Modeling Analysis of Biosparging at the Sanitary Landfill

by

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**MODELING ANALYSIS OF BIOSPARGING
AT THE SANITARY LANDFILL**

Task No. GW39-009

September 30, 1998

Prepared for:

Westinghouse Savannah River Company
Environmental Restoration Department
Aiken, South Carolina 29808

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1. Introduction

Groundwater beneath the Sanitary Landfill (SLF) at the U.S. DOE Savannah River Site (SRS) is contaminated with a number of constituents. The most widespread contaminants at the SLF that exhibit plume-like characteristics are trichloroethene (TCE) and vinyl chloride (VC). The Westinghouse Savannah River Company (WSRC) has proposed to treat this contamination with a bioparging system that will stimulate TCE and VC biodegradation by providing microbial nutrients (triethyl phosphate and nitrous oxide) and energy sources (oxygen and methane) with the use of two horizontal wells. These wells were installed in 1997 and 1998 as a part of the planned bioparging system.

This report presents the results of a groundwater modeling study that evaluates the performance of the bioparging system at the SLF. Numerical model simulations based on the Conceptual Site Model (CSM) presented in Section 2 of this report are used to predict the effectiveness of two horizontal bioparging wells, to select appropriate locations for monitoring the performance of the bioparging system, and estimate the overall time for operation of the bioremediation system. In this report a variety of relevant site characteristics and processes are reviewed, including site-specific hydrogeology, contaminant distributions, bioparging parameters, aerobic biodegradation of vinyl chloride, and cometabolic (*methanotrophic*) biodegradation of TCE. Collectively, these characteristics and processes form the basis of the modeling approach for simulating flow and biological degradation of chlorinated compounds in the SLF groundwater. The construction of the models is described, followed by the results of simulation of the bioparging system. Several sensitivity simulations are presented to assess the effect of parameter uncertainty on model predictions. Finally, best estimates of projected efficiency, required remediation period, and locations for monitoring sites are discussed.

1.1 Background

The Sanitary Landfill is a 70-acre unlined landfill that received wastes from 1974 to 1994. It was originally opened in 1974 as a 32-acre site. In 1987, as the original site reached capacity, a 16-acre Northern Expansion and a 22-acre Southern Expansion were added (WSRC, 1996). Wastes were placed in trenches and covered with soil. Wastes included paper, cardboard, rags, plastic, cafeteria waste, rubber, paint cans, paint thinners, solvent rags, batteries, office furniture, construction debris, asbestos containing materials, and organic sludge skimmed from the wastewater treatment plant. Contamination is migrating from the original 32-acre site and the 22-acre Southern Expansion.

The constituents that are present at the SLF include benzene, vinyl chloride (VC), methylene chloride, 1,2-dichloroethane, 1,2-dichloropropane, 1,4-dichlorobenzene, gross alpha, lead, mercury, tetrachloroethene (PCE), trichloroethene (TCE), and tritium. The most widespread contaminants that exhibit spatial continuity are VC and TCE. Relatively distinct VC and TCE plumes have been identified along the downgradient edges of the landfill. The VC plume is present along the western edge of the SLF while the TCE plume occurs along the southern edge of the SLF.

In compliance with a settlement agreement reached between the DOE and the South Carolina Department of Health and Environmental Control (SCDHEC), the SLF was capped

during 1996 and 1997 and was certified closed in October 1997. The cap consists of a basal foundation layer, a geosynthetic gas vent layer, a geosynthetic clay liner, a flexible membrane liner, a geosynthetic drainage layer, geotextile filter material, topsoil, and vegetation. The cap is reported to have an efficiency of 99.87%, based on calculations performed with the Hydrologic Evaluation of Landfill Performance (HELP) model (WSRC, 1992).

From 1994 to 1996, WSRC conducted laboratory and field pilot studies to test the feasibility of using biosparging to control the VC and TCE plumes at the downgradient edges of the landfill (WSRC, 1994; 1996). These studies indicated that the in situ biodegradation of VC could be stimulated by sparging air into the VC-contaminated plume, while the in situ *methanotrophic* biodegradation of TCE could be stimulated by sparging methane, air, and gaseous nutrients nitrous oxide and triethylphosphate (TEP). Based on the findings of these studies, WSRC proposed to implement an in situ biosparging system as part of the corrective action plan. Two horizontal biosparging wells were installed in 1997 and 1998, one in the VC-contaminated zone along the southwestern edge of the SLF, and the other in the TCE-contaminated zone at the southern boundary of the SLF. Other than the initial performance testing that was conducted after installation, the wells have not been operated.

1.2 Objectives

The objectives of this modeling analysis are: (1) to simulate the effectiveness of biological degradation of chlorinated compounds in the groundwater, (2) to predict contaminant concentration levels at downgradient points of compliance (POC), (3) to provide input to determination of appropriate monitoring well locations, and (4) to estimate the time required for the operation of the bioremediation system. Concentrations of TCE and VC in the groundwater migrating from the SLF are expected to decrease significantly in the future because the cap recently installed over the main section and southern expansion has reduced leachate, and the implementation of the proposed biosparging system is expected to eliminate much of the TCE and VC by enhanced biodegradation processes. The modeling described here is used to simulate the decrease in TCE and VC that will occur as a result of both the implementation of the biosparging system and the installation of the cap.

1.3 Modeling approach

The SRS biosparging system was simulated by linking three complementary numerical codes as shown in Figure 1-1: One biosparging model (TRAMP) to simulate the bioactive zones occurring above the horizontal sparging wells; a second model (RT3D) to simulate the transport of the solutes (TCE and VC) from the landfill to the biosparging zone and to the downgradient wetlands and Upper Three Runs Creek; and a third model (MODFLOW) to establish the groundwater flow field in and around the SLF.

First, the flow model was constructed using the template of the previous (Intera, 1993a) flow model and calibrated against monitor well calibration targets. Output from the flow model was then used in the development of the biosparging model and the Sanitary Landfill solute transport model. The biosparging model was used to simulate TCE and VC biodegradation in North-South trending profile cross sections transecting each of the biosparging wells. The cross-sectional model simulates the processes along a groundwater flow line. The processes within this cross section are assumed to be representative of the processes along other flowlines that are

parallel to the flow line under consideration and intersecting the sparge well system. Since the TCE and VC plumes occur in separate locations and the composition of the biosparging gases will vary depending on the target plume, the biosparging of the TCE and VC plumes are modeled as separate systems. The simulations with the biosparging model provide a prediction of biosparging performance efficiency, as well as a prediction of the radius of influence extending from the sparging wells. Recommendation of future monitoring well locations is based on the radius of influence predicted by the biosparging model.

Once the radius of influence was predicted by the biosparging model, the Sanitary Landfill solute transport model was used to simulate the flux of TCE and VC from the landfill through the biosparging zones, and further downgradient. Like the biosparging model simulations, the simulations with the Sanitary Landfill model indicate the performance of the biosparging system, but in a more simplistic fashion, with substantially fewer parameters. In the final analysis, the performance of the biosparging system is determined based on the output from both the biosparging and Sanitary Landfill transport models.

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Figure 1-1 Relationship of codes used for biosparging analysis

2. Conceptual model

2.1 Site-specific conceptual hydrogeologic model

A conceptual hydrogeologic model succinctly describes the principal components of a groundwater flow system and is developed from regional, local, and site-specific data. The primary components of groundwater flow systems include: (1) areal extent and configuration of aquifers, (2) hydraulic properties of aquifers, (3) groundwater recharge and discharge zones, (4) groundwater sources and sinks, and (5) areal and vertical distribution of groundwater hydraulic head potential. These aquifer system components serve as a framework for the construction of a numerical groundwater flow model. This section summarizes the key features of the conceptual model.

The local hydrogeology of the study area is summarized in *Sanitary Landfill Hydrogeologic Characterization* (WSRC, 1991) and in *Summary Report for the Subsurface Characterization at the Sanitary Landfill* (O'Halloran, 1994). Several numerical models exist for the A/M area that include the SLF. Existing groundwater models for the A/M area are documented in *Regional Hydrogeologic Conditions and Evaluation of Chemical Transport in the Vicinity of the M-Area Settling Basin and Lost Lake* (SS Papadopolous and Associates, 1988a), *Local Hydrogeologic Conditions and Evaluation of Chemical Transport in the Vicinity of the M-Area Settling Basin and Lost Lake* (SS Papadopolous and Associates, 1988b), *A Groundwater Flow Model for the A/M Area of the SRS* (Beaudoin et al., 1991) and *A Transiently Calibrated Regional Groundwater Flow Model for the A/M Area* (Intera, 1993b). A groundwater flow model exists for the SLF and is documented in *Sanitary Landfill Local-scale Flow and Transport Modeling in Support of Alternative Concentration Limits Demonstrations* (Intera, 1993a).

The conceptual model of groundwater flow in the Steed Pond Aquifer for the local area surrounding the SLF is that net recharge from precipitation (approximately 14 in/yr except for the capped portion of SLF) flows underground and discharges to Upper Three Runs Creek (UTRC) to the south, wetlands to the south, and Tim's Branch to the east. It is expected that groundwater flows into the model area in the northern portions. It is expected that groundwater generally flows downward in recharge areas and upward in discharge areas near UTRC, wetlands, and Tim's Branch.

2.1.1 Areal extent and configuration of aquifers

The areal extent and configuration of the underlying aquifers and confining units in the Sanitary Landfill area has been characterized by several sources including SRS staff, the U. S. Geological Survey, and independent consultants (Fallaw and Sargent, 1986; Bledsoe, 1988; Aadland and Bledsoe, 1990; Fallaw, 1991; and Aadland et. al., 1992; O'Halleron, 1994; Aadland, 1995). The conceptual model is based on the information contained in these reports.

Several classifications and naming conventions have been used to describe the geologic setting in the SLF area. Figure 2-1 compares the configuration of stratigraphy in the Sanitary Landfill area from three separate reports. The conceptual model will focus on groundwater flow in the Steed Pond Aquifer that is underlain by the Crouch Branch Confining Unit.

The Steed Pond Aquifer is the uppermost aquifer with depths ranging from 80 to approximately 120 feet below land surface. Upper, middle, and lower portions of the Steed Pond Aquifer have been identified. For this conceptual model, the upper portion (D wells) will be from land surface to a depth of approximately 40 feet. The middle portion (C wells) will be between approximately 40 and 75 feet below land surface. The lower portion (B wells) will be between approximately 75 and 120 feet below land surface.

The Crouch Branch Confining Unit serves as a bottom for the conceptual model. The Crouch Branch Confining Unit separates the Steed Pond Aquifer and the Crouch Branch Aquifer. The Crouch Branch Confining Unit was described hydraulically by Geraghty & Miller (1985). The horizontal conductivity of the clays in this unit was determined to be 4.5×10^{-6} ft/day. The vertical conductivity was determined to be 7.4×10^{-3} ft/day (arithmetic mean) and 4.8×10^{-4} ft/day (geometric mean). For this local flow and transport model, it is assumed that flow through the Crouch Branch Confining Unit, both vertically and horizontally, is not significant for contaminants in the upper portion of the Steed Pond Aquifer flowing between the SLF and UTRC.

2.1.2 Hydraulic properties of aquifers

The well monitoring network in the SLF area contains 89 LFW (sanitary landfill) series wells. Eight LFW wells were installed in 1981, six wells in 1984, 17 wells in 1986, 26 wells in 1991, and 32 wells in late 1993-1994. Quarterly water level data are available for the older wells since mid-1984. Since 1996, 48 of the wells have been monitored on a quarterly basis (groundwater sampling and analysis and water level measurements). The 38 monitor wells in Table 2-1 show the proposed monitoring scheme for the SLF (WSRC-RD-95-1538). The LFW wells are screened in different aquifer horizons within the Steed Pond Aquifer. Most of these wells are completed in the upper portion across the water table and are designated as "D" wells. Some of the wells are installed in the middle portion of the aquifer, approximately 25 to 30 feet below the water table ("C" wells) or directly above the Crouch Branch Confining Unit ("B" wells).

Table 2-1. Proposed monitoring well scheme.

Background Well (4)	Point of Compliance Wells (9)		Plume Definition Wells (25)		
LFW-31	LFW-6R	LFW-59D	LFW-10A	LFW-63B	LFW-67C
LFW-43B	LFW 8R	LFW-61D	LFW-18	LFW-63C	LFW-67D
LFW-43C	LFW-23R	LFW-62D	LFW-21	LFW-63D	LFW-69C
LFW-43D	LFW-36R	LFW-68D	LFW-41R	LFW-64C	LFW-69D
	LFW-58D		LFW-45D	LFW-64D	LFW-71B
			LFW-47D	LFW-65B	LFW-71C
			LFW-56D	LFW-65C	LFW-71D
			LFW-60C	LFW-65D	
			LFW-60D	LFW-67B	

Several aquifer tests have been conducted at the SLF and in the A/M area. Table 2-2 summarizes the hydraulic properties of the upper, middle, and lower portions of the Steed Pond Aquifer as well as aquifer tests in the A/M area. Measured conductivities range from 5.2 ft/day

to 148.4 ft/day. The weighted average of arithmetic mean conductivities for the entire area is 32.7 ft/day.

A water table surface map (Figure 2-2) shows that groundwater flows from SRS plant north to SRS plant south across the site. The water table map was constructed using monitor well data from 2nd quarter, 1997 and from UTRC stream elevations. The horizontal gradient from north to south is approximately 0.007 ft/ft. Note that this map is based on water level data following cap installation. A small deflection in water-level contours is present beneath the cap because infiltration in this area is nearly eliminated.

Comparison of clustered wells that are screened in the upper, middle, and lower zones of the Steed Pond Aquifer allow for the measurement of vertical gradients. A comparison of water levels in March 1997 shows a downward gradient in 8 of the 11 well clusters. The difference in heads ranged from 0.0 feet at LFW 43C and 43D to 3.6 feet at LFW 63C and 63D. The average difference in heads, ignoring the large LFW 63 value, is 0.14 feet. Three wells showed an upward gradient in March 1997. The difference in heads ranged from 0.0 feet at LFW 71C and 71B to 1.0 feet at LFW 65D and 65C. The average difference in heads is 0.49 feet.

Table 2-2. Summary of aquifer tests in the SLF area.

Source	Aquifer	Type of test	Arithmetic mean (ft/day)	Geometric mean (ft/day)	Number of tests	
WSRC, 1996	Upper Steed Pond; SLF, VC Plume	Not listed	28		Not listed	SLF Specific
WSRC, 1996	Upper Steed Pond; SLF, TCE Plume	Not listed	65		Not listed	
O'Halloran, 1994	Upper Steed Pond	Slug	4.9	3.5	10	
O'Halloran, 1994	Middle Steed Pond	Slug	16.2	11.5	11	
O'Halloran, 1994	Lower Steed Pond	Slug	14.9	10.0	10	
Sirriner, 1991	Upper Steed Pond	Slug	19.5	10.7	14	
Sirriner, 1991	Middle Steed Pond	Slug	15.0	8.0	32	
Sirriner, 1991	Lower Steed Pond	Slug	14.8	14.1	16	Steed Pond Aquifer A/M Area
Marine and Bledsoe, 1985	Congaree	Slug	16.5	6.5	12	
Marine and Bledsoe, 1985	Lower Four Mile	Slug	27.7	10.0	3	
Sirriner, 1990	Congaree	Slug	14.3	5.2	8	
Sirriner, 1990	Lower Four Mile	Slug	40.0	24.6	12	
Geraghty & Miller, 1986	Congaree	Pump	46.8	43.9	7	
Geraghty & Miller, 1986	Lower Four Mile	Pump	52.2	42.9	7	
Sirriner, 1987	Congaree	Pump	148.4	66.0	4	
Sirriner, 1987	Lower Four Mile	Pump	119.1	103.6	7	

2.1.3 Groundwater recharge and discharge zones

Groundwater recharge is calculated as the net amount of precipitation less evaporation, runoff, and evapotranspiration that reaches the groundwater system. Groundwater recharge has been evaluated in several studies across SRS. In a simplistic approach, Parizek and Root (1986) calculated that 29.5% of precipitation enters the groundwater systems as recharge. Yearly rainfall in the A/M area from 1967 to 1987 ranged from 37 to 68 in/yr with an average of 47 in/yr (Beaudoin et. al., 1991). According to this approach, recharge should vary between 11 and 20 in/yr with an average of 14 in/yr. Other SLF and A/M area models have used a groundwater recharge rate of 15 in/yr (Geraghty & Miller, 1985; S.S. Papadopolous and Associates, 1986; Beaudoin et. al., 1991).

Initially, a recharge value of 15 in/yr will be assigned in the SLF model, which is consistent with the value used in the previous SLF model (Intera, 1993a).

2.1.4 Groundwater sources and sinks

The SLF area does not currently include any groundwater extraction or injection wells. Surface runoff basins on the west and south sides of the facility could serve as sources and/or sinks to the groundwater system. It appears from visual inspection that these basins would more likely serve as sources than sinks. However, data such as residence time or average depth of water in the basins are unavailable, therefore the significance of the basins on the localized groundwater system can only be estimated.

2.1.5 Areal and vertical distribution of groundwater hydraulic head potential

Groundwater flow in the SLF area is assumed to be primarily in the Steed Pond Aquifer. The Crouch Branch Confining Unit separates the Steed Pond Aquifer from the Crouch Branch Aquifer System. For the local SLF groundwater flow system, it is assumed that leakage between the Steed Pond and Crouch Branch aquifers is not significant.

2.2 Type and extent of groundwater contamination

Quarterly groundwater monitoring has identified two relatively distinct areas of groundwater contamination in the vicinity of the southern expansion of the SLF: a VC plume, and a TCE plume. These plumes developed prior to the installation of the cap, and are likely due, in part, to leachate fluxes generated by infiltration events (WSRC, 1996). The VC plume (generally between 2 and 60 ug/L with one measurement of 219 ug/L at LFW 36R in September 1997) is located along the western boundary of the landfill, with wastes in the main section of the landfill providing the putative source. Figure 2-3 shows the second quarter, 1997 isopleths for VC. Several lines of evidence suggest significant bioactivity within the vinyl chloride plume, including an absence of oxygen, low-redox conditions, an abundance of dissolved organic species, and elevated concentrations of Cl^- . Since VC is the daughter product of anaerobic TCE biodegradation, and no TCE has been detected in the vicinity of the VC plume, it is probable that the VC has occurred due to biodegradation of chlorinated solvent contamination in the main section of the SLF. WSRC (1996) hypothesized that high organic carbon content of the groundwater in this area of the site provided the electrons necessary to facilitate reductive dechlorination. These high organic carbon conditions likely also caused the anaerobic conditions which inhibit VC degradation. Biodegradation of VC is notoriously slow in the absence of oxygen. Therefore, attenuation of the VC plume is likely limited by oxygen availability.

The TCE plume (generally between 2 and 72 ug/L) is located along the southern boundary of the landfill (Figure 2-4). Wastes (e.g., solvent rags) in the southern expansion of the landfill are the likely source of the TCE plume, although TCE contamination has also been detected beneath the main section of the landfill in previous sampling events, suggesting that the main section is also a likely source. The southern (downgradient) extent of the TCE plume beneath the main section is unknown due to an absence of monitoring wells within the southern expansion. However, it is possible that continuity exists between the TCE contamination underneath the main section and the along the southern boundary. Several lines of evidence have been suggested that the natural bioactivity is limited in the vicinity of the southern TCE plume, including an absence of VC, and a prevalence of microaerophilic conditions (WSRC, 1996). The lack of bioactivity is likely attributable to a scarcity of organic carbon in this area.

For both the VC and TCE plumes, there are no data to suggest that nonaqueous phase liquids (NAPLs) are present. VC and TCE concentrations are relatively low, and no pure phases have been reported. Historical concentrations are several orders of magnitude below solubility limits for both constituents. These findings are encouraging in the context of a biosparging system, as bioremediation is not well suited to treating NAPL-contaminated aquifers. Despite a confirmed absence of NAPLs in the VC and TCE plumes, the nature and extent of the contaminant sources within the main section and southern expansion of the landfill have not been characterized.

2.3 SLF biosparging design

WSRC is in the process of implementing a biosparging system to treat the VC- and TCE-contaminated groundwater migrating from the SLF. The decision to implement the SLF biosparging system was preceded by extensive laboratory and field studies investigating the feasibility of biosparging techniques (WSRC, 1994; 1996). Specifically, these studies tested the feasibility of stimulating methanotrophic TCE biodegradation in the SLF aquifer sediments by providing air, methane, and gaseous nutrients (nitrous oxide and TEP). A variety of methane-oxidizing (a.k.a. methanotrophic) bacteria are known to be capable of cometabolizing TCE under various conditions. The feasibility of stimulating VC biodegradation by providing air and gaseous nutrients was also investigated. Together, these laboratory and field experiments determined that in situ conditions at the SLF are favorable for stimulating TCE biodegradation by sparging with air, methane, and nutrients and stimulating VC biodegradation by sparging air only. In addition, the feasibility of biosparging from horizontal wells for remediating TCE contamination was also tested and found to be favorable at M Area at SRS (U.S. DOE, 1995).

Based on the results of the feasibility studies, WSRC installed two horizontal biosparging wells along the periphery of the SLF southern expansion (Figure 2-5). Horizontal well SLH -1 was installed underneath the TCE plume at the southern boundary of the SLF, along a trend roughly parallel to the SLF boundary. Horizontal well SLH-2 was installed underneath the VC plume along the western perimeter of the southern expansion. Both wells were installed to a depth of approximately 60 feet below ground surface, within the saturated zone in the Steed Pond Aquifer. For both wells this depth is beneath the contaminated zone subject to remediation by biosparging. The in situ bioremediation optimization test determined that the aquifer properties within the vicinity of SLH-1 and SLH-2 are conducive to supporting biosparging (i.e., the high conductivity ($> 10^{-3}$ m/s) of the aquifer is favorable for supporting a flux of air, methane and gaseous nutrients from the sparging wells) (WSRC, 1996; 1997).

The objective of the biosparging system is to enhance the methanotrophic biodegradation of TCE and the aerobic biodegradation of VC. Using SLH-1 as the injection well, WSRC has proposed to sparge the TCE plume with air only. WSRC has proposed to use SLH-2 to sparge the VC plume with air and nutrients, without methane. Both the TCE and VC sparge wells are expected to be operated in a pulsed fashion, with pulses of gases emanating from the sparge wells up into the overlying contaminated zones.

Based on SLF biosparging pilot study conducted using vertical-well sparging system, WSRC (1997) recommended a range of injection compositions and schedules for sparging of the TCE plume. This injection schedule, which is shown in Table 2-3, entails a cycle of injection

pulses followed by off intervals. Air will be the primary gas injected, with small percentages of methane, nitrous oxide, and TEP also added. The rate of gaseous injection for the TCE biosparging (SLH-1) will be 240 scfm and the rate of air injection for the VC treatment system (SLH-2) will be 270 scfm.

Table 2-3. Injection schedules for the TCE plume biosparging well (SLH-1).

Schedule	Injection Interval	Off Interval	% methane	% N ₂ O	% TEP
A	8 hours per day every other day for one week	1 week	1	0.07	0.007
B	8 hours once a week	1 week	4	0.07	0.007

2.4 Site-specific conceptual biosparging model

With regard to the system chemistry, there will be two primary differences between the TCE biosparging system and the VC biosparging system. First, the TCE biosparging system will include methane in the injection well, while the VC biosparging system will not. Second, the TCE biodegradation reaction will proceed cometabolically, with methane concentration playing a substantial role, while the VC biodegradation will proceed in a dissimilar fashion, with VC acting as the primary substrate. Due to these differences, and the spatial separation of the TCE and VC plumes, the TCE and VC biosparging systems will be modeled separately using the core biosparging model.

The biosparging conceptual model can be viewed as possessing three components: 1) a ground-water flow field; 2) an injection schedule with specified pressures and injection rates; and 3) a biokinetic element that dictates TCE and VC biodegradation kinetics. From a conceptual standpoint, the performance of the TCE and VC biosparging systems will proceed as follows. At present, a fairly well-defined contaminant mass exists above each of the sparging wells. The contaminant mass can be computed from the TCE and VC isopleths shown in Figures 2-3 and 2-4. As shown in those figures, initial concentrations of VC and TCE range from 2 to 60 ppb. It is assumed that the main section and southern expansion of the SLF act as constant sources of VC and TCE, respectively. The flux of contaminant from the SLF TCE and VC plumes is a function of groundwater flow rates, and contaminant retardation (sorption). The groundwater flow regime that transports the contaminants to the biosparging well areas will be governed by the same features described in Section 2.1, as well as advection and dispersion. As indicated in Table 2-2, the hydraulic conductivity of the Steed Pond Aquifer has been estimated to be between 5 and 150 ft/d in the SLF and A/M Area.

When the biosparging commences, the injected sparge gases will begin to desaturate the previously saturated porous media overlying the sparge wells. This will occur as a result of the sparge gases displacing water. The flux of gases will form a sparged zone in which the injected gases are present in the majority of pore space in any given aquifer unit. The size and extent of the sparged zone will be a function of aquifer properties (permeability and porosity) and injection pressures. The migration of gas from the sparge well can be described in terms of injection pressures (bubbling pressures and capillary pressures), densities of the injected gases, relative (air/water) permeabilities, formation porosity, and air/water partitioning. As sparging

proceeds, the sparged zone will grow until it reaches a dynamic steady state in which each subsequent pulse results in a sparged zone of the same size as the zone resulting from the previous pulse. As biosparging proceeds, advection will continue to feed TCE and VC into the respective biosparging zones.

As with any normal application of biosparging technology, the fate of the VC and TCE within the sparging zones above will be governed by two primary processes: biodegradation and volatilization (Johnson et al, 1993; Johnson, 1998). Because VC and TCE are volatile compounds, a portion of the VC and TCE dissolved in the saturated zone will partition into the vadose zone. Air-water partitioning of VC and TCE will be a function of vapor pressures, which are described by Henry's Law constants. Injecting gases during biosparging might further facilitate some partitioning between the saturated and vadose zones, but this will be minimized by use of low flow rates and the pulsed injection schedule. With most biosparging systems, biodegradation can be maximized and volatilization minimized when low sparging rates are applied (Miller et al, 1991; Dupont et al, 1991; Johnson, 1998). The balance between biodegradation and volatilization can best be addressed through monitoring and adjustments during start-up and operation.

Consistent with existing academic conventions regarding subsurface fate and transport (Borden and Bedient 1986; Widdowson et al. 1988; Celia et al. 1989; Semprini and McCarty 1991, Clement et al. 1998), it is assumed that biodegradation of VC and TCE and consumption of oxygen in the sparged zones will proceed by Monod kinetics. That is, it is assumed that VC and TCE will biodegrade with variable order kinetics that will depend on and be coupled to biomass growth. It is implicitly assumed that only the aqueous phase VC and TCE will biodegrade. Since aquifer bacteria favor growth on surfaces, it is assumed that bacterial transport will not be a significant process during biosparging. Initial cell concentrations for methanotrophs are on the order of 10^3 cells/mL (WSRC, 1997).

In the VC biosparging system, VC biodegradation will proceed by double Monod kinetics, in which substrate utilization and biomass growth are directly coupled to oxygen consumption during biodegradation. Few models are available to describe the cometabolic biodegradation of TCE coupled to methane, but Semprini and McCarty (1991) used a triple Monod model to describe this process at a field site. This triple Monod approach links TCE biodegradation to methane biodegradation and oxygen consumption. It is assumed that the same model will apply to the TCE biosparging zone at the SLF.

Figure 2-1 Configuration of stratigraphy in the Sanitary Landfill area.

Explanation

- Monitor well information used for water table contouring

150 Water table elevation in feet, msl

TITLE		Water table elevations 4th quarter, 1991	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	ND	FIGURE: 2-2
	DRAFTED BY	PAW	
	FILE NAME	WT-97.WOR	
	DATE	9/28/98	

p:\srs\lan_land\gis\workspac\ce2.wor

Explanation

- ⊕ Monitor well
- ★ Sampled well
- 10 — Concentration contour intervals of 2, 10, and 20 ug/L

TITLE		TCE concentrations 2nd quarter, 1997	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	ND	FIGURE: 2-4
	DRAFTED BY	PAW	
	FILE NAME	TCE2.WOR	
	DATE	8/12/98

Explanation

- ★ Point of compliance monitor well
- ☼ Plume definition monitor well
- Background monitor well

TITLE		Horizontal well locations	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	ND	FIGURE: 2-5
	DRAFTED BY	PAW	
	FILE NAME	HOR_WELL.WOR	
	DATE	8/12/98	

3. Sanitary Landfill Groundwater Flow Model

The groundwater flow model was based on the previous groundwater flow model for the SLF (Intera, 1993a). Groundwater flow simulations were executed using GWVISTAS as a pre-processor for the USGS MODFLOW-96 code (Harbaugh and McDonald, 1996). The existing uniform grid was refined in the area of the horizontal wells, four layers were used to describe the Steed Pond Aquifer (as opposed to one), and limited recharge (0.13% of average recharge) was introduced in the capped landfill areas. Boundary conditions and drain elevations were systematically lowered to account for a calibration period with lower water levels.

Groundwater flow model development proceeded in a three step process, shown in Figure 3-1. First, the previous MODFLOW groundwater model was run and compared to Intera's reported results. The models matched exactly. Second, the model was re-gridded and re-layered, run, and compared to reported model results. The re-gridded and re-layered model agreed with the previous model results. A new set of calibration target points was utilized after the model was re-layered. Third, the re-gridded and re-layered model was used to simulate the capped landfill. Comparison of these results indicated that the model required calibration to match the June 1997 conditions. This process involved working with SRS staff to determine representative capped conditions. Following calibration, results from the groundwater flow model were used to establish boundaries and initial conditions for the biosparging model and the SLF solute transport model.

3.1 Model construction

3.1.1 Discretization

A variable-spaced finite-difference grid, shown in Figure 3-2, was used in the groundwater flow model. This grid has a minimum grid spacing of 25 feet to allow for adequate resolution near biosparging injection wells. The Intera (1993a) SLF groundwater model from which this model is based had uniform 100-foot grid spacing. A maximum grid spacing of 100 feet was utilized to extend the model to significant hydrogeologic boundaries. The re-gridded model has 136 rows and 148 columns (20,128 grid cells per layer). The grid is oriented to the SRS plant coordinate system which is rotated 36° 22' west of north. The lower left-hand corner of the model has coordinates (39000, 78500) in SRS plant coordinates. The upper right hand corner of the model has coordinates (49000, 88500) in SRS plant coordinates.

The re-gridded model divides the Steed Pond aquifer into four layers. The one layer of the previous model was divided so that new layers 1 and 2 are above the horizontal injection wells, new layer 3 contains the horizontal injection wells, and new layer 4 contains the portion of the Steed Pond aquifer below the wells. Two layers were included above the injection wells to allow for the representation of hydraulic gradients. For each node of the model, the saturated thickness was computed and divided into layers as a percentage of the saturated thickness (see Figure 3-3). The bottom 57% was defined as layer 4 and corresponds with B wells. Between 57% and 77% from the bottom was defined as layer 3 that corresponds with C wells. Between 77% and 87% was defined as layer 2. The top 13% of the saturated thickness was defined as layer 1. D wells are within layers 1 and 2. The Steed Pond Aquifer is bound below by the Crouch Branch Confining System.

3.1.2 Initial and boundary conditions

The initial conditions consist of hydraulic head values at each node. The initial head values consisted of the simulated hydraulic head values from the Intera (1993a) flow model. Initial conditions were updated to simulate the June 1997 capped conditions.

Boundary conditions around the edge of the model (shown in Figure 3-2) were assigned in the SLF model consistent with the types of boundary conditions used in the previous SLF groundwater model (Intera, 1993a). General head boundary conditions were assigned on the southern edge to represent UTRC, on the eastern edge to represent Tim's Branch, and on the western edge to represent an unnamed tributary. Specified heads were assigned on the northern edge consistent with regional conditions. Drain cells were assigned in the southern portion of the model to represent existing wetlands. Extraction and/or injection groundwater wells were not simulated within the area of this model.

As the general head and specified head boundary conditions reflect the heads in the transient groundwater system, these boundary conditions were updated to represent the June 1997 capped conditions. Background groundwater elevations in the SLF area not affected by the landfill capping were consistently lower in June 1997 than September 1991, the calibration period for the previous SLF model. Figure 3-4 compares 1991 versus 1997 rainfall amounts. In 1991, the four months preceding the calibration period had a total rainfall of 31.5 inches of rain while the four months preceding the 1997 calibration period totaled 14.2 inches. Table 3-1 compares the water levels in several background SLF area monitor wells. On average, June 1997 water levels were 3.74 ft lower than September 1991 conditions. Using an iterative process involving the calibration statistics, the boundary conditions in the northern portion of the 1997 SLF model were lowered 4.1 ft.

Table 3-1. Comparison of September 1991 and June 1997 monitor well water elevations.

Well ID	September 1991 water level (ft, msl)	June 1997 water level (ft, msl)	Difference
LFW 31	167.28	163.70	3.58
LFW 43D	167.78	163.88	3.90
LFW 43C	167.94	164.08	3.86
LFW 43B	166.80	163.18	3.62
		Average:	3.74

3.1.3 Model parameters

Horizontal hydraulic conductivity and recharge were the primary flow model parameters. Table 3-2 lists the flow model parameters and current values in the existing calibrated groundwater flow model using June 1997 calibration targets.

Recharge was lowered to 12 inches per year, which is consistent with the lower amount of rainfall in the four months preceding June 1997. Recharge was added at a reduced rate in the

capped area consistent with the approved efficiency of 99.87%. Recharge was increased to four times average recharge amounts in the three drainage basins on the west, east, and south sides of the SLF. Figure 3-5 shows the drainage basins that act as recharge areas.

Table 3-2. Flow parameters.

Parameter	Intera (1993a) model	HSI GeoTrans (1998) model
Horizontal hydraulic conductivity	35 ft/day - uniform	Layer 1: 21 ft/day - uniform Layer 2: 70 ft/day - uniform Layer 3: 70 ft/day - uniform Layer 4: 70 ft/day - uniform
Recharge	14 in/yr - uniform	Capped landfill: 0.03 in/yr Drainage basins: 48 in/yr Remainder of model: 12 in/yr

3.2 Flow model calibration

Calibration of a groundwater flow model refers to the process of adjusting model parameters to obtain a reasonable match between observed and simulated water levels. In general, model calibration is an iterative procedure that involves variation of hydraulic properties and/or boundary condition to achieve the best match between observed and simulated water levels. During model calibration, water level observations were used as the primary constraints for the calibrated parameter values.

3.2.1 Calibration targets

For the calibration of a steady-state flow model, the goal in selecting calibration targets was to define a set of water-level measurements that represent the average elevation of the water table at locations throughout the model domain. 42 monitor wells within the model domain were used to calibrate the flow model. All monitor wells in the SLF area with reported June 1997 measurements were used. Table 3-3 lists the calibration targets, June 1997 water levels, and the depth to the screened interval portion of the well. Figure 3-5 shows the distribution and location of these calibration targets. The target wells were screened in the upper, middle, and lower portions of the Steed Pond Aquifer.

Table 3-3. Observed water levels, June 1997 and representative model layer.

Monitor Well	Water Level	Depth to Screened Interval
LFW 6R	152.8	13.7 - 33.7
LFW 8R	148.9	13.6 - 33.6
LFW 10A	147.0	15 - 45
LFW 18	150.1	14 - 44
LFW 21	144.7	15 - 45
LFW 23R	149.1	30 - 50
LFW 31	163.2	61 - 82
LFW 36R	144.5	24.4 - 44.4
LFW 41R	142.7	27.4 - 47.4
LFW 43B	163.7	100.6 - 110.6
LFW 43C	163.9	62 - 72
LFW 43D	164.1	30 - 50
LFW 45D	151.2	9.7 - 29.7
LFW 47D	148.4	5 - 24.8
LFW 48C	148.2	Not listed
LFW 56D	144.7	4.5 - 24.6
LFW 58D	141.1	18 - 38
LFW 59D	142	16 - 36
LFW 60C	137.6	46.8 - 56.8
LFW 60D	137.9	11.4 - 31.4
LFW 61D	142.6	16 - 36
LFW 62C	142	Not listed
LFW 62D	142.2	15 - 35
LFW 63B	139.7	89.8 - 99.8
LFW 63C	139.7	59.8 - 69.8
LFW 63D	140	19.8 - 39.8
LFW 64C	139.8	57 - 67
LFW 64D	140.0	15 - 35
LFW 65B	137.6	82.6 - 92.6
LFW 65C	137.6	50 - 60

LFW 65D	137.8	14.8 - 34.8
LFW 66C	139.7	Not listed
LFW 66D	140.8	Not listed
LFW 67B	138.6	89.8 - 99.8
LFW 67C	138.1	58.8 - 68.8
LFW 67D	140.6	14.8 - 34.8
LFW 68D	141.7	14.8 - 34.8
LFW 69C	137.6	55 - 65
LFW 69D	137.5	5 - 25
LFW 71B	137.4	77.9 - 87.9
LFW 71C	137.6	54.8 - 64.8
LFW 71D	136.9	10 - 30

The primary calibration targets were the water-level measurements in wells. Less quantitative targets such as flow directions and hydraulic gradients were also used to guide the calibration effort. Discharge to wetlands and UTRC was not used because the stream data were limited and somewhat variable.

3.2.2 Calibration procedure

The existing model (Intera, 1993a) was not calibrated to capped conditions, therefore, the capped simulation required calibration. For best calibration results, calibration of a model should rely on discrete measurements to produce answers that are not subject to contouring interpretations and artifacts. In the calibration of a groundwater flow model, the use of point data eliminates the potential for interpretive bias that may result from attempting to match contoured potentiometric surfaces. In calibrating the groundwater flow model for the SLF area, the water-level calibration targets measured in monitor wells throughout the model domain were used.

The primary criterion for evaluating the calibration of the groundwater flow model was examining the difference between simulated and observed water levels at the calibration targets. A residual or model error at point i , e_i , is defined as the difference between the observed and simulated hydraulic head measured at point i :

$$e_i = h_i - \hat{h}_i$$

where h_i is the measured value of hydraulic head at point i and $\hat{h}_i$ is the simulated value at point i . A residual with a negative sign indicates over-prediction by the model (i.e., the simulated head is higher than the observed head). Conversely, a positive residual indicates under-prediction.

The calibration also seeks to minimize the residual sum of squares (RSS):

$$RSS = \sum_{i=1}^n (h_i - \hat{h}_i)^2$$

where n is the total number of calibration targets. The RSS is the primary measure of model fit. The residual standard deviation (RSTD), which normalizes the RSS by the number of calibration targets and number of estimated parameters (p) is defined as:

$$RSTD = \sqrt{\frac{RSS}{n - p}}$$

The RSTD is useful for comparing model calibrations with different numbers of calibration targets and estimated parameters. Another calibration measure is the mean of all residuals. A mean residual significantly different from zero indicates model bias.

Calibration criteria serve to guide the calibration process and serve as a basis for acceptability of the model. It is important to note that different combinations of parameter values frequently yield similar results with a groundwater flow model, such that many satisfactory combinations of parameter values may be found with respect to the calibration criteria. Ideally, calibration criteria are selected to narrow the range of parameter values. The primary calibration criteria used for the steady-state capped flow model were:

1. Reproduce water levels to within the target value. For areas where there are reliable data, this generally corresponds to matching observed heads within a mean absolute error of two feet.
2. Ensure that the spread of the water level residuals are such that the residual standard deviation, RSTD, is less than ten percent of the change in head across the model domain. This spread corresponds to a RSTD of less than $(170-140)/10$ or three feet in the site area.
3. Ensure that the frequency of water level residuals are normally distributed about a residual of zero.
4. Produce water level residuals that are randomly distributed in space.

3.3 Flow model assessment

The groundwater flow model at the SLF agrees with observed capped conditions. Lower hydraulic conductivities are used in the upper portion of the Steed Pond aquifer. Higher conductivities (i.e. 70 ft/day), that are within aquifer test predictions, are used in the lower portions of the Steed Pond aquifer. A below normal recharge of 12 inches/year was used to simulate June 1997 conditions. Water elevations immediately beneath the SLF are observed to be lower than simulated, indicating more impact from the capped conditions than simulated. The discrepancy between observed and simulated conditions beneath the landfill cap may be due to localized heterogeneity that is not taken into account in the model. Another possible explanation

is measurement error that results from changes to the datum due to extension of wells when the cap was installed. The limited amount of simulated decline of water-levels due to capping is consistent with simulations by Intera (1993a) that predicted a maximum decline of 0.5 feet in the central portion of the landfill.

The calibrated groundwater flow model provides the basis for the two-dimensional biosparging model and the three-dimensional sanitary landfill model (RT3D). The groundwater flow model provides the boundary conditions to establish the flow field in the biosparging model. The groundwater flow model provides the water elevations and groundwater velocities for RT3D.

3.4 Calibration results

Twenty-four simulations were made with the groundwater flow model to (1) verify conversion from the Intera (1993a) model, (2) obtain a calibration, and (3) assess model sensitivity. Sensitivity simulations were performed as a part of the calibration procedure (runs SLF 17 and SLF 23), therefore a formal sensitivity analysis is not repeated. Table 3-4 summarizes the flow model simulations.

The calibrated groundwater flow model provides a representative fit to observed data and inferred flow directions as shown in Figure 3-6. Figure 3-7 shows modeled versus observed hydraulic heads and a histogram of residuals. The residual standard deviation of 1.15 feet is well within the goals of the calibration. The mean error of 0.04 feet and normal distribution around 0 indicates that there is no positive or negative bias to the residuals.

Table 3-5 shows the modeled and observed water-levels at individual well locations. In general, there does not appear to be any spatial bias to the modeled results, except possibly beneath the capped portion of the SLF. The modeled decline in water-levels does not appear to be as great as the observed decline. Whether this is a result of the measurement error or the model not simulating the effectiveness of the cap accurately is unclear.

3.5 Alternative Flow Representation for Transport Sensitivity

For later use in our RT3D transport model sensitivity analyses, the SLF MODFLOW model was re-run with a uniform hydraulic conductivity value of 35 ft/day and a base recharge rate of 15 in/year. These values of conductivity and recharge may be more consistent with other flow models of the site. Additionally, the general head boundaries on the eastern and western edges were removed to simulate a no-flow (flow-line) condition on these edges, and the vertical anisotropy was reduced from 100:1 to 10:1 (vertical conductivity of 3.5 ft/day).

This representation of the aquifer system produced a head field that matched observed conditions fairly well, but did not calibrate as well as the base model, SLF 24. The alternative representation had a residual standard deviation of 1.53 feet and a residual mean of 0.24 ft, with only 3 of the target wells more than 2 feet out of calibration. While not as good as the original calibrated model, this representation was used to show the effect of a different conductivity/recharge combination on predicted TCE and VC concentrations in RT3D (presented in Section 5).

Table 3-4. Sanitary Landfill groundwater simulations.

Simulation	Layers	Rows	Columns	Description
SLF1	1	100	100	Duplication of Intera (1993) model
SLF2	1	136	148	Regridded duplication of Intera (1993) model
SLF3	4	136	148	Relayering of Intera (1993) model - 10:1 horizontal to vertical anisotropy - Residual mean increased 0.3 feet
SLF4	4	136	148	Relayering of Intera (1993) model - 3:1 horizontal to vertical anisotropy - Residual mean increased 2.3 feet
SLF5	4	136	148	Relayering of Intera (1993) model - 50:1 horizontal to vertical anisotropy - Residual mean increased
SLF6	4	136	148	Changed calibration targets to June, 1997 - 10:1 horizontal to vertical anisotropy - SLF not simulated as capped
SLF7	4	136	148	Capped landfill - Calibration targets of June, 1997
SLF8	4	136	148	Capped landfill
SLF9	4	136	148	Capped landfill - Calibration run for Kx (1,2,3)
SLF10	4	136	148	Capped landfill - Recharge reduced from 14 to 12 in/yr
SLF11	4	136	148	Capped landfill - Calibration run for Kx(1,2), Kz(1,2) and recharge
SLF12	4	136	148	Capped landfill - Lowered constant head cells in north by 3.6' based on background water levels
SLF13	4	136	148	Capped landfill - Lowered boundary conditions in east and west
SLF14	4	136	148	Capped landfill - 100:1 vertical anisotropy
SLF15	4	136	148	Capped landfill - Lowered Kx to 10 ft/day
SLF16	4	136	148	Capped landfill - Wells used to simulate capped landfill
SLF17	4	136	148	Capped landfill - Calibration run for Kx (1,2,3)
SLF18	4	136	148	Capped landfill - Added settlement basins in the south, west, and east with elevated recharge
SLF19	4	136	148	Capped landfill - Increased recharge to settlement basins

SLF20	4	136	148	Capped landfill - Increased K_x to 30 ft/day
SLF21	4	136	148	Capped landfill - Lowered recharge to 13 inches/yr
SLF22	4	136	148	Capped landfill - Lowered drains and specified heads by 1.1 ft
SLF23	4	136	148	Capped landfill - Calibration for K_x (1,2,3,4), K_z (1,2) and recharge - $K_x = 70$ ft/day for layers 2, 3, and 4
SLF24	4	136	148	Capped landfill - Using values from calibration run SLF 23

Table 3-5. Modeled and observed water levels.

Monitor Well	Simulated in Model Layer	June 1997 Water level	Simulated level	Residual
LFW 6R	1	152.8	151.5	1.3
LFW 8R	1	148.9	148.3	0.6
LFW 10A	1	147.0	150.3	-3.4
LFW 18	1	150.1	152.1	-2.0
LFW 21	1	144.7	149.0	-4.3
LFW 23R	2	149.1	149.0	0.1
LFW 31	3	163.2	162.1	1.1
LFW 36R	1	144.5	145.5	-1.0
LFW 41R	1	142.7	142.5	0.2
LFW 43B	4	163.7	162.8	0.9
LFW 43C	3	163.9	163.0	0.9
LFW 43D	2	164.1	162.9	1.2
LFW 45D	1	151.2	150.3	0.9
LFW 47D	1	148.4	147.9	0.5
LFW 48C	3	148.2	147.7	0.5
LFW 56D	1	144.7	144.7	0.0
LFW 58D	1	141.1	141.0	0.1
LFW 59D	1	142	141.2	0.8
LFW 60C	3	137.6	137.5	0.1
LFW 60D	1	137.9	137.5	0.3
LFW 61D	1	142.6	141.6	0.9
LFW 62C	3	142	141.3	0.7
LFW 62D	1	142.2	141.2	1.0
LFW 63B	4	139.7	139.4	.03
LFW 63C	3	139.7	139.5	0.2
LFW 63D	1	140	139.5	0.5
LFW 64C	3	139.8	139.6	0.1
LFW 64D	1	140.0	139.4	0.5
LFW 65B	4	137.6	137.8	-0.2

LFW 65C	3	137.6	137.8	-0.3
LFW 65D	1	137.8	137.9	-0.2
LFW 66C	3	139.7	139.8	-0.1
LFW 66D	1	140.8	139.8	1.0
LFW 67B	4	138.6	139.6	-1.1
LFW 67C	3	138.1	139.7	-1.6
LFW 67D	1	140.6	139.8	0.8
LFW 68D	1	141.7	141.1	0.6
LFW 69C	3	137.6	136.9	0.7
LFW 69D	1	137.5	136.7	0.8
LFW 71B	4	137.4	137.9	-0.5
LFW 71C	3	137.6	137.8	-0.3
LFW 71D	1	136.9	137.8	-0.9

Step 1

Run Existing SLF MODFLOW model

Compare to Intera (1993a) model,
calibrated to 4th quarter 1991

Step 2

Re-grid and re-layer SLF MODFLOW model

Add cluster wells as calibration targets

Compare to Intera (1993a) model,
calibrated to 4th quarter 1991

Step 3

Simulate June 1997 capped conditions

Calibrate to June 1997 calibration targets

Figure 3-1 Flow model construction methodology

88,500

SRS Northing
(136 rows)

78,500

39,000

SRS Easting
(148 columns)

49,000

TITLE		Sanitary landfill model grid		FIGURE: 3-2
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	ND		
	DRAFTED BY	PAW		
	FILE NAME	GRID3.WOR		
	DATE	9/28/98		

p:\srs\san_land\gis\workspac\layers.wor

TITLE		Sanitary landfill model Steed Pond aquifer layering	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	ND	FIGURE: 3-3
	DRAFTED BY	PAW	
	FILE NAME	LAYERS.WOR	
	DATE	9/29/98	

1991 Rain Data

1997 Rain Data

HSI GEOTRANS

REVISED	DATE	BY	DESCRIPTION

CHECKED BY: GWC DATE: Sept 98

APPROVED BY: PFA DATE: Sept 98

APPROVED BY: DATE:

Simulation SLF24

SLF groundwater flow model

Figure 3-4
1991 versus 1997 monthly rainfall amounts

Scale: None Date: Sept. 1998

Prepared By: HSI GEOTRANS By: PAW

Explanation

- Drainage basin (area of additional recharge)
- Calibration Targets

TITLE		Distribution and location of 1997 calibration targets	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	NDD	FIGURE: 3-5
	DRAFTED BY	PAW	
	FILE NAME	TARG_97.WOR	
	DATE	9/29/98

Explanation

Calibration Targets

150

Simulated water table elevation
in feet, msl

0

800

1600

SCALE IN FEET

TITLE

Simulated Water Table
Elevation (feet, msl)

LOCATION

Savannah River Site, Aiken, SC

**HSI
GEOTRANS**
A TETRA TECH COMPANY

CHECKED BY	ND
DRAFTED BY	PAW
FILE NAME	WT-97sim.WOR
DATE	9/29/98

FIGURE:

3-6

HSI GEOTRANS			
REVISED	DATE	BY	DESCRIPTION
CHECKED BY: GWC		DATE: Sept 98	
APPROVED BY: PFA		DATE: Sept 98	
APPROVED BY:		DATE:	

SLF groundwater flow model

Figure 3-7
Simulated versus observed heads and residual histogram

Scale: None Date: Sept. 1998
Prepared By: HSI GEOTRANS By: PAW

Simulation SLF24

4. Biosparging model

4.1 Code selection

The code utilized for this biosparging simulations is named TRAMPP (Travis and Rosenberg 1997), which is an updated version of TRAMP (Travis, 1993). The model developed with the TRAMP/TRAMPP codes will be referred to as "the biosparging model" throughout the remainder of this report. This 3-D code was developed by the Los Alamos National Laboratory (LANL) to support the TCE biosparging field demonstration conducted at the SRS M Area during 1992 to 1993 (Travis and Rosenberg 1994; 1997). The model simulates 2-phase (air, water) flow and transport of contaminants in porous media, coupled with microbial growth and contaminant biodegradation. The model flow, transport, and reaction equations are solved using an integrated finite difference, implicit time-stepping, residual-reducing Newton-Raphson algorithm. Reasons for selecting this code for modeling biosparging at the SLF include:

- It is a comprehensive, state-of-the-art model designed to simulate contaminant biodegradation in air-water systems, including biosparging systems;
- It was developed for the purpose of simulating the methanotrophic biodegradation of TCE in horizontal well biosparging demonstration conducted at SRS M Area. This same type of biosparging will be used at the SLF. Only one other known ground water fate and transport model is capable of modeling this specific reaction;
- The model has been successfully applied using the results from the M Area field test. In addition, the model has been applied at a variety of other sites, in 2-D and 3-D applications;
- The capabilities of the model are extensive, including contaminant partitioning among the saturated and vadose zones, unsteady air and water flow (i.e., can accommodate pulsed injections), rate-limited sorption, Monod-type cometabolic biodegradation, as well as nutrient limitation and predator (protozoa) grazing; and
- The author of the code, Bryan Travis of LANL, has generously supplied a copy of the code with the stipulation that it be only be applied for this SLF biosparging modeling task.

The code provided by LANL contains two sets of equations that are solved simultaneously. The first set of equations describes the 3-D flow of air and water in heterogeneous porous media. Flow is modeled by mass conservation equations plus Darcy's law for each phase. These flow equations include terms for porosity, phase saturation, fluid pressure and density, and velocity (as modified for relative permeability and viscosity). The second set of equations describes the biodegradation of the substrate (e.g. TCE and CH_4 , if desired) and the consumption of O_2 by Monod kinetics. The code is capable of using triple Monod kinetics ($\text{TCE}/\text{CH}_4/\text{O}_2$) to simulate the methanotrophic cometabolic biodegradation of TCE, and double Monod kinetics (VC/O_2) to simulate the bio-oxidation of VC. The code implicitly assumes that interphase partitioning for TCE, VC, O_2 and CH_4 occurs rapidly, such that a local equilibrium is achieved and Henry's Law coefficients are appropriate to describe this process. The model is

also capable of simulating equilibrium and rate-limited sorption, transport and biological uptake of nutrients, as well as predator (protozoa) grazing on the bacterial population involved in degrading the organic contaminants. Details of the code and the governing equations are provided in Appendix A and in Travis and Rosenberg (1997).

4.2 Model construction

As described in section 2.4 of this report, the TCE and VC biosparging systems were modeled separately because of the spatial separation between the TCE and VC plumes, and because the chemistry of the sparge gases differs between the two systems (i.e. TCE system will receive air, methane and nutrients, while the VC system will only receive air). By running separate simulations for each system, the biochemistry unique to each system was more accurately described than could have been accomplished by running a unified simulation for both systems.

In applying the code to simulate the biosparging systems at the SLF, several assumptions were made regarding biodegradation processes at the SLF. Some of these assumptions simplified the model complexity, and allowed model runs to be performed efficiently. These assumptions are as follows:

- Acclimated bacterial populations capable of mediating the desired biodegradation reactions are present in the aquifer zones targeted for biosparging;
- TCE will biodegrade wherever bacteria, O_2 , CH_4 , and TCE are present simultaneously;
- VC will biodegrade wherever bacteria, O_2 and VC are present simultaneously;
- Biokinetic parameters from relevant studies at SRS and other non-SRS sites and laboratory experiments are appropriate to describe TCE and VC biodegradation at the SLF;
- Relative permeability between air and water is adequately described by the Brooks and Corey (1964) saturation relationships;
- Two fluid phases exist in the biosparging zones: air and water. No NAPL is present in the biosparging zones;
- The average subsurface temperature in the vicinity of the SLF is $19^\circ C$ (WSRC 1996);
- Nitrous oxide and TEP will be present where ever O_2 and CH_4 are present together. Thus, nutrient-limitation will be excluded from the biosparging model;
- Since TCE concentrations at the SLF are relatively low, product toxicity will not be a factor affecting biodegradation kinetics;
- Predation will not be a significant process in the TCE and VC biosparging systems. Predation is a theoretical, unproven aspect of bioremediation engineering that has been

studied very little in the scientific literature. The vast majority of bioremediation models do not recognize this process. In addition, protozoa and their importance in the SLF aquifer sands has not been quantified. For these reasons, it is inappropriate at this time to include predation in the biosparging model; and

- The representative cross-sectional profiles can be applied along the entire length of the injection wells, therefore necessitating only one 2-D profile for each injection well.

4.2.1 Model domain

The biosparging simulations are constructed as 2-D cross-sectional planes that transect each of the horizontal sparge wells (i.e., the x-dimension is a distance in a direction perpendicular to the sparge well, and the z-dimension is depth). This approach is consistent with the application of the biosparging model for the M Area simulations (Travis and Rosenberg, 1994). Each transect (TCE and VC) is modeled separately. Figure 4-1 shows the cross-sectional profile for the TCE plume and SLH-1. Figure 4-2 shows the cross-sectional profile for VC and SLH-2. Each transect is orientated in-line with the hydraulic gradient at the site which is approximately North-South.

Horizontally, the model grid extends approximately 400 ft upgradient for the TCE cross-sectional profile and 600 ft upgradient for the VC cross-sectional profile and 400 ft downgradient of the horizontal sparge well. A horizontal grid spacing of 10 ft is utilized near the sparge well (within approximately 90 ft both upgradient and downgradient), with increased horizontal grid spacing at greater distances from the sparge well (maximum horizontal grid spacing is 25 ft). Vertically, the model domain includes the entire sequence of saturated and unsaturated sediments (Steed Pond Aquifer) overlying the sparging well, and extends down to the top of the Crouch Branch Confining Unit (which is represented as a no-flux boundary). Table 4-1 details the vertical layering for the two transect models.

Table 4-1. Vertical layering for the transect models.

	Transect Model
Unsaturated Zone	30 ft (6 layers @ 5 ft each) elev. 164 to 134 ft msl
Saturated Zone Above Sparge Zone	20 ft (4 layers @ 5 ft each) elev. 134 to 114 ft msl
Sparge Zone	20 ft (5 layers @ 4 ft each) elev. 114 to 94 ft msl
Saturated Zone Below Sparge Zone (but above the Crouch Branch Unit)	45 ft (9 layers @ 5 ft each) elev. 94 to 49 ft msl

The sparge well itself is located within the 4-foot layer in the middle of the domain.

Because a cross-sectional modeling approach is utilized, there is only one cell in the direction parallel to the sparge well. A cell width of 9 ft is assigned in the model, which represents 1% of the 900-foot length of the actual sparge well. Note that since the model only represents 1% of the length of the sparge well, only 1% of the anticipated air flow is specified in the model input data.

4.2.2 Initial and boundary conditions

The top boundary of the model domain is open to the atmosphere except for the northern most 100 ft of the TCE cross-sectional profile that is simulated as capped. The bottom boundary (The Crouch Branch Unit) is modeled as an impermeable (no-flow) barrier. The upgradient and down-gradient boundaries are assigned as fixed boundaries (i.e., do not change with time), and initial pressures are assigned such that hydrostatic conditions are represented. The hydraulic gradient of 0.005 ft/ft was established consistent with the SLF groundwater flow model. This is similar to the gradients observed at each transect location.

The initial O₂ concentration is set at 0 mg/L in the VC plume, and at 2 mg/L in the TCE plume area. These concentrations are consistent with those reported by WSRC (1996). Permeability is set to 10 darcys in the horizontal direction, and a 10:1 vertical anisotropy is assumed. This horizontal permeability is similar to a water hydraulic conductivity of 35 ft/day (Freeze and Cherry, 1979, p.29) which is a conservative estimate based upon the capped flow model and is consistent with previous SLF flow models. Other relevant hydrogeologic input parameters used in the biosparging model are specified in Table 4-2. These parameters are appropriate for medium-grained sand similar to the type found in the zones intended for sparging at the SLF. Chemical parameters necessary for the model are provided in Table 4-3. Due to the low organic carbon content of the SLF aquifer sands (WSRC 1996), sorption of TCE and VC is assumed to be insignificant over the time-scales expected for the TCE and VC biosparging systems. Consequently, sorption is not included in the biosparging model.

Table 4-2. Baseline hydrogeologic parameter values for biosparging model (From Travis and Rosenberg, 1994).

Initial Saturation (%)	27
Coefficients for Brooks-Corey (1964) Formulation for relative permeabilities and matric potentials as a function of water saturation	
Bubbling Pressure (kPa)	10
pore-size distribution index (0-1)	0.62
Irreducible saturation (%)	25

Table 4-3. Baseline chemical parameter values for biosparging model (values are appropriate for the average temperature in the SLF subsurface - 19°C).

	VC	TCE	CH ₄ *	O ₂ *
Henry's Law coefficient (dimensionless)	0.87 **	0.28 **	27	29
Water Diffusivity (D _w) (cm ² /s)	8.5 ⁻⁶ +	10 ⁻⁵ *	10 ⁻⁵	10 ⁻⁵
Air Diffusivity (D _a) (cm ² /s)	0.11 ++	0.1 *	0.23	0.14

* Values from Travis and Rosenberg (1997).

** Value by the method of Gossett (1987).

+ Value calculated by the method of Hayduk and Laudie (1974).

++ Value calculated by the method of Fuller et al. (1966).

The baseline injection schedule for the TCE sparging simulations was Schedule A, which was previously shown in Table 2-2. This same injection schedule was used for the VC sparging simulations, except that methane or nutrients were excluded from the injections. The baseline injection rates are 240 and 270 scfm for SLH-1 and SLH-2, respectively.

The initial concentrations of TCE and VC were assigned conservatively based upon quarterly sampling results in 1996 and 1997. The TCE concentration (shown in Figures 2-4 and 5-2) was assigned at 25 µg/L in a slug that extended 300-ft upgradient and 25 ft downgradient from the sparge well at a depth from 109 ft to 139 ft. The VC concentration (shown in Figures 2-3 and 5-3) was assigned at 25 µg/L in a slug that extended 500-ft upgradient and 108 ft downgradient from the sparge well at a depth from 109 ft to 139 ft. These concentration profiles conservatively define TCE and VC plumes.

4.2.3 Model parameters

The biokinetic reaction equations used to model contaminant biodegradation are provided in Appendix A. None of biokinetic parameter values in these equations have been directly measured for the site-specific bacteria at the SLF. Therefore, the same parameter values as those used by Travis and Rosenberg (1997) for the M Area biosparging demonstrations were utilized for the TCE simulations. Biokinetic parameter estimates for the VC simulations were

determined from relevant studies on aerobic biodegradation of vinyl chloride and other hydrocarbons. Biokinetic parameter values are shown in Table 4-4 (TCE parameters were only used in TCE simulations, and VC parameters were only used in VC simulations). Note that these parameters are assumed to reflect an in-situ temperature of 19° C , and are assumed to be constant in time and space. Note also that not all the biokinetic parameters appearing in the governing equations (Appendix A) are included in Table 4-4. Parameters related to processes that will not be simulated in the biosparging zone (e.g. nutrient-limitation, product toxicity, and predation) were excluded from Table 4-4.

Table 4-4. Baseline biokinetic parameter values used in biosparging simulations.

Parameter	Symbol	Value	Reference
Initial value of microbes (bacteria)	M_{TCE} M_{VC}	1×10^{-12} g/mL 1×10^{-9} g/mL	Travis and Rosenberg 1997 and Norland et al. 1987
Background growth rate of microbes	k_c	3×10^{-7} g cells/g substrate/s	Travis and Rosenberg 1997
Microbial half saturation Concentration	K_{TCE} K_{CH_4} K_{VC} K_{O_2}	0.1 mg/L 0.4 mg/L 0.79 mg/L 0.1 mg/L	Chang & Alvarez-Cohen 1995 Graham et al. 1993 Bradley and Chapelle 1998 Semprini and McCarty 1991
Max. rate of substrate Utilization	K_{TCE} K_{CH_4} K_{VC}	5×10^{-5} g TCE/g cells/s 3×10^{-5} g CH ₄ / g cells/s 1.4×10^{-5} g VC/g cells/s	Chang & Alvarez-Cohen 1995 Graham et al. 1993 Bradley and Chapelle 1998; Clement et al. 1998
Microbial yield per unit Growth substrate consumed	Y_{CH_4} Y_{VC}	0.5 g cells/g CH ₄ 0.1 g cells/g VC	Semprini and McCarty 1991 Clement et al. 1998
Mass ratio of O ₂ consumed per mass substrate consumed	F_{TCE} F_{CH_4} F_{VC}	0.3 g O ₂ /g TCE 4.0 g O ₂ /g CH ₄ 1.3 g O ₂ /g VC	Travis and Rosenberg 1997 Travis and Rosenberg 1997 Weidemeier et al. 1996
Microbial decay rate	k_d	1.5×10^{-6} /s	Semprini and McCarty 1991

4.3 Biosparging model simulations

4.3.1 Base case simulation

Several simulations were performed with the biosparging model using the previously described model domain, initial and boundary conditions, and biokinetic parameters. The developer of the code, Dr. Bryan Travis of Los Alamos National Laboratory, was very helpful in establishing the initial model setup. Separate simulations were performed to predict biodegradation within the TCE and VC plumes and the radius of influence extending from the respective sparge wells. The radius of influence predicted by these simulations was used as an initial condition for the SLF transport model simulation (Section 5).

The biodegradation at SLH-1 in the TCE plume was simulated first with no action and then under the scheduled methane and nutrient injection. When no action is taken, the TCE plume is subject to volatilization, advection, dispersion, sorption, and anaerobic degradation. Note that conditions at the SLF (low organic carbon) will minimize or eliminate sorption effects. Figure 4-3 shows the movement of an initial TCE slug of 25 ug/L. The scheduled methane and nutrient injection significantly enhanced TCE removal through biodegradation and air-water partitioning. TCE within the radius of influence of the injection well is biologically remediated to below 1 ug/L within 100 days. Figure 4-4 shows the movement and biodegradation of an initial TCE slug of 25 µg/L. Figure 4-5 shows the corresponding methane concentrations under the scheduled injections. The biological removal of TCE and the presence of methane strongly correlate and illustrate the radius of influence of SLH-1. The simulated radius of influence is therefore determined to be between 50 ft and 70 ft after 300 days, depending upon depth.

The biodegradation at SLH-2 in the VC plume was also simulated with no action and then under the scheduled air injection. When no action is taken, the VC plume is subject to volatilization, advection, dispersion, sorption, and oxygen-limited aerobic degradation. Note that conditions at the SLF (low organic carbon) will minimize or eliminate sorption effects. Figure 4-6 shows the movement of an initial VC slug of 25 µg/L. The scheduled air injection provides an oxygen source that significantly enhances the biodegradation of VC. Figure 4-7 shows the movement and biodegradation of an initial VC slug of 25 µg/L. The VC within the radius of influence is reduced by the operation of the injection well down to a concentration between 1 and 5 µg/L after 200 days. Some VC mass was initially south of the injection well and is not within the well's radius of influence. The predicted radius of influence is approximately 60 feet.

4.3.2 Sensitivity analysis

The sensitivity analysis was conducted using an approach similar to that described by Travis and Rosenberg (1997). The sensitivity of the enhanced removal of VC and TCE due to microbial degradation was evaluated through a series of simulations in which biokinetic parameters of the system will be varied one at a time. The parameters included in this analysis will be k_{TCE} , k_{CH_4} , K_{CH_4} , k_{VC} , and K_{VC} . Using the TCE parameters as an example, the change in simulated efficiency of biosparging well was defined as:

$$\text{Change in Efficiency} = \left(\frac{\Delta TCE_{\text{sensitivity}} - \Delta TCE_{\text{base}}}{\Delta TCE_{\text{base}}} \right)$$

where ΔTCE is the total TCE removed by biosparging. The base subscript refers to the set of baseline conditions defined in the previous section.

Nine simulations have been made with the biosparging model to evaluate a range of expected biodegradation efficiencies with the remedial systems for the TCE and VC plumes. Various biokinetic and hydraulic parameters were varied to test model sensitivity and evaluate uncertainty in the predicted results. Table 4-5 shows the change in removal efficiencies based upon the sensitivity simulations. In each sensitivity case, a more conservative value was used which would reduce removal efficiency except for the case in which the initial bacteria concentrations in the VC plume simulation were increased by an order of magnitude.

Consistent with expectations, the biosparging model is most sensitive to the no action case, indicating that TCE and VC removal would be significantly less in the absence of biosparging. The TCE model is sensitive to the half saturation for methane and the methane utilization, which indicates that TCE removal is sensitive to the amount of available methane.

Table 4-5. Sensitivity Simulations for biosparging model input parameters.

	Change in parameter	Change in efficiency after 350 days
TCE Simulations		
input parameter:		
No injection	No air, methane and/or nutrient injection	- 27.1%
Anisotropy	Increased anisotropy from 10:1 to 100:1 (conservative assumption)	- 0.3%
BIGKA	Increased the half saturation for methane from 0.4E-6 g/mL to 0.4E-5 g/mL (conservative assumption)	- 16.2%
Predation	Sensitivity to predation (conservative assumption)	- 1.5%
SMKA	Decreased methane utilization from 3E-5 g/g/s to 3E-6 g/g/s (conservative assumption)	- 16.9%
SMKB	Decreased TCE utilization from 5E-5 g/g/s to 5E-6 g/g/s (conservative assumption)	- 6.2%
BIGKN	Increased the half saturation for nutrients from 1.0E-6 g/mL to 1.0E-5 g/mL (conservative assumption)	- 7.7%
VC Simulations		
input parameter:		
No injection	No air injection	- 6.9%
Initial bacteria	Increased the initial bacteria concentration from 1.0E-9 g/mL to 1.0E-8 g/mL (non-conservative assumption)	+ 1.3%
BIGKA	Increased the half saturation for methane from 0.8E-6 g/mL to 0.8E-5 g/mL (conservative assumption)	- 0.5%
SMKA	Decreased VC aerobic utilization from 1.4E-5 g/g/s to 1.4E-6 g/g/s (conservative assumption)	- 0.5%

4.4 Biosparging model assessment

The biosparging simulations are a simplified representation of the complicated multiphase flow transport system in the vicinity of the sparging wells. The potential range of biokinetic parameters, as well as system heterogeneity, lead to model results with a high level of uncertainty. The model results show that both SLH-1 and SLH-2 are effective in treating the TCE and VC plumes, respectively. Both treatment programs are markedly more effective than natural attenuation. The placement of the biosparging well upgradient of a sizable portion of both the TCE and VC plumes is the largest limitation to the overall effectiveness of the overall treatment program. The overall time required for operation is suggested to be a function of the travel time for the contaminants to reach the biosparging zone. Based on these travel times and

all the model assumptions stated previously, a 5 year operation period is expected for the VC plume, and 4 year operation period is expected for the TCE plume. A monitoring well network with upgradient and downgradient wells is suggested (see Section 6.3) to monitor system performance.

Domain for the TCE cross-sectional profile

TITLE		Biosparging model cross-sectional profile location for TCE	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	ND	
	DRAFTED BY	PAW	
	FILE NAME	tceXSECT.WOR	
	DATE	9/15/98	
FIGURE:			4-1

Domain for the VC cross-sectional profile

TITLE		Biosparging model cross-sectional profile location for VC	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	ND	FIGURE: 4-2
	DRAFTED BY	PAW	
	FILE NAME	vcXSECTS.WOR	
	DATE	9/15/98

Contour intervals of 1, 5, and 25 ug/L of TCE
Injection well located at X=400, Z=109 (Note: no injection in this simulation)

Figure 4-3. TCE base case modeling results for no injection.

North End

0 Days

South End

100 Days

200 Days

300 Days

Contour intervals of 1, 5, and 25 ug/L of TCE
Injection well located at X=400, Z=109

p:\ers\lan_land\surfer\tr22_tce.srf

Figure 4-4. TCE bioparging modeling results for scheduled methane injection.

Figure 4-5. TCE biosparging modeling results showing methane concentrations.

North End

0 Days

South End

100 Days

200 Days

300 Days

Contour intervals of 1, 5, and 25 ug/L of VC

Injection well located at X=600, Z=109 (Note: no injection for this simulation)

Figure 4-6. VC base case modeling results for no air injection.

Figure 4-7. VC base case modeling results for scheduled air injection.

5. Sanitary Landfill Solute Transport Model

5.1 Code selection

The flow and transport of TCE and VC through a bioactive zone requires sophisticated numerical modeling. RT3D, a modular computer code for simulating reactive multi-species transport in three-dimensional groundwater systems, was selected to simulate groundwater flow and transport. RT3D (Clement, 1998) is one of the best available models for simulating contaminant fate and transport from the landfill, through the bioactive zone, and downgradient of the bioactive zone. The RT3D code is unique in that it includes an implicit reaction solver that makes the code sufficiently flexible for simulating various types of chemical and microbial reaction kinetics. RT3D uses MODFLOW to develop the groundwater flow field, similar to the method used by MT3D (Zheng, 1990). RT3D is therefore highly compatible with the groundwater flow model, which uses MODFLOW.

The RT3D code includes two pre-programmed reaction modules that can be used to simulate aerobic and anaerobic breakdown of chlorinated solvents and a pre-programmed reaction module for a double Monod model. The intended purpose of the double Monod model is to simulate the reaction between an electron donor (e.g. VC) and an electron acceptor (e.g. O_2) mediated by actively growing bacteria cells living in both aqueous and soil phases. The modules assume that the degradation reactions occur only in the aqueous phase.

RT3D is used to predict the effectiveness of the two horizontal biosparging wells. Isopleths for TCE and VC are generated from RT3D predictions. The predictions are also used to provide recommendations for monitor well locations.

5.2 Model construction

The RT3D solute transport model is based on the MODFLOW groundwater flow model described in Section 3. The calibrated flow model provides the flow field (groundwater heads and fluxes) for the transport model. Model discretization is not changed, but chemical transport is only modeled in the area of the sanitary landfill and south to the modeled wetlands and stream (Figure 5-1). "Windowing" the analysis in this manner is more efficient and reduces simulation times. In the transport model, advection, dispersion, and chemical biodegradation processes are simulated. As a conservative assumption, sorption is not modeled, and diffusion is neglected because it is much smaller than macroscopic dispersion. The model is not capable of simulating volatilization. As an initial assumption, the effective porosity of the aquifer is set to 20% and the longitudinal dispersivity is set to 50 feet (maximum Peclet number of 2 at 100 ft grid spacing). The horizontal transverse dispersivity and the vertical dispersivity are set to one tenth of the longitudinal dispersivity, or 5 feet. All RT3D parameter values are listed in Table 5-1.

Table 5-1. Base case parameters in the RT3D SLF model.

Parameter	Value
Effective porosity	20%
Longitudinal dispersivity	50 ft
Horizontal Transverse dispersivity	5 ft
Vertical dispersivity	5 ft
First-order TCE decay rate in bioactive zone	0.08 d ⁻¹
Specific utilization rate of VC by microbes	1.25 d ⁻¹
Concentration of microbes utilizing VC	1 µg/L
Half-saturation constant for VC	790 µg/L
Half-saturation constant for oxygen	100 µg/L

Two constituents of concern are simulated in separate model runs: TCE and vinyl chloride. The initial concentrations for TCE (Figure 5-2) and vinyl chloride (Figure 5-3) in the upper two model layers were based on contour maps of average 1996 and 1997 concentrations (from quarterly monitoring). The initial concentrations of TCE and vinyl chloride are zero in model layers 3 and 4. No additional sources of these constituents are simulated, representing no further contributions from the SLF. This assumption is made because the highly efficient cap prevents virtually any percolation through the SLF. Only dissolved-phase TCE and vinyl chloride transport is simulated, as with the biosparging model in Section 4.

The upstream-weighted finite-difference method is used to solve the advection-dispersion equation for transport of dissolved TCE and vinyl chloride. RT3D uses adaptive time stepping to keep the solution stable and to keep the Courant number less than 1.0 (Courant number = $V\Delta t/\Delta l$). The biodegradation processes for these two constituents are handled differently, as explained in the next two sub-sections.

5.2.1 TCE biodegradation

Injection of air, methane and nutrients will stimulate the methanotrophic biodegradation of TCE in the sparge zones emanating from SLH-1. The biosparging model (Section 4) modeled this process using a sophisticated expression for triple Monod kinetics (TCE loss coupled to methane and oxygen consumption, and biomass growth coupled to methane). RT3D does not have the capability to explicitly model this TCE biodegradation coupled with methanotrophic growth. However, RT3D does have the capability to model first-order biodegradation of TCE. Consequently, a first order approximation is used to describe TCE biodegradation in the sparge zone created by SLF-1. Within this zone, first-order decay of TCE is assumed, as described by:

$$\frac{dC_T}{dt} = -k_T C_T \quad (5-1)$$

where C_T is the concentration of TCE [M/L³] and k_T is the first order rate constant for TCE degradation [T⁻¹]. Outside the TCE degradation zone, no decay is simulated for TCE — only dispersion and advection.

The methane and nutrients are introduced into the aquifer through the biosparging well SLH-1, which is in model layer 3. The injected air mixture moves outward and upward from the horizontal well to create the degradation zone. As an initial assumption, the TCE degradation zone extends 60 feet from the well in layers 1 through 3 (Figure 5-4). The 60-foot radius is based on the biosparging model results described in Section 4 and on a rule of thumb for sparge systems: the horizontal radius of influence is approximately equal to the depth below the water table. The TCE decay rate, k_T , is initially assumed to be 0.08 d^{-1} , based on a site-specific estimate of methanotrophic TCE biodegradation (Figure 3-10 in WSRC, 1994, adjusted for temperature).

5.2.2 Vinyl chloride biodegradation

Unlike TCE, aquifer bacteria can biodegrade vinyl chloride as a primary energy source. Therefore biodegradation of vinyl chloride can be described by double Monod kinetics. RT3D is capable of explicitly modeling this process. Consequently, a double Monod model is assumed, with vinyl chloride acting as an electron donor for the microbes, and oxygen acting as the electron acceptor (Clement et al, 1998):

$$\frac{dC_v}{dt} = -\mu C_x \left(\frac{C_v}{K_v + C_v} \right) \left(\frac{C_o}{K_o + C_o} \right) \quad (5-2)$$

where C_v , C_o , and C_x are the aqueous concentrations of vinyl chloride, oxygen, and bacterial cells respectively $[\text{M/L}^3]$, μ is the specific utilization rate $[\text{T}^{-1}]$, K_v is the half-saturation constant for vinyl chloride (M/L^3) and K_o is the half-saturation constant for oxygen $[\text{M/L}^3]$. This process also results in oxygen uptake given by:

$$\frac{dC_o}{dt} = Y_{o/v} \frac{dC_v}{dt} = -Y_{o/v} \mu C_x \left(\frac{C_v}{K_v + C_v} \right) \left(\frac{C_o}{K_o + C_o} \right) \quad (5-3)$$

where $Y_{o/v}$ is the amount of oxygen utilized per unit of vinyl chloride utilized. This coefficient, determined from stoichiometric relationships, is 1.3 (Weidemeier, 1996).

Since this process can be limited by the availability of oxygen, the model also simulates the transport of oxygen. Initially, an anaerobic condition is imposed over the area of contamination due to bacterial uptake (Figure 5-5). Elsewhere, the concentration is initially set to $5000 \text{ } \mu\text{g/L}$, and the concentration of oxygen in precipitation recharge is also set to $5000 \text{ } \mu\text{g/L}$. Under actual site conditions, the concentration of dissolved oxygen in the background groundwater may be closer to the saturated value of $9200 \text{ } \mu\text{g/L}$, however, $5000 \text{ } \mu\text{g/L}$ is used as a conservative, lower-bound initial assumption. Another conservative assumption is that the anaerobic zone extends into layer 3 — deeper than the area of contamination.

A zone of constant oxygen concentration is simulated near well SLH-2. Like the TCE degradation zone, this oxygenated zone is assumed to extend 60 feet from the well in layers 1-3 (Figure 5-6) (see section 5.2.1 for rationale for selecting 60 foot zone of influence). In this zone, the concentration of oxygen due to biosparging is set to $9000 \text{ } \mu\text{g/L}$, which is near the saturated dissolved oxygen concentration.

The bacterial concentration is assumed to be at a steady-state constant value, initially set to 1 $\mu\text{g/L}$ (consistent with the biosparging model). Though the bacterial concentration would grow as a result on vinyl chloride and oxygen uptake, and a portion of the bacterial population would move along with groundwater flow, these processes are not easily quantified with available information. Note that neglecting bacterial growth as a result of biodegradation is a conservative assumption.

The initial values used for the specific utilization rate and the half-saturation constants were taken from relevant literature. The specific utilization rate, μ , is set to 1.25 d^{-1} (representative of bacterial degradation of hydrocarbons, Clement et al, 1998), the vinyl chloride half-saturation, K_V , is initially 790 $\mu\text{g/L}$ (extrapolated from Bradley and Chapelle, 1998), and the oxygen half-saturation, K_O , is 100 $\mu\text{g/L}$ (Clement et al, 1998; Semprini and McCarty, 1991). Note that these values are consistent with those used in the biosparging model.

5.3 Sanitary Landfill solute transport model simulations

Several simulations were made with the Sanitary Landfill Solute Transport model to evaluate a range of expected biodegradation efficiencies with the remedial systems for the TCE and vinyl chloride plumes. Various degradation and transport parameters were varied to test model sensitivity and evaluate uncertainty in the predicted results.

5.3.1 TCE transport and decay

Base Case

With base case (initial) values for all parameters, the TCE plume moves toward the southern wetlands, with the maximum aquifer concentration decreasing to 1 $\mu\text{g/L}$ in 800 days. Figure 5-7 shows the plume movement over the first 400 days. Note that some of the initial TCE plume is initially south of the degradation zone and is therefore not subject to decay. The amount of mass removed by biodegradation is shown in Figure 5-8.

No Degradation (Tracer) Case

In another model run, the biodegradation rate is set to zero to show what would happen under a "no action" alternative with the contaminant acting as a conservative tracer. Due to dispersion, the maximum concentration in the plume decreases, but not as fast as in the base case. The plume movement over time is shown in Figure 5-9.

Sensitivity to Decay Rate Constant

In another simulation, the decay rate, k_T , is reduced by a factor of 10 to 0.008 d^{-1} in the TCE degradation zone. This results in less mass removal (Figure 5-8) and a plume movement similar to the no-degradation case (Figure 5-10).

Sensitivity to Effective Porosity

The effective porosity is reduced from 20% to 15% in another simulation. As a result of this change, solute moves faster through the aquifer and has less opportunity to decay (Figure 5-8). Figure 5-11 shows the plume movement for this case.

Sensitivity to Dispersivity

Another sensitivity simulation is conducted with all dispersivities reduced to 20% of their original value (10 feet longitudinal, 1 foot transverse, maximum Peclet number of 10). This keeps the plume from spreading as much as it crosses the degradation zone, leading to a higher rate of removal (Figure 5-8), but slightly higher peak concentrations at later times (Figure 5-12).

Sensitivity to Alternative Flow Representation

Finally, a sensitivity simulation is made with base case transport parameters, but with an alternative representation of the flow field (from Section 3.5). The alternative flow field, which does not calibrate as well as the base case flow field, was created using a uniform hydraulic conductivity of 35 ft/day and a base recharge rate of 15 in/yr. In this simulation, slightly more TCE mass is degraded (Figure 5-8), and the plume movement (Figure 5-13) is similar to that of the base case.

5.3.2 Vinyl Chloride transport and decay

Base Case

Using initial parameter values for all transport and double-Monod degradation parameters, the vinyl chloride plume is reduced to 1 $\mu\text{g/L}$ in about 800 days. The plume movement is shown in Figure 5-14. The VC degradation rate is largely the result of the assumed initial bacterial concentration and the assumed values for μ , K_v , and K_o . Some of these assumptions are addressed in sensitivity simulations discussed below. Figure 5-15 shows the vinyl chloride mass removal for the base case and the sensitivity simulations.

No Remediation Case

Another simulation is run to show the effect of the "no action" alternative. In this simulation, the constant concentration zone for oxygen at SLH-2 is not modeled. The result is only slightly less mass removal (Figures 5-15 and 5-16). Note that biodegradation still occurs in this simulation whenever oxygen is present (unlike in the TCE simulations where degradation is confined to a small zone around SLH-1). Transport of oxygen into the zone of vinyl chloride contamination results from both dispersion from the surrounding oxygen-rich groundwater and recharge of oxygen-rich groundwater.

No Degradation (Tracer) Case

For comparison purposes, a simulation is made with no biological uptake of chemicals ($\mu=0$). This simulation, which transports the vinyl chloride plume as a conservative tracer, results in a much larger plume size than the base case (Figure 5-17).

Sensitivity to Low Oxygen conditions

A sensitivity simulation was made with an initial oxygen concentration of zero throughout the aquifer and an oxygen concentration of zero for precipitation recharge. With these assumptions, the only source of oxygen in the model comes from the biosparge well SLH-2. This conservative case represents a scenario where the entire background oxygen supply is used by microbes that do not degrade vinyl chloride. In this case, the degradation of VC is more often oxygen limited and the rate of VC utilization is reduced (Figure 5-15). Figure 5-18 shows the plume movement for this simulation.

Sensitivity to Bacterial Concentration

Perhaps the most important parameter affecting the rate of biodegradation on vinyl chloride is the microbial concentration, C_x . An initial estimate of 1 $\mu\text{g/L}$ (aqueous) was used for the base case. In a sensitivity simulation, the bacterial concentration is raised to 30 $\mu\text{g/L}$. With the high value for C_x (Figures 5-15 and 5-19), the plume disappears much faster than in the base case. The distinct difference between this sensitivity run and the base case is a result of the large difference (~ 1.5 orders of magnitude) in bacterial concentrations simulated. Note that the specific utilization rate, μ , would have the same sensitivity to a parameter change (see equation 5-2), but μ is based on literature values and is not likely to vary over such a wide range.

In order to get an adequate understanding of the quantity, type, and degradation effectiveness of the microbial population, more site-specific data are needed. Not that measurement of system effectiveness using monitor wells (as proposed in Section 6) would provide a good indication of microbial characteristics.

Sensitivity to Vinyl Chloride Half-Saturation Constant

There is also uncertainty in the half-saturation constant K_v , a measure of the bacterial affinity for vinyl chloride as an electron donor. In a sensitivity simulation K_v is raised by a factor of 10 to 7900 $\mu\text{g/L}$, to simulate a weaker bacterial affinity for vinyl chloride. As shown in Figures 5-15 and 5-20, this simulation results in a more slowly-decaying plume. Note that the half-saturation constant for oxygen, K_o , is better known than K_v and is not varied in this sensitivity analysis.

Sensitivity to Effective Porosity

As with TCE, a simulation is made to show the effect of lower porosity (15%) on the transport and degradation of vinyl chloride. The faster solute movement results in slightly more dispersive mixing and slightly more degradation, as shown in Figures 5-14 and 5-20.

Sensitivity to Dispersivity

Another sensitivity simulation analyzes the effect of dispersivity uncertainty on vinyl chloride transport and decay. Slightly less degradation occurs in this case due to decreased mixing between the vinyl chloride and oxygen (Figure 5-15). The plume stays smaller with higher peak concentrations (Figure 5-22) as a result of the decreased dispersion.

Sensitivity to Alternative Flow Representation

Finally, a sensitivity simulation is made with base case transport parameters, but with an alternative representation of the flow field (from Section 3.5). The alternative flow field, which does not calibrate as well as the base case flow field, was created using a uniform hydraulic conductivity of 35 ft/day and a base recharge rate of 15 in/yr. In this simulation, slightly more vinyl chloride mass is degraded (Figure 5-15), and the plume movement (Figure 5-23) is similar to that of the base case.

5.4 Sanitary Landfill solute transport model assessment

The Sanitary Landfill Solute Transport model simulations effectively show contaminant movement and decay over time in three dimensions. Since RT3D does not model multi-phase flow or complex reactions, some simplifying assumptions are required to model the biological processes affecting TCE and VC degradation, as discussed in Sections 5.2.1 and 5.2.2. In

particular, the TCE degradation process is simplified to a first-order decay formulation in the zone of influence for SLH-1. Degradation of VC is simplified by assuming a constant, steady-state bacterial concentration in the double Monod model. Unlike the biosparging models, volatilization is not considered.

The base case simulation for the TCE plume predicted that the biosparging system would effectively remediate nearly 35% of TCE mass in the aquifer after one year of biosparging system operation. The model predicted that additional removal efficiency would be constrained by groundwater transporting the TCE out of the zone of influence and the sparge well. In the vicinity of the sparging well, the model predicted that the groundwater would be completely remediated after one year operation of the sparging system. However, downgradient of SLH-1 it was predicted a small, dilute TCE plume would remain naturally attenuating beneath the edge of the wetlands.

Note that these results are in general agreement with the biosparging model results. Both models predict that TCE contaminated groundwater upgradient of the sparge zone will be remediated within a year, but that groundwater flow will reduce efficiency by drawing TCE out of the zone of influence. These results indicate that system performance will be governed, in part, by groundwater flow rates.

The base case results for vinyl chloride indicates degradation rates similar to that of TCE, but the location of the degradation is not constrained to the sparge well radius-of-influence. Because degradation can take place wherever there is oxygen, and because the model allows oxygen into the VC plume (by dispersion and recharge), the simulation predicts little effect of adding oxygen by the sparge well.

Although these results might suggest that only minimal biosimulation can be achieved by air-sparging in the VC plume, another factor not considered by model could change this outcome. The high dissolved organic content of the VC plume (WSRC, 1996) likely exerts a significant oxygen demand that reduces O_2 available for VC biodegradation. Since this additional oxygen demand is not simulated in this model, the effect of air-sparging on biostimulation in the VC plume will likely be more substantial than predicted here. In addition, a significant quantity of VC will be removed due to air-water partitioning, and this process is not described by this model.

Contrast these results with those from the biosparging model results that show markedly increased degradation around the sparge well. This difference is probably due to the more sophisticated biological representation in the biosparging model (which allows for bacterial growth and decay) and the simulated volatilization of VC in biosparging.

For TCE, the most important parameter affecting biodegradation efficiency is the first-order decay rate k_T . As shown in a sensitivity simulation, slower decay rates can significantly reduce the effectiveness of the biosparging system. However, the rate chosen for the base case (0.08 d^{-1}) was derived from SLF soil experiments, and is likely to be a reasonable estimate. The decay rate is related to the concentrations of methane, bacteria, and nutrients in the bioactive zone.

Similarly, the most important variables affecting VC degradation are bacterial concentration, specific utilization rate, and the VC half-saturation constant. While in the base

case simulation the VC plume is degraded in a time frame of a few years, other plausible values for certain variables could significantly increase the rate of degradation.

According to these simulations, the bioremediation system is more effective for TCE removal than for VC removal, as compared to a "no action" alternative. This result is primarily due to a different simulation approach for the two constituents. For TCE, biodegradation can only occur in the zone of influence around SLH-1. Conversely, VC degradation can occur anywhere in the aquifer, provided there is oxygen present. Because oxygen is naturally introduced to the VC plume (via recharge and mixing with background groundwater), the oxygen added by the sparge system is only marginally effective for biostimulation. Unlike TCE, the VC plume begins degrading even before it passes through the bioremediation system. In addition, the removal mechanisms not described by these simulations (i.e. air-water partitioning) will cause significant VC removal.

Transport Not Simulated

File: lcbund.srf
Drafted: Greg Council 9/16/98

Figure 5-1
Area Where Transport
is Simulated with RT3D

SRS
Sanitary
Landfill

Concentration Scale in ppb

File: Ini-TCE.srf
Drafted: Greg Council 9/16/98

**SRS
Sanitary
Landfill**

**Figure 5-2
Initial Concentration
of TCE**

Concentration Scale in ppb

File: Ini-VC.srf
Drafted: Greg Council 9/16/98

**HSI
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A TETRA TECH COMPANY

**SRS
Sanitary
Landfill**

**Figure 5-3
Initial Concentration
of Vinyl Chloride**

TCE Degradation Zone

Figure 5-4
TCE Degradation Zone

File: TCE-Zone.srf
Drafted: Greg Council 9/16/98

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A TETRA TECH COMPANY

SRS
Sanitary
Landfill

Concentration Scale in ppb

File: Ini-OX.srf
Drafted: Greg Council 9/16/98

**SRS
Sanitary
Landfill**

**Figure 5-5
Initial Concentration
of Dissolved Oxygen**

Constant Oxygen Concentration Zone

Figure 5-6
Zone of Constant Dissolved
Oxygen Concentration

File: VC-Zone.srf
 Drafted: Greg Council 9/16/98

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Sanitary
Landfill

TCE Plume After 50 Days

TCE Plume After 100 Days

TCE Plume After 200 Days

TCE Plume After 400 Days

Concentration Scale in ppb

Note: Layer 1 concentration is shown.

Figure 5-7

TCE Plume Movement Base Case Simulation

File: slf40.srf
Drafted: Greg Council 9/16/98

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Landfill

Figure 5-8
TCE Mass Removal
in Various Model Simulations

File: tce1.xls
 Drafted: Greg Council 9/29/98

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Sanitary
Landfill

TCE Plume After 50 Days

TCE Plume After 100 Days

TCE Plume After 200 Days

TCE Plume After 400 Days

Concentration Scale in ppb

0 1500 3000

Scale in feet

Note: Layer 1 concentration is shown.

Figure 5-9

TCE Plume Movement No-Degradation Simulation

File: slf44.srf
Drafted: Greg Council 9/16/98

SRS
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Landfill

TCE Plume After 50 Days

TCE Plume After 100 Days

TCE Plume After 200 Days

TCE Plume After 400 Days

Concentration Scale in ppb

0 1500 3000

Scale in feet

Note: Layer 1 concentration is shown.
Decay Rate x 0.1

Figure 5-10
TCE Plume Movement
Slow-Decay Sensitivity Simulation

File: slf43.srf

Drafted: Greg Council 9/16/98

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Note: Layer 1 concentration is shown.
Porosity x 0.75

File: slf41.srf
Drafted: Greg Council 9/16/98

Figure 5-11
TCE Plume Movement
Low Porosity Sensitivity Simulation

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Landfill

TCE Plume After 50 Days

TCE Plume After 100 Days

TCE Plume After 200 Days

TCE Plume After 400 Days

Concentration Scale in ppb

0 1500 3000

Scale in feet

Note: Layer 1 concentration is shown.
Dispersivity x 0.2

File: slf42.srf
Drafted: Greg Council 9/16/98

Figure 5-12
TCE Plume Movement
Low Dispersivity Sensitivity Simulation

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Landfill

Note: Layer 1 concentration is shown.
Dispersivity x 0.2

File: slf45.srf
Drafted: Kelly Reese 9/29/98

Figure 5-13
TCE Plume Movement
Alternative Flow Sensitivity

SRS
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Landfill

Note: Layer 1 concentration is shown.

File: slf70.srf
Drafted: Greg Council 9/24/98

Figure 5-14
Vinyl Chloride Plume Movement
Base Case Simulation

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Landfill

Figure 5-15
Vinyl Chloride Mass Removal
in Various Model Simulations

SRS
 Sanitary
 Landfill

VC Plume After 50 Days

VC Plume After 100 Days

VC Plume After 200 Days

VC Plume After 400 Days

Concentration Scale in ppb

0 1500 3000

Scale in feet

Note: Layer 1 concentration is shown.

Figure 5-16 **Vinyl Chloride Plume Movement** **No Remediation Simulation**

File: slf71.srf
 Drafted: Kelly Reese 9/28/98

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Landfill

Concentration Scale in ppb

Note: Layer 1 concentration is shown.

File: slf72.srf
Drafted: Greg Council 9/24/98

Figure 5-17
Vinyl Chloride Plume Movement
No Degradation Simulation

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VC Plume After 50 Days

VC Plume After 100 Days

VC Plume After 200 Days

VC Plume After 400 Days

Concentration Scale in ppb

Note: Layer 1 concentration is shown.

File: slf77.srf
Drafted: Kelly Reese 9/28/98

Figure 5-18
Vinyl Chloride Plume Movement
Low Oxygen Simulation

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SRS
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Landfill

Note: Layer 1 concentration is shown.

File: slf73.srf
Drafted: Kelly Reese 9/28/98

Figure 5-19
Vinyl Chloride Plume Movement
High Bacterial Concentration Simulation

SRS
Sanitary
Landfill

VC Plume After 50 Days

VC Plume After 100 Days

VC Plume After 200 Days

VC Plume After 400 Days

Concentration Scale in ppb

Note: Layer 1 concentration is shown.

Figure 5-20

Vinyl Chloride Plume Movement High Half-Saturation Sensitivity Simulation

File: slf79.srf
Drafted: Kelly Reese 9/28/98

SRS
Sanitary
Landfill

VC Plume After 50 Days

VC Plume After 100 Days

VC Plume After 200 Days

VC Plume After 400 Days

Concentration Scale in ppb

Note: Layer 1 concentration is shown.

File: slf80.srf
Drafted: Kelly Reese 9/28/98

Figure 5-21
Vinyl Chloride Plume Movement
Low Porosity Sensitivity Simulation

HSI
GEOTRANS
A TETRA TECH COMPANY

SRS
Sanitary
Landfill

VC Plume After 50 Days

VC Plume After 100 Days

VC Plume After 200 Days

VC Plume After 400 Days

Concentration Scale in ppb

0 1500 3000

Scale in feet

Note: Layer 1 concentration is shown.

Figure 5-22

Vinyl Chloride Plume Movement Low Dispersivity Sensitivity Simulation

File: sif81.srf
Drafted: Kelly Reese 9/28/98

SRS
Sanitary
Landfill

Note: Layer 1 concentration is shown.

File: slf74.srf
Drafted: Kelly Reese 9/28/98

Figure 5-23
Vinyl Chloride Plume Movement
Alternative Flow Sensitivity

SRS
Sanitary
Landfill

6. Summary and Recommendations

This report has presented the results of a groundwater modeling study that evaluates the performance of the biosparging system at the SLF. Three separate computer models have been integrated and applied to determine the radius of influence of the injection wells, the effectiveness of the remedial measures, the overall time required for remediation and the optimum location for placement of monitor wells.

Simulations conducted with the biosparging model allowed a reliable prediction of system performance for the proposed SLF biosparging systems. These simulations allowed predictions of TCE and VC removal efficiencies, as well as system radius of influence (ROI). The simulations conducted with the biosparging model focused on groundwater quality in the vicinity of the sparging wells. A second model, referred to as the Sanitary Landfill solute transport model, was utilized to evaluate the biosparging system impact to ground water, on a larger, site-wide scale. These simulations were conducted with the three dimensional reactive fate and transport code, RT3D. Because RT3D does not explicitly model sparging (two phase, pressure-driven conditions), the ROIs predicted *a priori* from the biosparging model were used to define the spatial extent of the bioactive zone used in the RT3D simulations.

6.1 Radius of influence

The biosparging model simulated gas flux from the sparging well through the saturated zone, and up into the vadose zone. As sparging proceeded, the model predicted that gas would displace water in much of aquifer material adjacent to the sparge well. Injection rates and aquifer wetting properties are primary factors governing the radius of influence around the sparge well. For the TCE plume, the biosparging model predicted that the ROI around SLH-1 will range from 50 - 75 feet (average of ~ 60 feet), assuming the injection schedule and pressures used in these simulations. For the VC plume, the biosparging model predicted a ROI of 60 feet around SLH-2. These predictions are in excellent agreement with the ROI observed for the vertical well biosparging pilot study conducted at the SLF in 1996 (WSRC, 1996). It should be noted that, in practice, that gas flux from biosparging wells is often non-uniform, and may result in the creation of preferential flow paths that direct gas flow away from the well (Johnson et al., 1993). Such channeled flow was not modeled in this work. However, channeling in the SLF biosparging systems should be minimized under the injection schedule proposed because injection periods are short in duration. Channeling is favored under continuous, high rate injection schemes. In any case, performance monitoring should be conducted after system start-up to determine if channeling is reducing gas distributions and system performance.

6.2 Effectiveness of remedial measures

The biosparging model predicted that the portion of the TCE plume upgradient and in the immediate vicinity of sparge well SLH-1 will be remediated within 100 days of startup of air, methane, and nutrient injection. The model also predicted, however, that the portion of the plume that occurs downgradient of SLH-1 will be treated to a significantly smaller extent. As predicted by these simulations, treatment of the downgradient portion of the TCE plume will proceed at a slower rate. These simulations indicate that performance of the biosparging system

will be constrained by the ROI around the sparge well, and by groundwater flow drawing TCE downgradient, outside the ROI.

In general, the TCE simulations with RT3D agreed reasonably well with those of the biosparging model. The base case simulation with RT3D predicted that the part of the plume upgradient of the sparge well will be treated within 400 days. Downgradient of the sparge well, dispersion will slowly diminish TCE concentrations further.

The TCE plume extends 800 to 1000 ft upgradient of the injection wells. According to particle tracking simulations, the entire plume will pass the sparge well in about 4 years (Figure 6-1), with the center of the plume crossing the bioactive zone in about 400 days. This agrees with the calculated water velocity in the plume that ranges from 0.25 to 1.75 ft/day (from Darcy's Law with a gradient of 0.005 ft/ft, effective porosity of 20% and a conductivity range of 10 to 70 ft/day)

For VC, the two models give somewhat different results. While the biosparging model shows VC concentrations markedly decreasing near SLH-2, the RT3D model shows very little additional degradation at the sparge well. This difference arises from differing levels of complexity used to represent the biokinetic processes leading to VC reduction. Specifically, the biosparging model allows for volatilization of VC and allows the VC-degrading microbes to grow and decay. Neither model predicts that VC degradation will be limited by oxygen availability, and both models show a substantial decrease in VC mass due to biokinetic processes.

Both models indicate that the TCE sparge system (SLH-1) will be effective for enhancing degradation and reducing TCE groundwater concentrations. However, the models are less consistent on the added benefit of the sparge system at SLH-2. The biosparging model shows a significant improvement in VC removal, which RT3D does not. Given that the biosparging model provides a more detailed simulation of biosparging processes, the performance predicted by the biosparging model is like a more accurate representation that performance predicted by RT3D. From velocity calculations, particle-tracking simulations (Figure 6-1), and transport model simulations, the total time suggested for biosparging operation is 5 years. The system may be halted earlier if measured concentrations so dictate.

6.3 Monitor well locations

The combined flow modeling and biosparging modeling at the SLF help determine optimum locations for placement of monitoring wells to gauge the effectiveness of the treatment program. The proposed monitoring strategy includes (1) wells that are upgradient of the biosparging wells, (2) wells at the biosparging wells to monitor contaminant levels above the wells and below the wells, and (3) wells that are downgradient of the biosparging wells. The upgradient wells will serve to quantify the level of TCE and VC that remains to be treated. As the landfill is capped and any source is removed, the contaminant levels in these wells should diminish. The monitoring wells at the biosparging well will monitor the reduction in contaminants in the biosparging zone and monitor the possible flow of contaminants below the biosparging well at select locations. Some contaminants may preferentially flow beneath the biosparging wells due to the reduced permeability in the desaturated zone above the biosparging

wells. The downgradient wells will serve to demonstrate remediation. The downgradient wells should be the point of compliance wells.

Many monitoring wells exist in the SLF area that can be effectively used as part of the monitoring strategy. Figure 6-2 shows and Table 6-1 lists the proposed upgradient, injection well, and downgradient monitoring locations. The proposed upgradient and downgradient monitoring wells take advantage of existing LFW monitoring well locations. Four new shallow monitoring wells are proposed along SLH-1 at a spacing of 200 ft. Two deeper wells are proposed near two of the four shallow monitoring wells. Several monitor well clusters exist downgradient of SLH-1 that provide adequate monitoring points at several depths in the Steed Pond Aquifer. The shallow well above the injection well should be screened from 125 to 135 ft, msl or in the vadose zone to monitor volatilized contaminants. The deeper monitor well should be 20 ft downgradient of the injection wells and screened at a depth of 100 to 110 ft, msl. Three monitor well pairs are proposed along SLH-2 at a spacing of 300 ft. The monitor well pairs are the same construction as the SLH-1 monitor well pairs.

6.4 Limitations and uncertainties

Perhaps the greatest limitation of these simulations is the uncertainty associated with the source term. For the purpose of these simulations, it was assumed that there is no NAPL phase present at the SLF, and that all the TCE and VC is dissolved in groundwater. This assumption eliminates the possibility that remediation times could be constrained by rate-limited dissolution from a nonaqueous phase. If NAPLs are subsequently detected at the SLF, this assumption would be proven invalid, and new model simulations would be required to improve cleanup time estimates.

For the biosparging model, the injection cycle for both the TCE and VC sparging systems was assumed to occur as follows: 8 hrs injection per day, every other day for one week, followed a one week off period. The model set this exact biweekly on and off injection cycle to occur throughout the duration of the model run. For the TCE plume, the injection gas composition was assumed to be 1% methane, 0.07% nitrous oxide, and 0.007% TEP. For the VC plume, the injection gas was assumed to be air only. It was further assumed that the injection rates would be 240 scfm for the TCE plume, and 270 scfm for the VC plume. These assumptions regarding injection schedules, compositions, and rates were made on the basis of the WSRC 1997 report and conversations with WSRC. The WSRC 1997 report also recommended that when the biosparging actually commences, the system should be monitored closely to ascertain the effectiveness of these schedules and gas compositions. WSRC (1997) recommended that once the TCE and VC biosparging systems the injection schedule could be modified to improve performance. If the actual injection schedules, rates, and/or compositions used in the field should differ from those assumed here, this would reduce the applicability of these model simulations.

Numerous assumptions were made in developing the biosparging model to describe the physical behavior and biodegradation kinetics TCE, VC, CH₄, and O₂. Physical parameters included diffusivities and Henry's law. Biodegradation kinetic parameters included Monod substrate utilization rates, half saturation constants, growth rates, and stoichiometric yields. To the extent possible, uncertainty in the model parameters was minimized by: 1) using appropriate predictive equations, such as in the estimated parameter values for the Henry's law constant, air

diffusivity, and water diffusivity for vinyl chloride; 2) choosing appropriate biokinetic parameters that have been measured or applied at SRS (i.e. TCE parameters used in methanotrophic simulations at M Area; and 3) choosing appropriate biokinetic parameters from other relevant peer-reviewed research. Normally, the best use of Monod parameters in models is for systems in which those parameters have been measured directly. In the absence of direct measurements for these parameters at the SLF, every effort was made to use the most appropriate estimates from other relevant studies.

These limitations are not unique to this model, and are a common feature of most applied reactive fate and transport models. The models used for these simulations have been peer reviewed and applied at numerous sites, and represent the state-of-the-art in bioremediation modeling. The fact that the LANL code was developed and used to simulate the biosparging system at the SRS M Area lends confidence to the model findings presented herein.

6.5 Other Recommendations

In addition to the recommended locations for the monitoring wells, several recommendations can be made which serve to provide a better understanding of the subsurface system and how it can effectively be modified to remediate existing contaminant plumes. These recommendations are a direct result of the understanding that has been achieved from the modeling described in this report. These recommendations are first listed and then described below:

- Simulation of SLF biosparging based upon site specific data;
- Optimization of injection cycles; and
- Characterization of groundwater concentrations beneath the capped portion of the SLF.

Many of the parameters used in the SLF solute transport and biosparging models were based on parameters obtained from modeling and performance testing of a similar system at M-area. Although these parameters are believed to be representative of conditions at the Sanitary Landfill, updating parameters in the SLF models based on additional field testing or system performance during operation would provide increased confidence in modeled results. For example, updating the model during the early stages of operation could provide a better estimate of required time of operation. The key parameters that need to be better defined are the initial concentration of bacteria specific to TCE and VC, the growth rates, and the decay rates of these bacteria.

The assumptions regarding injection schedules, rates, and compositions used in the model were based on information provided by WSRC. These factors were not varied in the simulations to assess sensitivity. It could be useful to simulate several alternative injection plans and try to optimize system performance based on changes to injection schedules (length of injection, cycling scheme, resting periods, etc), rates, and compositions. Even though there is uncertainty in the model, comparison of some of these factors within the same analysis framework could provide information that would enhance the efficiency and operating costs of the system. For

example, a significant cost saving could be realized if methane volume or period of injection could be reduced.

Additional characterization of groundwater concentrations beneath the cap would be useful to verify the key assumption that the SLF is no longer serving as a source of contamination to the groundwater system. The assumption that there is no source and that the extent of the groundwater contamination is as modeled limits the time required to remediate the groundwater system. The configuration of horizontal sparge wells is capable of preventing contamination originating from the Sanitary Landfill from entering Upper Three Runs, however, the system must be in operation to be effective.

Table 6-1. Proposed monitor well locations.

TCE Plume	
Upgradient Monitor Wells	LFW 41 R
	LFW 59 B, C, D
	LFW 61 C, D
	LFW 62 B, C, D
Injection Well Monitoring Points	Four locations along SLH-1 as illustrated on Figure 6-3
Downgradient Monitor Wells	LFW 65 B, C, D
	LFW 67 B, C, D
	LFW 71 B, C, D
VC Plume	
Upgradient Monitor Wells	LFW 8 R
	LFW 36 R
	LFW 47 D
Injection Well Monitoring Points	Three locations along SLH-2 as illustrated on Figure 6-3.
Downgradient Monitor Wells	LFW 56 D
	LFW 58 D
	LFW 63 B, C, D
	LFW 64 B, C, D

Explanation

➔ Particle pathline (arrow shown every 200 days)

TITLE		Simulated Particle Pathlines from the TCE and VC Source Areas	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	NDD	FIGURE: 6-1
	DRAFTED BY	PAW	
	FILE NAME	PTRACKS.WOR	
	DATE	9/29/98

-
- 0 400 800
- SCALE IN FEET

TITLE		Distribution and location of proposed monitor wells	
LOCATION		Savannah River Site, Aiken, SC
HSI GEOTRANS A TETRA TECH COMPANY	CHECKED BY	ND	FIGURE: 6-2
	DRAFTED BY	PAW	
	FILE NAME	NEW_MWS.WOR	
	DATE	9/30/98	

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APPENDIX A:

Biosparging Core Model Governing Equations

LA-UR-93-479

**TRAMP (TRAc3D with Microbial Processes):
A Numerical Code for *In Situ* Bioremediation
Simulations**

**B. J. Travis
EES-5**

November 1993

LA-UR-93-479

**TRAMP (TRAcr3D with Microbial
Processes): A numerical code for *in*
situ bioremediation simulations**

B. J. Travis, EES-5

November 1993

Abstract

A computational model, TRAMP, has been developed to support a number of field tests of in situ bioremediation. TRAMP contains two sets of equations which are solved simultaneously. The first set includes the flow equations for unsaturated/saturated flow of air and water in heterogeneous, anisotropic porous media. These are time-dependent, three-dimensional equations which are solved using a finite difference, implicit time stepping algorithm. The second set of equations in TRAMP includes six nonlinear, coupled, time-dependent transport equations, one each for oxygen, two nutrients, two substrates (to allow for co-metabolic reactions), and microbes. Both anaerobic and aerobic conditions are included and Monod kinetics are assumed. TRAMP, for TRACr3d with Microbial Processes, is an extension of the TRACR3D code which simulates flow and transport of contaminants in porous media. This report describes the mathematical formulation and numerical methodology of TRAMP.

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1. Introduction

Organic materials such as chlorinated solvents and petroleum products are among the most common contaminants of ground water and soils. The conventional remediation approach has been to extract the contaminated ground water by pumping and then to treat the water at the surface. This 'pump-and-treat' approach has proven costly and less effective than expected in many cases. As a consequence, several new environmental restoration technologies are being investigated. One promising technology is *in situ* bioremediation.

At most sites, bacteria exist which can degrade a large variety of organic compounds, including many of the ones commonly found as ground water and soil contaminants. In the case of diesel oil or gasoline, native bacteria can often utilize these compounds directly as primary substrates. For chlorinated solvents, this is not the case. There are families of bacteria (and other micro-organisms such as fungi), however, which can co-metabolize many of these solvents in the presence of a primary substrate such as methane. This is possible because an enzyme the micro-organisms produce to metabolize the primary substrate fortuitously transforms other compounds. For example, the methanotrophs (methane-oxidizing bacteria) produce methane monooxygenase (MMO) which initiates the oxidation of methane. MMO has a low specificity, however, and can initiate the oxidation of other compounds, such as trichloroethylene. Because methanotrophs do not derive energy from the co-metabolism of these chlorinated solvents, they require a supply of methane, along with oxygen and nutrient (nitrogen/phosphate), at appropriate concentrations to stimulate their growth.

A computational model, TRAMP, has been developed jointly at Los Alamos National Laboratory (LANL) and HydroGeoChem Incorporated to support a number of field tests of *in situ* bioremediation. TRAMP calculates the transport of air, water and dilute contaminants plus bacterial metabolism of substrates, in porous media. TRAMP is capable of modeling both saturated and unsaturated flow and is not limited to the assumption of a steady flow field; all coupled flow and biokinetics codes of which we are aware [Molz *et al.*, 1986; Widdowson *et al.*, 1988; Celia *et al.*, 1989; MacQuarrie *et al.*, 1990; Rifai and Bedient, 1990; Semprini and McCarty, 1991; Kinzelbach *et al.* 1991; Wheeler *et al.* 1992] are limited to steady saturated flow fields. Compared to all of these other codes, TRAMP is broader and more sophisticated with respect to its capabilities. Most, for example, do not account for nutrient transport and co-metabolism [e.g., BIOPLUME II, Rifai and Bedient, 1990] and only one of these other recent codes is 3-D [Wheeler *et al.*, 1992].

TRAMP (TRACr3d with Microbial Processes) is an extension of the TRACR3D code which simulates flow and transport of contaminants in porous media [Travis, 1984; Travis and Birdsell, 1991]. TRACR3D is about to be qualified under the stringent software quality assurance requirements of the Yucca Mountain Project. TRAMP is an integration of TRACR3D with a sophisticated, relatively comprehensive biokinetics model developed by HydroGeoChem, Inc. [Bentley, 1990]. Both TRACR3D and TRAMP have been implemented on a number of computer systems, ranging from CRAYs to SUN workstations and they can be operated in 1-D, 2-D or 3-D mode.

This report gives a brief description of the mathematical formulation and numerical methodology used in TRAMP. Travis and Trent [1991] discuss the use of TRAMP in a study of a diesel oil spill at DOE's Sandia National Laboratory at Livermore. Travis *et al.* [1993] discuss the use of TRAMP in a study of bioremediation of chlorinated solvents, mainly trichloroethylene (TCE), at DOE's Savannah River site. A validation and verification report for TRAMP will be issued in the future.

2. Mathematical Formulation

TRAMP contains two sets of equations which are solved simultaneously. The first set includes the flow equations for unsaturated/saturated flow of air and water in heterogeneous, anisotropic porous media. These are time-dependent, three-dimensional equations which are solved using a finite difference, implicit time stepping algorithm. Material properties, such as porosity and permeability, can vary in space and the model allows considerable flexibility in boundary conditions and the location of injection/extraction wells. The flow equations are those included in TRACR3D [Travis and Birdsell, 1991]. Conservation of mass for the air phase is

Equation #1

$$\frac{\partial(\epsilon \rho_g f)}{\partial t} + \nabla \cdot (\rho_g \vec{u}_g) = \epsilon \dot{S}_g$$

and for the water phase is

Equation #2

$$\frac{\partial(\epsilon \rho_w \sigma)}{\partial t} + \nabla \cdot (\rho_w \vec{u}_w) = \epsilon \dot{S}_w$$

The momenta conservation equations are approximated by Darcy's law (for low Reynolds number flows):

Equation #3

$$\vec{u}_i = - \frac{k_i}{\mu_i} (\nabla P_i + \rho_i \hat{g})$$

where the subscript *i* refers to the air or water phase. The gas density is a function of pressure based on the ideal gas law. The numerical solution of the flow equations is not discussed here; the interested reader should consult Travis and Birdsell [1991].

The second set of equations in TRAMP includes six nonlinear, coupled, time-dependent transport equations, one each for oxygen, two nutrients, two substrates, and the microbes. Both anaerobic and aerobic conditions are included and Monod kinetics are assumed. Volatile constituents are assumed to partition between air and water phases according to Henry's Law. The relationship between the dissolved and sorbed phases is governed by an equilibrium sorption coefficient and a characteristic time scale such that transport between the phases can be modeled as instantaneous or time-dependent, as appropriate.

TRAMP is a general purpose code and therefore not all of its features may be needed at a specific site. The full equations are given here. The first equation in this set is the conservation equation for the first substrate, substrate A (Equation #4). This equation states that the change in the amount of A in a given space for a specific (short) time period is equal to the amount of A consumed, the amount of A advected into or out of the space, and the amount of A diffused/dispersed into or out of the space. Consumption of A depends on the concentrations of oxygen, A, a nutrient, and bacteria in a straightforward Monod form. Anaerobic consumption of substrate A is inhibited by oxygen.

Equation #4

$$\begin{aligned}
\frac{\partial(\epsilon(\sigma\rho_w + f H^A)[A]_w)}{\partial t} = & \\
& - \epsilon \sigma \rho_w k_A [M]_w \\
& * \left[\left(\frac{[A]_w}{K_A + [A]_w} \right) \left(\frac{[O_2]_w}{K_{O_2} + [O_2]_w} \right) \left(\frac{[N]_w}{K_N + [N]_w} \right) + J \left(\frac{[A]_w}{K'_A + [A]_w} \right) \left(\frac{[N]_w}{K'_N + [N]_w} \right) \left(\frac{I_{O_2}}{I_{O_2} + [O_2]_w} \right) \right] \\
& - \nabla \cdot ((\vec{u}_w + H^A \vec{u}_g)[A]_w) + \nabla \cdot (\epsilon(\sigma D_w^A + f H^A D_g^A) \nabla [A]_w) - (1 - \epsilon) \rho_s \frac{d[A]_s}{dt}
\end{aligned}$$

where

$$\frac{d[A]_s}{dt} = (K_d^A [A]_w - [A]_s) / \tau^A$$

In the expression for $d[A]_s/dt$, a small value of τ means that the concentration of A inside soil grains is in equilibrium with the water phase concentration, with the partitioning determined by K_d . A large value of τ means there is a significant time lag for equilibration between liquid and solid phases. This would be reflected in a rapid drop in air phase concentration after a vacuum extraction well is turned on, followed by a slow increase after the vacuum is turned off.

The second equation is the conservation equation for the second substrate, substrate B (Equation #5). This equation states that the change in the amount of B in a given space for a specific time period is equal to the amount of B degraded by microbes, the amount of B advected into or out of the space and the amount of B diffused/dispersed into or out of the space. The rate of degradation of B depends on the microbe concentration and the concentrations of oxygen, nutrient and B. Substrate A can also affect substrate B's metabolism by inhibiting it at and above moderate concentrations. In a simulation of biodegradation of trichloroethylene by methanotropic bacteria, for example, A would be methane and B would be trichloroethylene. In a simulation of biodegradation of diesel oil, A would be the diesel oil and there would be no B.

Equation #5

$$\begin{aligned}
\frac{\partial(\epsilon(\sigma\rho_w + f H^B)[B]_w)}{\partial t} = & \\
& - \epsilon \sigma \rho_w k_B [M]_w \\
& * \left\{ \left(\frac{[B]_w}{[B]_w + K_B (1 + [A]_w I_A)} \right) \left(\frac{[O_2]_w}{K_{O_2} + [O_2]_w} \right) \left(\frac{[N]_w}{K_N + [N]_w} \right) \right. \\
& \left. + J \left(\frac{[B]_w}{[B]_w + K'_B (1 + [A]_w I'_A)} \right) \left(\frac{[N]_w}{K'_N + [N]_w} \right) \left(\frac{I_{O_2}}{I_{O_2} + [O_2]_w} \right) \right\} \\
& - \nabla \cdot ((\vec{u}_w + H^B \vec{u}_g)[B]_w) + \nabla \cdot (\epsilon(\sigma D_w^B + f H^B D_g^B) \nabla [B]_w) - (1 - \epsilon) \rho_s \frac{d[B]_s}{dt}
\end{aligned}$$

where

$$\frac{d[B]_s}{dt} = (K_d^B [B]_w - [B]_s) / \tau^B$$

The third equation is the conservation equation for oxygen (Equation #6). This equation states that the change in the amount of oxygen in a given space for a specific time period is equal to the amount of oxygen consumed, the amount of oxygen advected into or out of the space, and the amount of oxygen diffused/dispersed into or out of the space.

Equation #6

$$\begin{aligned} \frac{\partial \epsilon (\sigma \rho_w + f H^{O_2}) [O_2]_w}{\partial t} = & - \epsilon \sigma \rho_w [M]_w \left(\frac{[O_2]_w}{K_{O_2} + [O_2]_w} \right) \left(\frac{[N]_w}{K_N + [N]_w} \right) \\ & * \left[(F_A) (k_A) \left(\frac{[A]_w}{K_A + [A]_w} \right) + (F_B) (k_B) \left(\frac{[B]_w}{[B]_w + K_B (1 + A_w / I_A)} \right) \right] \\ & - \nabla \cdot (\vec{u}_w + H^{O_2} \vec{u}_g) [O_2]_w + \nabla \cdot (\epsilon (\sigma D_w^{O_2} + f H^{O_2} D_g^{O_2}) \nabla [O_2]_w) - (1 - \epsilon) \rho_s \frac{d[O_2]_s}{dt} \end{aligned}$$

where

$$\frac{d[O_2]_s}{dt} = (K_d^{O_2} [O_2]_w - [O_2]_s) / \tau^{O_2}$$

The fourth equation is the conservation equation for a nutrient (e.g., phosphate or nitrate) (Equation #7). This equation states that the change in the amount of nutrient in a given space for a specific time period is equal to the amount of nutrient consumed, the amount of nutrient advected into or out of the space, the amount of nutrient dispersed into or out of the space and the amount of nutrient returned to the system from dead and decaying microbes. An identical fifth equation allows for a second nutrient.

Equation #7

$$\begin{aligned} \frac{\partial [\epsilon (\sigma \rho_w + f H^N) [N]_w]}{\partial t} = & - \epsilon \sigma \rho_w F_N k_M [M]_w \\ & * \left\{ \left(\frac{[O_2]_w}{K_{O_2} + [O_2]_w} \right) \left(\frac{[N]_w}{K_N + [N]_w} \right) \left[k_A Y_A \frac{[A]_w}{K_A + [A]_w} + k_B \frac{\max(0, Y_B) [B]_w}{K_B (1 + [A]_w / I_A) + [B]_w} \right] \right. \\ & \left. + J \left(\frac{I_{O_2}}{I_{O_2} + [O_2]_w} \right) \left(\frac{[N]_w}{K_N + [N]_w} \right) \left[k_A Y_A \frac{[A]_w}{K_A + [A]_w} + k_B \frac{\max(0, Y_B) [B]_w}{K_B (1 + [A]_w / I_A) + [B]_w} \right] \right\} \\ & - \nabla \cdot (\vec{u}_w + H^N \vec{u}_g) [N]_w + \nabla \cdot (\epsilon (\sigma D_w^N + f H^N D_g^N) [N]_w) \\ & + \left[k_d \left(\frac{[O_2]_w}{I_{O_2} + [O_2]_w} \right) + k'_d \left(\frac{I_{O_2}}{I_{O_2} + [O_2]_w} \right) \right] [M]_w X_{dM} \end{aligned}$$

$$-(1 - \epsilon) \rho_s \frac{d[N]_s}{dt}$$

where

$$\frac{d[N]_s}{dt} = (K_d^N [N]_w - [N]_s) / \tau^N$$

The final equation (Equation #8) describes the conservation of bacteria. The terms on the right hand side represent, respectively, growth due to degradation of substrates A and B, loss due to microbial death, and growth based on consumption of any naturally occurring organic material in the soil. The bacteria are assumed to be immobile so there are no advection and dispersion terms. All of the microbial activity takes place in the liquid phase. It is also assumed that the constituents in the water and bio-films are well-mixed so that there is no gradient and no mass transfer delay within the fluid layer. The consumption terms depending on B in equations #7 and #8 allow for the possibility that some bacteria may actually gain energy from breakdown of B. However, if B is toxic or inert, the term will disappear.

Equation #8

$$\begin{aligned} \frac{d[M]_w}{dt} = & k_M [M]_w \left\{ \left(\frac{k_A Y_A [A]_w}{K_A + [A]_w} \right) + \left(\frac{k_B \max(0., Y_B [B]_w)}{K_B (1 + [A]_w / I_A) + [B]_w} \right) \left(\frac{[N]_w}{K_N + [N]_w} \right) \left(\frac{[O_2]_w}{K_{O_2} + [O_2]_w} \right) \right. \\ & + J \left(\frac{k_A Y_A [A]_w}{K_A + [A]_w} \right) + \left(\frac{k_B \max(0., Y_B [B]_w)}{K_B (1 + [A]_w / I_A) + [B]_w} \right) \left(\frac{[N]_w}{K_N + [N]_w} \right) \left(\frac{I_{O_2}}{I_{O_2} + [O_2]_w} \right) \left. \right\} \\ & - \left[k_d \left(\frac{[O_2]_w}{I_{O_2} + [O_2]_w} \right) + k_d' \left(\frac{I_{O_2}}{I_{O_2} + [O_2]_w} \right) \right] [M]_w + k_d [NOC] \end{aligned}$$

The symbols used in equations 1-8 are defined in Table 1.

Table 1. Symbols.

	anaerobic parameters
ϵ	porosity
k	permeability
ρ	density
μ	viscosity
σ	water phase saturation
τ	characteristic time scale for diffusion of species into/out of soil particles = $d^2/4D_s$, where d is the particle diameter and D_s is the diffusion coefficient in the solid phase, assumed to be 10^{-10} cm ² /s
A	substrate A
B	substrate B
B_R^i	nonlinear term for specie i representing biological metabolic reactions
$[C]_i$	concentration of specie i in liquid phase, g/cm ³
D	dispersivity/diffusivity
F	the mass ratios of oxygen consumed per mass of substrate/nutrient
f	air phase saturation
g	gas phase
$\hat{g}$	gravity acceleration
H	Henry's Law coefficient
I	inhibition half saturation concentration (the substrate/nutrient concentration at which the maximum utilization rate is reduced by half)
i	refers to one of the species
J	ratio of anaerobic to aerobic utilization rates
K	half saturation concentration (the substrate/nutrient concentration at which the utilization rate is half the maximum)
k	maximum rate of substrate utilization
k_c	background growth rate of microbes
K_d	equilibrium sorption coefficient
k_d	death rate of microbes
L_i	differential operator for the i th specie
M	microbes (bacteria)
N	nutrient
NOC	natural organic carbon
O ₂	oxygen
R	factor corresponding to non-equilibrium sorption effect
s	sorbed phase
$\dot{S}$	mass source or sink
t	time
$\vec{u}$	velocity vector
w	liquid water phase
X_{dM}	fraction of dead microbes converted to available nutrients
Y	the microbial yield per unit of substrate consumed

3. Numerical Methodology

The partial differential equations that describe the transport and interactions of the model's six species (two substrates, oxygen, two nutrients and bacteria) must be solved numerically. There are many algorithms that can be used, each with its particular advantages and disadvantages. The approach taken here is to use finite difference approximations to the governing equations and to treat nonlinearities in the equations in an iterative fashion.

The general form of the transport differential equations in conservative form is:

Equation #9

$$L_i(C_i) = \frac{\partial [C_i(\epsilon \sigma \rho_w + \epsilon f H^i + (1-\epsilon) \rho_s K_d^i R^i)]}{\partial t} + \nabla \cdot ((\bar{u}_w + H^i \bar{u}_g) C_i) - \nabla \cdot [\epsilon (\sigma D_w^i + f H^i D_g^i) \nabla C_i] - \epsilon \sigma \rho_w B_R^i(C_1, C_2, C_3, C_4, C_5) = 0$$

where L_i is a symbol for the total operator on C_i , R^i accounts for noninstantaneous sorption, and B_R^i is a nonlinear term describing reactions between specie i (one of the substrates, oxygen, nutrient or bacteria) and the other components. The other symbols in equation #9 are defined in Table 1. At the initial time, values of C_i are specified in each grid cell and on the boundaries. Subsequent values of C_i at discrete time intervals are calculated through a finite difference approximation to equation #6 and the associated boundary conditions.

There are two basic processes represented by equation #9: (1) transport by advection and diffusion, and (2) growth and decay reactions. Treating these two processes separately is the basis for the iterative solution technique. We approximate the operator by two operators:

Equation #10

$$L_i^d = \hat{L}_1^d + \tilde{L}_1^d$$

L_i^d is a finite difference approximation to the differential operator L_i of equation #9. The two operators are:

Equation #11

$$(\tilde{L}_1^d)^k = A_1^{n+1} C_1^k - A_1^n C_1^n + \frac{\Delta t}{\Delta \Omega} \sum_{j=1}^6 (\bar{u}_w + H^i \bar{u}_g)_j (C_j)^k \Delta a_j - \sum_{j=1}^6 \epsilon (\sigma D_w^i + f H^i D_g^i)_j \frac{\Delta a_j}{\Delta x_j} [(C_j)^k - (C_i)^k] - \frac{\epsilon \sigma \rho_w}{2} (B_R^{i,n} + B_R^{i,k-1}) \Delta t$$

and

Equation #12

$$(\hat{L}_1^d)^k = A_1^{n+1} C_1^{n+1} - A_1^{n+1} C_1^k - \frac{\epsilon \sigma \rho_w \Delta t}{2} (B_R^{i,n+1} - B_R^{i,k-1})$$

The superscript 'n' refers to time level n and superscript 'n+1' to the next time point ($t^{n+1} = t^n + \Delta t$), Δt is the current value of the time step, the superscript 'k' refers to an intermediate value between time levels n and n+1, Δa_j is the area of the j-th face of a grid cell, $\Delta \Omega$ is grid cell volume, Δx_j is the distance between cell centers on the j-th side of each grid cell, A_i is equal to $(\epsilon \sigma + \epsilon f H_i + (1-\epsilon) p_s K_d^i R_i)$, and Σ represents summation over the faces of a grid cell.

The iterative solution of equations #11 and #12 is accomplished in the following manner. From knowledge of the values of C_i^n at the previous time step and the latest iteration in the current time step, C_i^{k-1} , equation #11 is solved implicitly for C_i^k . This step emphasizes the transport processes of equation #9. Next, equation #12 is solved. This step emphasizes the reactions between species. In equations #11 and #12, $B_R^{i,k-1}$ is evaluated using C_i^{k-1} values. (On the first iteration of a time step $C_i^{k-1} = C_i^n$). The term $B_R^{i,n+1}$ must be evaluated at the unknown n+1 time level. Since it is nonlinear, we expand it in a Taylor series around C_i^k . The operator is now:

Equation #13

$$(\hat{L}_i^d)^k = A_i^{n+1} C_i^{n+1} - A_i^{n+1} C_i^k - \frac{\epsilon \sigma}{2} \rho_w \Delta t (B_R^{i,k} - B_R^{i,k-1} + \sum_{m=1}^6 \frac{\partial B_R^{i,k}}{\partial C_m} (C_m^{n+1} - C_m^k))$$

In equation #13, only the first derivative terms of the Taylor series expansion are kept as shown. (This is equivalent to a Newton-Raphson solution.) Equation #13 is iterated in each grid cell until differences in the C_i^{n+1} on successive iterations fall below a specified tolerance (typically on the order of 10^{-12} to 10^{-16}). Since each B_R^i depends on the concentrations of all 6 species, a set of 6 simultaneous equations are solved in each grid cell. When equation #13 has converged in each cell, equation #11 is solved again, using the results of the last solution of #13 to evaluate the $B_R^{i,k-1}$ term in equation #11. This process is repeated until convergence on equation #9 occurs. The process is then repeated for the next time step.

Mass balance errors for the six species over an entire simulation involving strongly nonlinear behavior usually remain less than 1% and frequently much less than 1%. (Mass balance for the flow equations is generally accurate to one part in 10^6 or better.)

This procedure has the advantage of minimal computer memory requirements. Rather than solving the L_i^d simultaneously over the entire grid, for a total of $6N_c^2$ equations and a matrix solution for one $(6N_c^2) \times (6N_c^2)$ matrix (assuming a 2-D grid of $N_c \times N_c$ cells), we solve $(I_0)N_c^2$ (6x6) matrices, which is faster if I_0 (number of iterations of equation #11) is $< N_c$, and requires much less storage regardless of the value of I_0 . For weakly reacting conditions, I_0 is usually 2 or 3; for strongly reacting conditions, I_0 can reach values of 10-12. The disadvantage is that the equation solution may not be as robust as a fully simultaneous method. However, experience shows that the method is stable and acceptably efficient for problems of interest.

The total effort to solve equation #9 is then the solution of $I_0 \times 6$ matrices of size $N_c^2 \times N_c^2$ for solution of each equation #11 and $(I_i)(I_0)(N_c^2)$ matrices of size 6×6 for equation #13. Here, I_i is the number of iterations of equation #13 for each of the I_0 iterations of equation #11. Generally, $I_i \approx 2$. The $N_c^2 \times N_c^2$ matrices of equation #11 are banded, so the effort required is proportional to only $6(N_c^2)$ rather than N_c^4 . So the final tally is approximately $6(I_0)$ solutions of a $6(N_c^2)$ matrix plus $2I_0(N_c^2)$ solutions of a 6×6 matrix, per time step.

The velocity and saturation fields used in equation #9 are obtained from a numerical solution of the two phase Darcy flow and mass continuity equations. The numerical methods employed to solve these equations are described in detail in *Travis and Birdsell* [1991].

4. Model Input

The format of the input file has been changed from that used in TRACR3D. The namelist format has been dropped. The new input format is more portable, and just as convenient. Input quantities for TRAMP are those described for TRACR3D [Travis and Birdsell, 1991] plus the additional input variables for the biokinetics package listed in Table 2 and a few other minor changes. In the TRAMP input file, the next to the last entry for the keyword TABMAT is reserved for the typical soil grain diameter (cm). Also, the keywords CIN and SNIN are modified slightly. SNIN doesn't have to be $K_d \cdot \text{CIN}$ and CIN entries can represent water phase concentrations or air phase concentrations, or the total amount in both phases.

Table 2. TRAMP Input Parameters.

IBIODEG	Flag used to control the biokinetics package. 0 = No biokinetics calculated 1 = Biokinetics calculated
BIGKA	Half saturation for substrate A under aerobic conditions
BIGKB	Half saturation for substrate B under aerobic conditions
BIGKO	Half saturation for oxygen under aerobic conditions
BIGKN	Half saturation for nutrients under aerobic conditions
BIGKAP	Half saturation for substrate A under anaerobic conditions
BIGKNP	Half saturation for nutrients under anaerobic conditions
BIGIO	Oxygen inhibition concentration
SMKA	Aerobic maximum substrate A utilization per M per time
BIGJ	Factor converting SMKA to anaerobic analog
SMKB	Aerobic maximum substrate B utilization per M per time
BIGIA	Inhibition of B by A (> 0), half-concentration
BIGFA	Factor for consumption of O_2 mass per mass of A
BIGFB	Factor for consumption of O_2 mass per mass of B
SMKN	Rate of anaerobic nutrient production of microbial population
BIGFN	Consumption of nutrient per mass of M
BIGFSB	Fractional release of nutrient per mass of M
SMKSB	Death rate of M for aerobic conditions
SMKSBP	Death rate of M for anaerobic conditions
BIGYM	Yield of M mass per substrate A mass
BIGYM2	Yield of M mass per substrate B mass (can be negative if B is toxic)
BIGC	Natural organic carbon concentration
SMKC	Natural organic carbon decay rate
SMKM	Additional factor for conversion rate for microbes
XMAXGM	Maximum concentration of bacteria

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