>Rate Model</td>
<td>1.28 \times 10^{-3}</td>
<td>4.73 \times 10^{-8}</td>
<td>3.99 \times 10^{-3}</td>
</tr>
</tbody>
</table>

This suggests that a different \( K_f \) would better describe the rate study results. The rate experiments, single and bisolute, indicate a \( K_f \) slightly different from the equilibrium studies for the Traverse City material. Of the two experiment types, the equilibrium results were most sensitive to scatter; outliers were more difficult to identify and may have had an effect on the apparent \( K_f \). For these reasons the sorption rate coefficients were re-estimated assuming the same degree of nonlinearity (same Freundlich \( n_f \)) and a single point \( K_f \) estimated from the rate curves at long incubation time. The \( C_e \) at 2000 hours was estimated graphically from the rate curves, and \( q_e \) was calculated by the appropriate mass balance for each solute. This new \( K_f \) may approximate true equilibrium better. Re-estimation of the \( K_f \) and \( D_s \) yielded the values listed in Table 13. The fits are shown as a dashed line in Figures 53 to 56. Though the mean squared errors generally appear better, the fits are not significantly improved. The very fast initial sorption is not described well.
Figure 53. Single-solute TCB-Wagner experimental results with best fit diffusion rate models.

Wagner, TCB $C_0 = 1020 \ \mu g/L$

- $K_r = 0.221 \ (\mu g/g)(L/\mu g)^n$
- $K_r = 0.192 \ (\mu g/g)(L/\mu g)^n$
Figure 54. Single-solute lindane-Wagner experimental results with best fit diffusion rate models.

- ○○○○○ Wagner, Lindane $C_0 = 1947$ $\mu g/L$
- $K_r = 0.084 (\mu g/g)(L/\mu g)^n$
- $K_r = 0.127 (\mu g/g)(L/\mu g)^n$
Figure 55. Single-solute TCB-Traverse City experimental results with best fit diffusion rate models.

Traverse, TCB \( C_0 = 441 \mu g/L \)

- \( K_r = 2.23 \times 10^{-3} \left( \mu g/g \right) \left( L/\mu g \right)^n \)
- \( K_r = 1.72 \times 10^{-3} \left( \mu g/g \right) \left( L/\mu g \right)^n \)
Figure 56. Single-solute lindane-Traverse City experimental results with best fit diffusion rate models.

Traverse, Lindane $C_0 = 765$ µg/L

$K_f = 7.11 \times 10^{-4}$ (µg/g)(L/µg)$^n$

$K_f = 1.28 \times 10^{-3}$ (µg/g)(L/µg)$^n$
by the model. Adding to the model an expression for nearly instantaneous sorption would better describe the data.

Some general inferences can be made, however, from this modeling effort. The apparent diffusivity is inversely related to the strength of solute sorption. The diffusion rate of TCB was significantly slower than that of lindane on the same solid. This is in agreement with the inverse relationship between sorption rate and partitioning coefficient ($K_p$) found by Brusseau and Rao (1989b) for 61 hydrophobic chemicals. Intraorganic matter diffusion was concluded as the probable cause by the authors. The results herein do not provide a means to differentiate between intraorganic matter diffusion, retarded pore diffusion, or surface diffusion as the rate controlling mechanism. In addition, pore spaces may be at least partially filled with organic matter, such that distinctions between pore diffusion and intraorganic matter diffusion are difficult to separate physically or conceptually.

The time required for equilibration may be roughly estimated from the fitted models for the non-degrading solute. The Traverse City system has reached equilibrium at 42 days with a $C_e/C_o = 0.3$, while the Wagner system requires approximately 85 days to reach a $C_e/C_o = 0.1$. Although these values are rough estimates, the significance of the numbers is this: the estimated diffusion rates cause significantly long equilibration times in the context of the sorption rate literature. Sorption rates should not be ignored if accurate predictive transport modeling is desired.
7 Significance of Results

7.1 Overview

The results of the experimental work presented in the previous chapters showed several significant phenomena:

1. sorption equilibrium relationships were clearly and consistently nonlinear;
2. sorption rates were slow compared to the time scales normally allowed to approach equilibrium in the experimental work published to date;
3. sorption rate effects explain the majority of the often-observed apparent desorption hysteresis; and
4. competitive sorption effects were observed to be of minor importance in batch studies, but significant competition was observed in column experiments using the same materials.

These effects led to long solute concentration profiles for the organic solute sorption-desorption experiments performed in this work; similar results have been observed by other investigators. The tail on a desorption elution profile can be extremely important, since mandated aquifer cleanup levels often correspond to drinking water quality standard levels. Drinking water quality standards may be several orders of magnitude less than the maximum solubility of a contaminant in water. This suggests that the existence of long solute tails, even if of a relatively low concentration, can play an important role in determining the cost of aquifer restoration.

From a practical perspective, it is important to interpret the significance of small-scale laboratory findings with respect to expected behavior at the field scale. Such analysis is important for determining the relative importance of various nonideal effects as a function of scale and other system variables—such as solute source condition. The results of this research may be examined with respect to several considerations at the field scale:

1. the effect of nonlinear sorption equilibrium on solute distributions;
2. the effect of sorption rates on solute distributions;
3. the effect of multiple components on solute distributions; and
4. the relative importance of nonideal solute sorption behavior (i.e., nonlinear equilibrium, noninstantaneous rates, and solute competition) compared to subsurface heterogeneity.

The sections that follow examine these considerations.
7.2 Nonlinear Equilibrium Effects

The degree of nonlinearity observed in this work is described by the range of values for the Freundlich exponent—0.70 ≤ nf ≤ 1.00. The effect of such nonlinearity is to steepen the sorption portion of a solute concentration profile and smear the desorption portion of a solute concentration profile. This suggests concentration profiles arriving close to one throughput unit (dimensionless time accounting for sorption and advective travel rate), and desorption tails that have long tails of a relatively low concentration. This predicted desorption behavior agrees with field scale observations that show that pump-and-treat methods lead to a rapid decline in solute concentration followed by a long sustained tail (Travis and Doty, 1990).

Previous analysis (Miller et al., 1989) showed that log dimensionless concentration as a function of log dimensionless time (throughput) was a linear relationship, the slope of which was directly related to nf. An important finding from this work related to this observation is that the lower bound on nf appears to be much higher than previously presumed. This results directly from the evidence presented to show that the majority of the observed desorption hysteresis is an artifactual consequence of improper account of prolonged sorption and desorption rate effects. A rough quantitative account of the importance of this factor can be observed from previous simulations performed by Miller et al. (1989). For nf ≤ 0.8 a decrease in nf of 0.2 corresponds to about an order of magnitude increase in throughput to reach a $C/C_0 = 10^{-6}$ during elution. This suggests that raising the lower bound estimate on nf from 0.3 (corresponding to desorption hysteresis) to 0.7 would decrease the estimated required cleanup time to reach the example action level by two orders of magnitude. The predicted time required would be on the order of 35 throughput units (i.e., $\bar{t} = 35$), although the actual time is weakly dependent upon other system parameters such as $K_f$, and $D_x$. This estimated time far exceeds the estimate for linear sorption, $n_f = 1$, to reach the same level, which is on the order of $\bar{t} = 2$. In summary of this point, nonlinear sorption is a significant factor affecting cleanup times for low action levels, but the significance of nonlinear equilibrium is decreased substantially if hysteresis is not operative.

7.3 Rate Effects

The results presented previously for lindane sorption to the Wagner material can be evaluated to determine the effect of sorption and desorption rates on solute concentration distribution profiles and cleanup times. It is well known that a complete dimensionless analysis of such systems is not possible, since some model parameter specific dependency remains (Bahr and Rubin, 1987; Jennings, 1987; Miller et al., 1989). However, as a first-cut analysis, neglecting degradation, the time required to approach equilibrium in the experimental systems investigated here is on the order of 0.7 yr. In approximate terms, deviations from instantaneous assumptions can be observed if the travel time of interest is less than 10 times the time required to approach sorption equilibrium in a batch system.
For travel times of the same order of magnitude or less than the equilibrium time, these differences become quite significant (Miller et al., 1989). Based upon this reasoning, significant deviations from local equilibrium behavior should routinely be expected in field situations. For aquifer restoration purposes, these effects will tend to be less important than nonlinear equilibrium effects, especially when low solute concentration action levels are required.

7.4 Multicomponent Effects

Since little evidence for either competitive effects on sorption rates or equilibrium were found in batch work performed in this study, multicomponent effects at the field scale would be presumed to be small. Two considerations temper this conclusion.

First, a factor of two difference was observed in the arrival of the $C/C_0 = 0.1$ point for lindane in a bisolute system, which appeared to be the result of competitive equilibrium effects—judging by the similar shape of the solute concentration profiles. Such a result would be expected to translate to the field scale.

Second, typical field-scale contamination often consists of many compounds often at high concentrations—especially close to a contaminant source. As the number of solutes increase so too would the expected effect of solute competition on decreasing the time required for a first arrival at a given point. Significant deviation from single-solute behavior could exist in such cases. Further experimental work is needed to establish the importance of this consideration.
References


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