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Application of Horizontal Flow Treatment Wells for In Situ Treatment of Perchlorate Contaminated Groundwater

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APPLICATION OF HORIZONTAL FLOW TREATMENT WELLS FOR *IN SITU* TREATMENT OF PERCHLORATE CONTAMINATED GROUNDWATER

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Abstract

Groundwater contamination by perchlorate has recently been recognized as a significant environmental problem across the United States, and especially at Department of Defense facilities. In this study, a model is used to evaluate the potential of an innovative *in situ* bioremediation technology using Horizontal Flow Treatment Wells (HFTWs) to manage perchlorate-contaminated groundwater. The technology uses HFTWs to mix an electron donor into perchlorate-contaminated groundwater in order to promote reduction of the perchlorate by indigenous microorganisms in bioactive zones within the aquifer, as well as recirculate the contaminated water between treatment well pairs to achieve multiple passes of contaminated water through the bioactive zones. The model used in this study couples a three-dimensional fate and transport model, which simulates advective/ dispersive transport of solutes induced by regional groundwater flow and operation of the HFTWs, with a biodegradation model that simulates perchlorate reduction, as well as reduction of competing electron acceptors in the groundwater, by indigenous microorganisms. The model was applied to an example site to demonstrate how *in situ* perchlorate treatment might be implemented. A sensitivity analysis using the model is also conducted to evaluate which engineered and environmental parameters most affect technology performance. Model simulation results demonstrate that this technology may be effective in managing perchlorate-contaminated groundwater. The recirculation induced by the HFTW system results in increased treatment efficiency, as compared to treatment that would be achieved by a single pass of contaminated water through the bioactive zones. It was observed that the model was very sensitive to several kinetic

parameters, indicating that a fruitful area for future research would be to study how these important parameters can be accurately quantified for given geochemical and microbiological conditions. The model presented in this study is an important tool in helping to design field evaluations of the technology. These evaluations will be essential in ultimately transitioning the technology for application at perchlorate-contaminated groundwater sites throughout the Department of Defense.

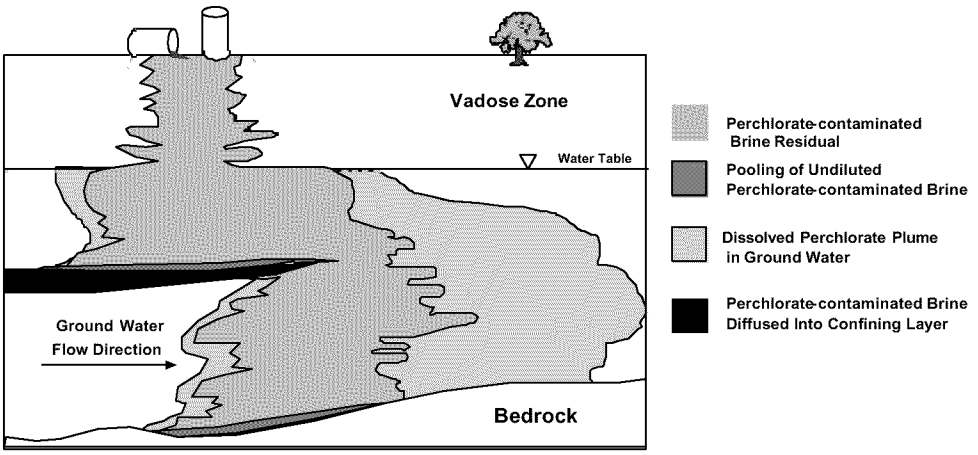
APPLICATION OF HORIZONTAL FLOW TREATMENT WELLS FOR *IN SITU* TREATMENT OF PERCHLORATE CONTAMINATED GROUNDWATER

1.0 INTRODUCTION

1.1 MOTIVATION

Perchlorate (ClO_4^-) potentially contaminates the drinking water of 12 million people in the United States and research into technologies that can be used to deal with perchlorate contamination in groundwater has only recently started (Logan, 1998). Ammonium perchlorate (NH_4ClO_4) is used extensively throughout the Air Force and Department of Defense (DoD) as the primary oxidizer in the rocket fuel used in solid rocket boosters. *In situ* remediation of perchlorate in groundwater (that is, remediation that occurs in place, without the need to pump perchlorate contaminated groundwater to the surface) is one of the DoD's research priorities (Environmental Security Technology Certification Program (ESTCP), 2000; Kowalczyk, 2001). The ESTCP request for proposals for fiscal year 2002 noted that, "…a number of DoD facilities are now faced with the challenge of remediating groundwater contaminated with perchlorate." Perchlorate is very mobile and can persist for decades under typical groundwater conditions (Urbansky, 1998). The National Academy of Sciences (2000) reported that the natural attenuation of perchlorate has a low likelihood of success given our current level of understanding, thereby emphasizing the need for an engineered approach to manage the contaminant. Even though perchlorate is very soluble in water, it is believed that sites typically consist of a source area of undiluted perchlorate-contaminated brine, along with a plume of perchlorate-contaminated groundwater (see Figure 1.1) (Flowers and Hunt, 2000). As of

2001, there have been no full-scale implementations of *in situ* perchlorate-contaminated groundwater remediation technologies (Roote, 2001).



After NRC (1994) and Flowers and Hunt (2000)

Figure 1.1 Conceptual depiction of perchlorate plume from perchlorate brine source area

Perchlorate is a health concern because it obstructs the production of thyroid hormone by hindering the uptake of iodide into the thyroid gland (Wolf, 1998), though the health effects of low doses of perchlorate over long periods of time has yet to be established (Pontius *et al.*, 2000). There also is concern about unknown developmental effects of perchlorate ingestion on neonates and children. Specifically, there have been reports on the potential for perchlorate to cause congenital hypothyroidism, a cause of mental

retardation in unborn babies (Lamm and Doemland, 1999). While there are some data on the effects of high-level doses of perchlorate on adults, when the data are extrapolated to effects at low doses and effects on other subpopulations, uncertainty increases (Lamm and Doemland, 1999). This uncertainty is the EPA's motivation for continued research on effects of perchlorate-contaminated waters on human and ecosystem health (Sterner and Mattie, 1998).

Because of this uncertainty, there is no established federal drinking water standard for perchlorate, though perchlorate is on the Contaminant Candidate List (CCL) for study for possible regulation (EPA, 2001). The California Department of Health Services led the regulatory effort in 1997 by issuing a provisional reference dose (RfD) of 18 ppb (18 $\mu g\ L^{-1}$) (California Department of Health Services, 2001). EPA regions and various state regulatory agencies have put forth cleanup standards in the range of 1.5 – 31 ppb (EPA Region 9, 1999). Due to the potential health risks, emerging regulations, and the widespread occurrence of perchlorate on DoD facilities, technologies that can deal with the problem are being sought.

Horizontal flow treatment wells (HFTWs), in conjunction with chemical and biological processes, have been used effectively for the *in situ* remediation of chlorinated ethene-contaminated groundwater, and their potential applications have been the subject of a number of studies (McCarty *et al.*, 1998; Ferland, 1999; Fernandez, 2001; Stoppel, 2001). McCarty *et al.* (1998) demonstrated that trichloroethene (TCE) could be successfully destroyed *in situ* using a pair of HFTWs to inject toluene, hydrogen peroxide, and oxygen

into contaminated groundwater at Site 19, Edwards Air Force Base (AFB), CA. Mixing of these compounds into the contaminated groundwater resulted in *in situ* zones of bioactivity where the TCE was destroyed by biological processes. Figure 1.2, which depicts an operating concept similar to that which was applied at the Edwards AFB site, shows a dual screened treatment well pumping in a downflow mode alongside a treatment well pumping in an upflow mode. In the upflow treatment well, the lower screen is the extraction screen while the upper screen serves as the injection screen, while conversely in the downflow well, the lower screen injects water into the aquifer and the upper screen extracts water. In the aquifer around the injection screens, bioactive zones form where indigenous bacteria degrade the target contaminant. Figure 1.3 shows the pattern of recirculation created by the HFTW system that results in the contaminated groundwater passing multiple times through the bioactive zones. This recirculation significantly increases the effectiveness of the treatment process. In the case of the Edwards Air Force Base field demonstration, downgradient TCE concentrations were 2-3% of upgradient concentrations, even though a single pass through a bioactive zone only removed 85% of the contaminant (McCarty *et al.*, 1998). In addition to providing high levels of treatment, HFTWs also reduce risk and costs by treating contaminants in the subsurface, without the need to pump contaminant aboveground.

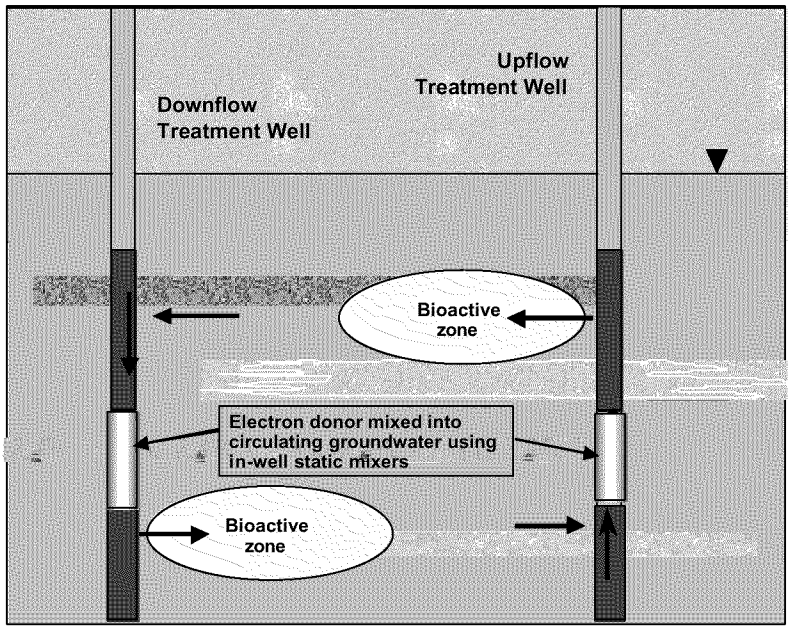


Figure 1.2 HFTW operating concept

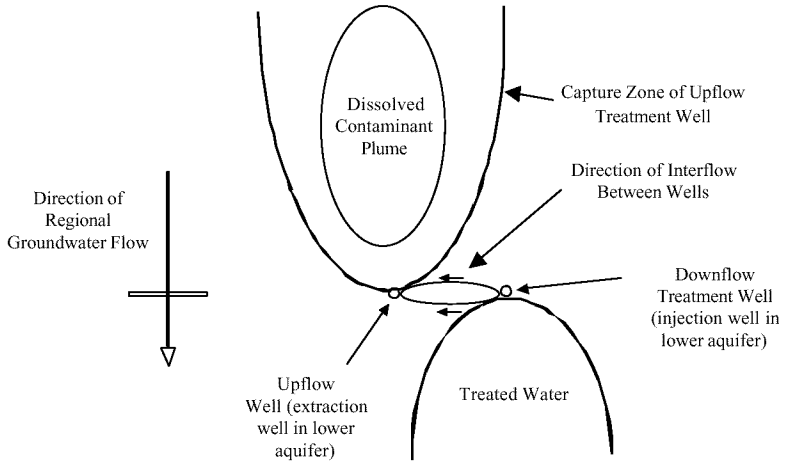


Figure 1.3 Plan view of HFTW system showing flow lines in lower part of aquifer

Laboratory studies show that perchlorate-contaminated groundwater and wastewater can be reduced to innocuous end products by either physicochemical or biological processes. Physicochemical perchlorate treatment processes studied include perchlorate reduction by metallic iron using ultraviolet light to promote the reaction (Gurol and Kim, 2000), reduction of perchlorate by titanous ions in ethanolic solution (Earley *et al.*, 2000; Amadei and Earley, 2001), electrochemical reduction (Urbansky and Schock, 1999), reverse osmosis (Urbansky and Schock, 1999) and ion exchange (Guter, 2000; Tripp and Clifford, 2000; Batista *et al.*, 2000; Venkatesh *et al.*, 2000; Brown *et al.*, 2000, Gu *et al.*, 2000a,b). The main biological processes studied in the laboratory involve perchlorate biodegradation promoted by the addition of an electron donor (such as acetate, ethanol, lactate, and hydrogen gas) (Rikken *et al.*, 1996; Logan, 1998; Miller and Logan, 2000; Giblin *et al.*, 2000a; Giblin *et al.*, 2000b; Herman and Frankenberger, 1999; Herman and Frankenberger, 1998; Cox *et al.*, 2000). The microorganisms use perchlorate as the electron acceptor, reducing it to chloride ions and water. Laboratory studies have also researched and documented the ubiquity and multiplicity of microorganisms from diverse environments that are capable of reducing perchlorate (Coates *et al.*, 1999; Coates *et al.*, 2000; Wu *et al.*, 2001). Based on these studies, there may be a potential for effective *in situ* treatment of perchlorate-contaminated groundwater using chemical or biological processes in conjunction with HFTWs.

1.2 RESEARCH OBJECTIVE

This thesis research will develop and implement a model to increase our understanding of how an HFTW system can be used to remediate perchlorate-contaminated groundwater. After a review of potential chemical and biological processes that may be applied in an

HFTW system to treat perchlorate, a technology model will be developed by incorporating a sub-model of the most suitable process into an HFTW hydraulic model. The technology model will then be used to provide a better understanding of how perchlorate contamination can be managed using HFTWs. The model will also serve as a tool to be used in the design and field implementation of HFTW systems to treat perchlorate contaminated groundwater.

1.3 RESEARCH APPROACH

(1) Begin with a literature review of potential physicochemical and biological treatment processes that can be used to treat perchlorate.

(2) A physicochemical or biological process that can treat perchlorate to below regulatory limits, and that is appropriate for in-well application as part of an HFTW system, will be selected and modeled.

(3) The model of perchlorate degradation will be incorporated into a numerical model of the HFTW system

(4) The combined technology model will be applied to determine how various environmental and engineered parameters influence the efficacy of *in situ* remediation of perchlorate-contaminated groundwater using this technology.

(5) The model and environmental data from an actual perchlorate-contaminated site will be used to simulate application of the technology at the site.

1.4 SCOPE AND LIMITATIONS OF RESEARCH

(1) After a literature review of candidate physicochemical and biological perchlorate destruction processes, a process that can degrade perchlorate to

below regulatory limits, and that is appropriate for in-well use, will be selected for modeling. If more than one process meets these criteria, additional criteria will be applied. These criteria may include such things as ease of modeling the candidate process, and potential for commercializing the process (e.g. availability of funds to evaluate the process in the field, marketability of the process).

(2) This model will be developed based upon a review of the literature and published laboratory data. No independent laboratory studies will be conducted as part of this research.

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter, we briefly review perchlorate health effects and regulatory issues, and then examine in some detail the literature that describes degradation mechanisms of perchlorate in water. We then review the physicochemical and biological processes that may potentially be useful in treating perchlorate-contaminated groundwater. We pay particular attention to models that can be used to describe the rate and extent of the reactions associated with these physicochemical and biological treatment processes, as well as the potential of applying these processes in-well. We also look at prior applications of processes, both *in situ* and *ex situ*, that have been used to remediate perchlorate-contaminated groundwater.

2.1.1 DEFINITIONS

Bifunctional anion exchange resin – A material that has two bound cationic groups (usually quaternary ammonium groups), one with long chains for higher selectivity and one with shorter chains for enhanced reaction kinetics (Gu *et al.*, 2000b)

Dissimilatory perchlorate reduction – the two-step process where perchlorate is reduced to chlorate and then chlorite in an energy-producing step (Maier *et al.*, 2000). The further reduction of chlorite to chloride is catalyzed by a chlorite dismutase enzyme that reduces the chlorite to molecular oxygen and chloride (Rikken *et al.*, 1996).

Dismutate – The breaking apart of the bonds in chlorite to produce molecular oxygen and water by specific enzymes.

Facultative anaerobes – microorganisms that preferentially use oxygen if it is present. However, these microbes can use other terminal electron acceptors when oxygen is not present (Maier *et al.*, 2000).

First-order reaction kinetics – A mathematical representation of a reaction rate that assumes the rate of change of a compound X is proportional to the concentration of compound [X] present (Clark, 1996). That is, $d[X]/dt = -k[X]$, where k, the proportionality coefficient, is defined as the first-order rate constant.

Fixed film bioreactor – A biological treatment reactor where the microorganisms are attached to a fixed bed media such as granular activated carbon (GAC) or sand (Montgomery Watson, 2000). Fixed film reactors can either be operated in up flow mode, where the bed media become fluidized (called fluid bed reactor), or down flow mode, where the bed is fixed (called fixed bed reactor) (Montgomery Watson, 2000; Logan, 2001b).

Half-life – A term used to describe the time it takes for half of the chemical of interest to degrade (Maier *et al.*, 1999). The use of the term half-life often implies first-order reaction kinetics. Note that the half-life is concentration independent, and strictly a function of the first-order reaction rate constant.

Hydrogen Release Compound™ (HRC) – A proprietary polylactate substrate developed by Regenesis Corporation that is specially formulated to slowly release lactic acid as it is hydrolyzed (Logan *et al.*, 2000). The lactic acid is used directly as a carbon and energy source by microorganisms (Logan *et al.*, 2000).

Microaerophilic –microorganisms that grow best under conditions of low dissolved oxygen (Maier *et al.*, 2000)

Pseudo first-order reaction – A reaction whose rate can be approximately described by first-order kinetics, even though the reaction mechanism may be complex, with the reaction rate a function of parameters other than the concentration of the reactant of interest. As an example, pseudo-first order kinetics may be observed when the reactant of interest reacts with a second compound, and the rate of destruction of the reactant of interest is described by second-order kinetics (rate is a function of the concentrations of both reactants). However, if the second reactant is at a high concentration that remains relatively constant, the reaction can be described by first-order kinetics (Clark, 1996).

Reductase – An enzyme that catalyzes reduction of a compound.

Selectivity coefficient – The affinity an ion exchange resin has for a particular ion. A generalized ion exchange reaction can be written as follows (Montgomery, 1985):

$$A^{n-} + n(R^+)B^- \leftrightarrow nB^- + (R^+)_n A^{n-}$$

where A is the anion in solution, B is the counterion initially attached to the resin, and R^+ is the positively charged functional group of the resin. From this an equilibrium expression can be written as (Montgomery, 1985):

$$K_{A,B} = \frac{(a_B)^n (a_{R_n A})}{(a_A)(a_{RB})^n}$$

In this equation a_A and a_B are the activities of ions A and B in a solution, and a_{RnA} and a_{RB} are activities of the ions in the resins (Montgomery, 1985). This $K_{A,B}$ is referred to as the selectivity coefficient.

Suspended growth bioreactor – A biological treatment reactor where water flows through a continuously stirred tank reactor (CSTR) and biomass is suspended in the water without a support medium (Montgomery Watson, 2000).

2.2 HEATH EFFECTS/REGULATORY ISSUES

As a major component in rocket fuel, perchlorate is thought to have been released into the environment decades ago, mostly from the then legal discharge of ammonium perchlorate (NH_4ClO_4) by manufacturing plants and the depots where rockets were serviced (Urbansky, 1998). Because of its stability and non-reactivity, perchlorate can potentially remain in the environment for many years. As discussed in Chapter 1, perchlorate is suspected to inhibit the human thyroid gland's normal uptake of iodine (Wolff, 1998). However, there is uncertainty as to the exact health threat posed by perchlorate ingestion through contaminated groundwater, and whether current levels of perchlorate contamination are significant enough to cause adverse health effects (Lamm *et al.*, 1999; Lamm and Doemland, 1999). There is current evidence, however, of some potentially serious health effects due to perchlorate ingestion. The EPA studied the health effects of perchlorate on patients with hypothyroidism in 1992 and found that over a two month period, doses of 6 µg per kg per day or more resulted in fatal changes to bone marrow (Urbansky, 1998). Also, Brechner *et al.* (2000) conducted a study on newborn babies in populations exposed and unexposed to perchlorate-contaminated drinking water. Their results suggested that even low levels of perchlorate might be associated with adverse health effects such as congenital hypothyroidism which may inhibit the child's cognitive, language, and hearing functional development (Brechner *et al.*, 2000). The results draw

attention to the need for further study of the impact of low levels of perchlorate exposure on humans (Brechner *et al.*, 2000).

Studies are ongoing to determine the effects of perchlorate on humans, animals, and ecosystems. Texas Tech University's Institute of Environmental and Human Health will soon begin a $4M project studying the environmental impacts of perchlorate on fish, amphibians, birds and mammals in the Waco Lake and Belton Lake watersheds (Texas Tech, 2001). Lockheed Martin is funding a study that is aimed at determining perchlorate impacts upon humans. They are paying 100 volunteers $1,000 each to take either a placebo or a 3 mg dose of perchlorate (Lockheed Martin, 2001). It is undetermined whether the data gathered from the study will influence the EPA's cleanup standards for perchlorate (DENIX, 2001) but these ongoing studies are aimed at providing a sound scientific basis for perchlorate cleanup standards. Other ongoing efforts include studies on systemic toxicity, reproductive and developmental toxicity, genotoxicity, pharmokinetics, immunotoxicity, interspecies comparison of thyroid hormone response to ammonium perchlorate exposure, as well as studies on humans (TERA, 2001).

Environmental Protection Agency (EPA) Region 1 mandated that Camp Edwards on the Massachusetts Military Reservation must clean up their perchlorate-contaminated groundwater from 300 micrograms per liter ($\mu g\ L^{-1}$) to 1.5 $\mu g\ L^{-1}$ (Camp Edwards Letter, 2001). The Region 1 EPA based this mandate on the currently available provisional reference dose (RfD) that is used to quantify potential harm to human health, which

ranges from 0.0001 mg-kg^{-1}day^{-1} to 0.0005 mg-kg^{-1}day^{-1} (Camp Edwards Letter, 2001). The 1.5 µg L^{-1} cleanup standard is the perchlorate concentration in water that equates to the 0.0001 mg-kg^{-1}day^{-1} reference dose where a young child might be adversely affected, and therefore EPA Region 1 mandates this level of cleanup in keeping with prudent public health measures (MMR Project, 2001). The Region 9 EPA in California has also mandated regulations for perchlorate, establishing a 4 µg L^{-1} cleanup level for the Aerojet Superfund facility in July 2001 (Kowalczyk, 2001).

While there is currently no federal Primary Drinking Water Regulation for perchlorate, many states have taken action to set standards for perchlorate in drinking water. California set a provisional action level of 18 µg L^{-1} in 1997, mandating that water distribution systems shut down if perchlorate levels rise above this standard (EPA, 1999). Other states taking regulatory action include Texas which set an interim action level of 22 µg L^{-1} for perchlorate in drinking water, Arizona which set a provision health based guidance level of 31 µg L^{-1} in 1999, and Nevada which set a provisional site cleanup level of 18 µg L^{-1} in 1997 (EPA, 1999). Texas has recently (October 2001) lowered the water quality standard for perchlorate from 22 µg L^{-1} to 4 µg L^{-1} for residential groundwater and 7-10 µg L^{-1} for commercial or industrial groundwater (Kowalczyk, 2001). The Texas Natural Resources Conservation Commission has also required new Texas Pollution Discharge Elimination System (TPDES) permits, which require that perchlorate-contaminated stormwater be treated prior to discharge (Kowalczyk, 2001). It should also be noted that the current detection limit of 4 µg L^{-1} was the result of a new ion chromatography (IC) method developed in 1997 (Logan, 2001b). An official EPA

mandated RfD for perchlorate is expected in June 2002, and a Safe Drinking Water Act Maximum Contaminant Level is expected by 2004 (Kowalczyk, 2001). We now move on to discuss the fate of perchlorate in the subsurface environment.

2.3 PERCHLORATE FATE IN THE SUBSURFACE ENVIRONMENT

2.3.1 ABIOTIC DEGRADATION

The perchlorate ion consists of a chlorine atom surrounded by four oxygen atoms in a tetrahedral geometry (Epenson, 2000). Ammonium perchlorate is extremely water soluble (on the order of 200 g L^{-1}). Sodium, calcium and magnesium perchlorate salts have even higher water solubilities (Flowers and Hunt, 2000). The ammonium salt dissociates completely in groundwater, where the NH_4^+ cation is typically biodegraded leaving behind the perchlorate (ClO_4^-) ion (Urbansky, 1998).

Perchlorate exhibits unusual behavior in chemical reactions. Perchlorate is a very strong oxidizing agent and in theory it should be highly reactive, oxidizing almost any substance it comes into contact with. In practice, however, it is very slow to react under most circumstances and it is not reduced or precipitated by common chemical agents used for these purposes (Urbansky, 1998). Equations 2.1 and 2.2 are the redox half-reactions for perchlorate reduction to chloride and chlorate respectively, with their associated reduction potentials (Emsley, 1989):

$$ClO_4^- + 8H^+ + 8e^- \leftrightarrow Cl^- + 4H_2O \qquad E^o = 1.287\ V \quad (2.1)$$

$$ClO_4^- + 2H^+ + 2e^- \leftrightarrow ClO_3^- + H_2O \qquad E^o = 1.201\ V \quad (2.2)$$

The positive values for reduction potential in both reactions indicate the reduction to chloride or chlorate is thermodynamically feasible (Urbansky, 1998). Thus it is concluded from the observed sluggish behavior that kinetics, not thermodynamics, dominates the behavior of perchlorate in the environment (Urbansky, 1998). Because of these slow kinetics, perchlorate in the environment is relatively persistent. However, recent studies have shown that microorganisms in the environment can catalyze perchlorate reduction, thereby facilitating perchlorate biodegradation. We will now discuss these biotic degradation processes.

2.3.2 BIOTIC DEGRADATION

The biological processes studied in the laboratory involve perchlorate biodegradation under anaerobic conditions in the presence of an electron donor (such as acetate, lactate, or hydrogen gas) (Logan, 1998). Typically facultative anaerobic microorganisms oxidize the electron donor, use perchlorate as the electron acceptor, and in the process reduce perchlorate to chloride ions and oxygen (Coates *et al.*, 2000). Complete oxidation of the electron donor produces carbon dioxide and water. Biomass is also produced (Rikken *et al.*, 1996). Equation 2.3 below is an example chemical redox equation with perchlorate as the electron acceptor and acetate as the electron donor (Milazzo and Caroli, 1978).

$$CH_3COO^- + ClO_4^- \rightarrow 2HCO_3^- + H^+ + Cl^- \qquad (2.3)$$

While the biochemical pathways for the reduction of perchlorate are not precisely known, good evidence exists to support the three-step microbial degradation pathway proposed by Rikken *et al.* (1996):

$$ClO_4^-\text{ (perchlorate)} \rightarrow ClO_3^-\text{ (chlorate)} \rightarrow ClO_2^-\text{ (chlorite)} \rightarrow Cl^-\text{ (chloride)} + O_2 \qquad (2.4)$$

During the first two intermediate reductions an electron donor is used by bacteria, producing carbon dioxide, water, and biomass (Rikken *et al.*, 1996). It is generally accepted that microbes reduce perchlorate to chlorate and then to chlorite using enzymes (perchlorate reductase and chlorate reductase) that catalyze this reduction and enable the microbes to use the energy for cellular respiration (Urbansky and Schock, 1999). The third step involves an enzyme (chlorite dismutase) that dismutates chlorite to produce chloride and oxygen (Rikken *et al.*, 1996). It has been observed that perchlorate reduction under anaerobic growth conditions is directly proportional to the appearance of chloride, indicating that complete perchlorate reduction (to chloride and oxygen) is possible (Rikken *et al.*, 1996). It can be seen from Equation 2.1 that the complete reduction of perchlorate requires a total of eight electrons. Rikken *et al.* (1996) reported that the four-electron reduction of perchlorate to chlorite using acetate as the electron donor is energetically favorable. The final four-electron reduction that converts chlorite to chloride and oxygen is not energetically favorable, but is facilitated by the enzyme chlorite dismutase - believed to be produced by the bacteria to detoxify chlorite, which is a biotoxin (Rikken *et al.*, 1996). The biochemical mechanism by which the chlorite dismutase enzyme acts has been studied in depth (van Ginkel *et al.*, 1996). Chlorite is not expected to accumulate in solution to toxic levels because the chlorite dismutase enzyme has much greater activity than either the perchlorate- or chlorate-reductase enzymes. For instance, Herman and Frankenberger (1998) found for *Wollinella succinogenes* HAP-1 that the chlorite dismutase enzyme had an activity 1000 times larger than the perchlorate or chlorate-reductase activities. This dissimilatory perchlorate

reduction pathway is believed to be the reductive pathway followed by most perchlorate-respiring microorganisms (Kim and Logan, 2001).

Many studies have been done in the laboratory that attempt to characterize the microorganisms able to degrade perchlorate and explain what conditions are favorable or detrimental to their growth. Table 2.1 summarizes known laboratory research conducted to date on perchlorate respiring microorganisms along with the electron donors tested.

Table 2.1 Summary of laboratory research on perchlorate biodegradation (after Logan, 1998)

	Growth Substrate Tested			
Culture	Growth	No Growth	Reference	Notes
V. dechloraticans	Acetate, ethanol, (glucose)	Lactose, starch; salts of oxalic and citric acids	Korenkov *et al.* (1976)	Poor growth, and only in the presence of a small amount of acetate (Korenkov et al., 1976).
GR-1	Acetate, propionate, caprionate, malate, succinate, lactate	Glucose, arabinose, mannose, mannitor, N-acetylglucosamine, maltose, gluconate, adipate, phenyl acetate	Rikken *et al.* (1996)	Grown on mineral salts medium in microcosm. Cultures started with activated sludge from domestic wastewater treatment
GR-1	Acetate		Kengen *et al.* (1999)	Batch study. In depth research into perchlorate reductase enzyme found chlorate, nitrate, iodate, and bromate were also reduced.
W. Succinogenes - HAP-1	H_2 and aspartate, fumarate, malate; mixture of H_2 and pyruvate, succinate, acetate, whey powder, peptone, yeast extract, brewers' yeast, casamino acids, cottonseed protein	Glucose, fructose, galactose, lactose, sucrose, butyrate, citrate, formate, propionate, benzoate, ethanol, methanol, 1-propanol, starch	Wallace *et al.* (1996)	
Mixed	Acetate, butyrate, citrate, lactate, propionate, pyruvate, succinate, glucose, fructose, lactose, sucrose, ehanol, methanol, nutrient broth, peptone, yeast extract, casamino		Attaway and Smith (1993)	
Consortium	Acetate		Logan *et al.* (1999)	Fixed bed bioreactor
Consortium	H_2 gas		Logan *et al.* (1999)	Unsaturated multiphase bioreactor
perc1ace	Acetate, fumarate, propionate, succinate, casamino acids, nutrient broth, peptone, tryptic soy broth, yeast extract	Citrate, formate, glucose, lactose, sucrose, fructose, starch, methanol, ethanol	Herman and Frankenberger (1999)	Batch and column studies. Able to use oxygen and nitrate as electron acceptors; could not use Fe(III), Mn(IV), or sulfate

Table 2.1 Continued - Summary of laboratory research on perchlorate biodegradation (after Logan, 1998)

	Growth Substrate Tested			
Culture	Growth	No Growth	Reference	Notes
perc1ace	Acetate		Giblin *et al.* (2000a)	Column Study w/ and w/o recycling
Autotrophic consortium	H_2 gas, bicarbonate, and carbon dioxide		Giblin et al. (2000b)	Batch and Packed bed bioreactor studies
Autotrophic consortium	H_2 gas and carbon dioxide		Miller and Logan (2000)	Packed-bed biofilm reactor operated in unsaturated flow mode
Isolate JM (*Dechlorimonas sp.*)	H_2 gas and carbon dioxide		Miller and Logan (2000)	Batch Study. Able to use oxygen, nitrate, chlorate, and perchlorate as electron acceptors; could not use sulfate
Consortium	Methanol, ethanol, and methanol/ethanol mixture		Green and Pitre (2000)	Lab pilot study and full-scale results of GAC and sand fixed bed bioreactors
Isolates WD, TTI, CL, NM, SIUL, MissR, CKB, PS, SDGM, Iso1, Iso2, NSS, PK	Acetate, benzene, hexadecane, toluene	H_2 , fructose, on anoxic basal media amended with glucose, yeast extract, casamino acids	Coates *et al.* (1999)	Batch studies. Able to use chlorate, perchlorate, oxygen as electron acceptors.
Isolates PS and WD	Acetate, proponate, butanoate, *iso*- butanoate, valerate, ethyl alcohol, pyruvate, lactate, succinate, malate, fumarate, casamino acids	H_2, by fermentation on basal media amended with glucose, yeast extract, and casamino acids	Michaelidou *et al.* (2000)	Batch studies
Isolate KJ	Acetate		Kim and Logan (2001b)	Fixed film bioreactor study. Removal rate=18.1 mg/L-min
Consortium	Acetate		Kim and Logan (2001b)	Fixed film bioreactor study. Removal rate=1.8 mg/L-min
In situ consortium	Ethanol, molasses, manure		Cox *et al.* (2000)	Microcosm studies, used actual site soil to simulate aquifer material with no isolation or culture of bacteria.
Isolate KJ, PDX, and mixed	Polylactate compound HRC^{TM} (lactic acid)		Logan et al. (2000)	Batch experiments
Isolate CKB	Acetate		Bruce *et al.* (1999)	Batch experiments
Consortium	Acetate		Kim and Logan (2001a)	Fixed Bed Bioreactor
Inoculum GSL, SBW, and SBB	Acetate		Logan *et al.* (2001)	High-Salinity Solution Batch experiments

These studies examined various electron donors and their ability to be used by microorganisms to promote perchlorate biodegradation. Whether the studies were batch, column, or bioreactor, each observed significant perchlorate removal rate and extent by the perchlorate respiring microorganisms under anaerobic conditions. Other studies have documented the ubiquity and diversity of perchlorate respiring microorganisms that have the ability to carry out this relatively newly discovered metabolic activity (van Ginkel *et al.*, 1996; Coates *et al.*, 1999; Coates *et al.*, 2000; Hunter, 2001; Wu *et al.*, 2001; Zhang *et al.*, 2001).

2.3.3 EFFECT OF GROUNDWATER CHEMISTRY ON FATE

Groundwater may contain several chemical species capable of serving as electron acceptors. Nitrate (NO_3^-) and oxygen are very commonly found in groundwater (Giblin *et. al.*, 2000a). It is generally believed that perchlorate reduction is inhibited by high concentrations of nitrate and oxygen for most organisms (Logan, 1998). Indigenous microorganisms typically utilize oxygen first, then nitrate, then other oxidized electron acceptors, in this case perchlorate (Stumm and Morgan, 1993; Maier *et al.*, 2000). Exceptions are the isolates *W. succinogenes* (HAP-1) and *A. thermotoleranticus* (Logan, 1998), and mixed cultures that have been shown to reduce perchlorate even though both nitrate and oxygen are present. Another notable exception was discovered in the research of Giblin *et al.* (2000a), who isolated the bacterium perclace that was able to respire on perchlorate in the presence of nitrate (though not in the presence of oxygen). Herman and Frankenberger (1999) observed that the presence of nitrate initially decreased the efficiency with which perclace reduced perchlorate. However, this reduced removal efficiency was temporary. After two days in a batch system with 62 mg L^{-1} NO_3^- and

varying perchlorate concentrations (0.089, 0.92, 12.0, and 122 mg L^{-1} ClO_4^-) present, both the ClO_4^- and the NO_3^- were reduced by an order of magnitude (Herman and Frankenberger, 1999). To test the ability of perclace to reduce perchlorate in the presence of nitrate in a flowing system, groundwater with 0.130 mg L^{-1} perchlorate along with 125 mg L^{-1} NO_3^- was passed through a sand column with a 3 hour residence time (Herman and Frankenberger, 1999). After a day of acclimation, the effluent perchlorate concentration was undetectable and nitrate was reduced to less than 1 mg L^{-1} (Giblin *et al.,* 2000a). In follow-on studies, Giblin *et al.* (2000a) demonstrated in both batch and packed column experiments that perclace could reduce perchlorate and nitrate simultaneously (Giblin *et al.*, 2000a). With perchlorate influent concentrations of 0.738 mg L^{-1} and NO_3^- concentrations of 26 mg L^{-1}, the perclace inoculated sand column removed perchlorate and NO_3^- to below detectable levels at a residence time of 5 hours (Giblin *et al.,* 2000a). These studies suggest that in some strains of perchlorate reducing microorganisms, perchlorate reduction is not affected by the presence of nitrate at levels 100-1000 times higher than perchlorate (Giblin *et al.*, 2000a).

Another constituent of groundwater that may impact perchlorate biodegradation is dissolved oxygen. Perchlorate has been shown to be reduced under anaerobic conditions (Giblin *et al.*, 2000a; Herman and Frankenberger, 1999; Logan *et al.*, 2000; Rikken *et al.*, 1996). Most perchlorate respiring microorganisms have the ability to use both oxygen and perchlorate as electron acceptors, and have been reported to preferentially use oxygen as the electron acceptor before using perchlorate (Attaway and Smith, 1993; van Ginkel *et al.,* 1996). Since molecular oxygen is produced by the dismutation of chlorite

and is not toxic to these bacteria, it has been suggested that these microorganisms are microaerophilic or facultative anaerobes rather than strict anaerobes as was originally suggested (Coates *et al.*, 2000). Thus it is concluded that oxygen has the potential to inhibit the degradation of perchlorate and possibly require that more electron donor be present to deplete the oxygen sufficiently in order to promote perchlorate degradation.

2.4 POTENTIAL PERCHLORATE TREATMENT PROCESSES

2.4.1 PHYSICOCHEMICAL PROCESSES

Physicochemical processes have been shown capable of treating perchlorate-contaminated groundwater and wastewater. Some of the potential chemical processes studied include perchlorate reduction by metallic iron using ultraviolet light to accelerate the reaction (Gurol and Kim, 2000) and by titanous ions (Earley *et al.*, 2000). In addition, perchlorate can be removed from water by ion exchange, reverse osmosis, and electrochemical reduction. A review of the work that has been done using these physicochemical processes to treat perchlorate-contaminated water follows. Table 2.2 shows perchlorate physico-chemical treatment technology studies that have been completed or are currently underway in various scales in the field.

Table 2.2 Physico-chemical treatment processes (from Roote, 2001)

#	Project Name	Scale of Project/Target Media/Agency Involved	Treatment Technology Classification	Status of Project
1	Bifunctional Anion Exchange Resin Development -US Patent No 6,059,975-Regeneration	Lab/ Water/ Oak Ridge National Laboratory, University of Tennessee	Bifunctional Anion Exchange Resin	Completed
2	Bifunctional Anion Exchange Resin Pilot	Pilot/ Groundwater/ Oak Ridge National Laboratory, University of Tennessee, Radian	Bifunctional Anion Exchange Resin	Completed (2000)
3	Calgon Carbon Corp. - ISEP® Continuous Ion Exchange	Pilot/ Water/ Calgon Carbon Corp	ISEP® Continuous Ion Exchange	Completed
4	Calgon Carbon Corp. Ion Exchange Bed Regeneration/Umpqua Ion Exchange Bed Regeneration	Lab/ Water/ Calgon Carbon Corp and Umpqua Research Company	Ion Exchange Bed Regeneration Optimization/ Regeneration with Catalytic Oxidation System	Completed (1999)
5	Calgon Carbon Corp. Remediation of Seepage by Ion Exchange	Full-Scale/ Seepage Remediation/ Calgon Carbon Corp	Ion Exchange	In Progress (2000)
6	Catalytic Reduction Using Oxorhenium (V) Oxazoline Complexes	Bench/ Water/ UCLA	(Oxorhenium (V) Oxazoline Complexes)	Completed
7	Demonstration of Perchlorate Reduction in Rejectate from Reverse Osmosis	Lab-scale/ Groundwater and Drinking Water/ ARA & Foster Wheeler Environmental	Anaerobic Biodegradation with Reverse Osmosis	Completed (2000)
8	Full Scale ISEP ® Groundwater Treatment Plant	Full-Scale/ Water/ Calgon Carbon Corp	ISEP® Continuous Ion Exchange	Completed
9	Influence of Humic Substances and Sulfate on Ion Exchange Resins	Lab/ Water/ UNLV	Ion Exchange	Completed (2000)
10	Investigation of Methods for Perchlorate Destruction in Aqueous Waste Stream (AWWARF #2578 and #2536)	Lab/ Water/ Clarkson University & The Pennsylvania State University	Various Abiotic Technologies	In Progress (TBC 2000)
11	Transition Metal Oxygen and Oxo Complexes (NSF #9982004)	Lab/ Soil/ Iowa State University	Chemical Reduction (Catalysis)	In Progress (TBC 2000)
12	NASA/California Institute of Technology Jet Propulsion Laboratory, Ion Exchange Bed Regeneration	Pilot/Water/ Calgon Carbon Corp	Ion Exchange Bed Regeneration	Completed (1999)
13	Permeable Reactive Barrier Feasibility	Lab-scale/ Groundwater/ US DOE Los Alamos National Laboratory	Permeable Reactive Barrier	In Progress (2001)

Table 2.2 Continued - Physico-chemical treatment processes (from Roote, 2001)

#	Project Name	Scale of Project/Target Media/ Agency Involved	Treatment Technology Classification	Status of Project
14	Removal of Perchlorate and Bromate in Conventional Ozone/Gac Systems (AWWARF #2535)	Illinois and Metropolitan Water District of Southern CA (Los Angeles)	Ozone/ GAC	In Progress (TBC 2001)
15	Thermal Regeneration of Ion Exchange Brine	Lab-scale/ Groundwater and Drinking Water/ ARA	Thermal Regeneration of Ion Exchange Brine	Completed (1999)
16	Titanium Ions for Perchlorate Reduction	Lab/ Water/ Georgetown University	Chemical Reduction using Titanium III and Alcohol	In Progress (2000)
17	Treatability of Perchlorate in Groundwater Using Ion Exchange Technology (AWWARF #2532)	Lab/ Water/ Univ of Houston, Montgomery Watson, Johns Hopkins Univ	Ion Exchange Technology	In Progress (TBC 2001)
18	Treatability of Perchlorate-Containing Water by Reverse Osmosis and Nanofiltration (AWWARF #2531)	Lab/ Water/ Univ of Colorado, Nat. Inst of Stand and Tech.,and Metropolitan Water Dist. of Southern CA (LA)	Reverse Osmosis/ Nanofiltration	In Progress (TBC 2001)
19	Treatability Studies for Perchlorate Treatment	Lab-scale/ Surface Water Outfalls/ US DOE Los Alamos National Lab	Anion Exchange	In Progress (2001)
20	US-Switzerland Cooperative Research; Mobility and Interactions of Major Ions in Soils	Lab/ Soil/ Louisiana State Univ, Swiss Federal Institute of Tech	Ion Exchange Processes in Soil	Completed
21	Zero Valence Reduction or Adsorption on Fe0 and Goethite	Bench/ Water/ San Diego State Univ	Chemical Reduction (Fe0, Goethite)	Completed (1999)

2.4.1.1 ION EXCHANGE

Several studies have looked at how perchlorate contaminated water can be treated using ion exchange (IX) processes (Guter, 2000; Tripp and Clifford, 2000; Batista *et al.*, 2000; Venkatesh *et al.*, 2000; Brown *et al.*, 2000, Gu *et al.*, 2000a). In this process, resins that have a high affinity for the perchlorate ion remove it from the water (Guter, 2000). Equation 2.5 is an example chemical equation describing perchlorate removal by a strong base anion exchange resin (Batista *et al.*, 2000):

$$\text{Resin} - Cl^- + ClO_4^- \leftrightarrow \text{Resin} - ClO_4^- + Cl^- \qquad (2.5)$$

Once all of the ion exchange sites have been filled with perchlorate, perchlorate will no longer be removed from the influent water and breakthrough will be observed. Breakthrough is the time at which perchlorate is measured at certain unacceptable levels in the effluent relative to the influent concentration (Batista *et al.*, 2000). When this occurs, the ion exchange resin must be regenerated to be able to continue removing perchlorate. Equation 2.6 describes the regeneration process (Batista *et al.*, 2000):

$$\text{Resin} - ClO_4^- + NaCl \leftrightarrow \text{Resin} - Cl^- + Na^+ + ClO_4^- \qquad (2.6)$$

During regeneration, the resin is flushed with sodium chloride. The chloride ion replaces perchlorate on the resin and the perchlorate is washed out in a concentrated brine waste solution (Batista *et al.*, 2000).

One advantage of this method of treatment is its ability to achieve very low levels of perchlorate in the treated water (Gu *et. al.*, 2000a). Another advantage is the fact that IX has the capability to remove other anionic groundwater contaminants such as nitrate and sulfate (Venkatesh *et al.*, 2000). One major disadvantage of this treatment process is the problem surrounding the ultimate disposal of the concentrated perchlorate brine that is produced when the IX resins are regenerated (Batista *et. al.*, 2000). To deal with this problem Gu *et al.* (2000a) and Batista *et al.* (2000) have suggested a possible combination of ion exchange with a biological treatment process where the perchlorate would be removed from the water by ion exchange and then the concentrated perchlorate brine wastewater would be treated biologically. Batista *et al.* (2000) researched the use of weak anion exchange resins that have the potential to be effectively regenerated with

ammonium hydroxide rather than sodium chloride. This would produce a waste regenerant solution containing ammonium hydroxide (a microbial nutrient) that may be more easily biodegraded than the high salinity waste that is produced using strong IX resins, which may inhibit biodegradation (Batista *et al.*, 2000). Equations 2.7 through 2.9 are the hypothesized steps in the weak anion exchange process (Batista *et al.*, 2000):

$$[R_3N:] + H_2O + CO_2 \leftrightarrow [R_3NH^+]HCO_3 \quad (2.7)$$

$$[R_3NH^+]HCO_3 + NaClO_4 \leftrightarrow [R_3NH^+]ClO_4 + NaHCO_3 \quad (2.8)$$

$$[R_3NH^+]ClO_4 + NH_4OH \leftrightarrow [R_3N:] + NH_4ClO_4 + H_2O \quad (2.9)$$

The tertiary amine group on the resin ([R_3N]) is carbonated in equation 2.7 by passing CO_2-saturated water over the basic form of the resin (Batisata, *et al.*, 2000). The bicarbonate ion is then exchanged for perchlorate in equation 2.8, and finally the resin is regenerated in equation 2.9 using ammonium hydroxide (Batisata, *et al.*, 2000). Studies identified some acrylic weak base resins that removed perchlorate successfully and at the same time were effectively regenerated with a caustic solution of sodium hydroxide (Batista *et al.*, 2000).

While disposing of the regeneration brine is one problem, the regeneration process itself is another problem. Perchlorate is not easily removed from the IX resins by conventional sodium chloride brines (Batista *et. al.*, 2000). A recent study addressing this problem by Gu *et al.* (2001) has demonstrated an effective means of regenerating special, highly selective anion exchange resins more efficiently, thus recovering more of the resin for further perchlorate treatment. They found that tetrachloroferrate ($FeCl_4^-$) anions that

were formed in a solution of ferric chloride ($FeCl_3$) and hydrochloric acid (HCl) used as a regenerant recovered nearly 100% of the anion exchange sites in as few as 5 bed volumes of the regenerant solution (Gu *et al.*, 2001). This new method of regenerating perchlorate-saturated resins has the potential to decrease cost, and waste volume while increasing regeneration efficiency when compared to typical ion exchange regeneration practices (Gu *et al.*, 2001).

Various IX processes involving anions have been modeled. Sengupta and Lim (1988) used a model to accurately predict chromate breakthrough and simulate chromate IX in fixed bed column runs with multiple ion species present in the water. Others have modeled IX processes focusing on cations (Bellot *et al.*, 1999; Schiewer and Volesky, 1995; Schiewer and Volesky, 1996; Yang and Volesky, 1999). Limited modeling work has been performed on perchlorate removal with IX. One study by Guter (2000) involved development of a two-part model. The first objective was to develop a model that would predict the selectivity coefficients for several anions (including perchlorate) on four resins based on resin structure and the molecular structure of the target anion (Guter, 2000). The investigators used computational molecular mechanics to accomplish this (Guter, 2000). The second objective was to determine how the selectivity coefficients would impact the treatment costs by running computer simulations of treatment experiments (Guter, 2000). In particular, the researchers simulated column experiments under various conditions to determine the efficiency of perchlorate removal by various IX resins (Guter, 2000). The model required inputs of untreated water composition, selectivity coefficients for each ion in the untreated water (determined by

computational molecular mechanics), initial resin composition, total ion capacity, and regenerant strength and composition (Guter, 2000). The output data from the model simulations included regenerant quantity and cost, treated water composition, breakthrough curves, wastewater quantity and composition, regeneration rinse curves, final resin composition at various bed depths, data snapshots at various run times, and plant design (Guter, 2000).

2.4.1.2 TITANOUS IONS

Earley *et al.* (2000) discussed the mechanism of perchlorate destruction using titanous ions [$Ti(H_2O)_6^{3+}$] in ethanol. The basic chemical equation involving perchlorate and titanium(III) is (Urbansky, 1998):

$$8Ti^{3+} + ClO_4^- + 8H^+ \rightarrow 8Ti(IV) + Cl^- + 4H_2O \qquad (2.10)$$

Earley *et al.* (2000) hypothesized that perchlorate might be effectively destroyed by trivalent titanous ions and that a media of ethanol increases the rate of destruction by several orders of magnitude. It is believed that the rate of the Ti(III)-perchlorate reaction is increased in the ethanolic solution due to the enhanced formation of perchlorato complexes in the less polar (compared to water) surroundings (Earley *et al.*, 2000). The authors of the study asserted that this process might be a stepping-stone for discovering a practical method of perchlorate destruction in environmental contamination applications.

Recently, Amadei and Earley (2001) reported two more potential catalysts of perchlorate destruction by titanous ions that achieve even higher rates of destruction than the ethanolic media. They studied two catalysts, a macrocyclic ligand called cyclam and a related ligand called CYCAPAB [6-amino-6-(4-aminobenzyl)-1,4,8,11-

tetraazalcyclotetradecan] that they synthesized (Amadei and Earley, 2001). These catalysts enabled perchlorate reduction to proceed at rates as high as 41.0 x 10^4 s^{-1} (Amadei and Earley, 2001). The kinetics for perchlorate destruction in these studies were pseudo first-order (Amadei and Earley, 2001).

2.4.1.3 METALLIC IRON/UV LIGHT

Gurol and Kim (2000) showed that perchlorate in contaminated water can be reduced to chloride and water when exposed to metallic iron (Fe^0) and UV light in an anoxic environment. The reaction involved is (Gurol and Kim, 2000):

$$4Fe^0 + ClO_4^- + 8H^+ \rightarrow Cl^- + 4Fe^{2+} + 4H_2O \qquad (2.11)$$

The rate of perchlorate reduction was found to be dependent on the concentration of Fe^0 and the intensity of the UV light (Gurol and Kim, 2000). The researchers hypothesized that the perchlorate ion adsorbed first to the metallic iron and then the iron was oxidized, with the electron transfer facilitated by the UV light (Gurol and Kim, 2000). They observed a 77% reduction of 1 mg L^{-1} perchlorate by 100 g L^{-1} of Fe^0 in 3 hours. However, to achieve such high perchlorate degradation, very high intensity UV light (total UV intensity of 0.9 W cm^{-2} generated using up to 16 low pressure mercury lamps) was needed (Gurol and Kim, 2000).

2.4.1.4 REVERSE OSMOSIS

Reverse osmosis (RO) is another possible means of removing perchlorate from groundwater. The contaminated water is forced through a membrane that rejects all ions and concentrates it into a brine reject solution. The water passing through the membrane is deionized water. RO is a mature technology that is fairly well commercialized (Urbansky and Schock, 1999). RO has been increasingly implemented as a means of

purifying saline water as the earth's population rises and fresh water becomes progressively more scarce. Full-scale RO water purification units are in operation, processing as much as 72 million gallons per day (Buros, 2000). Disadvantages of RO for groundwater remediation include high operating costs, size of treatment units, and the need to treat and dispose of the concentrated brine that is produced. Advantages are that it removes a variety of contaminants including nitrate and sulfate at a variety of concentrations.

2.4.1.5 ELECTROCHEMICAL REDUCTION

Perchlorate can also be reduced by applying an electrical current to the water using a cathode made of such metals as platinum, tungsten carbide, ruthenium, titanium, aluminum, or carbon doped with chromium(III) oxide or aluminum dioxide (Urbansky, 1998). This technology has yet to be applied to groundwater remediation, and potential disadvantages include ion transport to the electrode, electrode corrosion, surface passivation, and natural organic matter adsorption to the surface (Urbansky and Schock, 1999). No studies have been conducted documenting rates of reduction or any other kinetic data.

2.4.2 BIOLOGICAL PROCESSES

The biological processes being studied to treat perchlorate in groundwater are simply engineered versions of the natural biological degradation processes discussed in section 2.3.2. Here, we focus on the application of these processes, as well as models that may be used to describe them. Initially, suspended growth reactors were used to treat industrial wastewater containing high concentrations of perchlorate from the washing of solid rocket booster motors (Attaway, 1994; ESTCP, 2000; Logan, 2001b). To treat

lower concentrations in groundwater and drinking water, fluidized- and fixed-bed reactors have been applied (Logan, 2001b). Both of these types of bioreactors have been successfully used to remove perchlorate from contaminated wastewater and groundwater in various studies and applications (Wallace *et al.*, 1998; Green and Pitre, 2000; Giblin *et al.*, 2000b; Miller and Logan, 2000; Hatzinger *et al.,* 2000; Logan *et al.*, 2001; Losi *et al.*, 2001; Polk *et al.*, 2001; Togna *et al.*, 2001). Table 2.3 shows the influent and effluent concentrations of perchlorate, detention times, and rates of perchlorate removal from different lab studies using fixed film bioreactors. Polk *et al.* (2001) also performed a lab study with a granular activated carbon (GAC) fluidized bed fixed film bioreactor in order to evaluate the possibility of full-scale implementation to treat perchlorate contaminated groundwater at Longhorn Army Ammunition Plant (LHAAP) (Texas). Perchlorate influent concentrations averaging 16,500 $\mu g\ L^{-1}$ were reduced to below 5 $\mu g\ L^{-1}$. Following this successful laboratory evaluation, a full-scale fluidized bed fixed film bioreactor with a capacity to treat 50 gallons per minute was installed at LHAAP (Polk *et al.*, 2001). Influent perchlorate concentrations similar to that of the laboratory experiments (11,000-23,000 $\mu g\ L^{-1}$) were reduced to below the treatment objective of 350 $\mu g\ L^{-1}$ within three weeks of inoculation, and have been routinely reduced to below the detection limit (4 $\mu g\ L^{-1}$) (Polk *et al.*, 2001). Additionally, both Hatzinger *et al.* (2000) and Greene and Pitre (2000) conducted similar pilot scale fluidized bed reactor studies followed by full scale implementations treating influent perchlorate concentrations from 13 $\mu g\ L^{-1}$ to 400 $mg\ L^{-1}$ to below 4 $\mu g\ L^{-1}$ using both sand and GAC media. These reactors, of course, were installed aboveground. *In situ* biodegradation is advantageous over *ex situ* because the contaminant does not have to be pumped to the surface for

aboveground treatment (Logan, 2001b). Biobarriers and injected substrates such as acetate or Hydrogen Release Compound® (HRC®) have been used to create the anaerobic conditions necessary for *in situ* bioremediation of perchlorate (Logan, 2001b; Logan *et al.,* 2000). Table 2.4 summarizes perchlorate biological treatment studies either completed or currently ongoing.

Table 2.3 Comparison of perchlorate reduction rates in different reactors (from Logan, 2001a)

		Perchlorate concentration (mg/L)	Perchlorate concentration (mg/L)				
Study	Substrate	In	Out	C_{lm} (Log-mean ClO_4 conc)	Reactor detention time (min)	Rate (mg/L-min)[a]	Reference
O1	BYF-100[b]	1500	<100[c]	517	70	20	Wallace *et al.*, 1998
O2	BYF-100[b]	500	<100[c]	249	28	14	Wallace *et al.*, 1999
O3	Acetate[d]	100	<1	21.5	180	0.55	Herman and Frankenberger, 1999
O4	Acetate	22.5	<0.004	2.61	30.4	0.74	Kim and Logan, 2000
O5	Acetate	20	<0.004	2.35	11	1.8	Kim and Logan, 2001
O6	Acetate[e]	19.6	<0.004[f]	2.31	1.08	18.1	Kim and Logan, 2001
O7	Acetate[d]	0.738	<0.004	0.15	150-600	0.0012-0.0049	Giblin *et al.,* 2000a
O8	Acetate[d]	0.13	<0.005	0.038	180	0.0007	Herman and Frankenberger, 1999
I1	Hydrogen	0.74	0.46	0.59	1.2	0.23	Miller and Logan, 2000
I2	Hydrogen	0.7	<0.004	0.13	40	0.017	Giblin *et al.,* 2000a

Note: O1-O8 = organic substrates; I1-I2 = inorganic substrates.

[a]Rates assume maximum values given for the outlet concentration.

[b]BYF-100 contains 54% naturally occurring protein,peptides,free amino nitrogen,vitamins,and trace elements.

[c]Removal based on 95% of samples.

[d]Pure cultural reactor using isolate perclace

[e]Pure cultural reactor using isolate KJ

[f]Removal based on 84% of samples.

Table 2.4 Biological treatment processes (from Roote, 2001)

#	Project Name	Scale of Project/Target Media/ Agency	Treatment Technology Classification	Status of Project
1	Aerojet Bioremediation of Soil from Former Burn Area by Anaerobic Composting	Pilot/ Soil/ Geoyntec, Inc.	Ex Situ Bioremediation/ composting	Completed (2000)
2	Aerojet Facility, Rancho Cordova, (Sacramento) CA	Pilot-, Full-Scale/Groundwater/ US Filter, Envirogen, Inc.	Four Anoxic Fluidized Bed Reactors, Pilot, Full-Scale Design, Startup, and	Completed (Started 1998)
3	Aerojet Facility, San Gabriel, CA	Pilot/ Groundwater/ US Filter, Envirogen	Anoxic Fluidized Bed Reactor	Completed
4	Aerojet In Situ Bioremediation Field	Pilot/ Groundwater/ Geosyntec, Inc.	In Situ Bioremediation	Completed (2000)
5	Anoxic Fluidized Bed Reactor (FBR) Optimization, Lawrenceville, NJ	Pilot/ Groundwater/ US Filter, Envirogen Inc.	Anoxic Fluidized Bed Reactor	Completed
6	Application of Bioreactor Systems to Low-Concentration Contaminated	Lab/ Water/ Northwestern Univ.	Bioreactor	In-Progress (TBC 2001)
7	Application of Bioreactor Systems to Low-Concentration Contaminated	Lab-pilot/ Water/ The Pennsylvania State Univ.	Packed Bed or Biofilm Bioreactors	In-Progress (TBC 2001)
8	Baldwin Park Operable Unit of San Gabriel Basin, CA	Pilot/ Groundwater/ BPOUSP, US EPA IX, Main San Gabriel Basin Water Master	Fluidized Bed Bioreactor	In-Progress (TBC 2001)
9	Biodegradation of Subsurface Pollutants by Chlorate-Respiring Microorganisms	Lab/ Soil, Water/ The Pennsylvania State Univ.	Chlorate Reducing Microorganisms (PRM) Physiology and Use of Chlorate as Electron Acceptor	In-Progress (TBC 2001)
10	Biological Treatment at Low Concentrations in Water - Phase 1	Bench/ Water/ Harding Lawson Associates	Fluidized Bed Bioreactor	Not Specified
11	Biological Treatment at Low Concentrations in Water - Phase 2	Pilot/ Water/ Harding Lawson Associates	Fluidized Bed Bioreactor	Not Specified
12	Bioremediation of Perchlorate in Groundwater	Lab/ Water/ Univ. of California	Anaerobic Bioremediation	In-Progress (TBC 2001)
13	Composting for Treatment of Explosives	Full-Scale / Soil/ US Army	Ex Situ Bioremediation/ composting	In-Progress (TBC 2001)
14	Confidential Chemical Company Site, High Concentration Perchlorate/Chlorate Treatment	Pilot/ Groundwater/ US Filter, Envirogen Inc.	Anoxic Fluidized Bed Reactor	Completed

Table 2.4 Continued – Biological treatment processes (from Roote, 2001)

#	Project Name	Scale of Project/Target Media/ Agency Involved	Treatment Technology Classification	Status of Project
15	Demonstration of Perchlorate Reduction in Rejectate from Reverse Osmosis	Lab-Scale/ Groundwater and Drinking Water/ ARA & Foster Wheeler Env.	Anaerobic Bioremediation with Reverse Osmosis	Completed (2000)
16	Former Army Ammunition Plant, U.S. Army Corps of Engineers	Pilot/ Groundwater/ US Filter and Envirogen Inc.	Anoxic Fluidized Bed Reactor	Completed
17	Full-Scale Design of a 1.2 MGD Groundwater Treatment Plant	Full-Scale Treatment Plant/ Groundwater/ ARA & Biothane Inc.	Anaerobic Bioremediation	Completed (2000)
18	*In Situ* Bioreduction and Removal of Ammonium Perchlorate (SERDP #CU-1162)	Lab/ Groundwater/ Southern Illinois Univ.	*In Situ* Bioremediation	In-progress (2001)
19	*In Situ* Bioreduction and Removal of Ammonium Perchlorate (SERDP #CU-1163)	Lab/ Groundwater/ Envirogen Inc.	*In Situ* Bioremediation	In-progress (2001)
20	*In Situ* Bioreduction and Removal of Ammonium Perchlorate (SERDP #CU-1164) Geosyntec Guelph Ontario	Lab/ Groundwater/ GeoSyntec Inc.	*In Situ* Bioremediation	In-progress (2001)
21	*In Situ* Bioreduction and Removal of Ammonium Perchlorate (SERDP #CU-1164)	Lab/ Groundwater/ University of Toronto	*In Situ* Bioremediation	In-progress (2001)
22	NASA/ California Institute of Technology Jet Propulsion Laboratory, Anoxic FBR	Pilot/ Groundwater/ NAVFAC, NFESC, US Filter and Envirogen Inc.	Anoxic Fluidized Bed Reactor	In-progress
23	NASA/ California Institute of Technology Jet Propulsion Laboratory, Packed Bed Reactor	Pilot/ Groundwater/ NFESC, Foster Wheeler Env. Corp., UC Riverside	Packed Bed Reactor	Pending
24	Patented Hall Bioreactor	Pilot/ Groundwater, EcoMat, Earth Tech, Inc.	Anoxic Bioreactor	Completed (2000)
25	Perchlorate Biodegradation Pilot-scale Design, Construction, and Demonstration	Pilot-Scale/ Effluent from the Washout of Minutemen Boosters/ ARA and Case	Anaerobic Biodegradation	Completed (1994)
26	*In Situ* Perchlorate Degradation	Lab/ Soil, Groundwater/ Penn State and Regenesis	Hydrogen Release Compound (HRC™)	In-Progress
27	Insoluble Organic Substrates ("Edible Oils") for Degradation of Perchlorate	Pilot/ Air Force Center for Environmental Excellence (AFCEE) Solutions - IES	*In Situ* Bioremediation	Planned (2001)
28	Isolation of Perchlorate Reducing Bacterial Culture	Laboratory-Scale/Effluent from the Washout of Minutemen Boosters/ARA	Anaerobic Biodegradation	Completed (1990)
29	Longhorn Army Ammunition Plant, Karnack, TX - *In Situ* Soil Bioremediation	Pilot/ Soil, Sediment/ University of Georgia	*In Situ* Bioremediation	Completed (2001)

Table 2.4 Continued – Biological treatment processes (from Roote, 2001)

#	Project Name	Scale of Project/Target Media/ Agency	Treatment Technology Classification	Status of Project
30	Low Temperature Biodegradation Studies	Lab-Scale/ Groundwater/ ARA	Anaerobic Biodegradation	Completed (2000)
31	Multi-Cell Respirometry Unit Test of Perchlorate Destruction	Lab/ Water/ Indian Head Division Naval Surface Warfare Center	*Ex Situ* Biological	In-Progress
32	Treatability Studies on Groundwater from Henderson, NV	Lab/Groundwater/ ARA and Biothane Inc.	Anaerobic Biodegradation	Completed (2000)
33	US Navy, Southern Division, NAVFAC, Groundwater Remediation, McGregor, Texas	Pilot-Scale/ Groundwater/ EnSafe Inc.	Fixed Film Bioreactor	In-progress (2001)
34	US Navy, Southern Division, NAVFAC, *In Situ* Groundwater Remediation,	Full-Scale / Groundwater/ EnSafe Inc.	Full-Scale *In Situ* Biobarrier	In-progress (2001)
35	US Navy, Southern Division, NAVFAC, Soil Remediation, McGregor, Texas	Full-Scale / Soil/ EnSafe Inc.	Anaerobic Treatment Cell	Completed
36	Prototype Design, Construction, and Demonstration	Prototype/ Effluent from the Washout of Minutemen Boosters/ ARA, Thiokol, and Case Engineering	Anaerobic Biodegradation	Completed (1997)
37	Prototype Process Optimization	Prototype Effluent from the Washout of Minuteman Boosters/ ARA and Thiokol	Anaerobic Biodegradation	Completed (2000)
38	Respiratory Enzymes Used for Perchlorate Reduction by Microorganisms	Lab/ Soil, Water/ The Pennsylvania State Univ.	Perchlorate Reducing Microorganisms (PRMs) Physiology	In-Progress (TBC 2003)
39	Rocket Manufacturing Site Soil Bioremediation by Anaerobic Composting	Pilot/ Soil/ Geosyntec Inc.	*Ex Situ* Bioremediation (Composting)	Completed (2000)
40	Soil Bioremediation of Perchlorate	Bench/ Soil/ Univ. of Georgia	Bioremediation	Completed
41	Transformation of Perchlorate by Newly Isolated Bacterium	Lab/ Water/ Azko Nobel Central Research	Isolation of Anaerobic Cultures	Completed (1996)

Giblin *et al.* (2000b) performed laboratory experiments examining the removal of perchlorate by an autotrophic consortium of microorganisms using hydrogen and bicarbonate as growth substrates under anaerobic conditions. They conducted

experiments on the consortium's ability to remove perchlorate from a mineral salt medium and then from a sample of perchlorate-contaminated groundwater from the San Gabriel Valley in California. They showed that levels of perchlorate found in typical contaminated groundwater could be removed to below the detection limit of 4 $\mu g\ L^{-1}$ when passed through a fixed-bed bioreactor at a flow rate of 1 mL min^{-1} (Giblin *et al.*, 2000b). The authors also showed that perchlorate removal efficiency was decreased by (1) decreasing pH, (2) increasing flow through the column, and (3) decreasing temperature (Giblin *et al.*, 2000b).

Miller and Logan (2000) also performed laboratory experiments with an autotrophic packed-bed biofilm reactor column using hydrogen gas as an electron donor and carbon dioxide as a carbon source. They isolated a bacterium called JM that is a hydrogen-oxidizing bacterium capable of using oxygen, nitrate, chlorate, and perchlorate as electron acceptors (Miller and Logan, 2000). The purpose of their research was to show that perchlorate could be removed from water under hydrogen-oxidizing conditions for use in drinking water applications (Miller and Logan, 2000). They note however, that the greatest potential application of biological perchlorate treatment systems is in groundwater remediation due to the reluctance of water utilities in the United States to use biological treatment systems for drinking water (Miller and Logan, 2000). Although their experimental methods were similar to the methods of Giblin *et al.* (2000b) described above, they operated their bioreactor in an unsaturated flow mode (but still under anaerobic conditions) much like a trickling filter in order to more effectively transport the hydrogen gas to the biofilm since hydrogen is only moderately soluble in water (Miller

and Logan, 2000). While it is believed that dissolved oxygen inhibits perchlorate reduction (Logan, 1998), the oxygen was not removed from the influent water in this experiment. They achieved higher than expected perchlorate removal rates (See Table 2.2, Study I1) (Miller and Logan, 2000).

Two examples of field applications of perchlorate bioremediation include the Aerojet Superfund Site located in Rancho Cordova, California and the Thiokol site in Brigham City, Utah. In October of 1998 construction was completed on a full-scale 3,400 gpm bioreduction plant that cost $5.0 million to build (Montgomery Watson, 2000). Contaminated groundwater containing 3,000 – 6,500 $\mu g\ L^{-1}$ perchlorate was pumped to this FBR treatment plant that reduced perchlorate concentrations to below 4 $\mu g\ L^{-1}$ with the capacity to treat 4,000 gpm (Montgomery Watson, 2000). The treated water was reintroduced to the subsurface through groundwater recharge wells (Montgomery Watson, 2000). In May of 2000, McMaster *et al.* (2001) demonstrated successful *in situ* bioremediation of perchlorate at this same site using a single recirculation well that extracted water from the aquifer, mixed in electron donor (acetate), and reintroduced it into the aquifer. Influent perchlorate concentration ranged from 10-15 mg L^{-1}. Indigenous microorganisms reduced the perchlorate to concentrations that were less than both the Provisional Action Level of California (18 $\mu g\ L^{-1}$) and the method detection limit of 4 $\mu g\ L^{-1}$ in under 60 days within 5 meters of the electron donor injection well (McMaster *et al.*, 2001).

At the Thiokol site, a suspended growth wastewater treatment bioreactor has been in operation since December of 1997 (Montgomery Watson, 2000). This bioreactor treats influent perchlorate concentrations of up to 5,000 mg L^{-1} down to below 4 µg L^{-1} at flow rates of 2,000 – 2,300 gpd (Montgomery Watson, 2000). The treated water is discharged into a sewage treatment plant that eventually discharges into a surface water stream (Montgomery Watson, 2000).

2.4.2.1 FIRST ORDER MODELS

Logan (2001a) compared the results from 10 different fixed film bioreactor experiments and demonstrated that first-order kinetics held for perchlorate degradation in reactors using organic substrates as electron donors (either acetate or a complex high-protein medium). Table 2.2 summarizes the studies performed using flow through bioreactors along with the perchlorate reduction rates and electron donors for the different reactors.

Cox *et al.* (2000) (see Table 2.1 for synopsis of study) performed various microcosm studies that used soil from two perchlorate-contaminated sites and amended the soils with electron donors, perchlorate reducing bacteria, or both. At the first site, the perchlorate concentrations ranged from 90 to 120 mg L^{-1} in the microcosms, and the investigators calculated perchlorate biodegradation half-lives (assuming first-order decay) ranging from 0.8 to 2 days, based upon the microcosm data (Cox *et al.*, 2000). At the second site, the perchlorate concentrations averaged 100 mg L^{-1}. From the data, the investigators calculated perchlorate biodegradation half-lives ranging from 1.2 to 1.8 days (Cox *et al.*, 2000). McMaster *et al.* (2001) in their studies at the Aerojet Superfund Site in Sacramento, California (mentioned earlier) observed *in situ* perchlorate biodegradation

half-lives that ranged from 0.2 to 1.8 days. These rates are consistent with the laboratory microcosm values reported by Cox *et al.* (2000).

2.4.2.2 MONOD MODELS

In addition to the first-order biodegradation kinetics model that was assumed in the above studies, another model put forth to explain the biodegradation of perchlorate in contaminated groundwater is a Monod kinetic model (Logan, 2000). Monod kinetics is based on the assumption that microbial growth is driven by consumption of a limiting growth compound or substrate (Schwartzenbach *et al.*, 1993). The exponential growth rate observed in a microbial population (when substrate is not limiting) eventually reaches a maximal growth rate either due to the organism's intrinsic growth rate for that particular substrate or because another factor becomes limiting (Schwartzenbach *et al.*, 1993). The Monod equation relating the microbial specific growth rate due to synthesis (μ_{syn}) to the concentration of the growth substrate is shown below (Equation 2.12). Here μ_{max} is the maximum specific growth rate of the microorganisms (Pitter and Chudoba, 1990), X is the concentration of active microorganisms, S is the concentration of the growth-limiting chemical, and K_s is the Monod constant, also called the half saturation concentration. Note by examining equation 2.12 that the Monod constant is the substrate concentration at which the microbial growth rate is half the maximum growth rate (Schwartzenbach *et al.*, 1993; Rittman and McCarty, 2001).

$$\mu_{syn} = \frac{1}{X}\frac{dX}{dt} = \mu_{\max}\left(\frac{S}{S + K_s}\right) \qquad (2.12)$$

Growing microorganisms also experience decay due to cell maintenance and other cell functions and a term to describe this behavior is needed. Endogenous decay will be

denoted by the parameter b with units of T^{1} (Rittman and McCarty, 2001). Equation 2.13) describes the endogenous decay rate

$$\mu_{dec} = \left(\frac{1}{X} \frac{dX}{dt} \right)_{decay} = -b \qquad (2.13)$$

where μ_{dec} is the specific growth rate due to decay in units of T^{1} (Rittman and McCarty, 2001). Combining equations 2.12 and 2.13 gives the net specific growth rate of active biomass (μ) as seen in equation 2.14 below (Rittman and McCarty, 2001).

$$\mu = \mu_{\max} \left(\frac{S}{S + K_s} \right) - b \qquad (2.14)$$

Now we want to link microbial growth with the use of electron donor. Defining r_{ut} as the overall rate of substrate utilization by a biomass at concentration X, we can write (Rittman and McCarty, 2001):

$$r_{ut} = -k_{\max} \left(\frac{S}{K_S + S} \right) \cdot X \qquad (2.14a)$$

Thus, the net rate of biomass growth ($r_{net} = \mu X$), becomes

$$r_{net} = Y_{biomass} \cdot k_{\max} \left(\frac{S}{K_S + S} \right) \cdot X - b \cdot X \qquad (2.14b)$$

Where k_{max} is the maximum specific rate of substrate use in units of [mass electron donor$*$(biomass)$^{-1}*$time^{-1}] and $Y_{biomass}$ is the biomass yield, defined as the biomass produced per mass of electron donor consumed in units of [biomass$*$(mass electron donor)$^{-1}$] (Rittman and McCarty, 2001). From Equation 2.14, we see that the maximum specific growth rate equals the maximum specific rate of substrate use multiplied by the biomass

$$\mu_{\max} = k_{\max} Y_{biomass} \qquad (2.15)$$

Equation 2.14 relates donor use and biomass growth, thus allowing us to use Monod kinetics, which describes microbial growth kinetics, to also describe the kinetics of substrate utilization.

Logan *et al.* (2001) performed laboratory experiments to obtain growth rates of perchlorate-respiring bacteria using different electron donors, as well as to obtain other kinetic parameters used in the Monod model. Of the ten bacteria that were isolated all were able to use oxygen and chlorate as terminal electron acceptors, and eight of these were able to degrade perchlorate. A summary of the maximum observed growth rates and kinetic parameters for growth on different electron acceptors is shown in Table 2.5. Table 2.6 shows the cell yields observed in the studies as compared to cell yields reported by others. Finally Table 2.7 shows the maximum growth rates reported by others. These laboratory studies provide parameter values that will be useful when applying a model to simulate perchlorate biodegradation. Comparing Table 2.5 and 2.7 shows that results from most studies are within an order of magnitude of each other.

Table 2.5 Summary of the maximum observed growth rates in batch culture and kinetic parameters for growth on the indicated electron donors of (per)chlorate-reducing isolates grown under aerobic or anaerobic conditions (from Logan *et al.*, 2001)

Isolate	Electron Donor	Electron Acceptor	Max observed μ (h^{-1})	μ_{max} (h^{-1})[a]	K_s (mg/liter)[a]
KJ	Acetate	Oxygen	0.27	0.25+-0.00	14+-1
		Chlorate	0.26	0.27+-0.03	60+-25[b]
		Perchlorate	0.14	0.20+-0.07[c]	470+-290[d]
PDX	Acetate	Oxygen	0.28	0.28+-0.01	2.7+-2.1[e]
		Chlorate	0.21	0.27+-0.02	75+-16
		Perchlorate	0.21	0.24+-0.03	45+-19[b]
	Lactate	Chlorate	0.15	0.13+-0.01	10+-4[c]
PDA	Acetate	Oxygen	0.64	NT[f]	NT
		Chlorate	0.18	NT	NT
		Perchlorate	NG[g]	NT	NT
PDB	Acetate	Oxygen	0.41	NT	NT
		Chlorate	0.26	NT	NT
		Perchlorate	NG	NT	NT

[a]The maximum growth rate and half-saturation contants, μ_m and K_s, obtained by a nonlinear regression analysis using data shown in Fig 2 (not shown) through 4 and are significant at P value of 0.01 except as noted.

[b]$P<0.10$

[c]$P<0.05$

[d]$P=0.14$

[e]$P=0.26$

[f]NT, not tested

[g]NG, no growth

Table 2.6 Comparison of cell yields in the presence of various electron acceptors of isolate KJ versus those reported by others (from Logan *et al.*, 2001)

Culture	Cell yield - $Y_{biomass}$ (g [DW]/g of acetate) with the following electron acceptor:			Reference
	Oxygen	Chlorate	Perchlorate	
KJ[a]	0.46+-0.07	.044+-0.05	0.50+-0.08	Logan *et al.*, 2001
GR1	0.27+-0.01	0.28+-0.01	0.24+-0.01	Rikken *et al.*, 1996
AB1	0.13+-0.04	0.10+-0.04	NT[b]	Olson, 1997
Mixed	NT	0.30+-0.61[c]	NT	Malmqvist *et al.*, 1991
	NT	0.12+-0.06	NT	Logan *et al*., 1998

[a]Cell yields for isolate KJ are not significantly different ($p>0.05$) for the three different electron acceptors.

[b]NT, not tested.

[c]Converted from grams of volatile suspended solids (VSS) per equivalent of available electrons to grams (DW) per gram of acetate by assuming that 0.85g of VSS = 1 g (DW) and that there are eight equivalents of available electrons per mole of acetate.

Table 2.7 Maximum reported growth rates of previously described chlorate- and perchlorate-respiring isolates or mixed cultures (from Logan *et al.*, 2001)

Culture	Electron Acceptor	Electron Donor	maximum growth rate, μ_{max} (h^{-1})	Reference
GR1	Chlorate	Acetate	0.1	VanGinkel *et al.*, 1996
	Oxygen		0.23	
	Oxygen + Nitrate		0.077	
AB1	Chlorate	Acetate	0.012	Olson, 1997
Perclace	Perchlorate	Acetate	0.07	Herman and Frankenberger, 1998
CKB	Chlorate	Acetate	0.28	Bruce *et al.*, 1999
Mixed	Chlorate	Acetate	0.085	Logan *et al.*, 1998
		GG[a]	0.2	
		Phenol	0.035	

[a]Glucose-glutamic acid (50:50 mixture)

2.4.2.3 DUAL-MONOD MODELS

Many investigators (e.g. Bouwer and McCarty, 1985; Molz *et al.*, 1986; Semprini and McCarty, 1991; Envirogen, 2001) use dual-Monod kinetics to describe microbial growth as a function of both electron donor and acceptor concentrations. The model is written as equation 2.16 below (Semprini and McCarty, 1991).

$$\frac{\partial X}{\partial t} = X \cdot k_{max} \cdot Y_{biomass} \cdot \left(\frac{C^{don}}{K_{SD} + C^{don}} \right) \cdot \left(\frac{C_A}{K_{SA} + C_A} \right) - b \cdot X \cdot \left(\frac{C_A}{K_{SA} + C_A} \right) \qquad (2.16)$$

where

X = concentration of active microorganisms (mg/L)

k_{max} = maximum utilization rate of electron donor (mg donor/mg biomass/day)

C^{don} = concentration of electron donor (mg/L)

K_{SD} = electron donor half saturation concentration (mg/L)

C_A = concentration of electron acceptor (mg/L)

K_{SA} = electron acceptor half saturation concentration (mg/L)

$Y_{biomass}$ = yield coefficient (mg biomass/mg donor)

b = biomass decay rate (1/day)

It should be noted that the decay parameter (b) in equation 2.16 is multiplied by a Monod term including the electron acceptor concentration (Semprini and McCarty, 1991). Modification of the decay rate by the Monod term makes the assumption that the rate of microbial decay is a function of the electron acceptor concentration. Apparently, this Monod term is included so that in areas of the aquifer with no acceptor present, biomass isn't reduced in the model to extremely low levels (since decay is stopped when acceptor concentration equals zero). Others (*e.g.* Borden and Bedient, 1986; Molz *et al.*, 1986) do not make the assumption that the microbial decay rate is affected by acceptor

concentration. Biomass decay rate values in the literature for perchlorate respiring microorganisms are very sparse, and range from 0.0026 – 0.043 day^{-1} (Envirogen, 2002b). Half saturation concentration values are also sparse and vary widely in the literature, especially since they are dependent on the specific experimental setup; microbial cultures, electron donors, and the specific electron acceptors tested (oxygen, nitrate, or perchlorate). These factors all contribute to the dissimilar values reported by different investigators.

Equation 2.17 below shows the rate of donor consumption dependent upon both the electron donor concentration and the electron acceptor concentration.

$$\frac{\partial C^{don}}{\partial t} = -k_{max} \cdot X\left(\frac{C^{don}}{K_{SD} + C^{don}}\right)\cdot\left(\frac{C_A}{K_{SA} + C_A}\right) \qquad (2.17)$$

Equation 2.18 describes the rate of electron acceptor consumption, which depends on both electron donor and acceptor, and is decreased as the biomass decays. Again note the decay rate parameter b on the far right hand side of the equation is modified by a Monod term with the electron acceptor concentration (Semprini and McCarty, 1991).

$$\frac{\partial C_A}{\partial t} = -k_{max} FX\left(\frac{C^{don}}{K_{SD} + C^{don}}\right)\cdot\left(\frac{C_A}{K_{SA} + C_A}\right) - b \cdot d_c f_d X\left(\frac{C_A}{K_{SA} + C_A}\right) \qquad (2.18)$$

where:

F = stoichiometric ratio of electron acceptor to electron donor utilization for biomass synthesis (g acceptor/g donor) (Semprini and McCarty, 1991)

d_c = cell decay oxygen demand (mg oxygen/mg biomass)

f_d = fraction of cells that are biodegradable

2.4.2.4 MULTI-ELECTRON ACCEPTOR DUAL-MONOD PERCHLORATE MODEL

The environmental firm Envirogen has developed a model for perchlorate biodegradation based on dual-Monod kinetics that incorporates changes in microbial populations, consumption of electron donor (acetate), and utilization of multiple electron acceptors. The details of the Envirogen model are presented below (Envirogen, 2001).

Electron Donor

The rate of utilization of the electron donor (acetate in our model) is described below. The modified dual-Monod model attempts to simulate the effect of competition between multiple electron acceptors on donor and acceptor utilization, and microbial growth. As mentioned in Section 2.3.3, indigenous microorganisms typically prefer oxygen to nitrate, and nitrate to perchlorate, as an electron acceptor because of the relative amount of energy available for growth (Stumm and Morgan, 1993; Coates *et al.*, 2000).

$$r_{donor} = \frac{dC^{don}}{dt} = -X \cdot (r_{don,oxy} + r_{don,nit} + r_{don,per}) \tag{2.19}$$

Note that r_{donor} is the rate of donor consumption (in units of donor mass per volume per time) in contrast to $r_{don,oxy}$, $r_{don,nit}$, and $r_{don,per}$, which are defined below as specific rates of donor utilization (in units of donor mass per biomass per time):

$$r_{don,oxy} = k_{\max}^{don/oxy} \left[\frac{C^{don}}{K_S^{don/oxy} + C^{don}} \right] \cdot \left[\frac{C^{oxy}}{K_S^{oxy} + C^{oxy}} \right] \tag{2.20}$$

$$r_{don,nit} = k_{\max}^{don/nit} \left[\frac{C^{don}}{K_S^{don/nit} + C^{don}} \right] \cdot \left[\frac{C^{nit}}{K_S^{nit} + C^{nit}} \right] \cdot \left[\frac{K_i^{oxy}}{K_i^{oxy} + C^{oxy}} \right] \tag{2.21}$$

$$r_{don,per} = k_{\max}^{don/per} \left[\frac{C^{don}}{K_S^{don/per} + C^{don}} \right] \cdot \left[\frac{C^{per}}{K_S^{per} + C^{per}} \right] \cdot \left[\frac{K_i^{oxy}}{K_i^{oxy} + C^{oxy}} \right] \cdot \left[\frac{K_i^{nit}}{K_i^{nit} + C^{nit}} \right] \tag{2.22}$$

r_{donor} = rate of electron donor consumption (mg donor/L/day)

$r_{don,oxy}$ = specific rate of electron donor consumption using oxygen as an electron acceptor (mg donor/mg biomass/day)

$r_{don,nit}$ = specific rate of electron donor consumption using nitrate as an electron acceptor (mg donor/mg biomass/day)

$r_{don,per}$ = specific rate of electron donor consumption using perchlorate as an electron acceptor (mg donor/mg biomass/day)

k_{max} = maximum specific rate of substrate utilization (mg donor/mg biomass/day);

$k_{max}^{don/oxy}$ = maximum specific rate of substrate utilization in the presence of oxygen when donor concentration is varied and limiting (mg donor/mg biomass/day);

$k_{max}^{don/nit}$ = maximum growth rate of substrate utilization in the presence of nitrate when donor concentration is varied and limiting (mg donor/mg biomass/day);

$k_{max}^{don/per}$ = maximum specific rate of substrate utilization in the presence of perchlorate when donor concentration is varied and limiting (mg donor/mg biomass/day);

C^{don} = concentration of the electron donor (acetate) (mg/L);

C^{oxy} = concentration of oxygen (an electron acceptor) (mg/L);

C^{nit} = concentration of nitrate (an electron acceptor) (mg/L);

C^{per} = concentration of perchlorate (an electron acceptor) (mg/L);

$K_S^{don/oxy}$ = half saturation concentration of the electron donor in the presence of oxygen when donor (acetate) concentration is varied and limiting (mg donor/L);

$K_S^{don/nit}$ = half saturation concentration of the electron donor in the presence of nitrate when donor (acetate) concentration is varied and limiting (mg donor/L);

$K_S^{don/per}$ = half saturation concentration of the electron donor in the presence of perchlorate when donor (acetate) concentration is varied and limiting (mg donor/L);

K_S^{oxy} = half saturation concentration when oxygen (an electron acceptor) concentration is varied and limiting (mg/L);

K_S^{nit} = half saturation concentration when nitrate (an electron acceptor) concentration is varied and limiting (mg/L);

K_S^{per} = half saturation concentration when perchlorate (an electron acceptor) concentration is varied and limiting (mg/L);

K_i^{oxy} = oxygen inhibition coefficient (mg/L);

K_i^{nit} = nitrate inhibition coefficient (mg/L);

X = concentration of active biomass (mg/L); and

t = time (days).

From equation 2.19 to 2.22, we see that the depletion of the donor is controlled by the oxygen concentration (if oxygen is present), the nitrate concentration (if nitrate is present), and by perchlorate concentration only if both oxygen and nitrate are not present. It has been observed in the laboratory that oxygen and nitrate have inhibiting effects on the microorganisms use of the lesser preferred electron acceptors (Envirogen, 2002b). Equation 2.21 includes an inhibition coefficient that serves to slow the rate of consumption of donor using nitrate as an electron acceptor if oxygen is present. Similarly, equation 2.22 includes inhibition coefficients that slow the rate of donor consumption using perchlorate as an acceptor if either oxygen or nitrate is present. The inhibition coefficients can be estimated as the half-saturation constant (Envirogen, 2001).

Microbial Population

Since microbial growth is due to consumption of the growth substrate, we can write:

$$\frac{dX}{dt} = Y_{biomass} \cdot r_{donor} - b \cdot X \qquad (2.23)$$

$Y_{biomass}$ = the biomass yield per mass of donor consumed (mg biomass/mg electron donor)

b = biomass decay rate (1/day)

where the second term on the right hand side accounts for biomass decay, which is modeled as a first-order decay process (note that in this model the decay parameter, b, is not modified by an electron acceptor Monod term as it was in Equation 2.16).

Electron Acceptors

The rate of utilization of the electron acceptors is modeled below. It can be seen that these rates are directly linked to the rate of utilization of the donor (acetate) through a factor (F), which is the stoichiometric yield coefficient for the electron donor-electron acceptor reaction.

Oxygen

$$r_{oxy} = \frac{dC^{oxy}}{dt} = -X \cdot (F_{oxy} \cdot r_{don,oxy}) \qquad (2.24)$$

Nitrate

$$r_{nit} = \frac{dC^{nit}}{dt} = -X \cdot (F_{nit} \cdot r_{don,nit}) \qquad (2.25)$$

Perchlorate

$$r_{per} = \frac{dC^{per}}{dt} = -X \cdot (F_{per} \cdot r_{don,per}) \qquad (2.26)$$

r_{oxy} = rate of oxygen consumption (mg oxygen/L/day);

r_{nit} = rate of nitrate consumption (mg nitrate/L/day);

r_{per} = rate of perchlorate consumption (mg perchlorate/L/day);

F_{oxy} = stoichiometric coefficient for the donor (acetate)-oxygen reaction (mg oxygen/mg donor) where the stoichiometric coefficient accounts for the electron acceptor requirement for biomass production based on the following stoichiometry ($C_5H_9NO_3$ represents the chemical formula for biomass) (Envirogen, 2002a):

$$O_2 + 0.64\,CH_3COOH + 0.056\,NH_4OH \leftrightarrow 0.056\,C_5H_9NO_3 + 0.168\,H_20 + 1.0\,H_2CO_3$$

F_{nit} = stoichiometric coefficient for the donor (acetate)-nitrate reaction (mg nitrate/mg donor) where the coefficient accounts for the electron acceptor requirement for biomass production (Envirogen, 2002a):

$$NO_3^- + 0.786CH_3COOH \leftrightarrow 0.056C_5H_9NO_3 + 0.47N_2 + 0.53H_20 + 0.29H_2CO_3 + HCO_3^-$$

and

F_{per} = stoichiometric coefficient for the donor (acetate)-perchlorate reaction (mg perchlorate/mg donor) where the coefficient accounts for the electron acceptor requirement for biomass production (Envirogen, 2002a):

$$ClO_4^- + 1.14CH_3COOH + 0.056NH_4OH \leftrightarrow 0.056C_5H_9NO_3 + Cl^- + 2.002H_2CO_3 + 0.16H_20$$

The values of F calculated from the above equations are 0.83, 1.3, and 1.45 respectively for oxygen/acetate, nitrate/acetate, and perchlorate/acetate. For given initial conditions,

the model (Equations 2.19-2.26) enables determination of the concentration of donor, acceptor, and biomass at any point in time.

Using this model to guide the collection of laboratory data, Envirogen conducted batch and column experiments to compute model parameter values. These values are reported below.

Table 2.8 Growth rate parameters with substrate varied (Envirogen, 2002b)

Parameter (units)	Value	Method of Determination
$k_{max}^{don/per}$ (1/d)	0.14	Determined by measuring OD550 [1] values of the culture with substrate [2] varied and acceptor in excess.
$k_{max}^{don/nit}$ (1/d)	0.145	Determined by measuring OD550 values of the culture with substrate varied and acceptor in excess.
$k_{max}^{don/oxy}$ (1/d)	0.21	Determined by measuring OD550 values of the culture with substrate varied and acceptor in excess.
$K_S^{don/per}$ (mg/L)	120	Determined by measuring OD550 values of the culture with substrate varied and acceptor in excess. Substrate concentration at 1/2 k_{max}
$K_S^{don/nit}$ (mg/L)	70	Determined by measuring OD550 values of the culture with substrate varied and acceptor in excess. Substrate concentration at 1/2 k_{max}
$K_S^{don/oxy}$ (mg/L)	90	Determined by measuring OD550 values of the culture with substrate varied and acceptor in excess. Substrate concentration at 1/2 k_{max}
[1]OD550 - Optical density at 600 nm		
[2]Substrate is acetate		

Table 2.9 Growth rate parameters with electron acceptor varied (Envirogen, 2002b)

Parameter (units)	Value	Method of Determination
$k_{max}^{per/don}$ (1/d)	0.071	Determined by measuring OD550 values of the culture with acceptor varied and substrate in excess
$k_{max}^{nit/don}$ (1/d)	0.21	Determined by measuring OD550 values of the culture with acceptor varied and substrate in excess
K_S^{nit} (mg/L)	180	Determined by measuring OD550 values of the culture with substrate varied and acceptor in excess. Nitrate concentration at 1/2 k_{max}
K_S^{per} (mg/L)	150	Determined by measuring OD550 values of the culture with substrate varied and acceptor in excess. Perchlorate concentration at 1/2 k_{max}

Table 2.10 Biomass yield ($Y_{biomass}$) and decay (b) parameters calculated using different electron acceptors (Envirogen, 2002b)

Parameter (units)	Value
Yield ($Y_{biomass}$), perchlorate (mg biomass /mg acetate)	0.173
Yield ($Y_{biomass}$), nitrate (mg biomass/mg acetate)	0.131-0.252
Yield ($Y_{biomass}$), oxygen (mg biomass/mg acetate)	0.317
Decay (b - 1/day), Perchlorate	0.0026-0.0169
Decay (b - 1/day), Nitrate	0.0026
Decay (b - 1/day), Oxygen	0.043

Table 2.10 shows the experimentally determined values of $Y_{biomass}$ and b for use in equation 2.23 for the three electron acceptors.

2.5 HORIZONTAL FLOW TREATMENT WELLS (HFTWs)

2.5.1 OPERATION OF HFTWs

As mentioned in Chapter 1, HFTWs have been used to successfully treat contaminated groundwater *in situ.* HFTWs can capture contaminated groundwater and treat it *in situ* using a chemical or biological treatment technology, while increasing overall contaminant destruction efficiency due to the re-circulation of the groundwater through

the treatment wells (McCarty *et al.*, 1998; Garrett, 1999; Ferland, 1999; Fernandez, 2001; Stoppel, 2001; Gandhi et al., 2002a,b). Both Ferland (2000) and Stoppel (2001) analyzed the use of HFTWs where palladium catalyst in-well reactors were used to destroy TCE. McCarty *et al.* (1998) analyzed the full-scale use of HFTWs in a biodegradation application with a configuration similar to that of Figure 2.1 at Edwards Air Force Base Site 19. The chosen treatment technology in this case was cometabolic biodegradation stimulated by the introduction of toluene (electron donor), oxygen (electron acceptor), and hydrogen peroxide into the aquifer at the injection screens of the upflow and downflow treatment wells. The HFTW system mixed the nutrients into the contaminated groundwater to promote microbially mediated destruction of TCE that occurred in the zones of bioactivity. In their research on *in situ* aerobic co-metabolic bioremediation of chlorinated ethenes, Goltz *et al.* (2001) have observed the effects of electron donor injection pulse schedules in HFTW systems. Short pulses of primary substrate at high concentrations result in less microbial growth near the wells since electron donor is able to disperse into portions of the aquifer away from the injection wells before being degraded (Goltz *et al.*, 2001). Benefits of pulsing in the chlorinated ethene application include greater remediation of contaminant due to reduction of competitive inhibition and reduction of well screen bioclogging (Goltz *et al.*, 2001). On the other hand, a study on *in situ* perchlorate bioremediation found that bioclogging was not an issue when injecting electron donor to stimulate microbial growth (McMaster *et al.*, 2001). In both chemical and biological applications, the HFTW circulation effect results in multiple passes of the contaminated groundwater through the treatment zones, which leads to much higher treatment efficiencies than would be observed in a simple single-pass treatment

technology (McCarty *et al.*, 1998). In this section we will review methods to analytically and numerically model groundwater flow, as well as groundwater contaminant fate and transport resulting from HFTW operation.

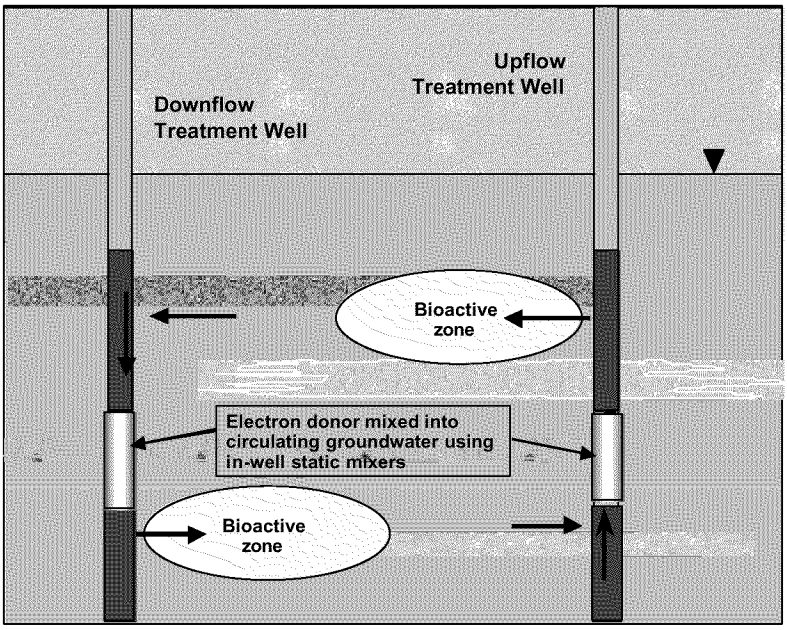


Figure 2.1 HFTW operating concept

2.5.2 MODELING

Three general types of models can be used to describe groundwater flow fields surrounding an injection or extraction well: numerical, semi-analytical, or analytical. Numerical models are typically used to simulate complex, heterogeneous, anisotropic, transient groundwater flow conditions. Analytical models are usually more simple models that require simplifying assumptions to reduce the complex differential equations to a manageable form. Analytical flow models traditionally assume steady-state

conditions in a homogeneous, isotropic, confined aquifer of constant thickness (Christ, 1997). While these assumptions may appear limiting, the models can be effectively used for screening and gaining insight into the process being modeled and can also be helpful when a lack of field data prohibits using the more complex numerical model (Christ, 1997). A semi-analytical model has characteristics of both numerical and analytical models. The following discussion will illustrate models that have been used to describe groundwater flow, as well as contaminant fate and transport, resulting from HFTW operation.

2.5.2.1 ANALYTICAL MODELS

Christ *et al.* (1999) developed an analytical model to investigate how multiple injection and extraction well pairs might be used to treat TCE–contaminated groundwater. For an HFTW system to operate correctly, it is important that the groundwater flow induced by the system predominantly be horizontal flow (Christ *et al.*, 1999). If water travels vertically, there is short circuiting of the flow between the injection and extraction screens of the same treatment well, severely impacting the treatment efficiency of the HFTW system (Christ *et al.*, 1999). Fortunately, horizontal flow will normally be induced by an HFTW system, since in most aquifers horizontal hydraulic conductivity is typically an order of magnitude greater than vertical hydraulic conductivity (Domenico and Schwartz, 1998; Christ *et al.*, 1999). These typical anisotropic conditions also permit the HFTW system to be modeled as two separate simultaneously operating extraction/injection well pairs.

When designing an HFTW system, the two key design variables are capture zone width and overall treatment efficiency. Capture zone width is a measure of the extent to which the contaminated groundwater plume will be captured for treatment. Overall treatment efficiency ($\eta_{overall}$) measures the extent of contaminant destruction by comparing contaminant concentrations upgradient (C_{in}) and downgradient (C_{down}) of the HFTW treatment system:

$$\eta_{overall} = 1 - \frac{C_{down}}{C_{in}} \qquad (2.27)$$

Figure 2.2 illustrates these important parameters for a two-well HFTW system (Stoppel, 2001). It depicts the upper portion of an aquifer where the upflow well is an injection well and the downflow well is an extraction well.

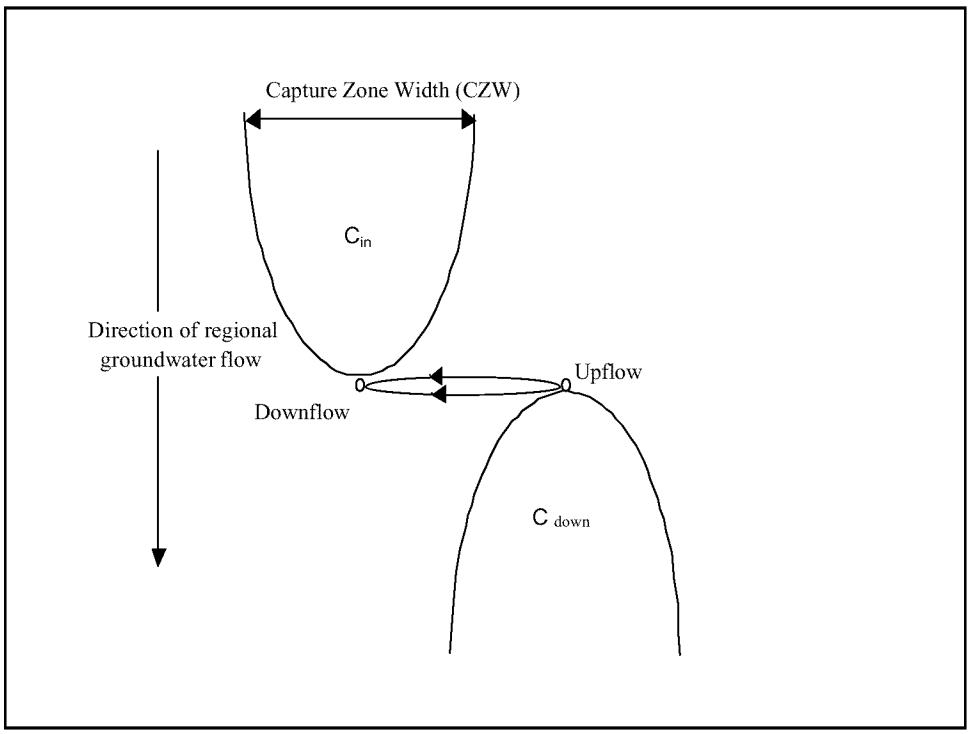


Figure 2.2 Plan view of 2-well HFTW system (upper aquifer shown) (After Stoppel, 2001)

Capture zone width and overall treatment efficiency can be determined by knowing the interflow between the treatment wells in the HFTW system, and the single-pass treatment efficiency of the technology being applied in the treatment wells. Interflow is defined as the fraction of the total groundwater pumped through an extraction screen that originated from the injection screen of an adjacent treatment well. Christ (1997) and Christ *et al.* (1999) present methods using complex potential theory for determining interflow based on aquifer (hydraulic gradient, hydraulic conductivity, aquifer thickness) and pumping well (pumping rate, distance between wells) characteristics. For details of these methods, the reader is referred to Christ (1997) and Christ *et al.* (1999).

The single-pass treatment efficiency is defined as the fraction of contaminant destroyed following a single-pass of contaminated groundwater through the treatment zone (Christ *et al.*, 1999; Stoppel, 2001). Single-pass treatment efficiency is a function of the technology that is applied in the treatment wells. For an analytical model of HFTW operation, contaminant destruction is typically described as a first-order process, dependent on the residence time of the contaminant in the treatment reactor (Ferland, 2000; Stoppel, 2001). Thus, for given aquifer and well characteristics, and knowledge of the first-order rate constant for contaminant destruction by the technology applied in the treatment wells, a designer can analytically determine the capture zone width and overall contaminant destruction effected by an HFTW system.

2.5.2.2 NUMERICAL MODELS

Numerical flow and transport models have been developed and used to simulate aerobic biodegradation of trichloroethene in an HFTW system (Huang and Goltz, 1998; Gandhi *et al.*, 2002a;b). The Huang and Goltz (1998) model is a three-dimensional model that combines steady-state flow, advective/dispersive transport of dissolved species, equilibrium or rate-limited sorption, and biodegradation. The model assumes microorganisms are stationary. The other chemicals dissolved in the groundwater (oxygen, electron donor, and TCE) are transported by the flowing groundwater (advection/dispersion) and affected by sorption.

The Huang and Goltz (1998) FORTRAN code uses a finite difference approach to numerically solve the three-dimensional partial differential equations describing fate and transport. The program MODFLOW (Harbaugh and McDonald, 1996) calculates the

steady-state conditions of flow in the aquifer, and these flow velocities are then used in a transport model, which simulates fate and transport of TCE, dissolved oxygen, toluene and bacteria (Huang and Goltz, 1998). The model incorporates dual-Monod kinetics to simulate the co-metabolic biodegradation taking place in the aquifer. The model also accounts for competitive inhibition of TCE destruction due to the presence of an electron donor. A finite difference grid, like one shown in Figure 2.2, is manually created using Visual MODFLOW. Its dimensions and specific cell composition can be varied, based on the system being modeled.

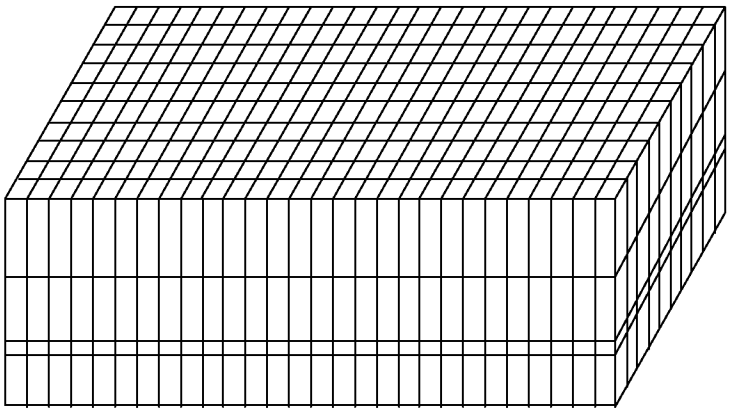


Figure 2.2 Example of a three dimensional finite difference grid (from Garrett, 1999)

Well locations in the three dimensional grid and pumping rates are specified in MODFLOW, along with boundary conditions. MODFLOW uses these data to calculate the steady state hydraulic head and velocity fields. The transport package of the computer program then uses the velocity data as well as the initial and boundary conditions of the electron donor, electron acceptors, and bacteria to calculate their concentrations over space and time. The concentrations of the components can be

monitored at any location on the grid, which allows the user to monitor the system and assess its performance. Setting up the model requires the user to input the contaminant source location, treatment well locations, grid cell size, number of grid cells, length of time steps, positions of observation points, and simulation time.

Gandhi *et al.* (2002a) also developed a three dimensional, numerical model that was used to simulate the Edwards AFB Site 19 HFTW system. This model had characteristics similar to the Huang and Goltz (1998) model, though it was based on finite elements which allowed for use of smaller grid dimensions near wells, where high spatial resolution was needed (Gandhi *et al.*, 2002a). Gandhi *et al.* (2002a) developed a flow model that described conditions at the Edwards site. The output of the flow model was then used in a fate and transport model. The fate and transport model simulated the same processes as were simulated by the Huang and Goltz (1998) model. The only differences between the two models were that the Gandhi *et al.* (2002b) model also accounted for TCE transformation product toxicity, and was based on finite elements, giving it greater flexibility. For further details regarding the mathematical formulation of the site model, the reader is referred to Gandhi *et al.* (2002b). The model fit the field data for TCE and dissolved oxygen well, and matched the toluene concentration data qualitatively (Gandhi *et al.*, 2002b). Based on the model analyses, it was concluded that the engineered flow field established by the HFTWs reduced the effect of site heterogeneities on the treatment system's performance (Gandhi *et al.*, 2002b). It was also concluded that the model was a useful tool in helping to interpret field results and evaluate technology performance (Gandhi et al., 2002b).

3.0 METHODOLOGY

3.1 INTRODUCTION

In this chapter, a process that can treat perchlorate to below regulatory limits and that is appropriate for in-well application in an HFTW system will be selected for further study. A submodel that simulates the selected treatment process will be developed and then combined with an appropriate HFTW flow model to create a technology model that will simulate the *in situ* destruction of perchlorate-contaminated groundwater using an HFTW system. The model will then be verified by running individual model components (with other components turned off) to ensure that output from each model component is behaving as expected. Finally we will discuss how the technology model will be used to answer the final two research questions: (1) how do environmental and engineering parameters influence technology efficiency, and (2) how might the technology be applied at an actual perchlorate-contaminated site.

3.2 SELECTION OF PERCHLORATE TREATMENT TECHNOLOGY

Table 3.1 compares the physicochemical and biological treatment technologies proposed in this research with regard to the criteria set forth in Chapter 1. In this section the treatment technologies will be evaluated and the most appropriate technology that can both reduce perchlorate-contaminated groundwater to below regulatory limits and be used in-well with an HFTW system will be selected. For the purposes of our evaluation, the current IC technology detection limit of 4 $\mu g\ L^{-1}$ will be used as the regulatory limit. As discussed in Chapter 2, it is currently projected that the regulatory limit will be some low level around 4 or 5 $\mu g\ L^{-1}$. However, the fact that a regulatory limit has yet to be

decided upon is important to this discussion, as it means that a treatment technology that provides some flexibility in achieving a treatment level is desirable.

The five physicochemical treatment technologies discussed earlier include ion exchange, titanous ion reduction, metallic iron/UV light reduction, reverse osmosis, and electrochemical reduction. Ion exchange (IX) has been used fairly extensively to remove perchlorate from industrial waste streams (Montgomery Watson, 1999; Venkatesh *et al.*, 2000). The major advantages of IX include the ability to remove perchlorate to below the current detection limit (4 $\mu g\ L^{-1}$) as well as the ability to remove various other contaminants. Disadvantages are the need to dispose of the waste regenerate brine and down time of the system to regenerate the IX resin. The IX process does not destroy the perchlorate, it only removes it from the groundwater and concentrates it. For use in an HFTW system the regenerate would need to be pumped to the surface for further disposal. For these reasons, IX does not appear to be a suitable technology candidate for in-well application in an HFTW system. The two titanous ion processes discussed in the literature review (titanous ion in ethanol solution and catalyst enhanced destruction) are newer technologies with very limited laboratory data. The processes have not yet been tested at pilot scale and no data exist to determine whether or not these technologies have the ability to degrade perchlorate to below regulatory limits rapidly enough for in-well use. Because of the newness of the technology and the limited kinetic data available, this technology also does not appear to be a suitable treatment technology for use in this system at the current time. The limited data on perchlorate reduction with metallic iron and UV light indicate that the technology is unable to remove perchlorate to below

regulatory levels at this stage in its development. It might also be a logistical problem to place the UV light source in-well. These challenges do not make this technology an appropriate candidate for in-well application. Reverse osmosis (RO) is a proven drinking water treatment technology that has the ability to remove perchlorate to below regulatory limits. However, it would be difficult to place a reverse osmosis system in-well because the size of an RO unit to treat typical flow rates would be excessive. For example, a well pumping 10 gallons per minute would require the RO unit to be about 10 feet by 4 feet by 6 feet and weight about 2000 pounds (Martin, 2001). The pumps needed to generate the pressure required to treat the water [(225-375 psi), Buros, 2000)], the size of the unit required, and the need for further treatment of the waste brine make this technology a poor candidate for in-well application. Electrochemical reduction is another mature treatment technology, though it has not yet been applied to treat contaminated groundwater (Urbansky and Schock, 1999). No studies have been conducted documenting whether perchlorate can be removed to below regulatory levels using electrochemical reduction. Also, difficulties applying this technology in-well are presented due to the relatively slow transport of the perchlorate ions to the electrode surface, electrode corrosion, surface passivation, and organic matter adsorption to the electrode surface (Urbansky and Schock, 1999). For these reasons electrochemical reduction does not seem well suited for application in an in-well system.

Table 3.1 Evaluation of treatment technologies

Treatment Process	Treat to Below Regulatory Limits (4 µg/L)?	Appropriate for In-well Application?	Comments
Physicochemical			
Ion exchange	Yes	No	Regenerant would need to be pumped to the surface for treatment/disposal
Titanous Ions	Unknown	No	Relatively untested, unknown application methods, limited kinetic data
Metallic Iron/UV Light	No	No	
Reverse Osmosis	Yes	No	System too large for in-well use. Brine would need to be pumped to the surface for treatment/disposal
Electrochemical Reduction	No	No	Cathode fouling from groundwater constituents would inhibit treatment
Biological			
Hydrogen Gas Reductant	Yes	Yes	
Acetate Reductant	Yes	Yes	
Lactate Reductant	Yes	Yes	

Let us now look at biological processes. First, biodegradation has been shown to effectively remove perchlorate from groundwater to below regulatory levels (Logan, 2001b). Second, it has removed perchlorate at rates that are fast enough to be useful in the HFTW system (Logan, 2001b). Third, it lends itself to in-well application better than

most other methods since only electron donor needs to be mixed into the groundwater to facilitate the bioremediation. The actual biodegradation occurs outside the well in the aquifer. It has been shown that perchlorate-degrading microorganisms are ubiquitous and are numerous at perchlorate-contaminated sites (Wu *et al.*, 2001). They can be stimulated to rapidly biodegrade perchlorate by the introduction of electron donor (Cox *et al.*, 2000). The electron donor chemical is degraded in the biodegradation process and therefore does not accumulate, which is important for an *in situ* groundwater remediation strategy. For these reasons, the treatment process selected for further study is *in situ* biodegradation.

3.3 TECHNOLOGY SUBMODEL

3.3.1 SUBMODEL SELECTION

In this section we choose the biological sub-model that will be used along with the chosen HFTW flow and transport model. As stated in Chapter 2 the main kinetic models that have been used to simulate perchlorate biodegradation are first-order, Monod, dual-Monod, and multi-acceptor dual-Monod models. First-order models offer a simple way of describing perchlorate degradation in the absence of any detailed knowledge of the destruction mechanism. Since several studies have documented the impacts of other groundwater constituents on perchlorate degradation, as described in section 2.3.2, it appears that the process can be modeled to a greater level of detail. Monod and dual-Monod models offer a greater degree of detail because they model the effect of the electron donor and/or acceptor on microbial growth, though these models do not account for the competition between electron acceptors that has been observed in the laboratory.

The multi electron acceptor dual-Monod biodegradation model proposed by Envirogen discussed in section 2.4.2.4 offers advantages over the first-order, Monod, and dual-Monod models. It allows for the observed competition between different electron acceptors to be modeled. Neither the first-order nor Monod models have this capability. Equation 2.19, which describes the rate of electron donor use by the microorganisms as a function of both microbial and electron acceptor concentration, incorporates this competition. The model also realistically incorporates the effect of both the electron donor and electron acceptor on the rate of perchlorate degradation, which neither first-order nor Monod models account for. The three rate parameters on the right-hand side of equation 2.19 model the degradation of oxygen, nitrate, and the target contaminant perchlorate, which are directly linked to the consumption of the electron donor. In addition, the model incorporates the effect of microbial growth on the perchlorate degradation. Envirogen (2002b) has used this model to simulate the laboratory data summarized in Tables 2.8 – 2.10.

3.3.2 SUBMODEL ASSUMPTIONS

(1) Cell yield ($Y_{biomass}$) and biomass decay (b) do not change with different electron acceptors (observed to be approximately true, see Table 2.6 and Table 2.10) (Logan *et al.*, 2001). While reported parameter values vary somewhat, $Y_{biomass}$ and b will be assumed constant in the interest of keeping the model relatively simple. This assumption will be tested in the sensitivity analysis.

(2) Maximum specific rate of substrate utilization (k_{max}) and donor half saturation concentration (K_S^{don}) do not change with the different electron acceptors; that is $k_{max} = k_{max}^{don/per} = k_{max}^{don/nit} = k_{max}^{don/oxy}$ and $K_S^{don} = K_S^{don/per} = K_S^{don/nit} = K_S^{don/oxy}$ (these

parameters are within the same order of magnitude, see Table 2.8, 2.9; Logan *et al.*, 2001). These assumptions will be tested in the sensitivity analysis.

(3) The values for the inhibition coefficients K_S^{oxy} and K_S^{nit} will be assumed equal to their respective half saturation concentrations K_i^{oxy} and K_i^{nit} (Envirogen, 2001).

(4) Electron donor sorption is assumed to be a linear equilibrium process.

(5) It will be assumed that the electron acceptors (ClO_4^-, NO_3^-, and O_2) are non-sorbing. Perchlorate has been reported to poorly sorb to mineral surfaces (Flowers and Hunt, 2000; Logan *et al.*, 2000) and there was no observed perchlorate sorption in sand batch tests. In the tests performed by Kim and Logan (2000) perchlorate breakthrough in a sand column was not distinguishable from an inert tracer (NaCl).

(6) Aside from the microorganisms oxygen, nitrate, and perchlorate will be the only groundwater constituents considered in the model.

(7) Electron donor will be assumed to be acetate for the purposes of this modeling effort. More has been published about perchlorate biodegradation using acetate as a donor than has been published using other electron donors. It is also a relatively accessible chemical that is not harmful to the environment and is expected to have a relatively inexpensive cost per volume treated (Kim and Logan, 2000).

(8) Perchlorate degrading microorganisms will be assumed ubiquitous at some steady state level throughout the aquifer (Coates *et al.*, 1999; Wu *et al.*, 2001).

3.3.3 SUBMODEL LIMITATIONS

While this submodel accounts for biodegradation parameters like multiple electron acceptor and electron donor concentrations, it does not track the products of perchlorate degradation. While it has been observed in the lab that these species (*e.g.* chlorate,

chlorite) do not typically accumulate in solution (Rikken *et al.*, 1996, Giblin *et al.* 2000a), there is a possibility that their presence will impact the rate and extent of biodegradation.

3.4 FLOW AND TRANSPORT MODEL

Three general types of models were discussed in Chapter 2 that can be used to describe contaminant fate and transport in groundwater flow fields induced by an HFTW system – numerical, semi-analytical, and analytical. Because of the non-linear biological submodel that was chosen above for this research, and the need to track fate and transport of five interacting constituents (electron donor, oxygen, nitrate, perchlorate, and microorganisms), a numerical flow and transport model was deemed best suited for this application. A numerical model also allows us to simulate heterogeneous, anisotropic, and non-steady flow conditions, should that be required. The numerical flow and transport model used in this study is based on the model developed by Huang and Goltz (1998) to simulate aerobic biodegradation of trichloroethene in an HFTW system. This specific numerical model was selected based upon the ease with which the author could access the computer code as well as the ability to readily obtain technical support from the model developers. It is a three-dimensional model that combines steady-state flow, advective/dispersive transport of dissolved species, equilibrium sorption, and biodegradation. The model assumes microorganisms are stationary, attached to the aquifer material. The other chemicals dissolved in the groundwater (oxygen, nitrate, perchlorate, and electron donor) are affected by advection, dispersion, and, in the case of the donor, sorption. Equations 3.1 through 3.4 are the three dimensional advection/dispersion equations that are used in the numerical model to describe transport

of the donor and three electron acceptors. The last term on the right hand side of these equations are the sink terms for the biodegradation reactions. In the original Huang and Goltz (1998) model, this term represented the cometabolic biodegradation of TCE. Applying these equations to perchlorate bioremediation, the last term represents biodegradation, modeled using the dual-Monod multi-electron acceptor biological submodel described in Section 2.4.2.4.

$$\frac{\partial C^{don}}{\partial t} \cdot R = D \cdot \nabla^2 C^{don} - v \cdot \nabla C^{don} + r_{donor} \qquad (3.1)$$

$$\frac{\partial C^{oxy}}{\partial t} = D \cdot \nabla^2 C^{oxy} - v \cdot \nabla C^{oxy} + r_{oxy} \qquad (3.2)$$

$$\frac{\partial C^{nit}}{\partial t} = D \cdot \nabla^2 C^{nit} - v \cdot \nabla C^{nitn} + r_{nit} \qquad (3.3)$$

$$\frac{\partial C^{per}}{\partial t} = D \cdot \nabla^2 C^{per} - v \cdot \nabla C^{per} + r_{per} \qquad (3.4)$$

The program MODFLOW (Harbaugh and McDonald, 1996) calculates the steady-state conditions of flow in the aquifer, and these flow velocities (v_x, v_y, and v_z) are then used in the transport model. Dispersion, which is not quantitatively important to this study, was modeled using numerical dispersion. As this study is focused on the groundwater flow and biological fate and transport processes, it was felt that numerical dispersion would provide an adequate qualitative representation of the dispersion process. Numerical dispersion is the result of truncation errors in the finite difference solution of the transport equations (3.1-3.4) (Charbeneau, 2000). These truncation errors add to the apparent dispersion seen in the simulation (Charbeneau, 2000). Since we are only using numerical

dispersion in this model (no value is input for the dispersion coefficients), the dispersion can be estimated in the x, y, and z directions as

$$D_{x,y,z} = \frac{v_{x,y,z}\Delta(d_{x,y,z})}{2} + \frac{(v_{x,y,z})^2 \Delta t}{2} \qquad (3.5)$$

where $v_{x,y,z}$ is the groundwater velocity in the x, y, and z directions, ?$d_{x,y,z}$ is the cell size in the x, y, and z directions, and ?t is the time step (Charbeneau, 2000). The transport model partial differential equations (Equations 3.1-3.4) are solved using a self-adaptive, partial implicit finite difference technique.

3.5 TECHNOLOGY MODEL

The technology model combines the selected treatment process submodel with the HFTW model. As determined previously we chose the biological treatment process modeled by the Envirogen dual-Monod multi-electron acceptor model coupled with the Huang and Goltz (1998) numerical HFTW model. The transport model (equations 3.1-3.4) is linked to the biological model through the last terms on the right hand sides of the equations. The r_{donor} in equation 3.1 is calculated using equation 2.19. The three electron acceptor biodegradation sink terms in equations 3.2 through 3.4 are calculated using equations 2.24-2.26 respectively, and are explicitly written below (assuming $k_{max} = k_{max}^{don/per} = k_{max}^{don/nit} = k_{max}^{don/oxy}$, $K_s^{don} = K_S^{don/per} = K_S^{don/nit} = K_S^{don/oxy}$):

$$r_{oxy} = \frac{dC^{oxy}}{dt} = -X \cdot F_{oxy} \cdot k_{\max} \left[\frac{C^{don}}{K_S^{don} + C^{don}}\right] \cdot \left[\frac{C^{oxy}}{K_S^{oxy} + C^{oxy}}\right] \qquad (3.6)$$

$$r_{nit} = \frac{dC^{nit}}{dt} = -X \cdot F_{nit} \cdot k_{\max} \left[\frac{C^{don}}{K_S^{don} + C^{don}}\right] \cdot \left[\frac{C^{nit}}{K_S^{nit} + C^{nit}}\right] \cdot \left[\frac{K_i^{oxy}}{K_i^{oxy} + C^{oxy}}\right] \qquad (3.7)$$

$$r_{per} = \frac{dC^{per}}{dt} = -X \cdot F_{per} \cdot k_{\max} \left[\frac{C^{don}}{K_S^{don} + C^{don}} \right] \cdot \left[\frac{C^{per}}{K_S^{per} + C^{per}} \right] \cdot \left[\frac{K_i^{oxy}}{K_i^{oxy} + C^{oxy}} \right] \cdot \left[\frac{K_i^{nit}}{K_i^{nit} + C^{nit}} \right] \quad (3.8)$$

The microbial growth/decay equation of the technology model is:

$$\frac{dX}{dt} = X \cdot \left[Y_{biomass} \cdot (r_{don,oxy} + r_{don,nit} + r_{don,per}) - b \right]; \quad X > X_{\min} \quad (3.9)$$

$$\frac{dX}{dt} = 0; X \le X_{\min}$$

where $r_{don,oxy}$, $r_{don,nit}$, and $r_{don,per}$ are defined by equations 2.20-2.22. Note equation 3.9 includes a "switch" to keep the microbial population from completely dying off in areas where there is no electron donor or acceptor. This is important, since one may see from looking at equations 2.20 through 2.22 that if the donor or all three acceptor concentrations are zero, the rate of donor utilization is zero (as expected), which leads to a loss of biomass (equation 3.9). This loss will continue indefinitely, with biomass concentrations reduced to extremely low values, until donor and acceptor concentrations rise above zero. In reality, however, it is likely that perchlorate-reducing microorganisms will be maintained at some low level (X_{min}) even if only trace amounts of electron donor or acceptor are present (Unz *et al.*, 1999; Coates *et al.*, 2000; Perlmutter *et al.*, 2001). The switch simulates this condition, by setting dX/dt in equation 3.9 to zero when X_{min} is reached. The combination of the transport equations (3.1-3.4), the biological reaction equations (3.6-3.8), and the biomass growth equation (3.9) will be referred to from now on as the technology model.

The first step in implementing the technology model was to set up hypothetical site conditions. Data from a perchlorate-contaminated site was applied to the model to more realistically simulate applications of this technology under real world conditions.
The site layout is designed to simulate conditions applicable to installing this technology in the middle of a large existing plume. We are modeling this scenario in anticipation of a future field-scale technology evaluation similar to the evaluation described by McCarty *et al.* (1998) where an HFTW system was used to cleanup a small portion of a large TCE plume at Edwards Air Force Base Site 19. The goal of this model setup is not to necessarily clean up the site or contain the plume, but simply to observe how the technology might work if it was implemented on a pilot scale at a real site. Table 3.1 shows the environmental parameters from seven perchlorate-contaminated sites. These data provide a sample range of values for the environmental parameters and choosing one allows us to create a model based upon actual field data to the greatest extent possible.

Table 3.2 Perchlorate-contaminated site data

	Site 1, CA (Cox, 2002)	Site 2, CA (Cox, 2002)	Site 3, CA (Cox, 2002)	Site 4, NV (Cox, 2002)	Edwards AFB Site 285 (IRP, 2000)	Longhorn Army Ammunition Plant, TX (Polk et al., 2001)	California Site (Hatzinger et al., 2000)
Aquifer Characteristics							
Hydraulic Conductivity (m/day)	9.144	2.59	8.717	7.6	-	-	-
Hydraulic Gradient	0.008	0.001	0.007	0.01	0.0023	-	-
Average Thickness of Aquifer (m)	18.23	15.24	15.24	30.48	18.45	-	-
Plume Characteristics							
Width of ClO4 Plume (m)	915	60	305	915	-	-	-
Length of ClO4 Plume (m)	2440	213	1300	4420	-	-	-
Oxygen Concentration (mg/L)	1 to 15	.1 to 1	42	2.8	-	3.8	-
Nitrate Concentration (mg/L)	24	0.5	4.3	60	0.18	1.9	1.5
Perchlorate Concentration (mg/L)	1 to 15	.1 to 1	4.3	330	1.6	14.7	6-8
Source Characteristics							
Continuing Source (yes/no)	yes	unknown	yes	yes	yes	-	-
Highest ClO4 Concentration (mg/L)	15	160	45	660	9.3	-	-

- Data not available

For the purposes of this study, the model will simulate operation of an HFTW remediation system at Site 4 Nevada (NV) (Table 3.2). The model will use, as closely as possible, data from the site. Site 4 NV was chosen because it had the largest hydraulic

conductivity and hydraulic gradient, which made simulation run times more manageable. Also, the groundwater components of interest in this study were present, and the average aquifer thickness (groundwater head) was convenient to model. Figure 3.1 depicts the site layout. Groundwater flows from east to west with a pore velocity of 0.279 m day^{-1}, which was calculated by applying Darcy's law using the hydraulic gradient and conductivity of Site 4 NV and assuming a porosity of 0.3. The perchlorate plume has an initial concentration of 330 mg L^{-1} throughout the site, and the western boundary of the site is a constant perchlorate source at the same concentration (330 mg L^{-1}). Similarly, the initial and boundary concentrations for oxygen and nitrate throughout the site and in the incoming groundwater are 2.8 mg L^{-1} and 60.0 mg L^{-1}, respectively. The three dimensional grid has four layers with a uniform horizontal hydraulic conductivity that is twenty times greater than the vertical conductivity. This anisotropy is assumed constant over the 32 meter deep and 105-meter square grid. The grid is made up of 35 columns and rows and the individual cell sizes are three meters square. The average hydraulic head in the model is 30.48 meters. The top layer represents an 8 meter deep zone, where the water table is located an average of 1.5 meters below the surface. The second and fourth layers (10 meters deep each) are where the upper and lower screens of the treatment wells are located, and the third layer (4 meters deep) separates the screened intervals. The two treatment wells are oriented perpendicular to the direction of groundwater flow and an observation well able to sample all four layers was placed 15 meters down gradient from the treatment wells. The time step used in the simulations was 0.010417 days (0.25 hours).

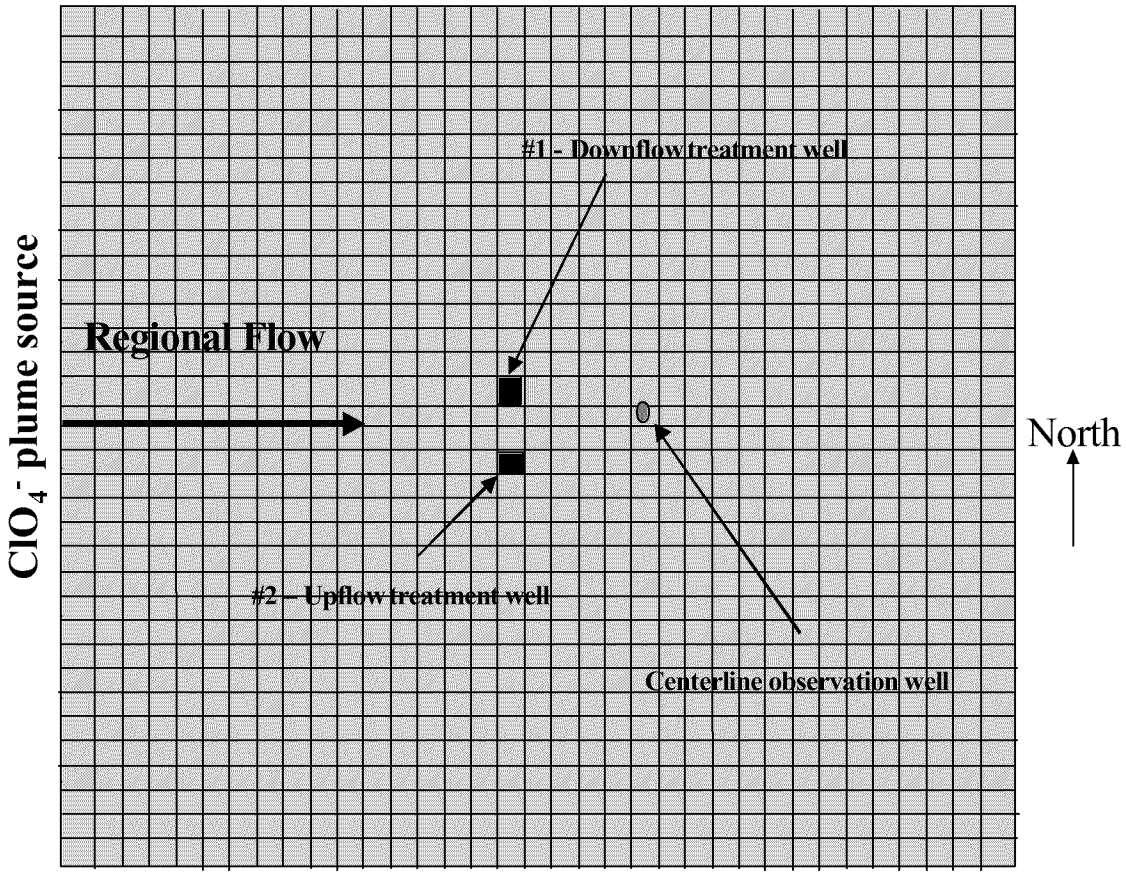


Figure 3.1 Model perchlorate contaminated site layout (after Garrett, 1999)

Table 3.3 shows the baseline kinetic parameters used in the biological submodel. As previously discussed, this model attempts to describe the competitive inhibition of two electron acceptors that are preferred over perchlorate, oxygen and nitrate. During the modeling effort an attempt was made to adhere closely to the kinetic parameters from Envirogen (2002b, see Tables 2.8 and 2.9). It should be noted that the values in the literature for half saturation concentrations (K_S^{don}, K_S^{oxy}, K_S^{nit}, and K_S^{per}) are meager and span a wide range (see Tables 2.5, 2.8, and 2.9). From Table 2.5, 2.8 and 2.9 literature values equivalent to K_S^{don} range from about 3 to 470 mg L^{-1} for acetate as the electron

donor depending on the electron acceptor and culture used in the experiment. In order to determine how model results are affected by uncertain half-saturation concentrations, sensitivity analyses will be conducted as part of this study. The values of these parameters used in this study (see Table 3.3) are within this range, though they deviate from the values determined in batch experiments conducted by Envirogen (2002b) (Table 2.8 and 2.9). Preliminary model simulations using K_S values from Tables 2.8 and 2.9 showed no appreciable oxygen, nitrate, or perchlorate removal after 400 days. Based on these preliminary results and the high variability of the half saturation concentration values from the literature, half saturation concentration parameters were used that were different from Envirogen (2002b) but still within a reasonable range, as determined by other studies (Table 2.5). Table 3.3 lists these values used in the model simulations. It is generally assumed that the inhibition factors due to oxygen (K_i^{oxy}) and nitrate (K_i^{nit}) are equal to their half saturation concentrations (K_S^{oxy} and K_S^{nit} respectively) (Envirogen, 2001). The stoichiometric coefficients used in the model are from the chemical reactions that include biomass growth (see section 2.4.2.4 and equations 2.24-2.26).

Table 3.3 Baseline kinetic parameters used in model simulations

Parameter	Baseline Value	Range Tested
k_{max}	0.21 mg donor/mg biomass/day	0.1, 0.21, 0.3 mg donor/mg biomass/day
K_S^{don}	10.0 mg/L	1.0, 10.0, 100.0 mg/L
K_S^{oxy}	10.0 mg/L	1.0, 10.0, 100.0 mg/L
K_S^{nit}	15.0 mg/L	1.0, 15.0, 150.0 mg/L
K_S^{per}	20.0 mg/L	2.0, 20.0, 200.0 mg/L
K_i^{oxy}	10.0 mg/L	1.0, 10.0, 100.0 mg/L
K_i^{nit}	15.0 mg/L	1.0, 15.0, 150.0 mg/L
$Y_{biomass}$	0.25 mg biomass/mg donor	0.1, 0.2, 0.25, 0.3 mg biomass/mg donor
F_{oxy}	0.83 mg oxygen/mg donor	N/A
F_{nit}	1.3 mg nitrate/mg donor	N/A
F_{per}	1.45 mg perchlorate/mg donor	N/A
b	0.01 1/day	0.002, 0.01, 0.05 1/day
X_{min}	0.01 mg/L	N/A

Table 3.4 shows the environmental parameters used in the model as well as the range of parameter values tested. As mentioned earlier, the baseline values of the parameters are taken from the Site 4, NV data from Table 3.2 The range of values chosen for vertical hydraulic conductivity were based upon three different horizontal to vertical hydraulic conductivity ratios, 1 to 1, 20 to 1, and 100 to 1. The goal was to observe how anisotropy impacted the perchlorate treatment effectiveness of this technology. Christ *et al.* (1999) note that the horizontal hydraulic conductivity must be about 20 times greater than that of the vertical hydraulic conductivity for an HFTW system to work effectively. Taking this to be true the baseline ratio of horizontal to vertical conductivity will be 20 to 1.

Table 3.4 Environmental parameters from Site 4, NV used in model simulations

Parameter	Baseline Value	Range Tested
Pore Water Velocity	0.279 m/day	N/A
Darcy Velocity	0.0836 m/day	N/A
Horizontal Hydraulic Conductivit	7.6 m/day	N/A
Vertical Hydraulic Conductivity	0.38 m/day	0.076, 0.38, and 7.6 m/day
Hydraulic Gradient	0.011 m/m	N/A
Porosity	0.3	N/A

In addition to the parameters in Table 3.4 that describe the site, the other important parameters that must be quantified describe the technology operation. These baseline engineering parameters as well as the range of values tested are specified in Table 3.5.

Table 3.5 Engineering parameters used in model simulations

Parameter	Baseline Value	Range Tested
Time-Averaged Electron Donor Concentration	600 mg/L	0-975 mg/L
Donor Injection Pulse Schedule	3 hrs on 5 hrs off	0.5, 3, 8 hrs on per 8 hrs
Well Spacing	15 m	9, 15, 39, 57, 69 m
Well Screen Lengths	10 m	N/A
Pumping Rate	100 m^3/day	25, 100, 150 m^3/day
Well	15 m	N/A

3.6 TECHNOLOGY MODEL VERIFICATION

One step in verifying a model is to break it down into smaller components by "turning off" portions of the model to ensure that each component works properly. To verify this model, we first eliminated flow through the treatment wells and set initial perchlorate concentrations throughout the site grid equal to zero so we could observe how perchlorate was transported from the western boundary by the natural gradient. As a second test, the

regional flow was stopped (by setting the regional hydraulic gradient to zero) and the transport of donor introduced into the aquifer by the treatment wells was tracked. Finally, for verification of the entire flow model, both the treatment wells and the regional groundwater flow were turned on but the initial and boundary concentrations for oxygen, nitrate, and perchlorate were set to zero. Donor was injected to calculate the interflow between the two treatment wells. The observed interflow was compared with the interflow calculated by an analytical model.

3.7 MODEL SIMULATIONS

After the verification tests were conducted, the model was operated with all systems on – the regional groundwater flow, the groundwater sources of perchlorate, oxygen, and nitrate, the pumping treatment wells, and the electron donor injection to stimulate the biomass growth. A series of simulations were performed to study the effects of environmental and engineered parameters on the efficacy of the application of HFTW's to *in situ* perchlorate bioremediation. The four ways used to interpret the results of the simulations were surface contour plots of the acceptor, donor, and microbial concentrations (in each of the four layers at points in time), breakthrough curves at a centerline downgradient monitoring well (able to monitor each of the four layers), breakthrough curves at monitoring wells placed in the injection well of treatment well #1, and total perchlorate mass degraded. These formats provided different indicators of technology performance.

The first series of simulations was run to obtain a baseline of the model's performance using the baseline values from Tables 3.3 – 3.5. The growth of biomass, the consumption

of oxygen, nitrate, and perchlorate, and the use of the electron donor were monitored and displayed both as contour plots and breakthrough curves. The second series of simulations was designed to study the effects of interflow on perchlorate treatment by varying both well spacing and pump rate. The wells were spaced as specified in Table 3.5 and all other parameters remained the same. The pumps were operated at rates specified in Table 3.5 and the mass of electron donor per day was held constant. The third series of simulations looked at the effects of varying time-averaged concentrations (TAC) of electron donor, as specified in Table 3.5. The pulse schedule remained constant throughout the simulations at 3 hours on and 5 hours off, and the wells were spaced 15 meters apart. The fourth series of simulations was designed to observe the effects of various horizontal to vertical hydraulic conductivity anisotropies. The ratios of horizontal to vertical hydraulic conductivity anisotropies studied were 1 to 1, 20 to 1, and 100 to 1. To vary the anisotropies the horizontal conductivity was held constant while the vertical hydraulic conductivity was varied, as indicated in Table 3.4. The fifth, sixth, and seventh series of simulations tested the impact of varying the kinetic parameters k_{max}, $Y_{biomass}$, and b as specified in Table 3.3. The eighth series of simulations tested each of the half saturation concentration parameters used in the model as specified in Table 3.3.

4.0 RESULTS AND ANALYSIS

4.1 INTRODUCTION

In this chapter we present and discuss the results obtained by applying the technology model (the numerical HFTW flow model coupled with the multi-electron acceptor dual-Monod biological model) developed in Chapter 3 to the site conditions at an actual perchlorate-contaminated site. We begin the chapter by verifying the model. Then we present and discuss results obtained from modeling the technology under site conditions similar to those found at Site 4 NV. We then conduct a sensitivity analysis, varying environmental and engineered parameters to see how these factors influence the efficacy of *in situ* bioremediation of perchlorate-contaminated groundwater. Finally, we test how sensitive the technology model results are to the values of various biological model kinetic parameters (k_{max}, $Y_{biomass}$, b, and all half saturation concentrations), in an attempt to determine which parameters impact simulation results the most.

4.2 MODEL VERIFICATION

As discussed in Chapter 3, the model was verified by breaking it down into smaller components to ensure that each component works properly. This was done by "turning off" various portions of the model. We first turned off the treatment wells, setting the pump rate to zero so that transport was just do to the regional groundwater flow. Additionally the perchlorate initial concentration throughout the grid was set to zero. An observation well was placed 45 meters from the west boundary of the grid. Figure 4.1 depicts the perchlorate breakthrough. Based on the pore water velocity of 0.279 m d^{-1}, the time for the perchlorate to arrive at the monitoring well should be about 162 days.

Using the model, the time to breakthrough of half of the steady-state perchlorate concentration was simulated at about 144 days, a difference of about 10%. The difference between the two times might be attributed to the fact that the numerical model includes perchlorate dispersion along with advective transport. The transport time estimated assuming adevctive/dispersive transport is expected to be less than the time that would be estimated considering advective transport only (Domenico and Schwartz, 1998, pg. 373).

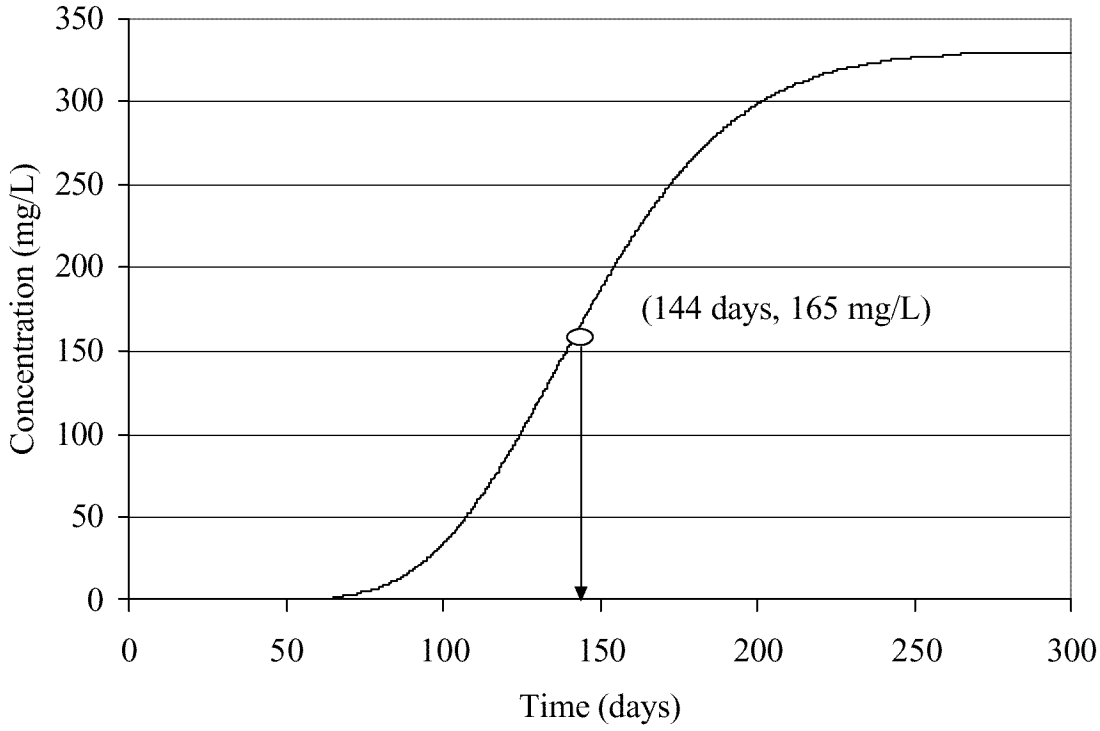


Figure 4.1 Perchlorate concentration breakthrough at observation well 45 m from west boundary (layer 2, 100 mg L^{-1} continuous injection)

The next step in the verification procedure was to ascertain that the model was properly simulating treatment well operation. The regional flow was set to zero, the treatment pump rates were set at 100 m^3 day^{-1}, sorption was turned off, and acetate was injected.

Acetate concentrations entering the downflow well in layer 2 (the extraction well) were monitored to simulate breakthrough of acetate at the extraction well as it was transported from the injection well. The wells were spaced 39 meter apart for this verification. Zhan (1999) developed an analytical solution to calculate the time of travel along the streamline directly connecting the two wells of an injection/extraction well pair:

$$t = \frac{2}{3}\left[\frac{(2\pi \cdot n \cdot B)}{Q}\right] \cdot d^2 \qquad (4.1)$$

In this equation (Zhan, 1999) n is the porosity, B is the aquifer layer thickness, Q is the pump rate, and d is half the distance between the wells. Based on numerical results from the model, the time to acetate breakthrough was about 30 days. The equation 4.1 analytical solution predicted a breakthrough time of 47 days. The difference in the arrival times predicted by the numerical and analytical solutions may be attributed to the spreading caused by dispersion in the numerical model. The analytical solution does not include the impact of dispersion, it is based upon purely advective flow. The arrival time predicted by the analytical solution would be expected to be later than the time predicted by a numerical solution that includes the impact of dispersion.

As the final step in the verification process, interflow predicted by the numerical and analytical models was compared. Using the numerical model, both the regional flow and the pumps were turned on and donor continuously added at the injection well in layer 2 to quantify recirculation. Hydraulic conductivity anisotropy was set high (100), in order to better compare numerical results with the analytical model that assumes two-dimensional flow between the treatment wells (infinite anisotropy). Under this scenario, donor behaved as a conservative tracer and it was possible to determine the interflow of the well

system by mass balance at the extraction well in layer 2.

$$Q_{recycle} = \frac{Q_{total} \cdot C_{measured}}{C_{injected}} \qquad (4.2)$$

$$Interflow = \frac{Q_{recycle}}{Q_{total}} \qquad (4.3)$$

At steady-state, the water flowing through the extraction well that originated at the injection well ($Q_{recycle}$) would have a donor concentration of $C_{injected}$. Thus, if we know the total flow rate (Q_{total}) and donor concentration ($C_{measured}$) in the extraction well, we can calculate interflow using equations 4.2 and 4.3 In this verification Q_{total} was100 m^3 day^{-1}, $C_{measured}$ was the steady state donor concentration at the extraction well (56.8 mg L^{-1}, see Figure 4.2), and $C_{injected}$ was 100 mg L^{-1}, resulting in a value of interflow (I) of about 0.57.

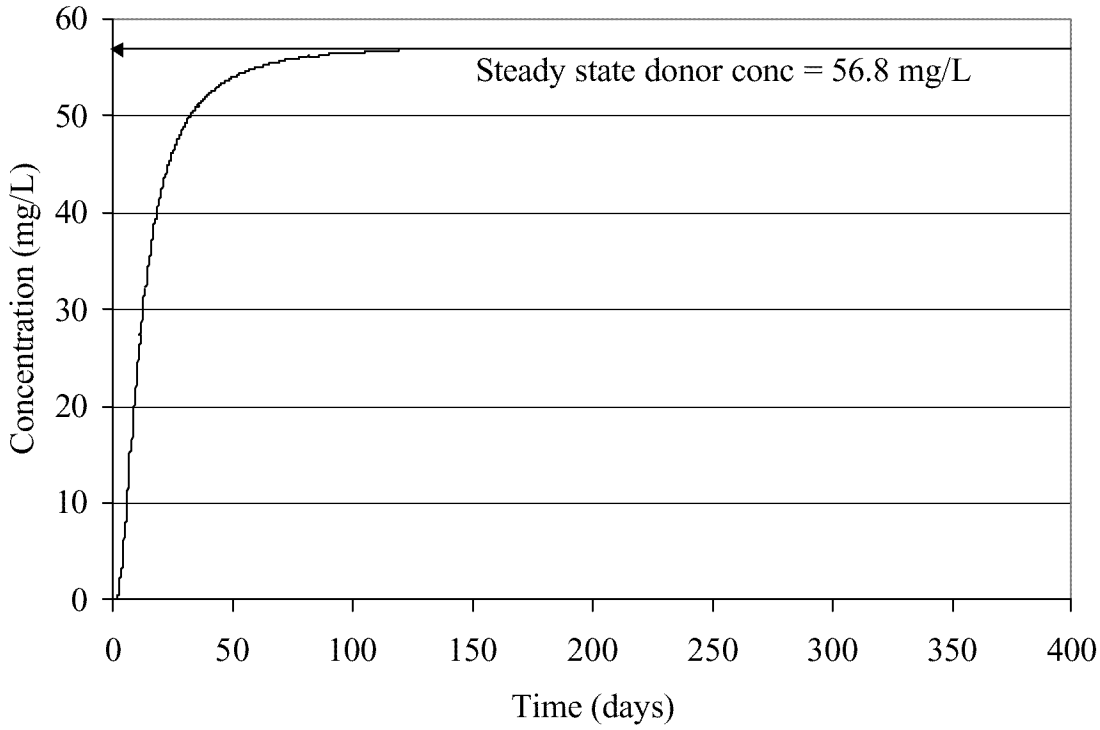


Figure 4.2 Donor breakthrough at layer 2 extraction well when 100 mg L^{-1} is continuously injected by layer 2 injection well

Christ *et al.* (1999) developed a method to analytically estimate the interflow of a two-dimensional injection/extraction well system (as discussed in Section 2.5.2.1). Using this method, the interflow was calculated as 0.59. It's expected that the analytical model, which assumes infinite anisotropy, would slightly over predict interflow. The fact that the interflow calculated from the numerical model (0.57) was close (and slightly less than) the analytically predicted interflow (0.59) gives us confidence the numerical model is accurately simulating flow in the recirculating well system.

4.3 TECHNOLOGY MODEL SIMULATION RESULTS

The model was first used to simulate technology application at a site that was constructed based upon contaminant and hydrogeologic conditions at Site 4 NV. In this section, we present and discuss the model results for baseline conditions, where the technology is applied using "best guess" values for engineered parameters. These best guess values were obtained based on the previous application of HFTWs at Edwards AFB (McCarty *et al.*, 1998) and the literature review of laboratory studies of perchlorate degradation kinetics. Figure 4.3 shows the concentration contours of the electron donor at 250 and 350 days respectively. The figure is a plan view of the 105 meter square model grid of the specified layer. The scale to the right of each graph is the concentration of the component in units of mg L^{-1}. This figure shows the injected electron donor transport by the regional water flow from west to east. These expanding concentration contours may be an indication that more electron donor is being added to the aquifer than can be used by the biomass to degrade the electron acceptors present. This excess substrate in the aquifer should not pose a water quality or regulatory problem, since acetate is environmentally harmless. Since perchlorate treatment is the goal, a conservative approach to donor addition should probably be taken to ensure as much perchlorate is destroyed as possible.

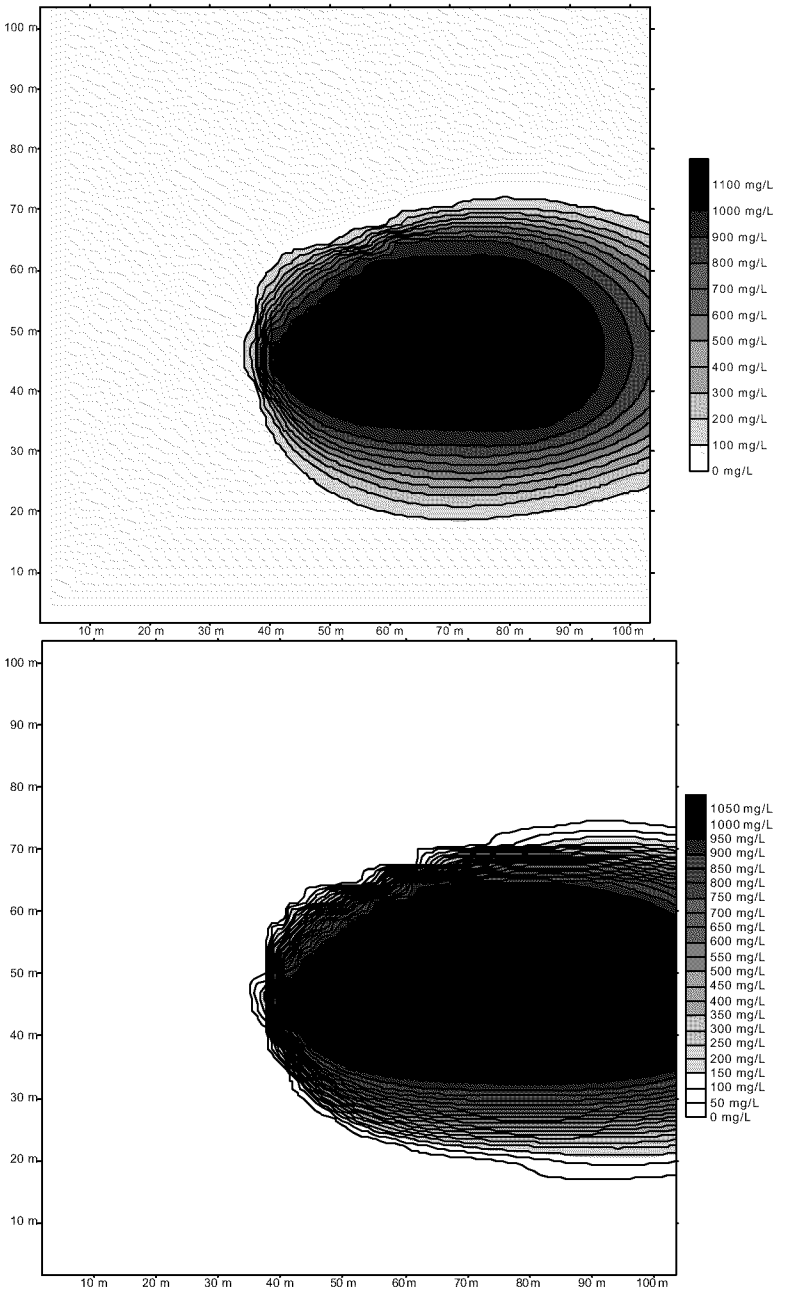


Figure 4.3 Electron donor concentration contours at 250 and 350 days respectively (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

Figure 4.4 shows the oxygen concentration contours at 250 and 350 days respectively. It can be seen that due to addition and mixing of donor into the groundwater, an oxygen-depleted "hole" develops and grows with time.

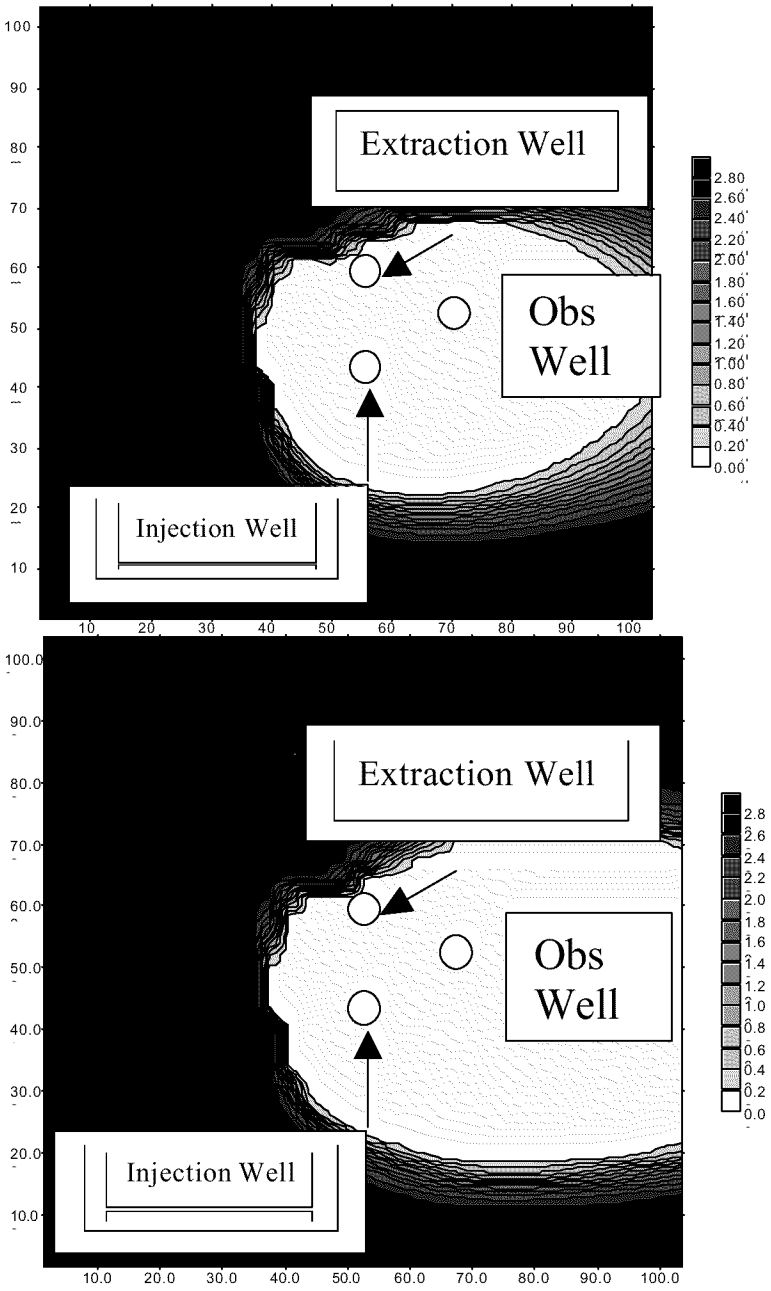


Figure 4.4 Oxygen concentration contours at 250 and 350 days respectively (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

Similarly, Figures 4.5 and 4.6 show growth over time of the nitrate and perchlorate holes, respectively, due to addition of electron donor, which is used by microorganisms to reduce the electron acceptors.

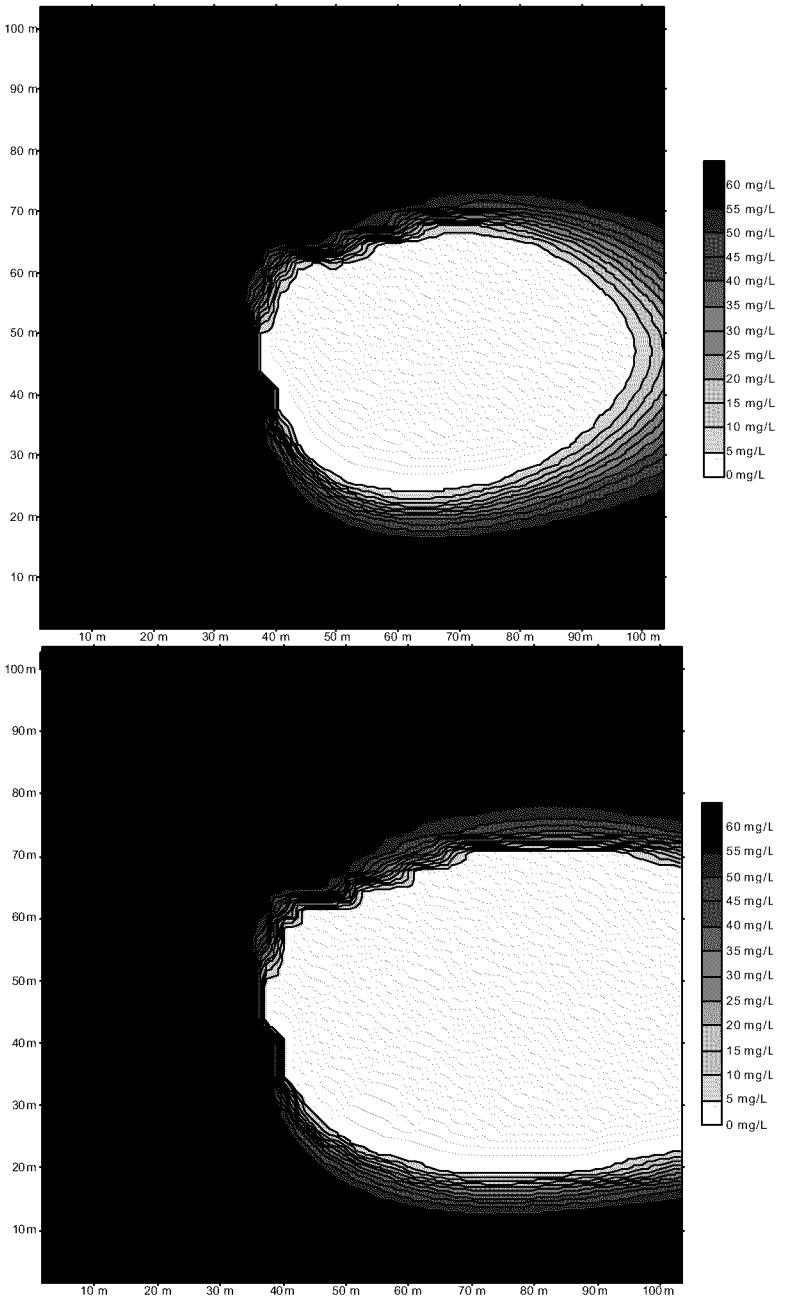


Figure 4.5 Nitrate concentration contours after 250 and 350 days respectively (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

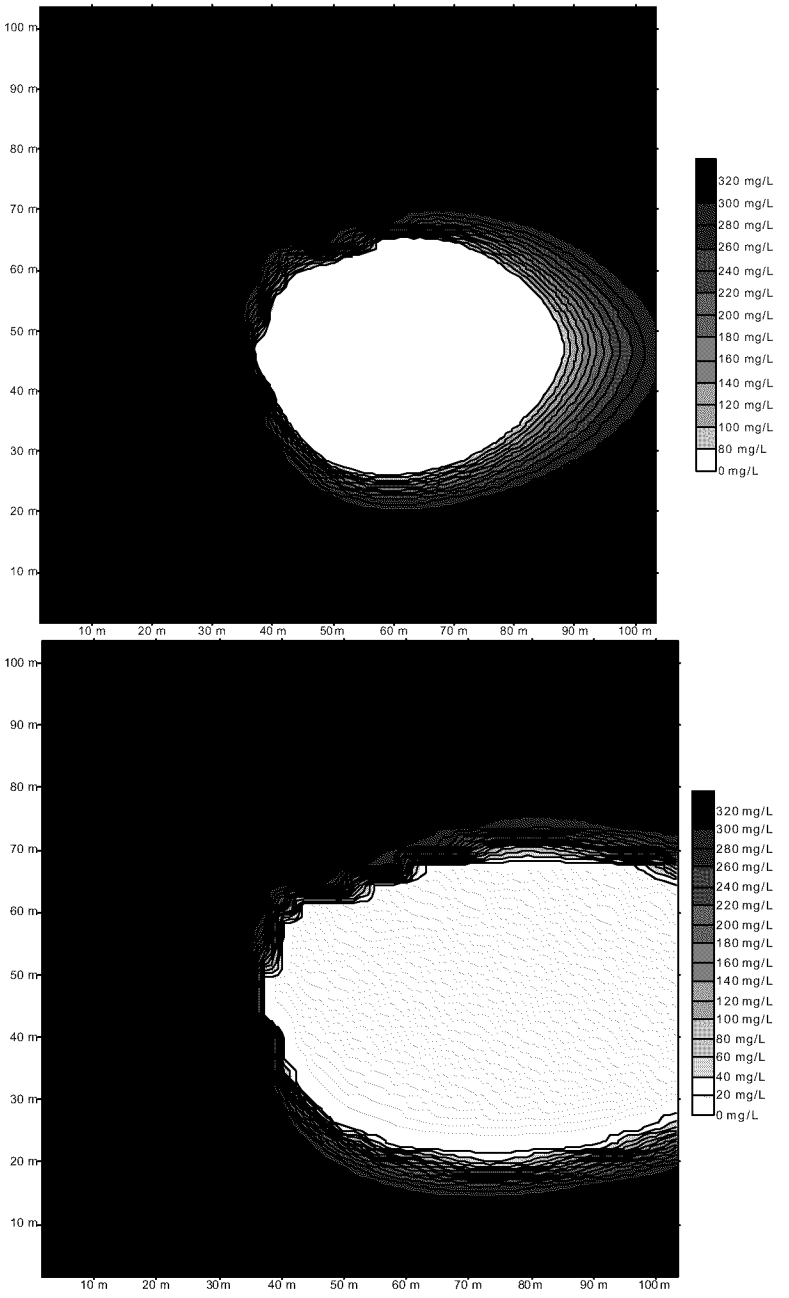


Figure 4.6 Perchlorate concentration contours after 250 and 350 days respectively (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

The electron acceptor holes are the result of growing biomass that consumes the electron donor and reduces the acceptors. Figure 4.7 shows the concentration contours of 5% of the initial concentrations for the three acceptors (oxygen, nitrate, and perchlorate) in layer

2 at 250 days. Observe how the oxygen hole is larger than the nitrate hole, which is larger than the perchlorate hole at this snapshot in time. This shows the expected behavior – that the oxygen is degraded preferentially before the nitrate, and likewise the nitrate before the perchlorate.

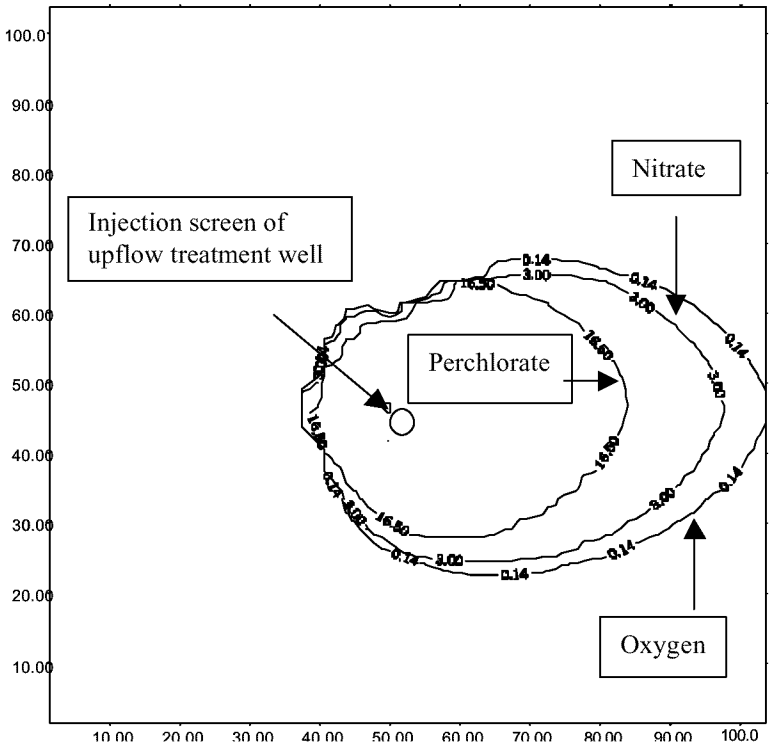


Figure 4.7 Contours of three electron acceptors at 5% of initial concentration (units of mg/L, layer 2, 250 days, donor TAC=600 mg L^{-1}, baseline kinetic data)

Figure 4.8 shows the growth and decay of the biomass at the point of injection in layer 4 compared with the growth and decay observed at the centerline observation well (15 meters down gradient) in layer 4. The biomass does not grow at either location until after about 150 days. At the injection well the population rises rapidly at 200 days, and then peaks at 325 days. The microbial population then decays to some steady state concentration (not shown), which is supported by the injection of electron donor and the

presence of electron acceptors that are continuously transported to the wells by the regional flow. At the centerline observation well the biomass peaks at about 225 days at a much lower concentration than the biomass concentration observed at the injection well. This may be due to lower amounts of donor and acceptor present in the treated water further downgradient. Based upon biomass growth observed at the treatment well and compared to the growth at the centerline observation well (Figure 4.8) it appears that the kinetic parameters, not the transport of growth substrates, are controlling the time at which degradation is observed. From the figure, we observe that the biomass at both locations begins growing at about the same time, and the biomass at the injection well does not dramatically increase until approximately 250 days after growth substrate begins to be added at the treatment wells. This lag in growth may indicate that kinetics rather than transport of donor or acceptor is the main factor controlling the time it takes for biomass to grow in response to donor addition.

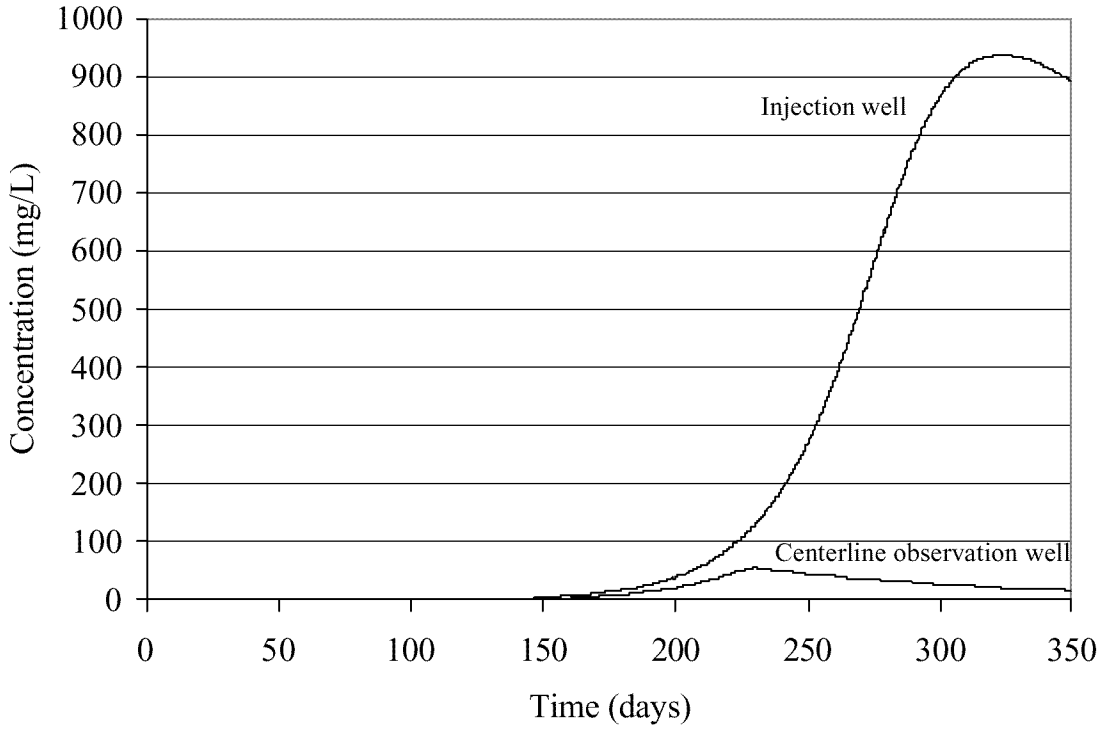


Figure 4.8 Biomass growth curves at point of injection and centerline observation well (layer 4, donor TAC=600 mg L^{-1}, baseline kinetic data)

Figure 4.9 shows the breakthrough behavior of all components at a downgradient observation well. As mentioned in chapter 3, the observation well is located 15 meters downgradient of the treatment wells. The figure shows compound concentrations in layer 2 (see Figure 3.1). Injection of donor starts at time zero and donor concentrations at the observation well gradually increase as donor is transported from the injection well to the observation well. It can be seen that the electron acceptors (oxygen, nitrate, and perchlorate) remain at their initial values until the water from the treatment wells breaks through at the observation wells. Since the biomass is not mobile the biomass growth observed at the centerline observation well is the result of the arrival of donor and residual acceptors. Biomass growth appears not to be the primary cause of the

degradation at the downgradient observation well. The reductions in nitrate and perchlorate observed at the downgradient observation well are most likely the result of the arrival of treated water from the region of high microbial growth surrounding the treatment wells. Near the treatment wells, once there is an abundance of electron donor and available acceptors, the biomass exponentially grows until eventually electron donor and acceptors are depleted (Figure 4.8). As the biomass population grows throughout the system (but especially close to the treatment wells) the electron acceptors are depleted rather rapidly along with the electron donor. It is difficult to determine the relative extent of electron acceptor degraded near the treatment wells as compared to degradation further downgradient. Because donor is traveling downgradient, treatment is occurring throughout the plume. However, based on relative biomass concentrations (see Figure 4.8), most of the degradation appears to occur near the treatment wells. Figure 4.9 also depicts the breakthrough of donor with no reaction taking place to give an indication of the amount of donor used for biodegradation. This curve was generated by injecting donor without any acceptors present so that the donor is behaving as a tracer.

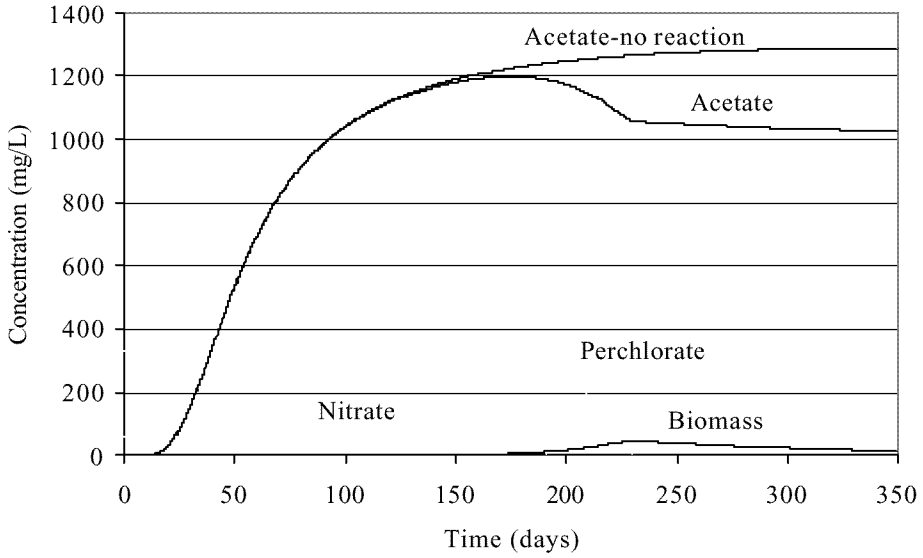


Figure 4.9 Breakthrough of all components (oxygen not seen) at centerline observation well (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

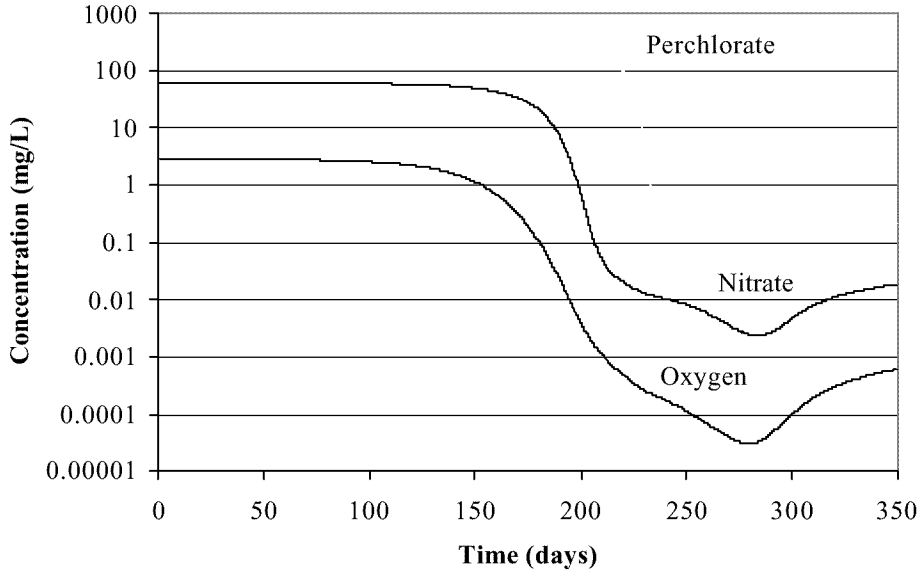


Figure 4.10 Breakthrough of electron acceptors at centerline observation well (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

Figure 4.10 shows a breakthrough curve of the electron acceptors at the centerline observation well on a log scale. As expected, oxygen is reduced before nitrate, which is reduced before perchlorate. Once the electron acceptors are depleted, the biomass cannot grow and therefore decays to some steady state value (not shown in Figure 4.9) where the population is maintained by the balance of incoming electron acceptors and donor. The slight rebound in the acceptor concentrations in Figure 4.10 may be due to the reduction in biomass as steady-state is approached.

Figures 4.11 and 4.12 below are included to give a picture of the perchlorate treatment in all four layers of the model grid. Figure 4.11 is the breakthrough of perchlorate in each layer at the centerline observation well. Figure 4.12 shows the concentration contour plots of perchlorate in layers 1 through 4. One potential disadvantage of the HFTW technology is that the treatment is better in the layers where the electron donor is injected. In this modeling effort, with anisotropic conditions set at 20 to 1, the flow between layers is somewhat restricted. Thus the donor that is injected by the 10 m screened treatment wells in layers 2 and 4 is transported mostly horizontally in that layer, with minimal transport vertically into the other layers. This is demonstrated in Figure 4.11, where the monitoring well downgradient shows very different perchlorate concentration breakthroughs in the different layers (note the log scale on the y-axis). Layer 1 shows the least amount of treatment, and this is expected since the only source of donor for treatment in this layer is the limited amount transported vertically from the injection screen in layer 2. Layer 2 shows slightly higher concentrations than are seen in layer 3, though reductions in concentration occur faster. The higher concentrations in layer 2 are

likely due to the fact that untreated water (particularly from layer 1) enters layer 2. Thus within layer 2 we are unable to achieve the lower treatment levels observed in layers 3 and 4 since the injected donor is inadequate in downgradient regions to stimulate enough biomass growth to degrade all the available acceptor. The fact that perchlorate concentrations in layer 2 are reduced before reductions are seen in layer 3 is due to the fact that donor is directly injected into layer 2, while reductions in layer 3 are due to the movement of donor and treated water from layers 2 and 4. Perchlorate levels in layer 4 are the lowest because it has only to degrade the incoming acceptors from layer 4 and infiltration from layer 3 – there is no lower layer for vertical transport of acceptors into layer 4.

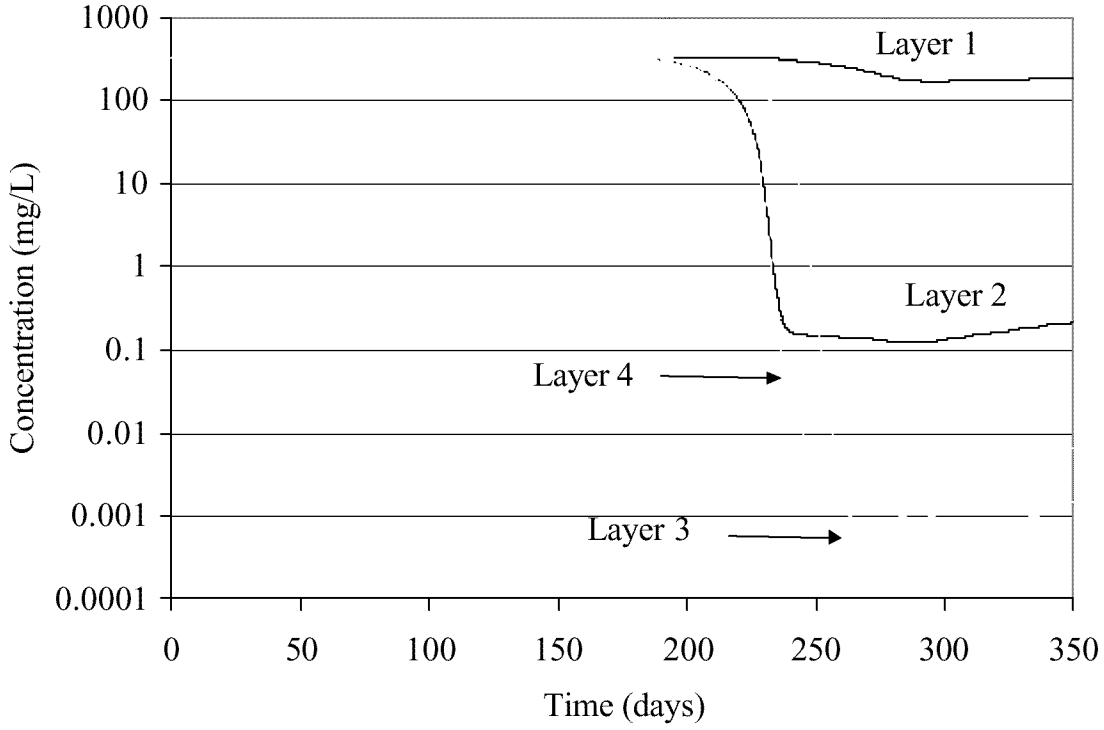


Figure 4.11 Log of perchlorate breakthrough concentrations at centerline observation well in all 4 layers (donor TAC=600 mg L^{-1}, baseline kinetic data)

Figure 4.12 shows spatially the treatment efficiency just discussed. This picture shows a few characteristics of the HFTW system. First, the concentration contour of perchlorate in layer 1 is smaller than layer 2, which is almost identical to the contour in layer 4 except for the location (it originates from the injection well of the downflow treatment well). The layer 3 contour shows that perchlorate degradation is impacted by the treatment zones in both layers 2 and 4.

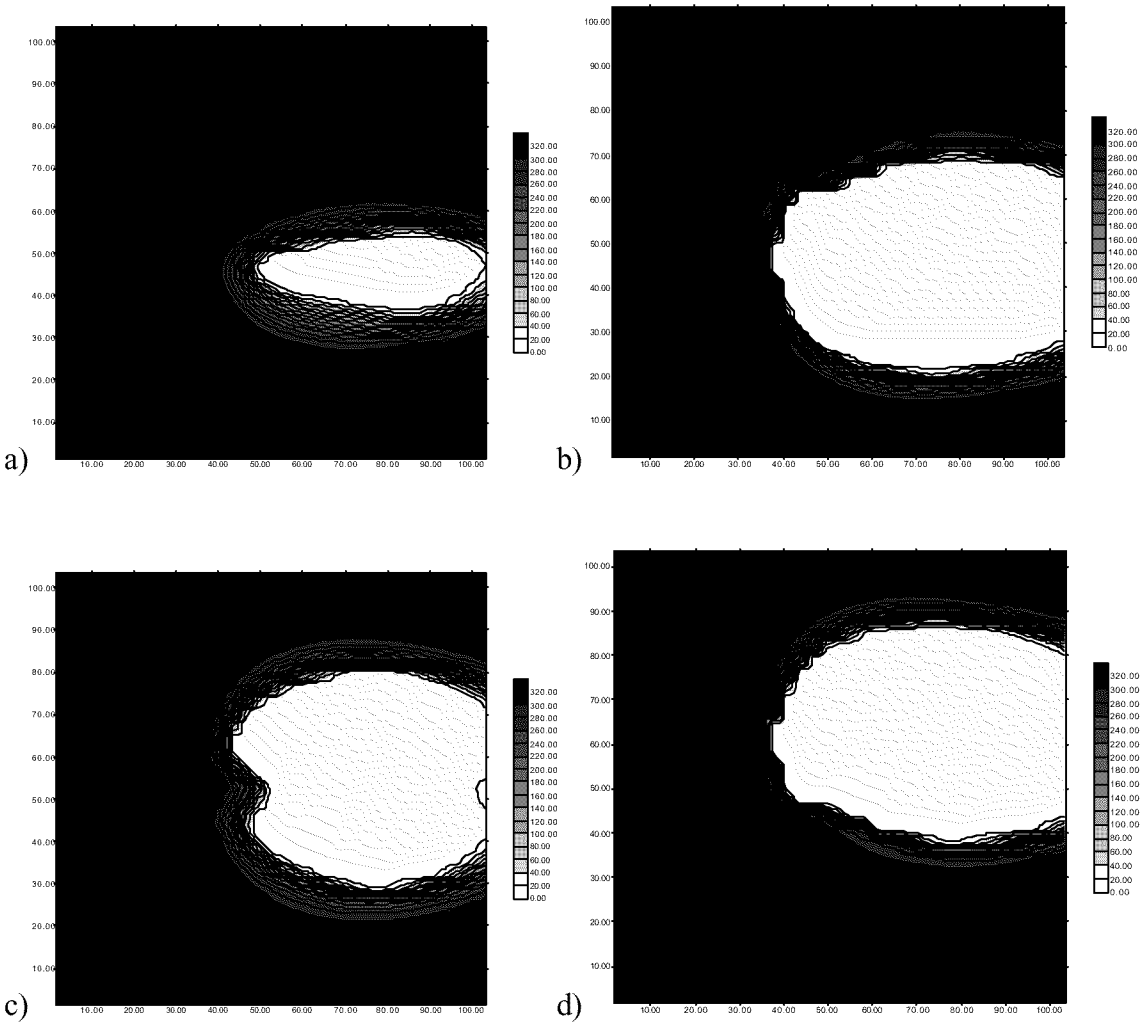


Figure 4.12 Perchlorate concentration contour in layers 1, 2, 3 and 4 (350 days, donor TAC=600 mg L^{-1}, baseline kinetic data)

Figures 4.11 and 4.12 also illustrate the extent of the treatment in each of the layers. As stated previously, one possible disadvantage of the HFTW technology is that treatment mainly occurs in the layers where electron donor is injected. However, it is apparent that to a certain extent treatment is occurring in all layers of the model. This demonstrates that more of the aquifer cross section can be treated than just the two layers where donor is injected.

4.4 SENSITIVITY ANALYSIS: VARYING ENGINEERING AND ENVIRONMENTAL PARAMETERS

In this section we investigate the effect of varying a variety of engineering and environmental parameters on the technology model simulation results. Specifically, we examine the effect of varying three engineering parameters (well spacing, time-averaged electron donor concentration, and electron donor pulse schedule) and one environmental parameter (anisotropy). The engineering and environmental parameter sensitivity results were analyzed within a 350-day window by examining breakthrough curves at the centerline observation well and the well #1 observation well, as well as contour plots and mass degraded information where applicable. Based upon the kinetic parameters used in this study, the 350-day time scale usually provided enough time to observe the important behavior simulated by the model. While longer run times may provide insight into the long-term performance of this technology, this study will focus on this 350-daytime frame. Reasons for this time frame include run time constraints and our specific interest in what the model shows regarding transient behavior and the interactions of the different compounds. The long-term behavior, which is important to technology implementation and determining the steady-state downgradient concentration levels achievable by the

technology is beyond the scope of this study and might be the subject of future optimization research.

4.4.1 INTERFLOW

4.4.1.1 WELL SPACING

Well spacing affects the interflow between the two treatment wells, which in turn affects the overall treatment efficiency of the system. Figures 4.13 and 4.14 show the effect of treatment well spacing on perchlorate breakthrough concentrations at the centerline observation well and at a well placed inside the injection screen of the treatment well, respectively.

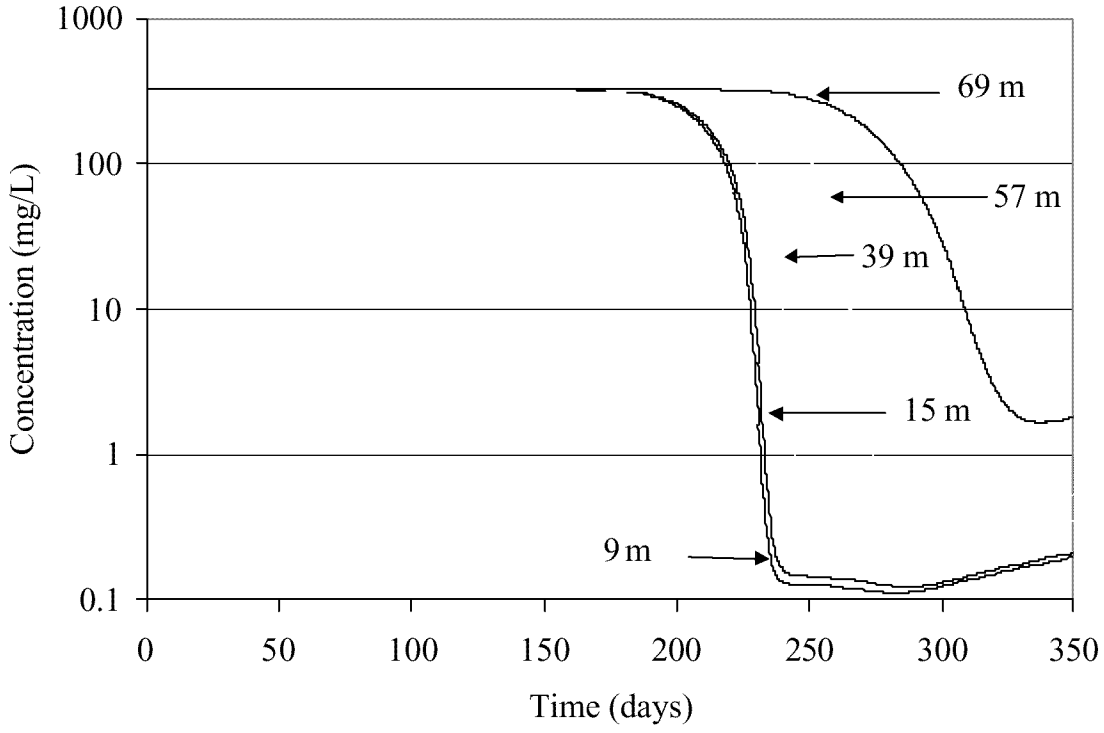


Figure 4.13 Effect of well spacing on perchlorate concentration at centerline observation well (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

The overall treatment efficiency, as determined by downgradient perchlorate concentrations, appears to be best with the wells closest together, and decreases as well spacing increases. This is due to the increased interflow that the smaller well spacings allow for. The Christ *et al.* (1999) analytical model estimated interflow ratios of 0.68, 0.59, 0.30, and 0.12 for well spacings of 9, 15, 39, and 57 meters respectively. However, the performance tradeoff that comes with the increased efficiency at the smaller well spacing is a reduced capture zone width. The closer the wells are together, the less upgradient groundwater the treatment wells are able to capture which results in less total treatment as measured by perchlorate mass degraded. Table 4.1 summarizes the mass of perchlorate degraded at different well spacings.

Table 4.1 Mass degraded at varying well spacings (all layers)

Wells Spacing	Mass Degraded
9 m	8,069 kg
15 m	10,105 kg
39 m	15,345 kg
57 m	17,168 kg

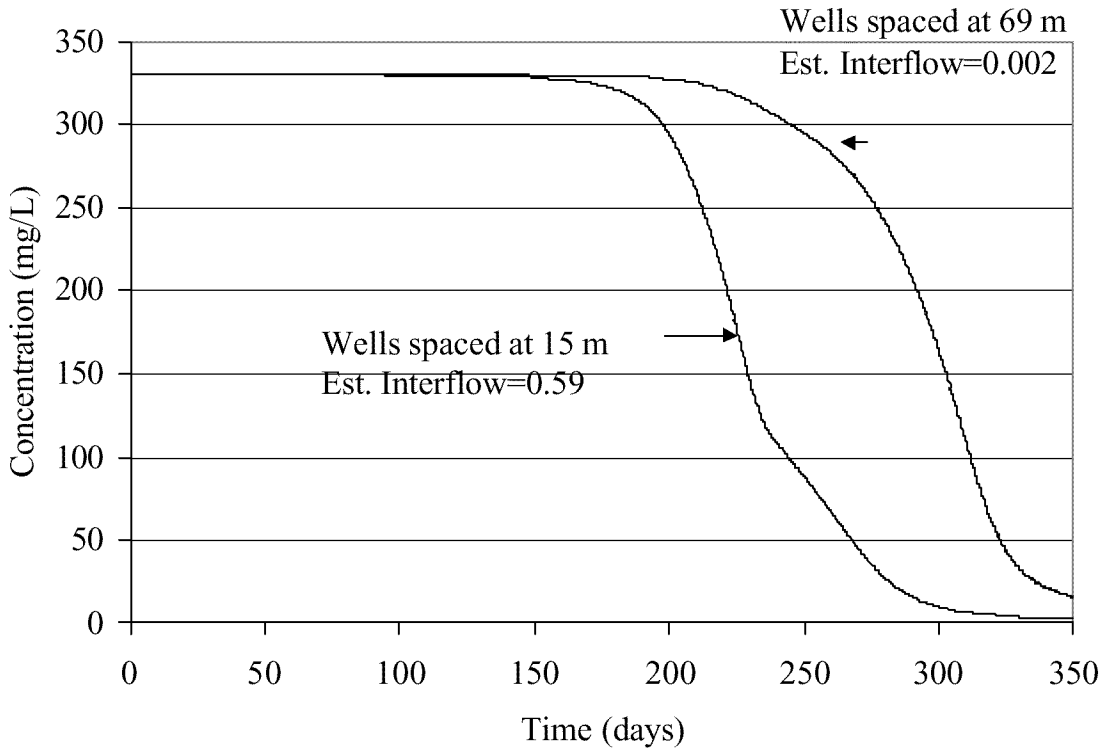


Figure 4.14 Effect of well spacing on perchlorate concentration at observation wells located in the injection screen of treatment well (layer 4, donor TAC=600 mg L^{-1}, baseline kinetic data)

Figure 4.15 illustrates this point further. It depicts the 5% concentration contour of the 330 mg L^{-1} initial concentration of perchlorate at two treatment well spacing configurations, 9m and 57 m in layer 2. The area of perchlorate treatment is much larger with the increased capture zone of the wells spaced at 57 meters compared with the wells spaced at 9 meters.

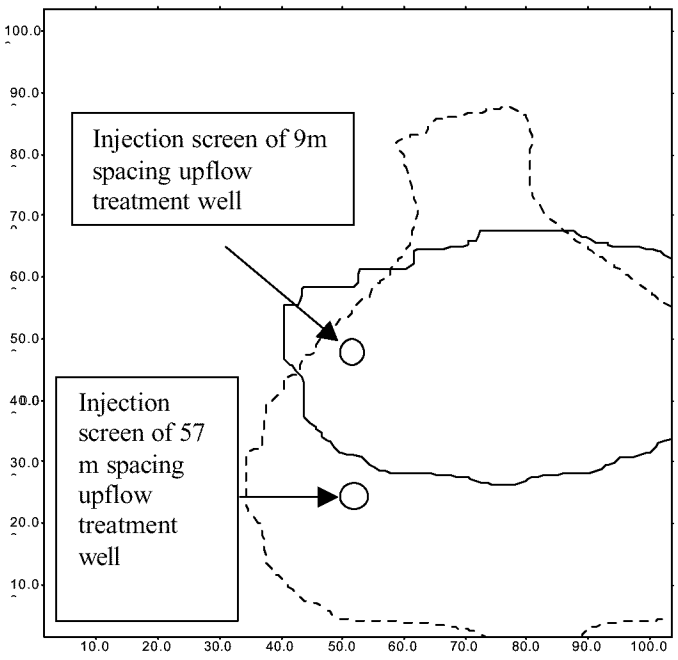


Figure 4.15 Concentration contours of 5% of initial perchlorate concentration using two different well spacing configurations (9m-solid and 57 m-dashed, layer 2,donor TAC=600 mg L^{-1}, baseline kinetic data)

4.4.1.2 TREATMENT WELL PUMP RATES

Another factor affecting the interflow between two HFTWs is the treatment well pumping rate. In this simulation, the mass per day of donor was set constant and perchlorate treatment was measured at the centerline observation well with the pumping rates set at 25 m^3 day^{-1} and 150 m^3 day^{-1}. The 25 m^3 day^{-1} and 150 m^3 day^{-1} systems had estimated interflows of 0.0874 and 0.67 respectively. Figure 4.16 below shows that perchlorate concentration reductions were achieved slightly faster with a 25 m^3 day^{-1} pumping rate, the higher pumping rate system achieved lower concentrations over the 400 day simulation. This higher treatment efficiency of the 150 m^3 day^{-1} system is most likely due to the increased recirculation. The faster response of the low pumping rate system is probably due to the decreased amounts of contaminated water treated by the

system. This allows the biomass in the treatment zone to grow and begin biodegradation more quickly.

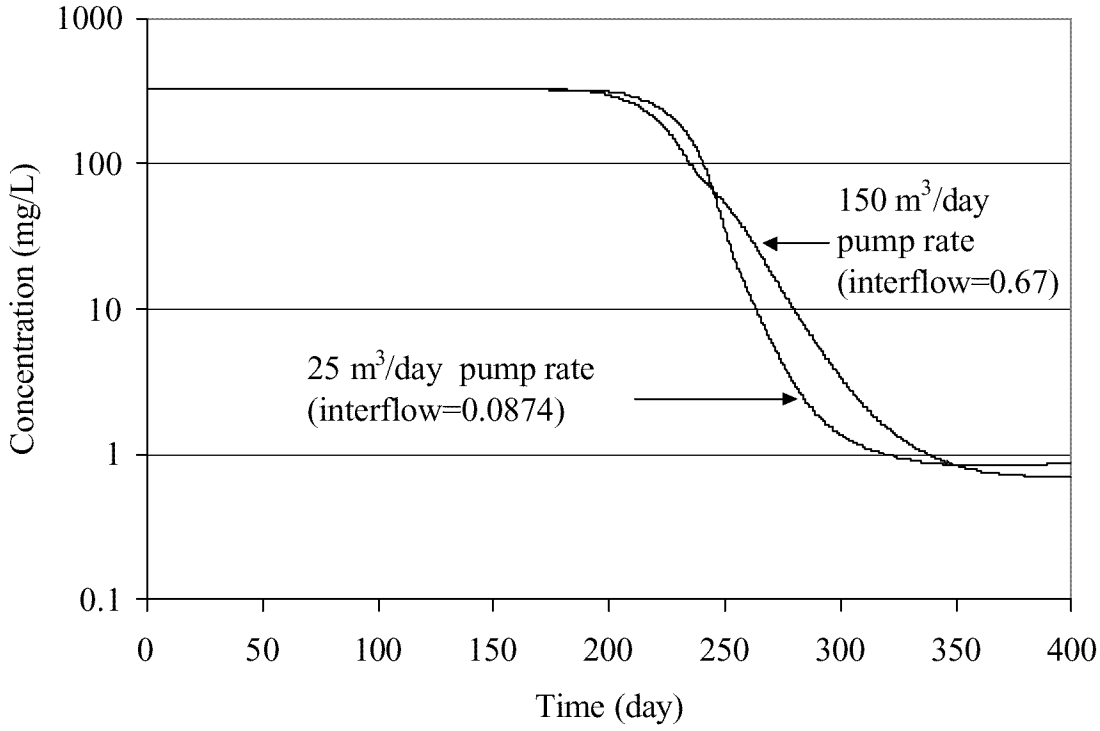


Figure 4.16 Effect of pumping rate on perchlorate concentration at centerline observation well (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

4.4.2 ELECTRON DONOR TIME-AVERAGED CONCENTRATION

The time-averaged concentration (TAC) of electron donor also has an impact on the treatment efficiency of this technology. Figure 4.17 shows perchlorate concentrations at a downgradient observation well when the electron donor TAC is varied.

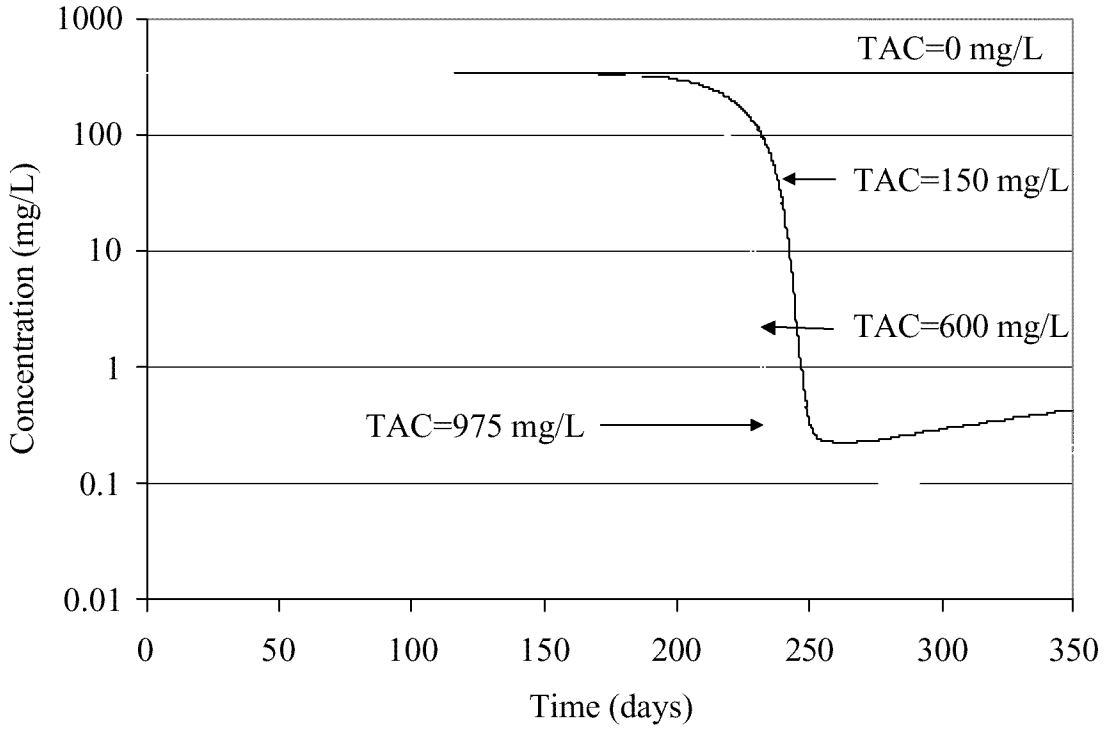


Figure 4.17 Effect of varying time averaged concentration (TAC) of electron donor on perchlorate concentration at centerline observation well (layer 2, baseline kinetic data)

The 975 mg L^{-1} TAC resulted in the fastest and most extensive degradation of perchlorate. From Figure 4.17, we see the TAC of electron donor could be manipulated to meet certain treatment goals. Figure 4.18 compares the perchlorate concentration contours of different electron donor TAC. The 600 mg L^{-1} TAC scenario created a larger "hole" in the perchlorate after 350 days than the 150 mg L^{-1} TAC scenario because the microbial population had more growth substrate to use, causing a faster and more extensive reduction of the electron acceptors.

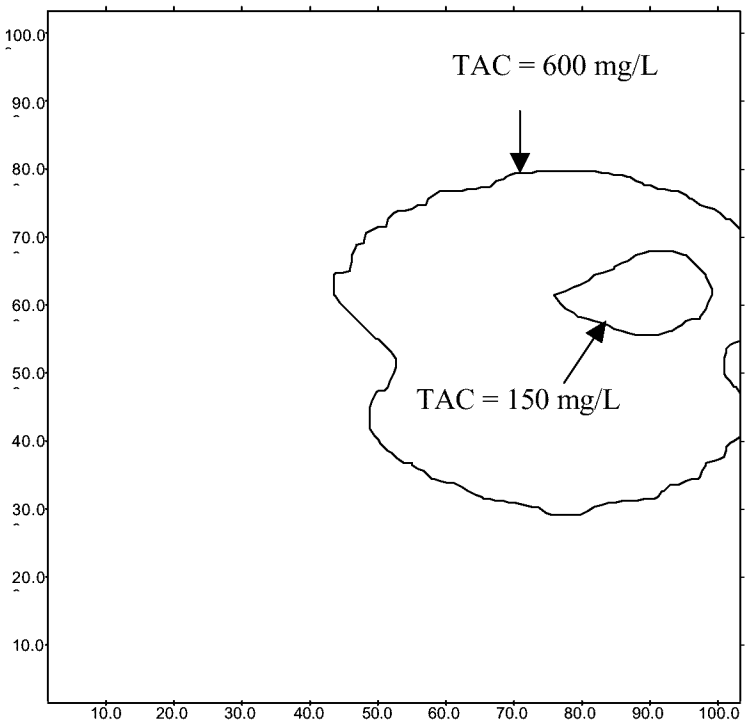


Figure 4.18 Perchlorate concentration contours (5% of initial concentration at two electron donor TACs (layer 3, 350 days, baseline kinetic data)

4.4.3 ELECTRON DONOR PULSE SCHEDULE

In this model, the electron donor pulse schedule may be varied by the user. That is, the user can specify the time period over which donor is injected, from 0 hours on/8 hours off to 8 hours on/0 hours off. The actual injected concentration is adjusted to maintain a constant time-averaged concentration in order to ensure the same mass per day is injected no matter what pulsing schedule is used. Previous studies (McCarty *et al.*, 1998; Goltz *et al.*, 2001) have demonstrated that pulsing the electron donor prevents excessive biomass growth near the treatment wells, thereby reducing bioclogging, and also allowing the electron donor to be transported further away from the wells. Figure 4.19 shows the breakthrough curves of perchlorate at the centerline observation well at varying pulse schedules (in the range of 0.5 hrs on/7.5 hrs off to 8hrs on/0 hrs off). It appears the more

continuous the pulse, the better the treatment. This might be due to the values of the kinetic parameters that we are using, which define a rather slow growing microbial population. The short pulses of high concentration may not stimulate growth as much as the continuous injection of lower concentrations. This is supported by the mass degraded information output from the model; with the short pulse scenario the model predicts degradation of about 7.3 kg of perchlorate over the course of the simulation whereas with the continuous pulse scenario, about 10.1 kg perchlorate degradation is predicted. Note, however, that the model does not simulate bioclogging of the well screens, so the possibly adverse effect of continuous electron donor injection does not impact the simulations.

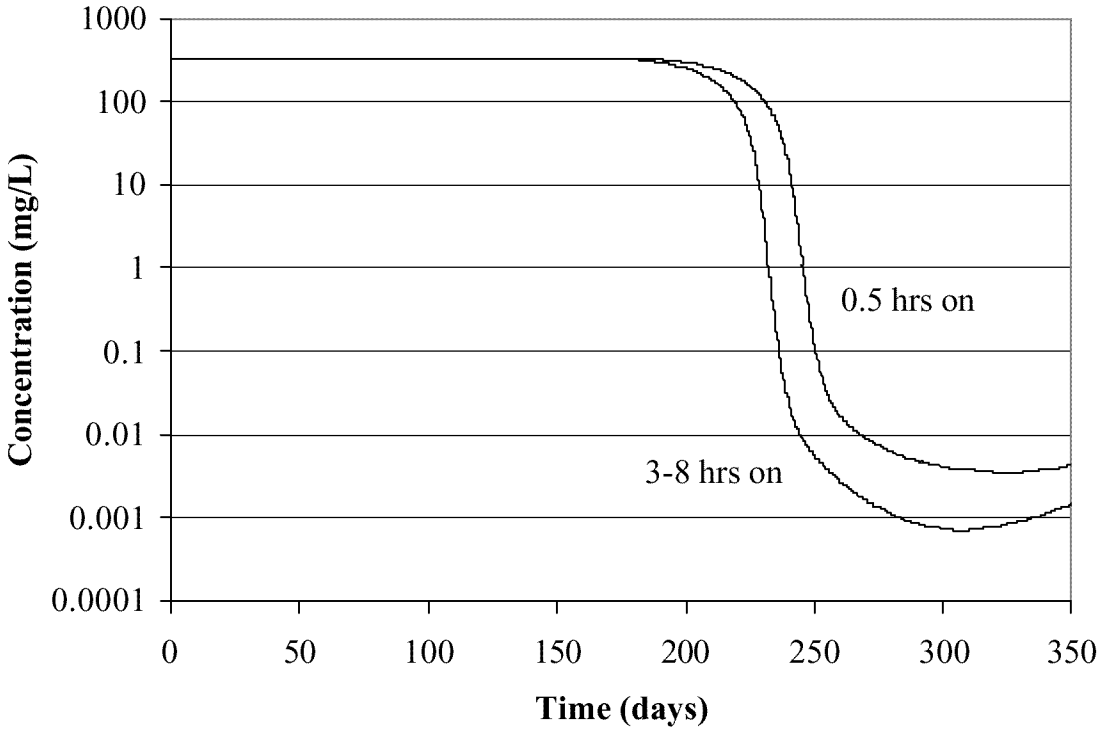


Figure 4.19 Effect of varying pulse schedules per 8 hour period on perchlorate concentration at centerline observation well (layer 4, donor TAC= 600 mg L^{-1})

4.4.4 ANISOTROPY

Site characterization is an important aspect of technology design, and knowing what data to focus the site characterization on could be of great advantage to engineers. One important aspect of the site where this technology might be implemented is the anisotropy of the horizontal and vertical hydraulic conductivities. This series of simulations explores the effect of horizontal to vertical hydraulic conductivity anisotropy on perchlorate treatment. Theoretically, the greater the ratio of horizontal to vertical hydraulic conductivity anisotropy, the greater the interflow will be between the two HFTWs, and the greater the interflow, the greater the overall treatment efficiency and the lower the downgradient contaminant concentrations (Christ *et al.*, 1999). As mentioned

in Chapter 2, if vertical hydraulic conductivity is close to the horizontal conductivity, there is a potential that flow short circuiting will occur between the upper and lower screens of a single treatment well, thus reducing the interflow and reducing the treatment efficiency. Figure 4.20 shows downgradient perchlorate concentrations at three different anisotropy values – 100 to 1, 20 to 1, and 1 to 1. The time at which degradation occurs is about the same in all three cases, but it seems that the smaller the anisotropy ratio, the better the treatment.

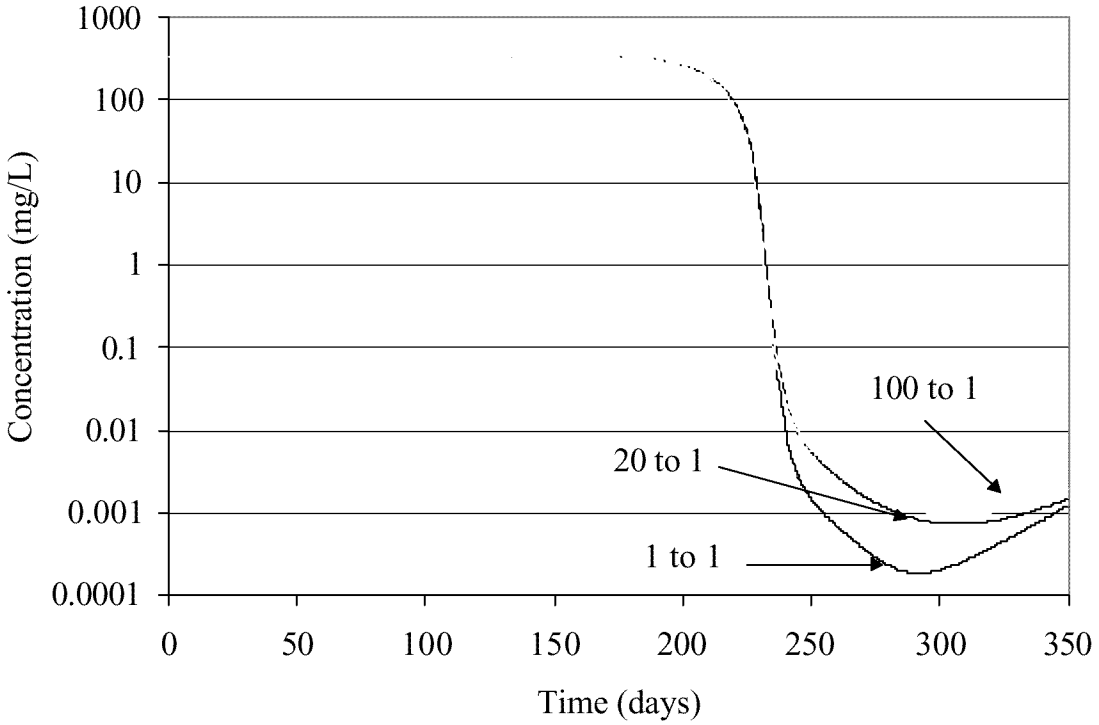


Figure 4.20 Effect of anisotropy on perchlorate concentration at observation well (layer 2, donor TAC=600 mg L^{-1}, baseline kinetic data)

This behavior might be explained by considering flow between layers. Recall from the discussion of Figure 4.11 that one explanation for the relatively high perchlorate concentrations in layer 2 was that layer 2 was affected by high perchlorate concentration

water flowing from layer 1. Lowering the anisotropy ratio would have two competing effects. Although a lower ratio would allow more water from layer 1 to flow into layer 2, it would also allow water in layer 1 (and layer 3) to receive more treatment in the treatment wells. Thus, the overall impact of lower anisotropy appears to be that water reaching the layer 2 observation well has lower concentrations of perchlorate. The slightly higher concentrations observed at the well when anisotropies are 20-1 and 100-1 are due to higher-concentration water from the unscreened layers (1 and 3) being transported vertically into layer 2. Figure 4.21 shows that perchlorate concentrations in the unscreened layer (layer 3) dramatically rise as anisotropy is increased. Another explanation of why the results in this study are different from those of Christ *et al.* (1999) might be related to the kinetic parameters used here for perchlorate degradation. The study of Christ *et al.* (1999), which simulated the impact of anisotropy on performance was examining aerobic cometabolism of TCE. Perchlorate biodegradation might happen quicker, which would mean that even though perchlorate-contaminated water might short-circuit between the injection/extraction screens of a single treatment well, destruction might be adequate, while short-circuiting of TCE in the TCE treatment system might result in significantly less treatment. Thus, in the case of perchlorate, short-circuiting of the flow due to isotropic conditions would not significantly reduce the treatment efficiency.

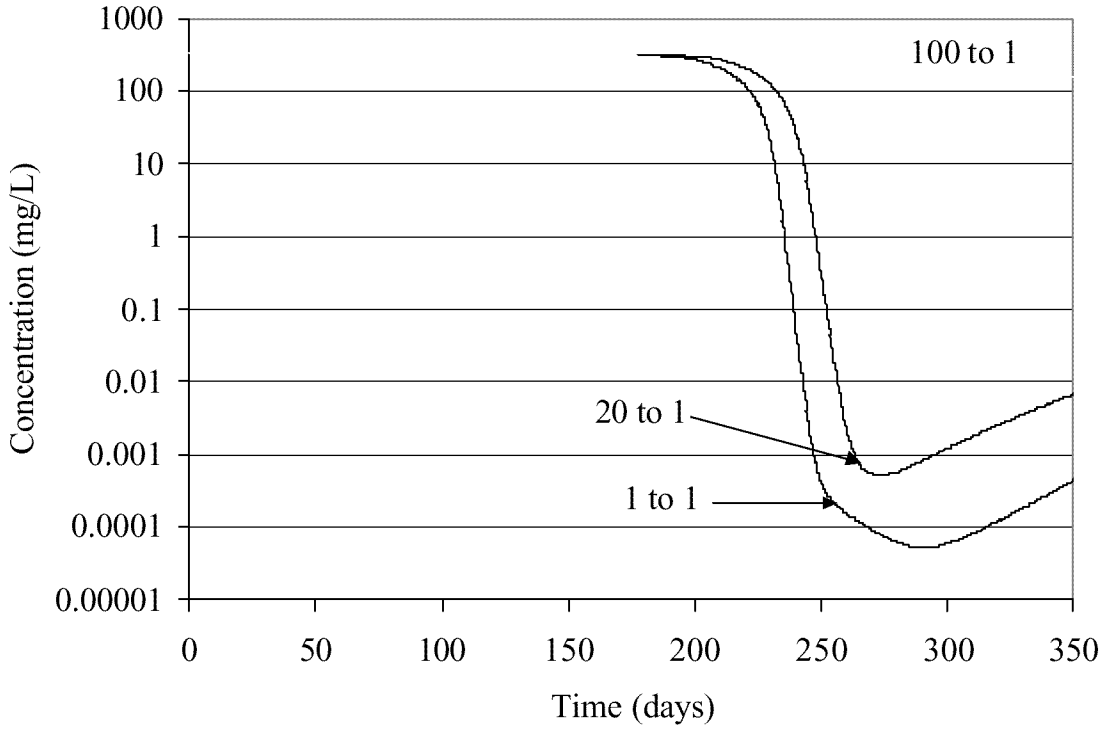


Figure 4.21 Effect of anisotropy on perchlorate concentration at observation well (layer 3, donor TAC=600 mg L^{-1}, baseline kinetic data)

4.5 SENSITIVITY ANALYSIS: VARYING KINETIC PARAMETERS

In this section, we explore the sensitivity of the model to changes in the values of kinetic parameters, maximum rate of donor utilization (k_{max}), cell yield ($Y_{biomass}$), biomass decay rate (b), and the half saturation concentrations of each component (K_S^{oxy} and K_I^{oxy}, K_S^{nit} and K_I^{nit}, and K_S^{per}). Figure 4.22 shows the downgradient perchlorate concentration at different values of k_{max}. From the model equations (3.1-3.9) it can be seen that the value of k_{max} is directly proportional to the value r_{don}, which is directly proportional to microbial growth.

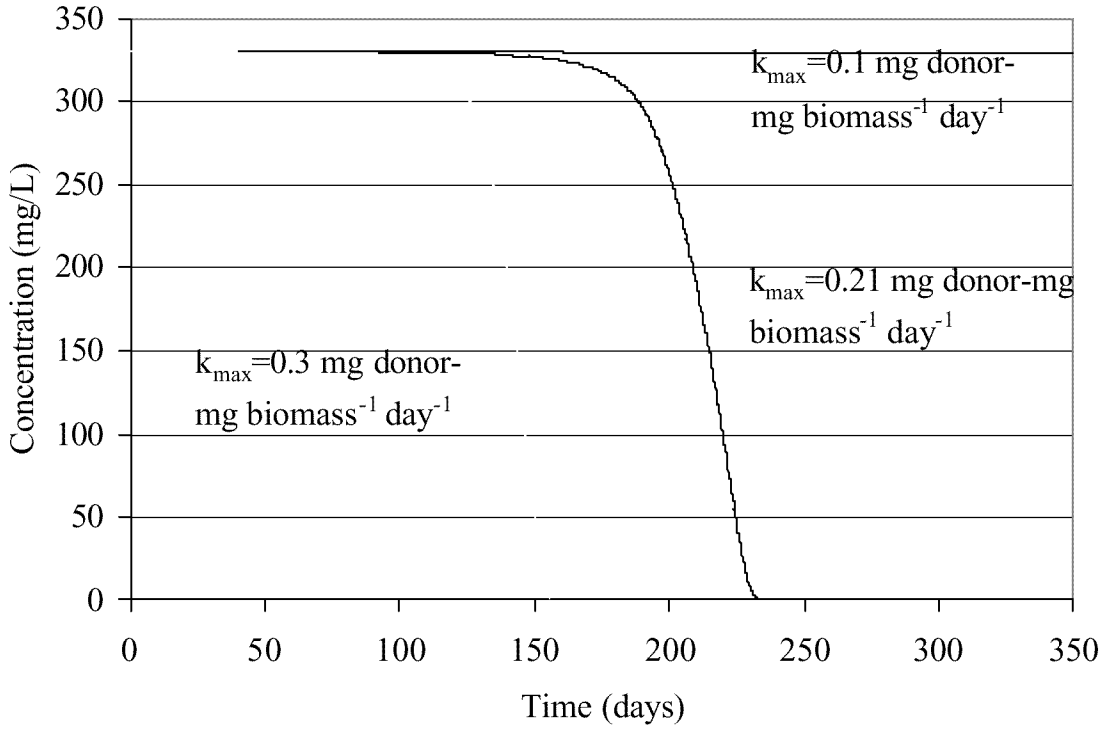


Figure 4.22 Effect of different k_{max} values on perchlorate concentration at observation well (layer 2, donor TAC=600 mg L^{-1})

When the value of k_{max} was increased to 0.3 mg donor mg biomass^{-1} day^{-1} the downgradient concentrations of perchlorate decreased at the observation well at about 150 days. This is because the rate at which the biomass was able to use the donor (recall the units of k_{max} are mg donor-mg biomass^{-1} day^{-1}) to deplete the acceptors was increased. When k_{max} is equal to 0.1 mg donor mg biomass^{-1} day^{-1} there is no perchlorate removal within the 350-day simulation time. The rate at which low downgradient concentrations are observed seems to be very sensitive to this parameter, which makes sense because in the model equations k_{max} is directly proportional to the rate of electron donor consumption thus directly affecting the biomass growth and the electron donor degradation (see equations 2.20-2.26). However, this downgradient concentration seems

to be only a rate effect because the lowest concentration reached in each scenario does not change significantly (not shown in Figure 4.22). The overall mass destroyed at each value of k_{max} tested is summarized in Table 4.1. As expected, the higher the max rate of substrate utilization the more total mass of perchlorate was degraded from all layers. Note that the perchlorate hole extends beyond the model grid boundaries, so the comparison does not capture all mass destroyed. But, it does provide another way to compare treatment efficacy when the boundary constraint is taken into consideration.

Table 4.2 Perchlorate mass degraded at varying values of k_{max} (all layers)

k_{max}	**Perchlorate Mass Degraded**
0.1 mg donor/mg biomass/day	25.0 kg
0.21 mg donor/mg biomass/day	10,100 kg[1]
0.3 mg donor/mg biomass/day	12,900 kg[1]
[1] Masses are underestimated due to degradation taking place outside model boundary	

Figure 4.23 below depicts the perchlorate concentration contours for k_{max} at 0.21 to 0.3 mg donor-mg biomass^{-1} day^{-1}. As would be expected, the perchlorate "hole" is significantly larger and extends further down gradient from the injection wells when k_{max} = 0.3 mg donor-mg biomass^{-1} day^{-1} than when k_{max} = 0.21 mg donor-mg biomass^{-1} day^{-1}. Note that the concentration holes extend beyond the grid boundary, so we can not quantify perchlorate mass destroyed.

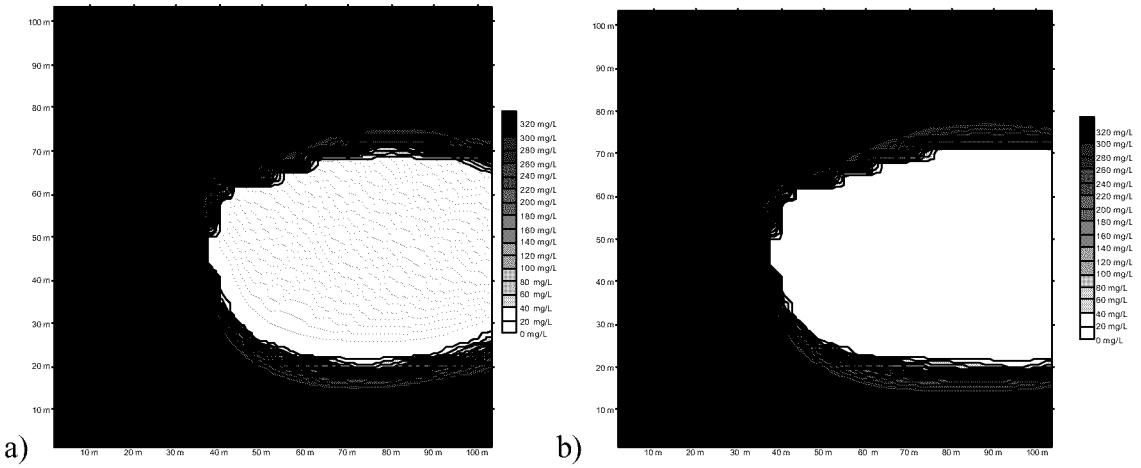


Figure 4.23 Perchlorate concentration contours at varying k_{max} values (a and b k_{max} values are 0.21 and 0.3 mg donor-mg biomass^{-1} day^{-1} respectively, layer 2, 350 days, baseline data)

Another kinetic parameter that directly affects the microbial growth (equation 3.9) is $Y_{biomass}$. Microbial growth is directly proportional to this term, which is defined as the biomass produced per mass of electron donor consumed (mg biomass-mg electron donor^{-1}). Figure 4.24 shows downgradient perchlorate concentrations for four different values of $Y_{biomass}$.

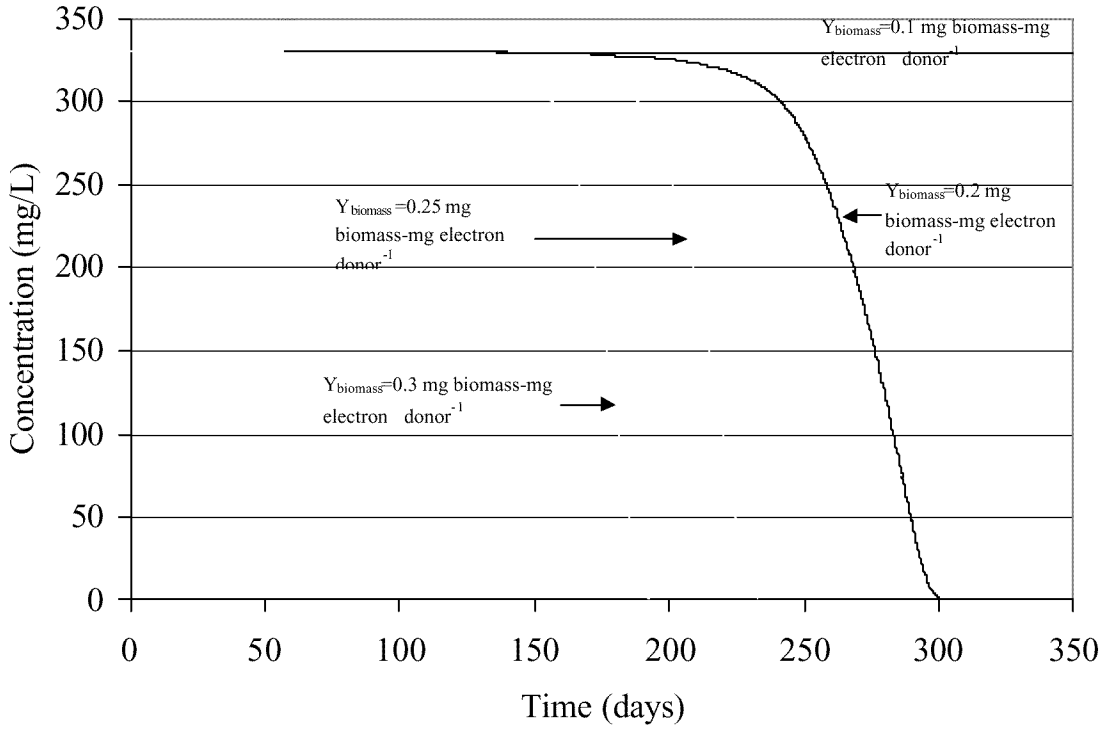


Figure 4.24 Effect of different $Y_{biomass}$ values on perchlorate concentration at observation well (layer 2, donor TAC=600 mg L^{-1})

It is apparent from Figure 4.24 that $Y_{biomass}$ has a similar effect on perchlorate treatment as k_{max}. The time at which perchlorate degradation occurs is reduced significantly by only slight changes in the $Y_{biomass}$ term. Only a small decrease in the value of $Y_{biomass}$ (from 0.2 to 0.1 mg biomass-mg electron donor^{-1}) is the difference between no treatment and significant treatment over the 350-day simulation. Figure 4.25 shows perchlorate

concentration contours at varying values of $Y_{biomass}$ to further demonstrate the impact of small changes to this kinetic parameter. The perchlorate hole grows significantly with each slight increase in Y_{biomss}.

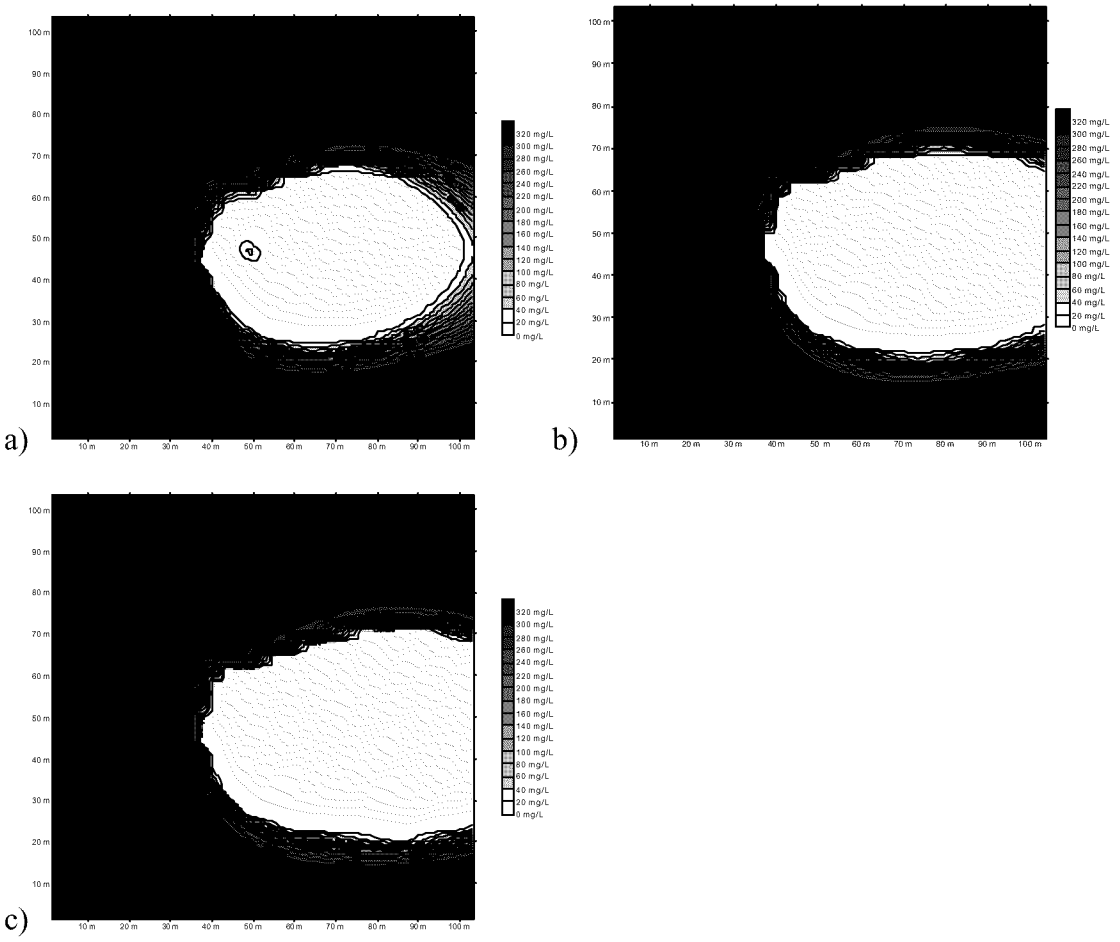


Figure 4.25 Perchlorate concentration contours at varying $Y_{biomass}$ values (a, b, and c $Y_{biomass}$ values are 0.2, 0.25, and 0.3 mg biomass-mg electron donor^{-1} respectively, layer 2, 350 days, baseline data)

Table 4.3 below summarizes the mass of perchlorate degraded at different values of $Y_{biomass}$. Note that at very low values of $Y_{biomass}$ (0.1 mg biomass-mg electron donor^{-1}), degraded mass is extremely small. Apparently, at these very low yields, biomass is insufficient to degrade significant amounts of perchlorate. With slight increases in the value, however, the mass degraded within the 350 day time frame grows significantly. The assumption from Chapter 3 that $Y_{biomass}$ is the same for each electron acceptor does not seem to be a good one since small changes in the parameter significantly affect model output. Accurately measuring the biomass yields for different acceptors and incorporating them into the model would appear to be important for technology design.

Table 4.3 Perchlorate mass degraded at varying values of $Y_{biomass}$ (all layers)

$Y_{biomass}$	**Perchlorate Mass Degraded**
0.1 mg biomass/mg electron donor	22 kg
0.2 mg biomass/mg electron donor	7,300 kg
0.25 mg biomass/mg electron donor	10,100 kg[1]
0.3 mg biomass/mg electron donor	11,600 kg[1]
[1] Masses are underestimated due to degradation taking place outside model boundary	

The model results are also sensitive to changes in the microbial decay rate constant (b). Varying the decay constants from 0.002, 0.01, to 0.05 day^{-1} resulted in large changes in the perchlorate concentration breakthrough curves downgradient as seen in Figure 4.26. As the rate at which the microbial population dies off increases, a smaller amount of biomass is available for treatment. The smaller the amount of biomass available for treatment, the more contaminant breaks through the bioactive zones to reach the downgradient monitoring well. The effect of b seems only to be a rate effect since the

long-term steady concentrations of perchlorate downgradient are similar, independent of decay rate.

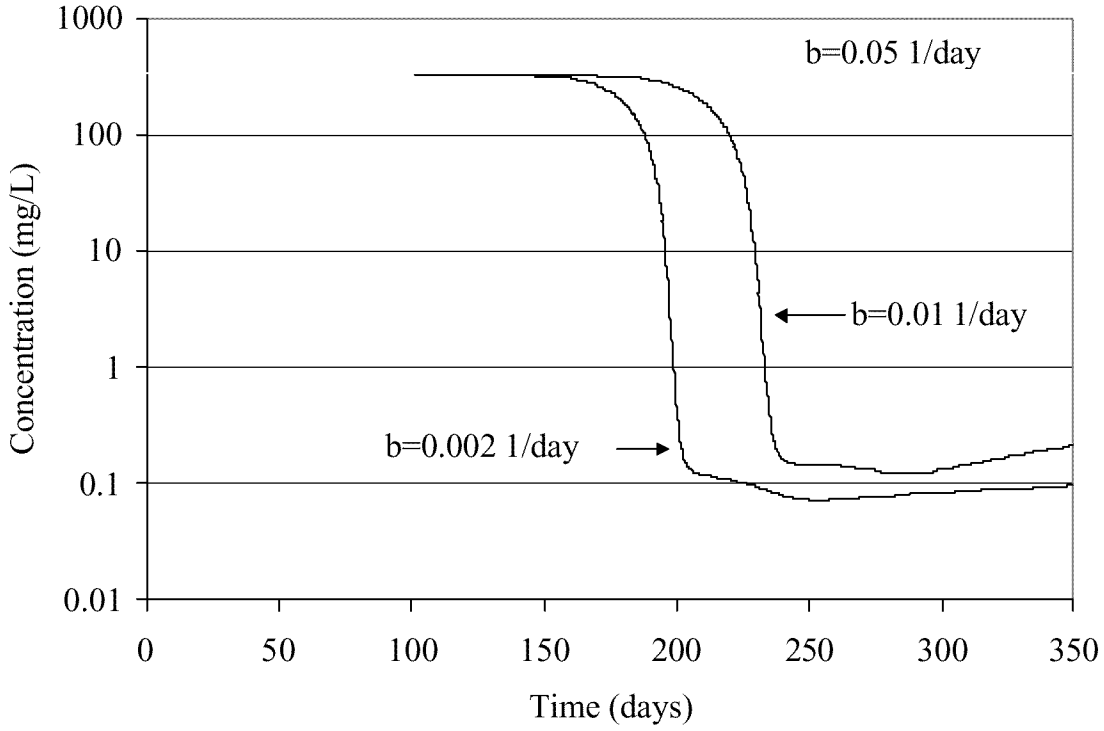


Figure 4.26 Effect of different decay constant values on perchlorate concentration at observation well (layer 2, donor TAC=600 mg L^{-1})

Table 4.4 summarizes the mass degraded within the model grid for varying values of biomass decay rate. For the 350 day time frame used in this study it seems that a biomass decay rate of somewhere around 0.05 day^{-1} causes the biomass to decay too rapidly to sustain any significant perchlorate degradation.

Table 4.4 Perchlorate mass degraded at varying values of biomass decay rate (all layers)

b	Mass Degraded
0.002 1/day	11,500 kg
0.01 1/day	10,000 kg
0.05 l/day	4.3 kg

The assumption from Chapter 3 that biomass decay rate is the same for each electron acceptor also does not seem to be a good one, as the impact of slight changes in yield is so significant.

The final series of simulations evaluated the half saturation concentrations and inhibition constants used in this modeling study, specifically K_S^{oxy}, K_i^{oxy} , K_S^{nit}, K_i^{oxy} , K_S^{per}, and K_S^{don}. Equations 2.20-2.22 contain these parameter values. It was mentioned in Chapter 3 that the inhibition coefficients are assumed to be the same as the half saturation concentrations. Figure 4.27 shows the downgradient concentration of perchlorate at varying values of K_S^{oxy} and K_i^{oxy} keeping $K_S^{oxy}=K_i^{oxy}$. It was observed that changing these parameters had very little effect on the downgradient concentration of perchlorate. In general a high value for the oxygen inhibition constant causes oxygen not to inhibit nitrate or perchlorate degradation. Low values cause nitrate and perchlorate to be inhibited significantly, depending on the relative values of the oxygen concentration compared with the oxygen inhibition constant (see equation 2.20-2.22). Specifically at low values of the oxygen inhibition constant, the oxygen degradation rate (r_{oxy}) and the rate of substrate utilization due to oxygen ($r_{don,oxy}$) are the fastest (i.e $r_{don,oxy}$ and r_{oxy} are the largest) and the perchlorate degradation rate (r_{per}) and the rate of substrate utilization due to perchlorate ($r_{don,per}$) are the most inhibited. The opposite is true at high values of

K_S^{oxy} and K_i^{oxy}. Thus r_{donor} remains relatively unchanged since its value is the aggregate of donor utilitization by all acceptors (equation 2.19). Since biomass growth is governed by r_{donor} (equation 2.23) the microbial population is not expected to change significantly with changes to K_S^{oxy} and K_i^{oxy}, causing little change to the downgradient concentration .

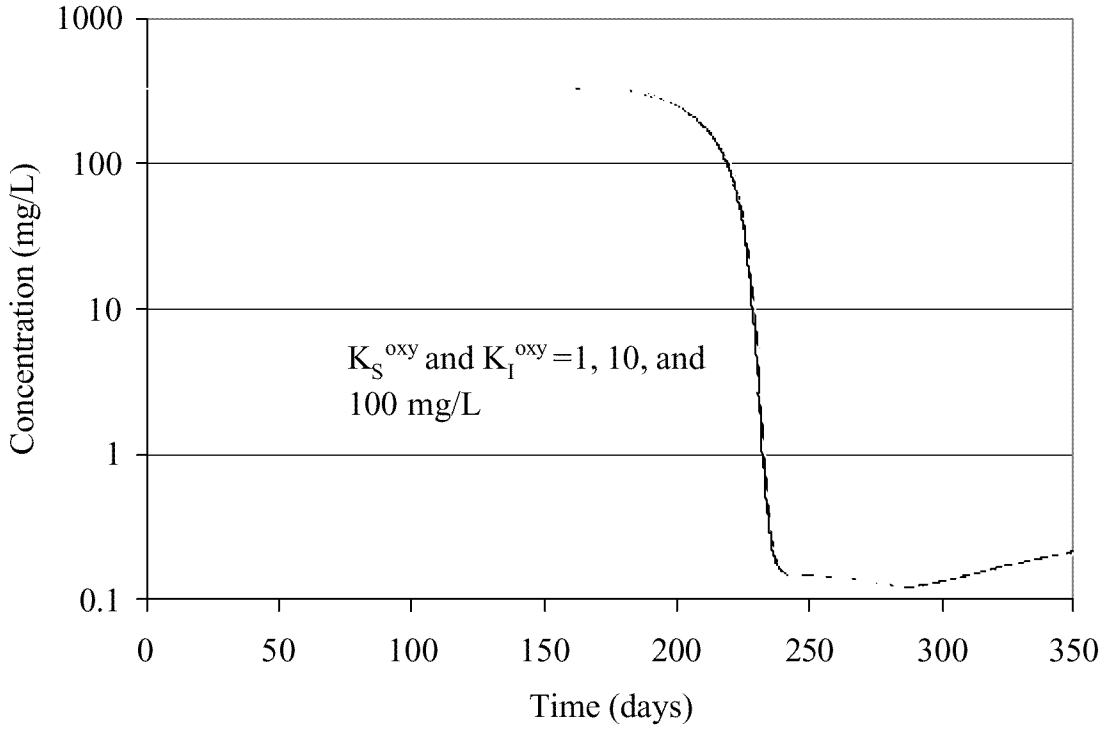


Figure 4.27 Effect of different oxygen half saturation concentration (K_S^{oxy}) and inhibition coefficient (K_i^{oxy}) values on perchlorate concentration at observation well (layer 2, TAC=600 mg/L)

Figure 4.28 shows the perchlorate concentration at varying nitrate half saturation concentrations and inhibition constants, and exhibits much of the same behavior for the same reasons discussed above for oxygen. The order of magnitude changes to the values cause little change to perchlorate concentration.

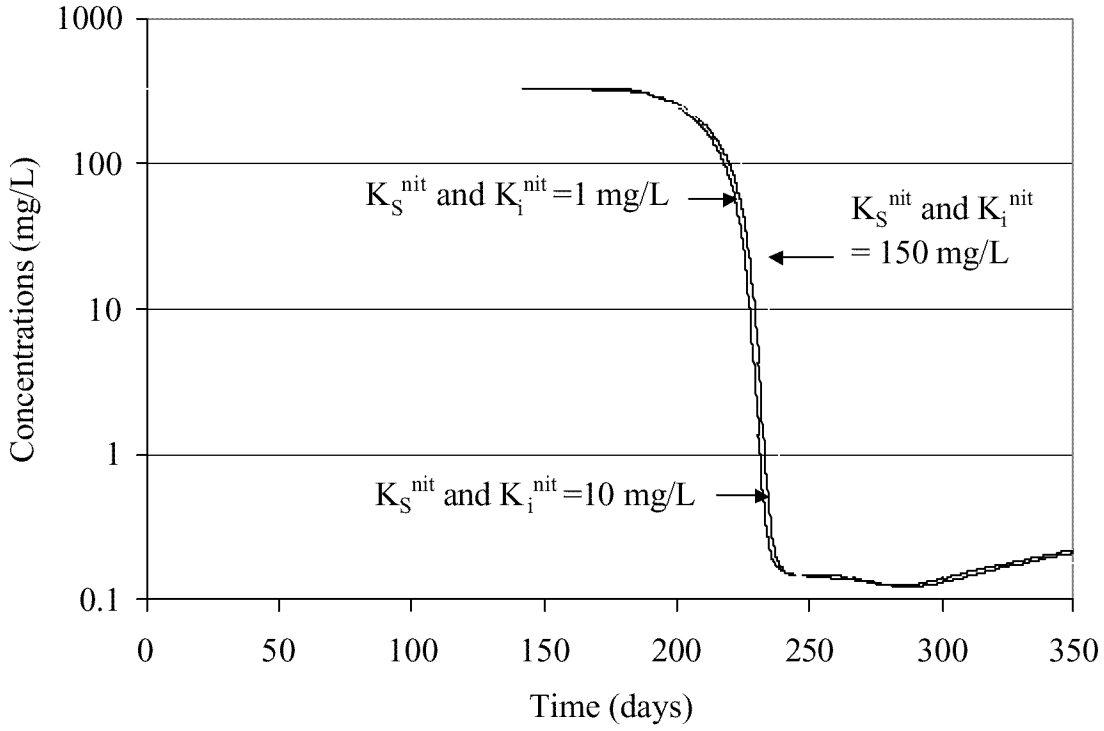


Figure 4.28 Effect of nitrate half saturation concentration (K_S^{nit}) and inhibition coefficient (K_i^{nit}) values on perchlorate concentration at observation well (layer 2, TAC=600 mg/L)

The effect of perchlorate half saturation concentration (K_S^{per}) on downgradient concentration is shown in Figure 4.29. Unlike the previous values for half saturation concentration, order of magnitude changes to K_S^{per} had a significant effect on the rate and extent of perchlorate concentration. Since K_S^{per} will increase both the perchlorate

degradation rate and the rate of substrate utilization due to perchlorate ($r_{don,oxy}$ and r_{oxy}) it is expected that changes to the perchlorate half saturation concentration would result in significant changes in model output.

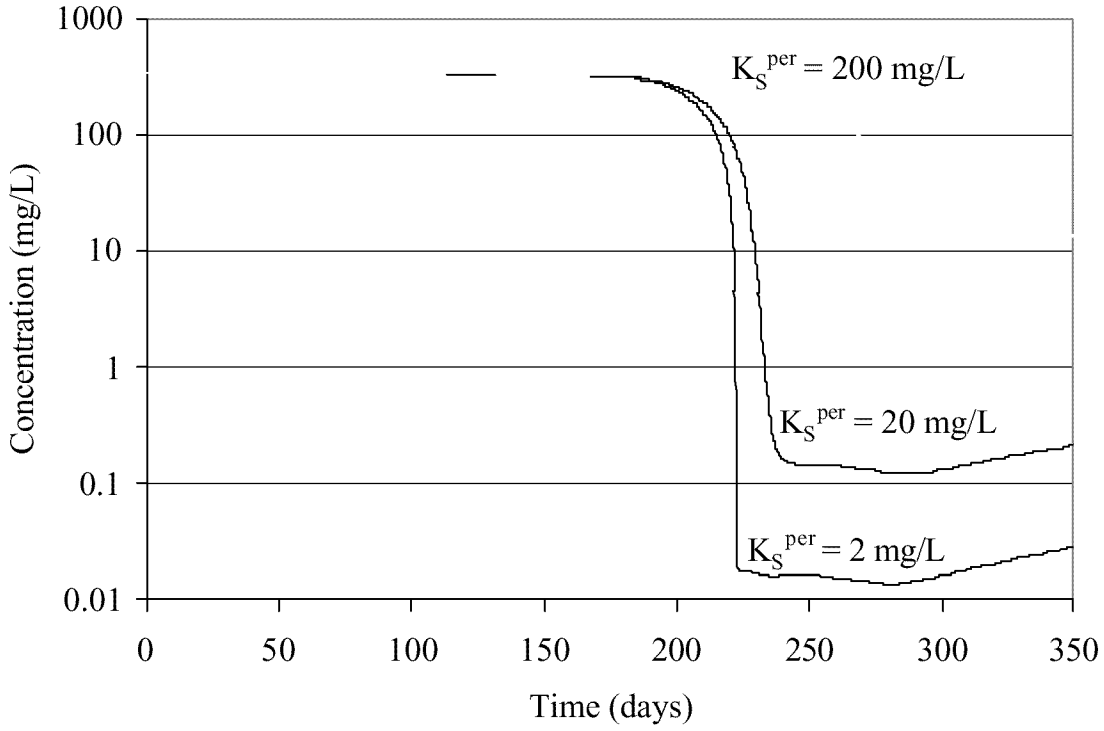


Figure 4.29 Effect of different perchlorate half saturation concentration values (K_S^{per}) on perchlorate concentration at observation well (layer 2, TAC=600 mg/L)

The final simulation tested the model response to changes in K_S^{don} (Figure 4.30). Equations 2.20-2.22 contain Monod terms with K_S^{don} that approach a maximum (almost 1) at low K_S^{don} values, and a minimum at high K_S^{don} values. The Monod term that contains K_S^{don} directly impacts the rate of donor consumption (r_{donor}) and the rate of perchlorate degradation ($r_{don,per}$), explaining the model's sensitivity to order of magnitude changes in K_S^{don} values.

Figure 4.30 illustrates the perchlorate concentration downgradient when K_S^{don} is varied.

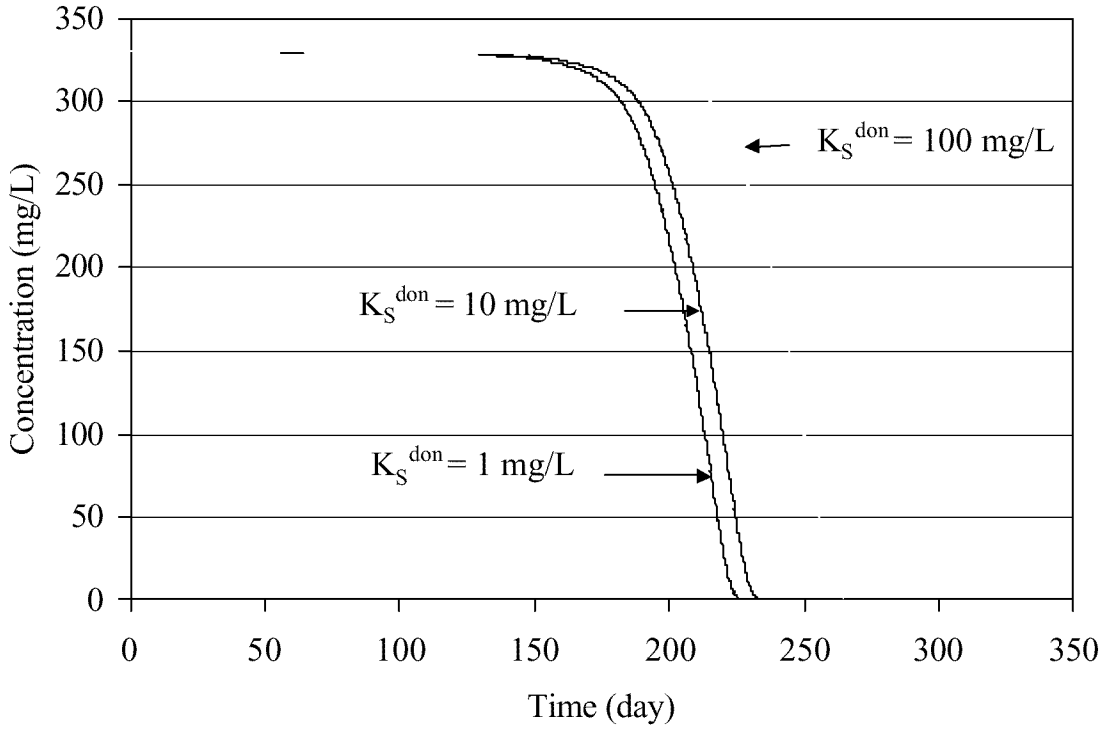


Figure 4.30 Effect of different donor half saturation concentration values on perchlorate concentration at observation well (layer 2, TAC=600 mg/L)

The observed sensitivity of k_{max} $Y_{biomass}$, b, K_S^{don}, and K_S^{per} emphasize the importance of accurately measuring these parameters to model the system.

5.0 CONCLUSIONS

5.1 SUMMARY

In this thesis, a technology model that combined a dual-Monod multi-electron acceptor biological submodel with the Huang and Goltz (1998) three-dimensional fate and transport model was developed, implemented, and applied to an example in situ perchlorate remediation based on Site 4, Nevada. Simulations of this technology at this site using laboratory kinetic values resulted in significant perchlorate removal in the presence of competing electron acceptors (oxygen and nitrate) in the HFTW recirculation system when electron donor (acetate) was injected.

5.2 CONCLUSIONS

Perchlorate plume containment appears to be possible using HFTWs coupled with *in situ* bioremediation. The technology model and the environmental, engineering, and kinetic parameters used in this study demonstrated that perchlorate can potentially be treated *in situ* using the HFTW technology.

Recirculation and mixing provided by the HFTW system may increase the overall effectiveness of the treatment system when compared with the treatment achieved by a single-pass of perchlorate-contaminated water through a bioactive zone. Model simulations with increased recirculation between the HFTW treatment wells due to smaller well spacing or increased pump rates indicate that the higher the recirculation, the better the overall perchlorate treatment. However, this increased treatment efficiency comes at the expense of the amount of upgradient perchlorate contaminated water that

can be captured by the treatment system. As recirculation increases, capture zone width decreases. This tradeoff would be addressed by designing a system with an adequate number of treatment wells to ensure both overall perchlorate destruction and capture objectives are met.

Changes in kinetic parameters have a greater influence on system performance in the HFTW system than changes to the well spacing, electron donor time averaged concentration, pulse schedule, or anisotropy. Analyses of the simulation results revealed that the treatment system performance was more sensitive to changes in the kinetic parameters (k_{max}, $Y_{biomass}$, b, K_S^{don}, and K_S^{per}) than the engineering parameters of well spacing or electron donor time averaged concentration. With regard to the engineered parameters, it appears that system performance is improved with continuous injection of donor in excess of that required and with wells spaced and pumping at a rate that allows for significant interflow. It also appears that this system may be effective under isotropic conditions, which is a different from what was concluded for a study of *in situ* bioremediation of TCE with HFTWs.

This model, by incorporating a biological submodel into the numerical HFTW flow model represents an important step in designing pilot scale systems. The model presented in this study may be used by researchers to design a pilot-scale technology application at a perchlorate-contaminated site.

5.3 RECOMMENDATIONS

Perform additional experiments to more fully determine kinetic parameters (k_{max}, b, $Y_{biomass}$, K_S^{oxy}, K_S^{nit}, K_S^{per}, K_i^{oxy}, and K_i^{nit}, and K_S^{don}). Literature values of these coefficients are highly variable and sparse. Additional experiments may provide further information on the effect that competing electron acceptors (oxygen and nitrate) have on perchlorate treatment, as well as furthering our understanding of the inhibition mechanism.

Revise model to account for biomass yield ($Y_{biomass}$) and biomass decay constant values for the different electron acceptors. The model was very sensitive to small changes in these values. Assuming them to be the same for different electron acceptors may not be a good assumption based upon model sensitivity to slight changes in these values.

Implement and monitor a pilot scale *in situ* HFTW bioremediation system. Implementing a pilot scale system modeled after the field evaluation of *in situ* bioremediation of TCE using HFTWs at the Edwards AFB Site 19 would provide valuable data and experience to guide implementation of this technology. Measuring kinetic parameters from the pilot scale would give more realistic parameters for use in technology design.

Optimize the technology model. In this study, a full sensitivity analysis, which would define technology performance capabilities and limitations, was not accomplished. An

optimization study, that attempts to determine "best" technology performance under various conditions, would serve to further our understanding of how the technology can potentially be applied.

Validate the technology model. Once data from a pilot scale demonstration of this technology are available, these data may be used to validate the model.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

Groundwater contamination by perchlorate has recently been recognized as a significant environmental problem across the United States, and especially at Department of Defense facilities. In this study, a model is used to evaluate the potential of an innovative *in situ* bioremediation technology using Horizontal Flow Treatment Wells (HFTWs) to manage perchlorate-contaminated groundwater. The technology uses HFTWs to mix an electron donor into perchlorate-contaminated groundwater in order to promote reduction of the perchlorate by indigenous microorganisms in bioactive zones within the aquifer, as well as recirculate the contaminated water between treatment well pairs to achieve multiple passes of contaminated water through the bioactive zones. The model used in this study couples a three-dimensional fate and transport model, which simulates advective/dispersive transport of solutes induced by regional groundwater flow and operation of the HFTWs, with a biodegradation model that simulates perchlorate reduction, as well as reduction of competing electron acceptors in the groundwater, by indigenous microorganisms. The model was applied to an example site to demonstrate how *in situ* perchlorate treatment might be implemented. A sensitivity analysis using the model is also conducted to evaluate which engineered and environmental parameters most affect technology performance. Model simulation results demonstrate that this technology may be effective in managing perchlorate-contaminated groundwater. The recirculation induced by the HFTW system results in increased treatment efficiency, as compared to treatment that would be achieved by a single pass of contaminated water through the bioactive zones. It was observed that the model was very sensitive to several kinetic parameters, indicating that a fruitful area for future research would be to study how these important parameters can be accurately quantified for given geochemical and microbiological conditions. The model presented in this study is an important tool in helping to design field evaluations of the technology. These evaluations will be essential in ultimately transitioning the technology for application at perchlorate-contaminated groundwater sites throughout the Department of Defense.

15. SUBJECT TERMS
Groundwater contamination, perchlorate, bioremediation, modeling

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