

AFIT/GEE/ENC/95D-04

**MACROSCALE DIFFUSION-LIMITED
SORPTION MODELING--A PRELIMINARY
MODELING EXERCISE
FOR A DOVER AFB SITE**

THESIS

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PRELIMINARY MODELING EXERCISE FOR A DOVER AFB SITE**

THESIS

**Presented to the Faculty of the Graduate School of Engineering
of the Air Force Institute of Technology
In Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Engineering and Environmental Management**

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Acknowledgments

I thank God and praise Him for seeing me through this difficult but rewarding experience. I hope that other researchers will gain insight from the perspective I present in this thesis. I believe that multi-disciplinary efforts such as this one hold the key to further understanding the complex processes that go on beneath our feet.

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Table of Contents

ACKNOWLEDGMENTS.....I

LIST OF FIGURES.....IV

LIST OF TABLES.....V

ABSTRACT.....VI

SECTION 1 - INTRODUCTION.....1

SECTION 2 - BACKGROUND.....4

2.1 NON-EQUILIBRIUM SORPTION.....4

2.2 THE SPLIT-OPERATOR APPROACH.....5

SECTION 3 - THE DOVER AFB SITE.....6

3.1 MATHEMATICAL MODEL.....6

3.2 SITE DESCRIPTION.....9

3.3 DEFINING THE MODEL IN SUTRA.....10

3.4 VALIDATION.....10

SECTION 4 - SIMULATIONS.....14

4.1 SHORT-TERM COMPARISON OF CI AND SO CODES.....16

4.1 SHORT-TERM REBOUND FROM DIFFERENT PUMP-DOWN TIMES..20

4.2 LONG-TERM REBOUND FROM DIFFERENT PUMP-DOWN TIMES...21

4.3 SHORT-TERM PULSED PUMPING SIMULATIONS.....22

4.4 LONG-TERM PULSED PUMPING.....25

SECTION 5 - CONCLUSIONS.....31

BIBLIOGRAPHY.....33

VITA.....36

List Of Figures

FIGURE 1	SCHEMATIC OF BOREHOLE, DRIVEPOINT.....11 AND MULTI-LEVEL PIEZOMETR LOCATIONS AT THE DOVER AFB FIELD SITE
FIGURE 2	VERTICAL CROSS SECTION OF CONCEPTUAL.....12 CELL WITH INITIAL CONDITION CONCENTRATION PROFILE REPRESENTED
FIGURE 3	COMPARISON OF 39 DAYS PUMPING OF CI.....17 AND SO CODES OBSERVED AT CENTRAL MONITORING POINT
FIGURE 4	COMPARISON OF REBOUND FOR THE CI AND.....18 SO CODES FOR DAYS 40 THROUGH 180 OBSERVED AT THE CENTRAL MONITORING POINT
FIGURE 5	REBOUND COMPARISON OF THREE PUMP-ON.....21 TIMES FROM 26 TO 180 DAYS OBSERVED AT CENTRAL MONITORING POINT
FIGURE 6	COMPARISON OF LONG-TERM REBOUND FOR.....22 DIFFERENT PUMP-ON TIMES OBSERVED AT CENTRAL MONITORING POINT
FIGURE 7	PULSED PUMPING: COMPARISON OF TWO.....23 REBOUND TIMES FOLLOWING 28.8 DAYS OF PUMPING OBSERVED AT CENTRAL MONITORING POINT
FIGURE 8	LONG-TERM COMPARISON OF PULSED AND.....28 CONTINUOUS PUMPING OBSERVED AT CENTRAL MONITORING POINT

List of Tables

TABLE 1	BASIC SIMULATION PARAMETERS.....	13
TABLE 2	SHORT-TERM PULSED PUMPING SIMULATION..... RESULTS	25
TABLE 3	LONG-TERM SIMULATION DATA FOR PULSED..... AND CONTINUOUS CASES	28

Abstract

A modification was made to the USGS SUTRA code which allowed the simulation of macroscale diffusion effects from specific layers. This modification utilized a split-operator finite element numerical technique to incorporate the macroscale diffusion. The code was applied to a conceptual site developed from a field site at Dover AFB, DL. Simulations were done to compare the modified code to the unmodified code which clearly showed the modified code as a closer representation of reality. Simulations were also done to study the effects of pulsed and continuous pumping within the time frame of a field experiment at Dover. These simulations indicated that the diffusion time scale was too long to be studied within the 180 days of the field study. Further investigation over a longer period of time provided the opportunity to study rebound effects due to macroscale diffusion. These simulations confirm the effectiveness of the macroscale model in representing actual physical processes.

Macroscale Diffusion-Limited Sorption Modeling-A Preliminary Modeling Exercise

For a Dover AFB Site

1. Introduction

Pump and treat (PAT) is used for remediation of approximately 2/3 of the existing 1200 Superfund sites. This number grows considerably larger when other non-Superfund sites are included [Travis and Doty, 1990]. At several superfund sites and specifically at Air Force Installation Restoration Process (IRP) sites, a great deal of time and money have been expended in an attempt to fully characterize the site and develop a timeline for remediation [Goltz, 1991]. In several of these cases, PAT performance has not been consistent with the timeline developed in preliminary modeling. Some examples of predictions differing from observed results include: cases in which health-based cleanup standards have never been met, cases in which it has taken longer than predicted to meet standards, and cases in which standards have been initially met and then violated in the future [Mackay and Cherry, 1989; Haley and others, 1991; Olsen and Kavanaugh, 1993]. This last phenomenon is commonly called "rebound".

There are several factors which may contribute to the discrepancy between predicted and observed cleanup times. The level of success achieved by PAT systems depends on the location of the contaminant in the porous media. If the contaminant is located in a region where it may be readily mobilized by advective flow, PAT is effective. If, however, a significant amount of the contaminant is located in zones that are not affected by advective flow, PAT cleanup times will be considerably longer than predicted [Rabideau and Miller, 1994]. These non-affected zones may be macroscopic in nature

such as zones where aqueous phase contaminant is in low hydraulic conductivity aquifer material, or microscopic in nature such as zones where mass transfer from sorption sites to the mobile aqueous phase is rate-limited [Keely, 1989; Mackay and Cherry, 1989; Haley et al., 1991; Wilson, 1992; Rabideau and Miller, 1994]. Pulsed pumping has been suggested by several authors to reduce the negative remediation effects stemming from these conditions [Keely et al., 1987; Keely, 1989; Adams and Virmontes, 1993; Caspers, 1994; Rabideau and Miller, 1994].

The rising cost of performing aquifer remediation, coupled with the current political climate demanding near-term results make it critically important that decisions made regarding groundwater cleanup be based upon the best available information [Adams and Virmontes, 1993; Caspers, 1994]. A primary source of information for remediation site managers is data from contaminant transport models [Goltz, 1991]. Several current groundwater contaminant transport models are based on the assumption of instantaneous sorption and desorption between the liquid and the solid phases. This assumption is commonly called the local equilibrium assumption (LEA). Its validity and applicability have been documented in the literature [Valocchi, 1985; Yu, 1985; Goltz and Roberts, 1986c; Valocchi, 1986, Mackay and other, 1986; Bahr and Rubin, 1987; Szecsody, 1988; Brusseau and Rao, 1989d; Brogan, 1991; Goltz, 1991b; Weber and others, 1991; Brusseau, 1992]. Considerable work has been done recently to develop models which accurately describe rate-limited sorption effects [Huso, 1989; Brogan, 1991; Adams and Virmontes, 1993; Caspers, 1994; Rabideau and Miller, 1994]. Most of these models utilize a two-zone description of a porous medium. They implement non-equilibrium

sorption in various ways, but all have considered non-equilibrium effects occurring throughout the porous medium on the microscopic scale. In the modeling effort described here, non-equilibrium sorption effects from only specific zones in the porous medium were investigated. In this study, the widely used USGS SUTRA code [Voss, 1984] was coupled with a two dimensional diffusion code to model non-equilibrium effects from specific layers only. This allowed the study of non-equilibrium sorption from a macroscopic view of specific zones. The use of specific layers or zones to model non-equilibrium sorption may more closely match model outputs to field data at specific sites.

A conceptual site model, developed from an existing site at Dover AFB, Delaware, was modeled. The first part of this work is a comparison of the unmodified version of the USGS SUTRA code to the modified version. This comparison was done to highlight the strengths of the modified code. The rest of the work focused on the study of the simulations done with the modified code over two time frames. The first time frame covered 180 days. The studies done within this time frame were in direct support of a field experiment being conducted at the Dover AFB site. In one study the cell was pumped for three different times and allowed to rebound until the end of the 180 day field experiment. The other short-term study was an investigation of pulsed versus continuous pumping and pulsed versus effective pumping. The long-term simulations were done over a four year time frame to study long-term diffusion effects which were not evident within the 180 days. The long-term simulations included a study of rebound for three different pump-down times and a study of pulsed versus continuous pumping.

2. Background

2.1 Non-Equilibrium Sorption

There are currently two major theories of why non-equilibrium sorption occurs on the microscopic or grain scale. The Retarded Intra-Particle Diffusion (RIPD) theory contends that molecules undergoing sorption must travel from sorption sites, deep within pores filled with immobile water, to the mobile/immobile water interface at the surface. This theory states that the reaction at the sorption site is fast compared to the diffusion through the immobile water. The Intra-Organic Matter Diffusion (IOMD) theory asserts that sorption sites are located within large organic molecules and that molecules must travel through immobile water within the flexible, polymerlike matrix of organic matter molecules to get to the mobile/immobile water interface. This theory once again assumes that the reaction at the sorption site is fast compared to the diffusion through the immobile water [Brusseau et al., 1989, Ball et al., 1991, Brusseau et al., 1991]. In both theories, diffusion is the rate-limiting step and a diffusion model should provide the most accurate representation of the either process[Ball et al., 1991]. The validity of the theories is site specific and often indistinguishable with the IOMD possibly being more correct for porous media with a high organic content and RIPD possibly being more correct for media with a low organic content.

Using a macro-diffusion approach incorporates the diffusion limiting process of both microscale theories into a macroscale model. In the macro-diffusion approach, rate-limited sorption occurs where heterogeneities produce diffusion dominated transport in zones of low permeability. An advantage of the macro-diffusion approach may be

experienced during preliminary modeling because it can be implemented without the additional parameters required by microscale models such as, particle size distribution, pore geometry, organic content of soil, and transfer constants. Site specific physical characteristics may lend themselves to this description, particularly in cases where the site is well stratified and the heterogeneity between layers overwhelms microscopic effects.

2.2 The Split-Operator Approach

The addition of diffusion sub-models to the advection dispersion (A-D) equation often results in systems of partial differential equations which are not easily solved [Miller and Rabideau, 1993]. Several authors have developed closed-form analytical solutions to systems with simple geometrics [Pellett, 1966; Rasmuson and Neretnieks, 1980; Valocchi, 1985; Goltz and Roberts, 1986], but systems which are more closely tied to reality require numerical methods. Two common approaches to solving these systems using numerical methods are: (1) solving the equations simultaneously and (2) using a split-operator approach to solve the equations separately at each time step [Miller and Rabideau, 1993].

In the early 70's, Yaneko[1971] popularized a class of solution methods known as the method of fractional steps. Split-operator procedures are a subset of this class. The split-operator approach has been used in several groundwater modeling applications as well as some biotransformation and biodegradation applications [Borden and Bedient, 1986; Kinzelbach et al., 1991; Valocchi and Malmstead, 1992]. The essence of the split-operator approach is that the governing equation is split into its transport and reaction operators and each is solved separately for each time step. This approach offers some distinct advantages over a simultaneous solution. First, the time scale of the reaction unit

processes may differ greatly from the time scale of the transport unit processes, resulting in numerical stiffness of the equation system if all equations are solved simultaneously. Utilizing different numerical time scales for each process eliminates stability problems due to the stiffness. Second, splitting the equations produces two sets of localized equations which may have known analytical solutions which may be exploited. Finally, separating the equations results in smaller systems of equations which may reduce overall computational time [Miller and Rabideau, 1993]. Miller and Rabideau [1993] provide a more in depth discussion of the technique of operator splitting.

3. The Dover AFB Site

3.1 Mathematical Model

The objective of this work was to develop a mathematical model which would account for rate-limited sorption from a single zone. This work was done to support a field study being conducted as well as a future three-dimensional modeling effort. The application code, USGS SUTRA, is a two-dimensional hybrid finite element/finite difference code. It incorporates nonuniform flow and spatial variability in flow and transport parameters as well as linear and non-linear equilibrium sorption [Voss, 1984]. By modifying the SUTRA code, it was possible to include all of the above variations as well as rate-limited sorption from a single layer. Rate-limited sorption was implemented in the modified code using a split operator technique and is referred to as the SO code or model. The unmodified SUTRA code includes the diffusion zone and solves it as part of its simultaneous solution. Therefore it is referred to as the clay included or CI code. A comparison of the CI and SO codes follows in the Simulation Runs section.

SUTRA simulates contaminant transport by combining two physical models, one to simulate the flow of ground water and the second to simulate the movement of a single solute in the ground water [Voss, 1984]. A development of these two models can be found in Caspers [1994] as well as in the SUTRA user's manual [Voss, 1984]. The separate balances for a single species stored in solution and on solid grains, are expressed, respectively, as follows [Voss, 1984]:

$$\frac{\partial(\theta\rho C)}{\partial t} = -f - \nabla(\theta\bar{v}C) + \nabla[\theta\rho(D + D_d^*)\nabla C] + \theta\rho\Gamma_w + Q_p C^* \quad (1)$$

and

$$\frac{\partial[(1-n)\rho_s F]}{\partial t} = f + (1-n)\rho_s \Gamma_s \quad (2)$$

where θ is the moisture content of the soil; ρ is the fluid density; C is the contaminant aqueous concentration; t is time; f is a volumetric adsorbate source; \bar{v} is the average fluid velocity; D is the coefficient of mechanical dispersion; D_d^* is the coefficient of molecular diffusion in a porous medium; Γ_w is an adsorbate mass source; $Q_p C^*$ is the dissolved species mass added by a fluid source with volumetric flow rate Q_p and concentration C^* ; n is the porosity; F is the mass of solute adsorbed on the solid per unit mass of solid; ρ_s is the solids density; and Γ_s is the rate of production of the solute per unit mass of solid

The addition of these two equations yields the general form of the total species mass balance used in SUTRA:

$$\frac{\partial(\theta\rho C)}{\partial t} = -\nabla[S_w \rho(q_{c, total})] - \frac{\partial\theta_s \rho_s F}{\partial t} - \theta_s \rho_s \Gamma_s + \theta\rho\Gamma + Q_p C^* \quad (3)$$

where θ_s is the solids volumetric fraction. Caspers [1994] and Voss [1984] discuss each term of the equation in detail and that information will not be repeated here.

The LEA assumption simplifies equation (2) by assuming equilibrium conditions between the two regions, mathematically expressed as

$$\frac{\partial C_s}{\partial t} = K_d \frac{\partial C}{\partial t} \quad (4)$$

where K_d is the linear distribution coefficient between soil and water; and C_s is the mass of solute adsorbed per unit dry mass of soil. [Szecsody, 1988]. The LEA model was used for all porous media in the unmodified code and for all except the bottom two loam layers in the modified code.

Physical non-equilibrium models are also commonly implemented by dividing the porous medium into a mobile and immobile region, so the non-equilibrium sorption affects the entire domain. Methods and results from implementing non-equilibrium sorption throughout the porous medium have been documented by other authors [Brusseu and Rao, 1989; Huso, 1989; Brogan, 1991; Adams and Virmontes, 1993; Caspers, 1994; Rabideau and Miller, 1994]. In the modification used for this research, the equilibrium immobile-mobile model used by SUTRA is left intact and a separate immobile zone is added.

$$R_s \frac{dC_s}{dt} = D_d^* \nabla^2 C_s \quad (5)$$

where R_s is the soil specific retardation factor. The separate immobile zone is modeled using a two-dimensional diffusion code developed by Pepper and Heinrich [1992]. In this macroscopic approach to non-equilibrium modeling, where the separate (diffusion-limited)

zone borders the 'equilibrium' domain, the diffusion code is used to calculate the concentration flux moving between the two regions.

$$\text{flux out of or into loam} = D_d^* \theta_s \nabla C_s \Big|_{\text{interface}} \quad (6)$$

This implementation is similar to that of Caspers [1994] and Rabideau and Miller [1994], but in those cases, mobile-immobile interaction was modeled at every node of the computational domain where as here it is only modeled at the interface nodes between the diffusion zone and the porous media.

3.2 Site Description

The site to be modeled, located at Dover AFB, Delaware, consists of two side-by-side cells which were constructed to allow forced-gradient field tests. The design of the site facilitates the side-by-side comparison of continuous and pulsed pumping remediation techniques. The cells were constructed in an area of pre-existing contamination. There are several contaminants present at the site, but for simplicity the experimenters have asked that the focus of this work be the flushing of tetrachloroethylene (PCE). The contamination profiles obtained during the early stages of site characterization suggest that a significant mass of contaminant exists in the lower three soil layers of the cells. The experimenters expect rate-limited sorption out of the lower two layers, an orange silty clay loam and a black silty loam, to be significant. This study served as a pre-modeling effort for both cells as well as an investigation into specified-zone sorption non-equilibrium.

Figure 1 is a top view of the site. For modeling purposes one conceptual cell was developed from a simple average of the two cells' dimensions. The conceptual cell is 10m x 4m x 10m. The cells are both heterogeneous but seem to be well stratified vertically. A

simplified conceptual model assuming perfect stratification was developed from early field data. A vertical cross section schematic is shown in figure 2. The conceptual initial condition concentration profile is also shown on figure 2. The concentrations are reported as bulk fluid-phase concentrations.

3.3 Defining the Model In SUTRA

The conceptual cell simulation parameters are listed in table 1. The split-operator code (SO) parameters and the clay included (CI) parameters were matched exactly whenever possible. The injection and extraction wells were simulated on the left and right perimeter nodes respectively. Both codes used no flow/zero-flux boundaries on top. The CI code used a no-flow/zero-flux boundary on the bottom while the SO code used a no flow/time-dependent flux boundary condition on the bottom. The time-dependent flux condition was determined from the results of the diffusion model for the clay layers. This diffusion model of the clay layers also had zero-flux boundary conditions along the sides and bottom of the clay; the top boundary condition was time dependent, coming from the SUTRA results of the mobile region model at the previous, split time-step.

3.4 Validation of Codes

The USGS SUTRA code has been validated against analytical solutions on several occasions. A validation is included in the user's manual [Voss, 1984] and Caspers recently validated it in his 1994 work. The diffusion code has also been validated against

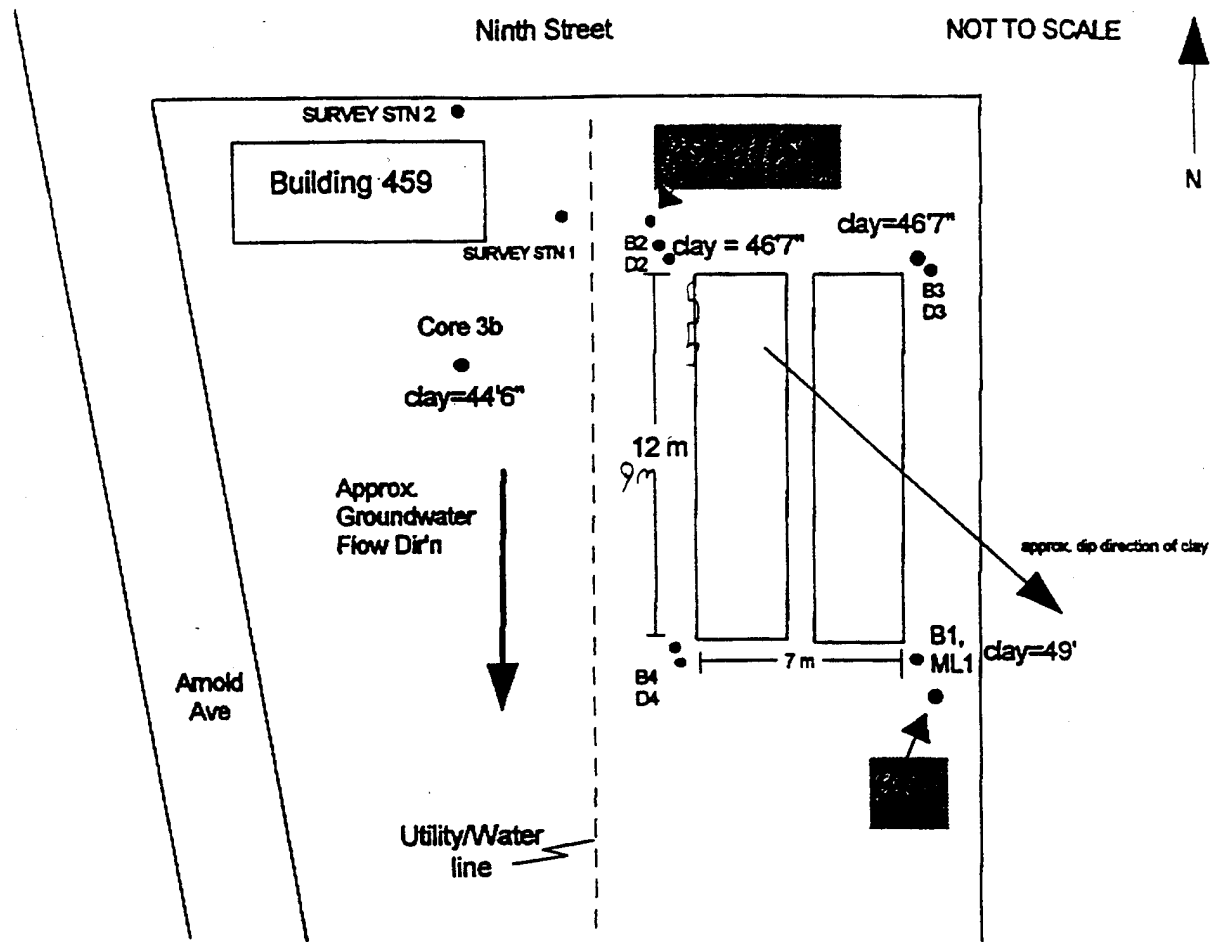


Figure 1. Schematic of Borehole, Drivepoint and Multilevel Piezometer Locations at the Dover AFB Field Site (not to scale)

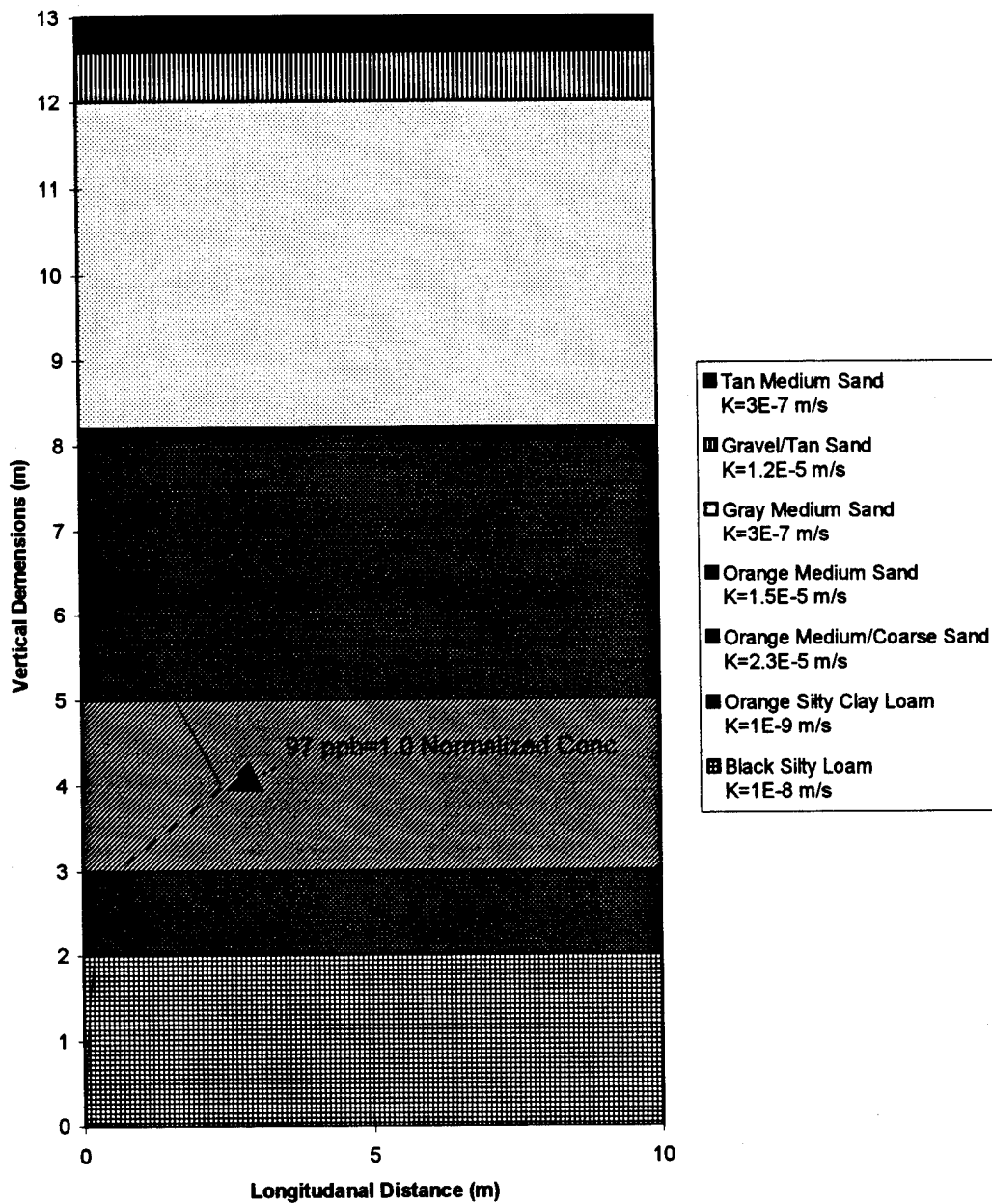


Figure 2. Vertical Cross Section of Conceptual Cell with Initial Condition Concentration Profile Represented

Table 1. Basic Simulation Parameters

Parameter	CI Value	SO Value
Porous Media Parameters		
Solid Matrix Compressibility, α [kg/ms^2] ⁻¹	2.0E-8	2.0E-8
Density of Solid grain, ρ_s [kg/m^3]	1810	1810
Fluid Compressibility, β [$\text{kg}/(\text{ms}^2)$] ⁻¹	4.40E-10	4.40E-10
Fluid Diffusivity, D_m [m^2/s]	8.3E-10	8.3E-10
Fluid Density, ρ_w [kg/m^3]	1000	1000
Fluid Viscosity, μ [kg/ms]	1.3E-3	1.3E-3
Porosity, ϵ	.36	.36
Longitudinal Dispersivity, d_L [m]	.23	.23
Transverse Dispersivity, d_T [m]	.023	.023
Numerical Parameters		
Number of Nodes	567	483/2601
Number of Elements	520	440/2500
Horizontal Grid Spacing [m]	.5	variable/.2
Vertical Grid Spacing [m]	.5	variable/.2
Time Steps	variable	variable
Length of Time Step [day]	1/20	1/20/1/10&1/2

an analytical solution. The combination of the codes to form the SO code was validated an additional two ways. First, a single data point from the field showed that the concentration went below the detection limit after 25 days of pumping. In computer simulations the value went below the detection limit at around 29 days. This is very close to the 25 days seen in the field experiment considering that the actual pump rate fluctuated at the beginning of the field experiment while in computer simulations it was held constant. Second, numerical refinement, both spatial and temporal resulted in consistent simulation output.

4 Simulation Runs for Dover AFB

There was a multitude of simulations which could have been run to compare and contrast the modified and unmodified codes, or to test the performance of a single code under different conditions. However, the simulations presented here focused on obtaining results which would provide insight to those conducting the field study. Unfortunately, the time frame of this work and that of the field experiment did not allow for the comparison of model data to field data. The experimenters hoped to use this study to gain insight on when and how long the flow in the pulsed pumping cell should be interrupted. Therefore they were interested in the magnitude of the rebound they could expect to see during interruptions of various lengths. The field experiment would collect pumping data for a period of approximately 180 days. All simulations which are contained within the 180 day period are referred to as short-term. Short-term simulations were done to provide immediately useful information to the field experimenters. Scaling arguments (see

equation 7 and calculation) and short-term simulations both indicated that diffusion out of the clay to equilibrium would require much more time than 180 days. To study the effects of long-term diffusion not evident during the 180 days, simulations over longer time periods were also accomplished. Simulations extending past the 180 day period are referred to as long-term. The effects of rebound and pulsed pumping were studied for both short-term and long-term simulations. Prior to examining these effects a comparison of the CI and SO codes was conducted to gain insight into the performance of the SO macro approach.

All of the simulations take place after allowing the initial condition to diffuse for 180 days. The conceptual concentration profile which was used as the initial condition is plotted on figure 2. The 97 ppb seen at the peak of the concentration profile is an aqueous concentration which was normalized to one for simulations. It is evident from the plot that there is a concentration gradient signifying the cell is not at equilibrium. The 180 day diffusion time matches the actual timeline between when the site was sampled and when the pumps were initiated. Additionally, the diffusion period smoothed out the sharp edges in the initial condition input file enhancing numerical stability.

The concentrations reported were observed at a central monitoring point in the grids approximately six inches above the orange silty clay loam, in the longitudinal center of the cell. This point was a close match to an actual monitoring well which was to be used to study rebound from the clay. The concentration was observed at other locations during simulation runs, but was only used to provide information to modelers, and is therefore not reported. One percent of the peak initial concentration was used as the

theoretical detection limit of the sampling equipment. This limit was based on an estimate from the field experimenters, prior to equipment arrival and testing. The initial peak concentration at the site was about 97 ug/L (see figure 2). One percent of this value is 1 ug/L or one part-per-billion which was considered within the capability of the sampling equipment prior to delivery and testing. The concentrations were normalized to the peak concentration therefore the detection limit used in the simulation runs was 0.01.

4.1 Short-Term Comparison of CI and SO Codes

Simulations of the tailing effect during pump-down periods and rebound during pump-off periods provided graphic comparisons of the two approaches. These results, coupled with a preliminary field result, clearly show that the form of the CI approach used in these simulations was not adequate to reflect the basic physics of the conceptual model. The pump-down period was complete when the average concentration of the water exiting the cell was below the detection limit. For the SO model this occurred at 39 days and for the CI model at 40 days. Figure 3 depicts the normalized concentration measured at the monitoring well at each time step. Although the endpoints occur at nearly the same time, it is apparent in figure 3 that the CI model shows significantly more mass removed. The greater amount of mass removed was possibly due to the fact that in the CI model the advective flow has access to the entire cell, while in the SO model the advective flow does not directly affect the bottom two layers. However, due to the low hydraulic conductivity in the lower layers, the velocity of the water was extremely small ($\approx 3.74E-10$ m/s) and the advection in the loam layers is negligible. Therefore a more significant reason for the greater amount of mass removed is that the CI model does not

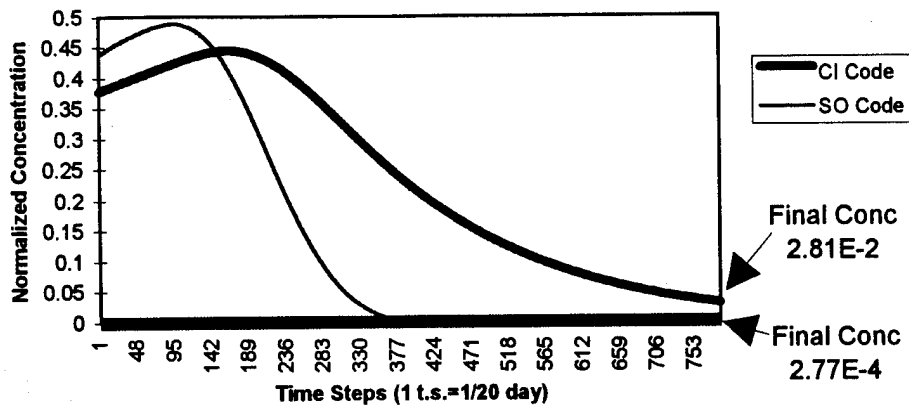


Figure 3. Comparison of 39 Days Pumping of CI and SO Codes Observed at Central Monitoring Point.

allow the flexibility of defining different distribution constants for the LEA models in the different layers. Therefore in the CI model the distribution constant was one-third of what it should have been for the orange silty clay loam and two orders of magnitude less than it should have been for the black silty loam. So, even though the hydraulic conductivity was low the mass was still mobilized out of the loam because the significant retardation in the loam layers was not accounted for in the CI model..

Figure 4 shows the concentration at each time step when the pumps are left off from day 40 until the end of the field experiment. Notice that the concentration of the CI code is decreasing instead of increasing as would be expected. This effect is probably a result of the phenomenon witnessed in figure 3, where there was a significant amount of mass mobilized from the loam layers. There is no significant mass of contaminant left to diffuse up to the monitoring well. In fact, the contaminant at the monitoring well appears

to be diffusing to a lower concentration area. This ultimately results in an under prediction of rebound.

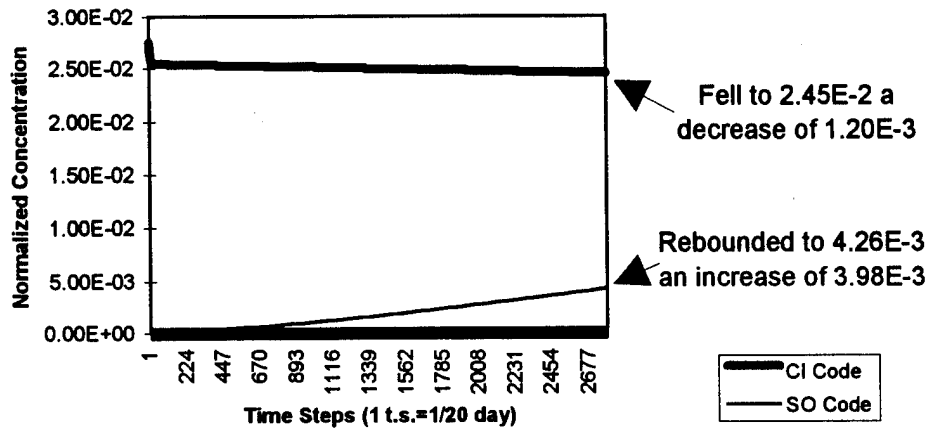


Figure 4. Comparison of Rebound for the CI and SO Codes for Days 40 through 180 observed at the Central Monitoring Point

A single preliminary measure was obtained from the field experimenters which indicated that the concentration in the central monitoring well went below the detection limit at around 25 days of pumping. This field data, the scaling calculation (equation 7), and the model output, evidence the shortcomings of the unmodified code making its inclusion in further simulation runs unnecessary. In particular the unmodified code does not allow the specification of retardation coefficients for the loam layers. The effects of this inflexibility are illustrated above where a significant amount of mass was mobilized from the clay at an unrealistically high rate (figure 3 and equation 7). This rapid transport ultimately caused the unmodified code to over predict mass transport from the loam and under predict rebound (figures 3 & 4). A positive result of the CI simulations was that in

many applications a large difference in hydraulic conductivity could cause stiffness in the numerical method resulting in instability of the flow solution, however; no instability was witnessed in the flow solutions. All simulations after this point were accomplished using the SO code.

Also at this point a new finite element grid with better resolution was employed to assist in the further study of pump-down and rebound times. The refinement can be seen in table 1. The number of elements increased from 440 to 2500 and the number of nodes from 483 to 2601. The previous grid was tight at the edges and loose in the middle to minimize boundary effects and enhance stability. The new grid is refined enough not to require similar tightening for stability. The remaining simulations were run at a slightly lower pump rate which more closely matched the one being used at the site. For all of the following simulations the time step will be 1/10 day for short-term and 1/2 day for long-term.

4.2 Short-Term Rebound from Different Pump-Down Times

In these simulations three different pump-down times were allowed to rebound until the end of the field study to study the rebound behavior of the cell. The first pump-off time came when the concentration in the monitoring well went below the detection limit. This occurred at 288 time steps or 28.8 days, very close to the time it takes to pump one pore volume and to when the field experimenters shut off their pumps the first time. Another pump-off time was determined when the effluent concentration went below the detection limit, 45.1 days. The horizontal concentration gradient across the bottom nodes was nearly zero at this time. The third pump-off time, 37 days, was the median value

between 28.8 and 45.1 days. This additional scenario was simulated to give the field experimenters greater insight on pump-down times. Figure 5 shows the pump-down and rebound concentrations for the different pump-down times from 26 to 180 days. The only curve that rebounds above the detection limit within the field study time is the shortest pump-off time of 28.8 days. This response was expected since the concentration had not decreased to as small a value as the other cases. This response along with the larger concentration increase could be expected since there was not only vertical diffusion from the clay, but horizontal diffusion from the higher concentration fluid to the right of the monitoring point as well. Horizontal diffusion is also witnessed for the 37 day pump-down curve. Note that although the largest rebound occurs in the shortest pump-on case, a calculation revealed that the largest amount of vertical diffusion from the loam occurred for the 45 day pump-down. Therefore, the largest contaminant rebound from the loam layers occurred for during the longest pump-on case. This was expected since the diffusion gradient in the vertical direction is the driving force behind the movement of contaminant from the loam to the aquifer and the 45.1 day pump-down creates the largest concentration gradient.

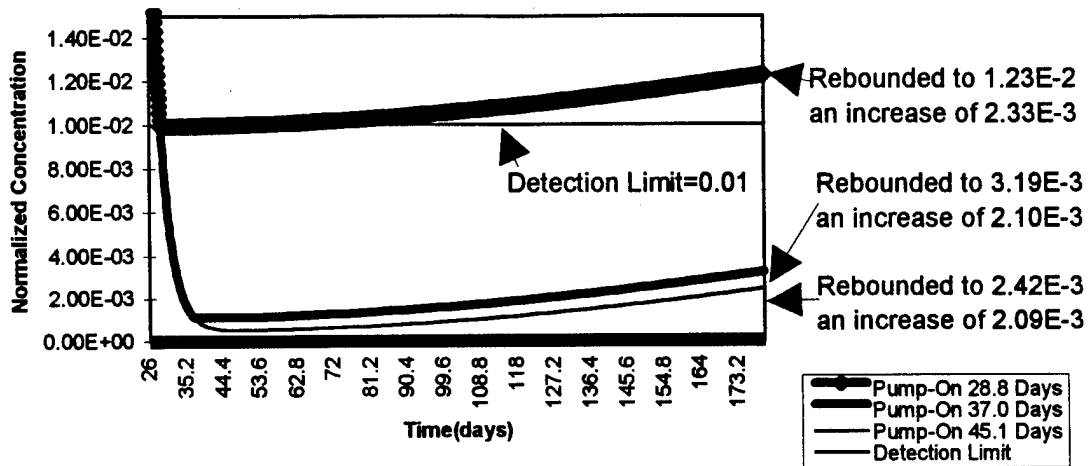


Figure 5. Rebound Comparison of Three Pump-On Times from 26 to 180 Days observed at Central Monitoring Point

4.3 Long-Term Rebound from Different Pump-Down Times

Although the concentrations of the longer pump-on times do not rebound above the detection limit within the time allotted for the field study they are increasing at the end of the field study. If allowed to rebound for a significantly longer period of time, such as four years, they too rebound past the detection limit. Figure 6 depicts the pump-down and rebound when the three are allowed to rebound for four years time. Notice that all three curves exceed the detection limit at the end of four years and that once again the 29 and 37 day pump-downs have a larger concentration increase due to horizontal diffusion. A decrease in the accuracy caused by changing the time step from 1/10 day to 1/2 day is evidenced by the 28.8 day concentration never dipping below the detection limit.

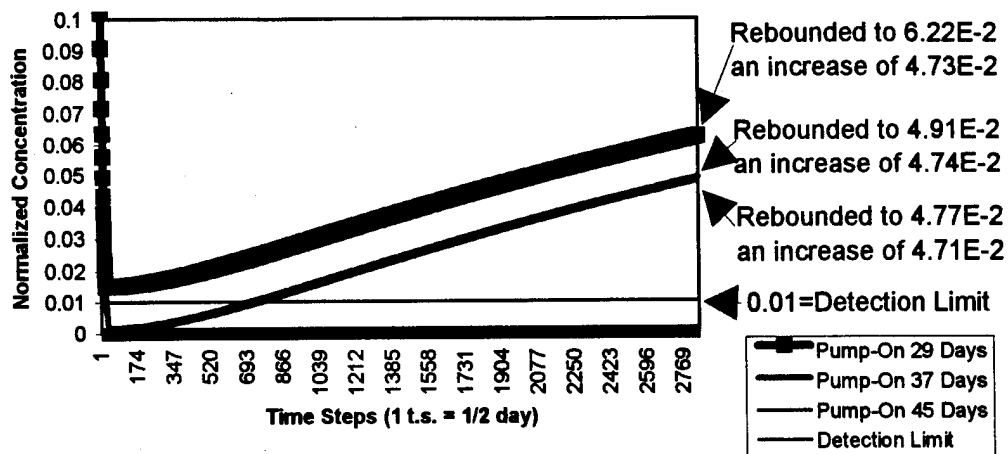


Figure 6. Comparison of Long-Term Rebound for Different Pump-On Times observed at Central Monitoring Point

4.4 Short-Term Pulsed Pumping Simulations

Of the three short-term pump-down times previously analyzed, the only one that rebounded past the detection limit within the 180 day study period was the 28.8 day pump-on time. For this reason and due to the fact that it was the closest to the first pump-off time used in the field study, pulsed pumping simulations were performed based on the 28.8 day pump-down time. Two pulsed pumping strategies were investigated. The first allowed the concentration to rebound to a level of $1.20\text{E-}2$ and then pumped it down below the detection limit. The $1.20\text{E-}2$ value was selected because it was close to the maximum value and the time required to achieve it allowed enough time to pump-down the concentration and still have time for another rebound within the 180 day study period. The other strategy allowed rebound to $1.10\text{E-}2$. This value was selected as an intermediate value between the maximum rebound and the detection limit, once again to

provide greater insight to the field experimenters.. The time required to achieve $1.10E-2$ was shorter and allowed a longer rebound period after the second pump-down. The longer rebound time was sufficient to allow rebound above the detection limit after a second pump-down. The concentration was pumped down a third time and allowed to rebound until the end of the study period. Figure 7 depicts the pulsed pumping strategies simulated.

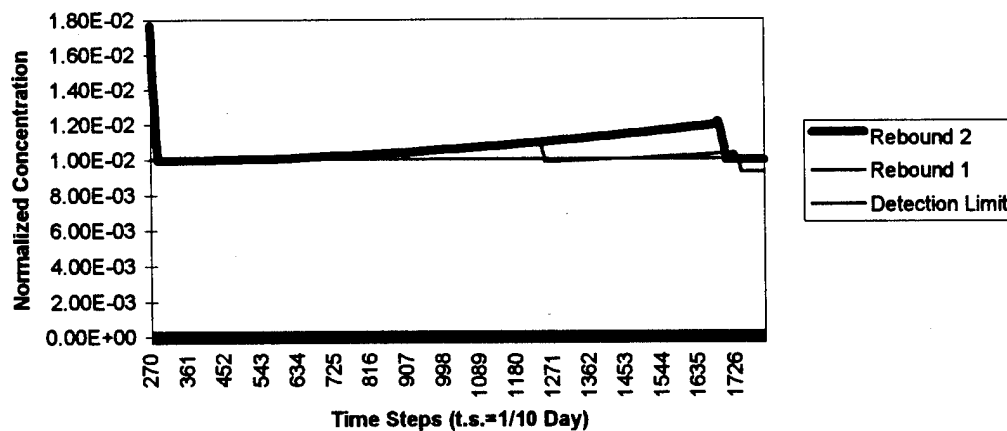


Figure 7. Pulsed Pumping: Comparison of Two Rebound Times Following 28.8 Days of Pumping observed at Central Monitoring Point

Consistent with the field study design, the pulsed pumping strategies were compared to the continuously pumped case. The pumps were run continuously, at the pump-on rate of the pulsed pumping simulations, for the duration of the 180 day field study. An estimate of the mass removed was calculated by integrating the breakthrough curves at the monitoring point. Table 2 provides a representation of mass removed, pumping duration, and volume pumped for the pumping strategies. The continuously

pumped strategy described above is in the column labeled Continuous. Although all three removed nearly the same amount of mass, the pulsed pumping strategies were six times as efficient as continuously pumping based on the mass removed per volume pumped. For further comparison, the amount of water pumped by the pulsed pumping strategies was spread out over six months resulting in two more continuous pumping schemes (termed 'effective pumping'). These very low pump rates increased the advective time scale and brought the time scales closer together for all of the layers. This lower pump rate resulted in almost six times more total mass removed and an order of magnitude increase in efficiency in the continuous pump. The data for the effective pumping cases appears in table 2 with Effective 1 corresponding to pulsed pumping strategy 1 and Effective 2 corresponding to pulsed pumping strategy 2. These results concur with the results of Harvey et al. [1994] in which they found continuous pumping at the effective rate to always be more efficient than pulsed pumping. Both strategies are based on the idea that pumping and treating relatively clean water is a waste of financial resources.

However, these additional effective pumping simulations are not always reasonable at field conditions. If the experimenters are attempting to do side by side comparisons, they do not know the duration of pumping a priori. Therefore it is impossible to get effective pump rates equivalent to pulsed pumping schemes. Additionally, there is usually not enough site information available before pumping to fully characterize the site and design a pulsed pumping scheme and a matching effective scheme. Another problem with the lower pump rates is time. If these effective pump rates were pulse pumped an even greater amount of mass would be removed. At some point the total time for remediation

must be considered. Effective pumping is more efficient in terms of mass removed, but pulsed pumping is more efficient in terms of time to lowest achievable concentration. Site managers must carefully assess their remediation goals considering such things as; human health and safety, legal requirements, political and social pressure, and cost. The results do confirm the efficiency based on mass removed per volume pumped of pumping at a rate just high enough to maintain plume containment [Rabideau and Miller, 1994].

Table 2. Short-Term Pulsed Pumping Simulation Results

	Pulsed 1	Pulsed 2	Continuous	Effective 1	Effective 2
Mass Removed 1st Pump	9.57	9.57	9.671155093	54.72048424	53.72063859
Duration of 1st Pump(days)	28.8	28.8	180	180	180
Volume Pumped(m3)	132.7104	132.7104	829.44	145.62	148.86
Mass Removed 2nd Pump	2.37E-02	1.26E-02	N/A	N/A	N/A
Duration of 2nd Pump(days)	2.1	1.2	N/A	N/A	N/A
Volume Pumped(m3)	9.6768	5.5296	N/A	N/A	N/A
Mass Removed 3rd Pump	N/A	1.48E-02	N/A	N/A	N/A
Duration of 3rd Pump(days)	N/A	1.4	N/A	N/A	N/A
Volume Pumped(m3)	N/A	6.4512	N/A	N/A	N/A
Total Mass Removed	9.59	9.60	9.671155093	54.72048424	53.72063859
Total Duration of Pumping	30.9	32.4	180	180	180
Total Volume Pumped(m3)	142.3872	149.2992	829.44	143.1	148.86
Efficiency(TMR/TVP)	0.067369	0.064275	0.011659861	0.382393321	0.360880281

4.5 Long-Term Pulsed Pumping Simulations

The extensive clay time scale limited the study of rebound that could be accomplished within the 180 day field study time frame. To gain a better understanding of the way the SO code was modeling non-equilibrium effects, a long-term pulsed pumping simulation was compared to a long-term continuous pumping simulation. For the pulsed pumping simulation the concentration was pumped down for 45 days. Short and long-term rebound data indicated that the 45.1 day pump-down time had the greatest amount of

rebound from the loam. Therefore of the three pump-down times previously examined, it was the most promising choice for exhibiting measurable rebound effects. A previous long-term rebound simulation indicated that two years pump-off time would allow sufficient time for rebound above the detection limit. The concentration was then pumped down for 50 days and allowed to rebound until the end of a four year period. The increase for the first rebound period was greater than that of the second as would be expected. The concentration was pumped down one final time for 50 days and allowed to rebound for two more years. The final pump-down was done to get a mass removed comparison to a continuously pumped case after 4 years and the final rebound was for comparison to the rebound that occurred following four years of continuous pumping. The increase following the final pulsed pump-down and the continuous pump-down was nearly identical. Interestingly the increase of the third rebound period was the same as the increase for the second period. If significant mass was being mobilized from the clay layer, the amount of the increase should continue to decrease as it did between rebounds 1 and 2. The fact that the last two rebounds for the pulsed pumping and the rebound for the continuous pumping are all the same indicates that there is still a significant amount of mass in the loam and that the only thing limiting mass transfer is time. The larger first increase was most likely due to the fact that there was a higher total concentration in the cell following the first pump-down than following the second resulting in a slight amount of horizontal diffusion.. Figure 8 gives a visual comparison of the long-term data.

As with the short-term pulsed pumping simulations, the total mass removed was nearly identical, however; the efficiency of pulsed pumping was an order of magnitude

greater than continuous pumping. These results are found in table 3. This improvement is significant for continuous PAT sites that are presently operating at long times with a low mass removed per volume efficiency. Simulation results suggest that if the disposal/treatment of the pumped water is a high cost item they could minimize cost by allowing diffusion based processes time to stabilize.

After three pump downs, the concentration continued to rebound to nearly the same level as previous rebounds. This rebound illustrated that there was still a significant mass of contaminant in the loam layers. This retention was expected based on scaling calculations using the effective diffusion constant of the contaminant in the clay and the thickness of the clay.

$$T = \frac{\text{DiffusionLength}^2}{D_m} \Rightarrow \frac{(2\text{m})^2}{8.3 \cdot 10^{-10} \frac{\text{m}^2}{\text{sec}}} = 152.717\text{yr} \quad (7)$$

Based on this calculation the time scale to clean up of this conceptual site is at least on the order of decades. These long-term pulsed pumping simulations confirm this basic calculation.

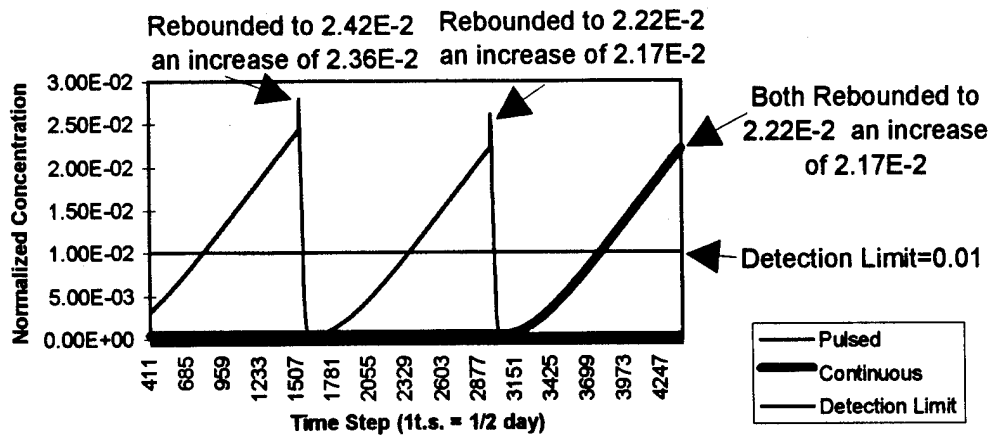


Figure 8. Long-Term Comparison of Pulsed and Continuous Pumping observed at Central Monitoring Point

Table 3. Long-Term Simulation Data For Pulsed and Continuous Cases

	Pulsed	Continuous
Mass Removed 1st Pump	9.808022752	10.48599567
Duration of 1st Pump(days)	45	1440
Volume Pumped(m3)	207.36	6635.52
Mass Removed 2nd Pump	0.369089233	N/A
Duration of 2nd Pump(days)	50	N/A
Volume Pumped(m3)	230.4	N/A
Mass Removed 3rd Pump	0.346560189	N/A
Duration of 3rd Pump(days)	50	N/A
Volume Pumped(m3)	230.4	N/A
Total Mass Removed	10.52367217	10.48599567
Total Duration of Pumping	145	1440
Total Volume Pumped(m3)	668.16	6635.52
Efficiency(TMR/TVP)	0.015750228	0.001580282

5. Conclusions

This research has investigated the modeling of a conceptual model based on an actual site. This investigation provided field experimenters with information regarding the length of the clay time scale and the ability of the current experimental design to study rebound from the clay within 180 days. A macroscale diffusion-limited sorption approach

to modeling sorption from a low hydraulic conductivity zone was introduced and implemented with success. The success achieved was evidence of the usefulness of this approach for preliminary modeling work when grain scale parameter estimates are difficult to obtain. Simulations which compared continuous, pulsed, and effective pumping showed that the preferred method depends on site specific remediation goals, however, pulsed and effective pumping were more efficient based on mass removed per volume pumped. This research also showed the weakness of an unmodified code that did not allow specific layer retardation factors to be defined. The following numbered statements summarize the conclusions drawn from this research:

1. The clay time scale was not compatible with the length of the field study and therefore it would be difficult for them to study rebound from the loam layers using the current experimental design.
2. The macro approach to modeling non-equilibrium sorption does not require microscale fitting parameters and for that reason may be preferred at early stages of modeling. It is capable of representing the diffusion processes that occur in reality without microscale parameters which are difficult to characterize.
3. The inflexibility of the unmodified SUTRA code made it impossible to insert the proper retardation factors for each layer. This inflexibility was the most likely cause for the exaggerated influence the advective flow had on the bottom two layers which resulted in the greater amount of mass being removed. This approach does not reflect the basic physics occurring in the loam layers. This approach may be valid if the retardation coefficient can be changed for each soil type.

4. Pulsed pumping at a given rate was more efficient than continuously pumping at that same rate over both a 180 day and a 4 year period and it removed roughly the same amount of mass. This result is important for field conditions where the flexibility of calculating effective continuous pump rates is not afforded. This conclusion (using a macro approach) supports the results of Harvey et al. [1994] in which pulsed pumping (using a micro approach) was shown to remove as much contaminant as continuous pumping at the same rate.
5. Pulsed pumping at a given rate was not as efficient as pumping at the effective rate for the short-term pulsed pumping simulation. Once again, this conclusion (using a macro approach) supports the results of Harvey et al. [1994] in which pumping at an effective rate was always more efficient than pulsed pumping (using a micro approach).
6. The larger concentration increase for the shorter pump-down times was evidence of horizontal diffusion. The horizontal diffusion effects were seen in both the short-term and long-term simulations.

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