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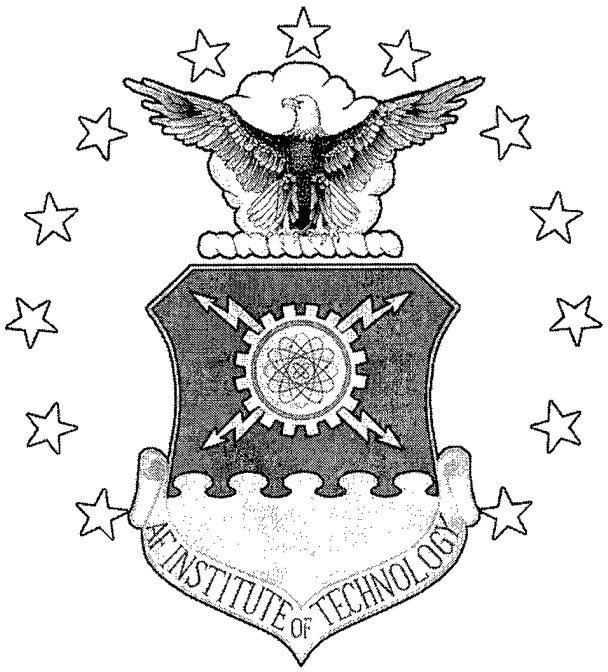
Modeling Chlorinated Ethene Removal in the Methanogenic Zone of Constructed Wetlands: A System Dynamics Approach

Randall L. Roberts



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THESIS

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AFIT/GEE/ENV/01M-17

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AFIT/GEE/ENV/01M-17

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THESIS

Presented to the Faculty

Department of Systems and Engineering Management

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Engineering and Environmental Management

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March 2001

AFIT/GEE/ENV/01M-17

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Acknowledgements

First I would like to my Lord and Savior Jesus Christ because with out him none of this would have been possible. I would also like to thank my wife for her patience, love, and support during this thesis effort, and for taking care of our twin boys. Next I would like to thank my advisor, Dr. Shelley, for his patience, support, insight, and confidence. This thesis effort would not possible without everybody's support. Thanks.

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Abstract

The purpose of this study is to gain understanding of the dynamics of the processes that degrade Perchloroethene (PCE) to ethene, within the confines of the methanogenic zone of a constructed wetland. A system dynamics modeling approach is used. This model is focused on determining conditions that will enhance contaminant degradation.

The chemical and biological processes within the methanogenic zone of a wetland system are extremely complex and dynamic processes. The model is broken up into three simultaneous processes: dechlorination, methanogenesis, and fermentation. The system behavior of the methanogenic zone can be adequately described by the classical formulations of representative microbial reactions acting simultaneously within each process in response to substrate limitation. The zone is assumed to be homogeneous and well mixed.

This study provides a fundamental understanding of the complex interactions within the methanogenic zone of a constructed wetland and gives some insight for implementation. Testing identified flow rate, hydrogen concentration, and initial PCE biomass as specific parameters, which could be optimized to have the most effect on contaminant fate.

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I. Introduction

Background

In the late 1970's, a number of groundwater plumes contaminated with chlorinated solvents were discovered under Air Forces bases. It was soon discovered that this problem was found throughout the Air Force and the Department of Defense (DOD). There are an estimated 7,300 sites contaminated with chlorinated solvents at 1,800 locations, owned by DOD (National Research Council, 1994). Chlorinated solvents are among the most common contaminants of groundwater. Nine of the 20 most common chemicals found in groundwater at Superfund sites are chlorinated solvents (National Research Council, 1997). These lower molecular weight chlorinated solvents, particularly trichloroethene (TCE), were used as solvents in routine maintenance and cleaning of everything from electronic components to jet engines, weapon systems, and septic tanks. Chlorinated solvents were also used as intermediates in chemical manufacturing and as carrier solvents for pesticides and herbicides. Typically, they were stored in bulk, usually in large underground storage tanks. As a result of their widespread use in industry, agriculture, commercial business, and homes, chlorinated solvents are among the most common ground water contaminants. Chlorinated solvents are persistent contaminants that stay in the environment a long time. Therefore, they pose a threat to public health, ecosystem viability, and funds associated with environmental protection and preservation.

TCE is relatively insoluble, is more dense than water, and tends to migrate toward the bottom of the groundwater aquifer where it will sorb and desorb onto the soil as it is slowly carried by the groundwater flow. TCE is a suspected carcinogen that is very volatile and is readily removed by air stripping (Masters, 1997). Biodegradation is very slow and will only occur if the conditions are conducive. The degradation pathway for TCE, under anaerobic conditions, is to isomers of dichloroethene (DCE): 1,1 DCE, cis-1,2 DCE, or trans-1,2 DCE. DCE is metal degreaser that was used in the manufacturing of a number of products, including vinyl chloride, fumigants, varnish removers, and soap compounds. It is not a known carcinogen, but high levels of exposure are known to cause injury to the central nervous system, liver, and kidneys. DCE is also quite soluble and is difficult to remove by air striping (Masters, 1997). Vinyl chloride is produced when DCE is reduced. Vinyl chloride is the most toxic of the chlorinated solvents. It is a known human carcinogen used primarily in the production of polyvinyl chloride resins.

The National Research Council has divided remediation into three general categories: 1) technologies for solidifiction, stabilization, and containment; 2) technologies using biological and/or chemical reactions to destroy or transform the contaminant; 3) technologies which separate the contaminant from the contaminated media, immobilize the contaminant and extract it from the subsurface.

Solidification and stabilization processes are generally appropriate for shallow contamination and soil treatment. These processes focus on decreasing the mobility and/or toxicity of the contaminant by reducing the solubility, volatility, or media permeability. Examples of this technology are asphalt batching, biostabilization, passive-reactive barriers, enhanced sorption, in-situ soil mixing, and lime addition (National

Research Council, 1997). Containment technologies incorporate physical or hydraulic barriers to prevent contaminant movement away from the zone of contamination. Technologies include pump and treat systems, and low permeability barriers utilizing slurry walls, sheet pile walls, and grout walls.

Biological and chemical processes transform contaminants into their daughter products. Biological processes (bioremediation) rely on microorganisms to transform the contaminant through varying reactions resulting in degraded compounds. Reactions may be aerobic or anaerobic and can be direct or cometabolic. Environmental conditions like temperature, pH, etc., impact microbial metabolism. Some biological treatment technologies are biopiles, bioventing and biosparging, composting, engineered in situ bioremediation, and natural attenuation (intrinsic bioremediation). Chemical processes transform the contaminant through chemical reactions. Chemical processes are used less than biological treatments. Chemical treatment technologies include oxidation, incineration, substitution, and zero-valent ion barriers. Biological and chemical processes are the only processes that can completely destroy an organic contaminant (Hoefar, 2000).

Separation, immobilization, and extraction technologies, separate the contaminant from the soil particles, immobilize it into the aqueous phase or airspace in the soil voids, and extract the contaminant to the surface. These technologies can use heat, chemicals, vacuums or electrical current to separate the contaminant from the soil and move it to the extraction zone (National Research Council, 1997).

Wetlands are unique ecosystems and are among the most important ecosystems on the Earth (Gosselink and Mitsch, 1993). Wetlands provide unique habitats for a wide

range variety of flora and fauna. They also perform functions in hydrologic and chemical cycles and they function as the downstream receivers of wastes from both natural and human sources (Gosselink, and Mitsch, 1993). Natural wetlands have been observed to remove contaminants from groundwater (Lorah and Olsen, 1999). The use of constructed wetlands to remove contaminants from groundwater has potential as an alternative for remediation. Capt. Colby Hoefar developed a fundamental model of the degradation processes in constructed wetlands in his thesis entitled "Modeling Chlorinated Ethene Removal in Constructed Wetlands: A System Dynamics Approach." This thesis provides a fundamental model, which can eventually be used by remediation managers to predict the performance of a constructed wetland in removing PCE (Hoefar, 2000).

Constructed wetlands are similar yet different than natural wetlands. The main difference is that seasonal changes in water depth that may affect the species composition and sediment biota of natural wetlands has all but been eliminated from constructed wetlands. This is because people have control over the water input and discharge. This creates controlled, steady water levels, which in turn create uniform hydrologic conditions and an absence of pattern effects (Kadlec and Knight, 1996). The constructed wetlands that will be used for this study are uniformly fed from the bottom. This creates a series of layers in the soil that the water and contaminant must pass through on the way up. The wetland is broken down into two distinct zones: the anaerobic (no oxygen present) zone and the aerobic (oxygen present) zone. The anaerobic zone can be broken into various levels of reduction potential. Various microbes thrive under the particular conditions and can degrade compounds accordingly. The biodegradation of highly chlorinated VOC's such as TCE is known to occur under a range of anaerobic conditions.

These conditions are nitrate reducing, iron-reducing, sulfate reducing, and methanogenic, with methanogenic being the most reduced condition. It is believed that under methanogenic conditions, as compared to less reducing conditions, dechlorination to nontoxic end products of ethylene and ethane occurs faster and is more likely to result in complete dechlorination (Lorah and Olsen, 1999). When there are organic materials present to provide the electron donors required for halorespiration, the complete destruction of perchloroethene (PCE) and TCE under anaerobic conditions involves consortia of many microorganisms working together (McCarty, 1997). Methanogens and halorespirators are entirely dependent on other anaerobes for providing their growth substrate (Zehnder, 1988). Under these anaerobic conditions there are microbes that hydrolyze complex materials to simple monomers. Then the same or other microbes ferment the monomers to alcohols and fatty acids for energy. Other microbes then oxidize the alcohols and organic acids to produce acetate and molecular hydrogen (H_2). Then a few competing microorganisms oxidize the acetate and hydrogen as electron donors in energy metabolism (McCarty, 1997). In the methanogenic zone of the wetland, the microbes that are in competition for the electron donors are the methanogens and the halorespirators. The methanogens use hydrogen ions (H^+) and carbon dioxide (CO_2) as electron acceptors. The halorespirators use the solvent (PCE or TCE) as the electron acceptor.

Problem Statement

Further detail needs to be added to the foundational model of the constructed wetlands in order to help improve understanding of the dynamic degradation processes. More detail needs to be added to the methanogenic zone, specifically the microbial

interactions that are taking place there because of hydrogen dependence and competition between methanogens and halorespirators that is not taken into account in Hoefar's model. Methane production was also very basic in the model.

The purpose of this thesis is to determine and explore the fundamental processes that occur in the methanogenic zone in the constructed wetlands that are responsible for the degradation of PCE and its daughter products. This thesis will take a system dynamics approach to model the dynamic interactions. This effort would serve to further improve the foundational model of constructed wetlands. This model would eventually be used in the application of a constructed wetland for PCE removal. This would allow remediation managers to predict performance over time and optimize controllable parameters for degradations. This model will be useful to decision makers, when they are trying to determine viable alternatives in ground water remediation.

System dynamics produces system behavior mechanistically by identifying and simulating the underlying fundamental process driving basic system behavior (Moorehead et al., 1996). The system dynamics approach captures the feedback loops, multiple interactions, time sensitive behavior, non-linear interactions, and changes in the system over time associated with extremely complex systems. A constructed wetlands is a complex system that involves many interactions among various entities and parameters. The simulation of a system dynamics model facilitates the study of internal interactions of complex systems, helps to explore the system behavior beyond the range of observed system behavior, and helps to identify how various parameters will affect the dynamic system.

Research Questions

1. What processes in the methanogenic region are most important in influencing chlorinated solvent degradation throughout the constructed wetland system?
2. What factors affect the competition for electron donors of the methanogens and halorespirators?
3. What combination of controllable parameters gives the maximum amount of degradation in the system as a whole?

Scope/ Limitations

This study will focus on the conditions in the methanogenic zone that are necessary for dechlorination of PCE. Dechlorination in the methanogenic zone depends upon the concentration of contaminant, the microbial consortia present (fermenters, methanogens, and halorespirators), and the ability of the halorespirators to compete for the electron donors, specifically hydrogen, over the methanogens. Complete dechlorination will occur once the other electron acceptors like sulfate, nitrate, and nitrite are depleted (McCarty, 1996). In the methanogenic zone these other electron acceptors are depleted rapidly; therefore, this study will assume that these electron acceptors have already been depleted. This model will focus on the competition between the halorespirators and methanogens. The effects of temperature and pH will not be taken into consideration for this model.

II. Literature Review

Introduction

Many chlorinated compounds are formed naturally; PCE and TCE are emitted during volcanic activity (Hoekstra and DeLeer, 1995). Therefore it should be no surprise that dehalogenating bacteria have been discovered, since bacteria have been on the earth since geological time began. Microbial dehalogenation should appear as another microbial adaptation to an available carbon and energy source. There are some anaerobic systems that only partially dechlorinate PCE, and there are some that can completely dechlorinate PCE to ethene or ethane (Tandol et al., 1994). These microbial populations show that oxygen is not required to completely dechlorinate to ethene and that, because these microbes can gain energy from the solvents, contaminated groundwater plumes may be self-enriching for the bacteria.

Constructed Wetlands

Constructed wetlands have the ability to provide the conditions necessary for microbial dehalogenation. There are two types of constructed wetlands: surface flow (SF) and subsurface flow (SSF). Since the constructed wetlands used for this study are uniformly fed from the bottom, the SSF wetlands will be the focus here.

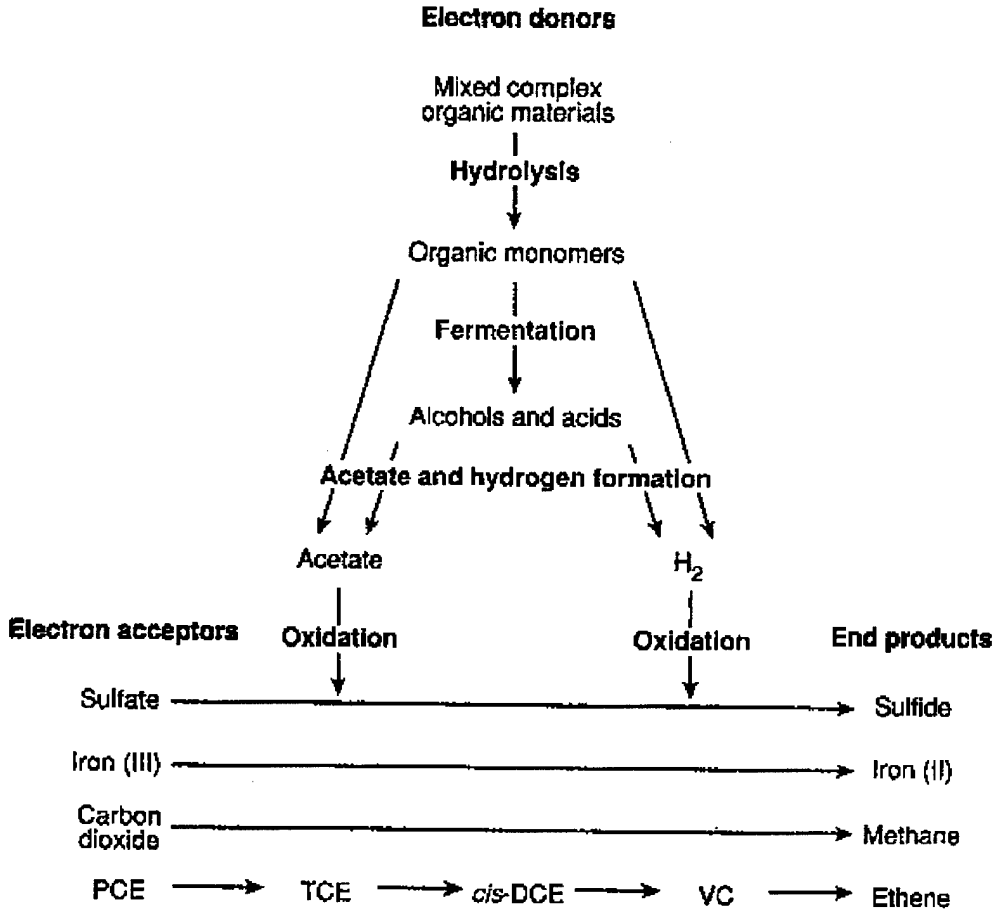
Subsurface flow wetlands use horizontal or vertical flow through sediment or constructed media of the wetland. Microbes can attach themselves to the media or to the roots of wetland plants. Generally, SSF wetlands have no standing water at the surface, although the sediment is saturated completely to the surface. Design components include an input device, the wetland basin, media (to include sediment), plants, and an output

device. For optimal performance, these systems must initiate and maintain a consistent flow through a permeable media (Kadlec and Knight, 1996).

The steady, vertical flow the constructed wetland creates a uniform hydrological condition and the absence of pattern effects (Kadlec and Knight, 1996). The wetland is broken down into two distinct zones: the anaerobic (no oxygen present) zone and the aerobic (oxygen present) zone. The anaerobic zone is the only zone that will be considered in this paper.

Anaerobic Zone

The anaerobic zone is where there is no oxygen present. There are many processes that take place in the anaerobic zone. Methanogens and dechlorinators are both anaerobic microorganisms. Both of them are entirely dependant on other anaerobic microbes to provide them with growth substrate (Zehnder, 1988). Under anaerobic conditions, there are microbes that breakdown complex materials to simple monomers (sugars, amino acids, organic acids) by hydrolysis. Then the same or other microbes ferment the simple monomers to alcohols and fatty acids for energy. Other microbes then oxidize the alcohols and organic acids to produce acetate and hydrogen (H2). Then a few competing microorganisms oxidize the acetate and hydrogen as electron donors in energy metabolism (McCarty, 1997). Figure 1 gives a graphical representation of some of the processes that occur in an anaerobic zone.



Detoxification: a competitive situation. Electron flow from electron donors to electron acceptors in the anaerobic oxidation of mixed and complex organic materials. Microorganisms that can use chlorinated compounds (PCE, TCE, cis-DCE, and VC) as electron acceptors in halorespiration compete for the electrons in the acetate and hydrogen intermediates with microorganisms that can use sulfate, iron (III), and carbon dioxide.

Figure 1. Taken From McCarty, 1997

Wetland Soil

Wetland soil is the medium in which many of the wetland chemical transformations take place, and it is also the primary storage of available chemicals for most wetland plants (Mitsch and Gosselink, 1993: 115). Wetland soil is often described as hydric soil. The U.S. Soil Conservation Service (1987) defines a hydric soil as "a soil that is saturated, flooded, or ponded long enough during the growing season to develop

anaerobic conditions in the upper part." There are two types of wetland soils: mineral soils or organic soils. Since nearly all soils have some organic content, a soil is considered a mineral soil if its organic content is less than 20 to 35 percent (on a dry weight basis (Mitsch and Gosselink, 1993: 116). Organic soils are different from mineral soils in several physiochemical features. Table 1 lists the differences.

Table 1. Comparison of Mineral and Organic Soils in Wetlands

	Mineral Soil	Organic Soil
Organic Content, percent	Less than 20 to 35	Greater than 20 to 35
Organic Carbon, percent	Less than 12 to 20	Greater than 12 to 20
pH	Usually circumneutral	Acid
Bulk Density	High	Low
Porosity	Low (45-55%)	High (80%)
Hydraulic Conductivity	High (except for clays)	Low to high
Water Holding Capacity	Low	High
Nutrient Availability	Generally high	Often low
Cation Exchange Capacity	Low, dominated by major cations	High, dominated by hydrogen ion

Source: taken from Mitsch and Gosselink, 1993

1. Organic soils have lower bulk densities and higher water-holding capacities than mineral soils.
2. Mineral and organic soils both have a wide range of possible hydraulic conditions. The hydraulic conditions for organic soils depend on the degree of decomposition. Organic soils may hold more water than mineral soils, however, given the same hydraulic conditions, they do not necessarily allow water to pass through more rapidly.

3. Organic soils generally have a greater amount of minerals tied up in organic forms unavailable to plant than do mineral soils. This does not mean that there are more total nutrients in organic soils. Very often the opposite is true in wetland soils. For example, organic soils can be extremely low in bioavailable phosphorous or iron content. These contents can be low enough to limit plant productivity (Mitsch and Gosselink, 1993).

The organic content of soils has some significance for the retention of chemicals in a wetland. Since organic soils have a higher cation exchange capacity than mineral soils, they can therefore remove some contaminants through ion exchange (Mitsch and Gosselink, 1993: 602). The organic matter in wetland soils varies generally between 15 and 75 percent (Mitsch and Gosselink, 1993: 602). Subsurface flow wetlands usually add organic matter such as composted mushrooms, peat, or detritus as one of the layers in order to help get them started. Many constructed wetlands avoid the use of organic soils because they are low in nutrients, can cause low pH, and often provide inadequate support for rooted aquatic plants (Mitsch and Gosselink, 1993: 602)

Competition between Methanogens and Dechlorinators

There is evidence that hydrogen is a key electron donor in the dehalogenation of *cis*-DCE to VC to ethylene (Yang and McCarty, 1998). The dechlorinating organisms compete for the electrons in hydrogen with organisms using other electron acceptors, like hydrogen-utilizing methanogens, homoacetogens, and sulfidogens (McCarty 1997b). Microorganisms preferentially utilize electron acceptors that provide the maximum free energy during respiration. Of the most common electron acceptors, oxygen provides the most free energy during electron transfer (Table 2). Microorganisms using nitrate,

Mn(IV), Fe(III), sulfate, and carbon dioxide for electron acceptors, receive less energy during electron transfer according to the order listed in Table 2 (Bouwer, 1992). Methanogens and dehalogenators are not competitive with nitrate, Mn(IV), Fe(III), and sulfate reducing microorganisms. Dehalogenators compete intensely with methanogens for hydrogen (Smatlak et al., 1996). The dehalogenating bacteria have the ability to use H_2 at lower levels than methanogens. However, at higher levels of H_2, the methanogens out-compete the dehalogenators for the hydrogen and dechlorination stagnates (Smatlak et al., 1996). Smatlak et al. found that deliberately choosing an electron donor whose fermentation results in a slow, steady low-level release of hydrogen, favored dechlorination.

Table 2. Electron Acceptors in Biotransformation Processes

Microbial Process	Electron Acceptor	Reaction	Free energy change ($\Delta G°$) at pH 7 (kcal/ equivalent)
Aerobic respiration	O_2	CH_2O (formaldehyde) + $O_2(g)$ = $CO_2(g) + H_2O$	-29.9
Denitrification	NO_3^-	$CH_2O + 0.8\ NO_3^- + 0.8\ H^+$ = $CO_2(g) + 0.4\ N_2(g) + 1.4\ H_2O$	-28.4
Mn(IV) reduction	Mn(IV)	$CH_2O + 2MnO_2 + 2\ HCO_3^- + 2\ H^+$ = $CO_2(g) + 2\ MnCO_3(s) + 3\ H_2O$	-23.3
Fe(III) reduction	Fe(III)	$CH_2O + 4\ FEOOH(s) + 4\ HCO_3^- + 4\ H^+$ = $CO_2(g) + FeCO_3(s) + 7\ H_2O$	-10.1
Sulfate reduction	SO_4^-	$CH_2O + 0.5\ SO_4^- + 0.5\ H^+$ = $CO_2(g) + 0.5\ HS^- + H_2O$	-5.9
Methanogenesis	CO_2	$CH_2O + 0.5\ CO_2(g) = CO_2(g) + 0.5\ CH_4$	-5.6

Taken from Bouwer, 1992

Fermentation

The fermentation process is important in the competition for hydrogen between methanogens and dehalogenators. Under anaerobic conditions, many different organic substrates become H_2 sources when fermented. The levels of H_2 resulting from their fermentation, however, can differ by orders of magnitude. This depends upon the intrinsic thermodynamics of the particular fermentation reaction (Fennell and Gossett, 1998). Four organic H_2 sources—butyric acid, ethanol, lactic acid, and propionic acid—have widely different H_2-production ceilings (i.e. maximum levels of H_2 that could be thermodynamically achieved via fermentation). Fennell et al. (1997) conducted studies of the effects of the fermentation of butyric acid, ethanol, lactic acid, and propionic acid on the degradation of tetrachloroethene. These studies demonstrated that substrates fermented only under low H_2 partial pressures (e.g. butyric and propionic acids) are superior donors for stimulating dechlorination while minimizing competing methanogens (Fennell et al., 1997). Yang and McCarty produce similar results with their comparative studies with benzoate and propionate. Benzoate, when used as a substrate, is fermented rapidly and thereby hydrogen is also rapidly produced. The hydrogen produced is over the methanogenic threshold level; therefore, most of the hydrogen is used by the methanogens. The fermentation of propionate, on the other hand, has a slower, longer lasting release of hydrogen because of the small propionate-utilizing population and thermodynamic regulation of the fermentation. The propionate fermentation produces a higher long-term hydrogen production rate that is below the threshold for methanogens. This limits methanogenesis and results in a higher rate of dechlorination (Yang and McCarty, 1998).

Methanogenesis

Methanogens are strictly anaerobic, unicellular organisms belonging to a phylogenetic domain, the archaebacteria. They are obligate anaerobes and are extremely sensitive to low levels of oxygen. Methanogens cannot effectively compete until nitrate, iron, and sulfate ions are reduced. Methanogens are not capable of using complex organic carbon compounds for food. They are entirely dependent on the metabolic activities of other anaerobes for providing their growth substrates (Zehnder, 1988). Fermentation of the various compounds leads to the production of methanogenic substrates (Zehnder, 1988). Methanogenic bacteria use the following as substrates: H_2 and CO_2, formate, acetate, methanol, and methylated acids (Zehnder, 1988). From these substrates two independent pathways are generally associated: the reduction of CO_2 with electrons from H_2 or fermentation of acetate to methane and CO_2. The following are the equations for these processes:

$$\text{Acetate} \rightarrow \text{Methane} + CO_2$$

$$CO_2 + 4\,H_2 \rightarrow \text{Methane} + 2\,H_2O$$

A Michaelis-Menten type kinetic equation, which incorporates the threshold for H_2 use by methanogens, is used to determine the methanogenesis from H_2. The equation is:

$$\left(\frac{dMt_{CH4}}{dt}\right)_{production} = k_{methane} X_{hydrogentroph} * \left(\frac{(Cw_{H2} - H_2 threshold_{meth})(Cw_{CO_2})}{(K_{S(H2)meth} + (Cw_{H_2} - H_2 threshold_{meth})) * (K_{S(CO2)} + Cw_{CO_2})}\right)$$

Mt_{CH4}	total CH_4 produced via hydrogenotrophs (mg)
k_{meth}	maximum rate of CO_2 utilization (mg/mg of VSS/d)
$X_{hydrogenotroph}$	hydrogenotrophic methanogenic biomass (mg of VSS)
Cw_{H2}	aqueous hydrogen concentration (mg/L)

Cw_{CO2}	aqueous carbon dioxide concentration (mg/L)
$K_{s(H2)meth}$	half-velocity coefficient for H_2 use by hydrogenotrophic methanogens (mg/L)
$K_{S(CO2)}$	half-velocity coefficient for CO_2 use by hydrogentrophic methanogens (mg/L)
H_2 threshold$_{meth}$	threshold for H_2 use by hydrogentrophic methanogens (mg/L)

Reductive Dehalogenation

Reductive dehalogenation is the removal of one or more chlorine atoms and replacing them with hydrogen. In dehalogenation, the chlorinated hydrocarbon is used as an electron acceptor. The electron donor is another organic compound such as lactate, acetate, methanol, glucose (Bouwer, 1994) or hydrogen. In effect, microorganisms "breath" the chlorinated compound in the same way aerobic organisms use oxygen (McCarty, 1997). There are microbial populations that are capable of dehalogenation. Some of the known bacteria that are capable of accomplishing this are: *Dehalospirillum multivorans, Dehalobacter restrictus* (PER-K23), Strain TT4B, and Strain 195 (Bagely, 1998).

PCE and TCE are highly chlorinated VOC's, therefore the carbon atoms have relatively high oxidation states. This allows them to be microbially reduced relatively easily under anaerobic conditions via reductive dehalogenation. The rate of reductive dehalogenation generally decreases as the degree of chlorination of the aliphatic hydrocarbon decreases. PCE is dehalogenated to TCE. Dehalogenation of TCE produces DCE. Several studies have shown that of the three possible isomers of DCE that cis-1,2-DCE predominates over trans-1,2-DCE and that 1,1-DCE is the least

significant intermediate (Bouwer, 1994). DCE is then reduced to vinyl chloride (VC), which can be reduced to ethylene and ethane. Ethylene and ethane are desirable non-toxic end products. However, DCE and VC are problematic daughter products. VC in particular is a known carcinogen. Chapelle (1993) states that it could be difficult to achieve desirable end products in most subsurface environments because of the lack of sufficient natural organic matter to provide electron donors.

Dehalogenation has been shown in the laboratory to occur under iron-, nitrate-, and sulfate-reducing and methanogenic conditions (Bouwer 1994). However the rates of dehalogenation of highly chlorinated VOC's tend to be greater under the highly reducing conditions of methanogenesis than under less reducing conditions (McCarty and Semprini, 1994). The kinetics of dechlorination are of Michaelis-Menten form wherein the rate of dechlorination is described by the chloroethene concentration as well as by the H_2 (electron donor) concentration (Fennell and Gosset, 1998). The equations used to describe dechlorination are exemplified by the equation for PCE:

$$\left(\frac{dMw_{PCE}}{dt}\right) = \frac{-k_{PCE}X_{dechlor}Cw_{PCE}}{K_{S(PCE)} + Cw_{PCE}} x \frac{(Cw_{H2} - H_2threshold_{dechlor})}{K_{S(H2)dechlor} + (Cw_{H2} - H_2threshold_{dechlor})}$$

Mw_{PCE}	total amount of PCE in the aqueous phase (mg)
k_{PCE}	maximum specific rate of PCE utilization (mg/mg of VSS/d)
$X_{dechlor}$	dechlorinator biomass (mg of VSS)
Cw_{PCE}	aqueous PCE concentration (mg/L)
$K_{S(PCE)}$	half-velocity coefficient for PCE use (mg/L)
Cw_{H2}	aqueous H_2 concentration (mg/L)
$K_{S(H2)dechlor}$	half –velocity coefficient for H_2 use by dechlorinators (mg/L)
$H_2\,threshold_{dechlor}$	threshold for H_2 use by dechlorinators (mg/L)

Other Models

Capt. Colby Hoefar developed a fundamental model of the degradation processes in constructed wetlands in his thesis entitled "Modeling Chlorinated Ethene Removal in Constructed Wetlands: A System Dynamics Approach." This thesis provides a fundamental model, which can eventually be used by remediation managers to predict the performance of a constructed wetland in removing PCE, and help them to develop a fundamental understanding of a wetland system and the mechanisms involved (Hoefar, 2000). The model succeeds in encapsulating the sequential degradation of PCE via microbial processes, while establishing the appropriate level of detail required for his study to model contaminant fate and transport within a wetland system. Capt. Hoefar's model closely portrays the structure of a natural system. The model is lacking detail of the interactions of microbes and the specific conditions in which they thrive (Hoefar, 2000). It may be important to further define the anaerobic methanogenic zone by adding hydrogen dependence and competition between the methanogens and halorespirers as evidence in the literature suggests (Yang and McCarty, 1998).

Wiedemeier et al. (1996) provides an overview of some of the many analytical and numeric fate and transport models that are currently available for evaluating contaminant transport and degradation. Most of these models were developed for fuel hydrocarbons. All but a few use first-order decay as the kinetic model for contaminant degradation. Some models have zero- or multiple- order options. RT3D, which includes a kinetics package for reductive dechlorination, BIOPLUME III, and UTCHEM incorporate more elaborate biodegradation schemes including Monod kinetics (Fennell and Gossett, 1998). One model includes kinetics for both chloroethene and electron

donor degradation, equations for the conversion of an applied donor to it end products, and competitive inhibition between PCE and TCE (Fennell and Gossett, 1998). These models, however, do not take into account the complex interactions that are present in a constructed wetland.

III. Methodology

The design of constructed wetlands for the removal of highly chlorinated compounds such as PCE or TCE is on the cutting edge of remediation technology. The methanogenic zone of the constructed wetland is made up of biodegradation processes that are very complex and involve countless interactions. A mechanistic model in conjunction with systems thinking allows the system behavior to be assessed over time. System dynamics captures feed back loops, multiple interactions, time sensitive behavior, non-linear interactions, and changes in the system over time associated with extremely complex systems like the methanogenic zone of a constructed wetland.

System dynamics reproduces system behavior mechanistically by identifying and simulating the underlying fundamental process driving basic system behavior in contrast to other modeling approaches, such as empirically based modeling, which ignore the underlying processes (Moorehead et al., 1996). Additionally, system dynamics facilitates the study of internal interactions of complex systems through the use of simulations. Simulations also allow for exploring the system beyond the range of observed system behavior and for providing insight into ramifications of various parameters on the dynamic system.

The methodology of this study will follow systems thinking and the modeling process. There are four distinct phases of the system dynamics modeling process. They are conceptualization, formulation, testing, and implementation. The system dynamics process is an iterative one. As a result, the processes may have to be repeated or reformulated in order to provide a true mechanistic representation of the biodegradation process within the methanogenic zone of a wetland.

Conceptualization

A model was developed by Captain Colby Hoefar in his thesis "Modeling Chlorinated Ethene Removal in Constructed Wetlands: A System Dynamics Approach". This model is based on a pilot concept that has been built by the Air Force Institute of Technology, Wright-Patterson AFB, OH. This model is a further development of the methanogenic zone of Capt. Hoefar's model. The methanogenic zone will be made of endemic wetland soil, rich in organic content. The organic content of wetland soil has been determined to be approximately 62%. The zone will be considered anaerobic. This is because the groundwater entering the zone will be depleted of oxygen and the zone will be completely saturated. The methanogenic conditions provide the necessary environment for the dechlorinating bacteria to be the primary reductive force within the methanogenic zone. This zone will be approximately eighteen inches deep. The expansion of the methanogenic zone will have the competition between the dechlorinating bacteria and the methanogens for hydrogen.

The reference mode represents the hypothetical behavior of the system based on a vague mental notion of the influences within the system. It should also be focused on the research question. As stated in Chapter 1, the primary research question is to look at the processes within the methanogenic zone and determine influences that affect the dechlorination process. The reference mode is a hypothetical outcome of the system that is based on the interactions among the mechanisms of the system. The perceived behavior of the reference mode is qualitative. This is because the outcomes from each of the mechanisms give a constant output; while on the other hand, the interactions between the mechanisms and their effects on the behavior of the system are not known. The

reference mode for this model is based on the known concentration of contaminant entering an uncontaminated wetland, becoming well mixed, and undergoing microbial degradation over time. It is the perceived behavior resulting from the interactions of the microbial processes, fermentation, methanogenesis, dechlorination, and transport.

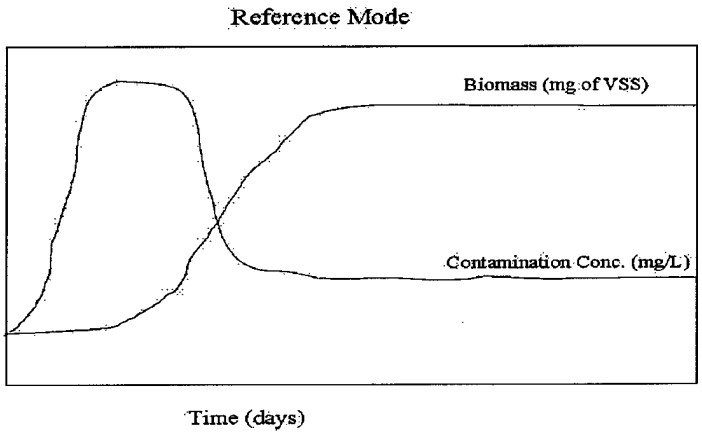


Figure 2. Reference Mode. Hypothetical behavior of system based on a qualitative mental notion of the influences within the system.

The reference mode shows that the concentration of the contaminant will start to build up in the methanogenic zone until the biomass starts to grow. The concentrations of the contaminant will then start to decrease and the rate of biomass growth will slow until the system reaches steady state. This is the basic reference mode for anything that is to be degraded by microorganisms.

The conceptualization of this model is based on the assumption that the system behavior of the methanogenic zone can be adequately described by the classical formulations of representative microbial reactions acting simultaneously in response to substrate limitation.

Formulation

The tool used to implement the model was the software package, STELLA 5.1.1, from High Performance Systems. The building blocks of the model are stocks or accumulations and flows or rates of movement to and from a stock. Knowledge of the processes that are occurring in the methanogenic zone is necessary in order to develop the model from the conceptual design. This model has been built using a mass balance approach.

The model has been developed so that it represents the processes that are occurring in two dimensions, based on a vertical cross-section of the methanogenic zone. The wetland physical parameters generally remain constant. The model is broken up into three simultaneous processes: dechlorination, methanogenic, and fermentation. The methanogenic zone is approximately 18" deep and is the deepest zone in the constructed wetland. As a result it will be the zone to come into contact with the contaminated groundwater.

The primary processes in the methanogenic zone are advection, fermentation, methanogenesis, and degradation. The goal of this project is to find optimal conditions for chloroethene degradation within the methanogenic zone of the constructed wetland. This will involve parameter variation and significance testing, as well as many other simulation tests. The results of these tests will be presented in the next chapter.

Methanogenic Zone Physical Parameters

Since this model is a more detailed part of Capt. Hoefar's model, the physical parameters have been taken from his model and modified to meet the needs of this work. The following table is a list of parameters and their initial values.

Table 3. Physical parameters and their initial values

PARAMETERS	INITIAL VALUES
Length	42.672 meters (60 feet)
Width	18.288 meters (30 feet)
Depth	.4572 meters (18 inches)
Sediment Porosity	.5

Fermentation

The model describing the fermentation process that degrades the H_2 donors uses Michaelis-Menten kinetics. The following equation is used in the model:

$$\frac{dMt_{donor}}{dt} = \frac{-k_{donor}X_{donor}Cw_{donor}}{Ks_{(donor)} + Cw_{donor}}$$

dMt_{donor} total amount of donor (mg)

k_{donor} maximum specific rate of donor degradation (mg/mg of VSS/d)

X_{donor} donor-fermenting biomass (mg of VSS)

$K_{S(donor)}$ half-velocity coefficient for the donor (mg/L)

Cw_{donor} donor concentration (mg/L)

The following chemical equations are the fermentation reactions that are used in the model:

$Butyrate^- + H_2O \rightarrow 2acetate^- + H^+ + 2H_2$

$Ethanol + H_2O \rightarrow acetate^- + H^+ + 2H_2$

$Lactate^- + 2H_2O \rightarrow acetate^- + HCO_3^- + H^+ + 2H_2$

$Propionate^- + 3H_2O \rightarrow acetate^- + HCO_3^- + H^+ + 3H_2$

$Ethanol + 2/3\ HCO_3^- \rightarrow 2/3\ propionate^- + 1/3\ acetate^- + 1/3\ H^+ + H_2O$

$3Lactate^- \rightarrow 2propionate + acetate + CO_2 + H_2O$

The following table is a list of parameters, initial values, and a reasonable range of values for the fermentation reactions.

Table 4. Fermentation parameters, their initial values, and reasonable values

PARAMETERS	BASELINE VALUE	REASONABLE RANGE OF VALUES	REFERENCE
k acetate	8 mg acetate/mg of VSS/d	3-8 mg acetate/mg of VSS/d	1,2
Ks acetate	59 mg acetate/L	25-59 mg acetate/L	1,2
k butyrate	10.243 mg butyrate/mg of VSS/d		1
Ks butyrate	2.89754 mg butyrate/L		1
k ethanol 1	24.302 mg ethanol/mg of VSS/d	0.5-25 mg ethanol/mg of VSS/d	1,2
Ks ethanol 1	.7837 mg ethanol/L	0.5 - 4 mg ethanol/L	1,2
k ethanol 2	24.302 mg ethanol/mg of VSS/d	0.5-25 mg ethanol/mg of VSS/d	1,2
Ks ethanol 2	.7837 mg ethanol/L	0.5 - 4 mg ethanol/L	1,2
k lactate 1	18.5966 mg lactate/mg of VSS/d		1
Ks lactate 1	.22525 mg lactate/L		1
k lactate 2	18.5966 mg lactate/mg of VSS/d		1
Ks lactate 2	.22525 mg lactate/L		1
k propionate	3.9125 mg propionate/mg of VSS/d	2-4 mg propionate/mg of VSS/d	1,2
Ks propionate	.83733 mg propionate/L	.8-18 mg propionate/L	1,2
1. Fennell and Gossett, 1998 2. Bagley, 1998			

Kinetic Model for Dechlorination

The kinetics equation for dechlorination used in the model can be found in Chapter 2. The kinetics are of Michaelis-Menten form. The rate of dechlorination is described not only by the chloroethene concentration but also by the H_2 concentration. The chemical equations used in the model are as follows:

$PCE + H_2 \rightarrow TCE + H^+ + Cl^-$

$TCE + H_2 \rightarrow$ cis-DCE $+ H^+ + Cl^-$

Cis-DCE + H_2 → VC + H^+ + Cl^-

VC + H_2 → Ethene + H^+ + Cl^-

The following table is a list of the parameters for the dechlorination equations and their initial values and a reasonable range of values.

Table 5. Dechlorination Parameters initial values and reasonable range of values

PARAMETERS	BASELINE VALUE	REASONABLE RANGE OF VALUES	REFERENCE
k PCE	7.164 mg PCE/mg of VSS/d	0.39-7.164 mg PCE/mg of VSS(day)	1,4
Ks PCE	.0896 mg PCE/L	.00995-.0896 mg/L	1,4
Ks(H2) PCE	1.8E-5 mg H_2 /L	1.8E-5 – 2E-4 mg H_2/L	2,1
Initial PCE biomass	10 mg of VSS		
k TCE	9.4608 mg TCE/mg of VSS/d	1.01-9.4608 mg TCE/ mg of VSS/d	1,4
Ks TCE	.07096 mg TCE/L	.07096 - .184 mg TCE/L	1,4
Ks(H2) TCE	2.8E-5 mg H_2/L	2.8E-5 - 2E-4 mg H_2/L	2,1
Initial TCE biomass	10 mg of VSS		
k DCE	6.9768 mg DCE/mg of VSS/d	.55-6.9768 mg DCE/mg of VSS/d	1,4
Ks DCE	.05233 mg DCE/L	.05233 - .3298 mg DCE/L	1,4
Ks(H2) DCE	4.2E-5 mg H_2/L	4.2E-5 - 2E-4 mg H_2/L	2,1
Initial DCE biomass	10 mg of VSS		
k VC	4.5 mg VC/mg of VSS/d	.2955-4.5 mg VC/mg of VSS/d	1,4
Ks VC	18.125 mg VC/L	.169-25 mg VC/L	1,4
Ks(H2) VC	3.4E-5 mg H_2/L	3.4E-5 - 2E-4 mg H_2/L	2,1
Initial VC biomass	10 mg of VSS		
H_2 Threshold - Dechlorination	4E-6 mg H_2/L		3
1. Fennell and Gossett, 1998 2. Ballapragada et al., 1997 3. Smatlak et al., 1996 4. Bagley, 1998			

Kinetics of Methanogenesis

The methanogenesis from H_2 and from acetate is also modeled using the Michaelis-Menten equation. The equation that was used in the model for hydrogentrophic methanogenesis can be found in Chapter 2. The chemical equations for methanogenesis are also found in Chapter 2. The rate for hydrogentrophic methanogenesis is described not only by the H_2 concentration, but also by the carbon dioxide (CO_2) concentration. The follow is a list of parameters for the methanogenic equations, initial values and a reasonable range of values.

Table 6. Hydrogentrophic Methanogenesis Parameters initial values and reasonable range of values

PARAMETERS	INITIAL VALUE	REASONABLE RANGE OF VALUES	REFERENCE
k methane	10.56 mg CO_2/mg of VSS/d	1.8 - 10.56 mg CO_2/mg of VSS/d	1,3
Ks(H2) Methane	1E-3 mg H_2/L	1E-3 – 1.92E-3 mg H_2/L	1,3
Ks CO_2	.25 mg CO_2/L		
Initial hydrogenotrophic biomass	1000 mg of VSS		
H_2 threshold - Methanogenesis	2.2E-5 mg H_2/L		2
1. Fennell and Gossett, 1998 2. Smatlak et al., 1996 3. Bagley, 1998			

Biomass Growth

In the model, biomass growth was modeled separately for each distinct group of organisms. The equation that was used is:

$$\frac{dX}{dt} = Y\left(\frac{-dMt}{dt}\right) - k_d X$$

dMt/dt	change in substrate of interest over time (mg/day)
Y	organism yield rate (mg of VSS/mg of substrate used)
X	biomass of the specific organism group (mg of VSS)

k_d death rate coefficient for the organism group (d^{-1})

The death rate coefficient, $k_d = .024\ d^{-1}$ (Fennell and Gossett, 1998), was assumed for all microbial groups. The death rate coefficient has also been modified so that it takes into account a maximum population for the biomass. In order to do this, a k_d factor is set so that it is variable based on biomass population/mass of soil. The equation for k_d is:

$$k_d = Bsline\_k_d + (k_d\_factor * (X * k))$$

k maximum specific rate of degradation (mg/mg of VSS/d)

The k_d_factor is taken from a graph that has the k_d_factor on the y-axis and the biomass population/mass of soil on the x-axis. This equation does not allow the biomass population to grow out of control.

The following table is a list of parameters for biomass growth, their initial values, and a reasonable range for their values.

Table 7. Biomass parameter initial values and reasonable ranges

PARAMETERS	INITIAL VALUE	REASONABLE RANGE OF VALUES	REFERENCE
PCE biomass yield	.0163 mg of VSS/mg of PCE	.01-.1 mg of VSS/mg of PCE	1
TCE biomass yield	.0205 mg of VSS/mg of TCE	.01-.1 mg of VSS/mg of TCE	1
DCE biomass yield	.0278 mg of VSS/mg of DCE	.01-.1 mg of VSS/mg of DCE	1
VC biomass yield	.0435 mg of VSS/mg of VC	.01-.1 mg of VSS/mg of VC	1
Hydrogentrophic Methanogenesis biomass yield	.715 mg of VSS/mg of H2 used	.1-1 mg of VSS/mg of H2 used	2
Acetate Methanogenesis biomass yield	.032 mg of VSS/mg of acetate	.01-.1 mg of VSS/mg of acetate	2
Butyrate biomass yield	.032 mg of VSS/mg of butyrate	.01-.1 mg of VSS/mg of butyrate	2
Ethanol 1 biomass yield	.043 mg of VSS/ mg of ethanol	.01-.1 mg of VSS/ mg of ethanol	2
Ethanol 2 biomass yield	.0644 mg of VSS/mg of ethanol	.01-.1 mg of VSS/mg of ethanol	2
Lactate 1 biomass yield	.039 mg o9f VSS/mg of lactate	.01-.1 mg o9f VSS/mg of lactate	2
Lactate 2 biomass yield	.062 mg of VSS/mg of lactate	.01-.1 mg of VSS/mg of lactate	2

Propionate biomass yield	.019 mg of VSS/mg of propionate	.01-.1 mg of VSS/mg of propionate	2
Bsln_k_d	.024/day	.001-.1/day	2
1. Bagley, 1998 2. Fennell and Gossett, 1998			

Equations used in forming the Model

The equations used to describe dechlorination are illustrated by the equation for PCE:

$$\left(\frac{dMw_{PCE}}{dt}\right) = \frac{-k_{PCE}X_{dechlor}Cw_{PCE}}{Ks_{(PCE)} + Cw_{PCE}} x \frac{(Cw_{H2} - H_2threshold_{dechlor})}{Ks_{(H2)dechlor} + (Cw_{H2} - H_2threshold_{dechlor})}$$

The following is the equation for hydrogentrophic methanogenesis:

$$\left(\frac{dMt_{CH4}}{dt}\right)_{production} = k_{methane}X_{hydrogentroph} * \left(\frac{(Cw_{H2} - H_2threshold_{meth})(Cw_{CO_2})}{(Ks_{(H2)meth} + (Cw_{H_2} - H_2threshold_{meth})) * (Ks_{(CO2)} + Cw_{CO_2})}\right)$$

The following equation is used for the fermentaion processes:

$$\frac{dMt_{donor}}{dt} = \frac{-k_{donor}X_{donor}Cw_{donor}}{Ks_{(donor)} + Cw_{donor}}$$

The following equation is used for biomass growth:

$$\frac{dX}{dt} = Y\left(\frac{-dMt}{dt}\right) - k_dX$$

The dMt/dt is the rate at which the existing microorganism population is degrading its specific substrate and uses the equation above for dechlorination, hydrogentrophic methanogenesis, and fermentation.

The following equation is used for the death rate k_d:

$$k_d = Bsline\_k_d + (k_d\_factor * (X * k))$$

Testing

Testing the Dynamic Hypothesis

Initial simulation tests will be run to determine whether the basic mechanism and interactions are sufficient and produce the appropriate behavior, reflecting the reference mode. If the behavior does not follow the reference mode, a review of the mechanisms and their interactions with each other is required to determine if those relationships are accurately represented. If the interactions among the mechanisms are reasonable and accurate, then the reference mode may need to be adjusted to reflect the appropriate behavior. The process of testing the model does not prove correctness, it merely creates confidence in the model. All parameters will be tested.

Structure Verification Test

This test compares the structure of the model directly with the structure of the real system that the model represents. Structure verification is made through people highly knowledgeable in the field of the system or through comparison of the model to systems found in the literature. To pass this test there must be no contradictions with the structure of the model to the real world system. However, levels of detail may be omitted providing the model sufficiently represents the real system.

Parameter Verification Test

The parameter verification test compares the model parameters to knowledge of the real system to determine if parameters correspond conceptually and numerically to real life. Behavioral tests can be run to help determine the validity of parameter values

by recognizing unreasonable behavior for the system when the model uses certain parameter values.

Extreme Condition Tests

Extreme conditions should be simulated to verify that behavior will remain reasonable in accordance with the extreme conditions. Much of the knowledge about real systems relates to the consequences of extreme conditions. If this knowledge is incorporated, the result is usually an improved model in the normal operating region. This test is used mostly on rate equations within the model. This is done by inducing an extreme condition to produce a predictable response, such as setting the utilization rate for PCE to zero; the output should be that no TCE is produced.

Behavior Reproduction Test

This test is used to determine how well the behavior of the model matches the hypothesized behavior of the real system. Creating the same behavior patterns is the goal of the test; so reproducing the exact numbers is not desired. Comparing the time sequence of relative variables of the hypothesized natural system to that of the model is of particular importance. The model should follow the same hypothesized timing sequence of the real system. The pattern of behavior should not be driven by inputs from outside the model boundary. Inputs from outside the system boundary should be like the concentration of the contaminant coming into the system. Changing the concentration of the contaminant coming in should not affect the pattern of the behavior.

Sensitivity Testing

This type of testing evaluates the sensitivity of model output to changing parameter values. This may offer insight into the processes or mechanisms that are the most sensitive to perturbations or changes to the model. The changing of the parameter values allows the associated behavior to be analyzed to determine the impact of those parameters on the behavior of the system.

Simulations

The following is a list of the tests that were run.

Verification Tests

This simulation is to verify that the hydrogen threshold for the methanogens and dechlorinators is working. The methanogens and the dechlorinators have a threshold that the hydrogen must reach in order for them to be able to use the hydrogen. In order to make sure that the model is running appropriately for the threshold, tests must be run at hydrogen concentrations below the dechlorinator threshold, above the dechlorinator threshold but below the methanogenic threshold, and above the methanogenic threshold. Three simulations will be run. In order to run the test the hydrogen concentration will be held constant at the desired test level. The dechlorinator threshold is 4 E-6 mg/L and the methanogenic threshold is 2.2 E-5 mg/L.

Validation Tests

Simulations need to be run to see how the model runs at extreme concentration of contaminants and if the behavior of the system at extreme conditions is logical. Two

simulations will be run with extreme values of 0 mg/L and 1000 mg/L of PCE entering the system.

The model needs to be tested to see if it can produce the behavior of the real system. The model will be run with its initial values.

The Ks values, k values death rates, and growth rates for all the microorganisms are values that affect the rates of degradation, methanogenesis, or fermentation. Tests need to be run with imaginary maximum and minimum values in order to determine how these parameters will affect the system and to see if the results are logical.

Sensitivity Analysis Tests

Since there is a wide range of values on the literature for the Ks(H2) values for PCE, TCE, DCE, and VC, simulations need to be run to determine how sensitive the system is to the changing of the Ks(H2) values. The values range from (μmol/L): PCE Ks(H2): 0.009-0.1; TCE Ks(H2): 0.014-0.1; DCE Ks(H2): 0.021-0.1; and VC Ks(H2): 0.017-0.1. Run one test with the upper values for each Ks(H2). Run one test with the values of .05 μmol/L for each Ks(H2) value and then run one test for the low values of the Ks(H2).

There is uncertainty in the amount of biomass that is initially in the system. By changing the initial value of the biomasses, it can be determined how much effect the initial value of the biomass will have on the system. There are twelve different biomasses. Five simulations will be run with each biomass while all the other initial biomasses will remain constant.

There is uncertainty in the values for the utilization rates of the chlorinated solvents. Running the simulations with varying utilization rates will show how sensitive

the system is to the utilization rate. The tests will be run by changing the utilization rate for each chlorinated solvent while holding the others constant. One simulation will be run at the bottom of the range, one in the middle and one at the high end of the range.

There is uncertainty in the utilization rate for hydrogentrophic methanogens. Running simulations with varying simulation rates can show how sensitive the system is to the hydrogentrophic methanogenic utilization rate. The simulations will be run by changing the utilization rate for the hydrogentrophic methanogens, while keeping all other variables constant. One simulation will be run at the bottom of the range, one in the middle, and one at the high end of the range.

There is uncertainty in the Ks values for PCE, TCE, DCE, VC, and hydrogentrophic methanogens. Simulations are needed to determine how much the Ks values for these chlorinated solvents will effect the system. Vary the Ks values for PCE, TCE, DCE, VC or hydrogentrophic methanogens and keep all the other Ks values constants. Three tests will be run for PCE, TCE, DCE, and hydrogentrophic methanogens. Five tests will be run with VC since the Ks values have a much broader range (2.7-400 μmol/L (Bagley, 1998)).

There is no certain death rate constant for the biomasses that are in the model. Simulations need to be run to determine sensitive the system is to the death rate constant. Run ten simulations with death rates between the ranges of: .001-.1.

There is uncertainty in the biomass yield rates for the biomasses in the model. The sensitivity of the model to changes in the biomass yield rates needs to be examined. Four simulations will be run for each biomass yield rate with differing numbers.

There is uncertainty in the Ks values for the organic compounds. Simulations need to run to determine how sensitive the system is to these values. The Ks values will be change for one organic acid and the rest will be held constant. Four simulations will be run for each organic acid.

There is uncertainty in the utilization rate values for the organic acids. Simulations need to run to determine how sensitive the system is to these values. The utilization rate values will be change for one organic acid and the rest will be held constant. 4 simulations will be run for each organic acid.

Implementation

The results from the simulations will be presented and discussed in the following chapter. Testing and verification procedures build confidence in the model and in the system dynamics approach. The model can be used to explore design criteria and operation parameters, which optimize the degradation of the contaminant once confidence in the model is achieved. Sensitivity analysis is used to determine specific parameters that have the most impact on the system. With this information, the model can be used as a management tool to assess various scenarios and optimize treatment conditions. The following tests were run as implementation of the system.

Implementation Tests

The amount of contaminant that comes into the system can change. By running these simulations we can see the effect of the incoming concentration of contaminant has on the system. We can possibly use it to try and optimize the system. The model will be tested by reducing the initial incoming concentration by 50% and then incrementally increasing it by 10% to 150% of the initial concentration.

The retention time of water in the constructed wetlands can be varied. The "desired" retention time for the water through the entire constructed wetland system is 5 to 15 days. The groundwater, however can have a retention time range between 1 to 25 days or larger. By varying the flow rates we can tell what kind of effects that retention times has on the system and the amount of contaminants that are degraded. Flow rates will be determined and simulated starting at 1 day retention time (through the entire system) and increased in 1 day increments to 25 days. The flow rate for the entire system will be divided by 1/3 to get the retention time for the methanogenic zone.

There is uncertainty in the concentration of organic compounds that will be generated. Running simulations, with varying concentrations of concentrations of organic compounds (butyrate, ethanol, lactate, and proionate) entering the system, will show how much of an effect the organic compound concentration will have on the amount of contaminant that is degraded. The amount of organic compounds that are fermented will affect the hydrogen concentration. The tests will be run be changing the inflow concentration of one of the organic compounds, while keep the others constant. The values will be in the range of 0.1 to 100 mg/L.

IV. Results and Discussion

The results of the testing and validation procedures, as described in Chapter 3, are evaluated here to provide confidence in the model and in the system dynamics modeling process. The behavior of the methanogenic zone as a whole and in part, will be discussed to provide a better understanding of the dynamic nature of contaminant removal within the methanogenic zone of a constructed wetland. This chapter will also serve to answer the research questions for which this study was intended.

As discussed in Chapter 3, the reference mode introduced the hypothetical behavior of the methanogenic zone system over a time horizon. Developing the framework required several iterations to ensure the resulting framework was essential and represented the actual structure of the methanogenic zone in a constructed wetland. The behavior of the system was the same as the reference mode.

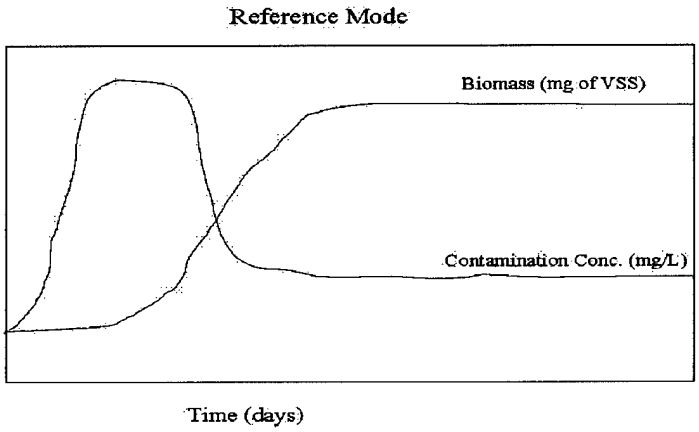


Figure 3. Reference Mode.

The reference mode was based on the perception that as the contaminant enters the methanogenic zone, microorganisms will reductively dehalogenate the contaminant. Figure 3 indicates that the contaminant concentration increases at a very high rate because there is initially a small population of microorganisms. The contaminant continues to climb in the zone until the microorganisms reach a population in which it is able to degrade the contaminant faster than the incoming concentration. This results in a decline in the contaminant concentration in the zone until the population and contaminant concentration reach a steady-state value. Figure 4 shows output from the model that verifies that the model structure qualitatively matches the reference mode behavior.

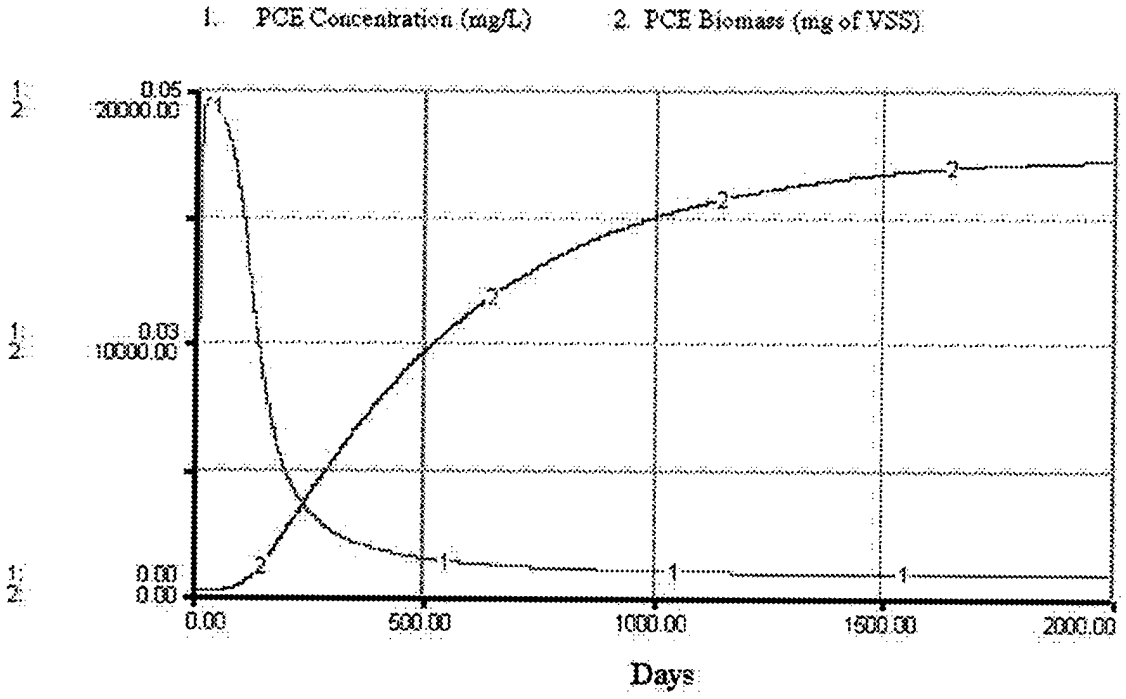


Figure 4. Simulated Reference Mode

It shows that the contaminant concentration increases very quickly due to a small initial population of microorganisms. Then as that microorganism population begins to increase, the contaminant concentration starts to decrease because the microorganisms are degrading more of the contaminant. The microorganism population continues to grow until a steady state is reached with the concentration of the contaminant.

Understanding the system and the interactions between the mechanisms in the system is the key to developing confidence in the model. Good structure and the appropriate level of detail help to build confidence in the model. The structure verification test compares the structure of the model to the structure of the system that the model represents. In this case it is the methanogenic zone of the constructed wetland. The model structure is presented in Appendix A. The structure of the model is built as discussed previously in Chapter 3. The model closely follows the information that is in the literature. There are many complex chemical and biological processes in the methanogenic zone of a constructed wetland. Therefore the model is broken up into three simultaneous processes: dechlorination, methanogenesis, and fermentation. Dechlorination and methanogenesis rely on fermentation to break down the complex organics and produce electron donors, like hydrogen, that they can use. This model assumes that the methanogenic zone is homogeneous and well mixed. These assumptions eliminate several orders of detail in the real system but are hypothesized to provide behavior consistent with the natural system. The development of the three simultaneous processes provide a sufficient level of detail for the model, yet remains general enough to gain understanding of the behavior of the methanogenic zone.

The model has a hydrogen threshold that must be reached before dechlorination and hydrogenotrophic methanogenesis can begin. In order to verify that the thresholds work, a test was run. The results show that at a concentration below the threshold levels of both dechlorination and hydrogenotrophic methanogenesis that neither reaction took place. At a hydrogen concentration level above the dechlorination threshold, but below the hydrogenotrophic methanogenesis threshold, there was dechlorination, but no methanogenesis. At a hydrogen concentration above both thresholds, both dechlorination and methanogenesis take place. This verifies that the threshold in the model is functioning.

The flow rate of the constructed wetland is a controllable variable. The flow rate is determined by how much retention time of the water. The flow rates used for the methanogenic zone were calculated, based on the retention time of the entire constructed wetland. Table 8 shows the retention time and flow rates that were used in the simulation.

Table 8 Retention Times and Flow Rates

RETENTION TIME (days)	FLOW RATES (gal/min)
1	98.08
3	32.69
5	19.62
7	14.01
10	9.81
13	7.54
17	5.77
22	4.46
25	3.92

These flow rates represent at range of retention time of 1-25 days with the retention time for a constructed wetland set usually between 5-15 days. These retention times were selected to give an overview of the behavior of the system as the flow rate was increased. Figure 5 shows the results of the simulation run with varying retention times in the system.

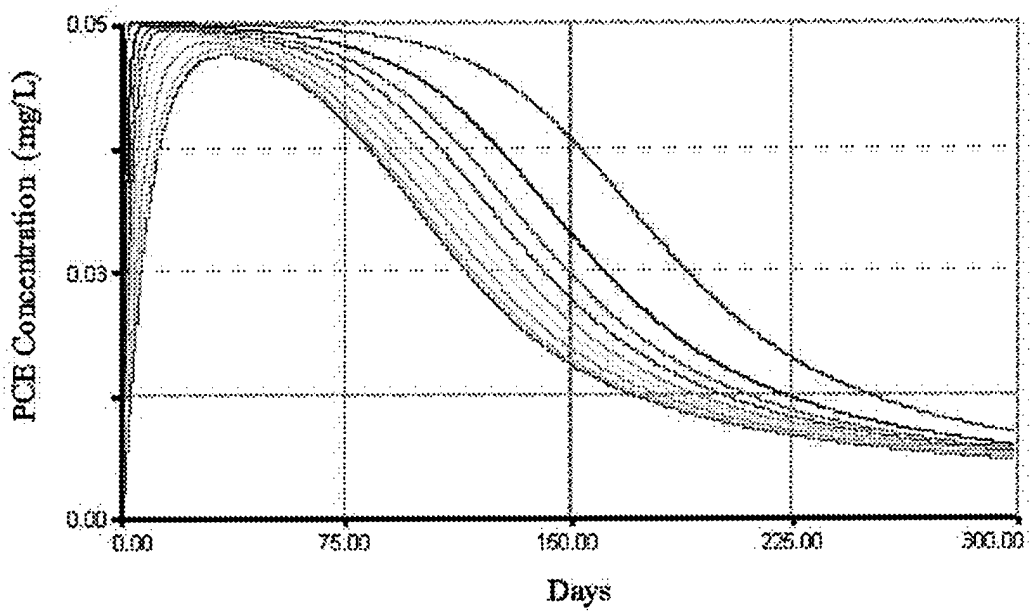


Figure 5. Effects of changes in the retention time on the degradation of PCE

The top curve represents a retention time of one day, and as you move down through the curves, the retention increases according to the values in Table 8. This graph shows the amount of PCE that is in the methanogenic zone. As the retention time of the water increases, the amount of PCE that is in the methanogenic zone decreases. This is because

the longer the water and contaminant are in the zone; the longer the microbes have to degrade the contaminant. The more contaminant that the microbes eat the more the microbe population grows. However, as the retention time in the system gets longer the less of an impact it has on the contaminant concentration in the methanogenic zone as the graph shows. A longer retention also allows for the contaminant to be more completely degraded. Figure 6 shows the TCE concentration in the system. The faster the PCE is degraded by the microbes the more TCE is produced so that the microbes that degrade TCE can start to degrade it and start to grow. The same principle applies for the DCE and VC with the final end product being ethene. The longer the retention time, the longer the contaminant is in the system for the microbes to degrade. The goal is to get the most efficient and complete degradation as possible.

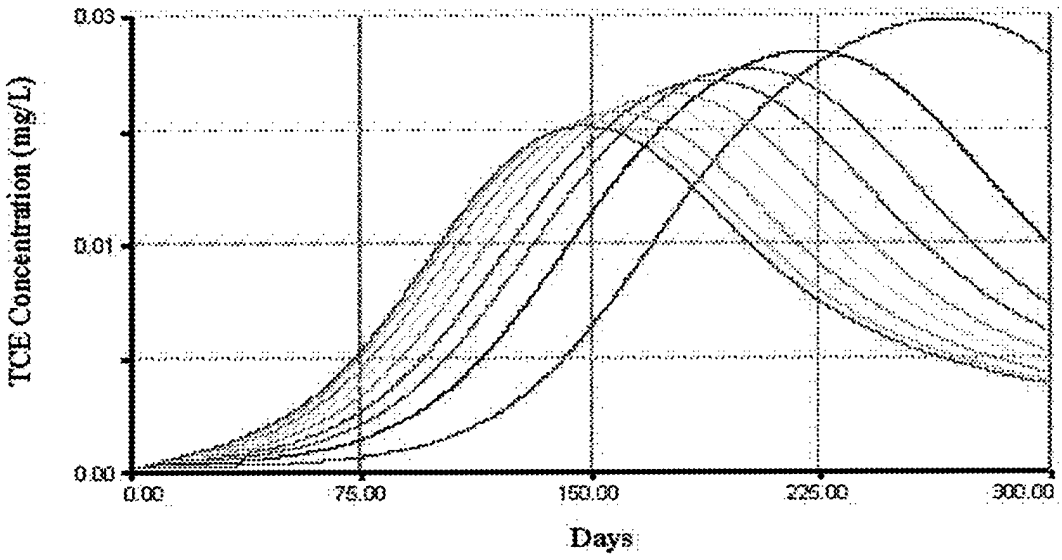


Figure 6. Effects of changes in the retention time on the degradation of TCE. The curve with the highest peak and furthest to the right is shortest retention time. The retention time increases as the curves move down and to the left.

The concentration of the incoming contaminant has an affect on the time to the steady state value that the system will reach. But steady state at 300 days is essentially the same for all concentrations. The Table 9 is a list of incoming contaminant concentrations that were used to produce Figure 7.

Table 9 Incoming Concentration of PCE

Incoming Concentrations of PCE (mg/L)	
1) .025	7) .055
2) .03	8) .06
3) .035	9) .065
4) .04	10) .07
5) .045	11) .075
6) .05	

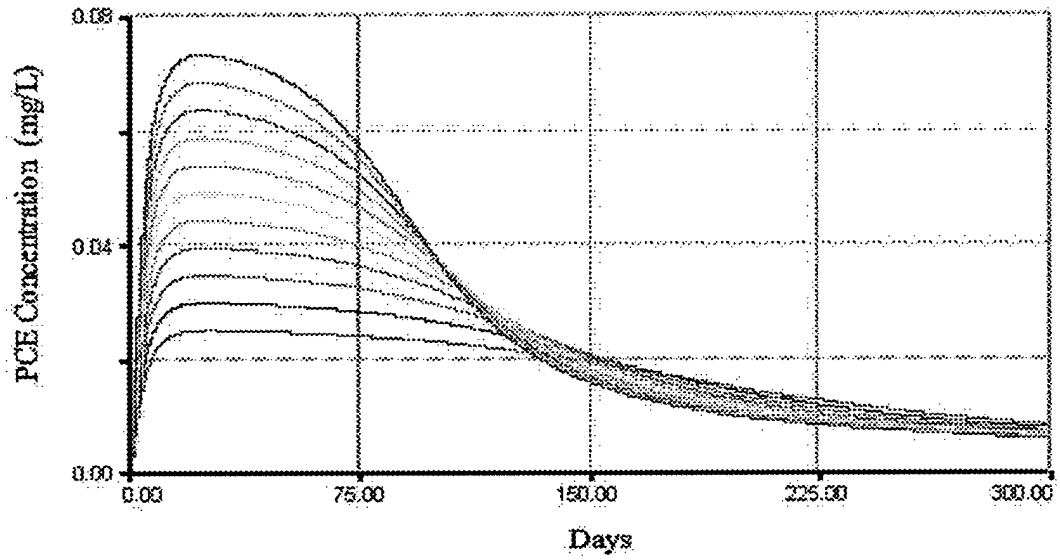


Figure 7. Effects of changing the incoming concentrations of PCE into the system. The curve with the highest peak has the highest incoming concentration of PCE. The concentration decreases as you move down the peaks of the curves.

The figure shows that as more PCE enters the methanogenic zone, the higher the initial rise in PCE in the system will be before it starts to decline. But when the contaminant concentration in the system starts to decline the curves begin to flip-flop. This is because the larger the concentration of contaminant, the more food the microbes have in order to grow. Therefore the microbe population grows and reduces the amount of contaminant in the system faster and to a greater extent. However, as Figure 8 shows, the system comes to the same steady state value, no matter what the incoming concentration. The concentrations that were used for this graph were 0.025, 0.035, 0.045, 0.055, 0.065, 0.075 mg/L of PCE coming into the methanogenic zone.

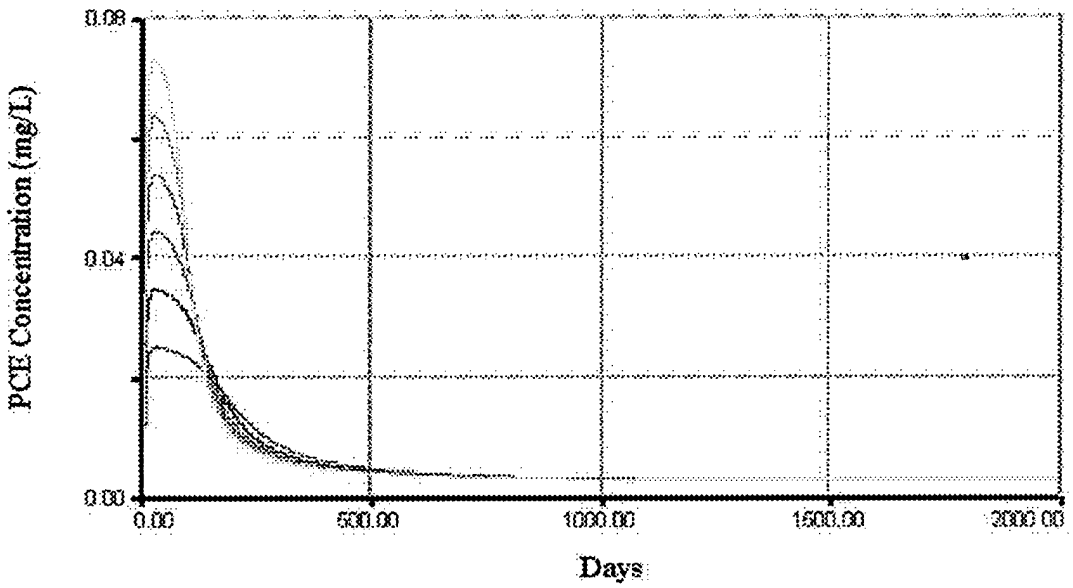


Figure 8. The effects of changing the incoming concentration of contaminant on the amount of contaminant at steady state. The curve with the highest peak has the highest incoming concentration of PCE. The concentration decreases as you move down the peaks of the curves.

The system reaches the same steady value no matter what the incoming concentration is because the biomass populations are increasing and degrading the increase in the contaminant. Figure 9 shows the PCE biomass for the same simulation in Figure 8. It shows that as the concentration of the contaminant increases, the PCE biomass also increases.

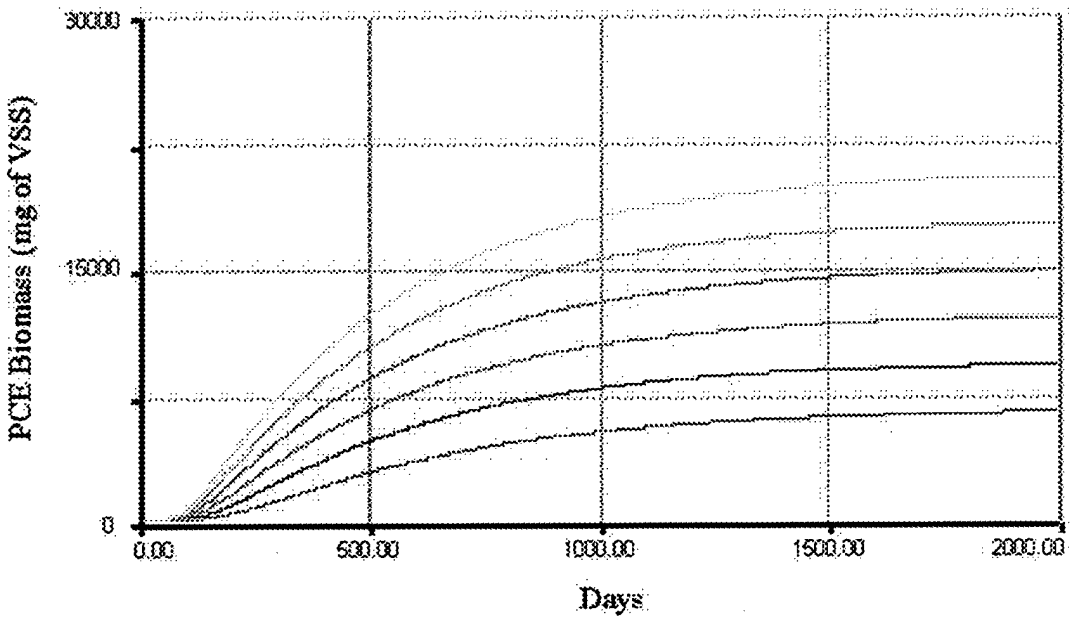


Figure 9. Effects of changing incoming concentrations on PCE biomass

The initial biomass of the dechlorinating microorganisms has a great effect on the amount of contaminant that will be in the system. The greater the initial biomass, the

smaller will be the peak of the concentration of the contaminant.

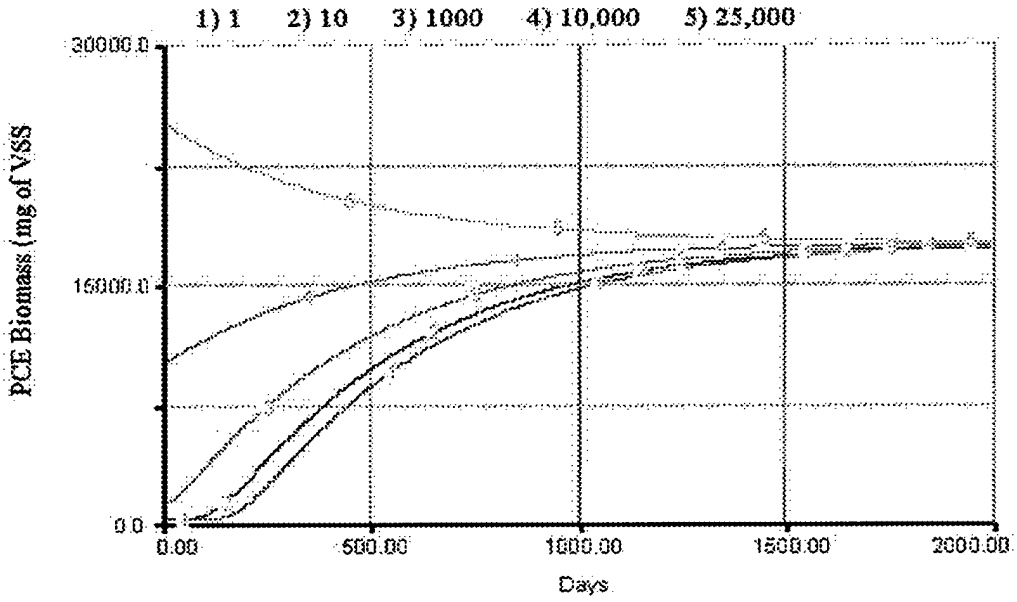


Figure 10. The effect of changing PCE initial biomass on PCE biomass.

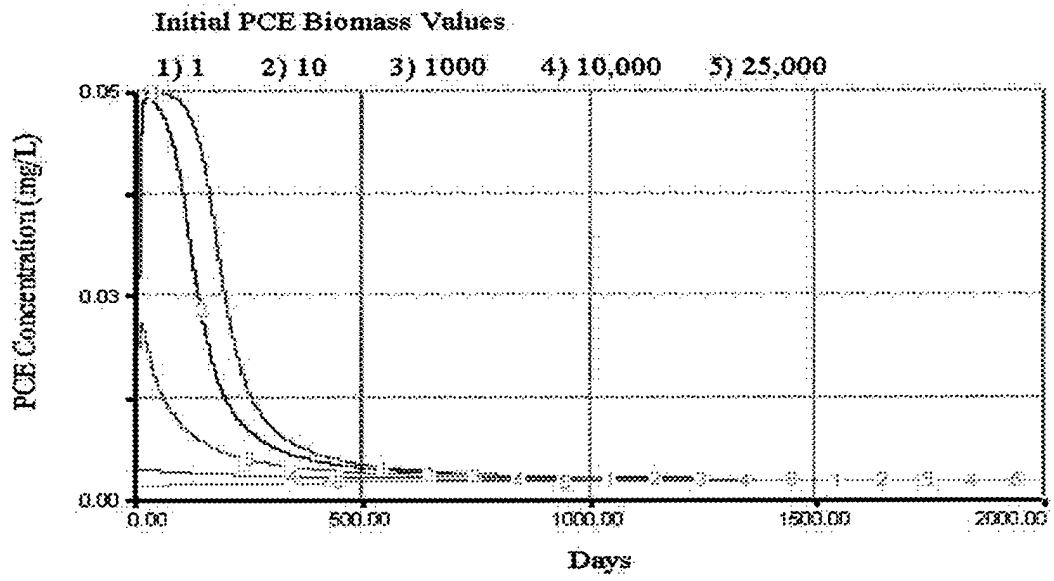


Figure 11. The effects of changing PCE initial biomass on the PCE concentration

Figure 10 shows the behavior of the PCE biomass as the initial PCE biomass is changed and Figure 11 shows how the concentration of PCE in the system is affected by the initial PCE biomass values. The steady state value for the concentration is the same, as is the biomass populations. The higher the initial population of PCE the more degradation takes place. This is because the larger biomasses degrade more PCE to TCE, and therefore, the TCE degrading population begins to grow sooner than with lower initial PCE biomass populations. Figure 12 shows the effect that the initial PCE biomass population has on the TCE biomass.

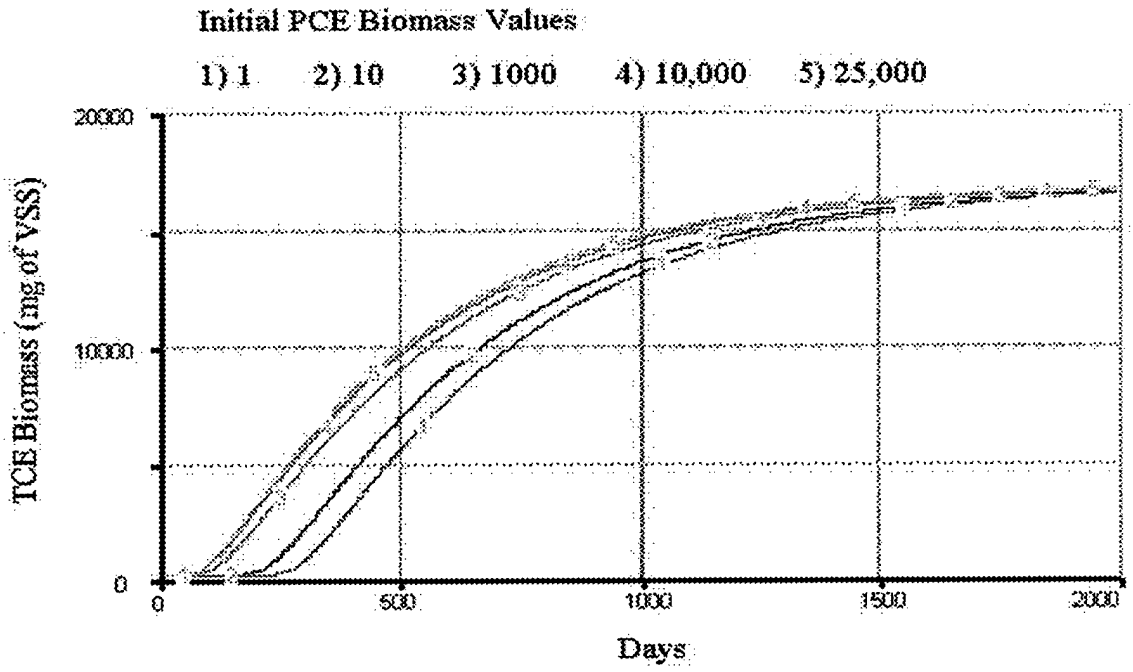


Figure 12. The effects of PCE initial biomass on TCE biomass

The rest of the degradation products follow the same pattern, just lagging behind. PCE degrades to TCE, TCE degrades to DCE, DCE degrades to VC, and VC degrades to ethene. The initial PCE biomass has a greater effect on degradation than changes to the

other chlorinated solvents biomass because it is at the top of the chain and affects everything after it. Changing the initial biomass populations of TCE, DCE, and VC just affect the concentration of the contaminant being degraded and contaminant below it in the degradation chain. Increasing all the initial populations will provide greater and more complete degradation of the contaminant initially. However, the system comes to approximately the same steady state values for the contaminants and the dechlorinating biomasses.

The hydrogenotrophic microorganisms and the fermenting microorganisms did not have an effect on the dechlorination of the contaminant. The simulations done with changing the initial biomasses of the hydrogenotrophic and fermenting microorganisms show that they had no effect on dechlorination. These graphs can be found in appendix ?.

Sensitivity tests were done with each of the parameters to determine what, if any, effect the parameters have on the model. For this model, the effect that the parameter has on dechlorination is what is being examined. Figure 13 is an example of a sensitivity analysis in which the degradation was sensitive to the changing parameter value. Figure 14 is an example of a sensitivity analysis in which contaminant degradation is not sensitive to the changing parameter value.

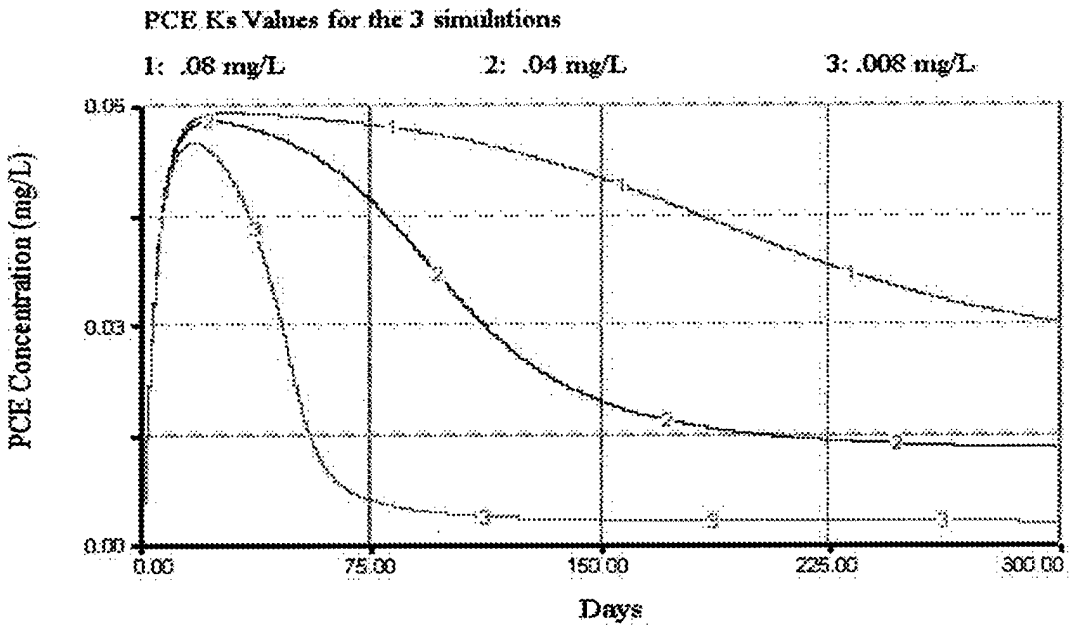


Figure 13. Example of a parameter that degradation of PCE is sensitive to.

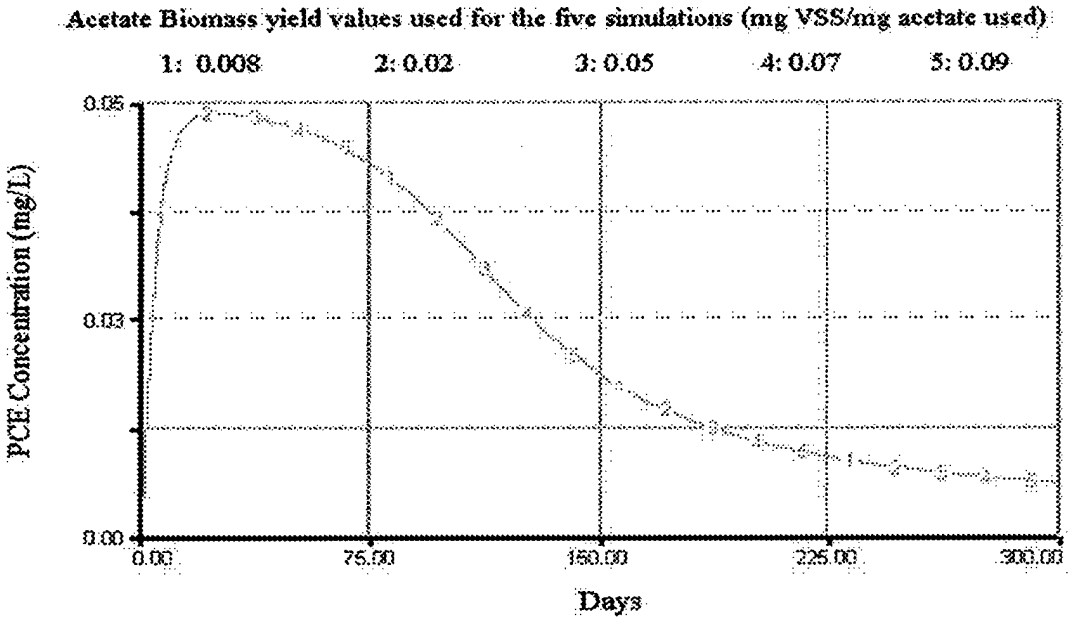


Figure 14. An example of a parameter that the contaminant degradation is not sensitive to

The following table is a summary of the parameters and how sensitive the model is to them.

Table 10 Sensitivity Analysis Summary for Dechlorination Parameters

PARAMETER	SENSITIVITY
k PCE	Sensitive
Ks PCE	Sensitive
Ks(H2) PCE	Not sensitive
Initial PCE Biomass	Sensitive
k TCE	Sensitive
Ks TCE	Sensitive
Ks(H2) TCE	Not sensitive
Initial TCE Biomass	Sensitive
k DCE	Sensitive
Ks DCE	Sensitive
Ks(H2) DCE	Not sensitive
Initial DCE Biomass	Sensitive
k VC	Sensitive
Ks VC	Sensitive
Ks(H2) VC	Not sensitive
Initial VC Biomass	Sensitive

The model was sensitive to most of the parameters for dechlorination. The parameters that did not affect dechlorination were the half–velocity coefficients for H_2 use by dechlorinators.

Table 11 Sensitivity Analysis Summary for Hydrogenotrophic Methanogenesis

PARAMETER	SENSITIVITY
k methane	Not sensitive
Ks(H2) Methane	Not sensitive
Ks CO_2	Not sensitive
Initial hydrogenotrophic biomass	Not sensitive

Table 12 Sensitivity Analysis Summary for Fermentation Parameters

PARAMETER	SENSITIVITY
k acetate	Not sensitive
Ks acetate	Not sensitive
Initial acetate biomass	Not sensitive
k butyrate	Not sensitive
Ks butyrate	Not sensitive
Initial butyrate biomass	Not sensitive
k ethanol	Not sensitive
Ks ethanol	Not sensitive
Initial ethanol biomass	Not sensitive
k lactate	Not sensitive
Ks lactate	Not sensitive
Initial lactate biomass	Not sensitive
k propionate	Not sensitive
Ks propionate	Not sensitive
Initial propionate biomass	Not sensitive

Table 13 Sensitivity Analysis Summary for Biomass Population Parameters

PARAMETER	SENSITIVITY
PCE biomass yield	Sensitive
TCE biomass yield	Sensitive
DCE biomass yield	Sensitive
VC biomass yield	Sensitive
Hydrogenotrophic Methanogenesis biomass yield	Not sensitive
Acetate Methanogenesis biomass yield	Not sensitive
Butyrate biomass yield	Not sensitive
Ethanol 1 biomass yield	Not sensitive
Ethanol 2 biomass yield	Not sensitive
Lactate 1 biomass yield	Not sensitive
Lactate 2 biomass yield	Not sensitive

Propionate biomass yield	Not sensitive
k_d	Sensitive

Of the dechlorination parameters, the model is most sensitive to the PCE parameters. While the model is sensitive to most dechlorination parameters, it is most sensitive to PCE parameters because they cause effects all the way down the dechlorination chain. While the other dechlorination parameters just affect there dechlorination process and the ones after them.

The amount of hydrogen that enters the system depends on the degradation of the butyrate, ethanol, lactate, and propionate. The amount of these materials in the system depends on the rate at which higher organic materials are broken down into these compounds. These compounds are then fermented to produce hydrogen and other products. The amount and the rate by which hydrogen is produced, affects the competition between the methanogens and the dechlorinators for hydrogen. Figures 15-22 are graphs of the same two simulations. Simulation 1 shows the effects of a low steady input of hydrogen into the system. Simulation 2 shows the effect on the degradation of the contaminant when the hydrogen has a high influx initially. Figure 14 shows the two hydrogen concentration behaviors. The first hydrogen concentration trace is a low steady influx of hydrogen into the system. The second trace has a quick influx of hydrogen initially that stimulates the biomass growth that causes the hydrogen to be consumed. This produces a numerical error in the model. However the behavior of the system is okay until this point and conclusions can be drawn on the behavior until the numerical error. In the real system, the hydrogen would be consumed immediately as it

enters the system. The model shows the hydrogen entering the system in one time step and then being consumed in the next time step. This is the numerical error.

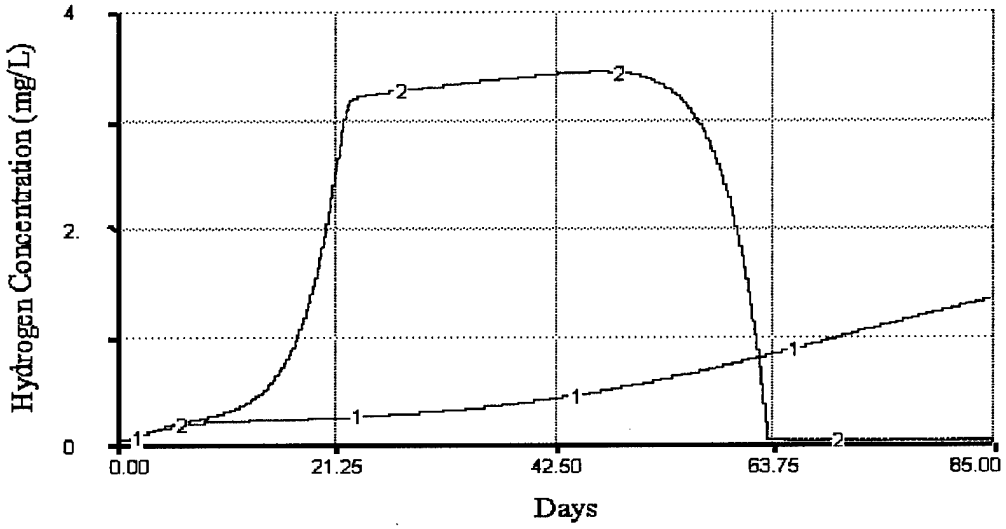


Figure 15. Hydrogen concentrations

A low steady influx of hydrogen into the system allows for more PCE to be degraded. This is because at low levels, the methanogens do not have enough hydrogen to grow as rapidly, so the dechlorinators can establish their presence. Figure 15 shows how the methanogens fare on the hydrogen. With high initial influx of hydrogen, the methanogens grow faster since there is more than enough hydrogen for both the methanogens and the dechlorinators and the methanogens have a higher yield rate.

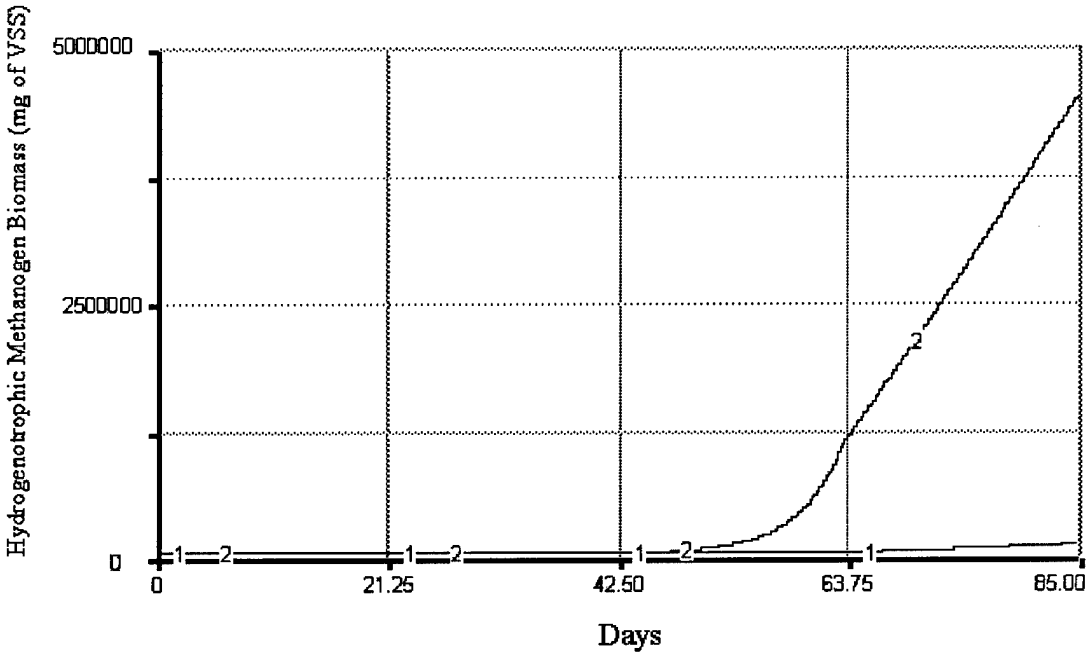


Figure 16. Hydrogenotrophic Methanogen Biomass

The PCE biomass (Figure 17) is a little delayed in growing in the second plot. This is because the hydrogen is used up in the in the second and there are more methanogens to compete for the hydrogen that is entering the system. Therefore since the biomass does not have as much hydrogen to use as an electron donor, it is delayed in growing. The lower the biomass population is, the slower the degradation of PCE and the slower the growth of the population will be.

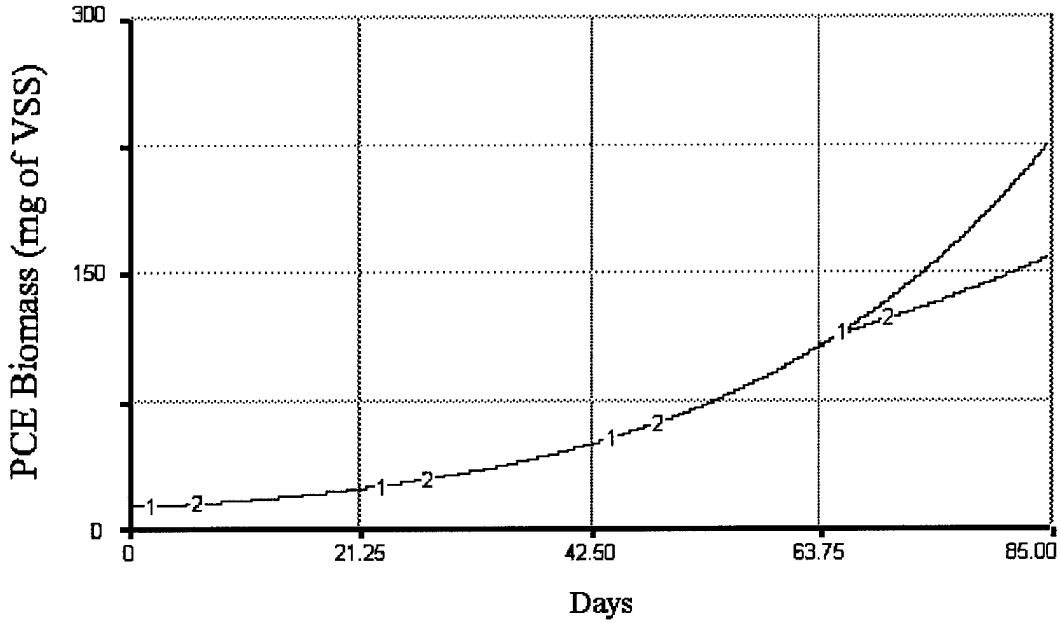


Figure 17. PCE Biomass

Figure 18 shows the how PCE concentration in the methanogenic zone is affected by difference in the hydrogen influx. The initial part the PCE concentration graphs are the same until the hydrogen in the system is used up in the second case. Then the PCE microbes are competing with the methanogens for the hydrogen that is then entering the system. The dechlorinators have the advance at low hydrogen concentration, however, the extremely large population of methanogens helps them to reduce or overcome that advantage.

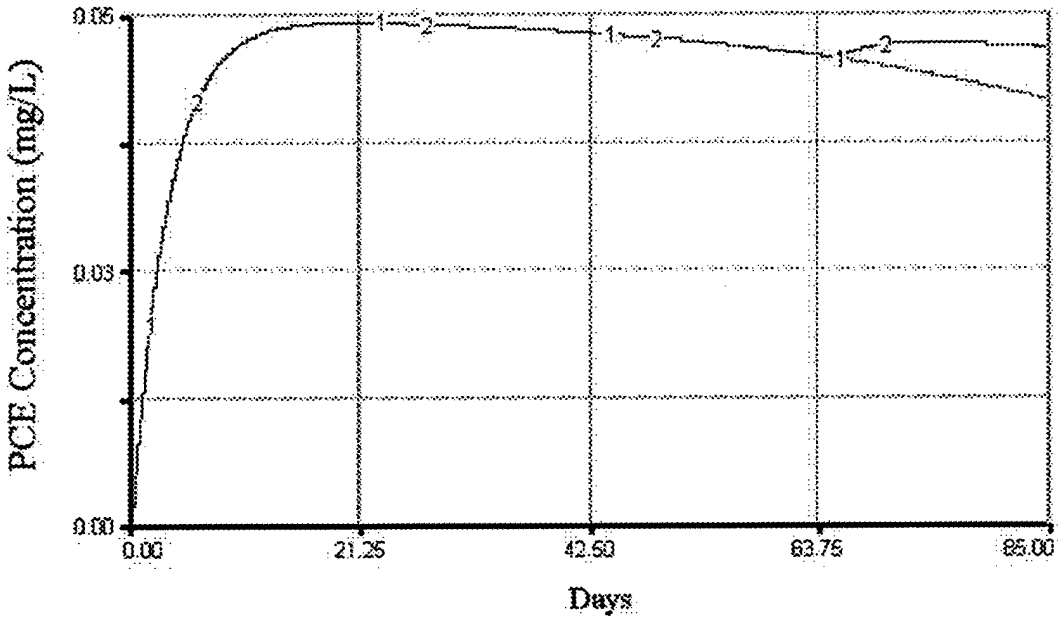


Figure 18. PCE Concentrations

Figure 19 shows how the rate of hydrogen influx into the system affects the concentration of TCE in the system. The slow down in the degradation of PCE in simulation 2 accounts for the drop in the concentration of TCE in the system. This lower amount of TCE in the system cause the TCE degrading biomass to slow their growth and thus affect how much TCE is degraded

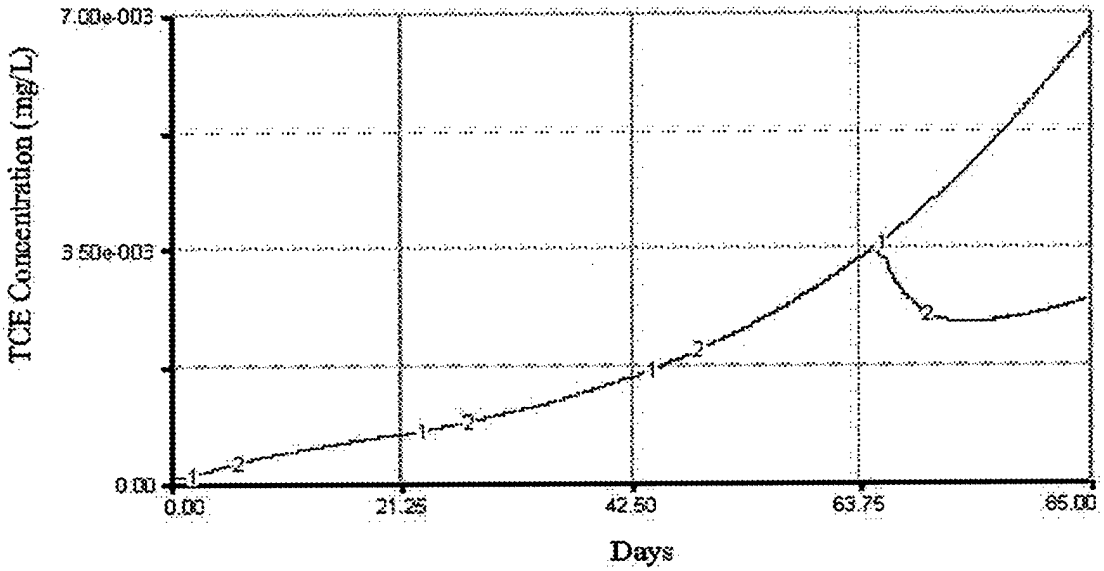


Figure 19. TCE Concentrations

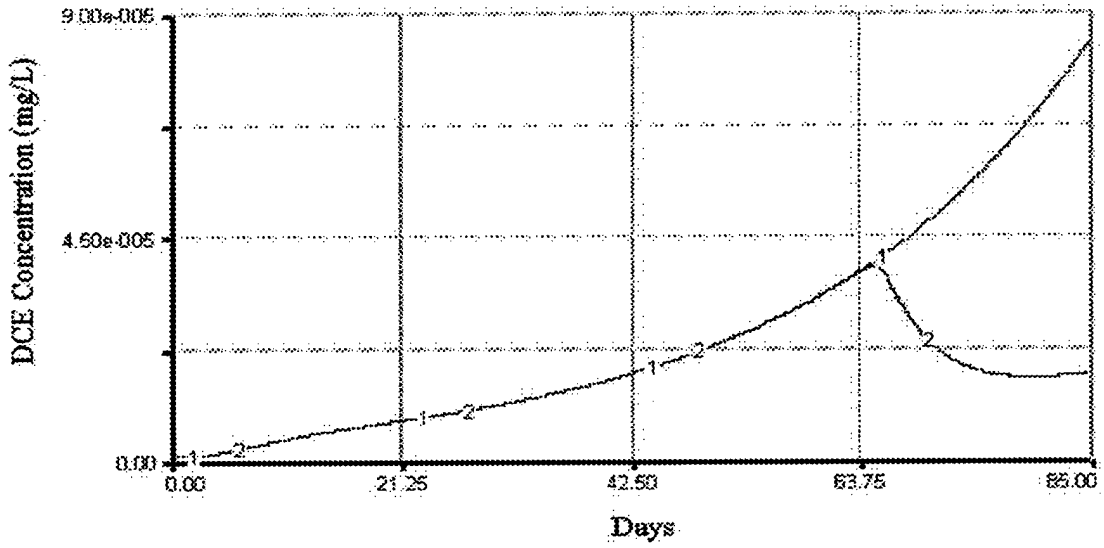


Figure 20. DCE Concentrations

The effects of the competition on the dechlorination of the contaminant keep getting worse and worse as the contaminant is being degraded. Figure 20 shows the DCE concentration in the system. The competition for the hydrogen also affects the growth of the microorganisms, which in turns affects the rate of degradation.

Figure 21 shows the VC concentration in the system during the two simulations. Ethene (Figure 22) is the final step in the degradation process for PCE.

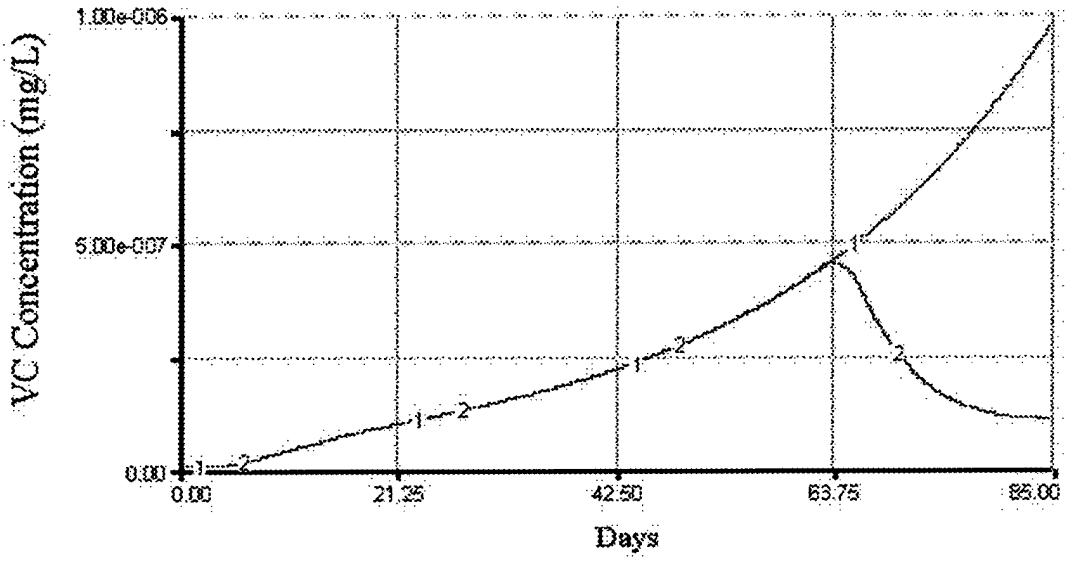


Figure 21. VC Concentrations

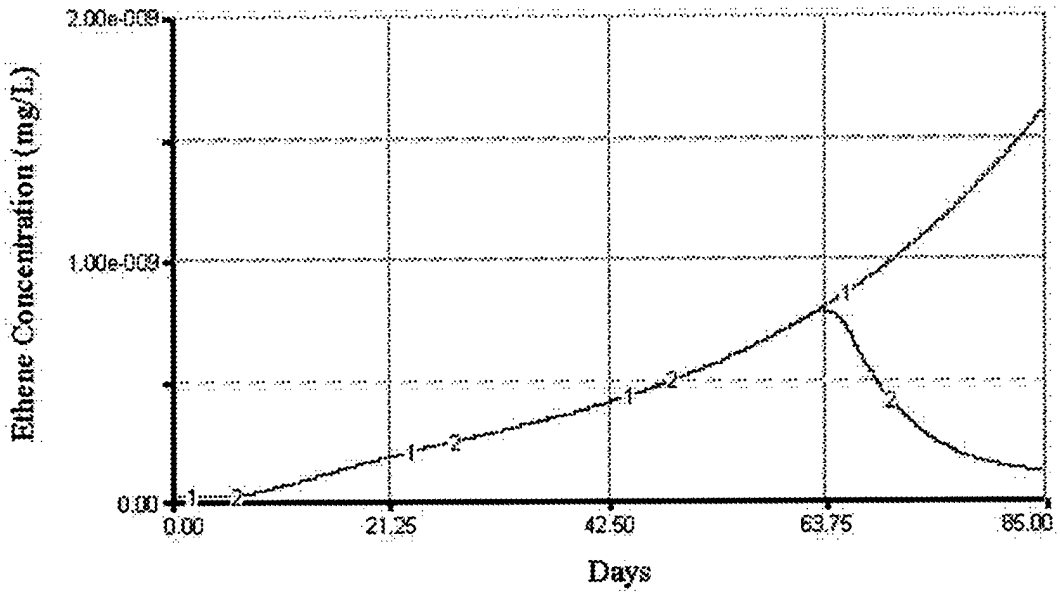


Figure 22. Ethene Concentrations

The rate and concentration of the hydrogen that comes into the wetland, affects the degradation of PCE. A low steady influx of hydrogen into the methanogenic zone of the constructed wetland allows for more dechlorination and more complete dechlorination in a shorter amount of time than a high quick influx of hydrogen into the system. This is because a high influx of hydrogen allows the methanogen population to become extremely large and compete for the limited amount of hydrogen that is entering the system.

V. Conclusions and Recommendation for Further Study

The purpose of this study was to develop a system dynamics model to reasonably describe contaminant fate and transport within the methanogenic zone of a constructed wetland. This includes determining the processes within the methanogenic zone that are most important in controlling contaminant fate, and the combination of parameters that optimize or limit the system.

The methanogenic zone of a wetland is a dynamic, complex system. Modeling the methanogenic zone proved to be a challenging task. Confidence in the model was built through verification and testing. Reasonable behavior resulted from a reasonable range of parameters. Based on the level of detail presented, this study provides a baseline understanding of the methanogenic zone and gives some insight for implementation. The thing that had the most effect on the decontamination of the chlorinated solvent was the influx of hydrogen. In order to have more complete degradation of PCE, the initial amount of hydrogen that enters the system needs to be low and steady until the microorganisms responsible for the degradation of the chlorinated solvents are firmly established. This allows them to better compete with the methanogens for the electron donors, especially hydrogen, in the system.

The initial amount of biomass also has a great affect on the degradation, especially the PCE degrading population. Increasing the population does not affect the steady state value of the contaminant in the system. It does however reduce the maximum concentration of the contaminant in the system. It also has a syngergistic affect other chlorinated solvents in the system.

Model Strengths

Given the model's purpose of providing further detail to Capt. Hoefar's model of contaminant degradation within the methanogenic zone of a constructed wetland, the model succeeds in capturing the sequential degradation of PCE via microbial processes. It also establishes the appropriate level of detail required for this study to model contaminant fate and transport within the methanogenic zone of a wetland system. Additionally, the model captures the necessary interactions and feedback loops between mechanisms of the system. The model provides a more detailed look at the methanogenic zone and the simultaneous reactions that take place there. This model can be incorporated into Capt. Hoefar's fundamental model of a constructed wetland in order to make that model better. The model also looks at the competition between the methanogens and dechlorinators and describes the factors that affect the competition.

Model Weaknesses

The model is limited in that there are interactions and limits that are not incorporated in the level of detail for this model. The model does not take into account the fact that many of the fermentation reactions and some of the chlorinated solvent reactions may be limited by inhibitions such as inhibition of fermentation when the concentration of the products of fermentation are too great in the system and an inhibition of the degradation of VC when the concentration of the other chloroethenes in the system is high. The rate at which the fermentation products (butyrate, ethanol, lactate and propionate) enter the system is not known. This creates some uncertainty in the model. Another weakness of the model is the numerical limitations of the software.

Areas for Further Research

1. The fermentation reactions are inhibited by high concentrations of products in the system. This is not reflected in the model. This inhibition could affect the rate and amount of hydrogen that enters the system through fermentation.
2. There is also evidence in the literature of an inhibition in the rate of VC degradation due to high concentrations of higher chlorinated ethenes (Bagley, 1998). There is also evidence of an inhibition of the growth of methanogens due to the presence of PCE (Bagley, 1998).
3. The model accounts for each of the degradation populations for each of the chlorinated solvents as separate populations. There is evidence in the literature that there are microorganisms that can completely degrade PCE to ethane (Maymo-Gatell et al., 1997). There are also microorganisms that can degrade both PCE and TCE. There are microorganism that can degrade DCE and VC (Bagley, 1998).
4. Further development is needs to be added to the fermentation process to include the break down of simple monomers like sugar, and amino acids into the products for fermentation.

Final Assessment of the Thesis Effort

Contaminant fate and transport within methanogenic zone of a wetland system is an extremely complex and dynamic process. The entities and mechanisms that drive the methanogenic zone behavior are dynamic. The ideal approach to gain understanding of the system is through the use of a model. The system dynamics approach to modeling lends itself nicely to such a challenging system because it allows insight into the behavior

of the overall system. By constructing the model and performing simulations with the model, one learns and begins to understand the complexity of the system, the interactions, interdependencies, and feedback loops and how they are all tied together to comprise the system.

The system dynamics process is favored over other modeling processes for this study as it develops insight to the behavior of the system as a whole versus one influential mechanism in the system. This model of the methanogenic zone of a constructed wetland can be added to Capt. Hoefar's model in order to provide a more complete model of a constructed wetland.

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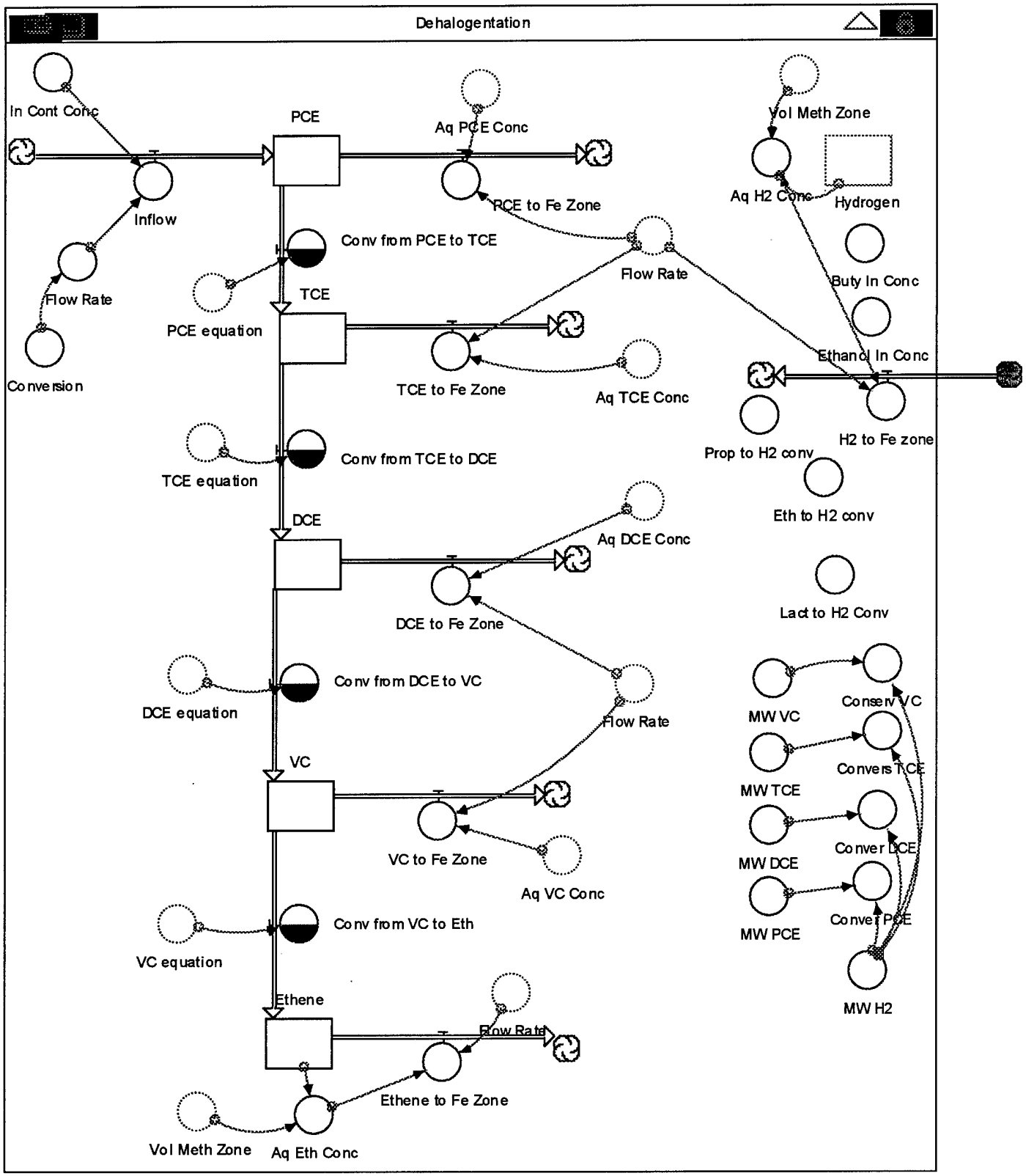
Appendix A


Dehalogentation
In Cont Conc
Inflow
Flow Rate
Conversion
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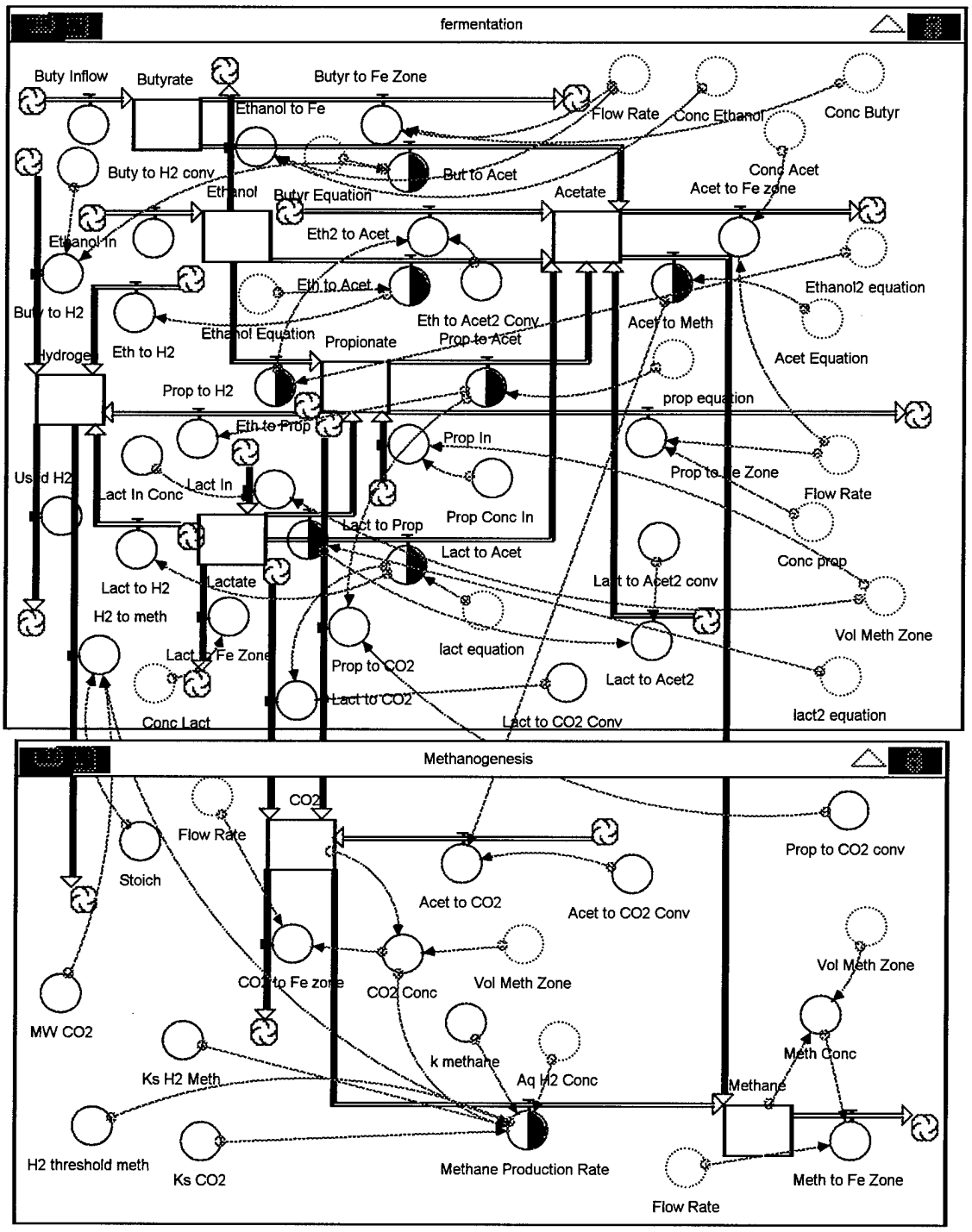
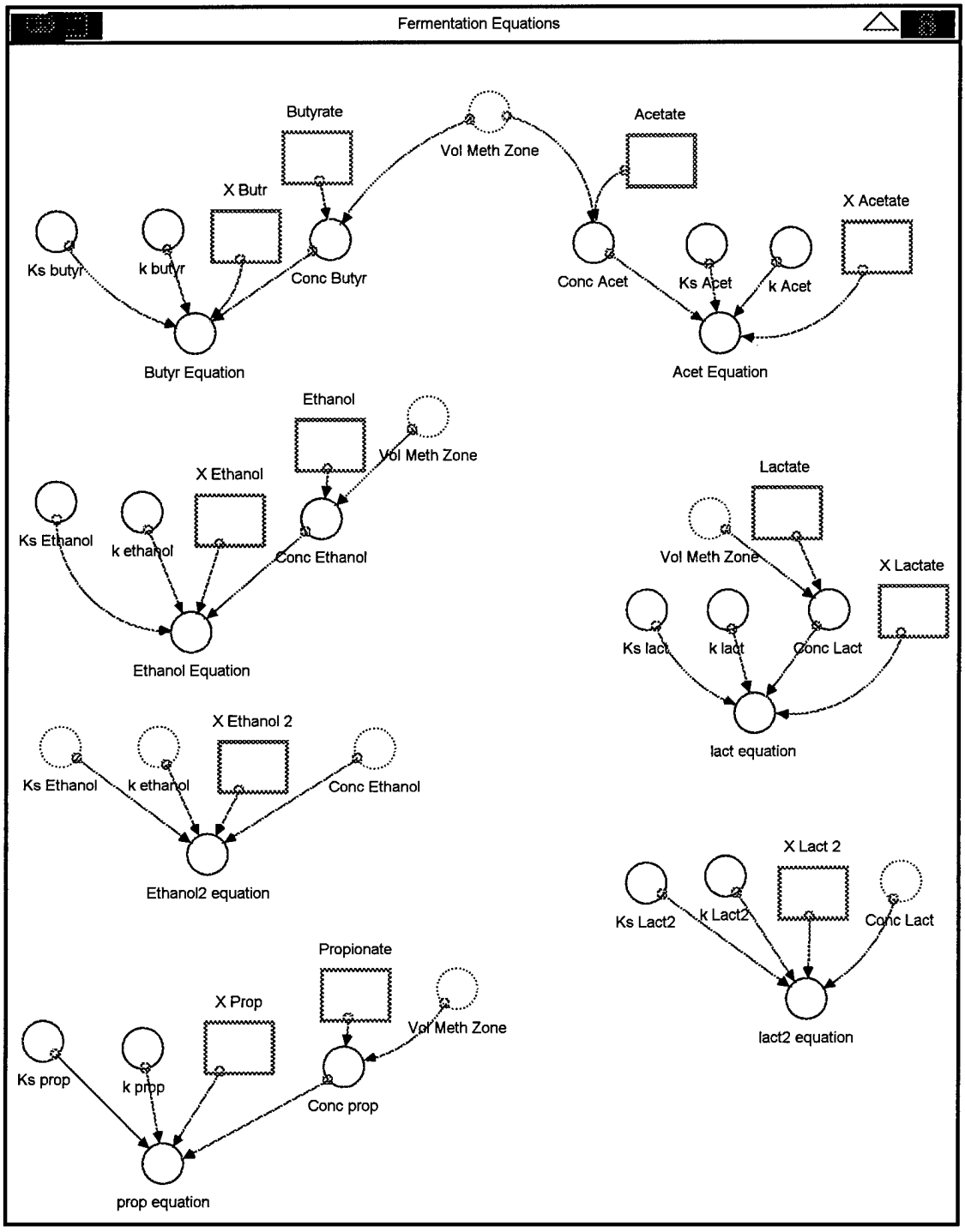
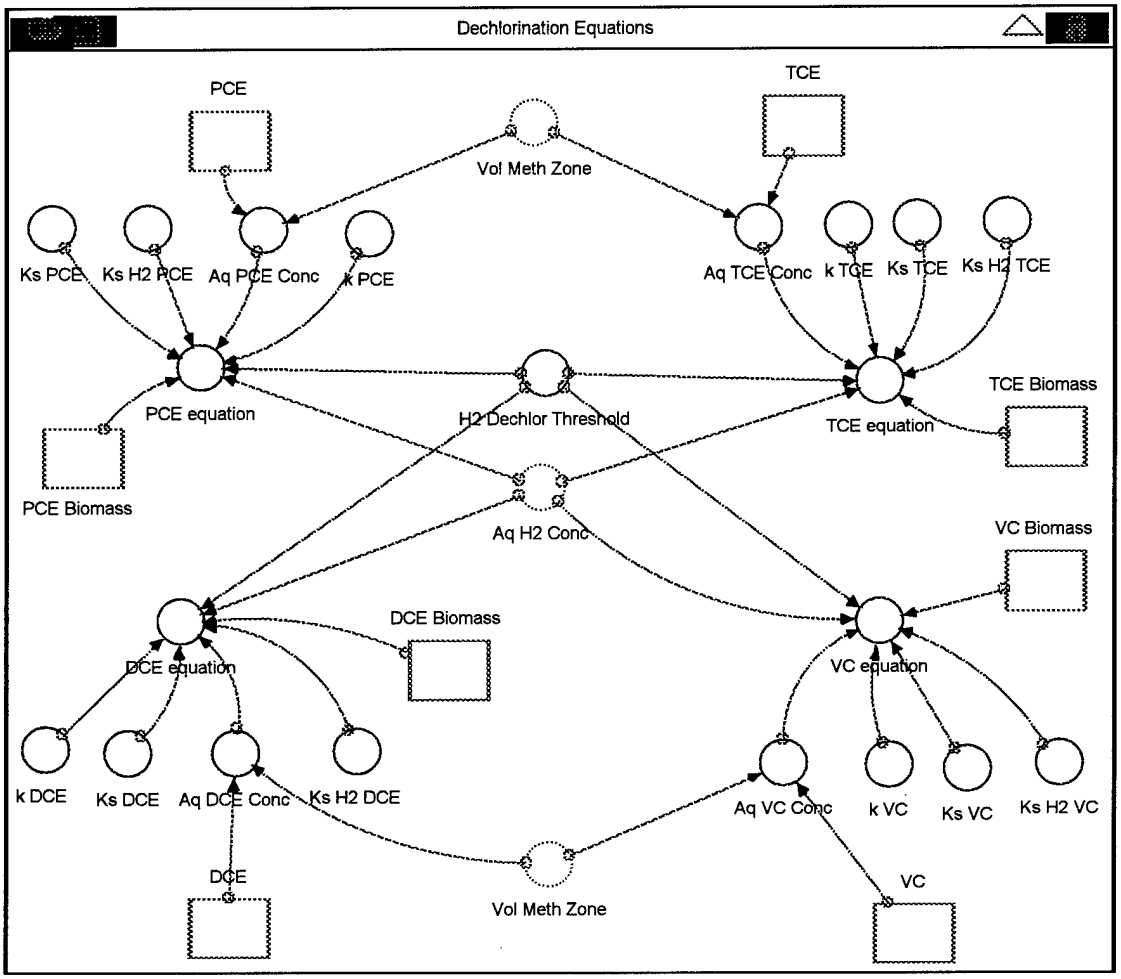
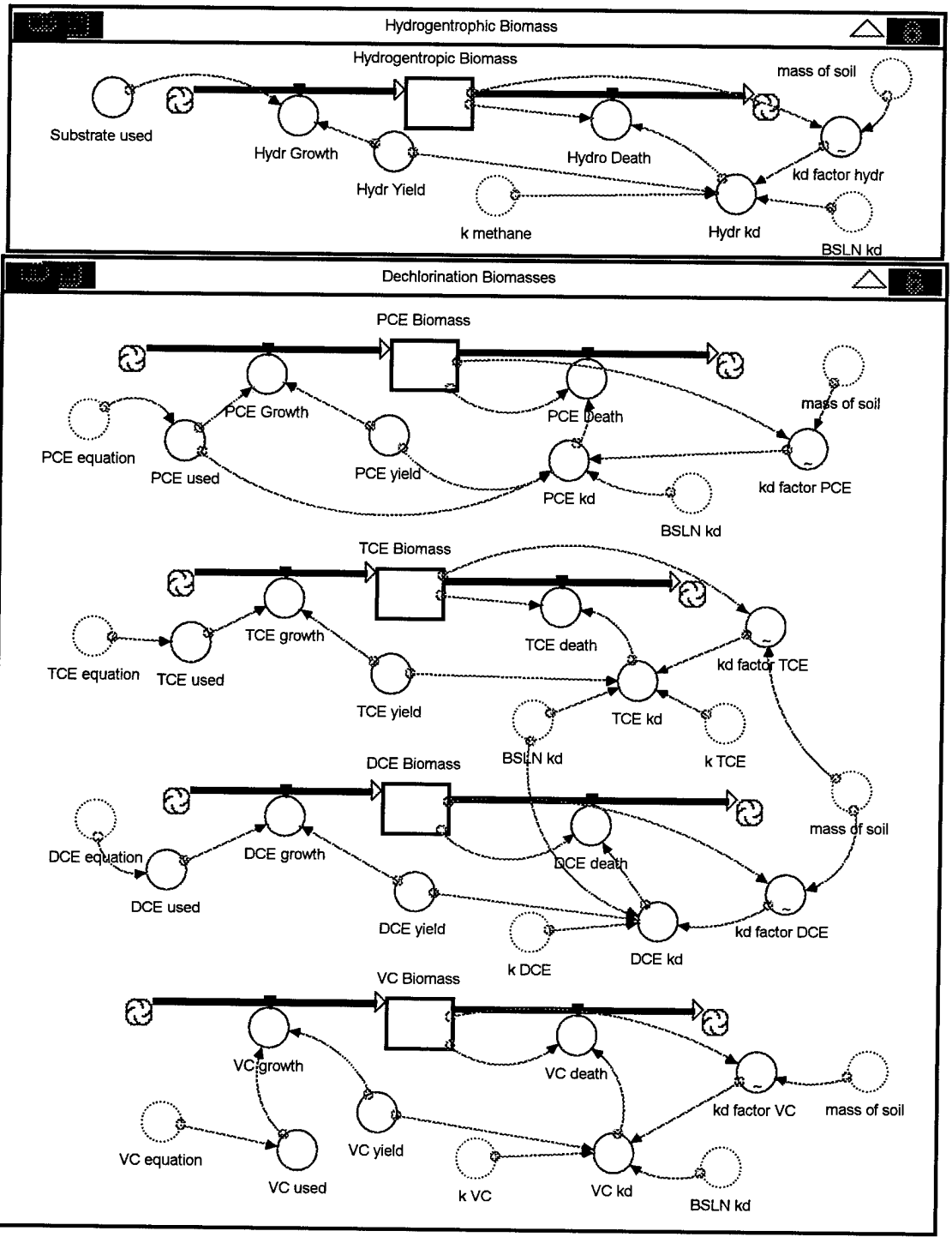
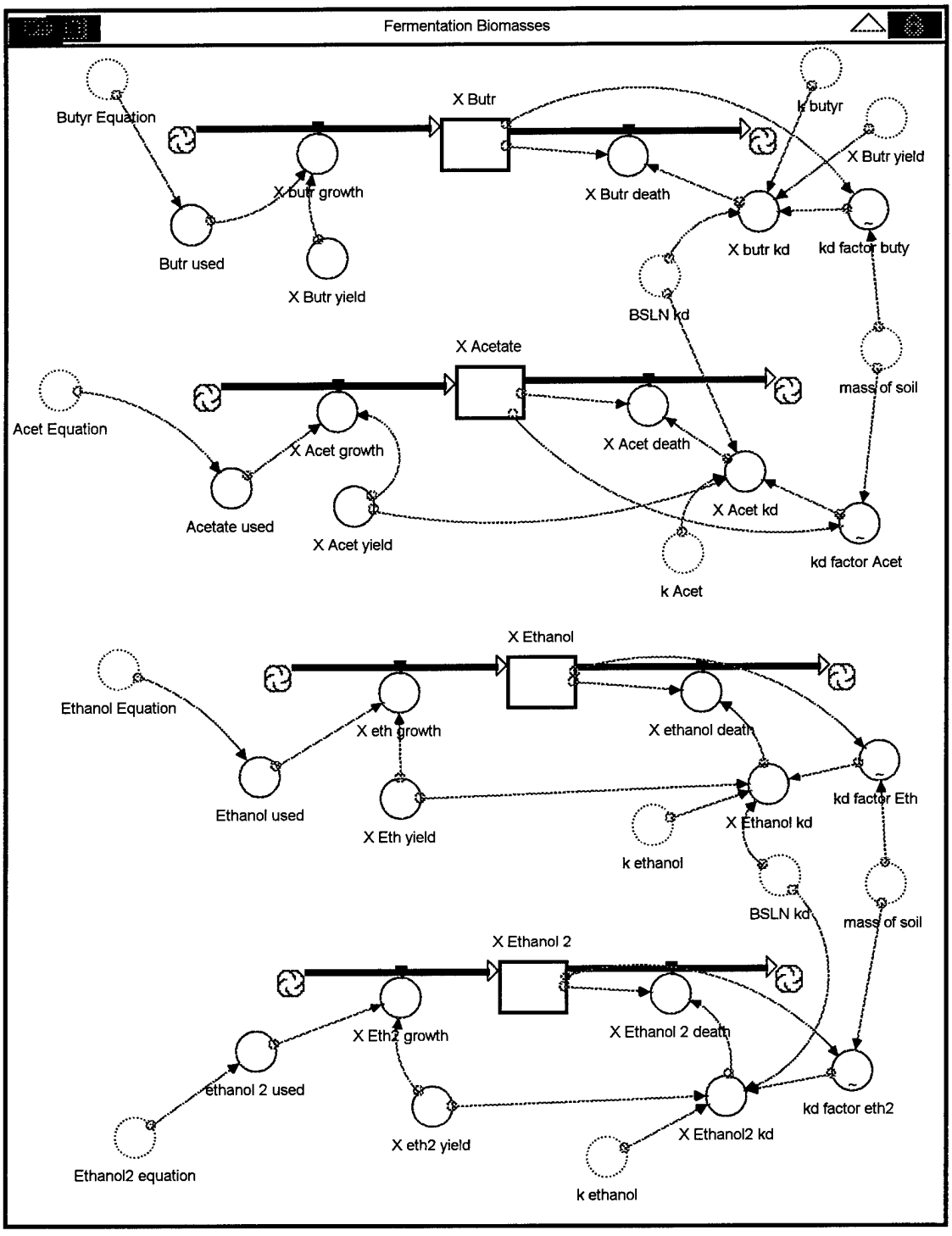
Aq PCE Conc
PCE to Fe Zone
Conv from PCE to TCE
PCE equation
TCE
TCE to Fe Zone
Aq TCE Conc
Flow Rate
TCE equation
Conv from TCE to DCE
DCE
Aq DCE Conc
DCE to Fe Zone
DCE equation
Conv from DCE to VC
Flow Rate
VC
VC to Fe Zone
Aq VC Conc
VC equation
Conv from VC to Eth
Ethene
Flow Rate
Ethene to Fe Zone
Vol Meth Zone
Aq Eth Conc
Vol Meth Zone
Aq H2 Conc
Hydrogen
Buty In Conc
Ethanol In Conc
Prop to H2 conv
H2 to Fe zone
Eth to H2 conv
Lact to H2 Conv
MW VC
Conserv VC
MW TCE
Convers TCE
MW DCE
Conver DCE
MW PCE
Convert PCE
MW H2

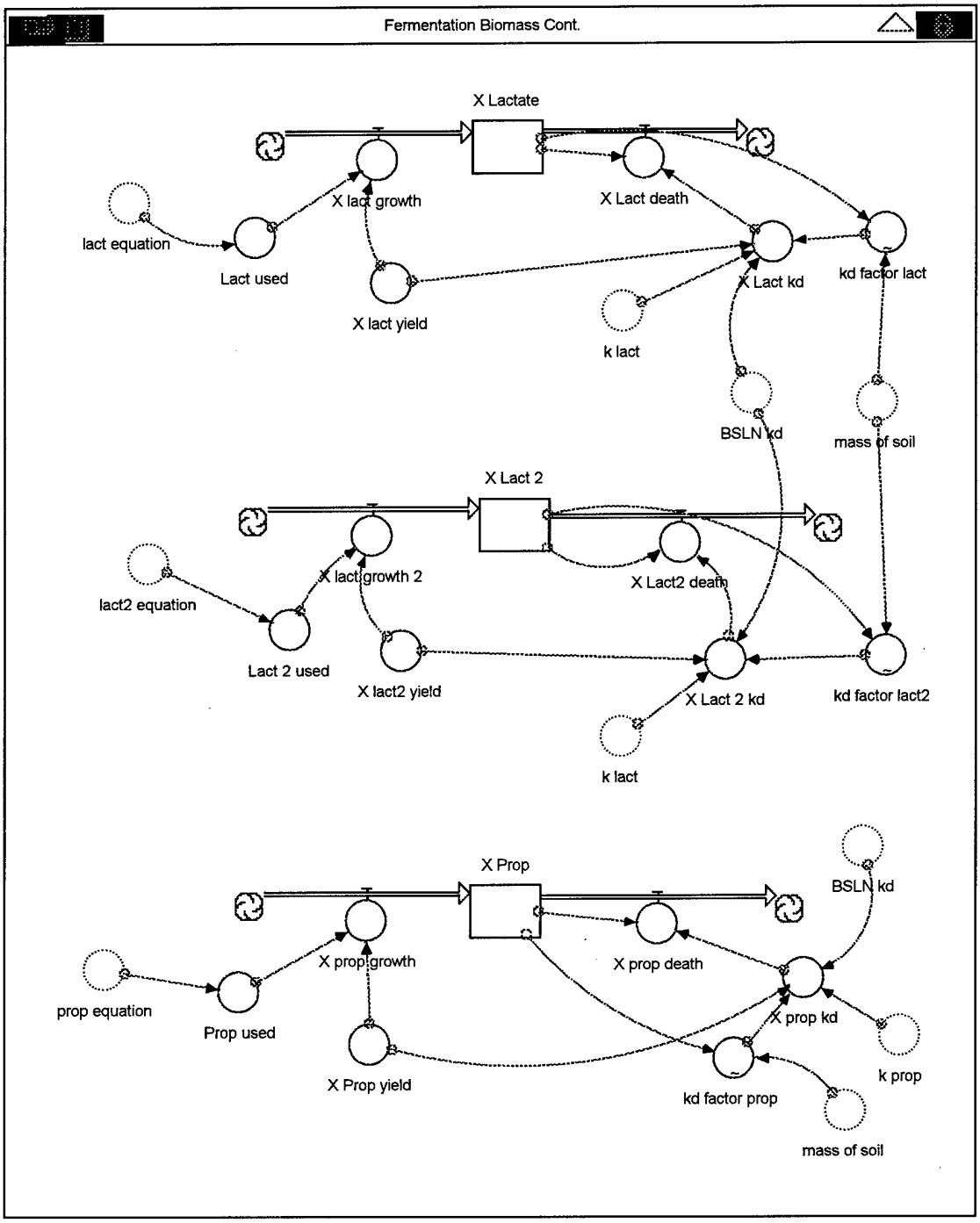

fermentation
Buty Inflow
Butyrate
Butyr to Fe Zone
Ethanol to Fe
Flow Rate
Conc Ethanol
Conc Butyr
Buty to H2 conv
But to Acet
Conc Acet
Ethanol
Butyr Equation
Acetate
Acet to Fe zone
Ethanol In
Eth2 to Acet
Eth to Acet
Ethanol2 equation
Buty to H2
Eth to Acet2 Conv
Acet to Meth
Ethanol Equation
Propionate
Prop to Acet
Hydroge
Eth to H2
Acet Equation
Prop to H2
prop equation
Eth to Prop
Prop In
Used H2
Lact In Conc
Lact In
Prop to Fe Zone
Flow Rate
Lact to Prop
Prop Conc In
Lact to Acet
Conc prop
Lact to H2
Lactate
Lact to Acet2 conv
H2 to meth
Vol Meth Zone
Lact to Fe Zone
lact equation
Prop to CO2
Lact to Acet2
Lact to CO2
Conc Lact
Lact to CO2 Conv
lact2 equation
Methanogenesis
CO2
Flow Rate
Prop to CO2 conv
Stoich
Acet to CO2
Acet to CO2 Conv
Vol Meth Zone
CO2 to Fe zone
CO2 Conc
Vol Meth Zone
MW CO2
Meth Conc
k methane
Ks H2 Meth
Aq H2 Conc
Methane
H2 threshold meth
Ks CO2
Methane Production Rate
Meth to Fe Zone
Flow Rate

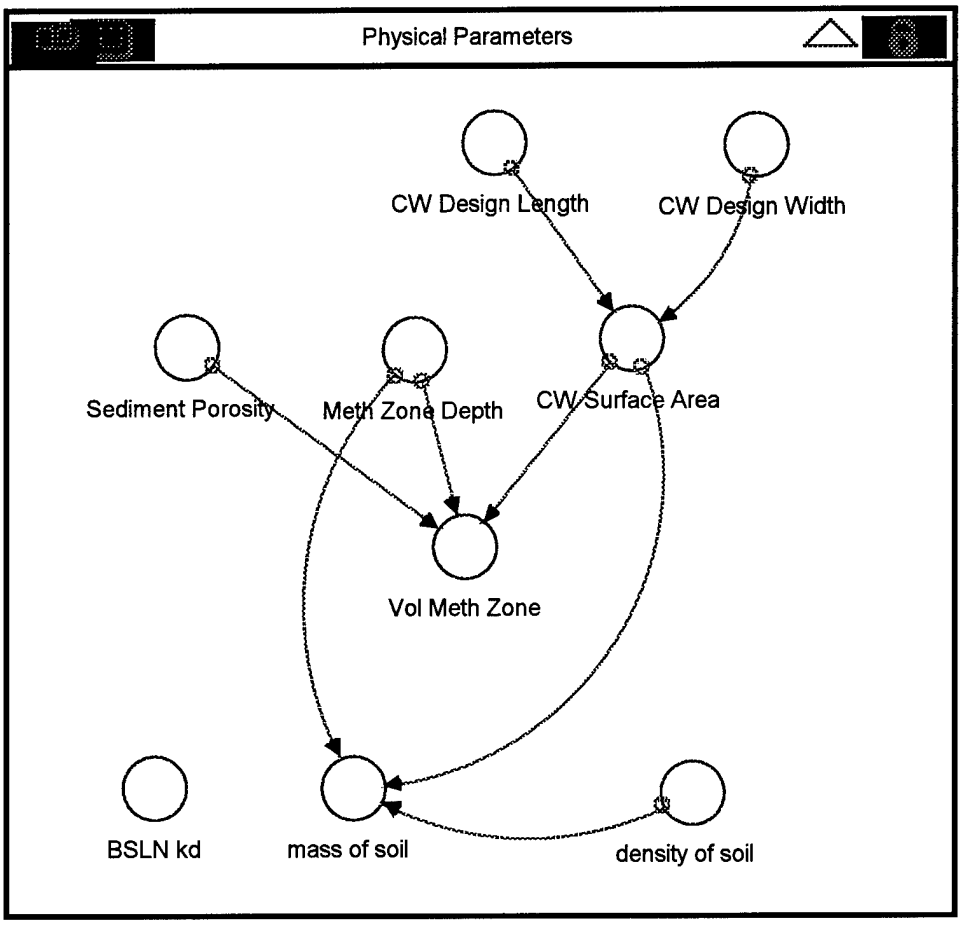

Fermentation Equations
Butyrate
Vol Meth Zone
Acetate
X Butr
X Acetate
Ks butyr
k butyr
Conc Butyr
Conc Acet
Ks Acet
k Acet
Butyr Equation
Acet Equation
Ethanol
Vol Meth Zone
X Ethanol
Ks Ethanol
k ethanol
Conc Ethanol
Ethanol Equation
Lactate
Vol Meth Zone
X Lactate
Ks lact
k lact
Conc Lact
lact equation
X Ethanol 2
Ks Ethanol
k ethanol
Conc Ethanol
Ethanol2 equation
X Lact 2
Ks Lact2
k Lact2
Conc Lact
lact2 equation
Propionate
X Prop
Vol Meth Zone
Ks prop
k prop
Conc prop
prop equation


Dechlorination Equations
PCE
TCE
Vol Meth Zone
Ks PCE
Ks H2 PCE
Aq PCE Conc
k PCE
Aq TCE Conc
k TCE
Ks TCE
Ks H2 TCE
PCE equation
H2 Dechlor Threshold
TCE equation
TCE Biomass
PCE Biomass
Aq H2 Conc
VC Biomass
DCE Biomass
DCE equation
VC equation
k DCE
Ks DCE
Aq DCE Conc
Ks H2 DCE
Aq VC Conc
k VC
Ks VC
Ks H2 VC
DCE
Vol Meth Zone
VC


Hydrogentrophic Biomass
Hydrogentropic Biomass
Substrate used
Hydr Growth
Hydr Yield
Hydro Death
mass of soil
kd factor hydr
k methane
Hydr kd
BSLN kd
Dechlorination Biomasses
PCE Biomass
PCE equation
PCE used
PCE Growth
PCE yield
PCE Death
mass of soil
kd factor PCE
PCE kd
BSLN kd
TCE Biomass
TCE equation
TCE used
TCE growth
TCE yield
TCE death
kd factor TCE
TCE kd
BSLN kd
k TCE
DCE Biomass
DCE equation
DCE used
DCE growth
DCE yield
DCE death
mass of soil
kd factor DCE
k DCE
DCE kd
VC Biomass
VC equation
VC used
VC growth
VC yield
VC death
kd factor VC
mass of soil
k VC
VC kd
BSLN kd


Fermentation Biomasses
Butyr Equation
X Butr
k butyr
X Butr yield
X butr growth
X Butr death
Butr used
X Butr yield
X butr kd
kd factor buty
BSLN kd
X Acetate
mass of soil
Acet Equation
X Acet growth
X Acet death
X Acet kd
Acetate used
X Acet yield
kd factor Acet
k Acet
X Ethanol
Ethanol Equation
X eth growth
X ethanol death
kd factor Eth
Ethanol used
X Eth yield
X Ethanol kd
k ethanol
BSLN kd
mass of soil
X Ethanol 2
X Eth2 growth
X Ethanol 2 death
ethanol 2 used
kd factor eth2
X eth2 yield
X Ethanol2 kd
Ethanol2 equation
k ethanol


Fermentation Biomass Cont.
X Lactate
X lact growth
X Lact death
lact equation
Lact used
X Lact kd
kd factor lact
X lact yield
k lact
BSLN kd
mass of soil
X Lact 2
X lact growth 2
X Lact2 death
lact2 equation
Lact 2 used
X lact2 yield
X Lact 2 kd
kd factor lact2
k lact
X Prop
BSLN kd
X prop growth
X prop death
prop equation
Prop used
X prop kd
k prop
X Prop yield
kd factor prop
mass of soil


Physical Parameters
CW Design Length
CW Design Width
Sediment Porosity
Meth Zone Depth
CW Surface Area
Vol Meth Zone
BSLN kd
mass of soil
density of soil

Appendix B

Dechlorination Biomasses

DCE_Biomass(t) = DCE_Biomass(t - dt) + (DCE_growth - DCE_death) * dt

INIT DCE_Biomass = 10
DCE_growth = DCE_used*DCE_yield
DCE_death = DCE_Biomass*DCE_kd
PCE_Biomass(t) = PCE_Biomass(t - dt) + (PCE_Growth - PCE_Death) * dt

INIT PCE_Biomass = 10
PCE_Growth = PCE_used*PCE_yield
PCE_Death = PCE_Biomass*PCE_kd
TCE_Biomass(t) = TCE_Biomass(t - dt) + (TCE_growth - TCE_death) * dt

INIT TCE_Biomass = 10
TCE_growth = TCE_used*TCE_yield
TCE_death = TCE_Biomass*TCE_kd
VC_Biomass(t) = VC_Biomass(t - dt) + (VC_growth - VC_death) * dt

INIT VC_Biomass = 10
VC_growth = VC_used*VC_yield
VC_death = VC_Biomass*VC_kd
DCE_kd = BSLN_kd+(kd_factor_DCE*(DCE_yield*k_DCE))
DCE_used = DCE_equation
DCE_yield = .0278
DOCUMENT: 2.7E-3 mg of VSS/umol of DCE used (Bagley, 1998) converted to mg of VSS/mg of DCE used
(2.7E-3 mg of VSS/umol of DCE used) * (umol DCE/97 E-6 g DCE) * (1 g DCE/1000mg DCE) = .0278 mg of VSS/mg of DCE used

PCE_kd = BSLN_kd+(kd_factor_PCE*(PCE_used*PCE_yield))
PCE_used = PCE_equation
PCE_yield = .0163
DOCUMENT: 2.7E-3 mg of VSS/umol of PCE used (Bagley, 1998) converted to mg of VSS/mg of PCE used
(2.7E-3 mg of VSS/umol of PCE used) * (umol PCE/165.8E-6 g PCE) * (1 g PCE/1000mg PCE) = .0163 mgof VSS/mg of PCE used

TCE_kd = BSLN_kd+(kd_factor_TCE*(k_TCE*TCE_yield))
TCE_used = TCE_equation
TCE_yield = .0205
DOCUMENT: 2.7E-3 mg of VSS/umol of TCE used (Bagley, 1998) converted to mg of VSS/mg of TCE used

(2.7E-3 mg of VSS/umol of TCE used) * (umol TCE/131.5E-6 g TCE) * (1 g TCE/1000mg TCE) = .0205 mgof VSS/mg of TCE used

VC_kd = BSLN_kd+(kd_factor_VC*(k_VC*VC_yield))
VC_used = VC_equation
VC_yield = .0435
DOCUMENT: 2.7E-3 mg of VSS/umol of VC used (Bagley, 1998) converted to mg of VSS/mg of VC used
(2.7E-3 mg of VSS/umol of VC used) * (umol VC/97 E-6 g VC) * (1 g VC/1000mg VC) = .0435 mg of VSS/mg of VC used

kd_factor_DCE = GRAPH(DCE_Biomass/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.2), (0.0035, 0.4), (0.004, 0.6), (0.0045, 0.805), (0.005, 1.00)
kd_factor_PCE = GRAPH(PCE_Biomass/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.00), (0.0035, 0.00), (0.004, 0.00), (0.0045, 0.00), (0.005, 0.00)
kd_factor_TCE = GRAPH(TCE_Biomass/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.205), (0.0035, 0.4), (0.004, 0.6), (0.0045, 0.795), (0.005, 1.00)
kd_factor_VC = GRAPH(VC_Biomass/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.205), (0.0035, 0.4), (0.004, 0.605), (0.0045, 0.8), (0.005, 1.00)

Dechlorination Equations

Aq_DCE_Conc = DCE/Vol_Meth_Zone
Aq_PCE_Conc = PCE/Vol_Meth_Zone
Aq_TCE_Conc = TCE/Vol_Meth_Zone
Aq_VC_Conc = VC/Vol_Meth_Zone
DCE_equation =
((k_DCE*DCE_Biomass*Aq_DCE_Conc)/(Ks_DCE+Aq_DCE_Conc))*((Aq_H2_Conc -H2_Dechlor_Threshold)/(Ks_H2_DCE+(Aq_H2_Conc-H2_Dechlor_Threshold)))
H2_Dechlor_Threshold = 4E-6
Ks_DCE = .05233
DOCUMENT: half-velocity coefficient for DCE use
.54 umol/L (Fennel and Gossett, 1998) converted to mg/L
(.54 umol DCE/L) * (96.9E-6 g DCE/umol DCE) * (1000 mg DCE/1 g DCE) = .05233 mg DCE/L

Ks_H2_DCE = 4.2E-5
DOCUMENT: half-velocity coeffiecient for H2 use by dechlorinators
21 nmol H2/L (Ballapragada et al., 1997) converted to mg H2/L
(21 nmol H2/L) * (2E-9 g H2/nmol H2) * (1000 mg H2/ 1 g H2) = 4.2E-5 mg H2/L

Ks_H2_PCE = 1.8E-5
DOCUMENT: half-velocity coefficient for H2 use by dechlorinators

9 nmol H2/L (Ballapragada et al., 1997) converted to mg H2/L
(9 nmol H2/L) * (2E-9 g H2/nmol H2) * (1000 mg H2/ 1 g H2) = 1.8 E-5 mgH2/L

Ks_H2_TCE = 2.8E-5
DOCUMENT: half-velocity coefficient for H2 use by dechlorinators
14 nmol/L (Ballapragada et al., 1997) converted to mg/L
(14 nmol H2/L) * (2E-9 g H2/nmol H2) * (1000 mg H2/ 1 g H2) = 2.8E-5 mgH2/L

Ks_H2_VC = 3.4E-4
DOCUMENT: half-velocity coefficient for H2 use by dechlorinators
17 nmol/L (Ballapragada et al., 1997) converted to mg/L
(17 nmol H2/L) * (2E-9 g H2/nmol H2) * (1000 mg H2/ 1 g H2) = 3.4E-5 mg H2/L

Ks_PCE = .0896
DOCUMENT: half-velocity coefficient for PCE use
.54 umol/L (Fennel and Gossett, 1998) converted to mg/L
(.54 umol PCE/L) * (165.8E-6 g PCE/umol PCE) * (1000 mg PCE/1 g PCE) = .0896 mg PCE/L

Ks_TCE = .07096
DOCUMENT: half-velocity coefficient for TCE use
.54 umol/L (Fennel and Gossett, 1998) converted to mg/L
(.54 umol TCE/L) * (131.4E-6 g TCE/umol TCE) * (1000 mg TCE/1 g TCE) = .07096 mg TCE/L

Ks_VC = 18.125
DOCUMENT: half velocity coefficient for VC use
290 umol VC/L (Fennel and Gossett, 1998) converted to mg VC/L
290 umol VC/L) * (62.5E-6 g VC/umol VC) * (1000 mg VC/1 g VC) = .16875 mg vc/L

k_DCE = 6.9768
DOCUMENT: maximum specific rate of DCE utilization
3 umol DCE/(mg VSS *h) (Fennel and Gossett, 1998) converted to 6.9768 mg TCE/(mg VSS*day)
1.8 umol DCE/(mg of VSS*h) * (96.9E-6 g DCE/umol DCE) * (1000 mg DCE/1 g DCE) * (24 h/day) = 7.164 mg DCE/(mg VSS*day)

k_PCE = 7.164
DOCUMENT: maximum specific rate of PCE utilization
1.8 umol PCE/(mg of VSS *h) (Fennel and Gossett, 1998) converted to 7.164 mg PCE/(mg VSS*day)
1.8 umol PCE/(mg of VSS*h) * (165.8E-6 g PCE/umol PCE) * (1000 mg PCE/1 g PCE) * (24 h/day) = 7.164 mg PCE/(mg VSS*day)

k_TCE = 9.4608
DOCUMENT: maximum specific rate of TCE utilization
3 umol TCE/(mg of VSS*h) (Fennel and Gossett, 1998) converted to 9.4608 mg TCE/(mg of VSS*day)
3 umol TCE/(mg of VSS*h) * (131.4E-6 g TCE/umol TCE) * (1000 mg TCE/1 g TCE) * (24 h/day) = 9.4608 mg TCE/(mg VSS*day)

k_VC = 4.5
DOCUMENT: maximum specific rate of VC utilization
3 umol VC/(mg VSS*h) (Fennel and Gossett, 1998) converted to 4.5 mg VC/ (mg VSS*day)
1.8 umol VC/(mg of VSS*h) * (62.5E-6 g VC/umol VC) * (1000 mg VC/1 g VC) * (24 h/day) = 7.164 mg VC/(mg VSS*day)

PCE_equation =
((k_PCE*PCE_Biomass*Aq_PCE_Conc)/(Ks_PCE+Aq_PCE_Conc))*((Aq_H2_Conc-H2_Dechlor_Threshold)/(Ks_H2_PCE+(Aq_H2_Conc-H2_Dechlor_Threshold)))
TCE_equation =
((k_TCE*TCE_Biomass*Aq_TCE_Conc)/(Ks_TCE+Aq_TCE_Conc))*((Aq_H2_Conc-H2_Dechlor_Threshold)/(Ks_H2_TCE+(Aq_H2_Conc-H2_Dechlor_Threshold)))
VC_equation =
((k_VC*VC_Biomass*Aq_VC_Conc)/(Ks_VC+Aq_VC_Conc))*((Aq_H2_Conc-H2_Dechlor_Threshold)/(Ks_H2_VC+(Aq_H2_Conc-H2_Dechlor_Threshold)))

Dehalogenation

DCE(t) = DCE(t - dt) + (Conv_from_TCE_to_DCE - Conv_from_DCE_to_VC - DCE_to_Fe_Zone) * dt

INIT DCE = 0
Conv_from_TCE_to_DCE(o) = TCE_equation
DOCUMENT: Inflow multiplier = stoich conversion * MW DCE/MW TCE
Inflow multiplier = 1 * 96.9/131.4 = .7376

Conv_from_DCE_to_VC(o) = DCE_equation
DOCUMENT: Inflow multiplier = Stoich conver from DCE to VC (1) * MW VC/MW DCE
Inflow multiplier = 1 * 62.5/96.9 = .6392

DCE_to_Fe_Zone = Flow_Rate*Aq_DCE_Conc
Ethene(t) = Ethene(t - dt) + (Conv_from_VC_to_Eth - Ethene_to_Fe_Zone) * dt

INIT Ethene = 0
Conv_from_VC_to_Eth(o) = VC_equation
DOCUMENT: Inflow multiplier = stoich conversion (1) * MW ethene/MW VC

Inflow multiplier = 1 * 28/62.5 = .4489

Ethene_to_Fe_Zone = Flow_Rate*Aq_Eth_Conc
PCE(t) = PCE(t - dt) + (Inflow - Conv_from_PCE_to_TCE - PCE_to_Fe_Zone) * dt

INIT PCE = 0
Inflow = In_Cont_Conc*Flow_Rate
Conv_from_PCE_to_TCE(o) = PCE_equation
DOCUMENT: Inflow multiplier = stoich conversion from PCE to TCE (1) * MW TCE/MW PCE
Inflow multiplier = 1 * 131.4/165.8 = .793

PCE_to_Fe_Zone = Aq_PCE_Conc*Flow_Rate
TCE(t) = TCE(t - dt) + (Conv_from_PCE_to_TCE - Conv_from_TCE_to_DCE - TCE_to_Fe_Zone) * dt

INIT TCE = 0
Conv_from_PCE_to_TCE(o) = PCE_equation
DOCUMENT: Inflow multiplier = stoich conversion from PCE to TCE (1) * MW TCE/MW PCE
Inflow multiplier = 1 * 131.4/165.8 = .793

Conv_from_TCE_to_DCE(o) = TCE_equation
DOCUMENT: Inflow multiplier = stoich conversion * MW DCE/MW TCE
Inflow multiplier = 1 * 96.9/131.4 = .7376

TCE_to_Fe_Zone = Flow_Rate*Aq_TCE_Conc
VC(t) = VC(t - dt) + (Conv_from_DCE_to_VC - Conv_from_VC_to_Eth - VC_to_Fe_Zone) * dt

INIT VC = 0
Conv_from_DCE_to_VC(o) = DCE_equation
DOCUMENT: Inflow multiplier = Stoich conver from DCE to VC (1) * MW VC/MW DCE
Inflow multiplier = 1 * 62.5/96.9 = .6392

Conv_from_VC_to_Eth(o) = VC_equation
DOCUMENT: Inflow multiplier = stoich conversion (1) * MW ethene/MW VC
Inflow multiplier = 1 * 28/62.5 = .4489

VC_to_Fe_Zone = Flow_Rate*Aq_VC_Conc
H2_to_Fe_zone = Aq_H2_Conc*Flow_Rate

OUTFLOW FROM: Hydrogen (IN SECTOR: fermentation)

Aq_Eth_Conc = Ethene/Vol_Meth_Zone
Aq_H2_Conc = Hydrogen/Vol_Meth_Zone
Buty_In_Conc = .7
Conserv_VC = MW_H2/MW_VC
Conversion = 5.45*1000
DOCUMENT: gal/min * 60 min/h * 24 h/day * 3.78E-3 m^3/gal * 1000 L/m^3 = L/day

Convers_TCE = MW_H2/MW_TCE
Conver_DCE = MW_H2/MW_DCE
Conver_PCE = MW_H2/MW_PCE
Ethanol_In_Conc = 5
Eth_to_H2_conv = .087
DOCUMENT: stoich conversion * MW H2/ MW ethanol
2 * 2/46.1 = .087

Flow_Rate = 7.66*Conversion
DOCUMENT: Expressed in liters per day, based on 75 gallons per minute flow rate.

In_Cont_Conc = .05
DOCUMENT: Groundwater concentration of contaminant converted to mg/L

Lact_to_H2_Conv = .044
DOCUMENT: stoich conversion * MW H2/ MW lactate
2 * 2/90.1 = .044

MW_DCE = 97
MW_H2 = 2
MW_PCE = 165.8
MW_TCE = 131.5
MW_VC = 62
Prop_to_H2_conv = .081
DOCUMENT: stoich conversion * MW H2/ MW propionate
3 * 2 / 74.1

Fermentation

Acetate(t) = Acetate(t - dt) + (Eth_to_Acet + But_to_Acet + Lact_to_Acet + Prop_to_Acet + Eth2_to_Acet + Lact_to_Acet2 - Acet_to_Meth - Acet_to_Fe_zone) * dt

INIT Acetate = 0
Eth_to_Acet(o) = Ethanol_Equation
DOCUMENT: Inflow multiplier = stoich conversion (1) * MW Acetate/MW Ethanol
Inflow multiplier = 1 * 59/46.1 = 1.28

But_to_Acet(o) = Butyr_Equation
DOCUMENT: Inflow Multiplier = stoich conversion (2) * MW Acetate/MW Butyrate

Inflow Multiplier = 2 * 59/87.1 = 1.35

Lact_to_Acet(o) = lact_equation
DOCUMENT: Inflow multiplier = stoich conver * MW Acet/MW Lact
Inflow multiplier = 1 * 59/90.1 = .65

Prop_to_Acet(o) = prop_equation
DOCUMENT: Inflow multiplier = stoich conv * MW Acetate/MW Propionate
Inflow multiplier = 1 * 59/74.1 = .8

Eth2_to_Acet = Eth_to_Prop*Eth_to_Acet2_Conv
Lact_to_Acet2 = Lact_to_Prop*Lact_to_Acet2_conv
Acet_to_Meth(o) = Acet_Equation
DOCUMENT: Inflow multiplier = stoich conversion (1) * MW Methane * MW Acetate
Inflow multiplier = 1 * 16/59 = .271

Acet_to_Fe_zone = Flow_Rate*Conc_Acet
Butyrate(t) = Butyrate(t - dt) + (Buty_Inflow - But_to_Acet - Butyr_to_Fe_Zone) * dt

INIT Butyrate = 0
Buty_Inflow = Buty_In_Conc*Vol_Meth_Zone
But_to_Acet(o) = Butyr_Equation
DOCUMENT: Inflow Multiplier = stoich conversion (2) * MW Acetate/MW Butyrate
Inflow Multiplier = 2 * 59/87.1 = 1.35

Butyr_to_Fe_Zone = Conc_Butyr*Flow_Rate
Ethanol(t) = Ethanol(t - dt) + (Ethanol_In - Eth_to_Acet - Eth_to_Prop - Ethanol_to_Fe) * dt

INIT Ethanol = 0
Ethanol_In = Vol_Meth_Zone*Ethanol_In_Conc
Eth_to_Acet(o) = Ethanol_Equation
DOCUMENT: Inflow multiplier = stoich conversion (1) * MW Acetate/MW Ethanol
Inflow multiplier = 1 * 59/46.1 = 1.28

Eth_to_Prop(o) = Ethanol2_equation
DOCUMENT: Inflow multiplier = stoich conversion (2/3) * MW Propionate/MW Ethanol
Inflow multiplier = 2/3 * 74.1/46.1 = 1.07

Ethanol_to_Fe = Flow_Rate*Conc_Ethanol
Hydrogen(t) = Hydrogen(t - dt) + (Buty_to_H2 + Eth_to_H2 + Prop_to_H2 + Lact_to_H2 - Used_H2 - H2_to_meth - H2_to_Fe_zone) * dt

INIT Hydrogen = 0

Buty_to_H2 = But_to_Acet*Buty_to_H2_conv
Eth_to_H2 = Eth_to_Acet*Eth_to_H2_conv
Prop_to_H2 = Prop_to_Acet*Prop_to_H2_conv
Lact_to_H2 = Lact_to_Acet*Lact_to_H2_Conv
Used_H2 =
Conv_from_PCE_to_TCE*Conver_PCE+Conv_from_TCE_to_DCE*Convers_TCE+Co
nv_from_DCE_to_VC*Conver_DCE+Conv_from_VC_to_Eth*Conserv_VC
H2_to_meth = Methane_Production_Rate*Stoich*(MW_H2/MW_CO2)
H2_to_Fe_zone (IN SECTOR: Dehalogentation)
Lactate(t) = Lactate(t - dt) + (Lact_In - Lact_to_Acet - Lact_to_Prop - Lact_to_Fe_Zone)
* dt

INIT Lactate = 0
Lact_In = Vol_Meth_Zone*Lact_In_Conc
Lact_to_Acet(o) = lact_equation
DOCUMENT: Inflow multiplier = stoich conver * MW Acet/MW Lact
Inflow multiplier = 1 * 59/90.1 = .65

Lact_to_Prop(o) = lact2_equation
DOCUMENT: Inflow multiplier = stoich conver * MW Prop/MW Lact
Inflow multiplier = 2/3 * 74.1/90.1 = .55

Lact_to_Fe_Zone = Conc_Lact*Flow_Rate
Propionate(t) = Propionate(t - dt) + (Eth_to_Prop + Lact_to_Prop + Prop_In -
Prop_to_Acet - Prop_to_Fe_Zone) * dt

INIT Propionate = 0
Eth_to_Prop(o) = Ethanol2_equation
DOCUMENT: Inflow multiplier = stoich conversion (2/3) * MW Propionate/MW
Ethanol
Inflow multiplier = 2/3 * 74.1/46.1 = 1.07

Lact_to_Prop(o) = lact2_equation
DOCUMENT: Inflow multiplier = stoich conver * MW Prop/MW Lact
Inflow multiplier = 2/3 * 74.1/90.1 = .55

Prop_In = Vol_Meth_Zone*Prop_Conc_In
Prop_to_Acet(o) = prop_equation
DOCUMENT: Inflow multiplier = stoich conv * MW Acetate/MW Propionate
Inflow multiplier = 1 * 59/74.1 = .8

Prop_to_Fe_Zone = Flow_Rate*Conc_prop
Lact_to_CO2 = Lact_to_Acet*Lact_to_CO2_Conv

INFLOW TO: CO2 (IN SECTOR: Methanogenesis)
Prop_to_CO2 = Prop_to_Acet*Prop_to_CO2_conv

INFLOW TO: CO2 (IN SECTOR: Methanogenesis)
Buty_to_H2_conv = .046
DOCUMENT: stoich conversion * MW H2/ MW Butyrate
2 * 2/87.1 = .046

Eth_to_Acet2_Conv = .43
DOCUMENT: stoich conversion * MW acetate/MW ethanol
1/3 * 59/46.1 = .43

Lact_In_Conc = .1
Lact_to_Acet2_conv = .22
DOCUMENT: Inflow multiplier = stoich conver * MW Prop/MW Lact
Inflow multiplier = 1/3 * 59/90.1 = .22

Lact_to_CO2_Conv = .163
DOCUMENT: stoich conversion * MW CO2/MW Lactate
1/3 * 44/90.1 = .163
Prop_Conc_In = .3

Fermentation Biomasses

X_Lactate(t) = X_Lactate(t - dt) + (X_lact_growth - X_Lact_death) * dt

INIT X_Lactate = 1000
X_lact_growth = X_lact_yield*Lact_used
X_Lact_death = X_Lactate*X_Lact_kd
X_Lact_2(t) = X_Lact_2(t - dt) + (X_lact_growth_2 - X_Lact2_death) * dt

INIT X_Lact_2 = 1000
X_lact_growth_2 = Lact_2_used*X_lact2_yield
X_Lact2_death = X_Lact_2*X_Lact_2_kd
X_Prop(t) = X_Prop(t - dt) + (X_prop_growth - X_prop_death) * dt

INIT X_Prop = 1000
X_prop_growth = Prop_used*X_Prop_yield
X_prop_death = X_Prop*X_prop_kd
Lact_2_used = lact2_equation
Lact_used = lact_equation
Prop_used = prop_equation
X_lact2_yield = .062

DOCUMENT: .00563 mg of VSS/total umol of lactate used (Fennel and Gossett, 1998) converted to .062 mg of VSS/mg of lactate used
(.00563 mg VSS/umol of lactate used) * (umol lactate/90.1E-6 g lactate) * (1 g lactate/1000 mg lactate) = .062 mg of VSS/mg of lactate used

X_Lact_2_kd = BSLN_kd+(kd_factor_lact2*(k_lact*X_lact2_yield))
X_Lact_kd = BSLN_kd+(kd_factor_lact*(k_lact*X_lact_yield))
X_lact_yield = .039
DOCUMENT: .00351 mg of VSS/total umol of lactate used (Fennel and Gossett, 1998) converted to .039 mg of VSS/mg of lactate used
(.00351 mg VSS/umol of lactate used) * (umol lactate/90.1E-6 g lactate) * (1 g lactate/1000 mg lactate) = .039 mg of VSS/mg of lactate used

X_prop_kd = BSLN_kd+(kd_factor_prop*(k_prop*X_Prop_yield))
X_Prop_yield = .019
DOCUMENT: .00144 mg of VSS/total umol of propionate used (Fennel and Gossett, 1998) converted to .019 mg of VSS/mg of propionate used
(.00144 mg VSS/umol of propionate used) * (umol propionate/74.1E-6 g propionate) * (1 g propionate/1000 mg propionate) = .019 mg of VSS/mg of propionate used

kd_factor_lact = GRAPH(X_Lactate/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.205), (0.0035, 0.405), (0.004, 0.61), (0.0045, 0.81), (0.005, 1.00)
kd_factor_lact2 = GRAPH(X_Lact_2/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.195), (0.0035, 0.395), (0.004, 0.605), (0.0045, 0.805), (0.005, 1.00)
kd_factor_prop = GRAPH(X_Prop/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.195), (0.0035, 0.405), (0.004, 0.605), (0.0045, 0.795), (0.005, 1.00)
X_Acetate(t) = X_Acetate(t - dt) + (X_Acet_growth - X_Acet_death) * dt

INIT X_Acetate = 1000
X_Acet_growth = X_Acet_yield*Acetate_used
X_Acet_death = X_Acetate*X_Acet_kd
X_Butr(t) = X_Butr(t - dt) + (X_butr_growth - X_Butr_death) * dt

INIT X_Butr = 1000
X_butr_growth = Butr_used*X_Butr_yield
X_Butr_death = X_Butr*X_butr_kd
X_Ethanol(t) = X_Ethanol(t - dt) + (X_eth_growth - X_ethanol_death) * dt

INIT X_Ethanol = 1000
X_eth_growth = X_Eth_yield*Ethanol_used
X_ethanol_death = X_Ethanol*X_Ethanol_kd
X_Ethanol_2(t) = X_Ethanol_2(t - dt) + (X_Eth2_growth - X_Ethanol_2_death) * dt

INIT X_Ethanol_2 = 1000
X_Eth2_growth = X_eth2_yield*ethanol_2_used
X_Ethanol_2_death = X_Ethanol_2*X_Ethanol2_kd
Acetate_used = Acet_Equation
Butr_used = Butyr_Equation
ethanol_2_used = Ethanol2_equation
Ethanol_used = Ethanol_Equation
X_Acet_kd = BSLN_kd+(kd_factor_Acet*(X_Acet_yield*k_Acet))
X_Acet_yield = .032
DOCUMENT: .00189 mg of VSS/total umol of acetate used (Bagely, 1998) converted to .032 mg of VSS/mg of acetate used
(.00189 mg VSS/umol of acetate used) * (umol acetate/59E-6E-6 g acetate) * (1 g acetate/1000 mg acetate) = .032 mg of VSS/mg of acetate used)

X_butr_kd = BSLN_kd+(kd_factor_buty*(X_Butr_yield*k_butyr))
X_Butr_yield = .032
DOCUMENT: .00279 mg of VSS/total umol of butyrate used (Fennel and Gossett, 1998) converted to .032 mg of VSS/mg of Butyrate used
(.00279 mg VSS/umol of butyrate used) * (umol butyrate/87.10E-6 g butyrate) * (1 g butyrate/1000 mg butyrate) = .032 mg of VSS/mg of butyrate used)

X_eth2_yield = .0644
DOCUMENT: .00297 mg of VSS/total umol of ethanol used (Fennel and Gossett, 1998) converted to .0644 mg of VSS/mg of ethanol used
(.00297 mg VSS/umol of ethanol used) * (umol ethanol/46.1E-6 g ethanol) * (1 g ethanol/1000 mg ethanol) = .0644 mg of VSS/mg of ethanol used

X_Ethanol2_kd = BSLN_kd+(kd_factor_eth2*(k_ethanol*X_eth2_yield))
X_Ethanol_kd = BSLN_kd+(kd_factor_Eth*(k_ethanol*X_Eth_yield))
X_Eth_yield = .043
DOCUMENT: .00198 mg of VSS/total umol of ethanol used (Fennel and Gossett, 1998) converted to .043 mg of VSS/mg of ethanol used
(.00198 mg VSS/umol of ethanol used) * (umol ethanol/46.1E-6 g ethanol) * (1 g ethanol/1000 mg ethanol) = .043 mg of VSS/mg of ethanol used

kd_factor_Acet = GRAPH(X_Acetate/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.195), (0.0035, 0.4), (0.004, 0.605), (0.0045, 0.805), (0.005, 1.00)
kd_factor_buty = GRAPH(X_Butr/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.175), (0.0035, 0.365), (0.004, 0.58), (0.0045, 0.8), (0.005, 1.00)
kd_factor_Eth = GRAPH(X_Ethanol/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.21), (0.0035, 0.41), (0.004, 0.61), (0.0045, 0.81), (0.005, 1.00)

kd_factor_eth2 = GRAPH(X_Ethanol_2/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.2), (0.0035, 0.405), (0.004, 0.595), (0.0045, 0.805), (0.005, 1.00)

Fermentation Equations

Acet_Equation = (k_Acet*X_Acetate*Conc_Acet)/(Ks_Acet+Conc_Acet)
Butyr_Equation = (k_butyr*X_Butr*Conc_Butyr)/(Ks_butyr+Conc_Butyr)
Conc_Acet = Acetate/Vol_Meth_Zone
Conc_Butyr = Butyrate/Vol_Meth_Zone
Conc_Ethanol = Ethanol/Vol_Meth_Zone
Conc_Lact = Lactate/Vol_Meth_Zone
Conc_prop = Propionate/Vol_Meth_Zone
Ethanol2_equation =
(k_ethanol*X_Ethanol_2*Conc_Ethanol)/(Ks_Ethanol+Conc_Ethanol)
Ethanol_Equation = (k_ethanol*X_Ethanol*Conc_Ethanol)/(Ks_Ethanol+Conc_Ethanol)
Ks_Acet = 59
DOCUMENT: half-velocity coefficient for acetate
1000 umol/L (Fennell and Gossett, 1998) converted to mg/L

Ks_butyr = 2.89754
DOCUMENT: half-velocity coefficient for butyrate
34.3 umol/L (Fennell and Gossett, 1998) converted to mg/L

Ks_Ethanol = .7837
DOCUMENT: half-velocity coefficient for ethanol
17 umol/L (Fennell and Gossett, 1998) converted to mg/L

Ks_lact = .22525
DOCUMENT: half-velocity cofficient for lactate
2.5 umol/L (Fennell and Gossett, 1998) converted to mg/L

Ks_Lact2 = .22525
Ks_prop = .83733
DOCUMENT: half-velocity coefficient for propionate
11.3 umol/L (Fennell and Gossett, 1998) converted to mg/L

k_Acet = 8
DOCUMENT: maximum rate of acetate utilization
5.65 umol acetate/(mg VSS*h) (Fennel and Gossett, 1998) converted to 8 mg acetate/(mg VSS*day)
(5.65 umol acetate/(mg VSS*h)) * (59E-6 g acetate/umol acetate) * (1000 mg acetate/1 g acetate) * (24h/day) = 8 mg acetate/(mg VSS*day)

k_butyr = 10.243
DOCUMENT: maximum specific rate of butyrate degradation
4.9 umol/(mg of VSS*h) (Fennel and Gossett, 1998) converted to 10.243 mg/(mg of VSS*day)
(4.9 umol/(mg of VSS*h)) * (87.1E-6 g butyrate/umol butyrate) * (1000 mg butyrate/1 g butyrate) * (24h/day) = 10.243 mg/(mg of VSS*day)

k_ethanol = 24.302
DOCUMENT: maximum specific rate of ethanol degradation
21.9 umol ethanol/(mg of VSS*h) (Fennel and Gossett, 1998) converted to 24.302 mg ethanol/(mg of VSS*day)
(21.9 umol ethanol/(mg of VSS*h)) * (46.1E-6 g ethanol/umol ethanol) * (1000 mg ethanol/1 g ethanol) * (24h/day) = 24.302 mg ethanol/(mg of VSS*day)

k_lact = 18.5966
DOCUMENT: maximum specific rate of lacate degradation
8.6 umol lactate/(mg of VSS*h) (Fennel and Gossett, 1998) converted to 18.5966 mg lactate/(mg of VSS*day)
(8.6 umol lactate/(mg of VSS*h)) * (90.1E-6 g lactate/umol lactate) * (1000 mg lactate/1 g lactate) * (24h/day) = 18.5966 mg lactate/(mg of VSS*day)

k_Lact2 = 18.5966
DOCUMENT: maximum specific rate of lacate degradation
8.6 umol lactate/(mg of VSS*h) (Fennel and Gossett, 1998) converted to 18.5966 mg lactate/(mg of VSS*day)
(8.6 umol lactate/(mg of VSS*h)) * (90.1E-6 g lactate/umol lactate) * (1000 mg lactate/1 g lactate) * (24h/day) = 18.5966 mg lactate/(mg of VSS*day)

k_prop = 3.9125
DOCUMENT: maximum specific rate of propionate degradation
2.2 umol propionate/(mg of VSS*h) (Fennell and Gossett, 1998) converted to 3.9125 mg propionate/(mg of VSS*day)
(2.2 umol propionate/(mg of VSS*h)) * (74.1E-6 g propionate/umol propionate) * (1000 mg propionate/1 g propionate) * (24h/day) = 3.9125 mg propionate/(mg of VSS*day)

lact2_equation = (k_Lact2*X_Lact_2*Conc_Lact)/(Ks_Lact2+Conc_Lact)
lact_equation = (k_lact*X_Lactate*Conc_Lact)/(Ks_lact+Conc_Lact)
prop_equation = (k_prop*X_Prop*Conc_prop)/(Ks_prop+Conc_prop)

Hydrogenotrophic Biomass

Hydrogentropic_Biomass(t) = Hydrogentropic_Biomass(t - dt) + (Hydr_Growth - Hydro_Death) * dt

INIT Hydrogentropic_Biomass = 1000
Hydr_Growth = Hydr_Yield*Substrate_used

Hydro_Death = Hydrogentropic_Biomass*Hydr_kd
Hydr_kd = BSLN_kd+(kd_factor_hydr*(Hydr_Yield*k_methane))
Hydr_Yield = .715
DOCUMENT: 1.43 E-3 mg of VSS/umol of H2 used my methanogens (Fennel and Gossett, 1998) converted to mg of VSS/mg of H2 used by methanogens
(1.43 E-3 mg of VSS/umol of H2) * (umol H2/2E-6 g H2) * (g H2/1000 mg H2) = .715 mg of VSS/mg of H2 used by methanogens

Substrate_used = H2_to_meth
kd_factor_hydr = GRAPH(Hydrogentropic_Biomass/mass_of_soil)
(0.00, 0.00), (0.0005, 0.00), (0.001, 0.00), (0.0015, 0.00), (0.002, 0.00), (0.0025, 0.00), (0.003, 0.2), (0.0035, 0.405), (0.004, 0.61), (0.0045, 0.805), (0.005, 1.00)

Hydrogenotrophic Methanogenesis

CO2(t) = CO2(t - dt) + (Prop_to_CO2 + Lact_to_CO2 + Acet_to_CO2 - Methane_Production_Rate - CO2_to_Fe_zone) * dt

INIT CO2 = 0
Prop_to_CO2 (IN SECTOR: fermentation)
Lact_to_CO2 (IN SECTOR: fermentation)
Acet_to_CO2 = Acet_to_Meth*Acet_to_CO2_Conv
Methane_Production_Rate(o) = (k_methane*CO2_Conc*(Aq_H2_Conc-H2_threshold_meth)*Hydrogentropic_Biomass)/((Ks_H2_Meth+(Aq_H2_Conc-H2_threshold_meth))*(Ks_CO2+CO2_Conc))
DOCUMENT: Inflow Multiplier = stoich conversion (1) * MW methane/MW CO2
Inflow multiplier = 1 * 16/44 = .364

CO2_to_Fe_zone = CO2_Conc*Flow_Rate
Methane(t) = Methane(t - dt) + (Methane_Production_Rate + Acet_to_Meth - Meth_to_Fe_Zone) * dt

INIT Methane = 0
Methane_Production_Rate(o) = (k_methane*CO2_Conc*(Aq_H2_Conc-H2_threshold_meth)*Hydrogentropic_Biomass)/((Ks_H2_Meth+(Aq_H2_Conc-H2_threshold_meth))*(Ks_CO2+CO2_Conc))
DOCUMENT: Inflow Multiplier = stoich conversion (1) * MW methane/MW CO2
Inflow multiplier = 1 * 16/44 = .364

Acet_to_Meth (IN SECTOR: fermentation)
Meth_to_Fe_Zone = Flow_Rate*Meth_Conc
Acet_to_CO2_Conv = .746
DOCUMENT: stoich conversion * MW CO2/MW Acetate
1 * 44/59 = .746

CO2_Conc = CO2/Vol_Meth_Zone

H2_threshold_meth = 2.2E-5
Ks_CO2 = .25
Ks_H2_Meth = 1E-3
DOCUMENT: half-veolcity coefficient for H2 use by hydrogentrophic methanogens .5 umol/L (Fennell and Gossett, 1998) converted to mg/L

k_methane = 10.56
DOCUMENT: 40 umol H2/(mg VSS*h) (Fennell and Gossett, 1997)
40 umol H2./(mg VSS*h) * 1umol CO2/4umol H2 * 44E-6 g CO2/1umol CO2 * 1000 mg/1 g * 24 hrs/d = 10.56 mg CO2/(mg VSS*d)

Meth_Conc = Methane/Vol_Meth_Zone
MW_CO2 = 44
Prop_to_CO2_conv = .594
DOCUMENT: stoich conversion * MW CO2/MW propionate
1 * 44/74.1 = .594

Stoich = 4

Physical Parameters

BSLN_kd = .0024
CW_Design_Length = 42.672
DOCUMENT: Length of constructed wetland, expressed in meters; equivelent to 180'

CW_Design_Width = 18.288
DOCUMENT: The design width of the constructed wetland, expressed in meters; equivelent to 60'

CW_Surface_Area = CW_Design_Length*CW_Design_Width
density_of_soil = 20000000000
DOCUMENT: 2 times the density of water (kg/m^3)

mass_of_soil = CW_Surface_Area*Meth_Zone_Depth*density_of_soil
Meth_Zone_Depth = .4572
DOCUMENT: From Colby's model; expressed in meters

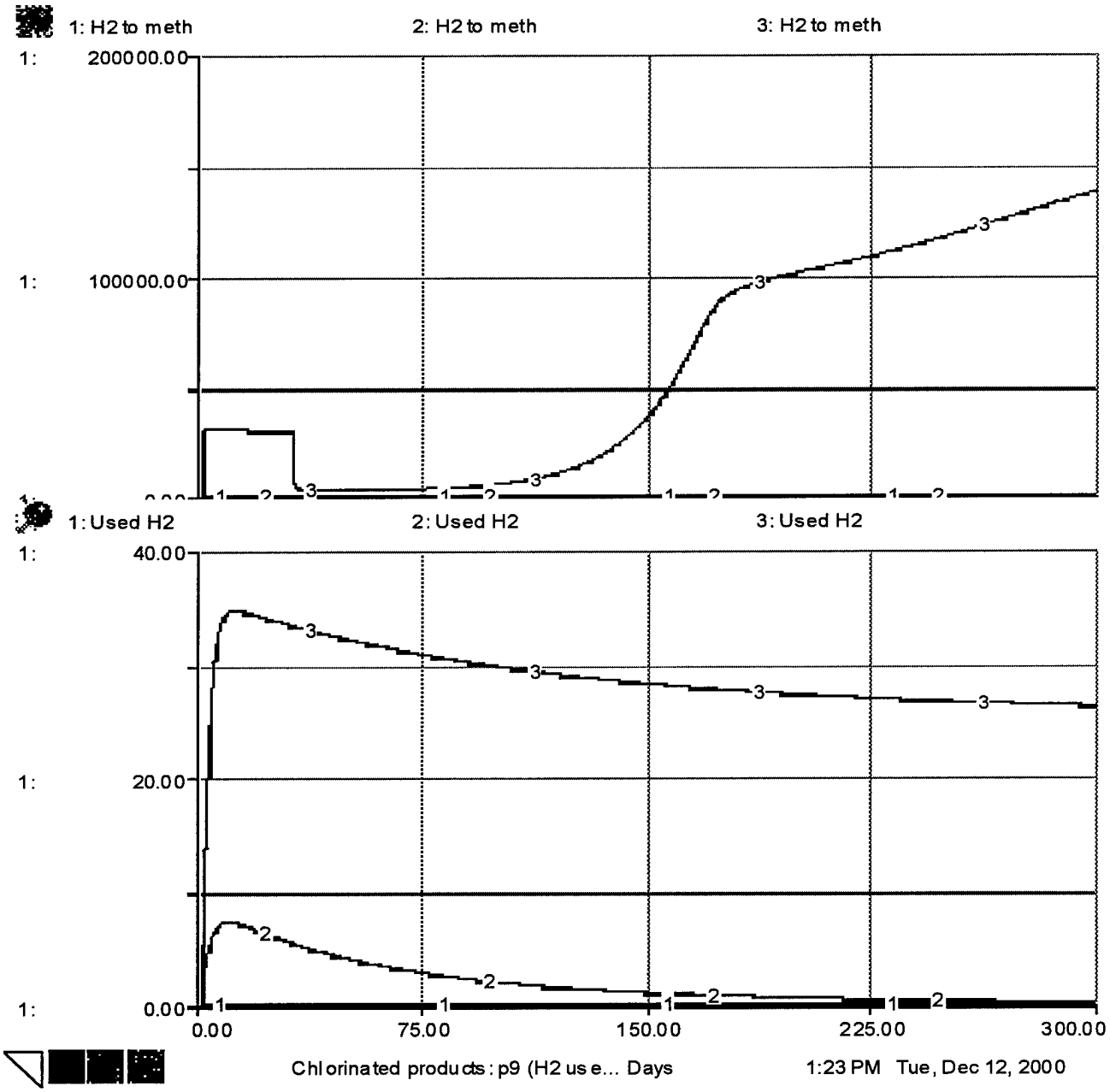
Sediment_Porosity = .5
DOCUMENT: Mineral soils generally range from 45% to 55% total pore space (Mitsch and Gosselink, 1993)

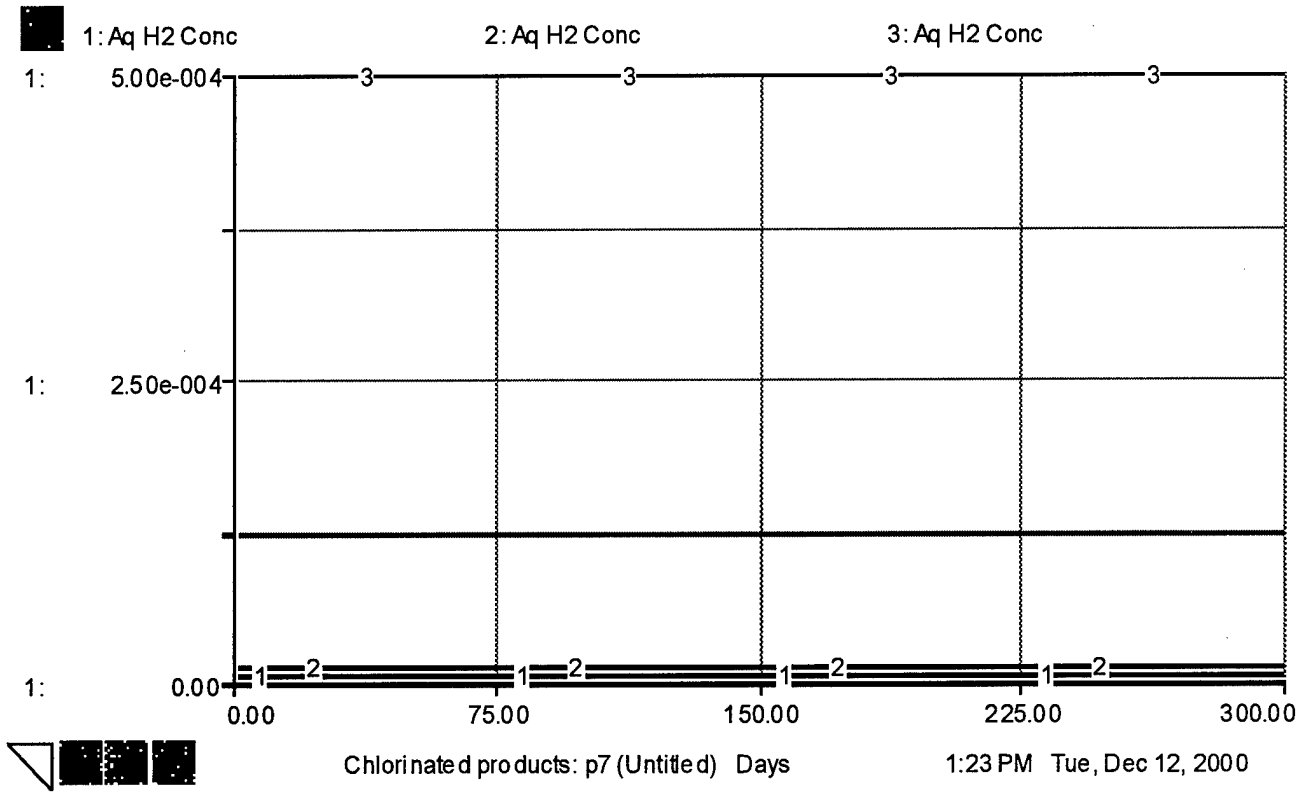
Vol_Meth_Zone = CW_Surface_Area*Meth_Zone_Depth*Sediment_Porosity*1000
DOCUMENT: Water volumein methanogenic zone in liters, converted from cubic meters (1000 L per cubic meter).

Appendix C

Simulation 1 (verification)

Simulation 1 was accomplished by removing the hydrogen stock from the concentration of hydrogen and just inputting a hydrogen concentration to see if the thresholds work.





1. Aq H2 Concentration = 3 E-6 mg/L
2. Aq H2 Concentration = 1 E-5 mg/L
3. Aq H2 Concentration = 5 E-4 mg/L

Dechlorinator Threshold = 4 E-6 mg/L

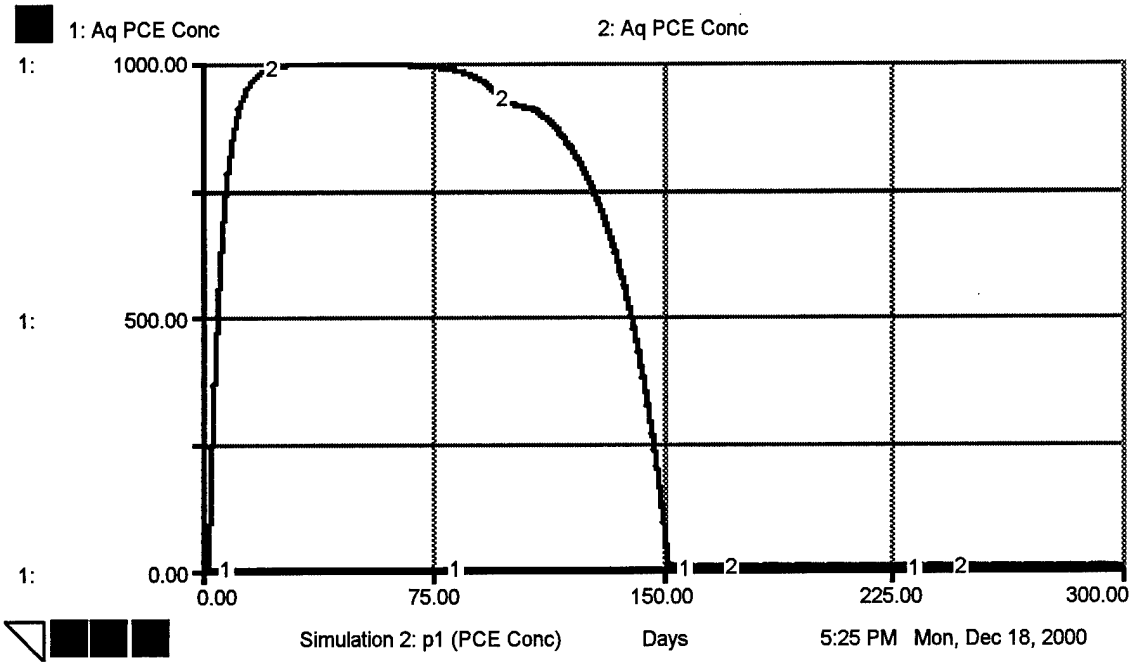
Hydrogenic Methanogenic Threshold = 2.2 E-5 mg/L

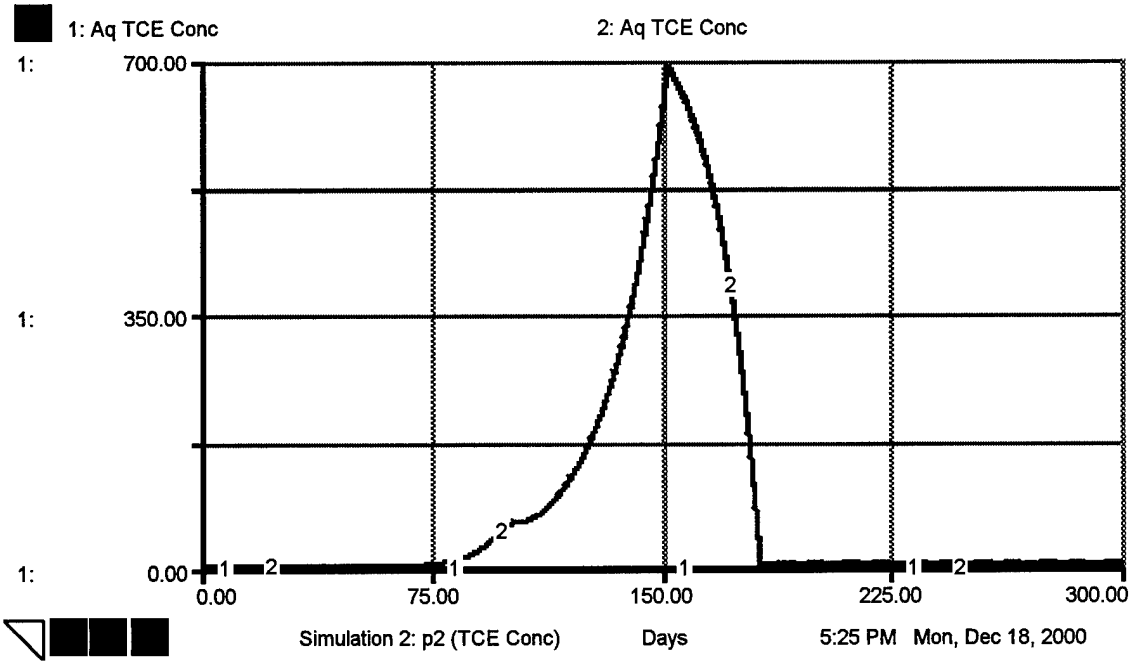
The graphs indicate that the threshold works.

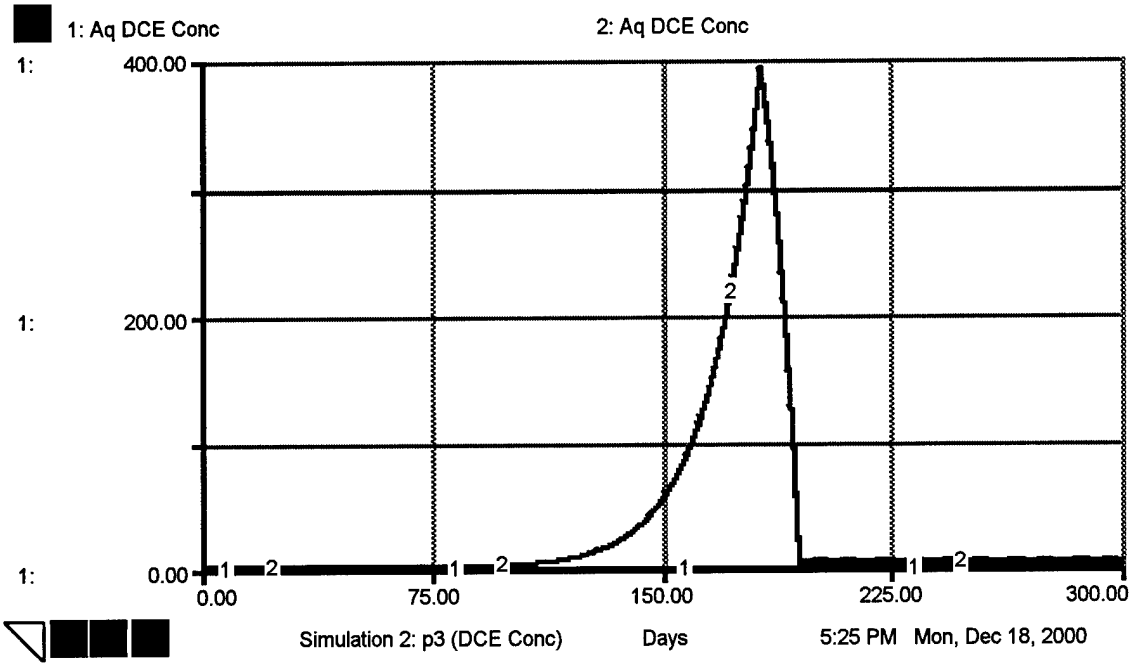
Simulation 2

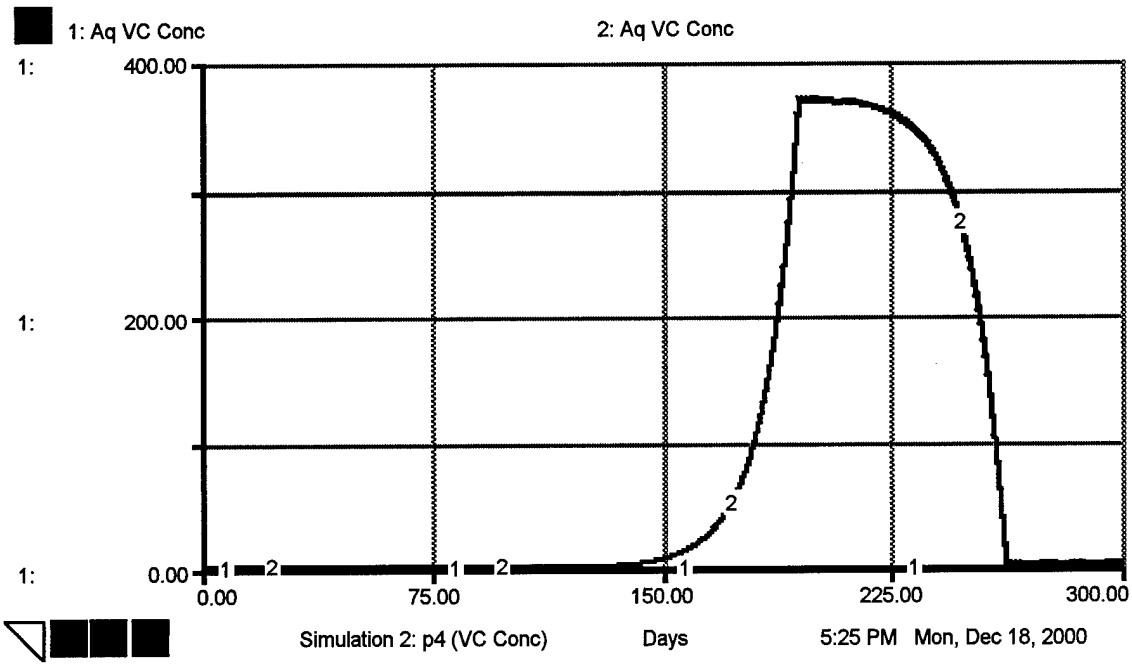
Used to determine how the system would react to extreme concentrations of in incoming concentration. The graphs show reasonable behavior.

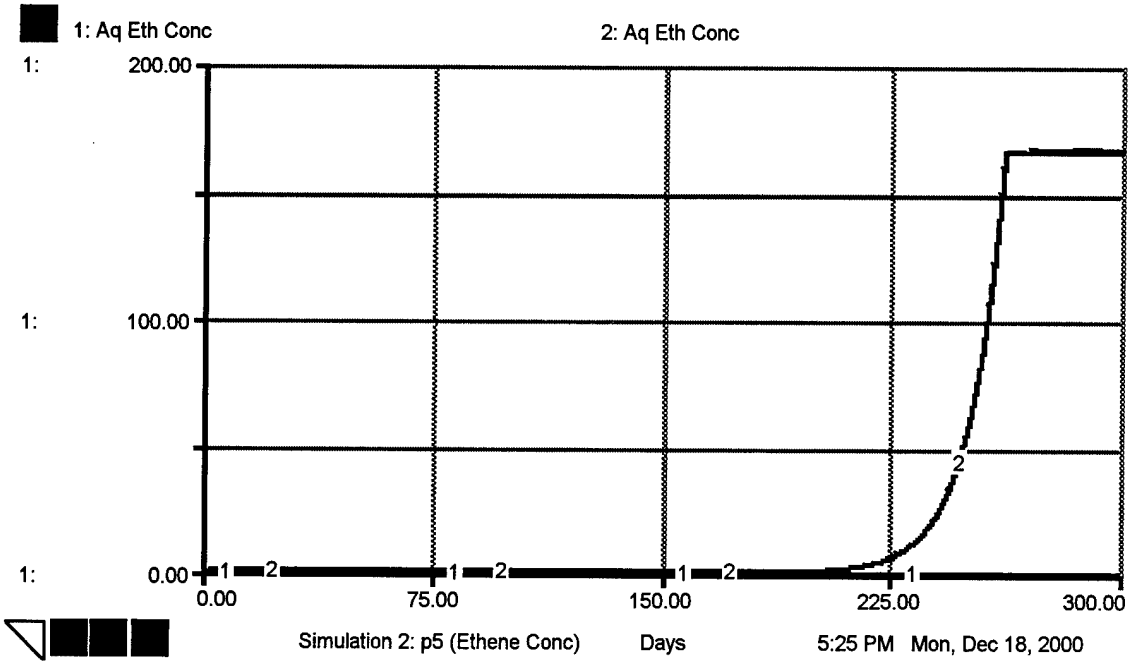
Run	Incoming PCE Concentration
1	0 mg/L
2	1000 mg/L





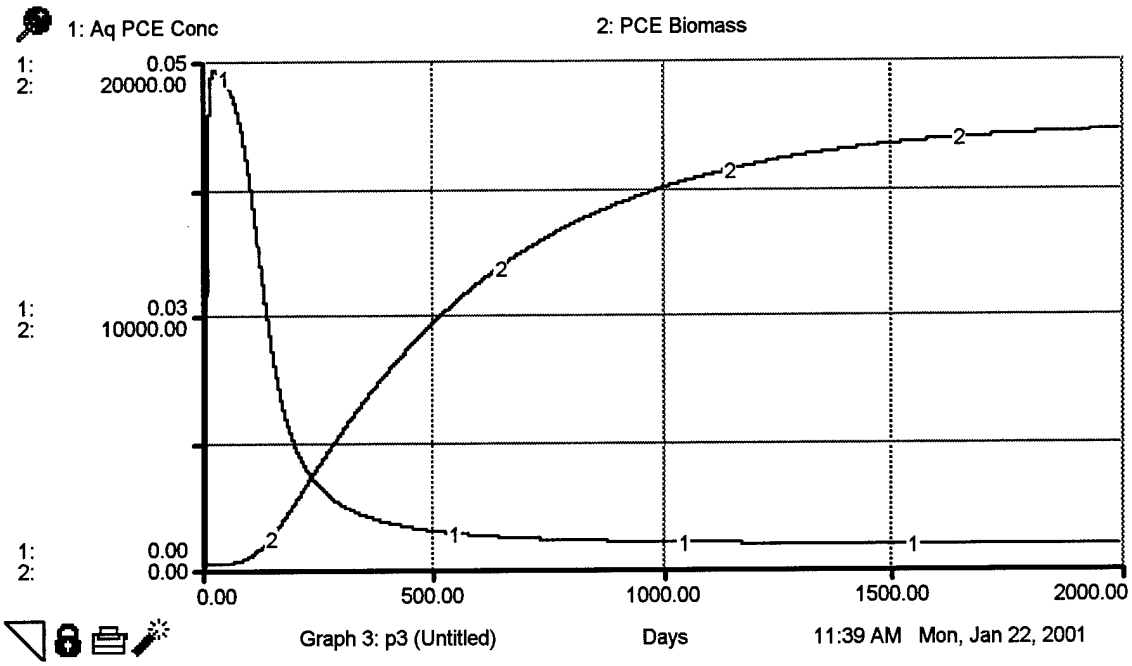

1: Aq DCE Conc
2: Aq DCE Conc
1:
400.00
1:
200.00
1:
0.00
0.00
75.00
150.00
225.00
300.00
Simulation 2: p3 (DCE Conc)
Days
5:25 PM Mon, Dec 18, 2000


1: Aq VC Conc
2: Aq VC Conc
1:
400.00
1:
200.00
1:
0.00
0.00
75.00
150.00
225.00
300.00
Simulation 2: p4 (VC Conc)
Days
5:25 PM Mon, Dec 18, 2000


1: Aq Eth Conc
2: Aq Eth Conc
1:
200.00
1:
100.00
1:
0.00
0.00
75.00
150.00
225.00
300.00
Simulation 2: p5 (Ethene Conc)
Days
5:25 PM Mon, Dec 18, 2000

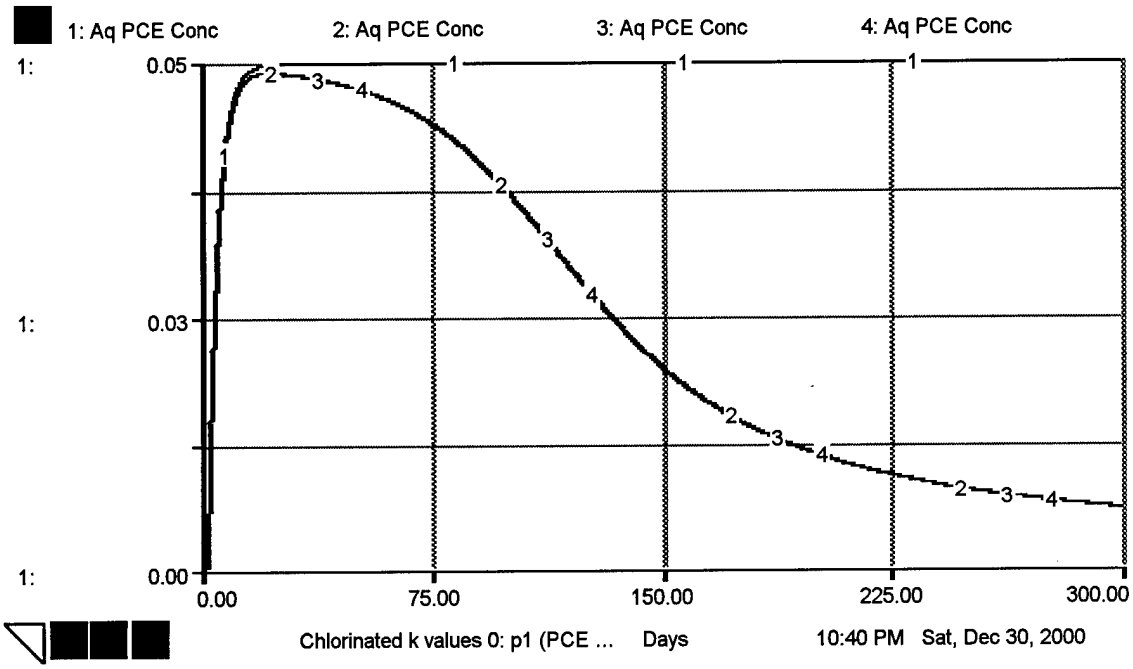
Simulation 3

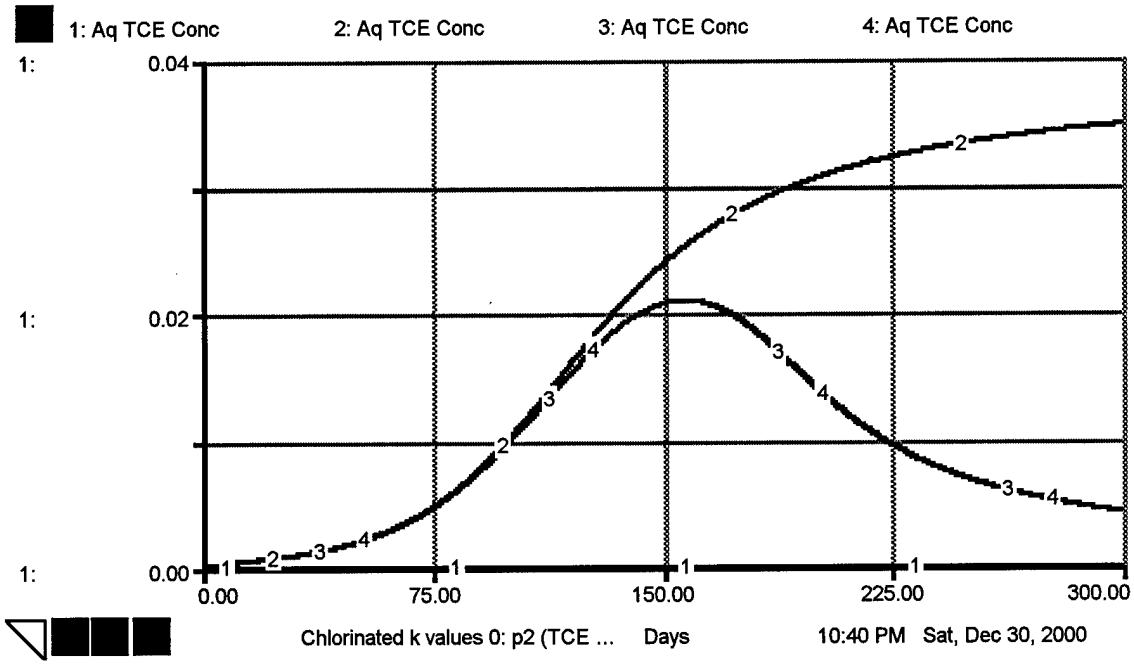
Test to see if the model can reproduce the hypothetical behavior of the system. The simulation was run with the initial values of the model.

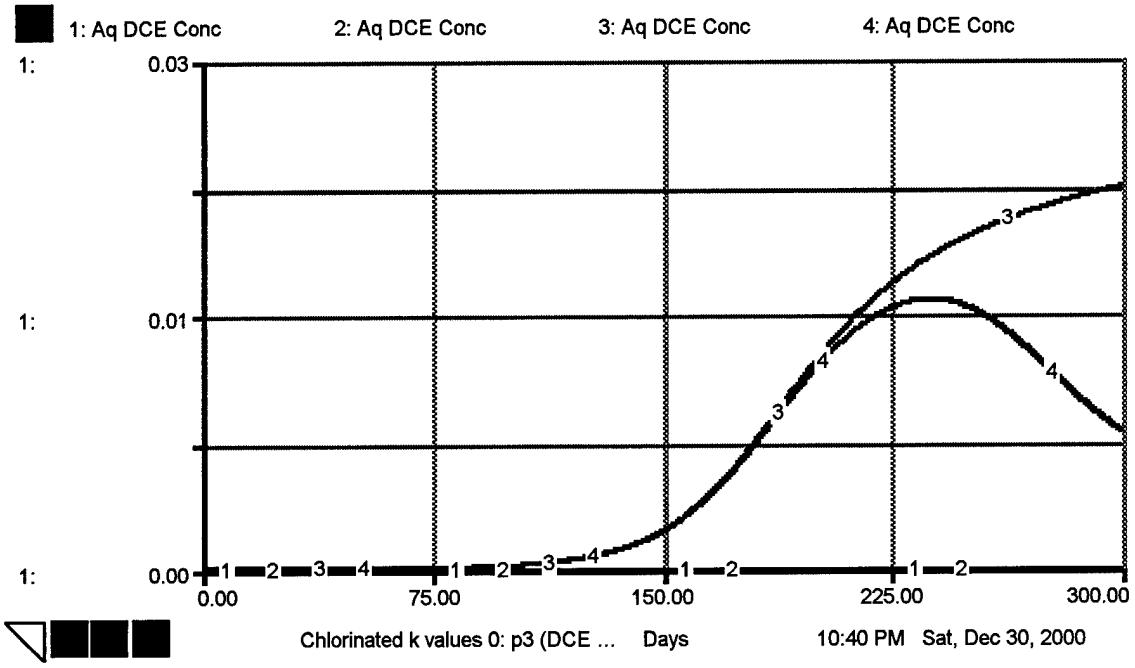


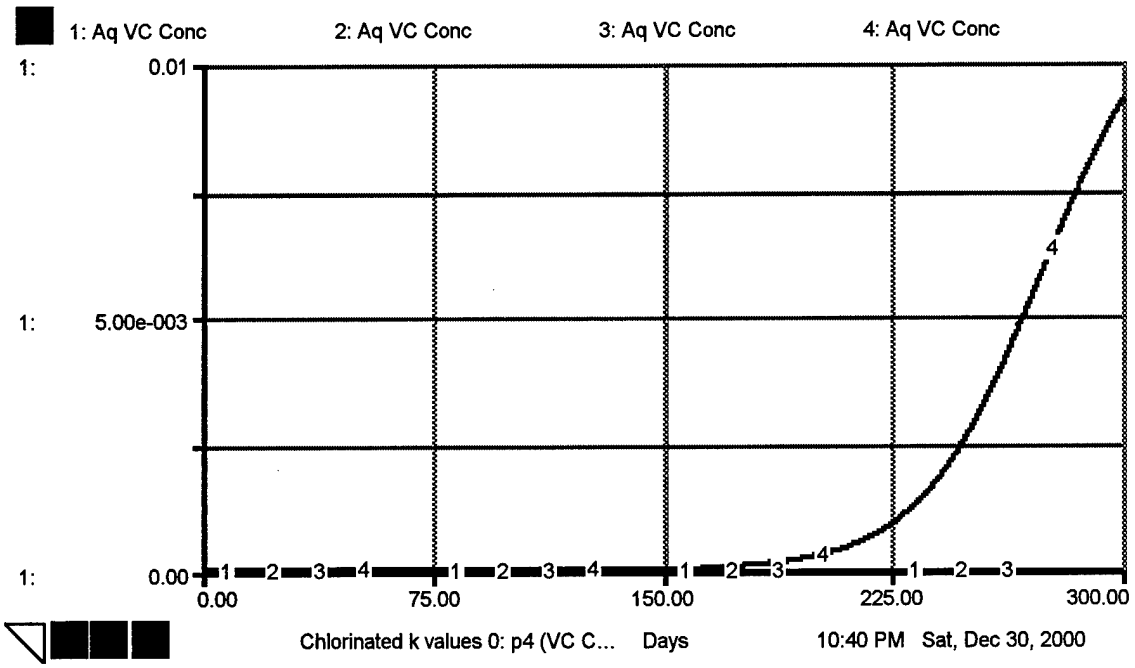
Simulation 4

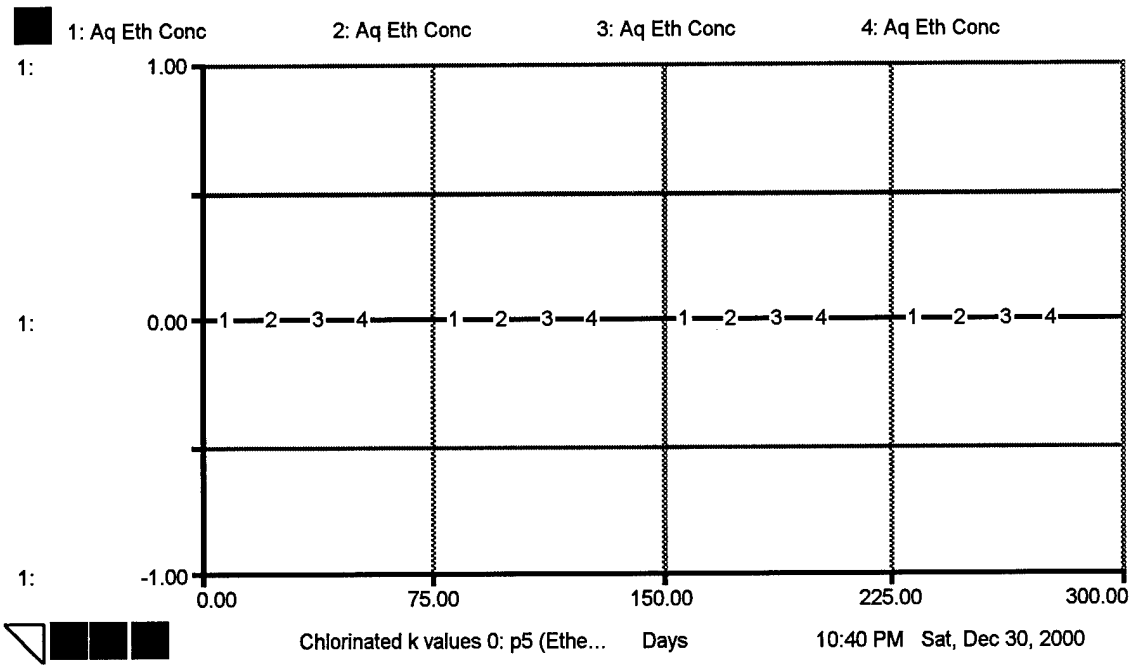
1. PCE utilization rate = 0
2. TCE utilization rate = 0
3. DCE utilization rate = 0
4. VC utilization rate = 0

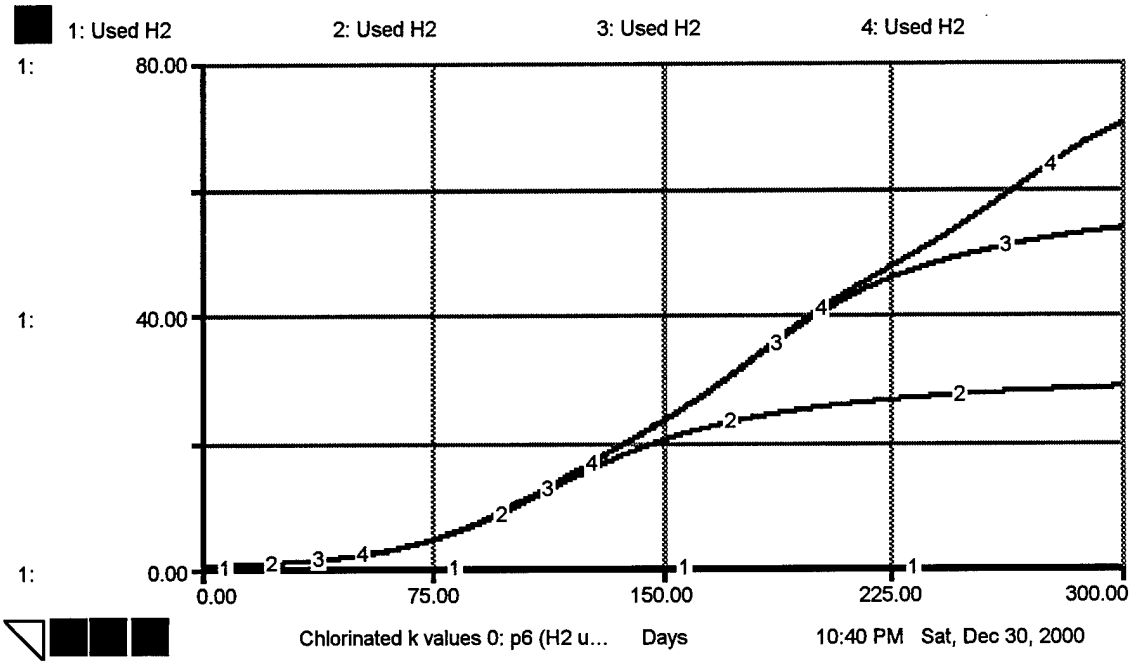




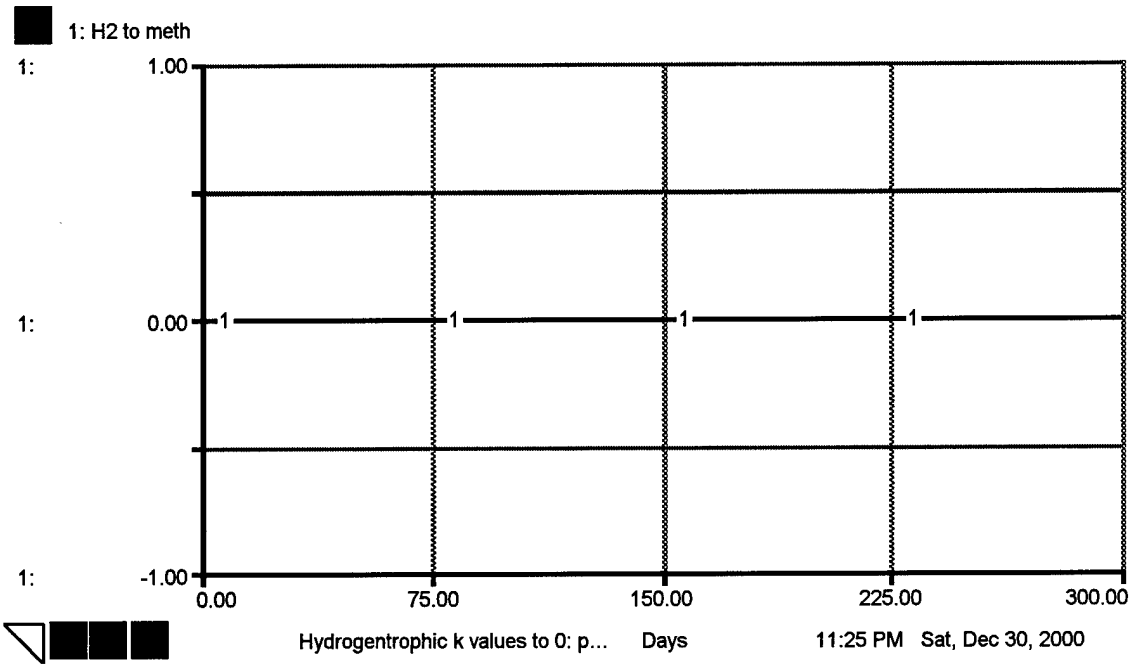

1: Aq DCE Conc
2: Aq DCE Conc
3: Aq DCE Conc
4: Aq DCE Conc
1:
0.03
1:
0.01
1:
0.00
0.00
75.00
150.00
225.00
300.00
Chlorinated k values 0: p3 (DCE ...
Days
10:40 PM Sat, Dec 30, 2000


1: Aq VC Conc
2: Aq VC Conc
3: Aq VC Conc
4: Aq VC Conc
1:
0.01
1:
5.00e-003
1:
0.00
0.00
75.00
150.00
225.00
300.00
Chlorinated k values 0: p4 (VC C...
Days
10:40 PM Sat, Dec 30, 2000

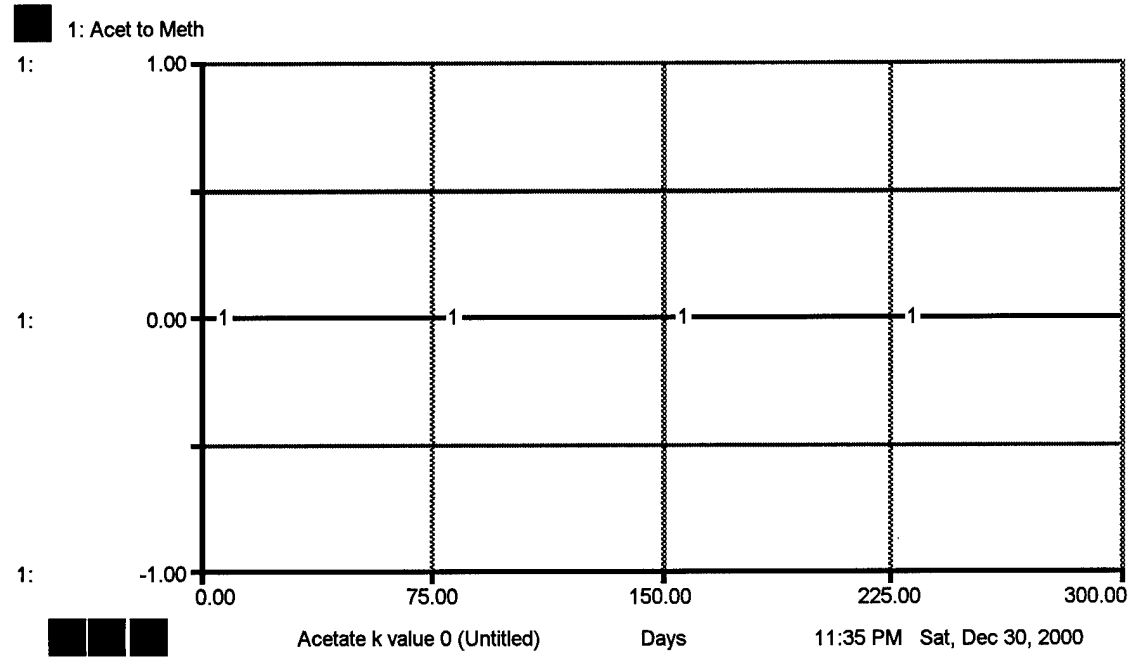

1: Aq Eth Conc
2: Aq Eth Conc
3: Aq Eth Conc
4: Aq Eth Conc
1:
1.00
1:
0.00
1:
-1.00
0.00
75.00
150.00
225.00
300.00
Chlorinated k values 0: p5 (Ethe...
Days
10:40 PM Sat, Dec 30, 2000


1: Used H2
2: Used H2
3: Used H2
4: Used H2
1:
80.00
1:
40.00
1:
0.00
0.00
75.00
150.00
225.00
300.00
Chlorinated k values 0: p6 (H2 u...
Days
10:40 PM Sat, Dec 30, 2000

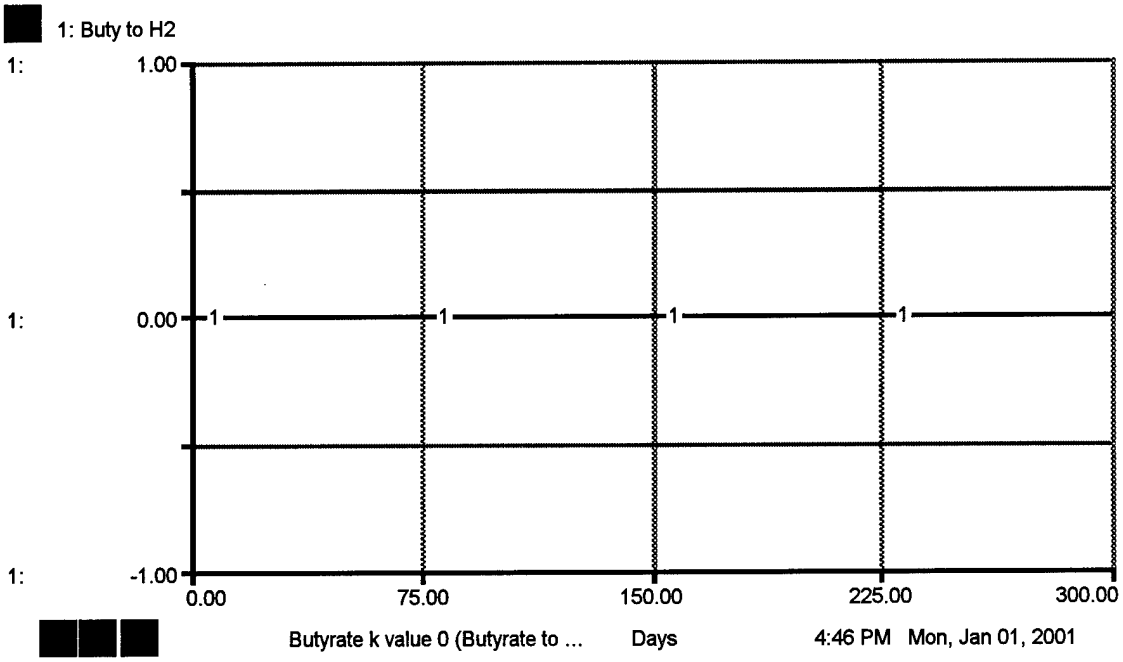
Hydrogentrophic k value to 0



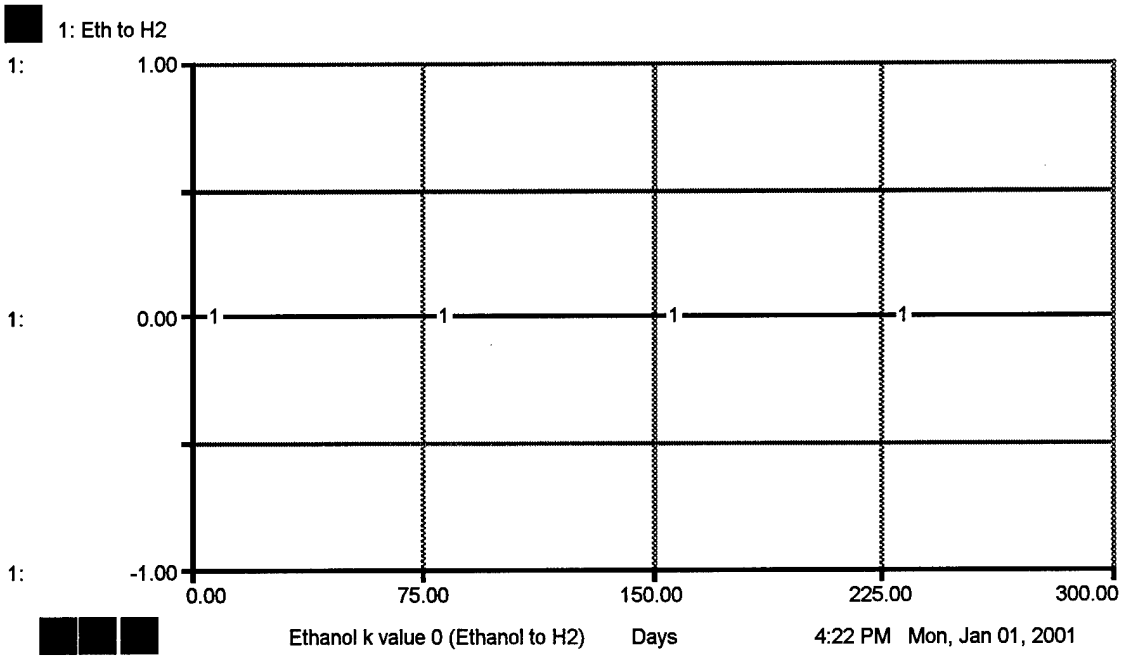
Acetate K value = 0



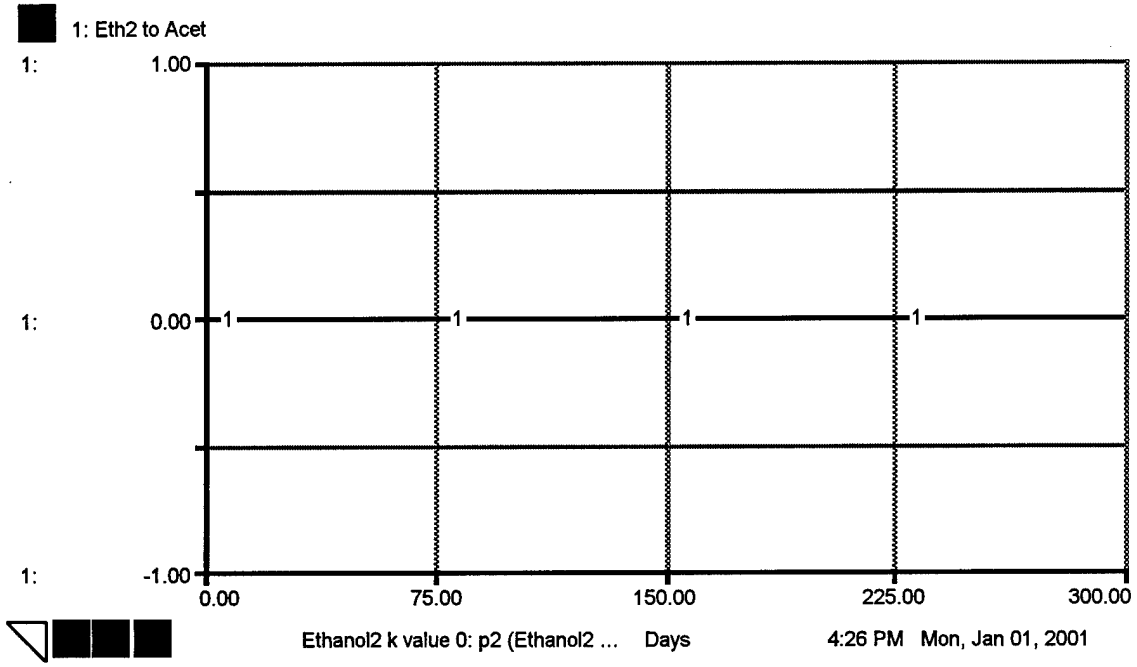
Butyrate k value = 0



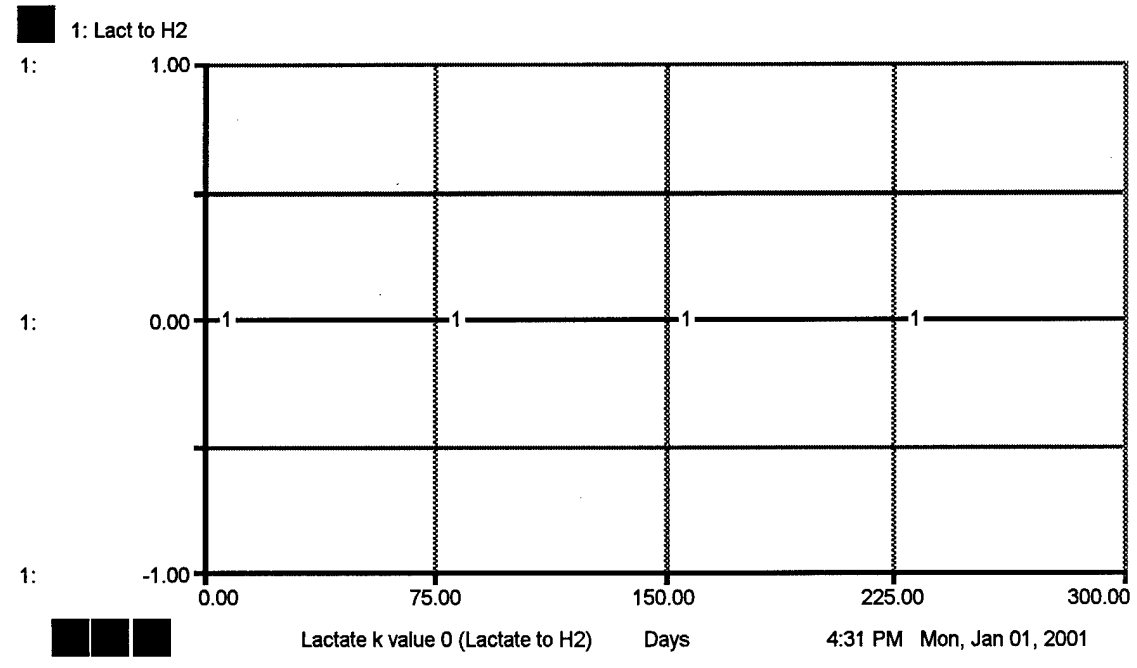
Ethanol k value = 0



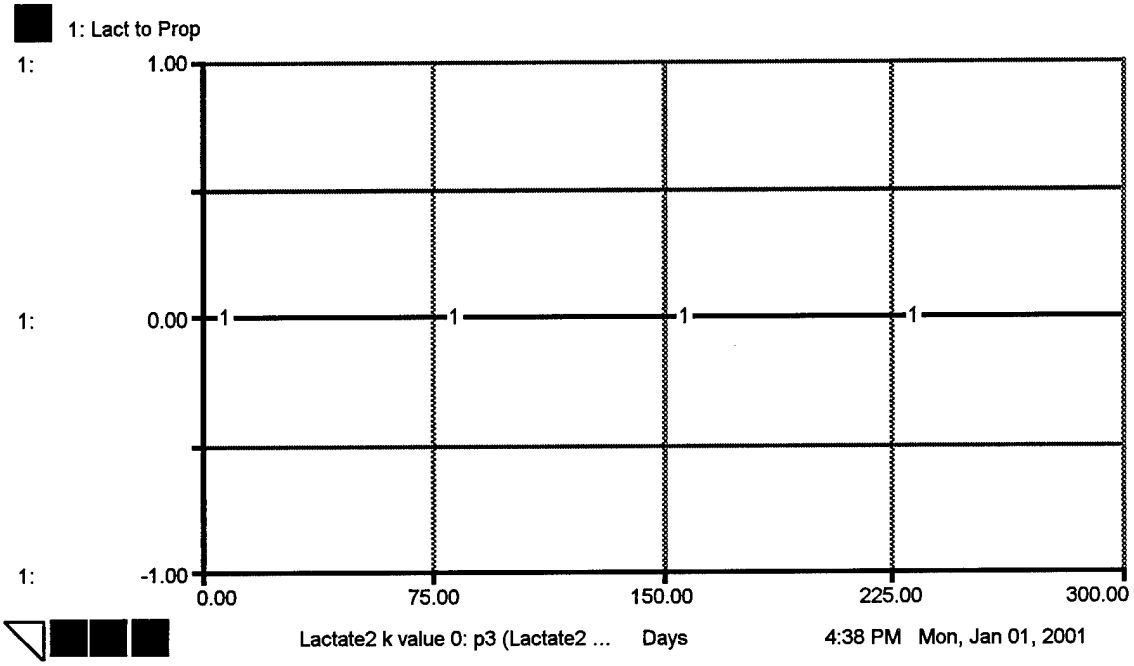
Ethanol 2 k value = 0



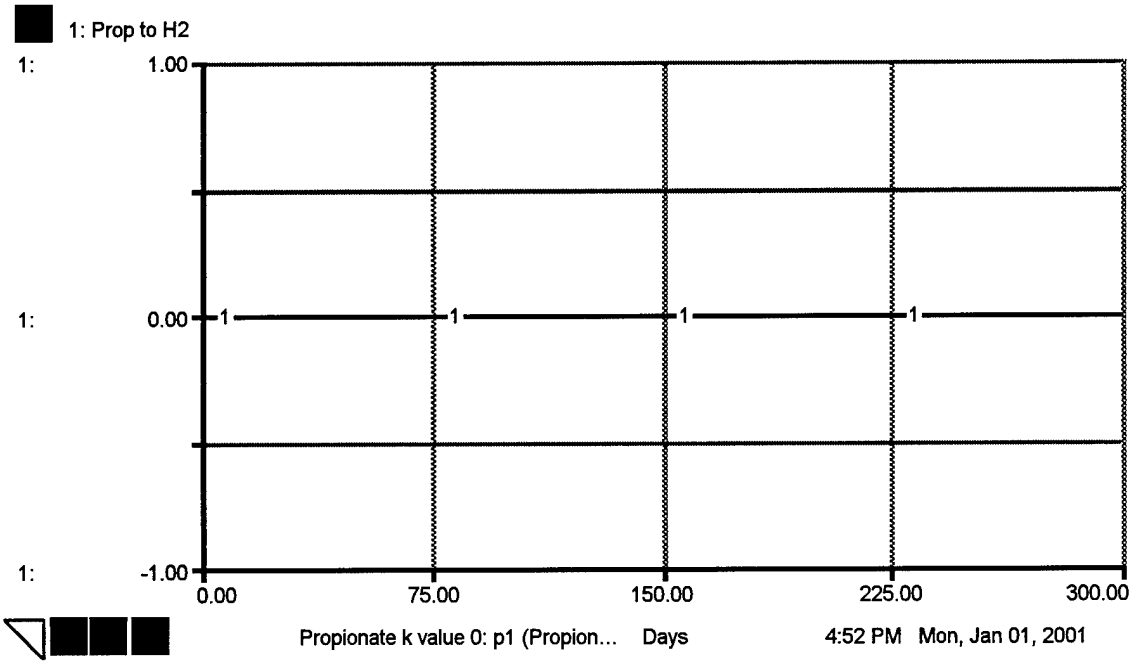
Lactate k value = 0



Lactate 2 k value = 0



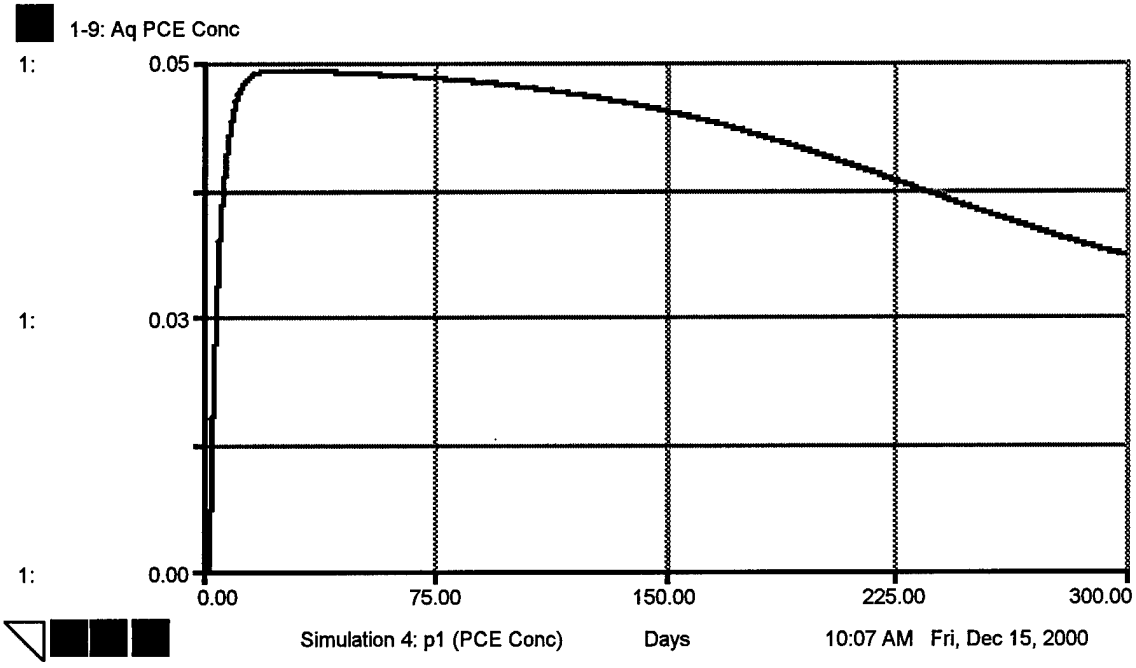
Propionate k value = 0



Simulation 5

Sensitivity analysis on the $Ks(H_2)$ values for PCE, TCE, DCE, and VC.

Run	$Ks(H_2)$
1	all low values
2	PCE = 1E-4 mg H_2/L
3	PCE = 2E-4 mg H_2/L
4	TCE = 1E-4 mg H_2/L
5	TCE = 2E-4 mg H_2/L
6	DCE = 1E-4 mg H_2/L
7	DCE = 2E-4 mg H_2/L
8	VC = 1E-4 mg H_2/L
9	VC = 2E-4 mg H_2/L

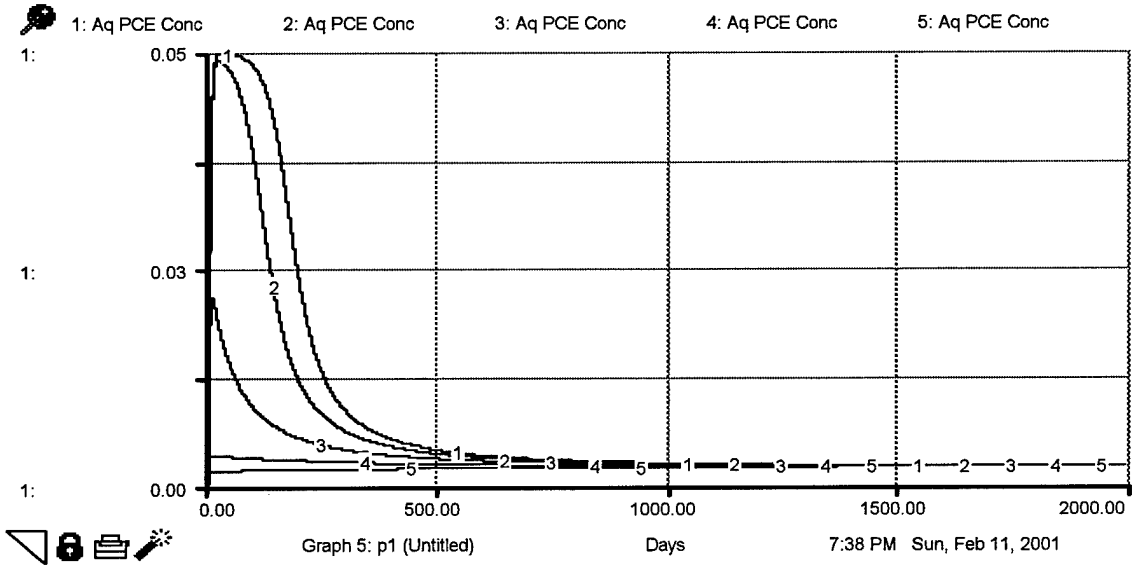


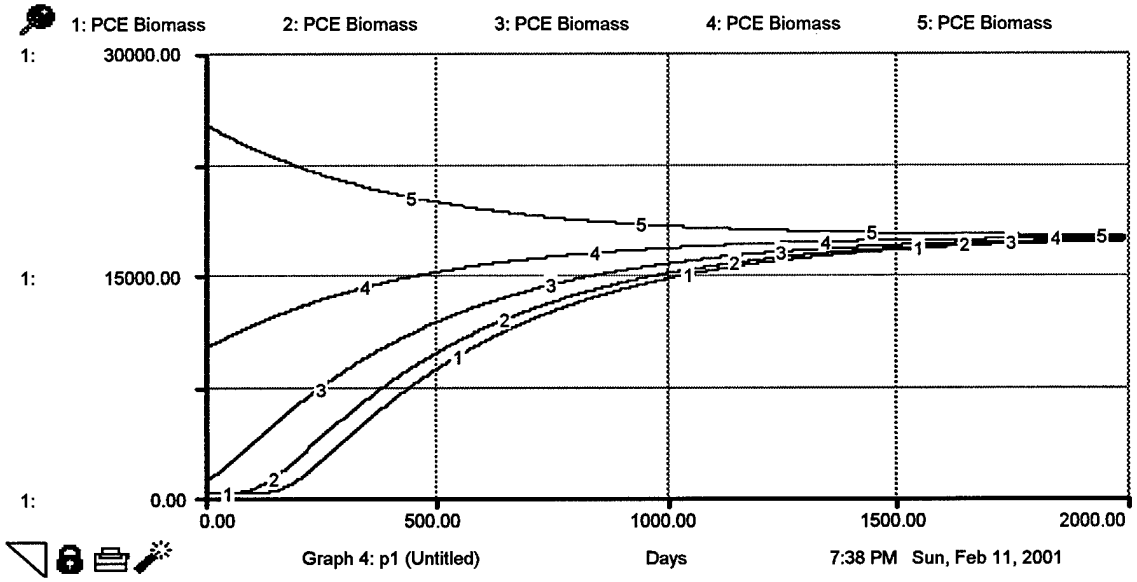
Simulation 6

The initial biomass populations are all held constant except for the one that is being changed.

PCE Initial Biomass

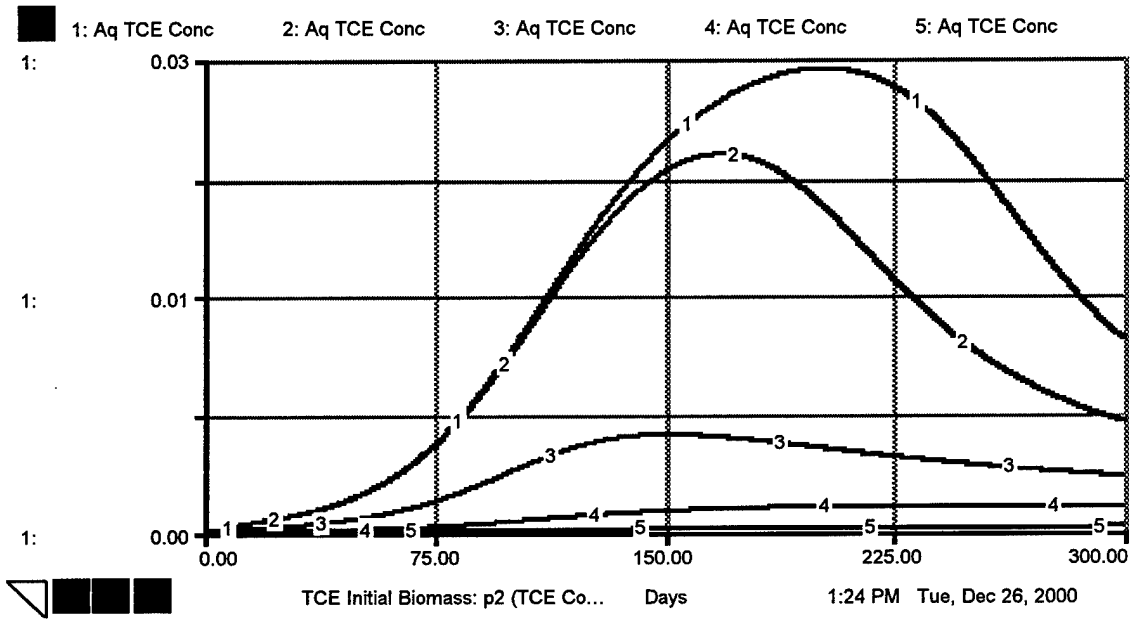
Run	PCE Initial Biomass (mg of VSS)
1	1
2	10
3	1000
4	10,000
5	25,000

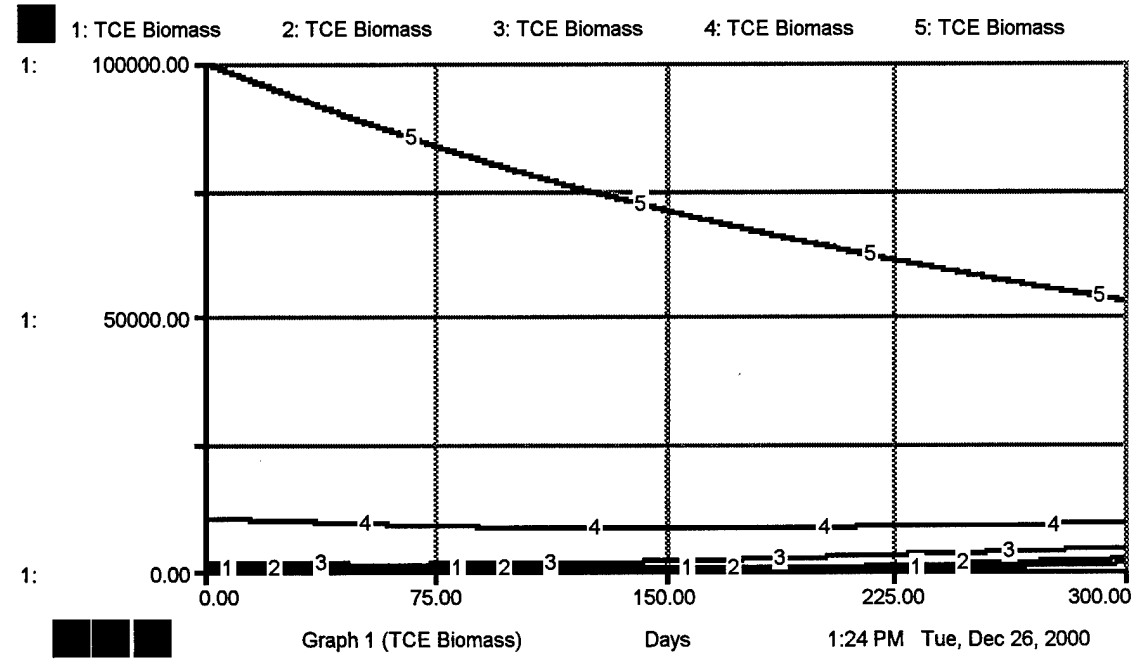




TCE Initial Biomass

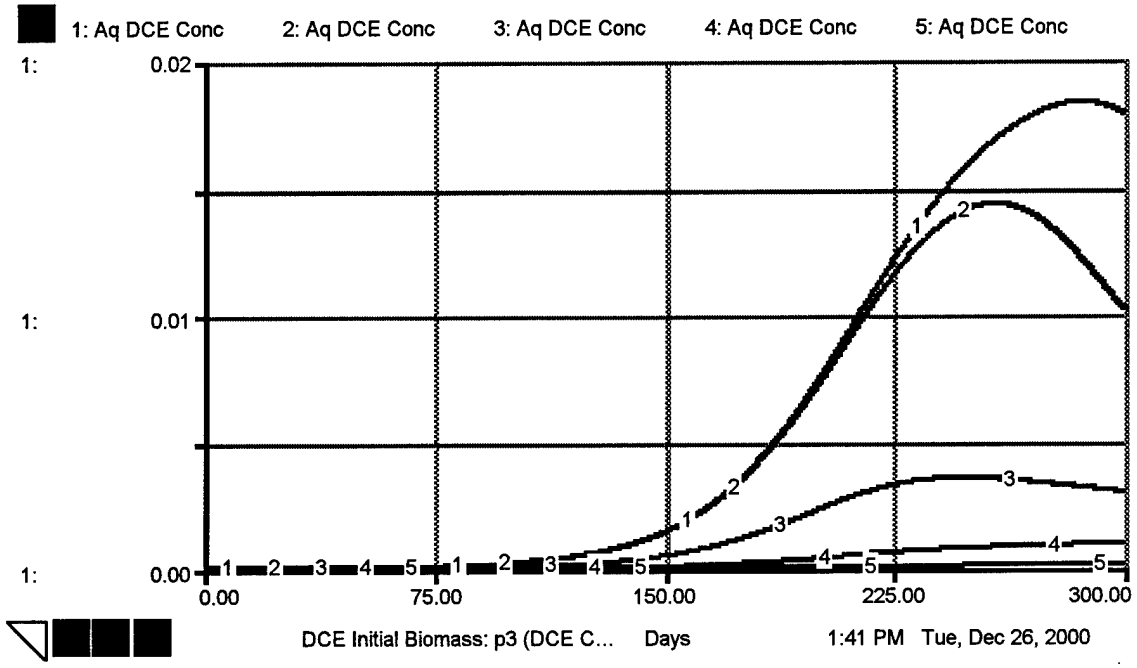
Run	TCE Initial Biomass (mg of VSS)
1	1
2	10
3	1000
4	10,000
5	100,000

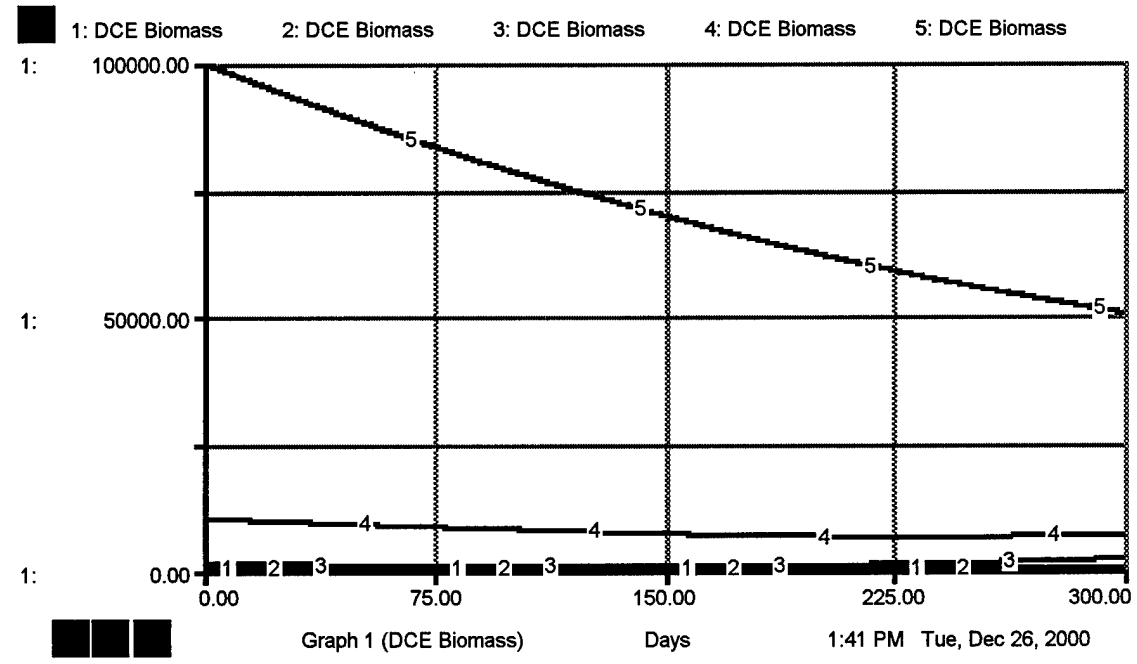




DCE initial biomass

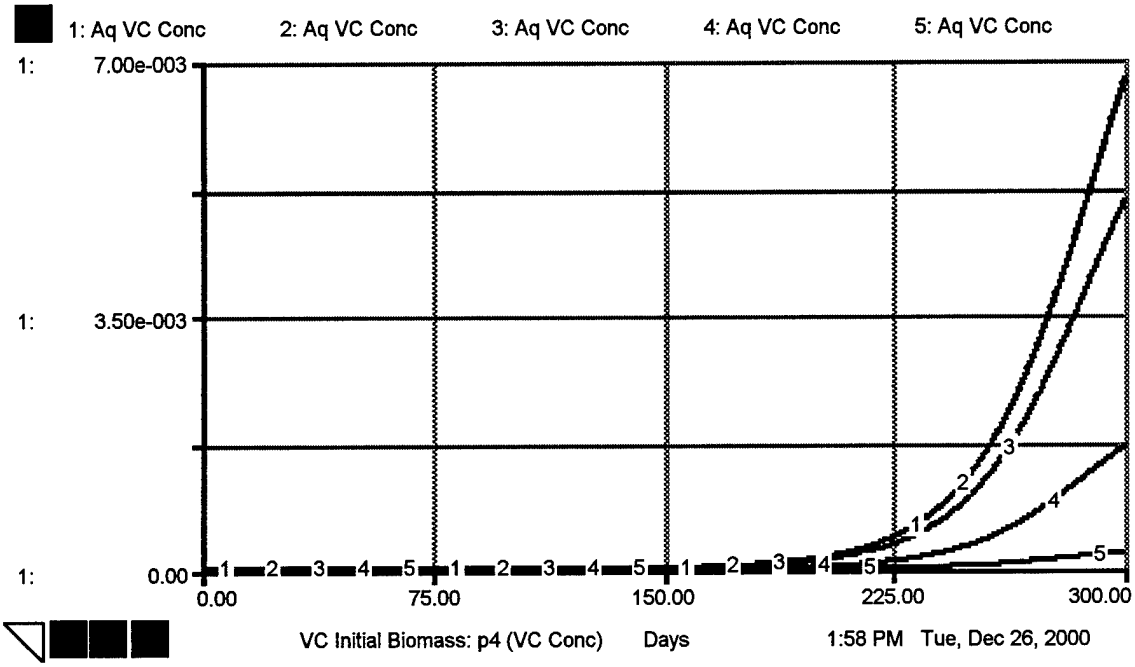
Run	DCE Initial Biomass (mg of VSS)
1	1
2	10
3	1000
4	10,000
5	25,000

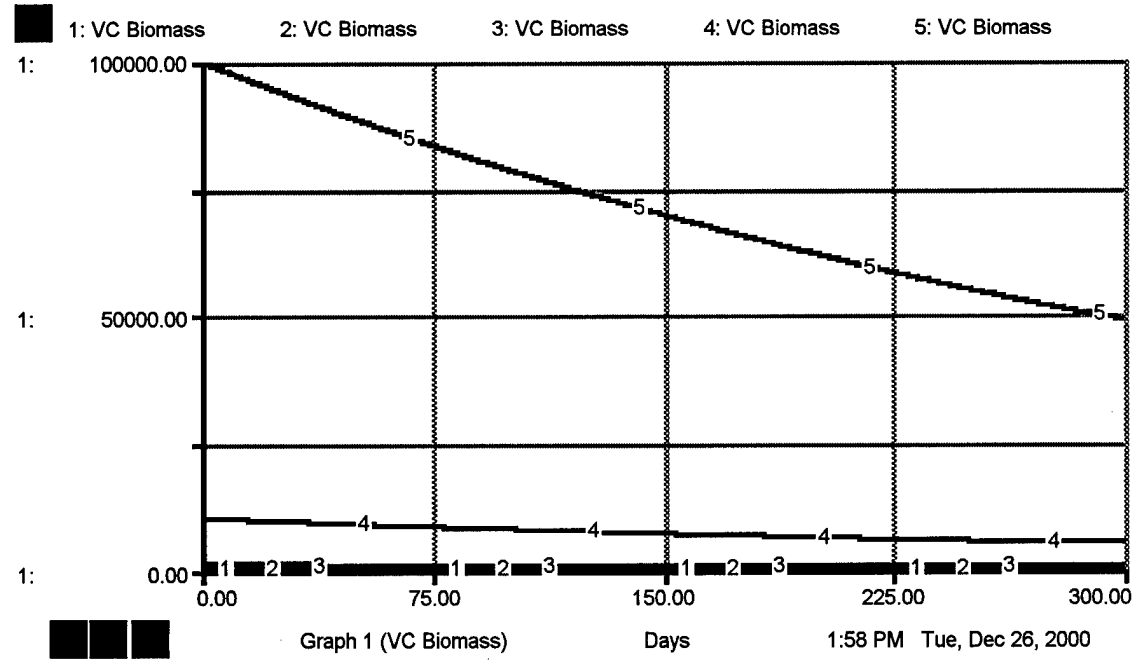




VC Initial Biomass

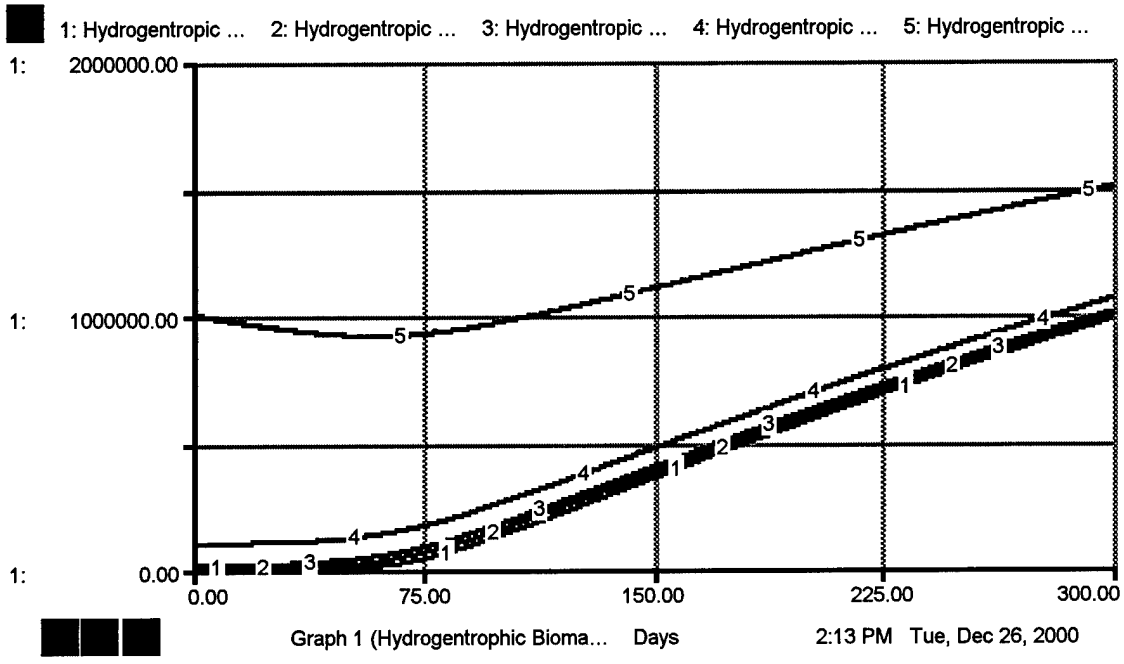
Run	VC Initial Biomass (mg of VSS)
1	1
2	10
3	1000
4	10,000
5	25,000

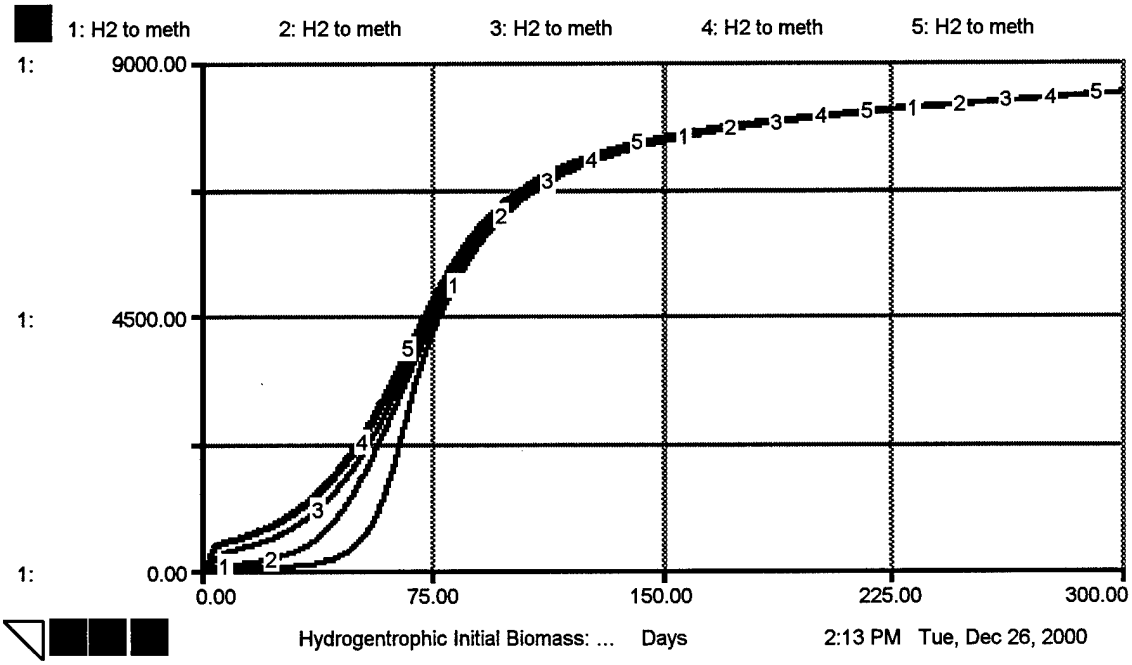


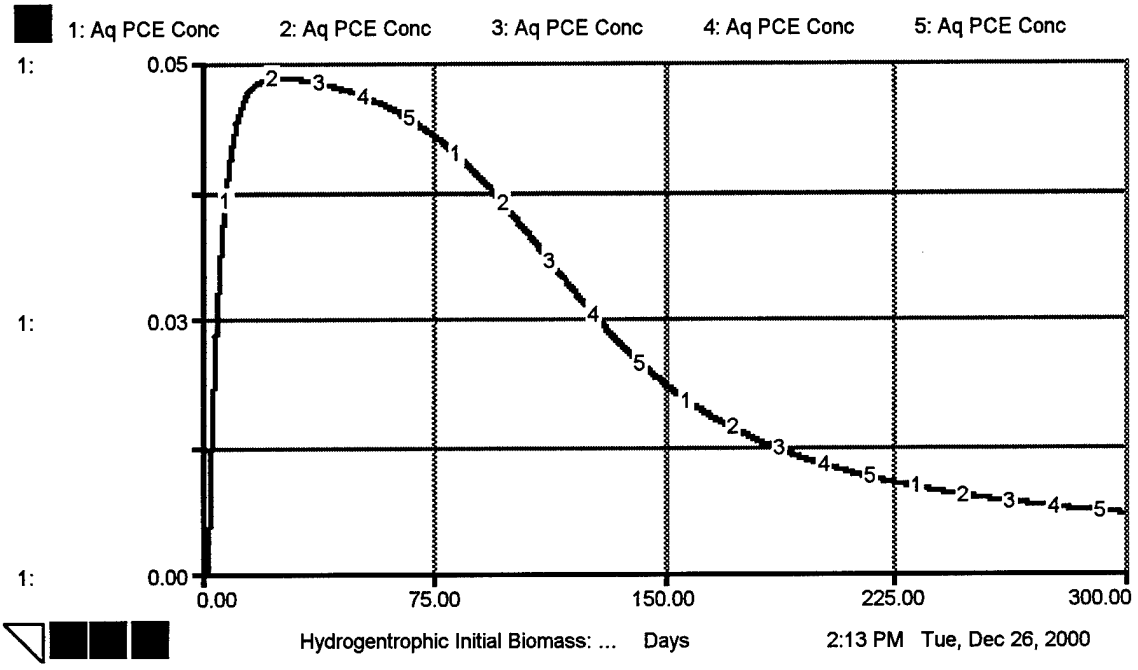


Initial biomass of hydrogenotrophic methanogens

Run	Hydrogenotrophic Methanogenic Initial Biomass (mg of VSS)
1	100
2	1000
3	10,000
4	100,000
5	1,000,000

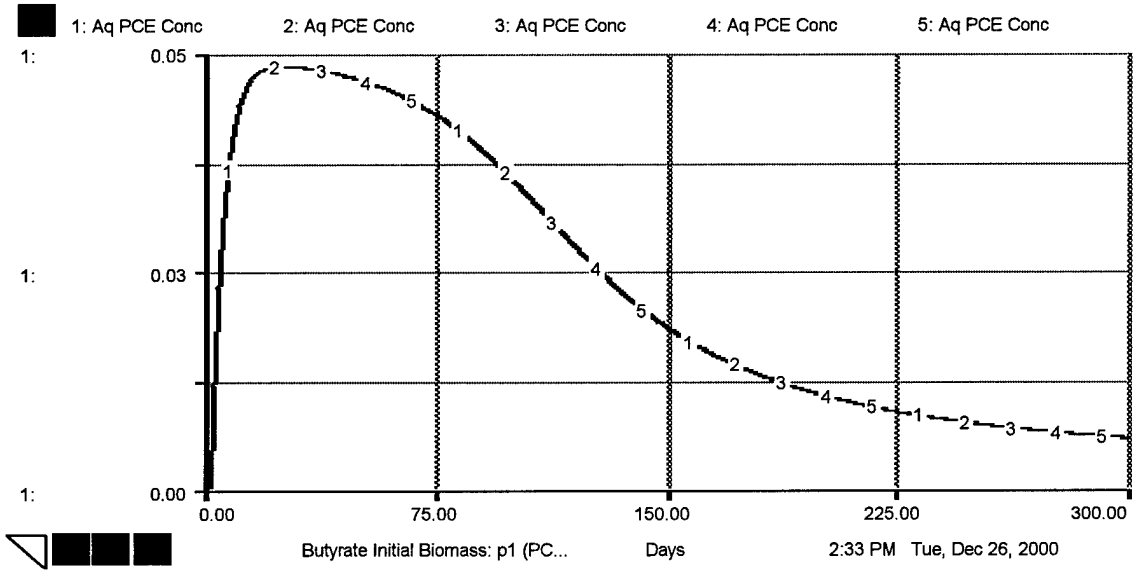


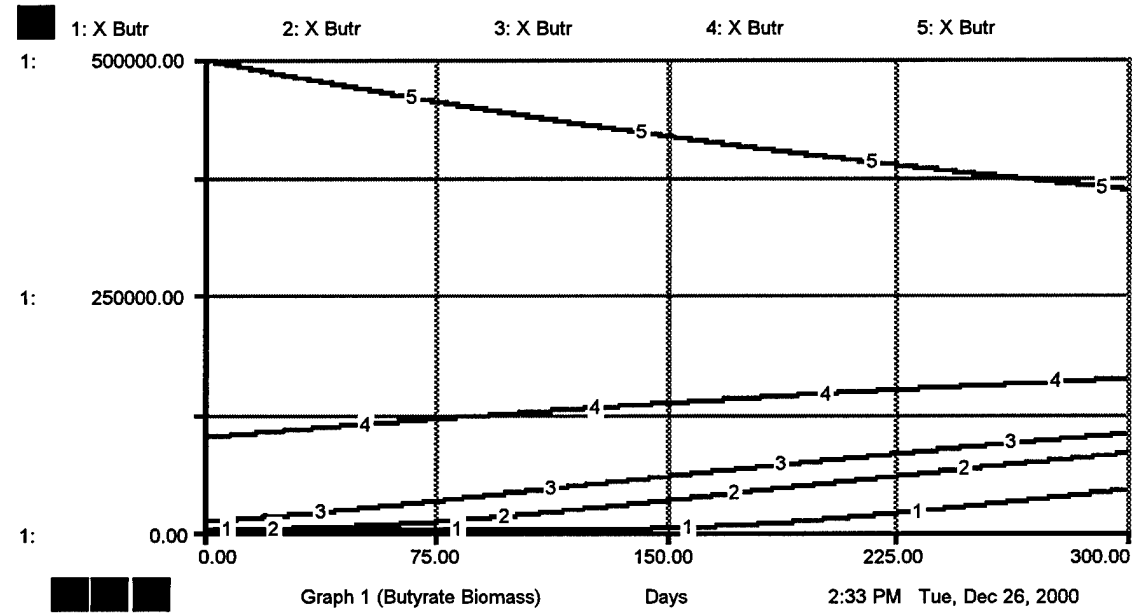



1: Aq PCE Conc
2: Aq PCE Conc
3: Aq PCE Conc
4: Aq PCE Conc
5: Aq PCE Conc
1:
0.05
1:
0.03
1:
0.00
0.00
75.00
150.00
225.00
300.00
Hydrogentrophic Initial Biomass: ...
Days
2:13 PM Tue, Dec 26, 2000

Fermentation initial biomass
Butyrate

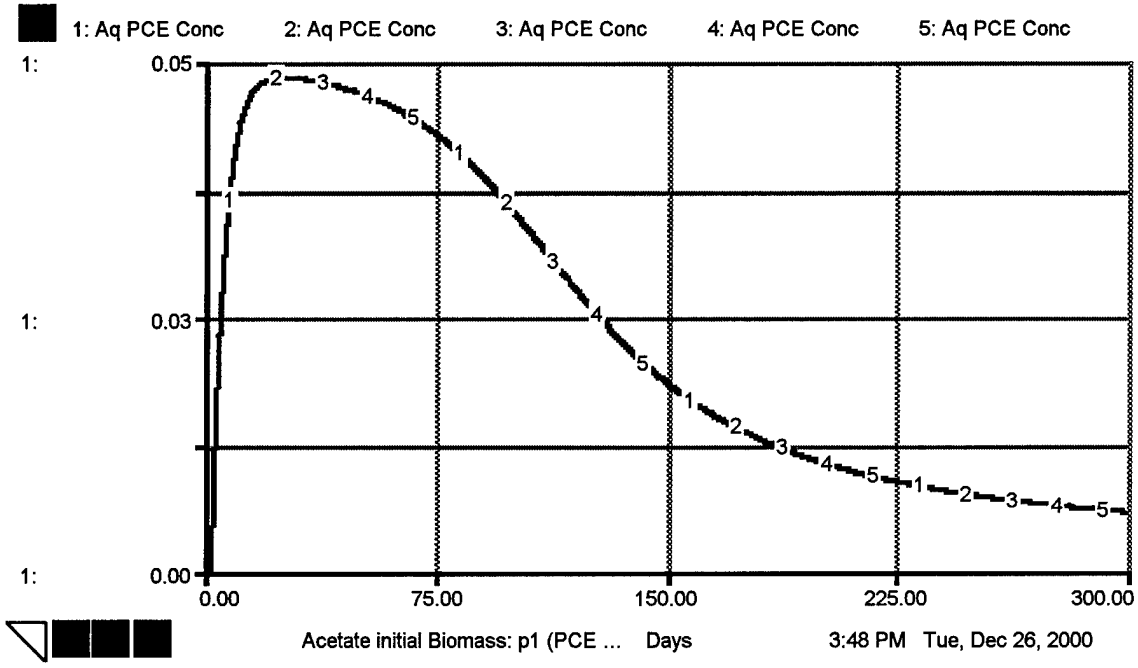
Run	Butyrate Initial Biomass (mg of VSS)
1	10
2	1000
3	10,000
4	100,000
5	500,000

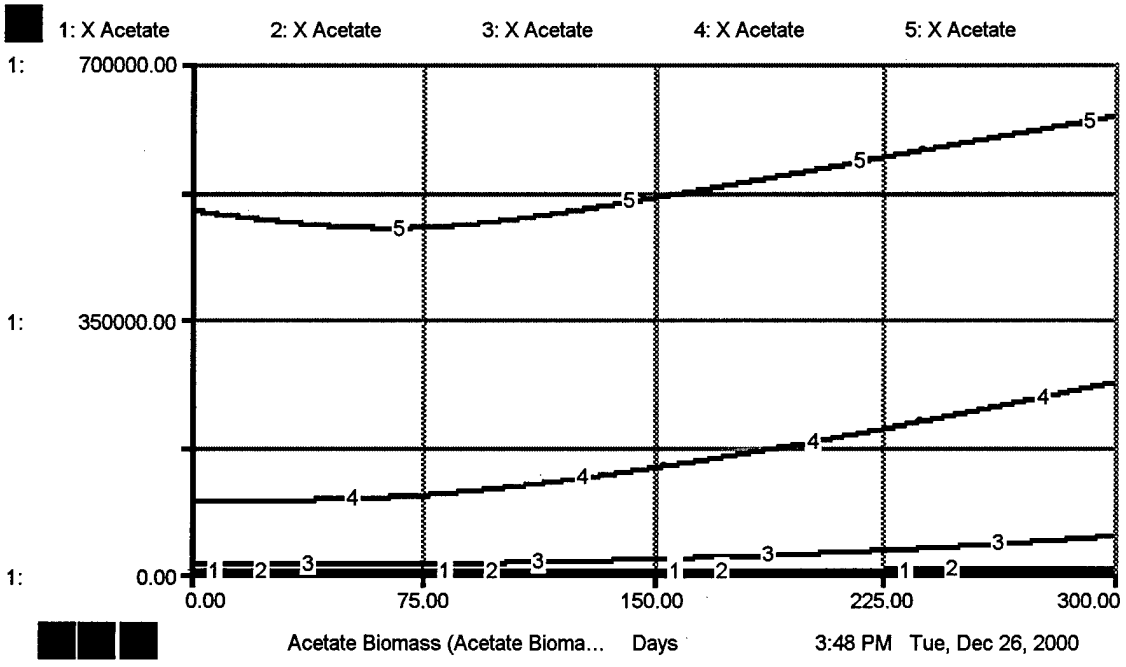




Acetate initial biomass

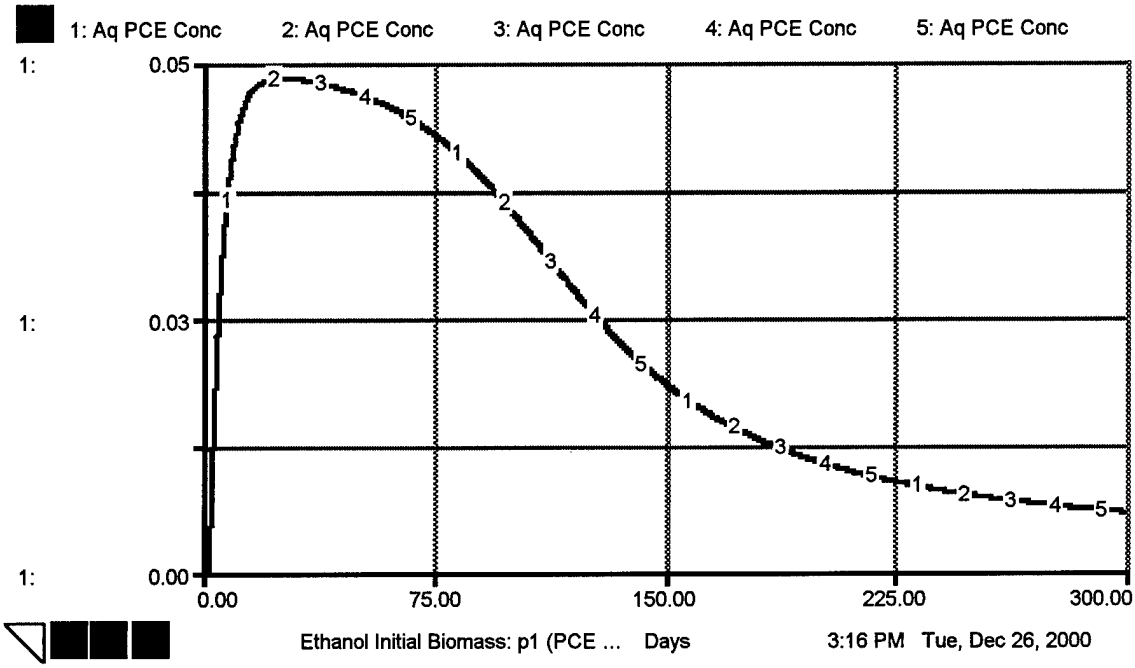
Run	Acetate Initial Biomass (mg of VSS)
1	10
2	1000
3	10,000
4	100,000
5	500,000

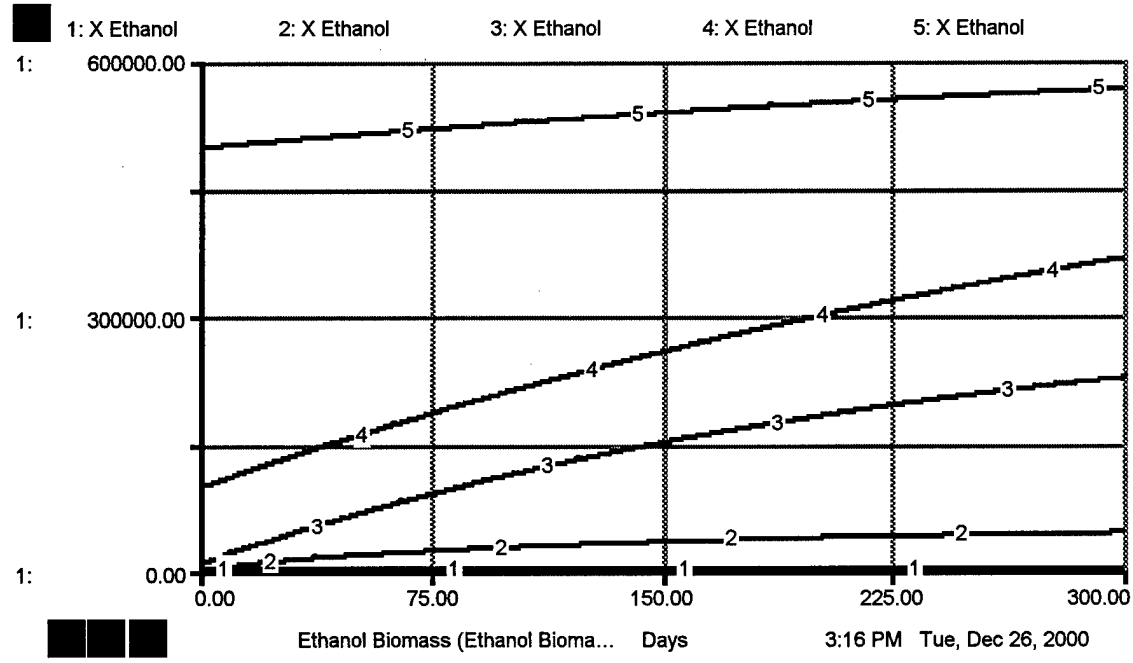




Ethanol Initial Biomass

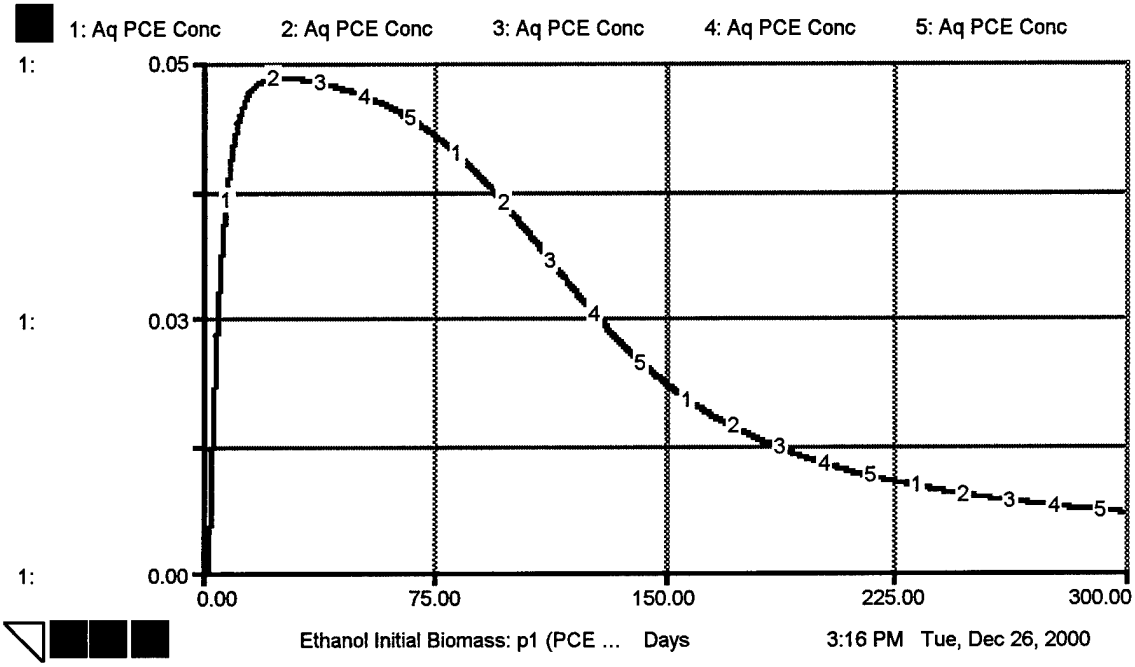
Run	Ethanol Initial Biomass (mg of VSS)
1	10
2	1000
3	10,000
4	100,000
5	500,000

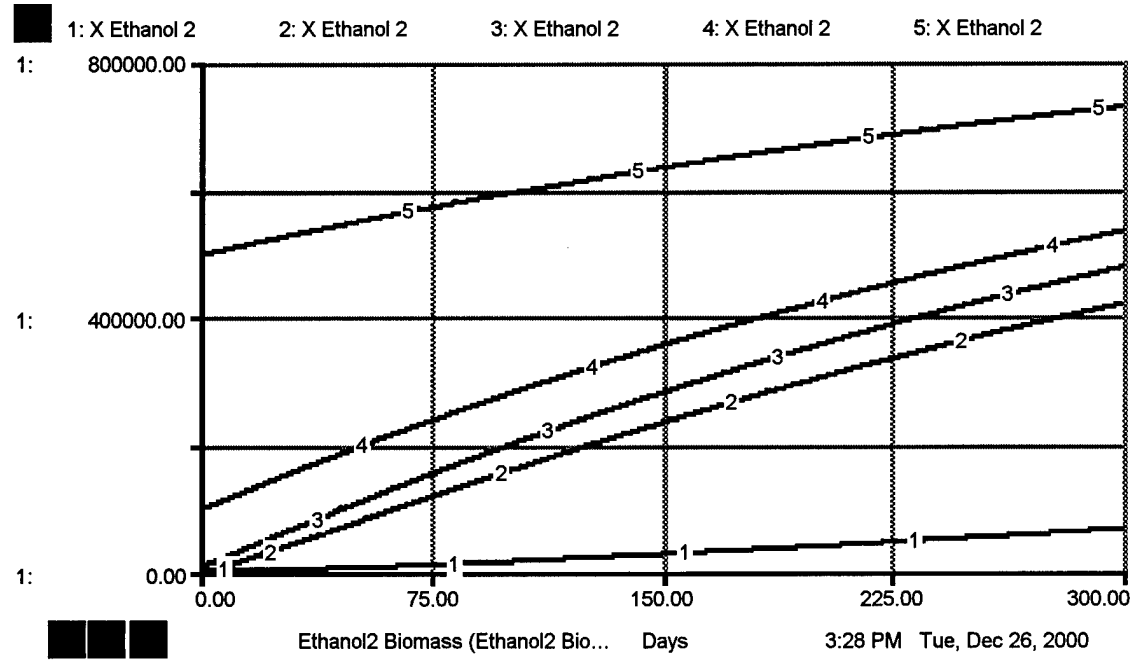




Ethanol 2 Initial Biomass

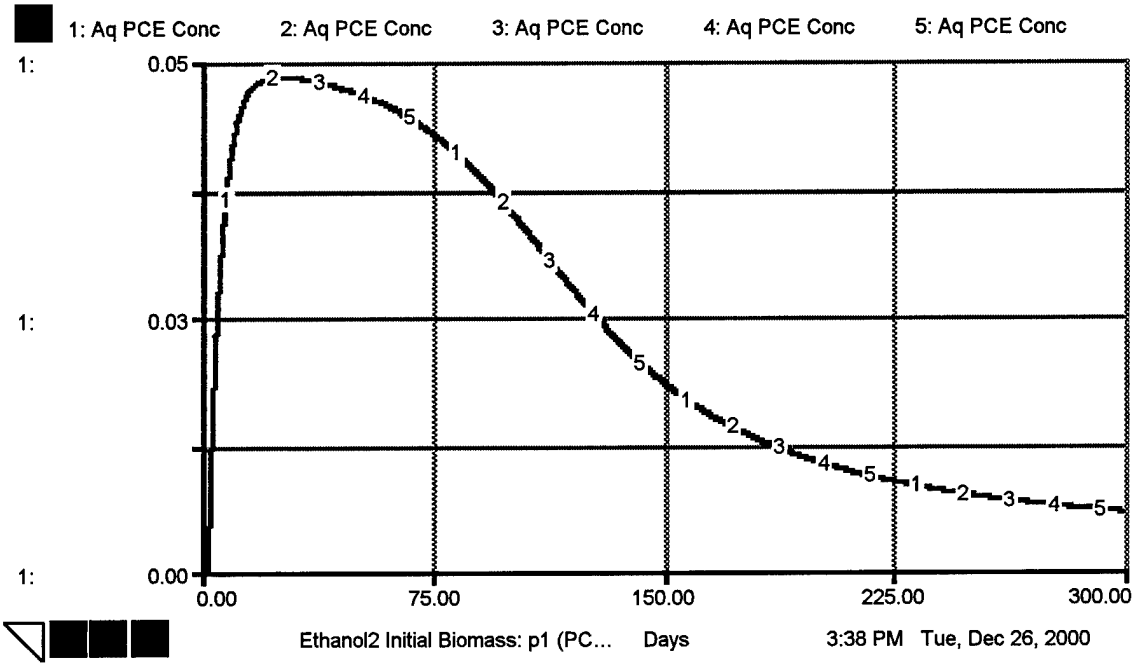
Run	Ethanol 2 Initial Biomass (mg of VSS)
1	10
2	1000
3	10,000
4	100,000
5	500,000

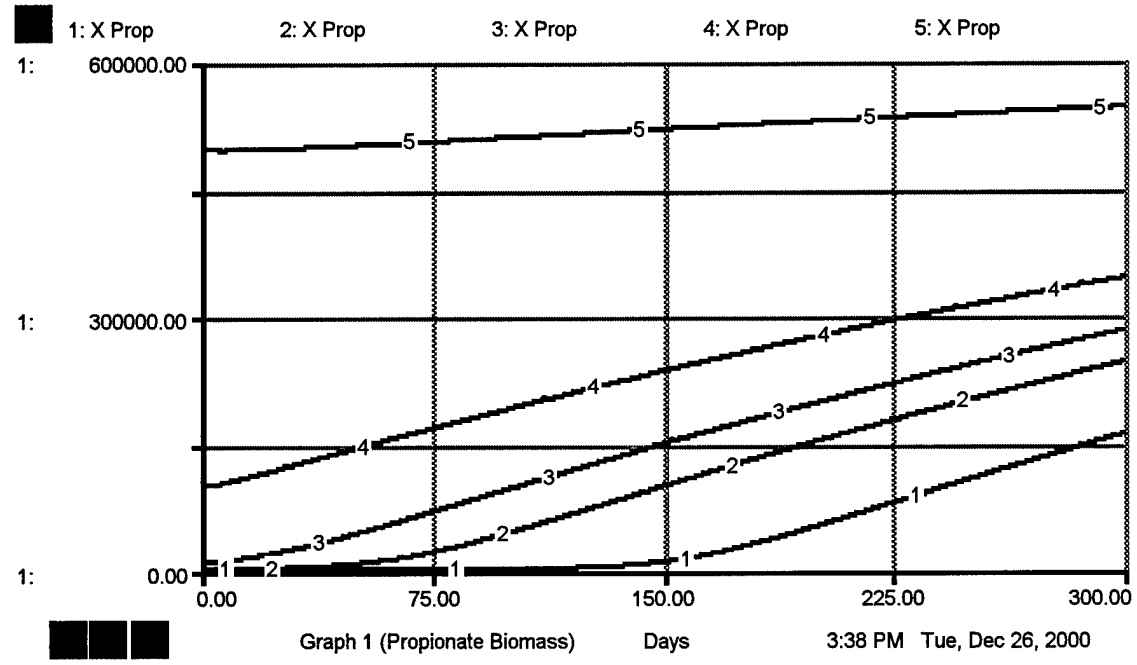




Propionate initial biomass

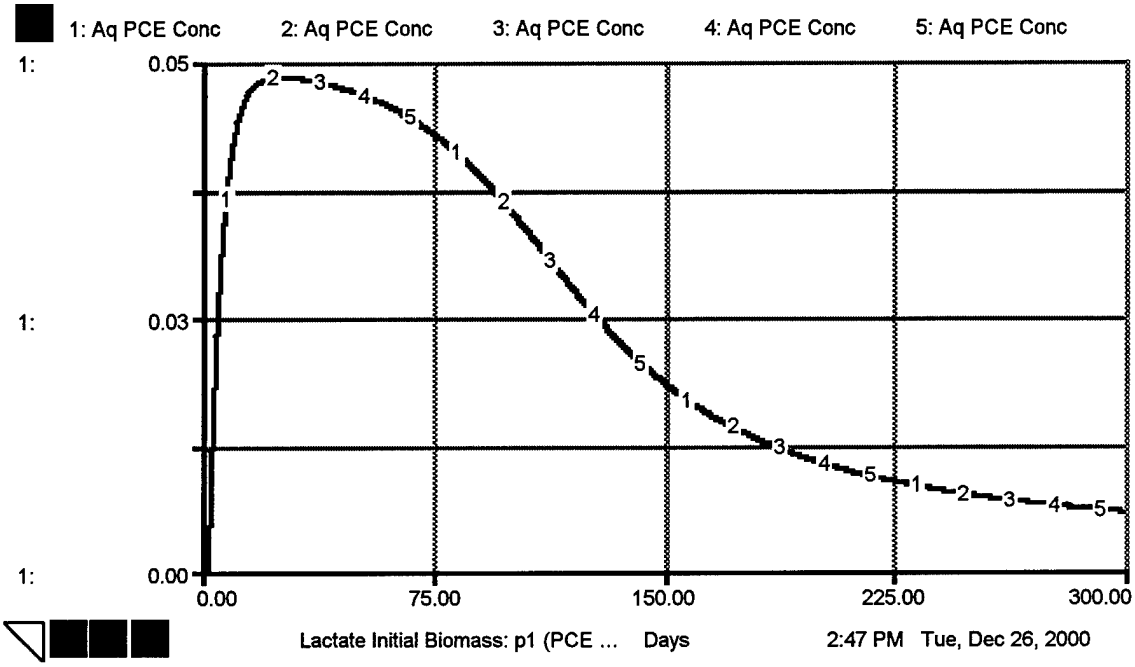
Run	Propionate Initial Biomass (mg of VSS)
1	10
2	1000
3	10,000
4	100,000
5	500,000

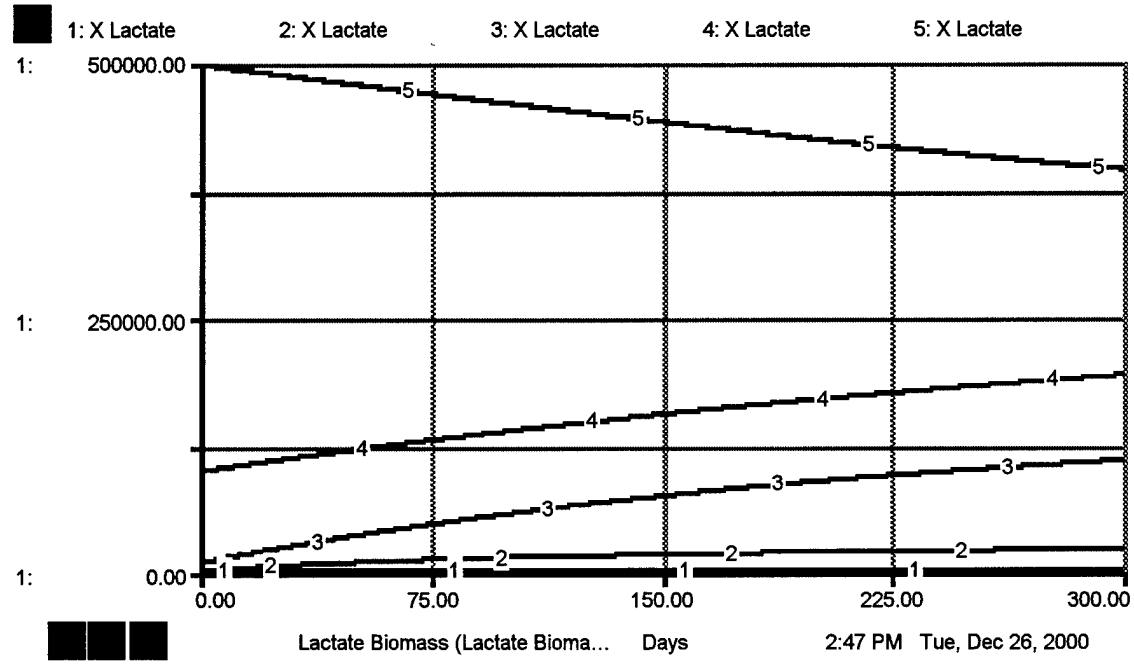




Lactate initial biomass

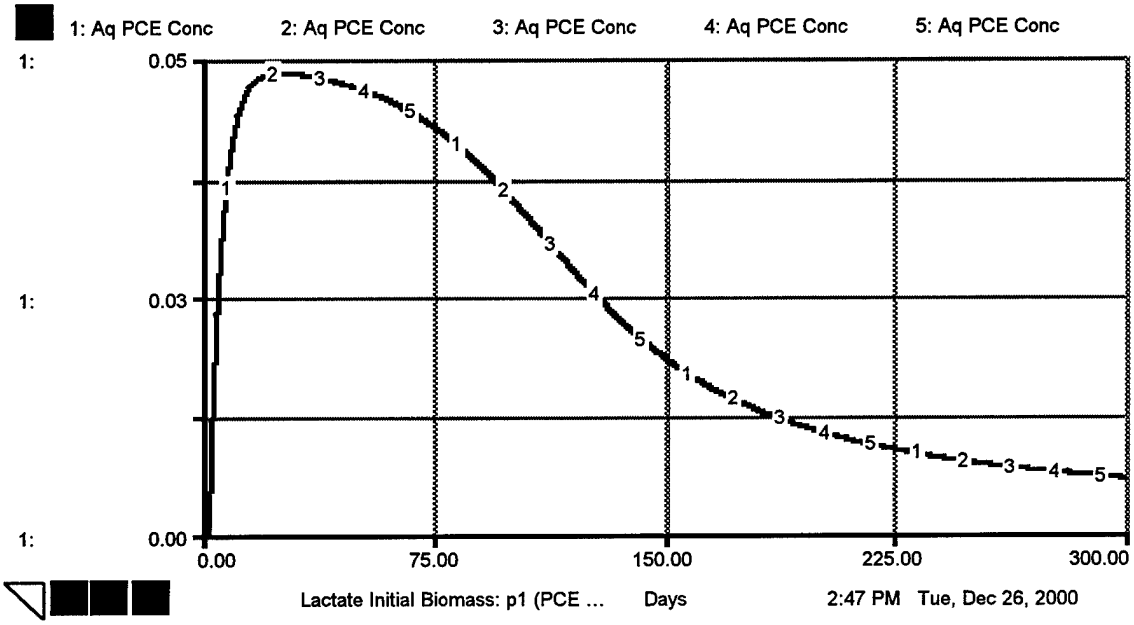
Run	Lactate Initial Biomass (mg of VSS)
1	10
2	1000
3	10,000
4	100,000
5	500,000

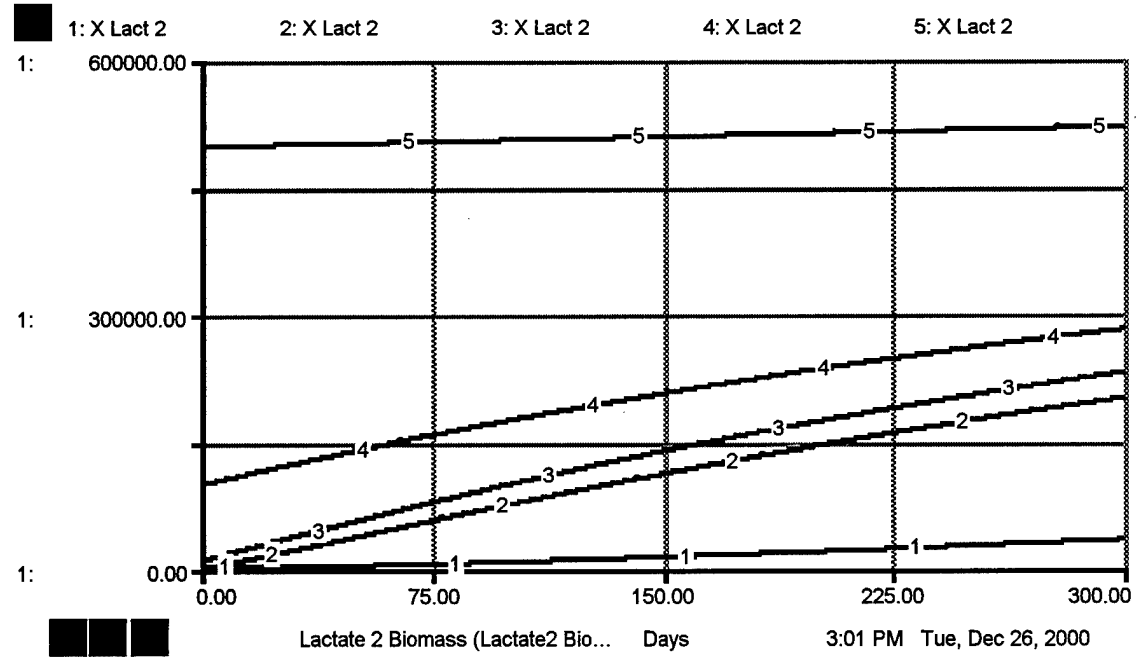




Lactate 2 initial biomass

Run	Ethanol 2 Initial Biomass (mg of VSS)
1	10
2	1000
3	10,000
4	100,000
5	500,000

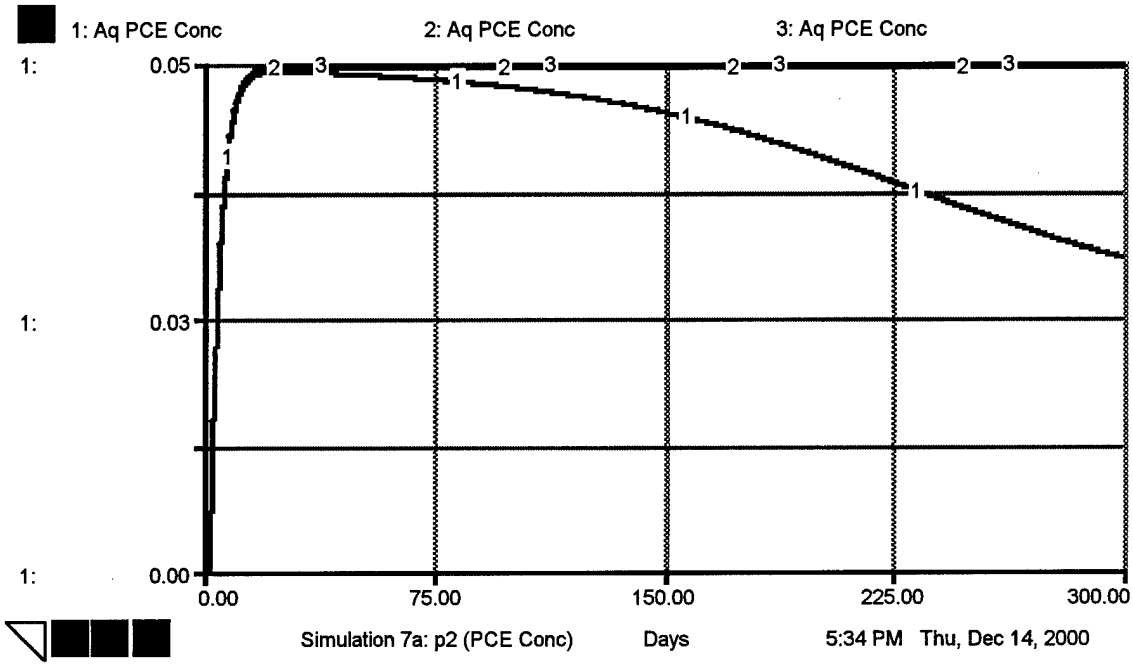




Simulation 7

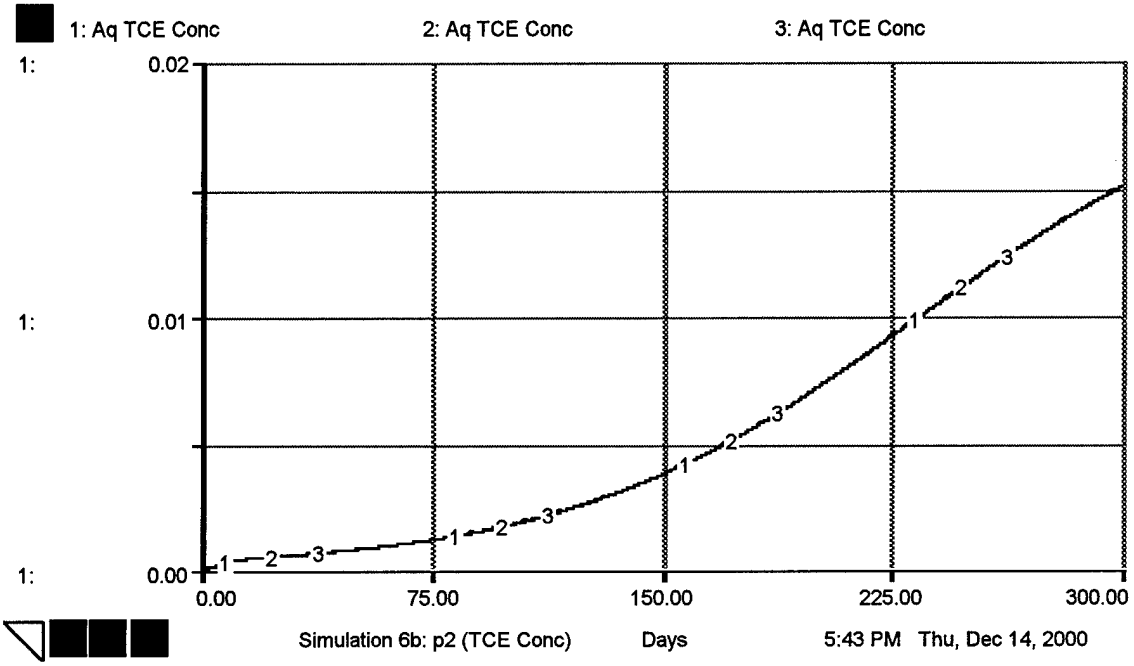
PCE utilization rate

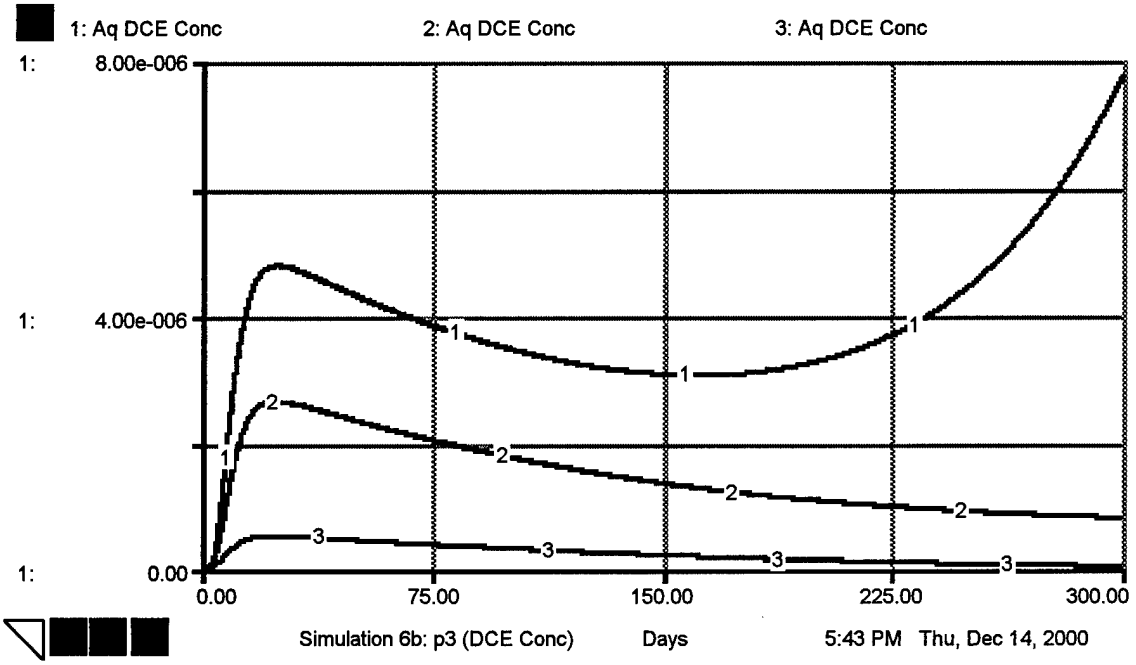
Run	PCE utilization rate (k) (mg/mg of VSS/d)
1	7.164
2	3.77
3	0.39



TCE utilization rate

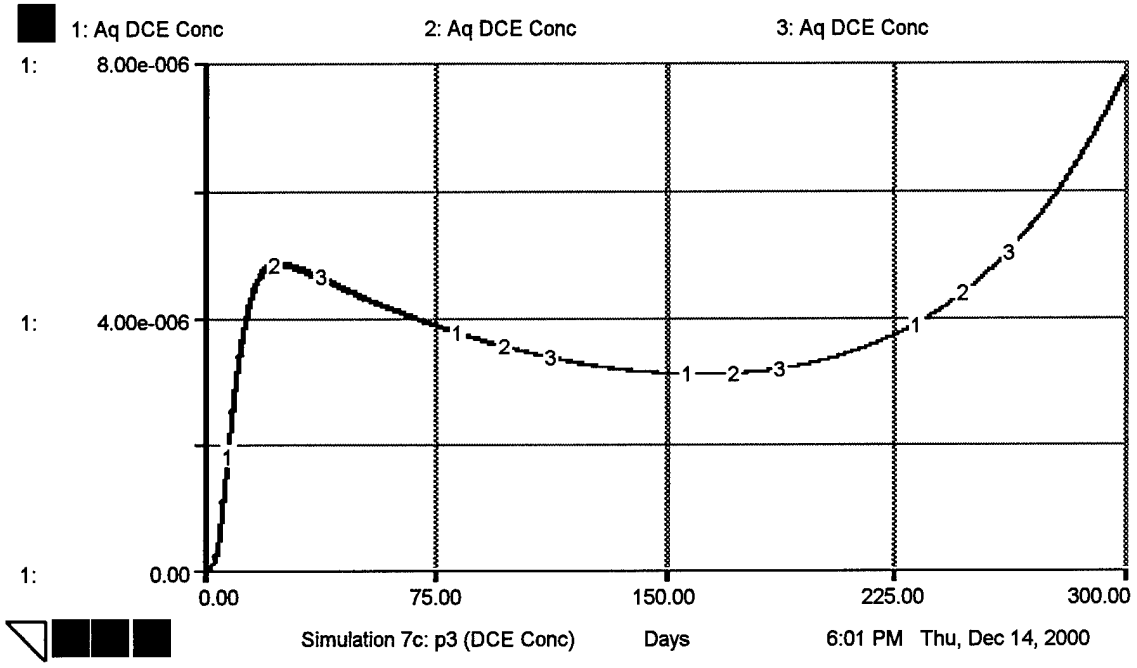
Run	PCE utilization rate (k) (mg/mg of VSS/d)
1	9.461
2	5.2355
3	1.01

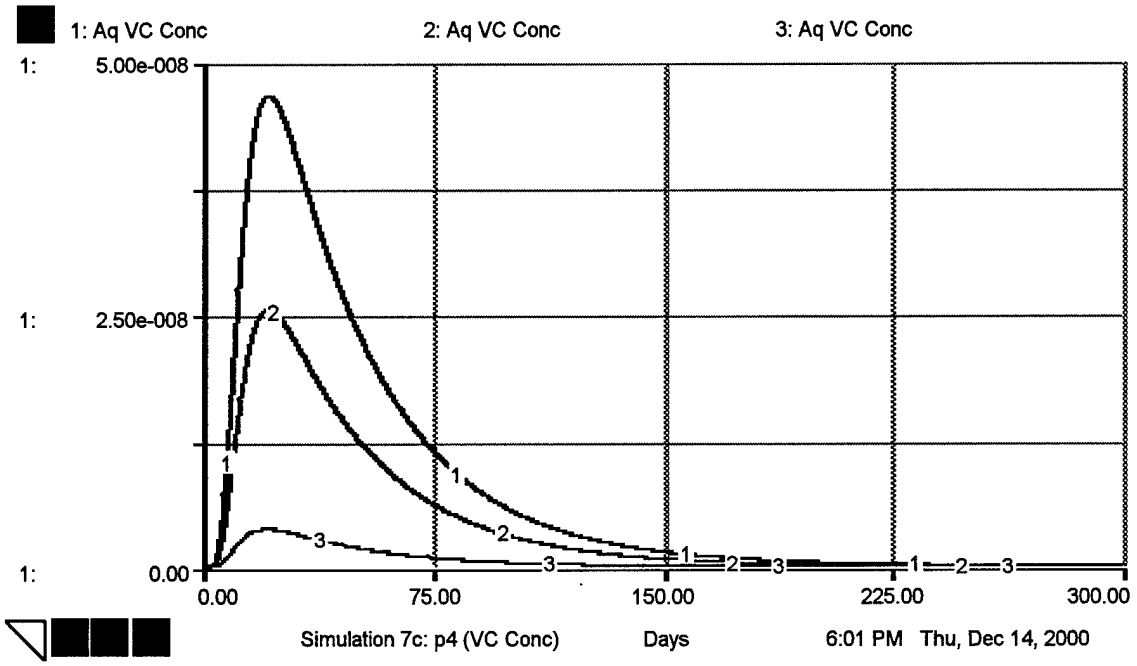




DCE utilization rate

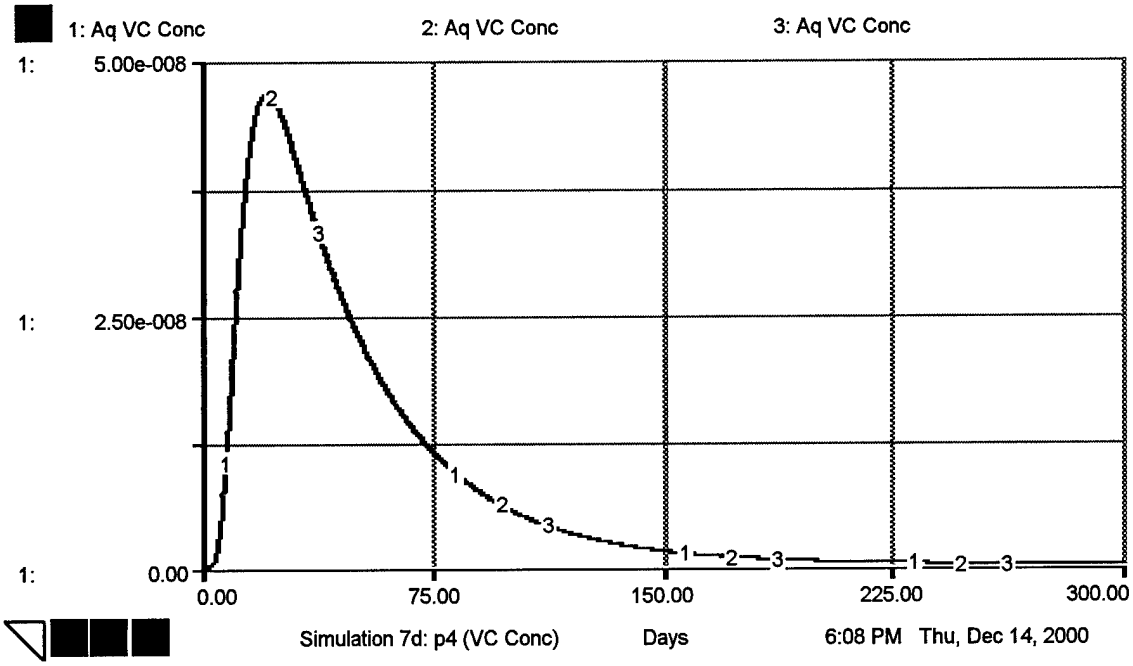
Run	DCE utilization rate (k) (mg/mg of VSS/d)
1	6.976
2	3.763
3	0.55

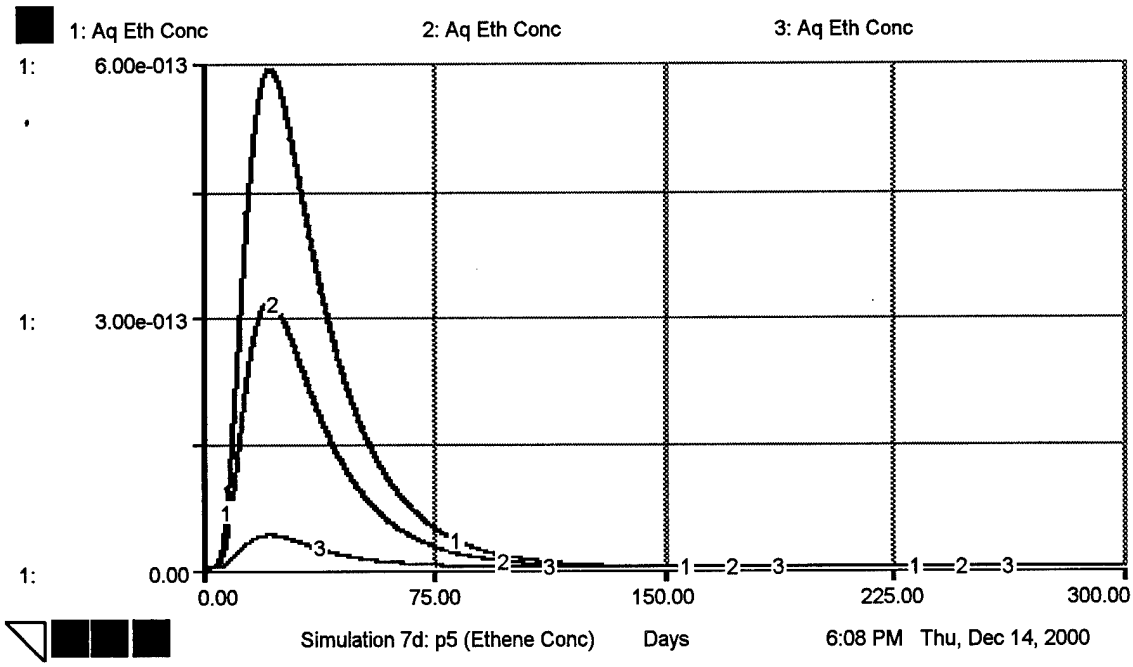




VC utilization rate

Run	VC utilization rate (k) (mg/mg of VSS/d)
1	4.5
2	2.4
3	0.2955

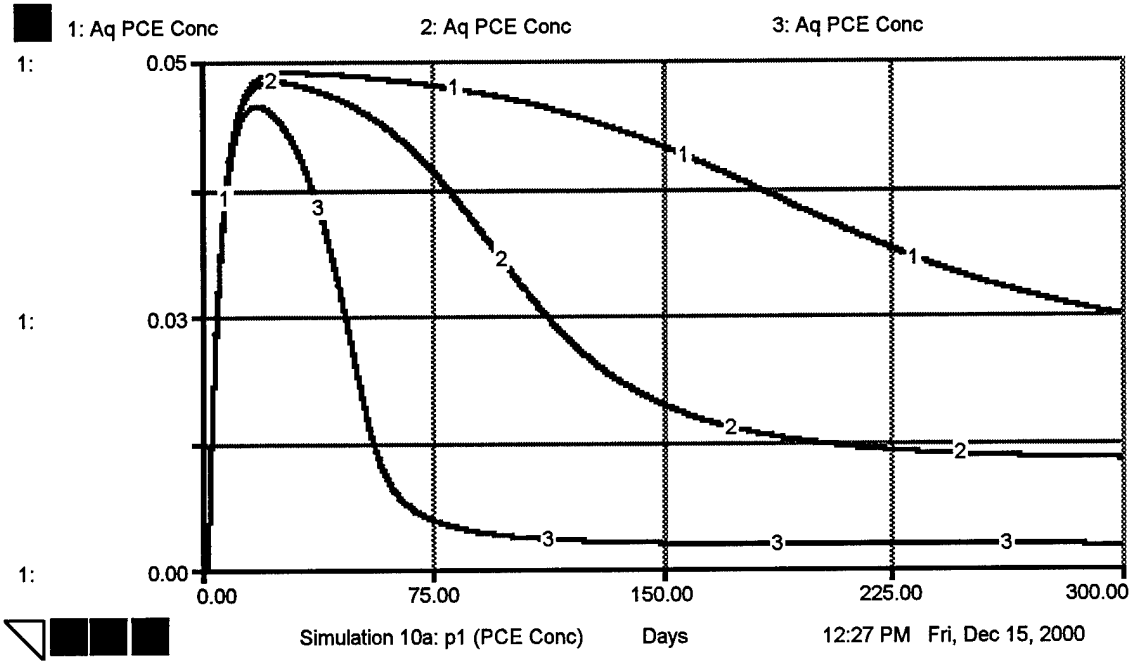




Simulation 9

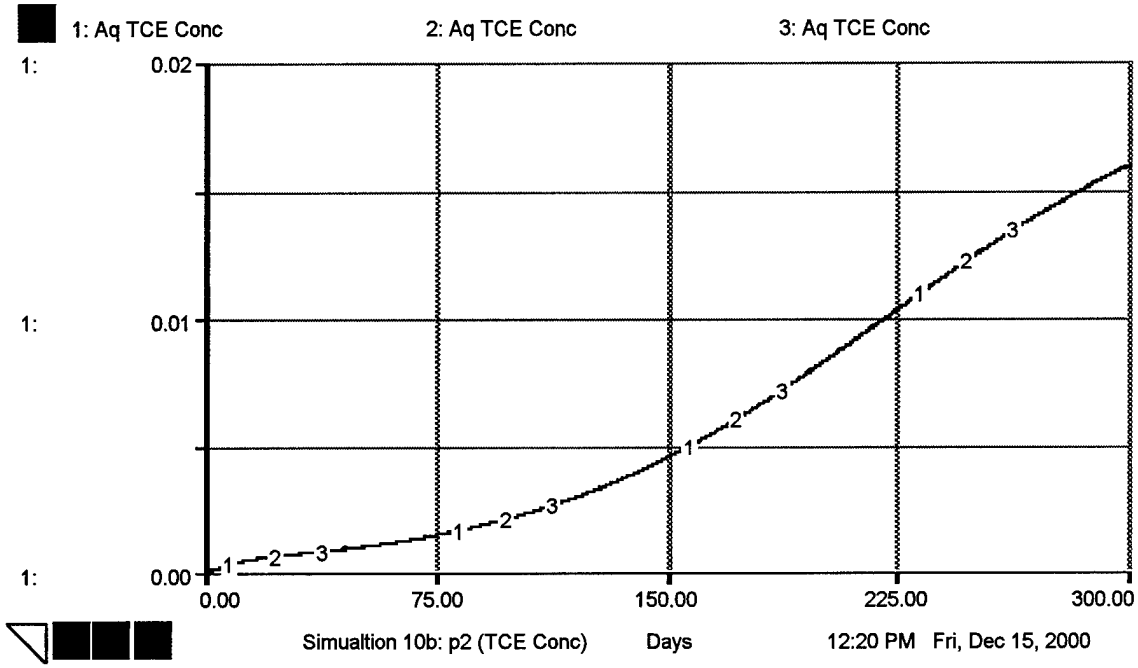
Ks values for PCE

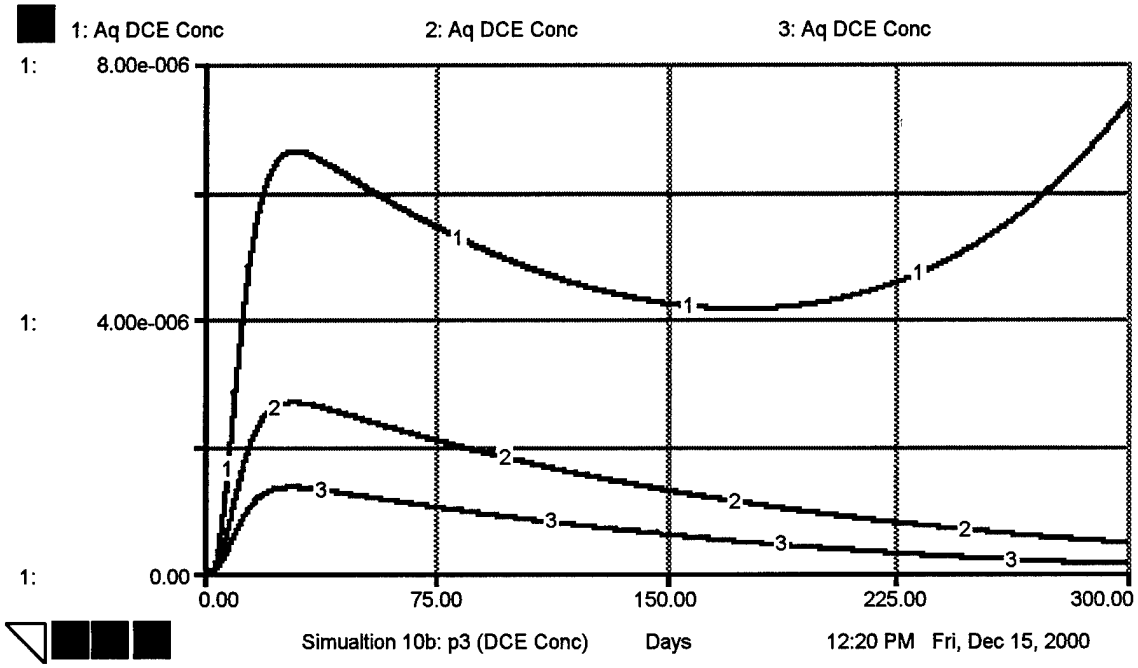
Run	PCE half-velocity coefficient (Ks) (mg/L)
1	0.08
2	0.04
3	0.008



Ks Values for TCE

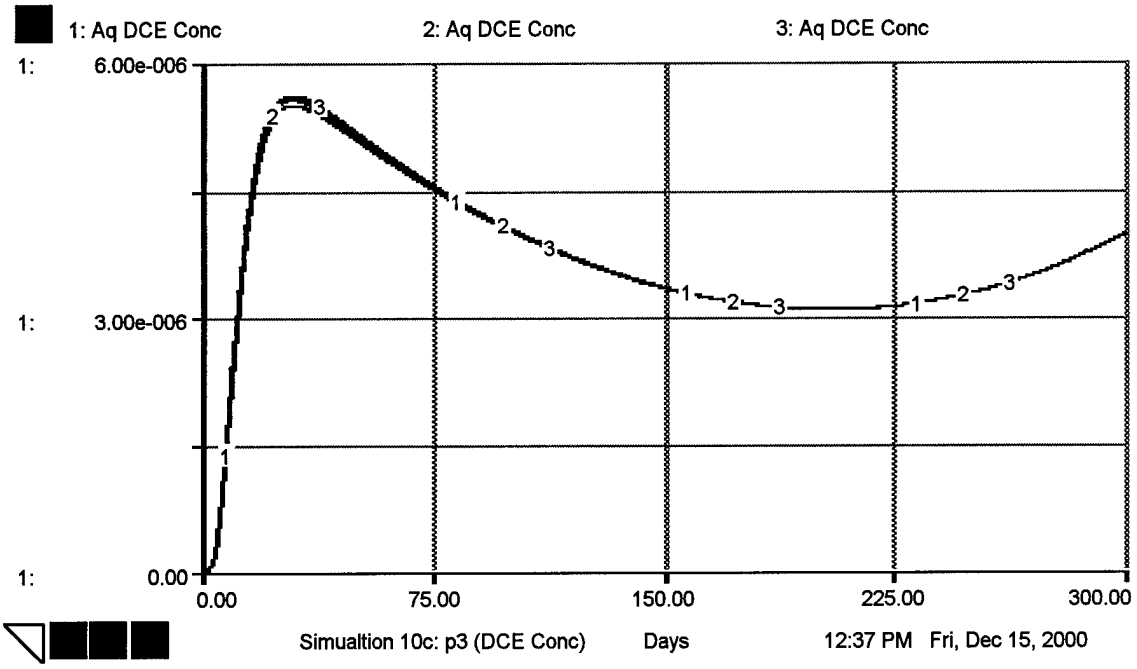
Run	TCE half-velocity coefficient (Ks) (mg/L)
1	0.06
2	0.15
3	0.3

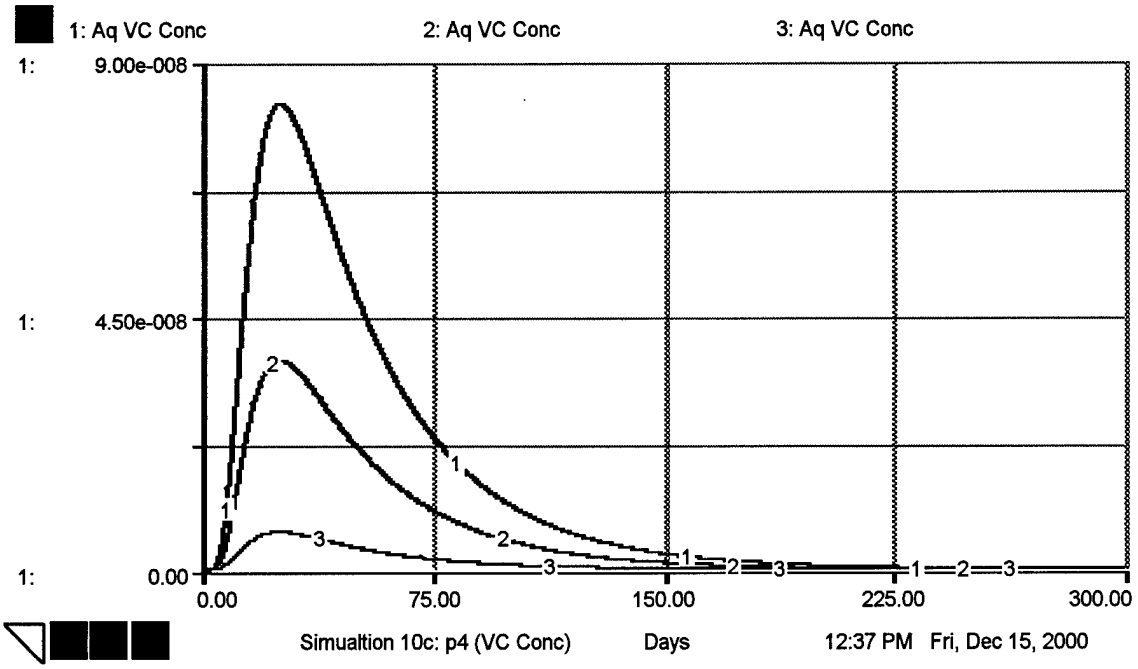




Ks values for DCE

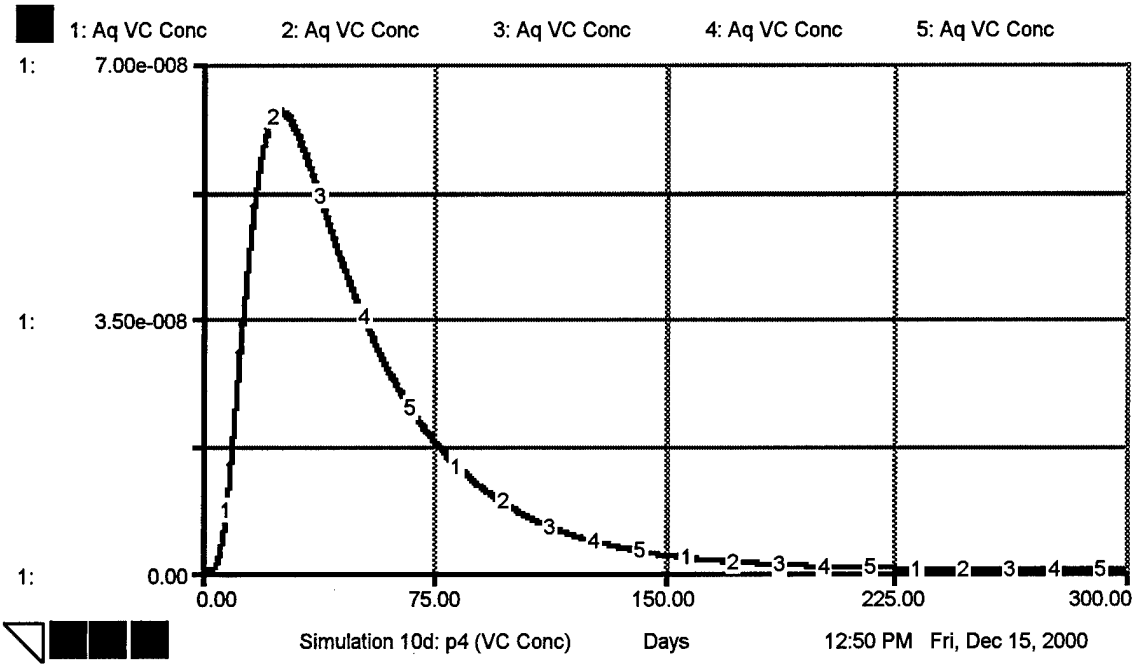
Run	DCE half-velocity coefficient (Ks) (mg/L)
1	0.04
2	0.09
3	0.5

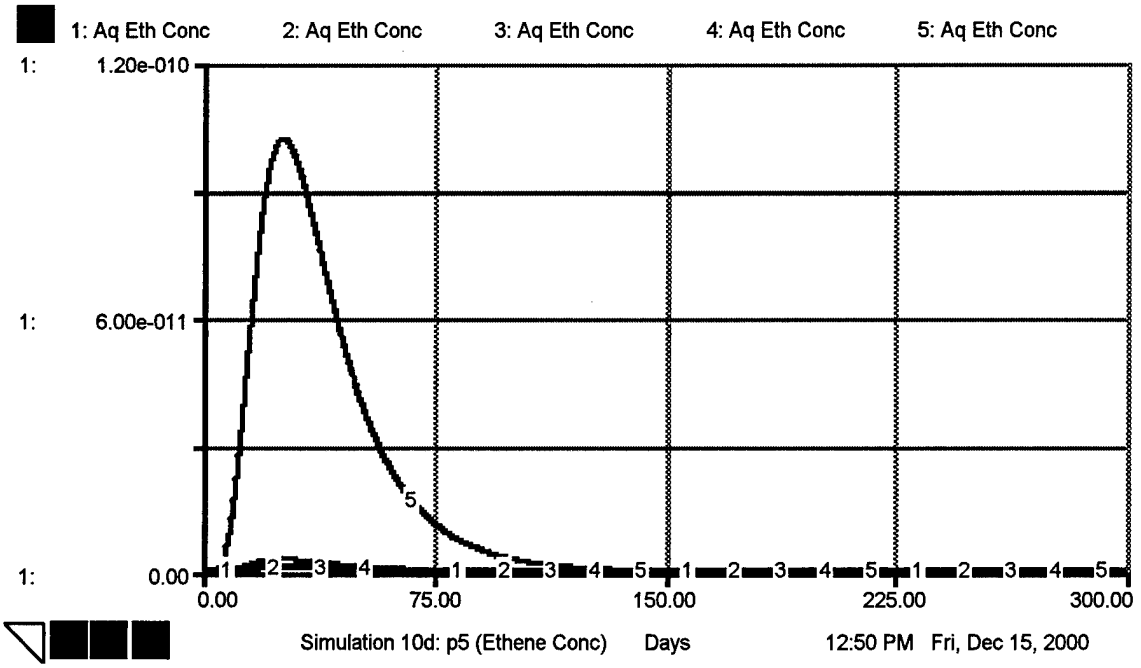




Ks values for VC

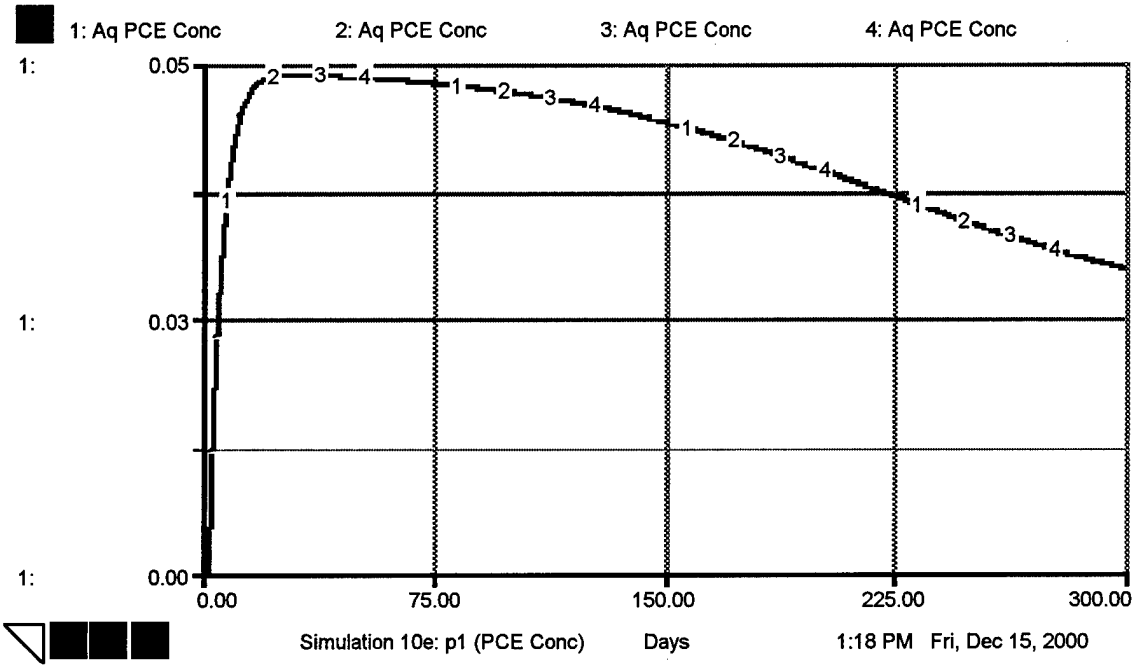
Run	PCE half-velocity coefficient (mg/L)
1	25
2	18.1221
3	12.5
4	6.25
5	.16875





Hydrogenotrophic Methanogens Ks values

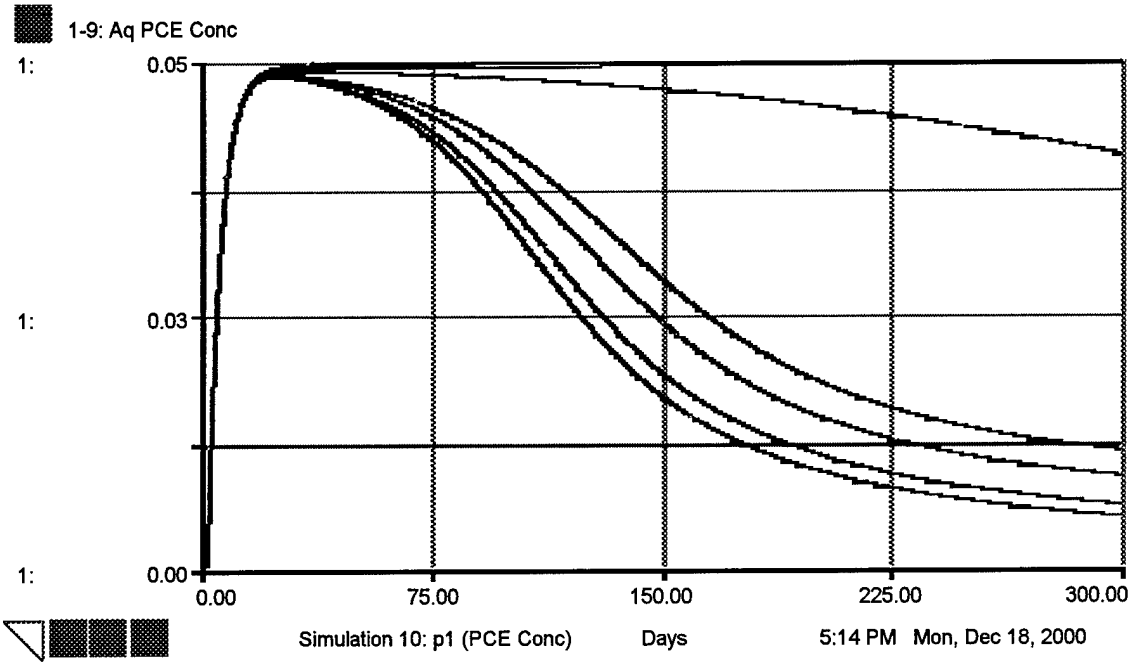
Run	Hydrogenotrophic methanogen half-velocity coefficient (Ks) (mg/L)
1	0.0008
2	0.001
3	0.004
4	0.01

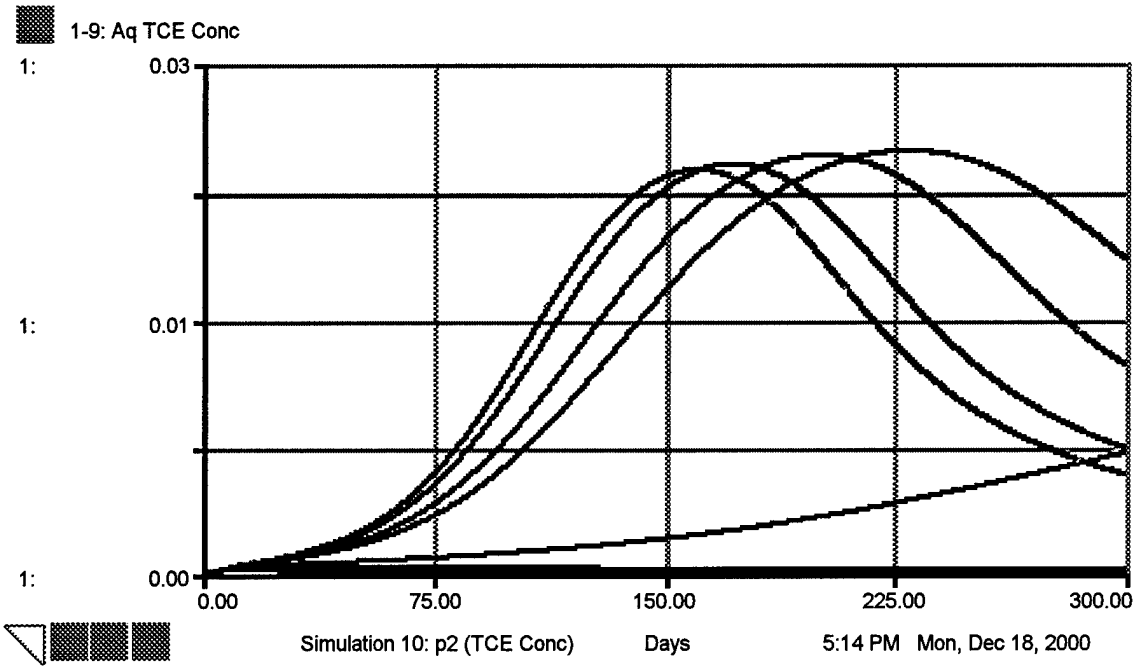


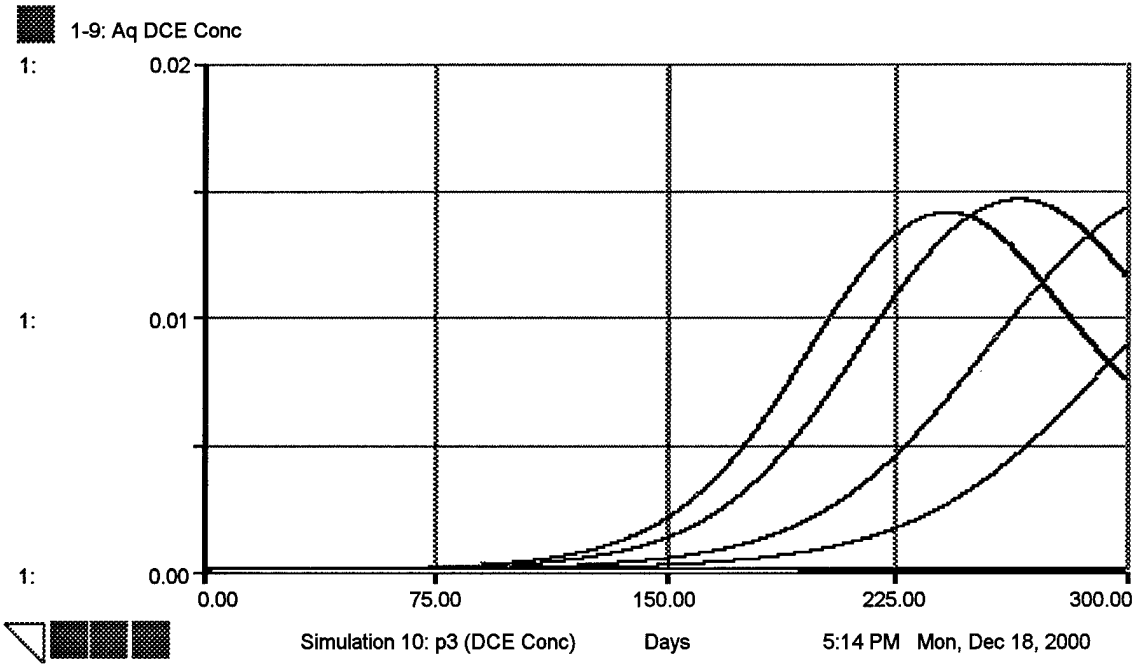
Simulation 10 Changing the Death Rate

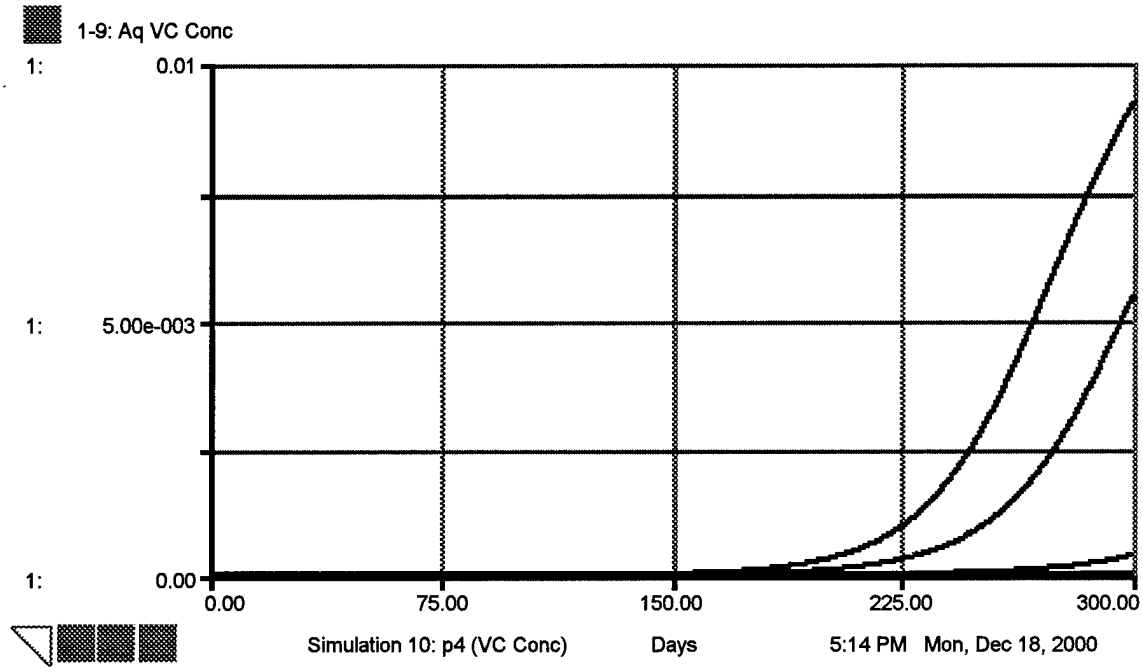
Run	Death Rate
1	0.001
2	0.003
3	0.007
4	0.01
5	0.03

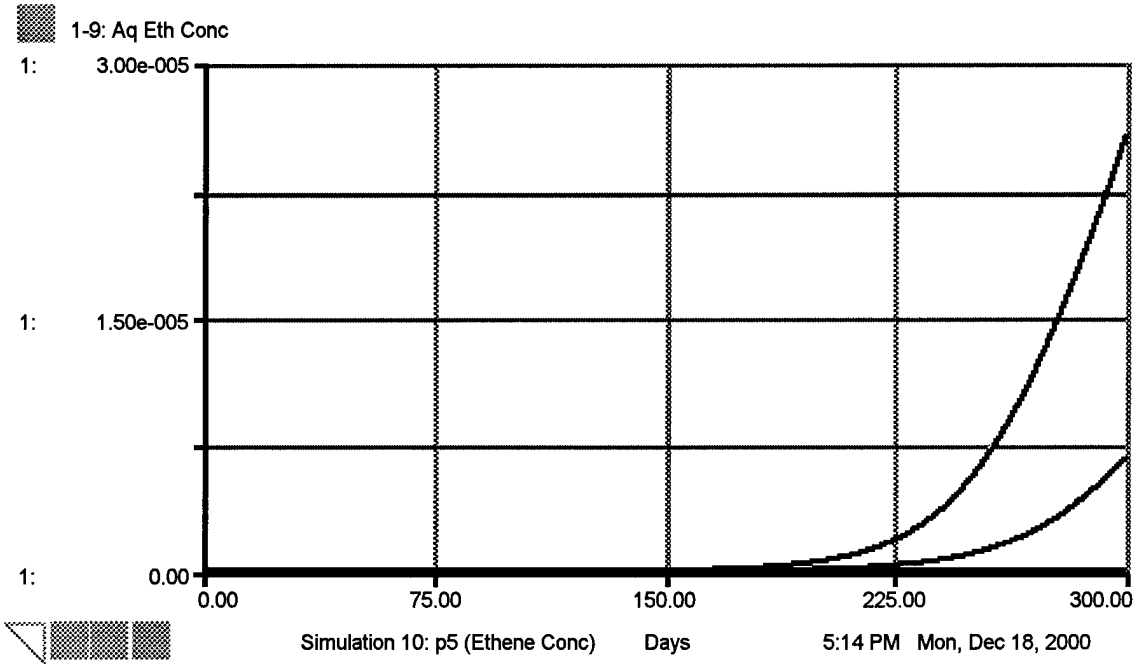
Run	Death Rate
6	0.045
7	0.06
8	0.075
9	0.1




1-9: Aq TCE Conc
1:
0.03
1:
0.01
1:
0.00
0.00
75.00
150.00
225.00
300.00
Simulation 10: p2 (TCE Conc)
Days
5:14 PM Mon, Dec 18, 2000


1-9: Aq DCE Conc
1:
0.02
1:
0.01
1:
0.00
0.00
75.00
150.00
225.00
300.00
Simulation 10: p3 (DCE Conc)
Days
5:14 PM Mon, Dec 18, 2000

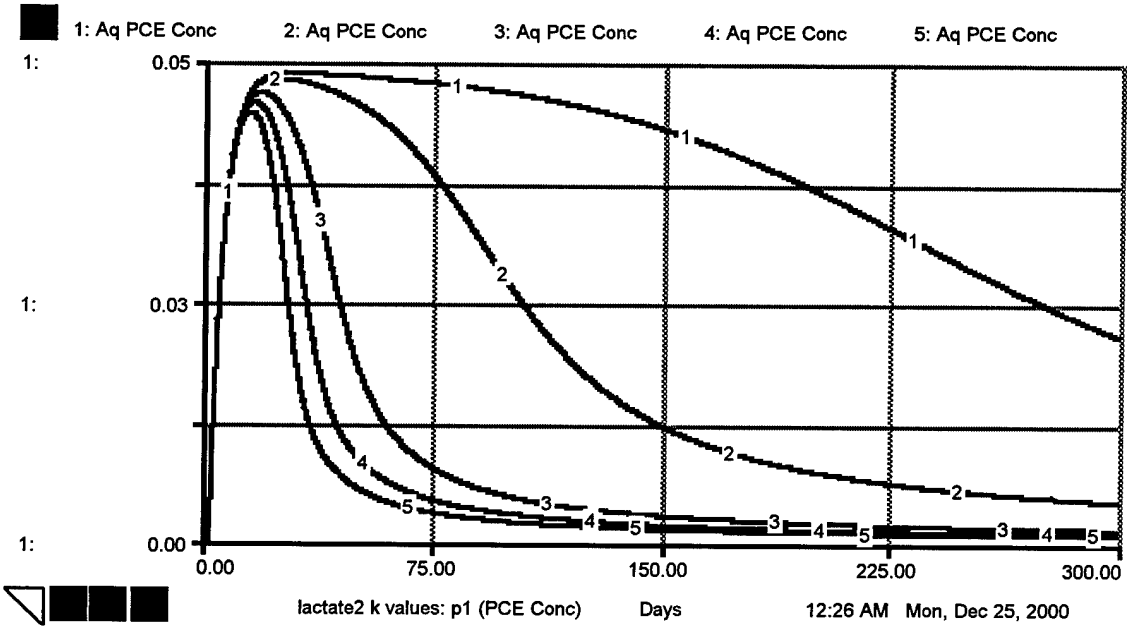

1-9: Aq VC Conc
1:
0.01
1:
5.00e-003
1:
0.00
0.00
75.00
150.00
225.00
300.00
Simulation 10: p4 (VC Conc)
Days
5:14 PM Mon, Dec 18, 2000

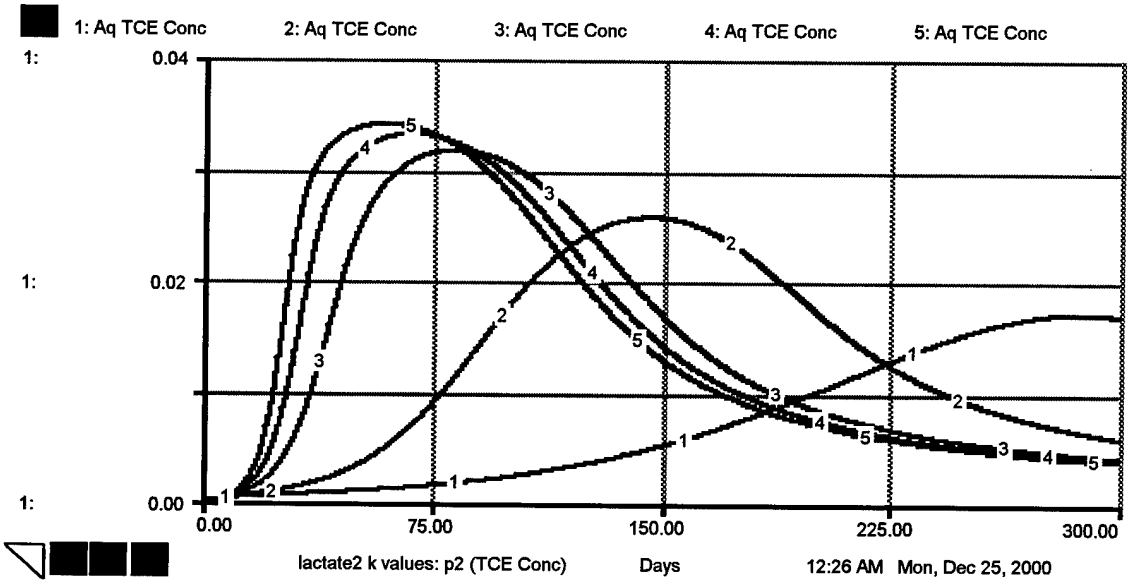

1-9: Aq Eth Conc
1:
3.00e-005
1:
1.50e-005
1:
0.00
0.00
75.00
150.00
225.00
300.00
Simulation 10: p5 (Ethene Conc)
Days
5:14 PM Mon, Dec 18, 2000

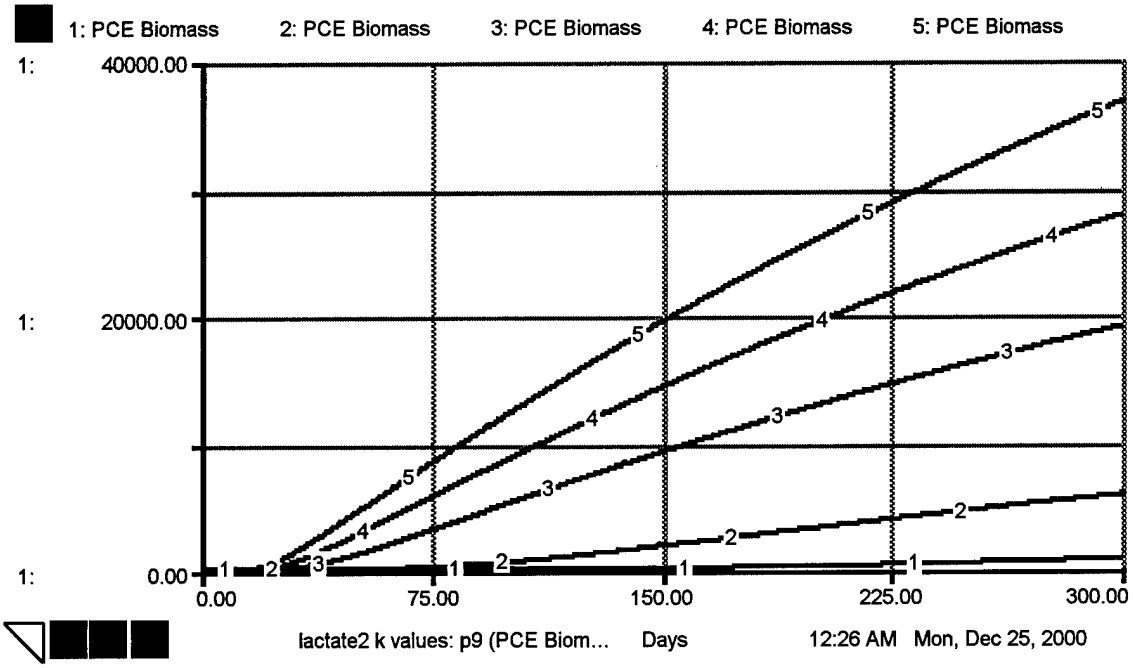
Simulation 11

PCE biomass yield

Run	PCE Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.09

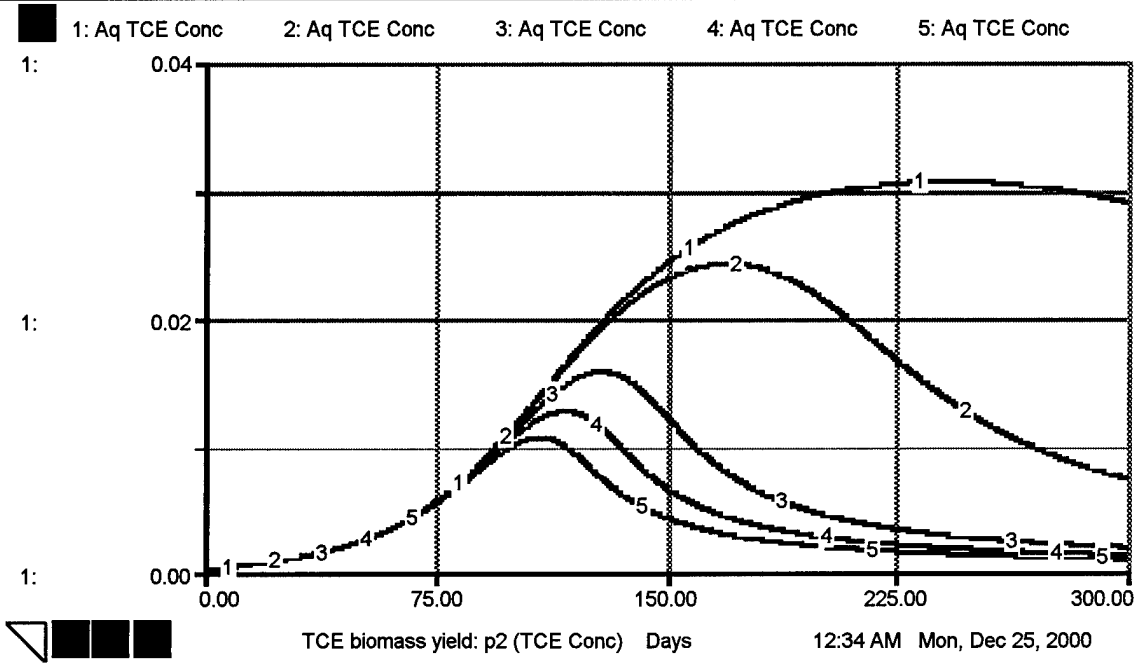


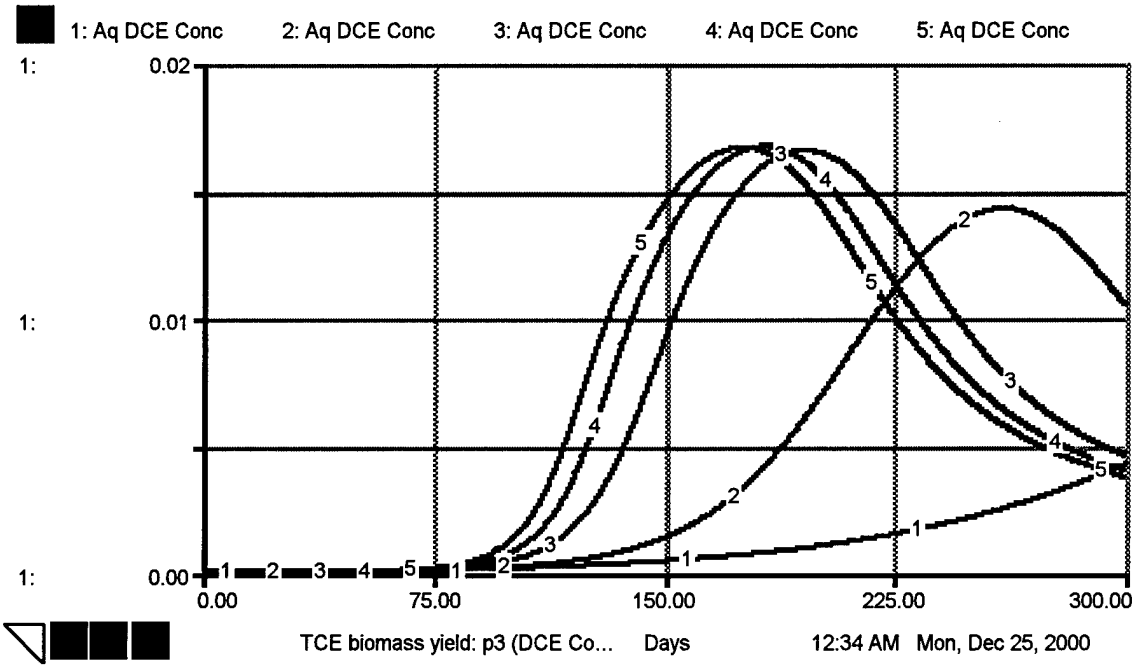


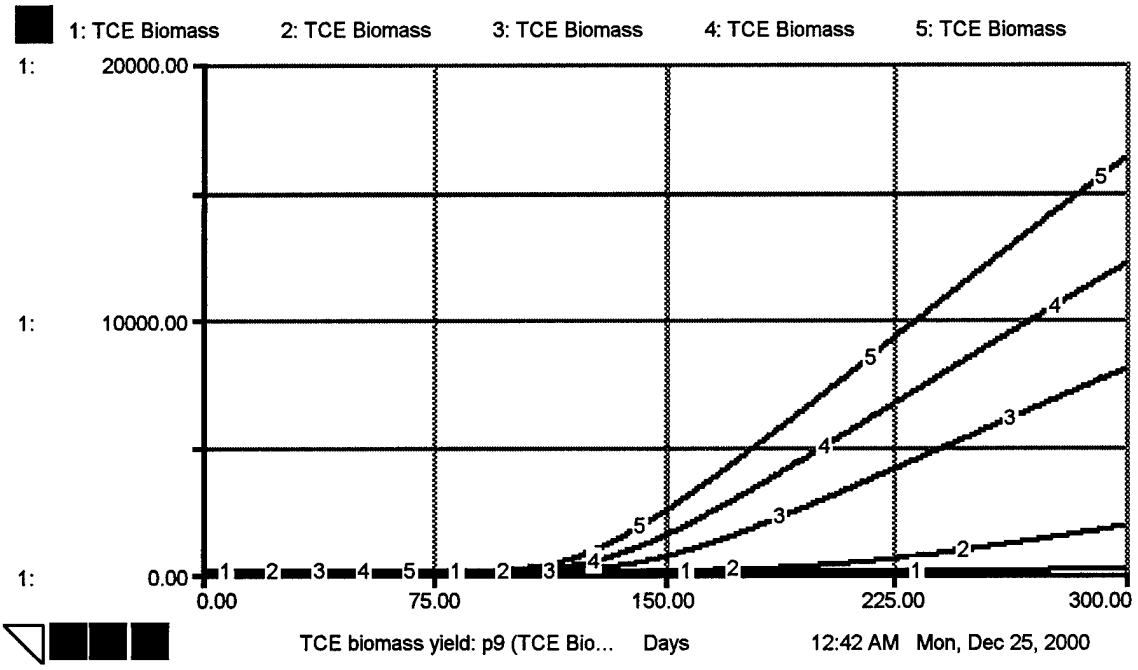

1: PCE Biomass
2: PCE Biomass
3: PCE Biomass
4: PCE Biomass
5: PCE Biomass
1: 40000.00
1: 20000.00
1: 0.00
0.00
75.00
150.00
225.00
300.00
lactate2 k values: p9 (PCE Biom...
Days
12:26 AM Mon, Dec 25, 2000

TCE biomass yield

Run	TCE Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.09

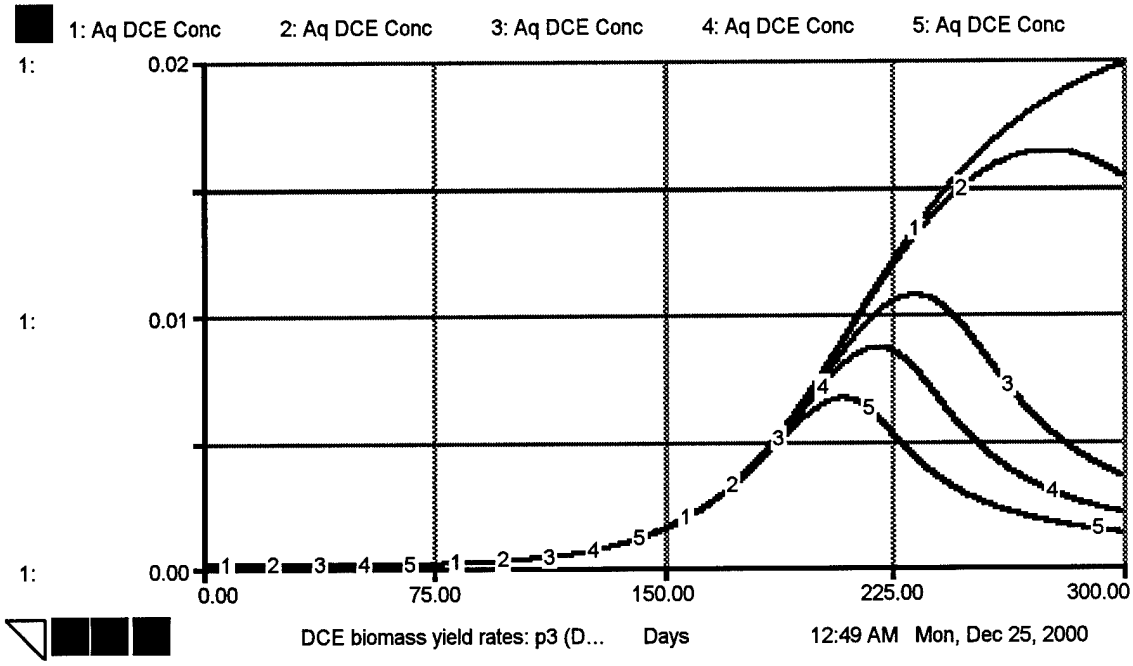


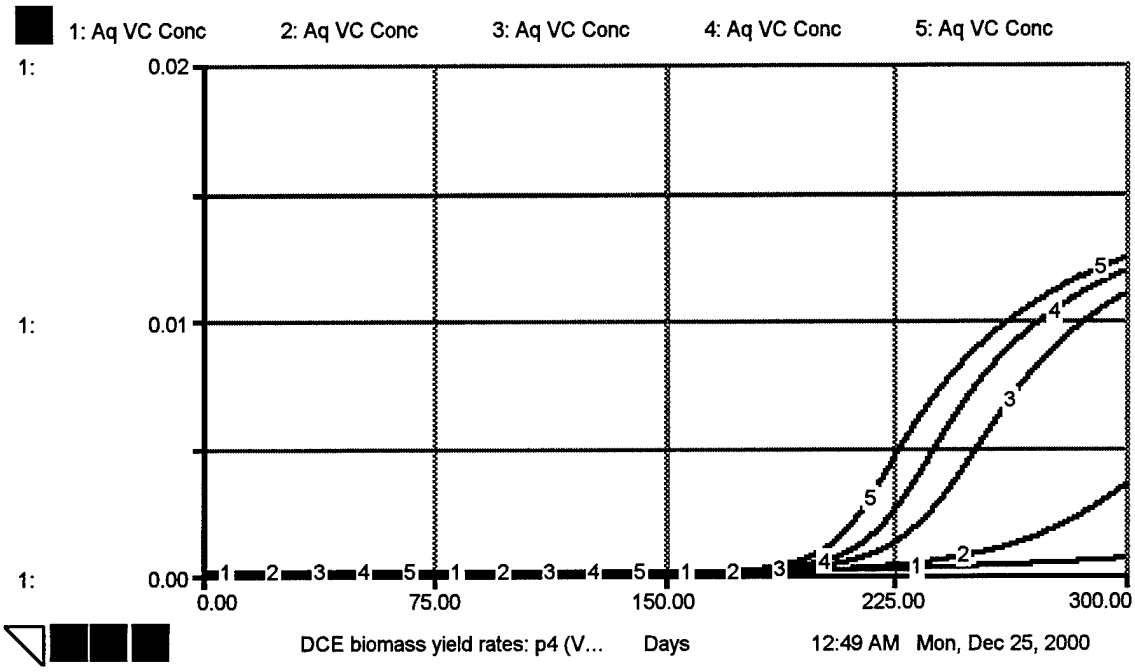


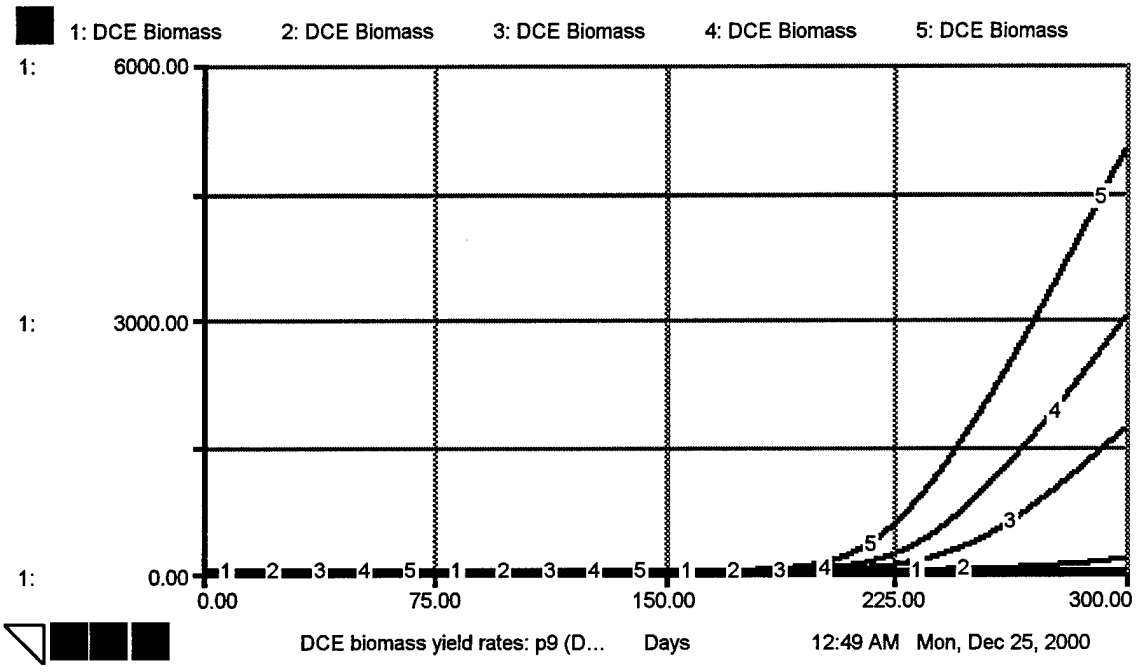

1: TCE Biomass
2: TCE Biomass
3: TCE Biomass
4: TCE Biomass
5: TCE Biomass
1: 20000.00
1: 10000.00
1: 0.00
0.00
75.00
150.00
225.00
300.00
TCE biomass yield: p9 (TCE Bio...
Days
12:42 AM Mon, Dec 25, 2000

DCE biomass yield

Run	DCE Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.09

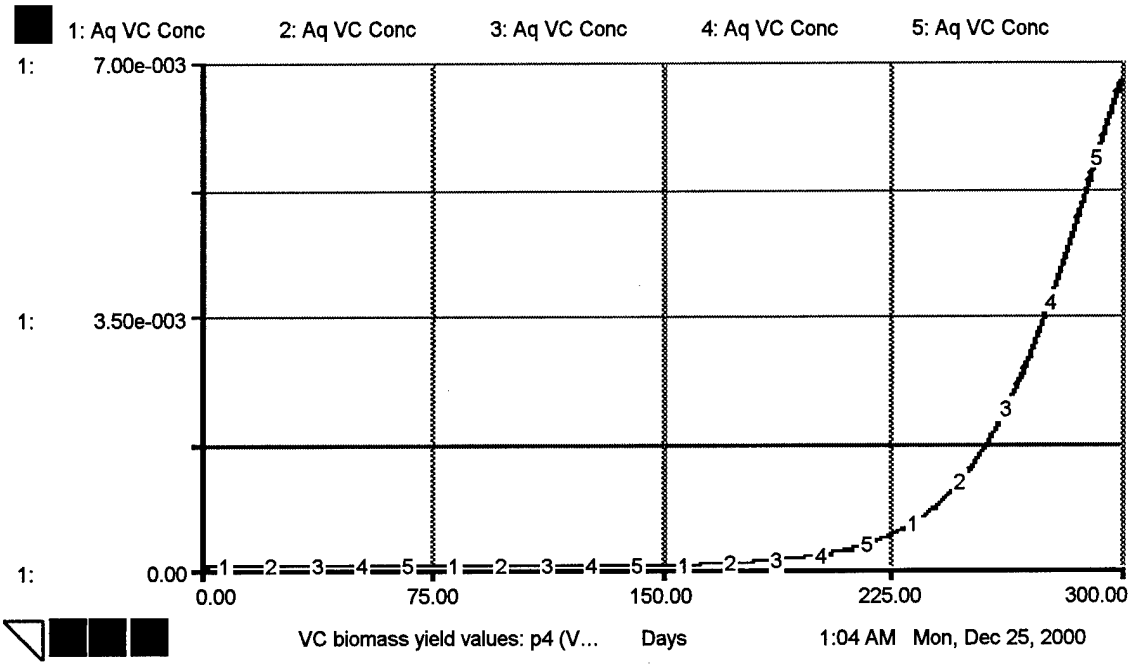


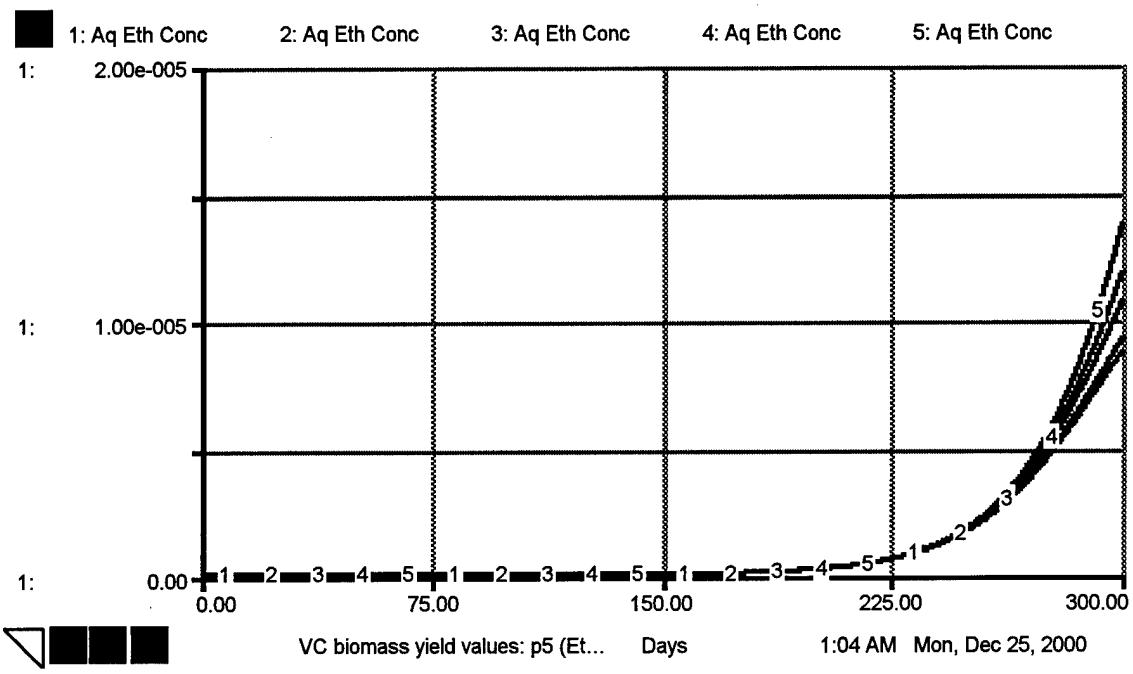

1: Aq VC Conc
2: Aq VC Conc
3: Aq VC Conc
4: Aq VC Conc
5: Aq VC Conc
1:
0.02
1:
0.01
1:
0.00
0.00
75.00
150.00
225.00
300.00
DCE biomass yield rates: p4 (V...
Days
12:49 AM Mon, Dec 25, 2000

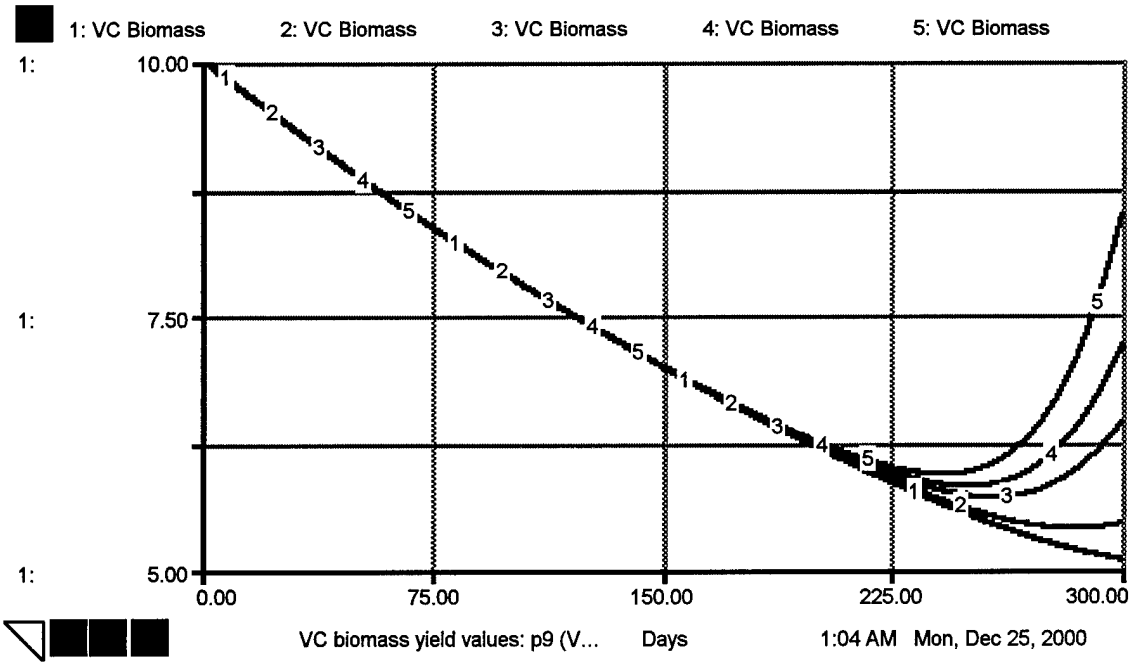

1: DCE Biomass
2: DCE Biomass
3: DCE Biomass
4: DCE Biomass
5: DCE Biomass
1:
6000.00
1:
3000.00
1:
0.00
0.00
75.00
150.00
225.00
300.00
DCE biomass yield rates: p9 (D...
Days
12:49 AM Mon, Dec 25, 2000

VC biomass yield

Run	VC Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.09

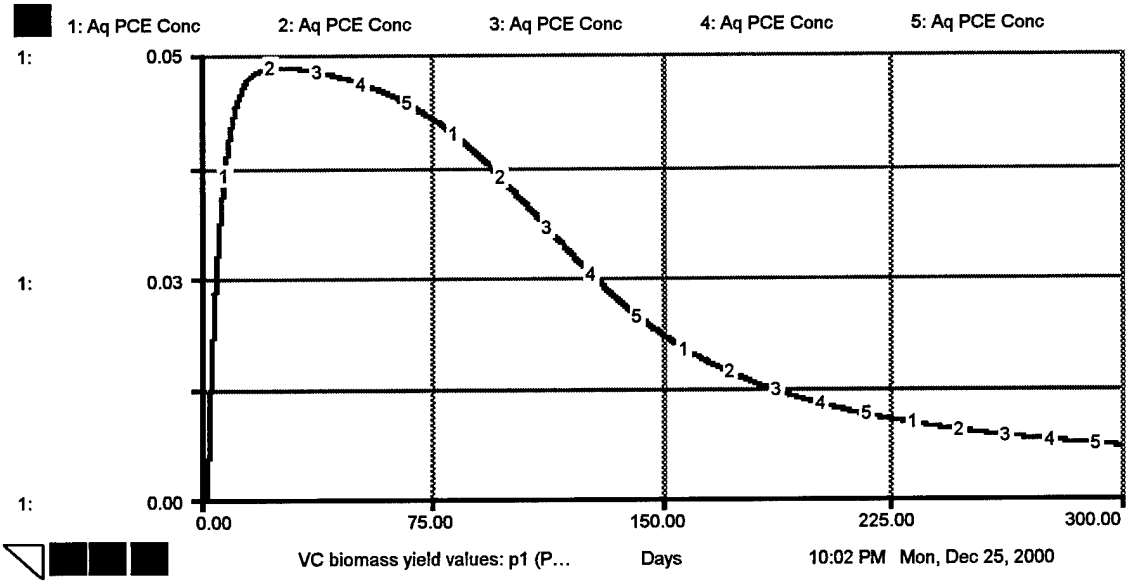


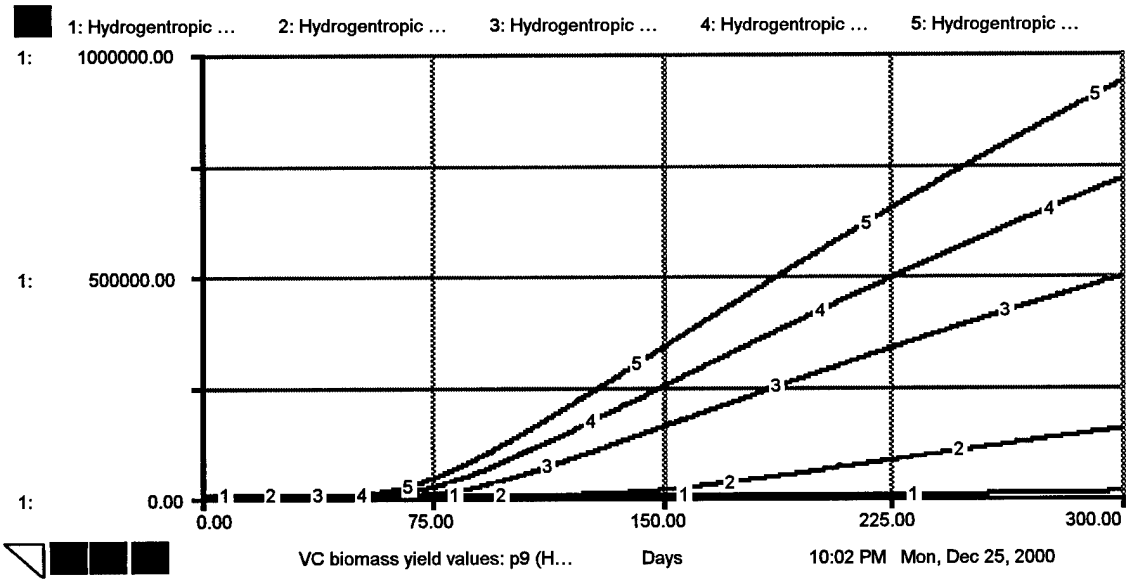

1: Aq Eth Conc
2: Aq Eth Conc
3: Aq Eth Conc
4: Aq Eth Conc
5: Aq Eth Conc
1: 2.00e-005
1: 1.00e-005
1: 0.00
0.00
75.00
150.00
225.00
300.00
VC biomass yield values: p5 (Et...
Days
1:04 AM Mon, Dec 25, 2000


1: VC Biomass
2: VC Biomass
3: VC Biomass
4: VC Biomass
5: VC Biomass
1: 10.00
1: 7.50
1: 5.00
0.00
75.00
150.00
225.00
300.00
VC biomass yield values: p9 (V...
Days
1:04 AM Mon, Dec 25, 2000

Hydrogenotrophic methanogen biomass yield

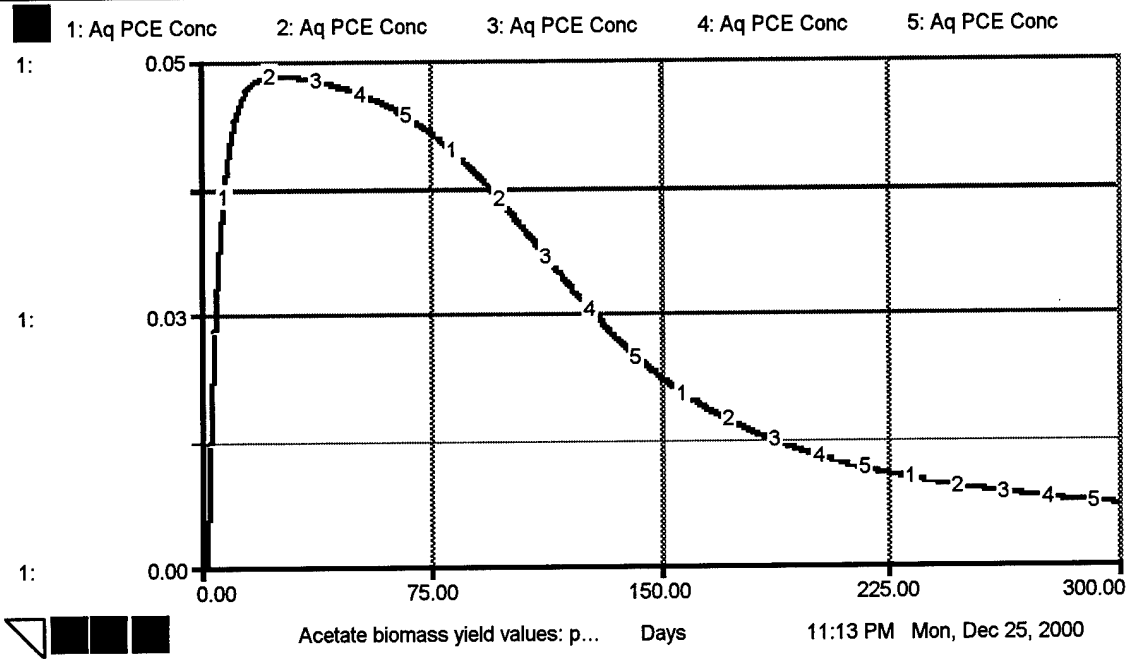
Run	Hydrogenotrophic methanogen Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.09

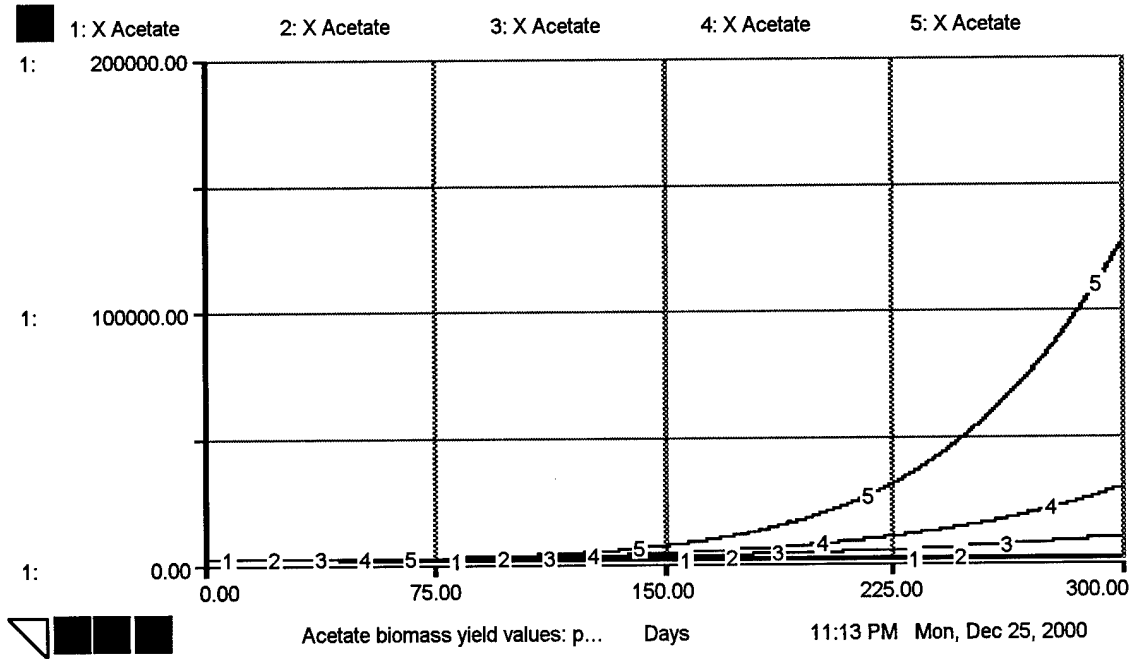




Acetate biomass yield

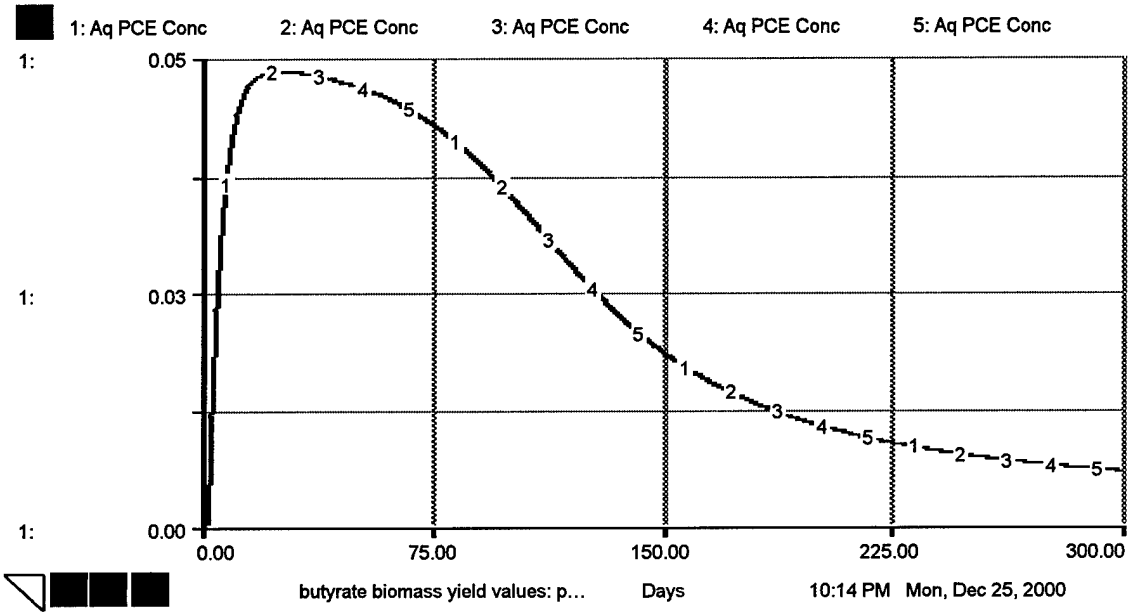
Run	Acetate Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.09

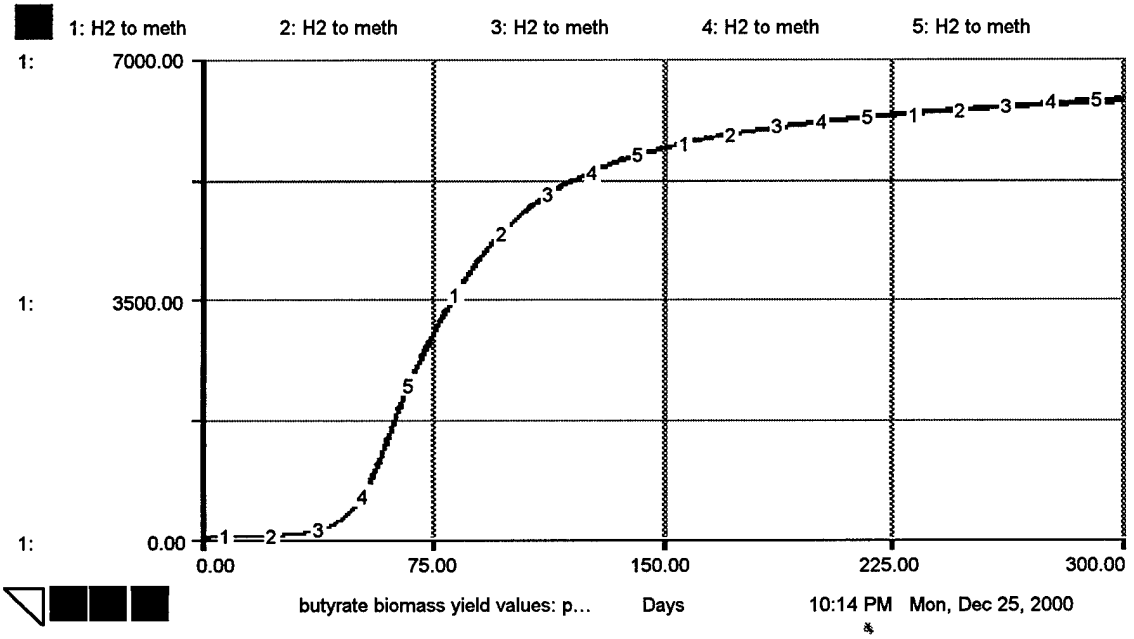




Butyrate biomass yield rate

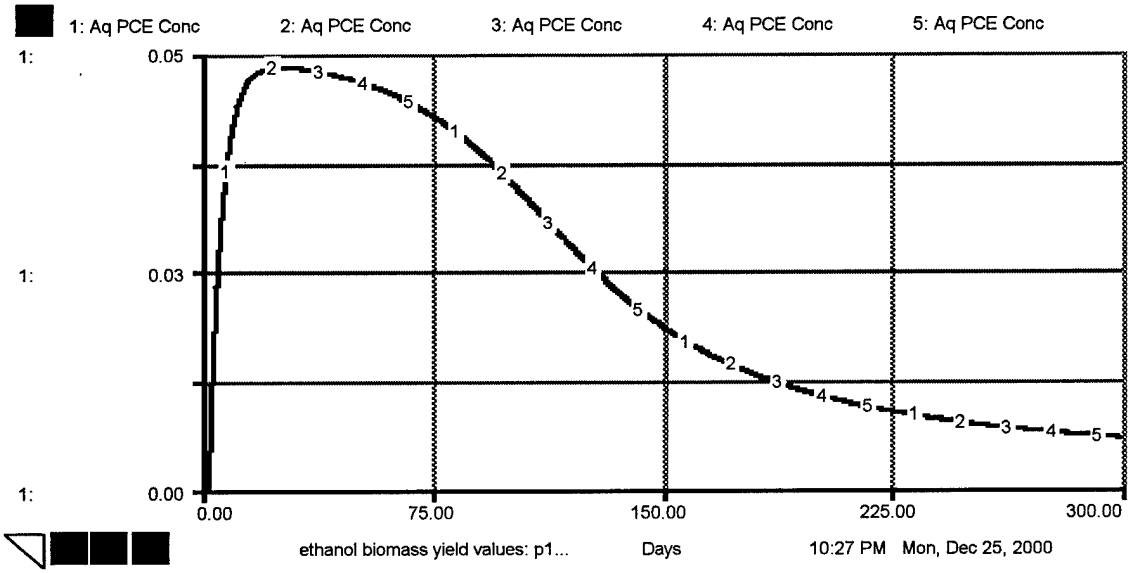
Run	Butyrate Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.1

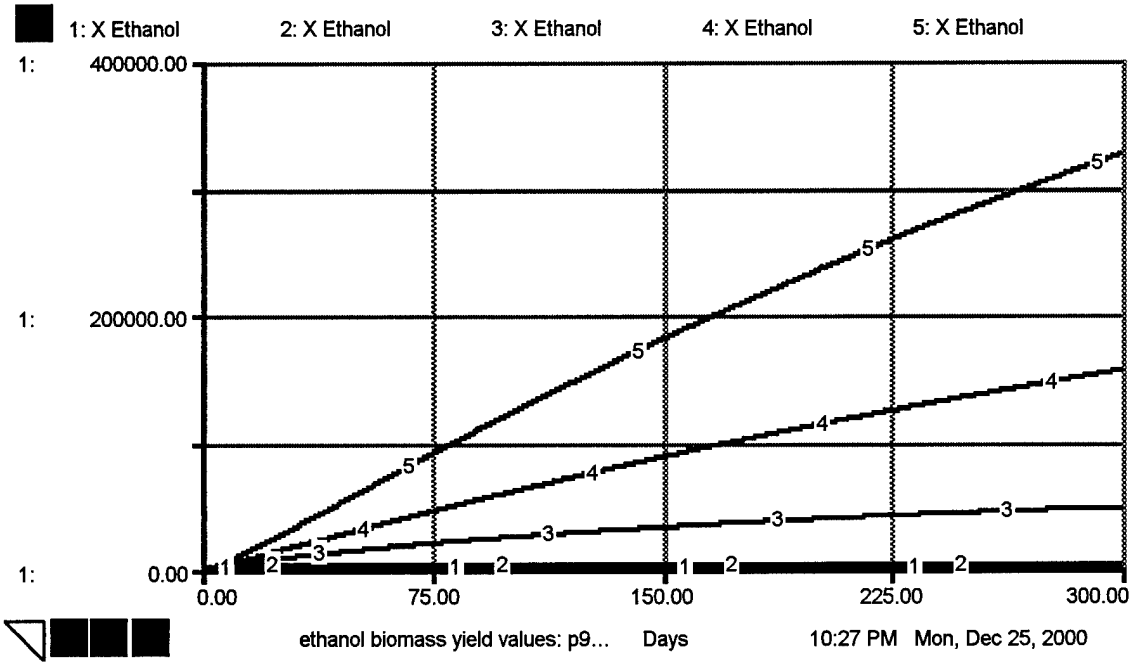




Ethanol biomass yield rate

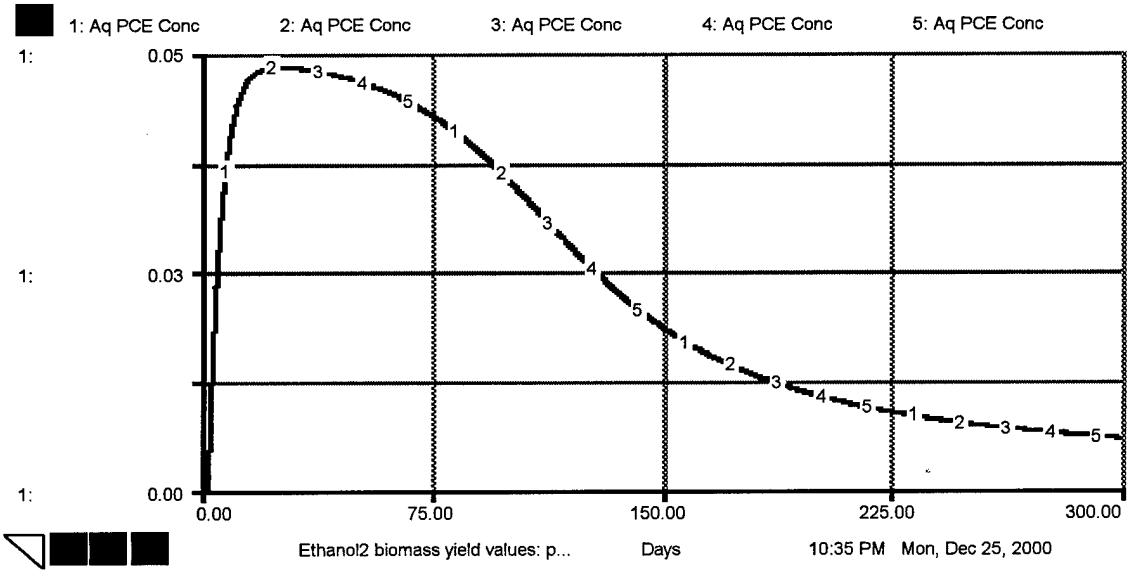
Run	Ethanol Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.1

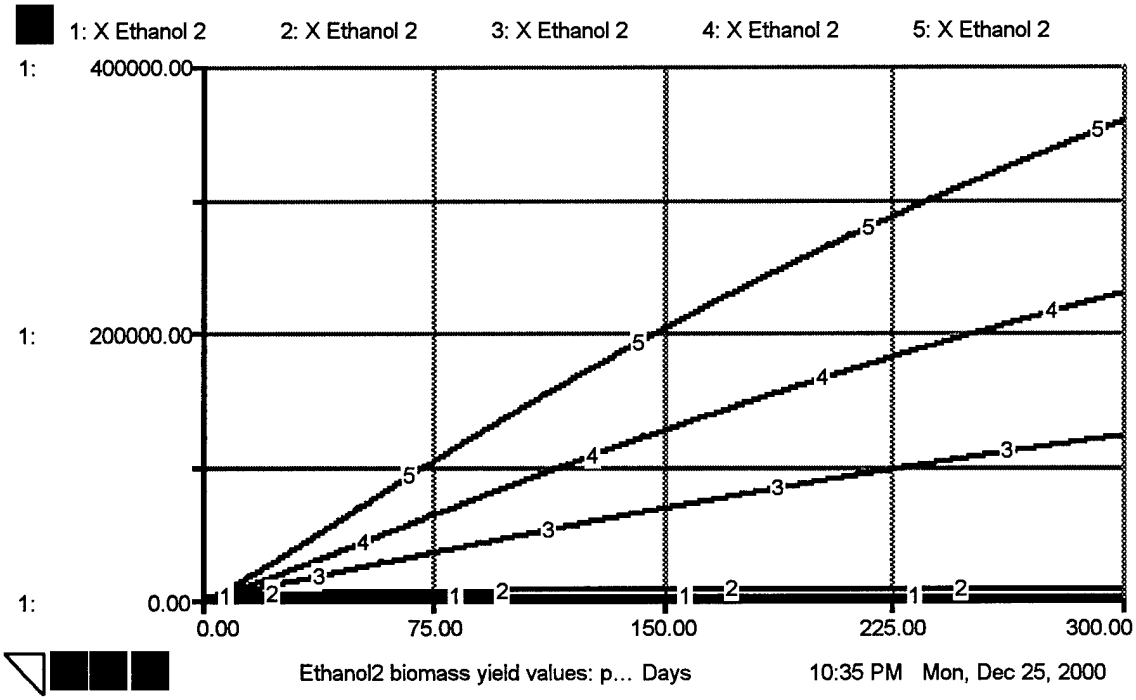




Ethanol 2 biomass yield rate

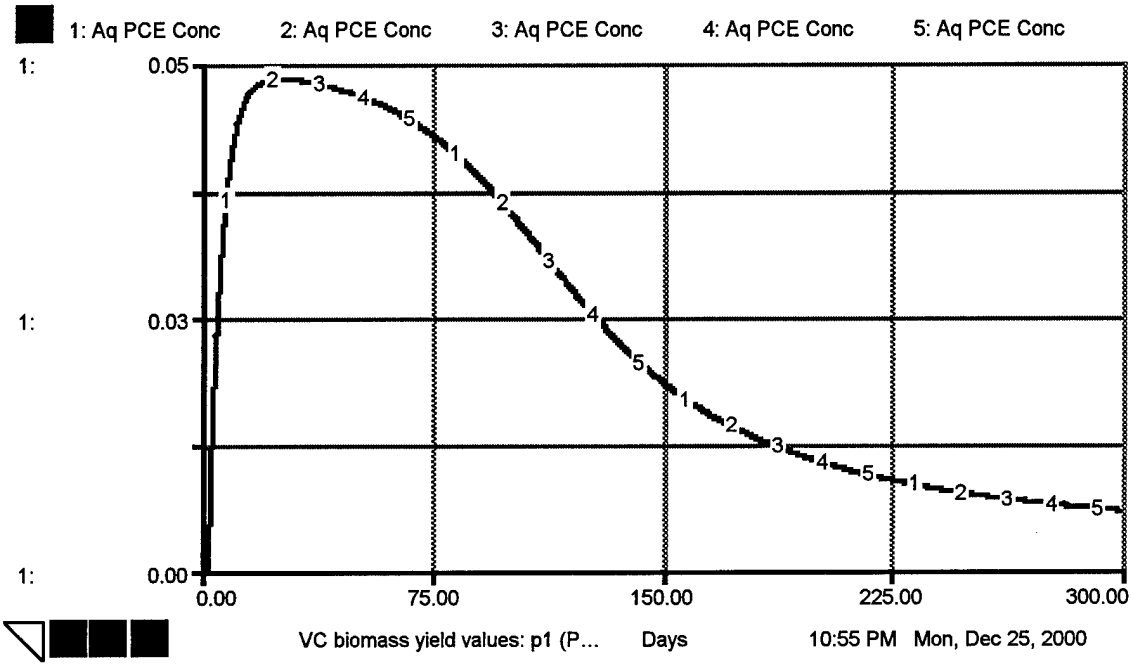
Run	Ethanol 2 Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.1

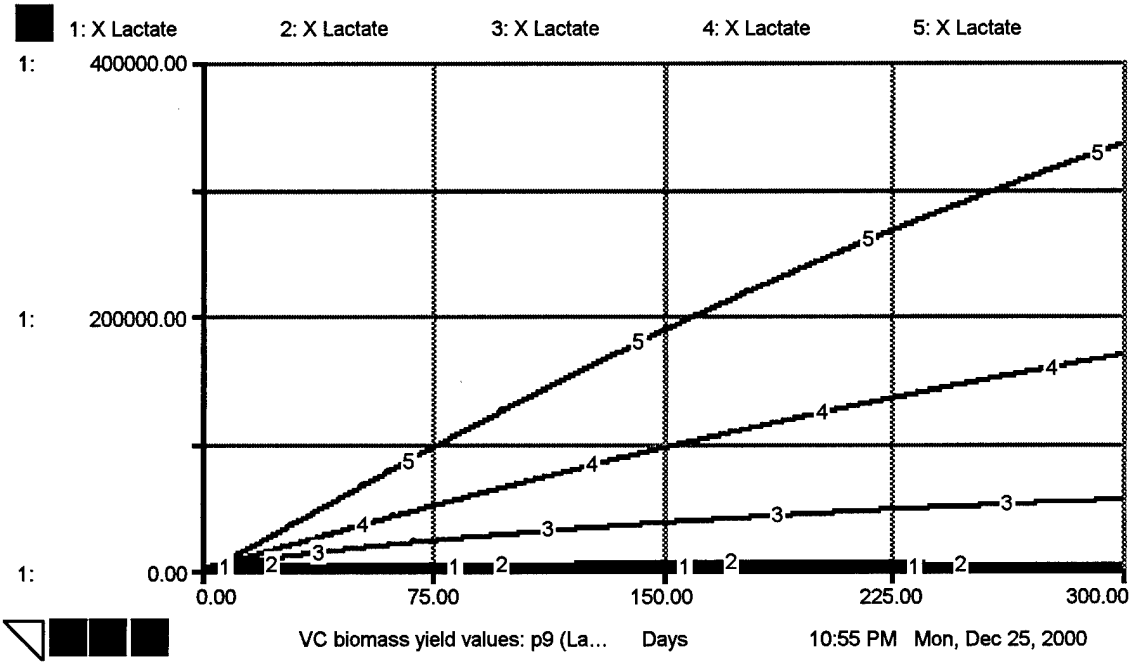




Lactate Biomass Yield Rates

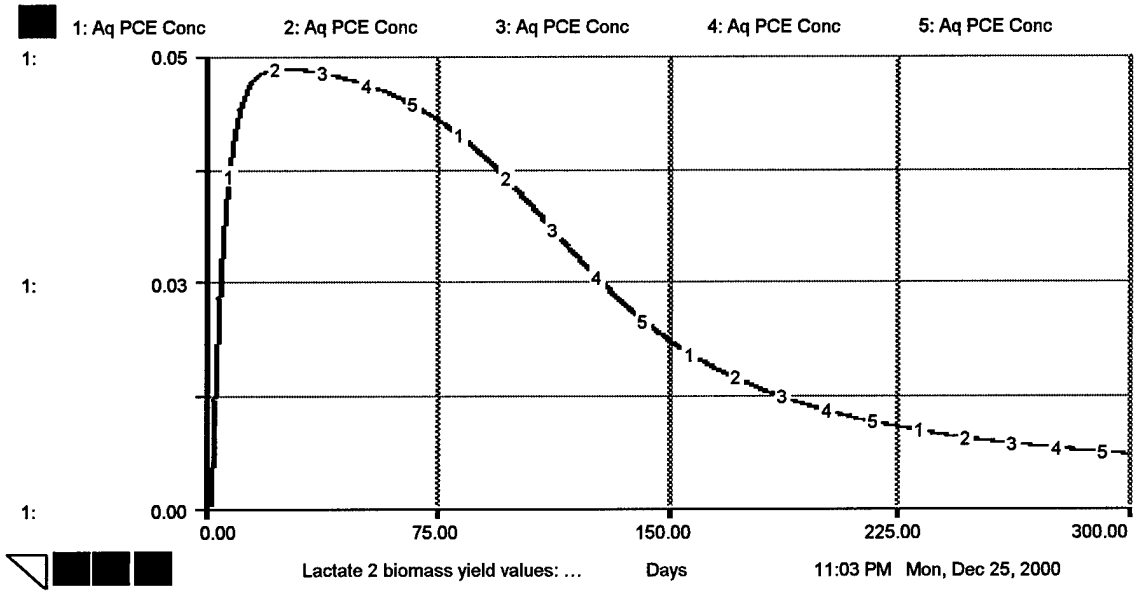
Run	Lactate Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.1

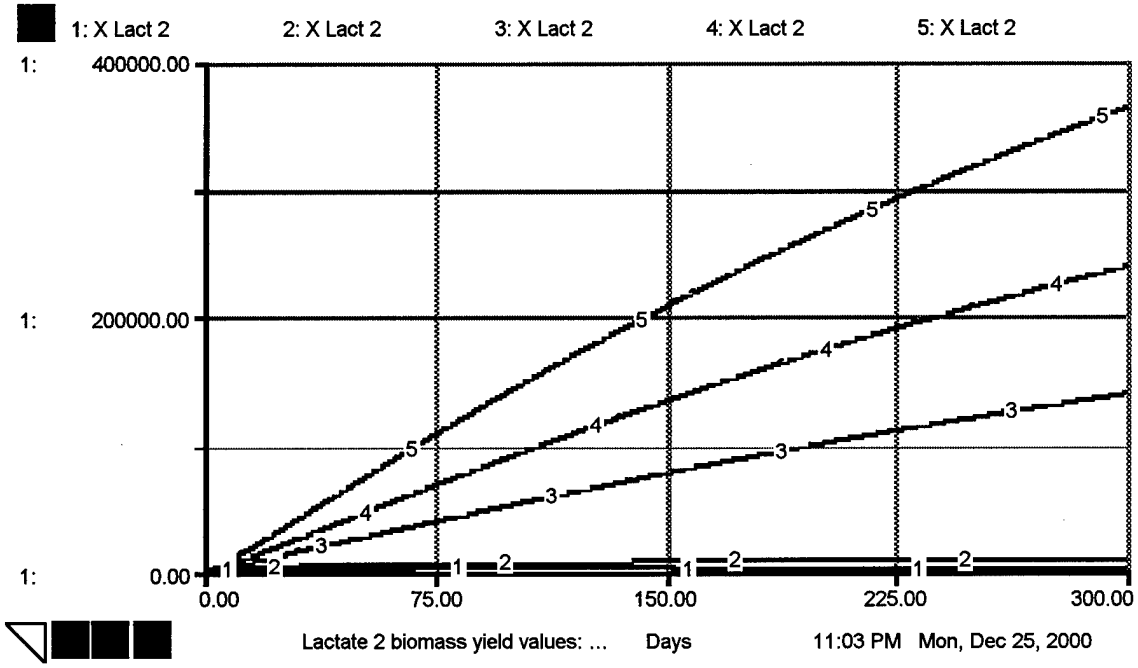




Lactate 2 Biomass Yield Rates

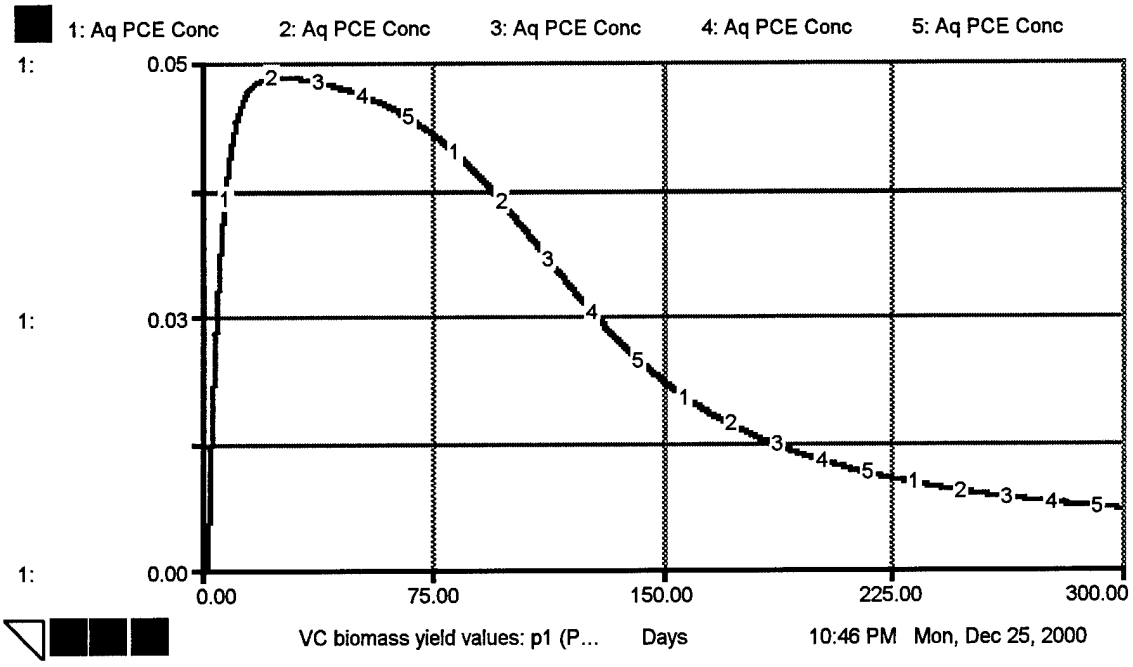
Run	Lactate 2 Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.1

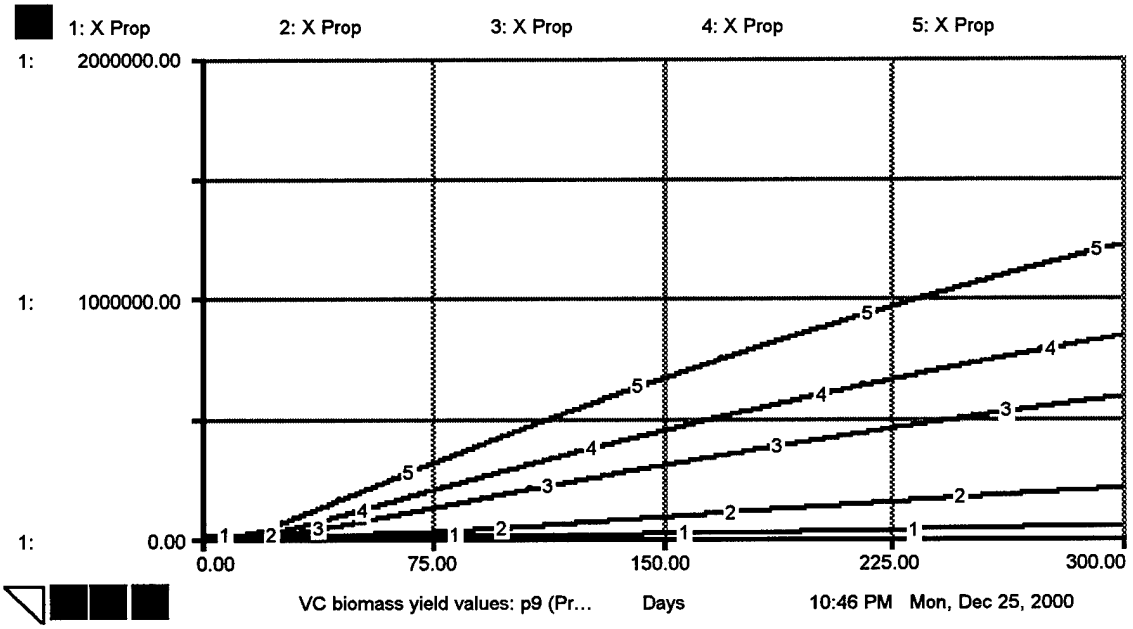




Propionate Biomass Yield Rate

Run	Propionate Biomass Yield (mg of VSS/mg of substrate used)
1	0.008
2	0.02
3	0.05
4	0.07
5	0.1

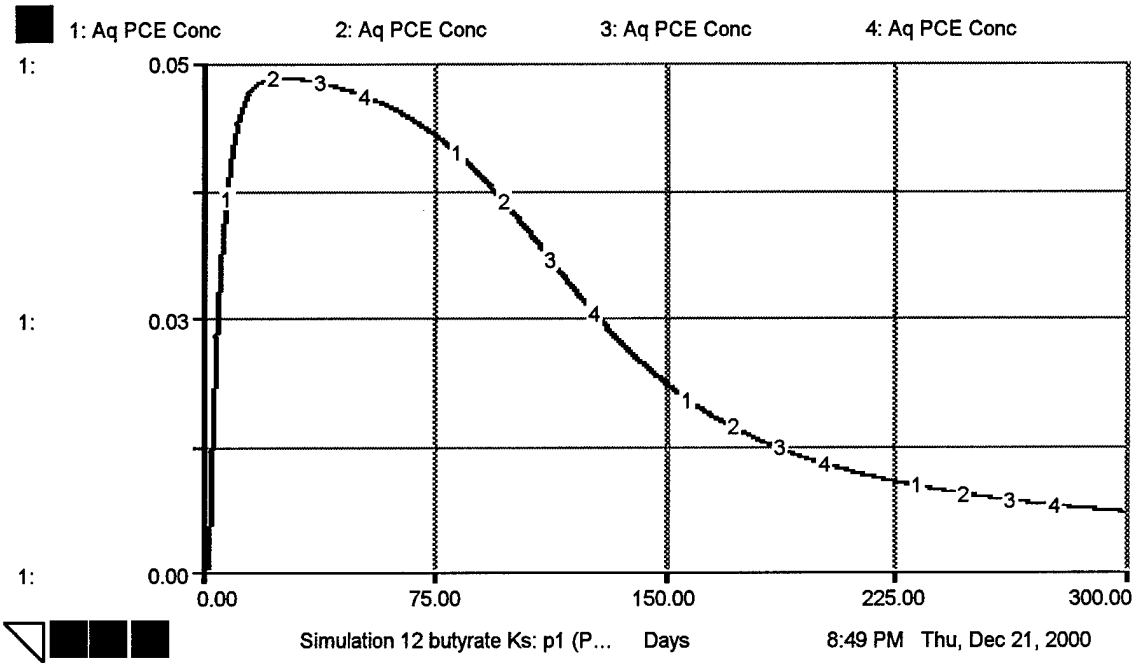


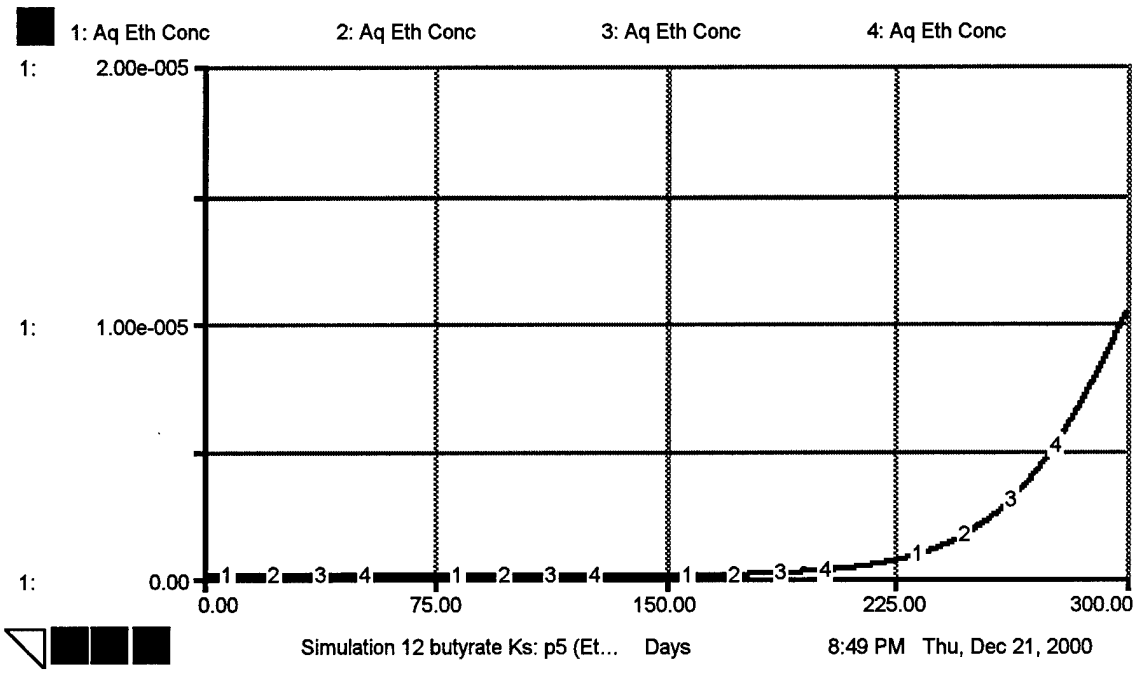


Simulation 12

Butyrate half-velocity coefficients

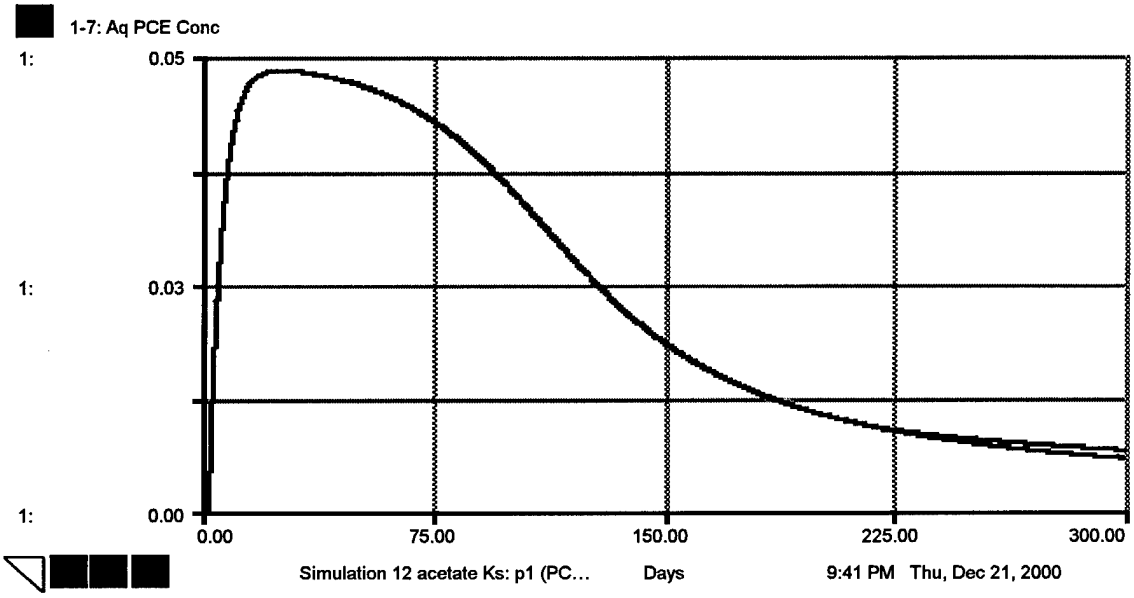
Run	Butyrate half-velocity coefficient (Ks) (mg/L)
1	0.5
2	1
3	3
4	5

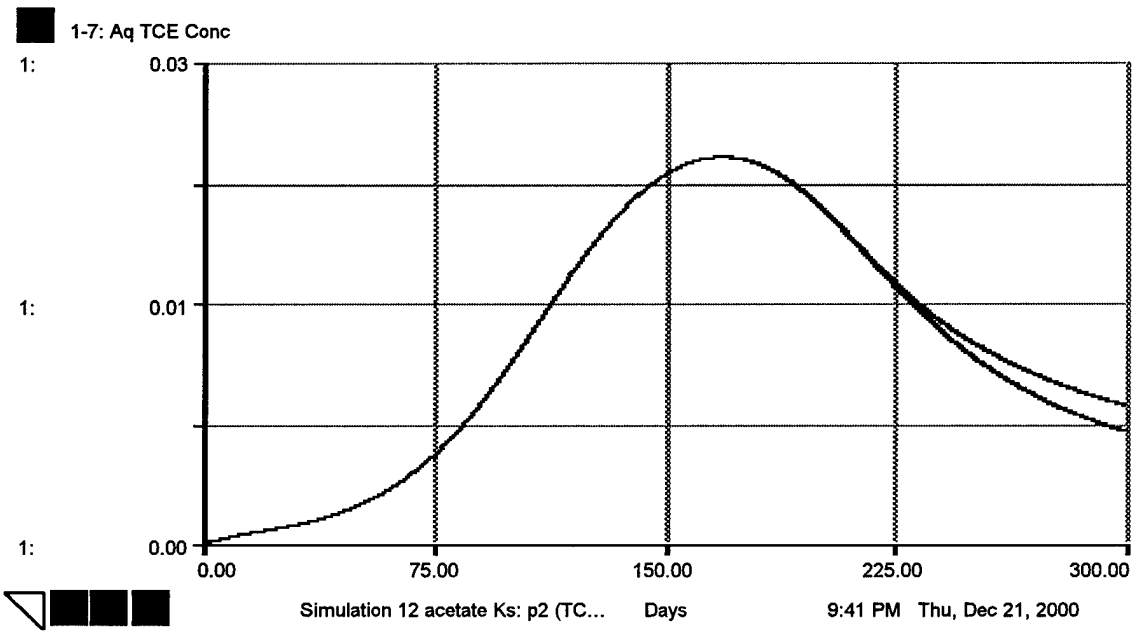



1: Aq Eth Conc
2: Aq Eth Conc
3: Aq Eth Conc
4: Aq Eth Conc
1: 2.00e-005
1: 1.00e-005
1: 0.00
0.00
75.00
150.00
225.00
300.00
Simulation 12 butyrate Ks: p5 (Et... Days
8:49 PM Thu, Dec 21, 2000

Acetate half-velocity coefficients

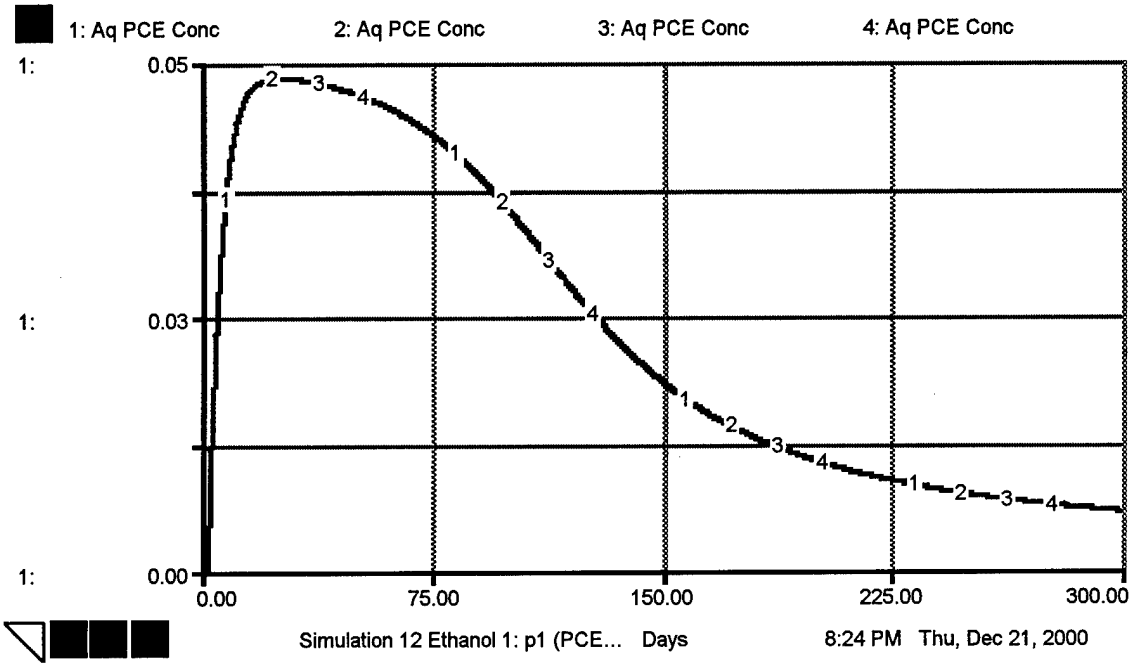
Run	Acetate half-velocity coefficient (Ks) (mg/L)
1	5
2	15
3	25
4	35
5	45
6	55
7	70

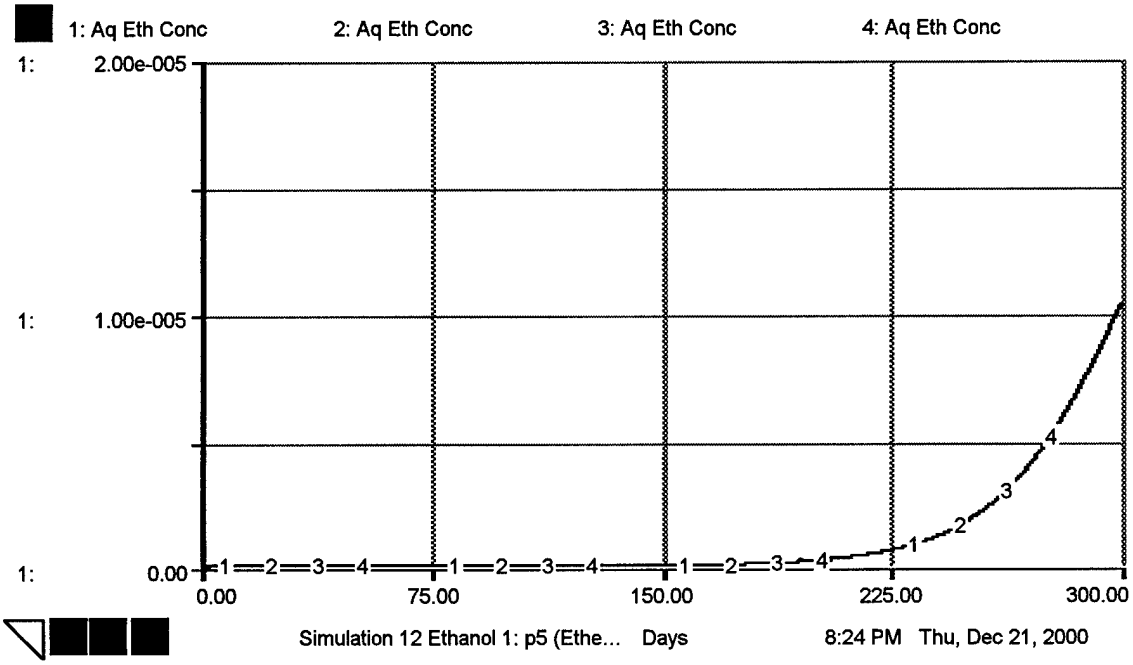




Ethanol half-velocity coefficients

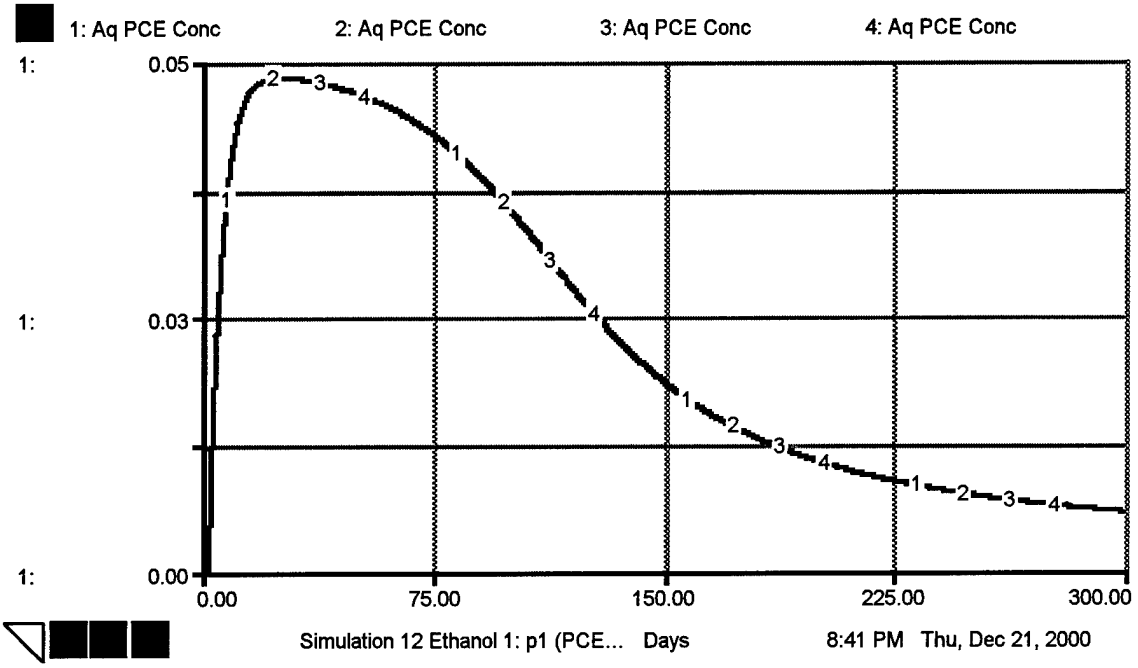
Run	Ethanol half-velocity coefficient (Ks) (mg/L)
1	0.5
2	1.5
3	3
4	5

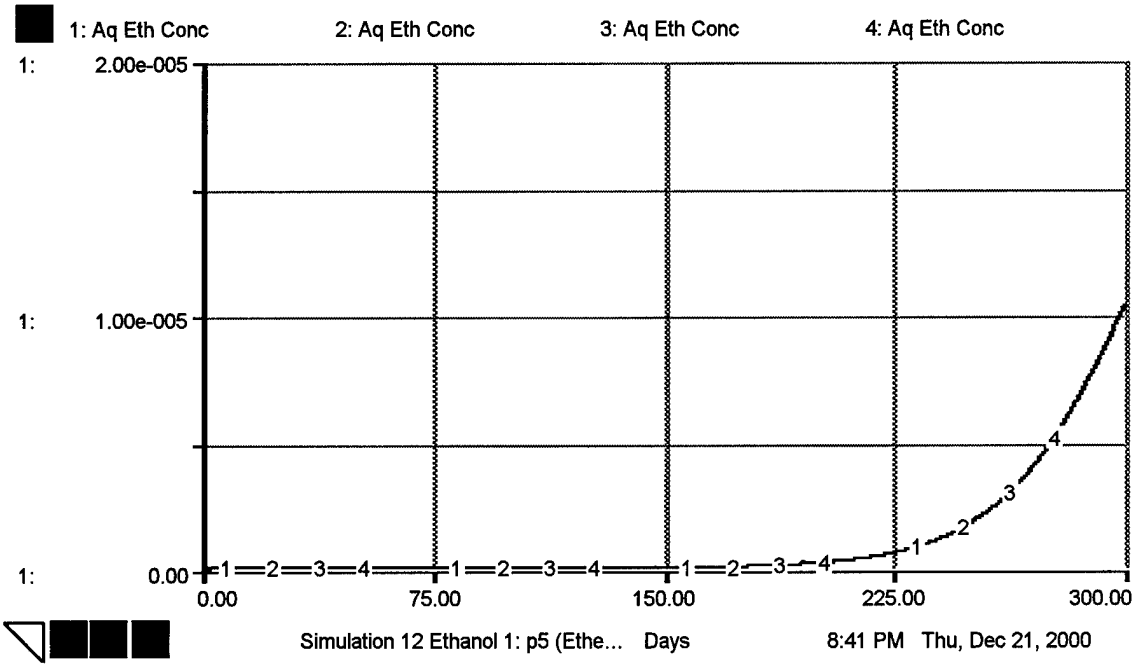




Ethanol 2 half-velocity coefficients

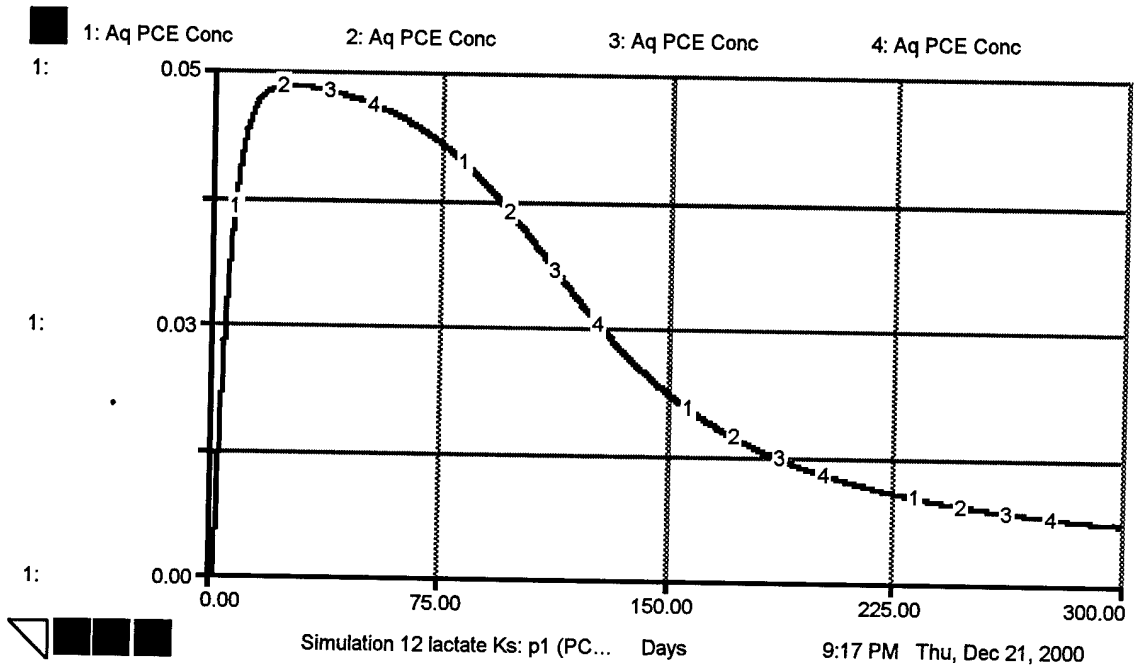
Run	Ethanol 2 half-velocity coefficient (Ks) (mg/L)
1	0.5
2	1.5
3	3
4	5

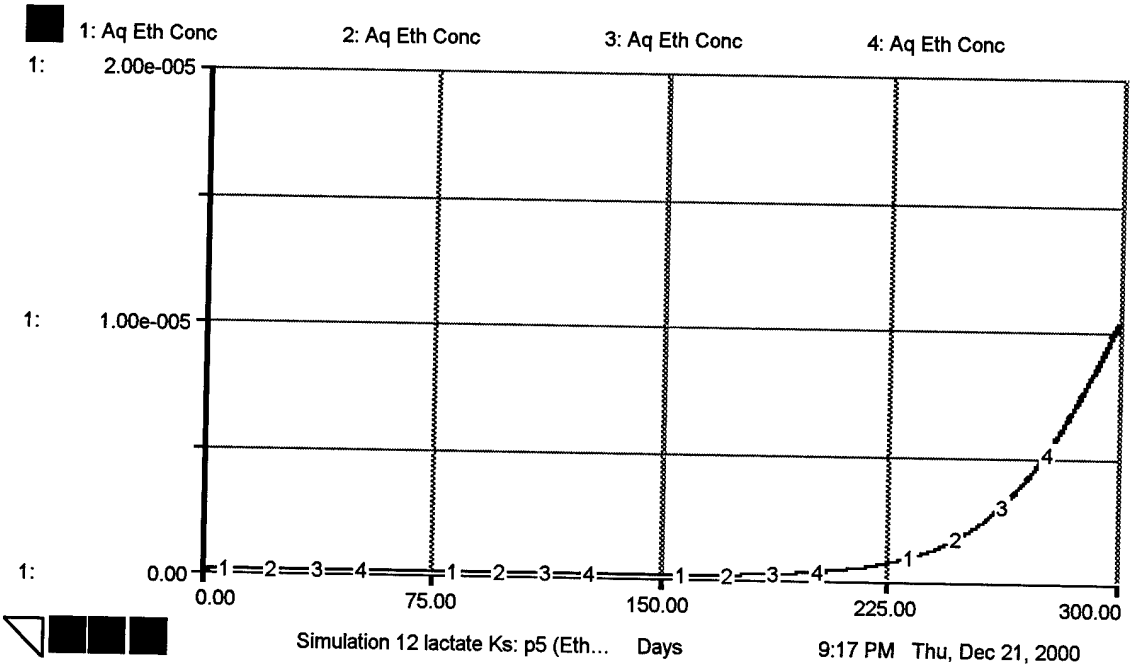




Lactate half-velocity coefficients

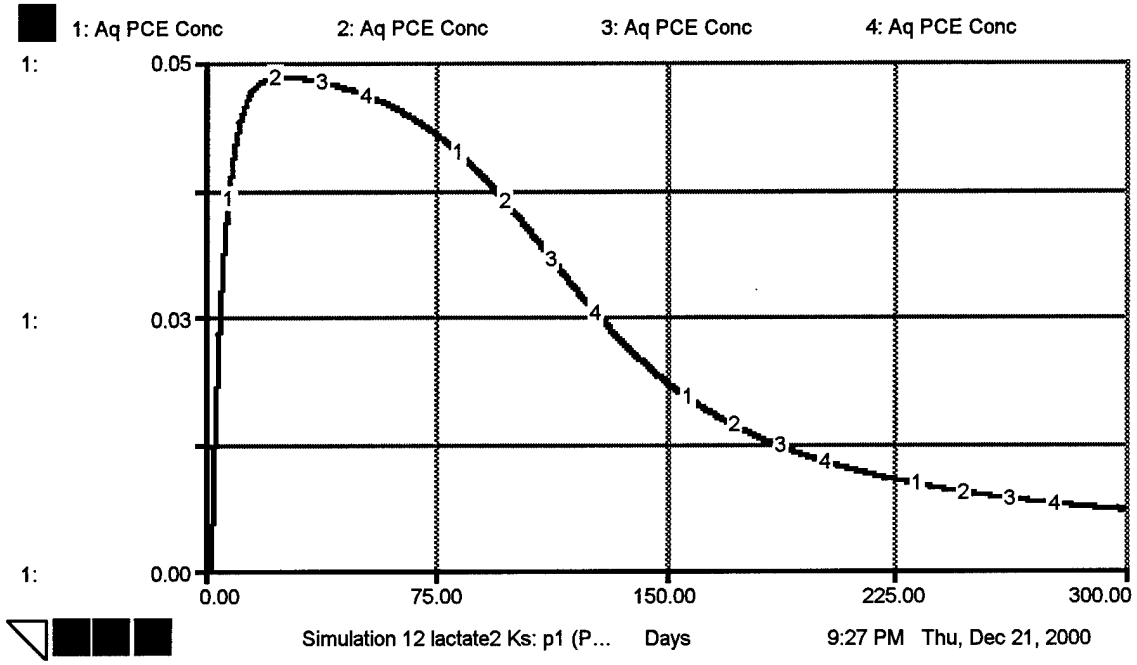
Run	Lactate half-velocity coefficient (Ks) (mg/L)
1	0.1
2	0.7
3	2
4	5

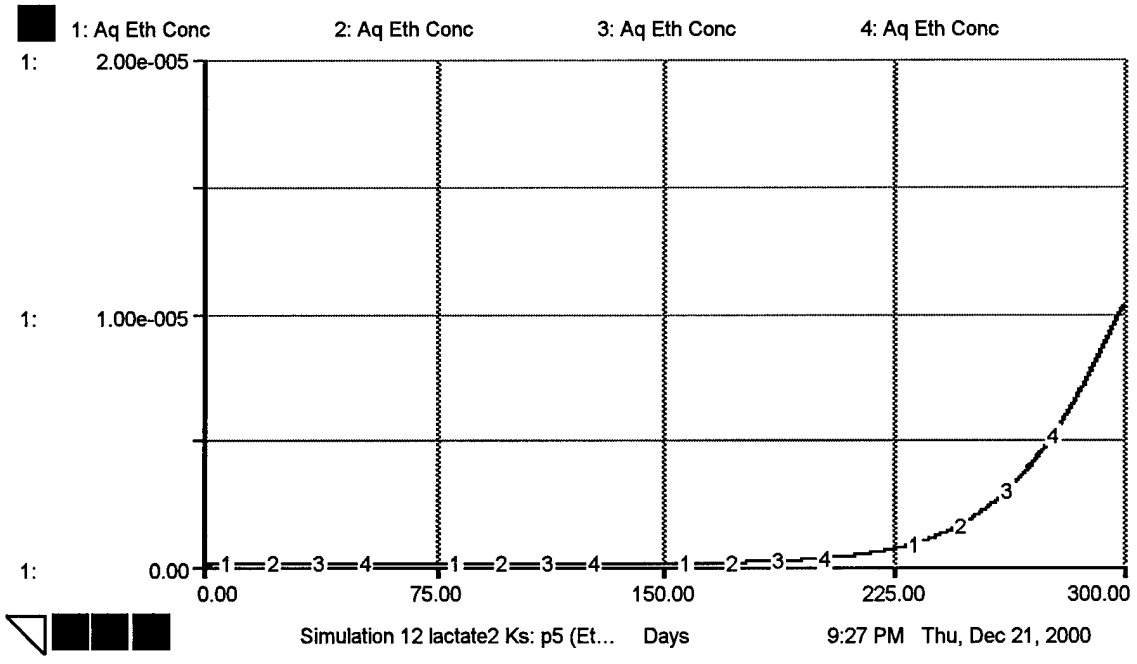




Lactate 2 half-velocity coefficients

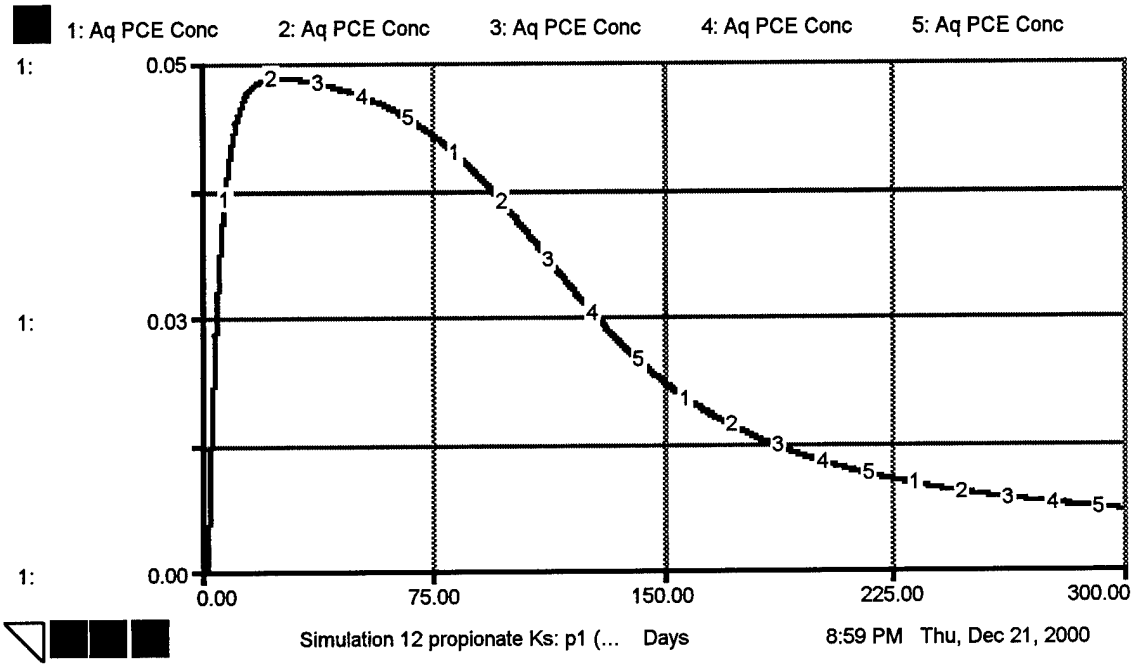
Run	Lactate 2 half-velocity coefficient (Ks) (mg/L)
1	0.15
2	0.7
3	2
4	5

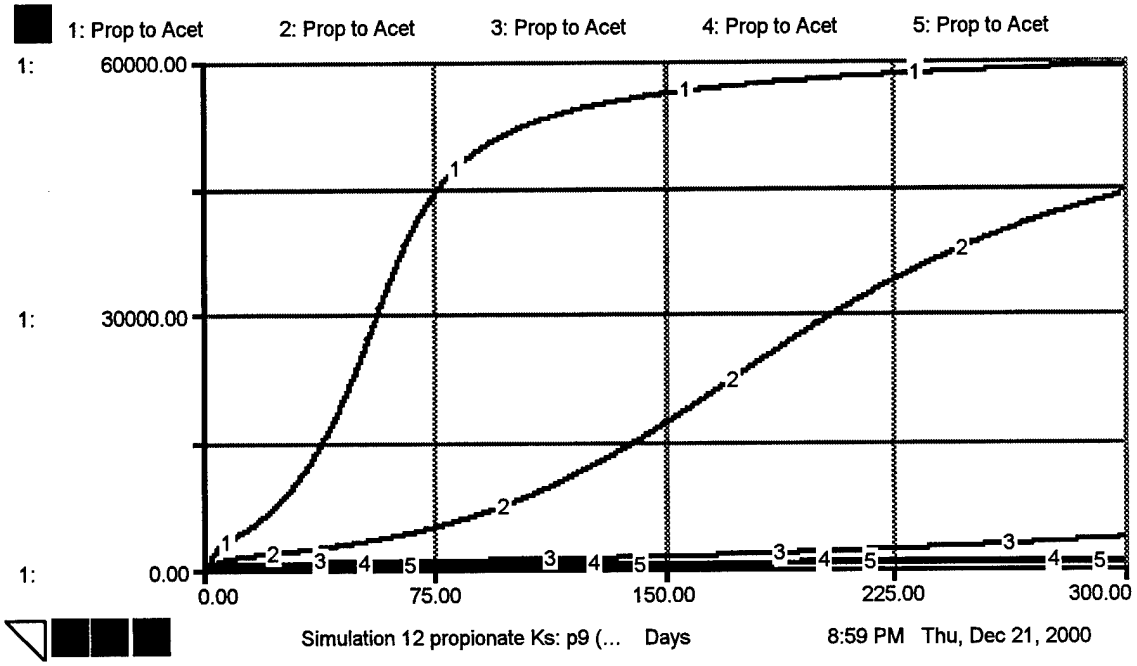




Propionate half-velocity coefficients

Run	Propionate half-velocity coefficient (Ks) (mg/L)
1	0.5
2	3
3	10
4	17
5	25

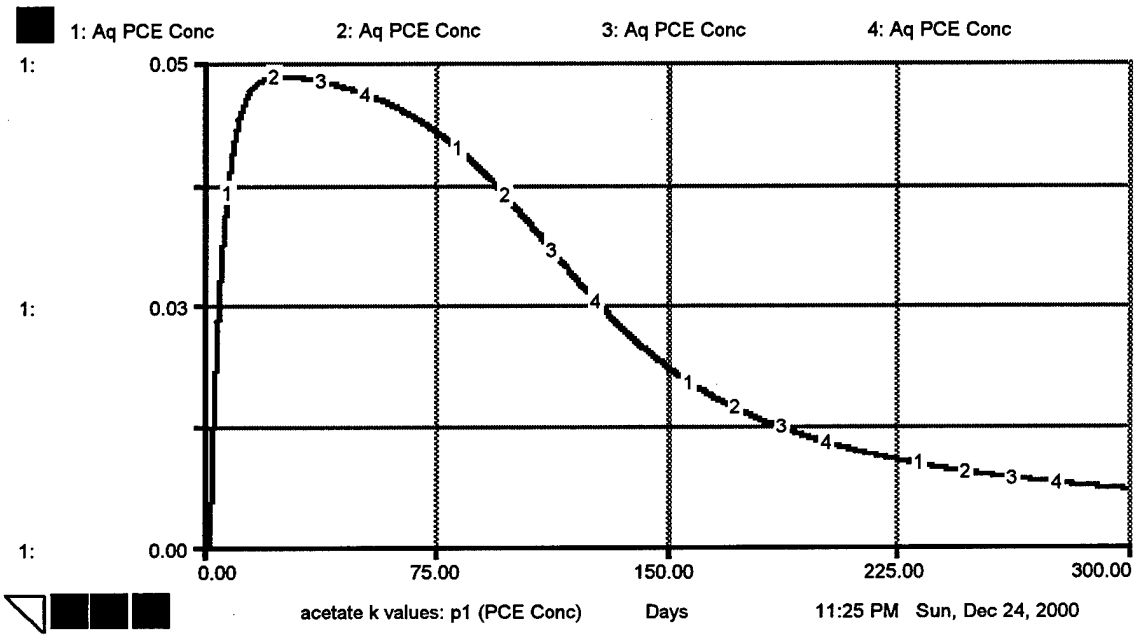


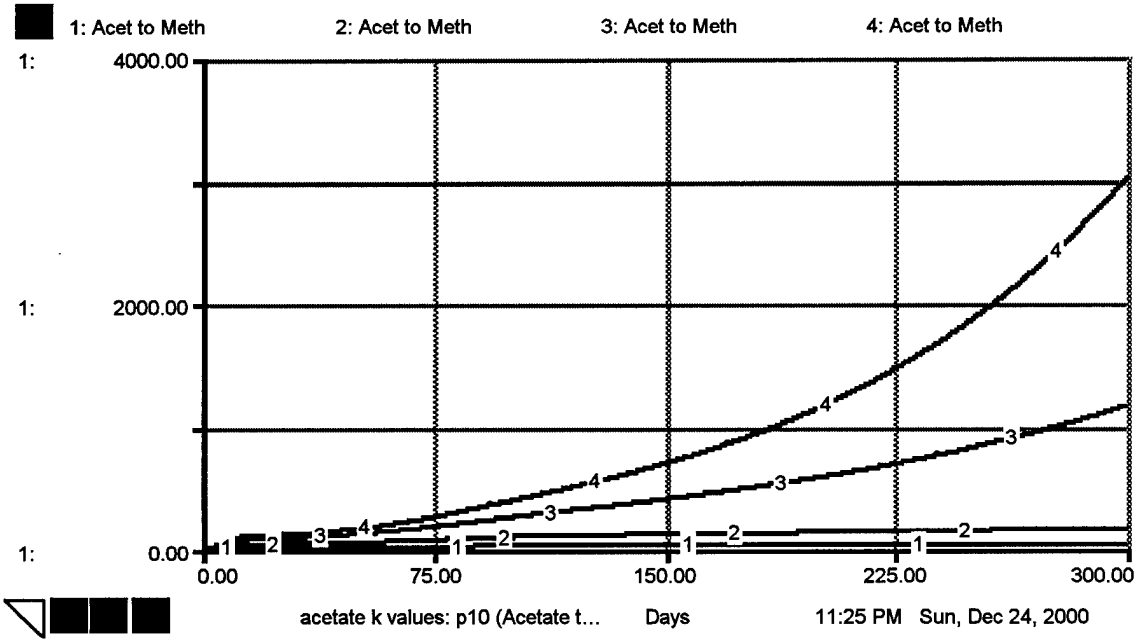


Simulation 13

Acetate utilization rate (k)

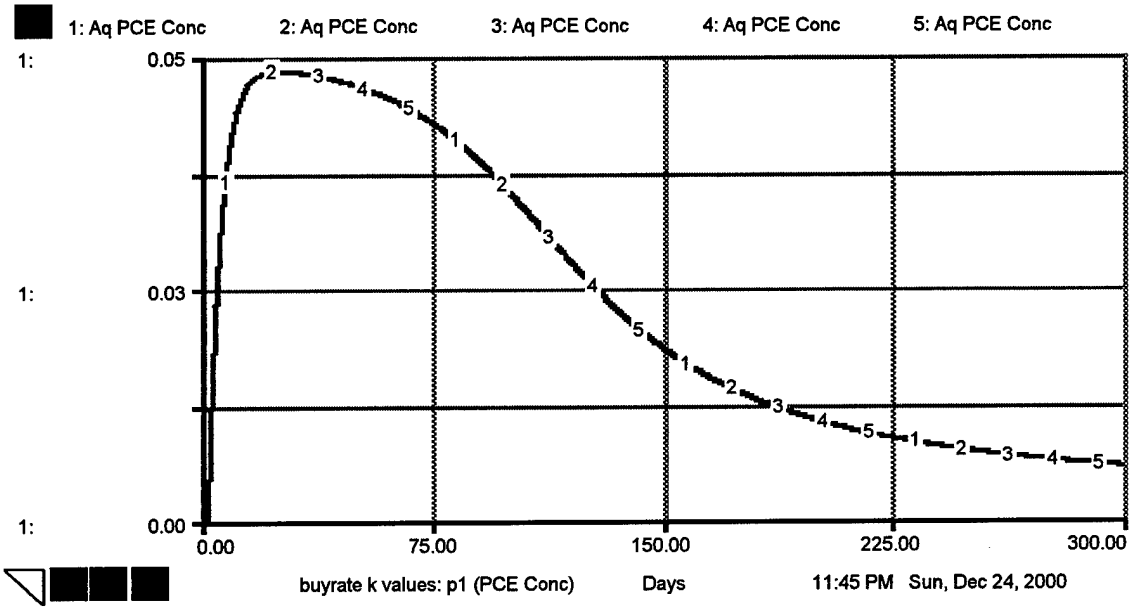
Run	Acetate utilization rate (k) (mg/mg of VSS/d)
1	1
2	4
3	9
4	12

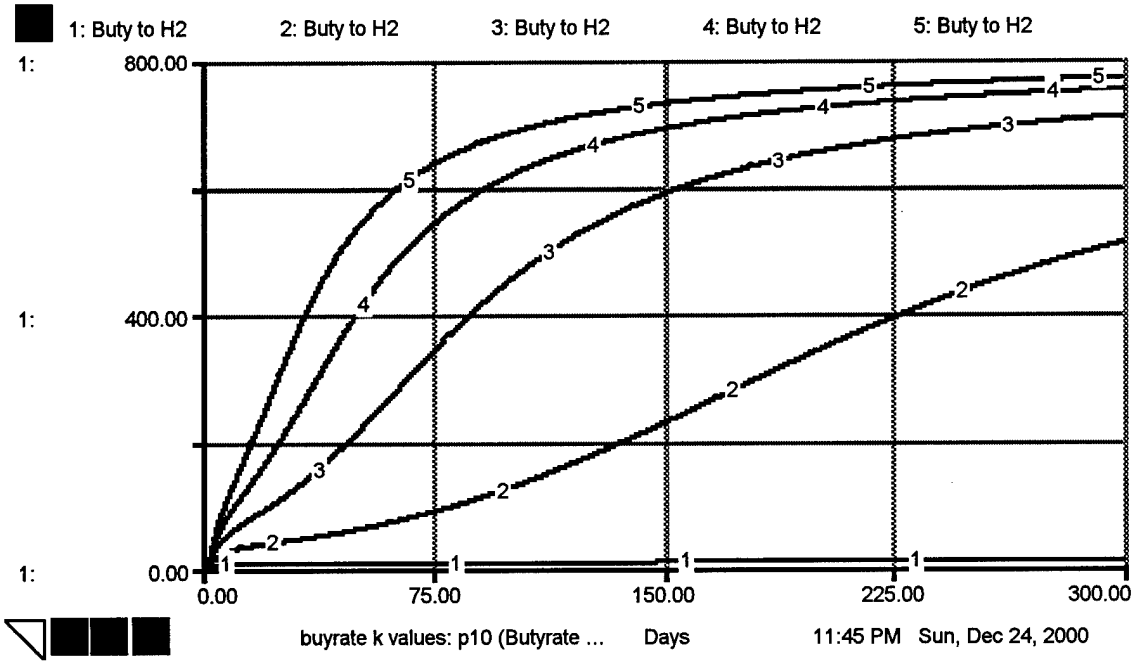




Butyrate utilization rate (k)

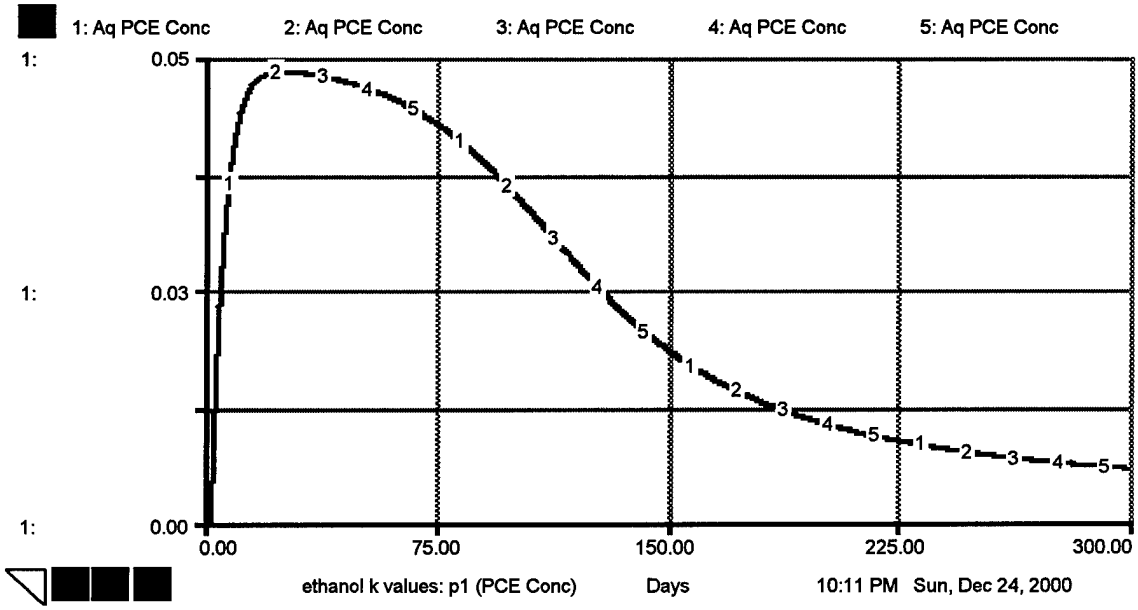
Run	Butyrate utilization rate (k) (mg/mg of VSS/d)
1	1
2	5
3	10
4	15
5	20

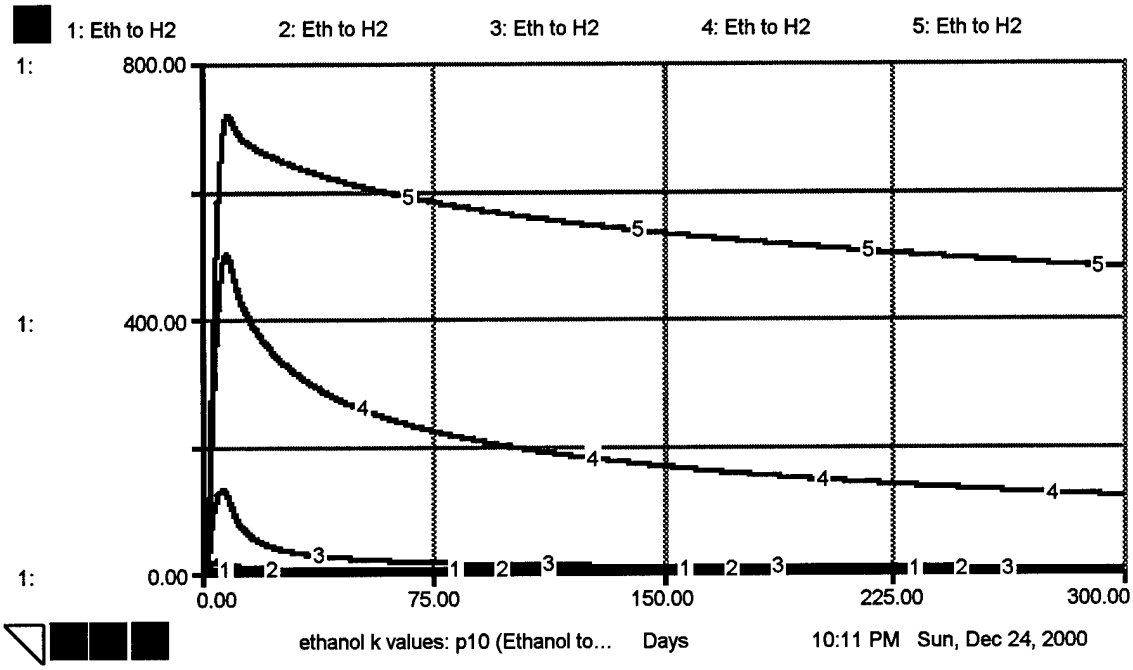




Ethanol utilization rate (k)

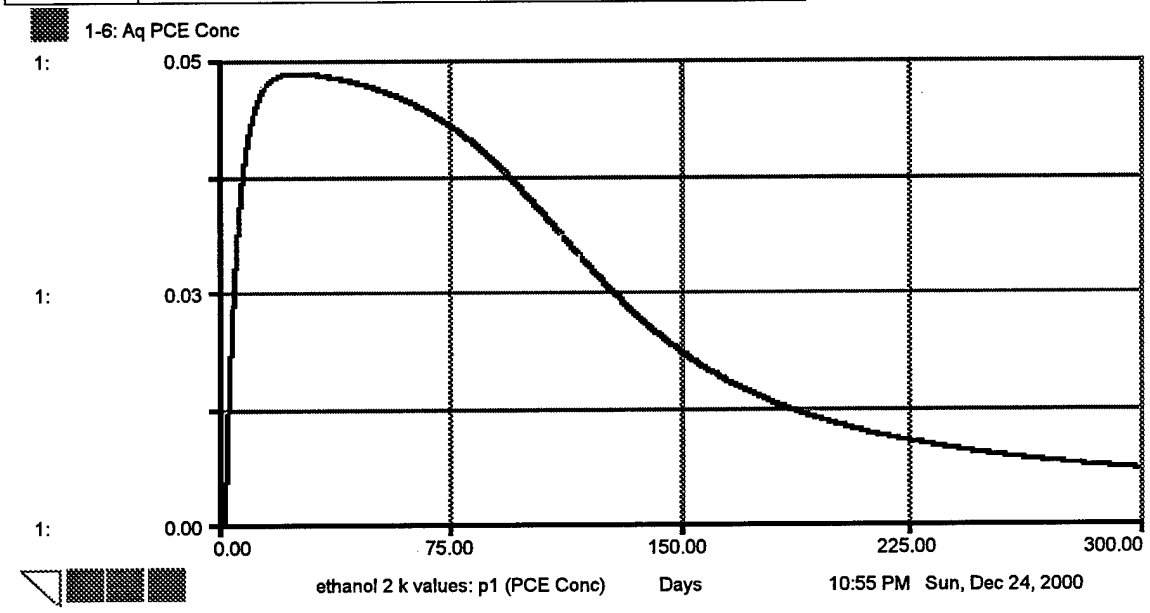
Run	Ethanol utilization rate (k) (mg/mg of VSS/d)
1	0.2
2	1
3	7
4	14
5	22

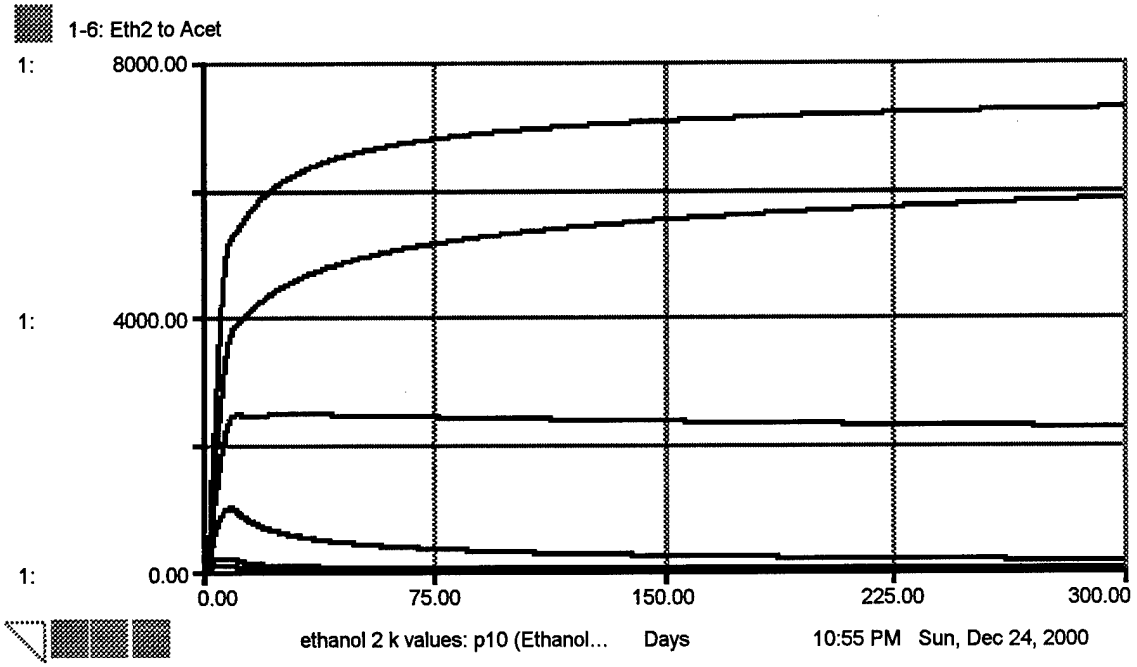



1: Eth to H2
2: Eth to H2
3: Eth to H2
4: Eth to H2
5: Eth to H2
1:
800.00
1:
400.00
1:
0.00
0.00
75.00
150.00
225.00
300.00
ethanol k values: p10 (Ethanol to...
Days
10:11 PM Sun, Dec 24, 2000

Ethanol 2 utilization rate (k)

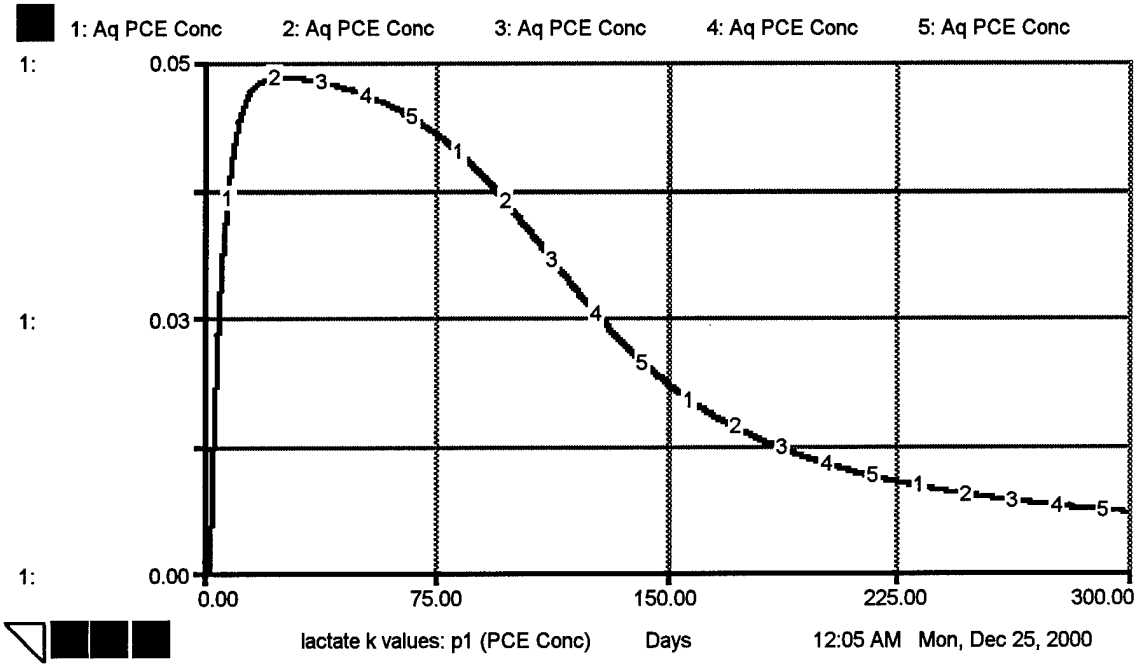
Run	Ethanol 2 utilization rate (k) (mg/mg of VSS/d)
1	0.6
2	2
3	8
4	15
5	21
6	30

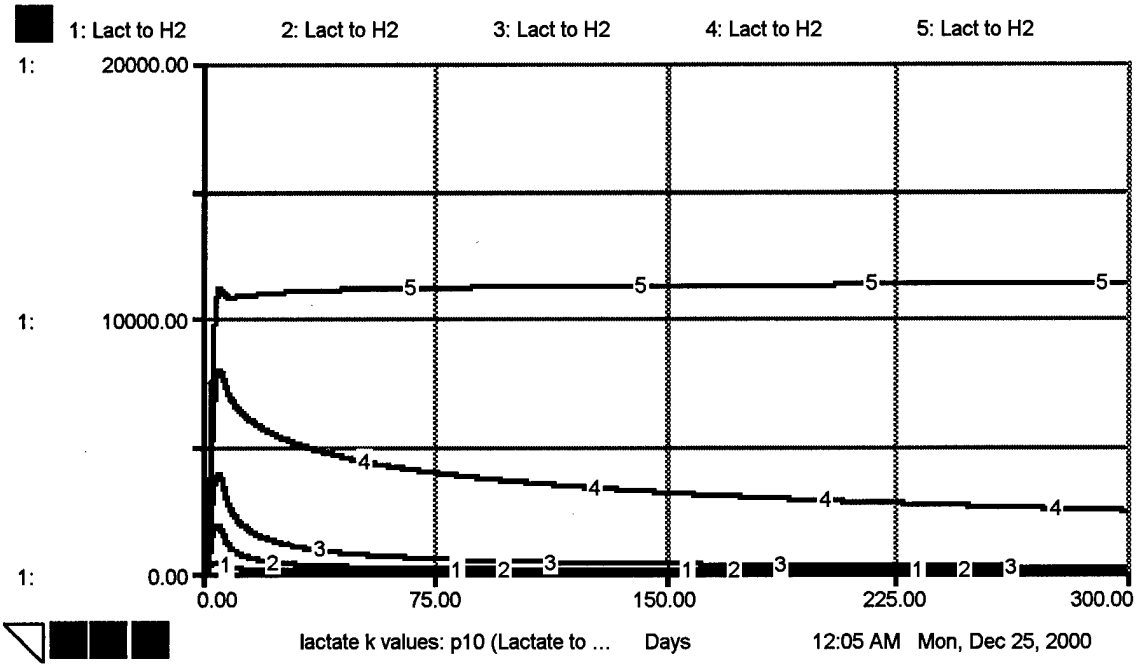




Lactate utilization rate (k)

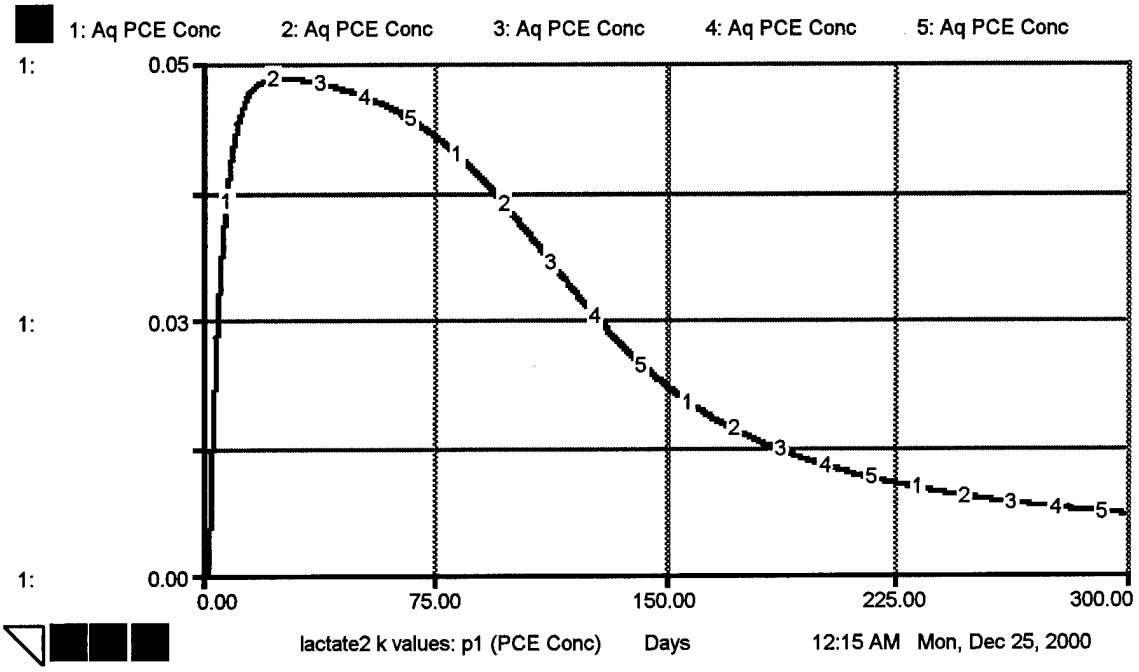
Run	Lactate utilization rate (k) (mg/mg of VSS/d)
1	1
2	5
3	10
4	20
5	30

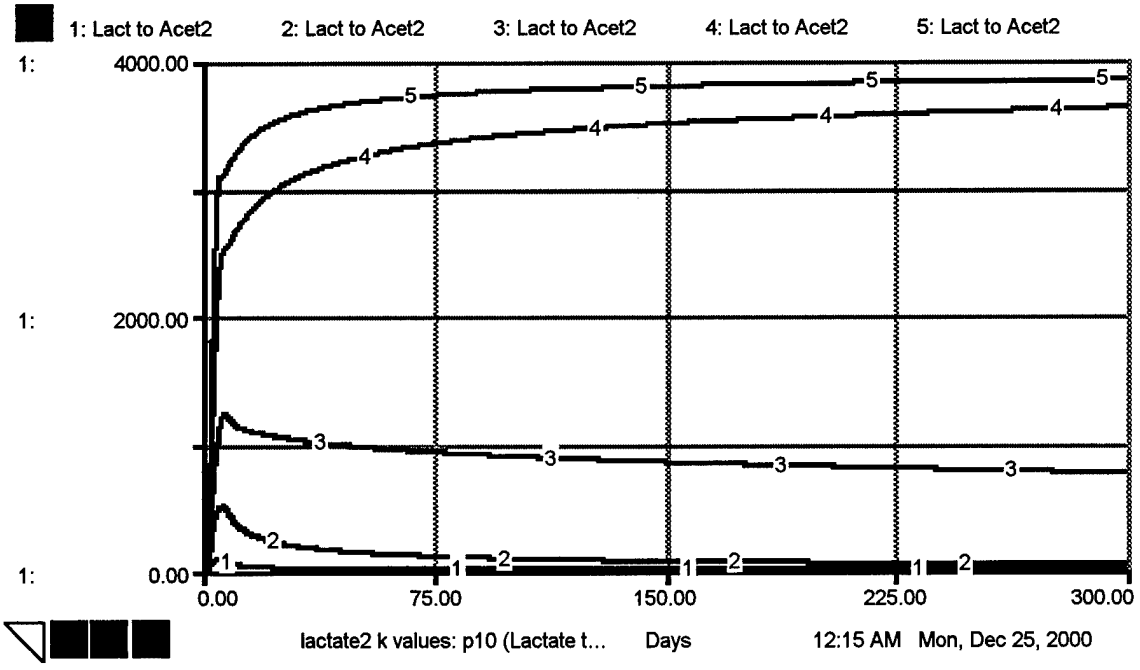




Lactate 2 utilization rate (k)

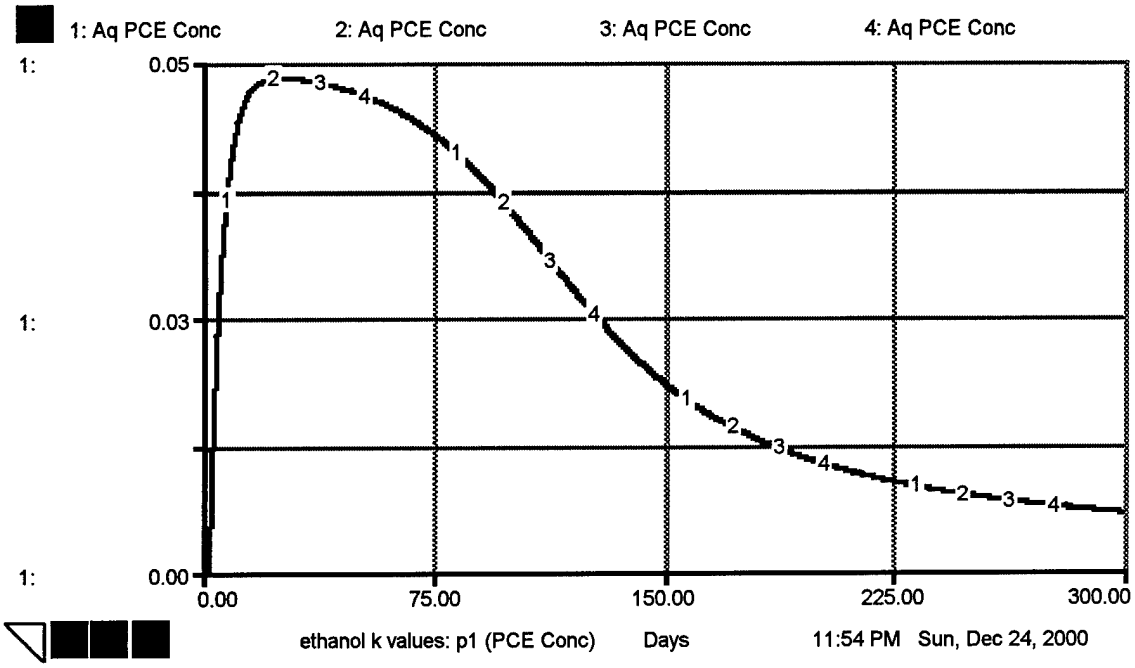
Run	Lactate 2 utilization rate (k) (mg/mg of VSS/d)
1	1
2	5
3	10
4	20
5	30

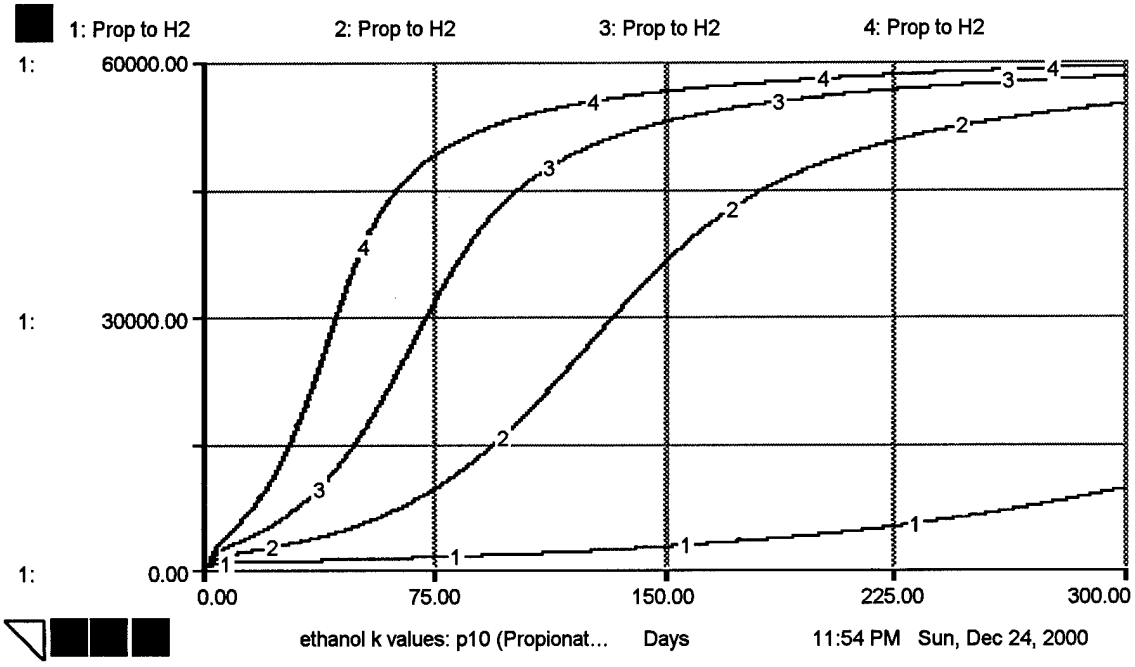




Propionate utilization rate (k)

Run	Propionate utilization rate (k) (mg/mg of VSS/d)
1	1
2	2.5
3	4
4	6

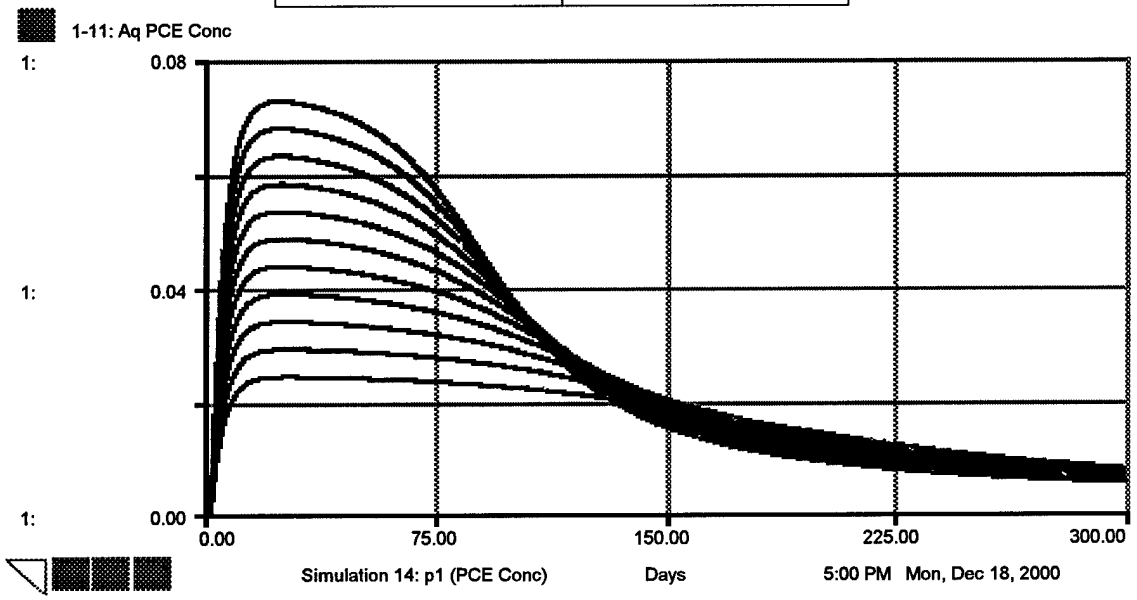


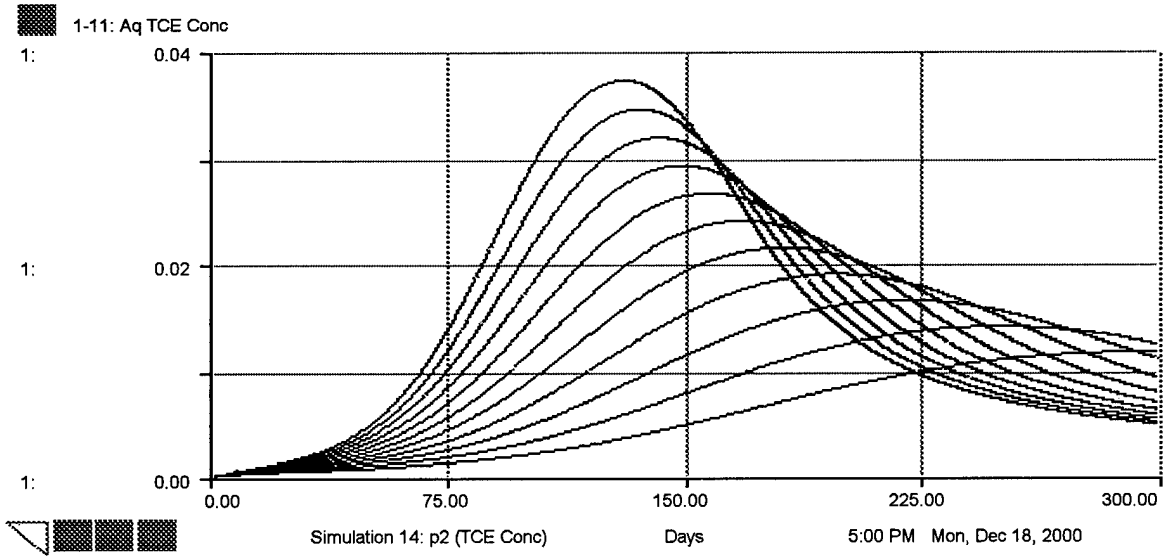


Simulation 14

Changes in the concentration of the incoming contaminant

Incoming Concentrations of PCE (mg/L)	
1) .025	7) .055
2) .03	8) .06
3) .035	9) .065
4) .04	10) .07
5) .045	11) .075
6) .05	

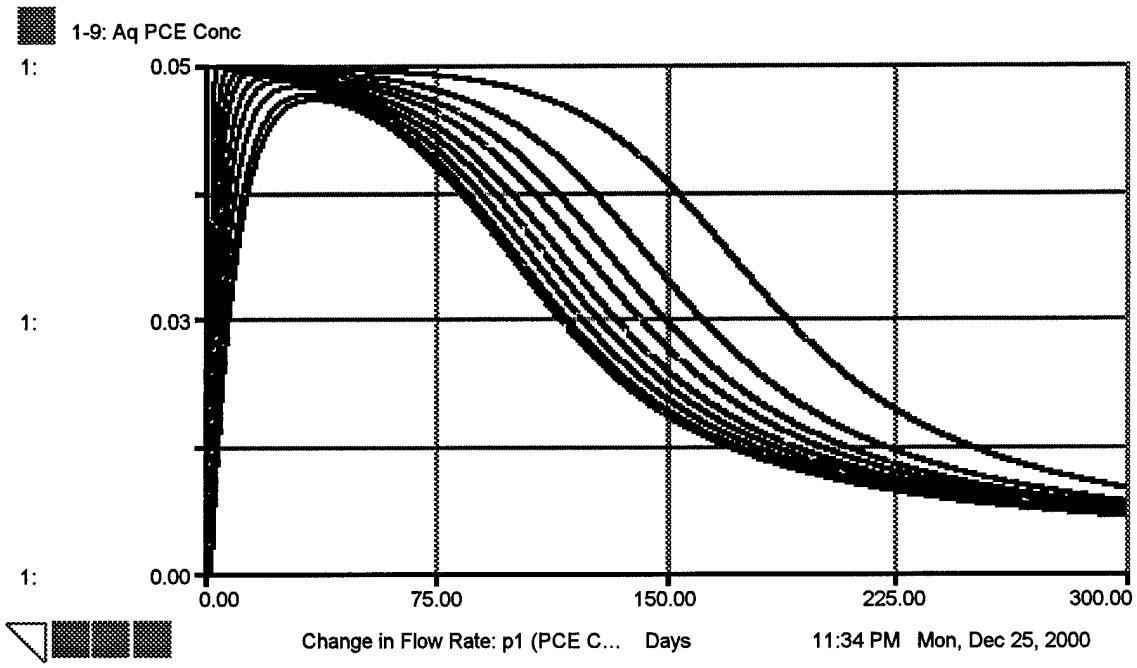


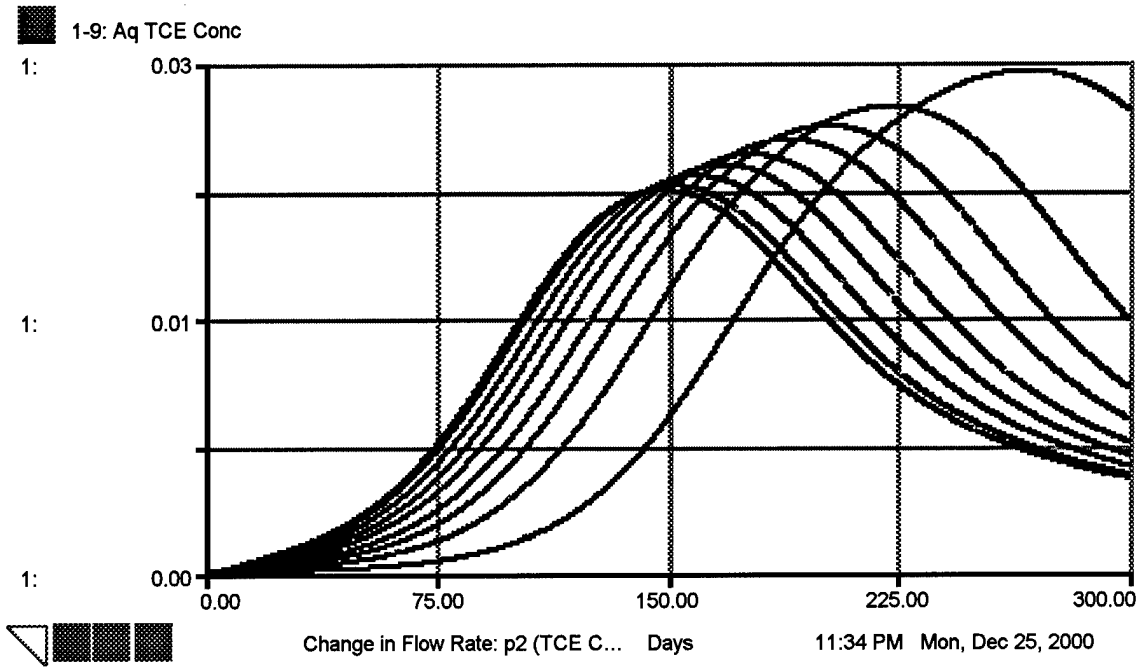


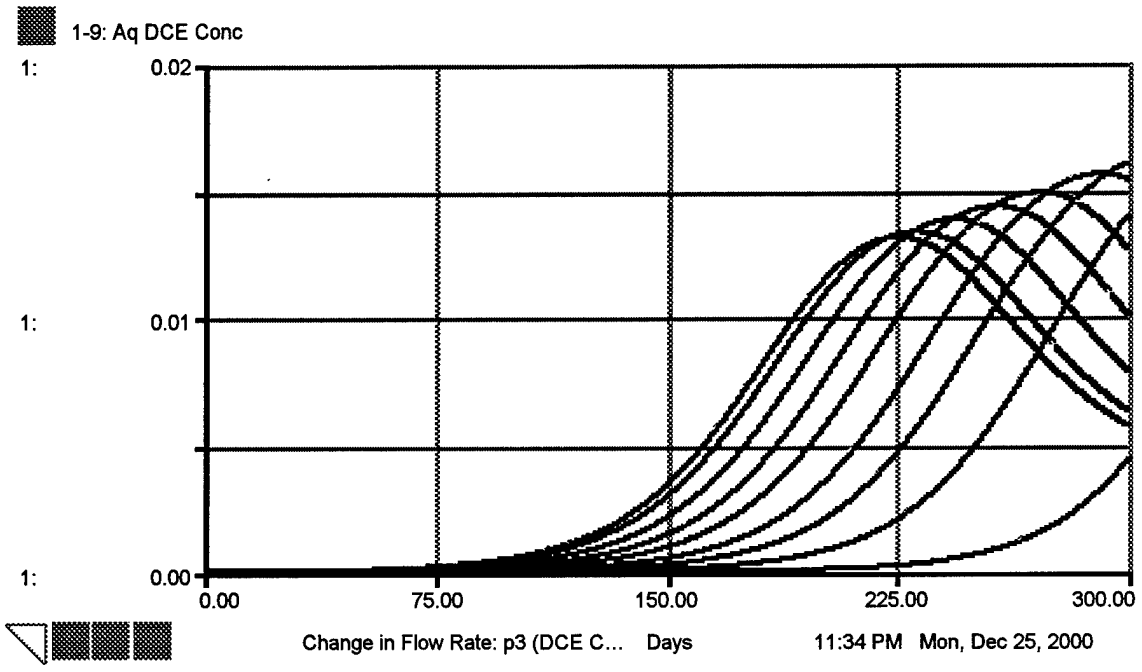
Simulation 15

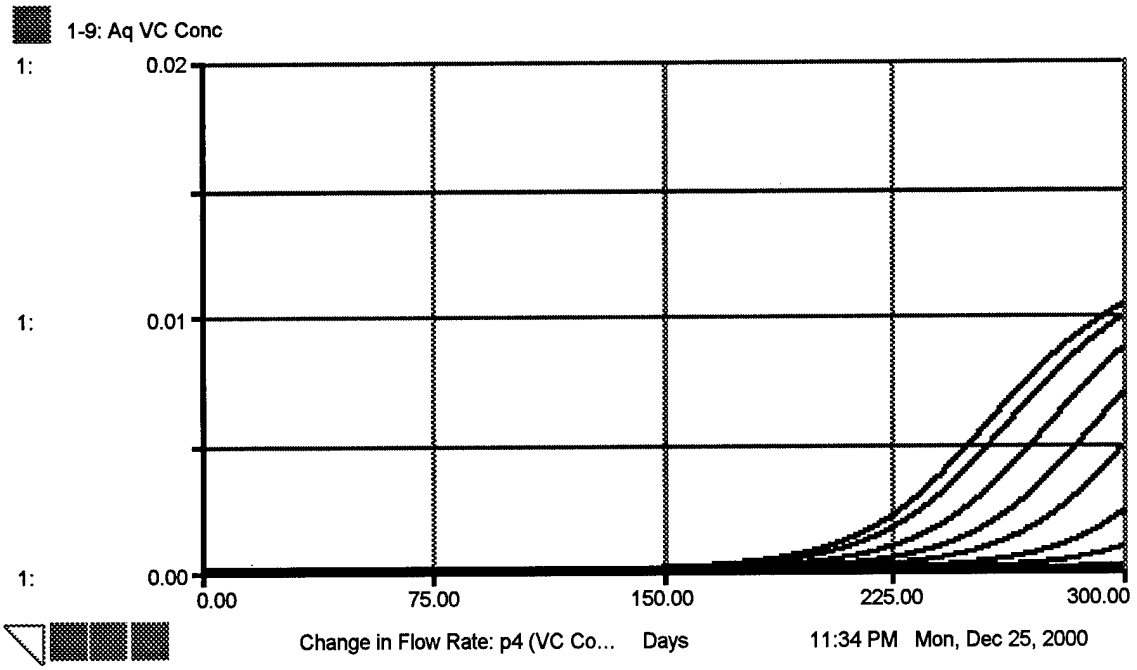
Simulation 15 Flow rate Changes

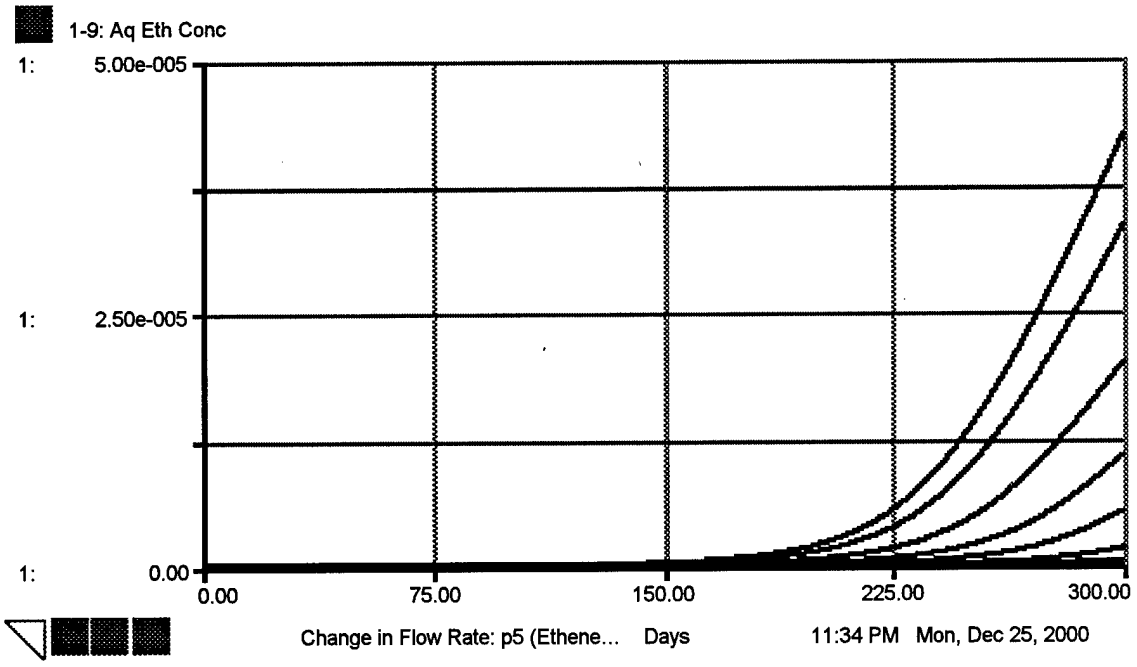
Run	RETENTION TIME (days)	FLOW RATES (gal/min)
1	1	98.08
2	3	32.69
3	5	19.62
4	7	14.01
5	10	9.81
6	13	7.54
7	17	5.77
8	22	4.46
9	25	3.92




1-9: Aq TCE Conc
1:
0.03
1:
0.01
1:
0.00
0.00
75.00
150.00
225.00
300.00
Change in Flow Rate: p2 (TCE C...
Days
11:34 PM Mon, Dec 25, 2000


1-9: Aq DCE Conc
1:
0.02
1:
0.01
1:
0.00
0.00
75.00
150.00
225.00
300.00
Change in Flow Rate: p3 (DCE C...
Days
11:34 PM Mon, Dec 25, 2000

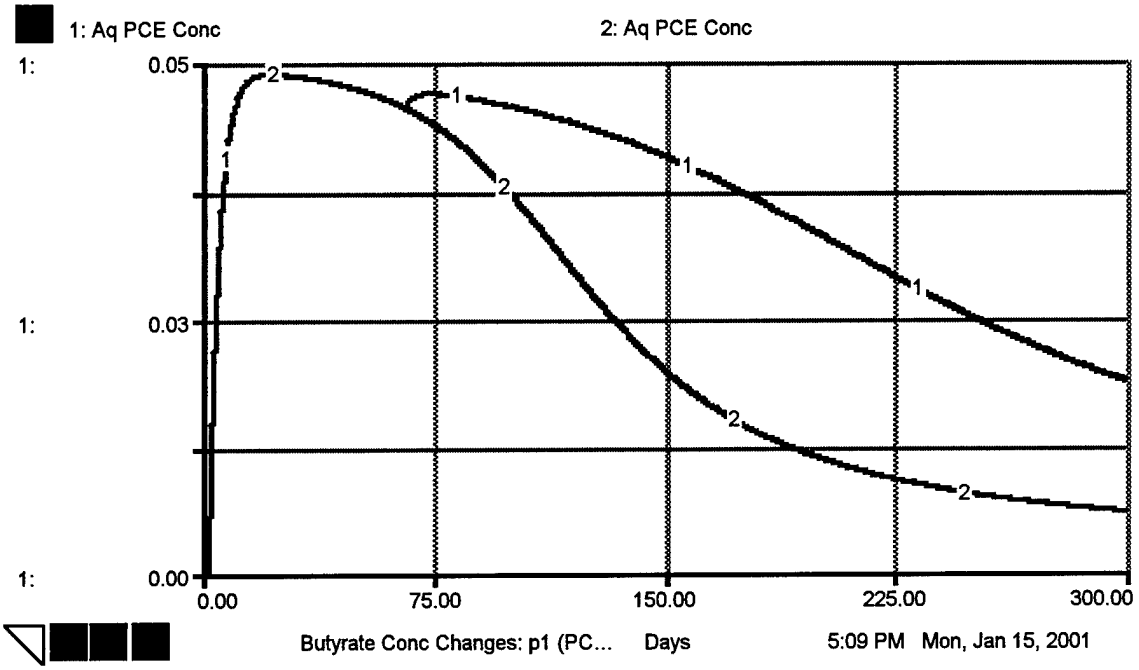

1-9: Aq VC Conc
1:
0.02
1:
0.01
1:
0.00
0.00
75.00
150.00
225.00
300.00
Change in Flow Rate: p4 (VC Co...
Days
11:34 PM Mon, Dec 25, 2000

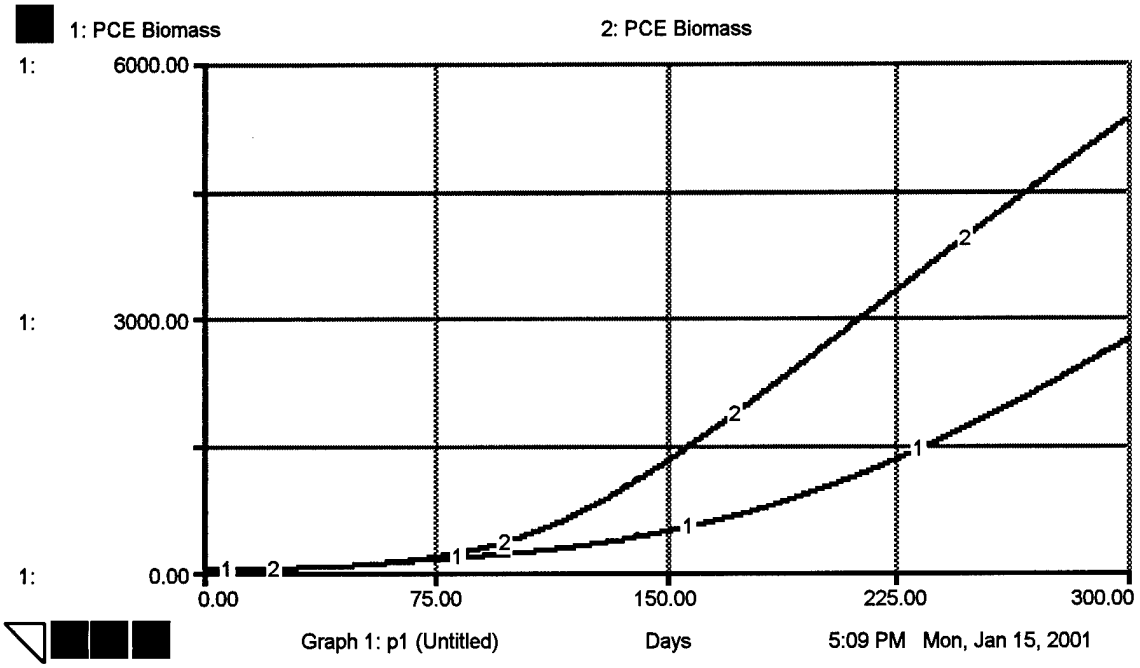

1-9: Aq Eth Conc
1:
5.00e-005
1:
2.50e-005
1:
0.00
0.00
75.00
150.00
225.00
300.00
Change in Flow Rate: p5 (Ethene...
Days
11:34 PM Mon, Dec 25, 2000

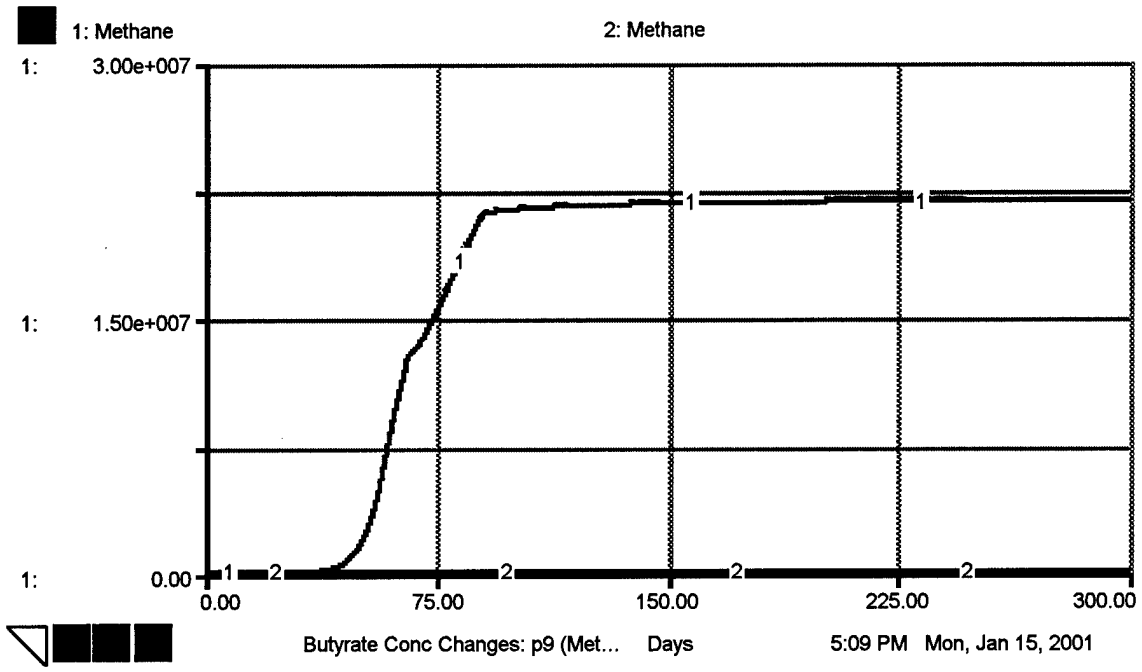
Simulation 16

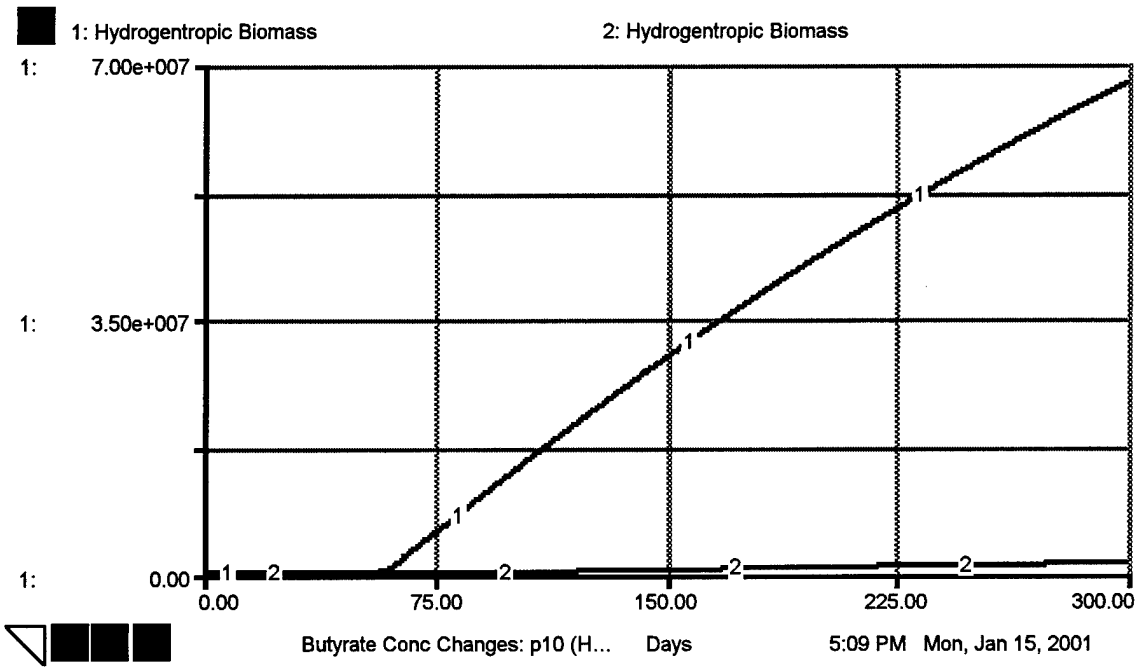
Butyrate Concentration Changes

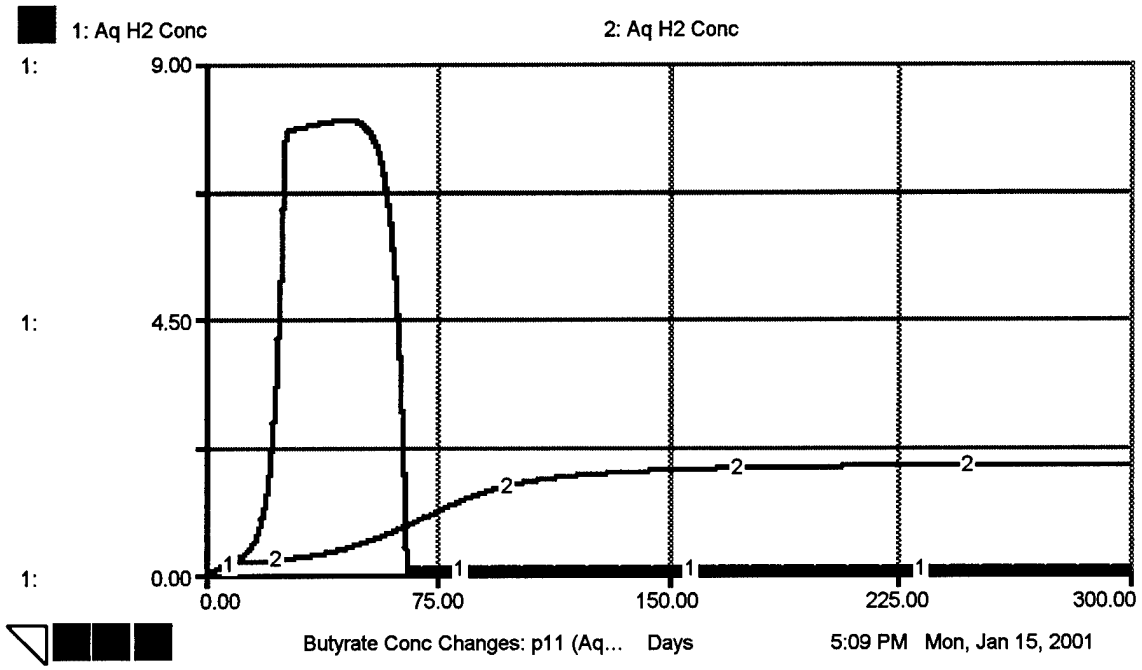
Run	Butyrate Concentration (mg)
1	.6
2	20





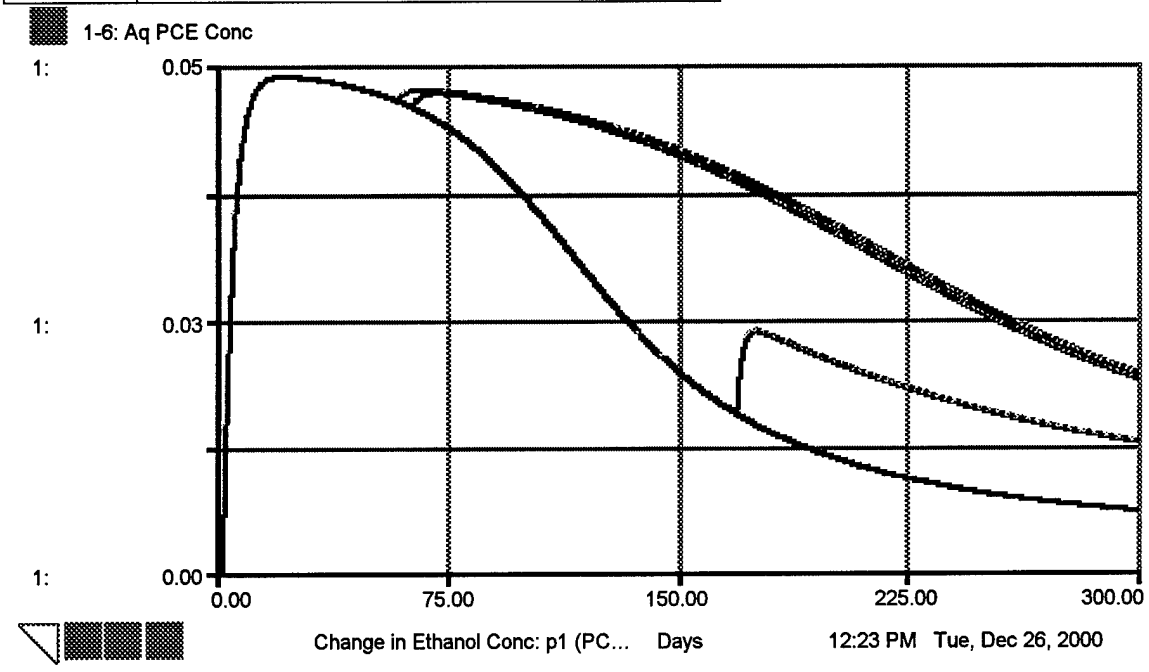

1: Methane
2: Methane
1: 3.00e+007
1: 1.50e+007
1: 0.00
0.00
75.00
150.00
225.00
300.00
Butyrate Conc Changes: p9 (Met...
Days
5:09 PM Mon, Jan 15, 2001

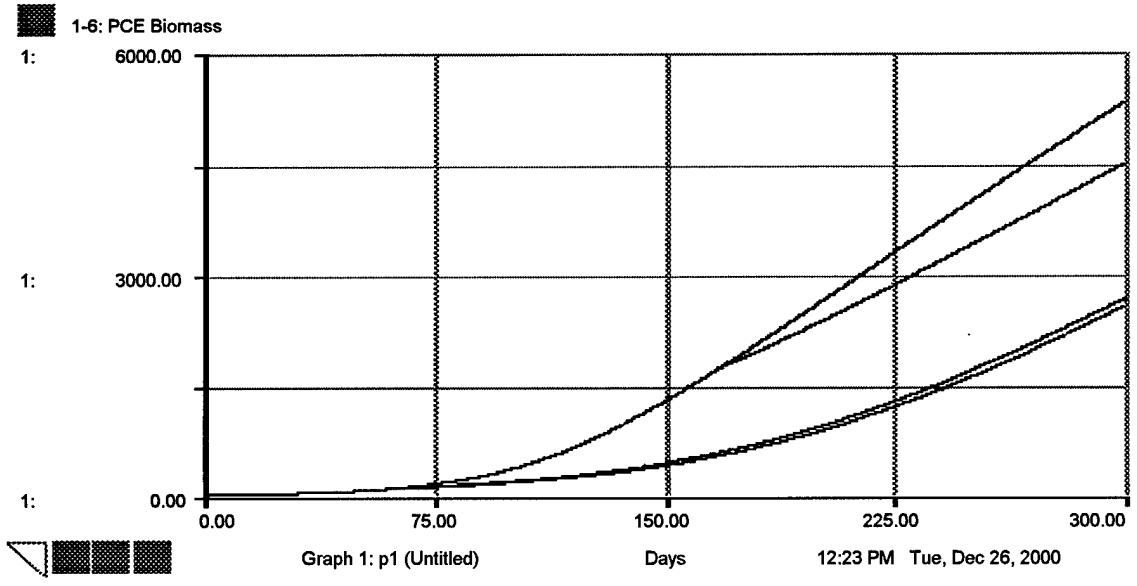

1: Hydrogentropic Biomass
2: Hydrogentropic Biomass
1: 7.00e+007
1: 3.50e+007
1: 0.00
0.00
75.00
150.00
225.00
300.00
Butyrate Conc Changes: p10 (H...
Days
5:09 PM Mon, Jan 15, 2001

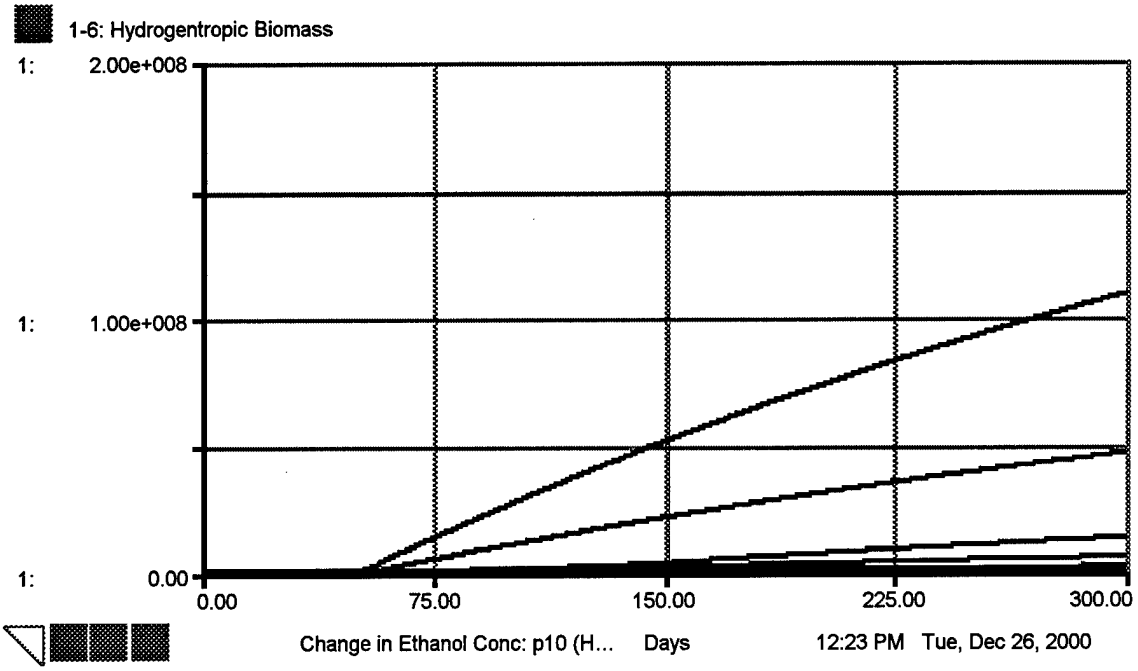

1: Aq H2 Conc
2: Aq H2 Conc
1:
9.00
1:
4.50
1:
0.00
0.00
75.00
150.00
225.00
300.00
Butyrate Conc Changes: p11 (Aq...
Days
5:09 PM Mon, Jan 15, 2001

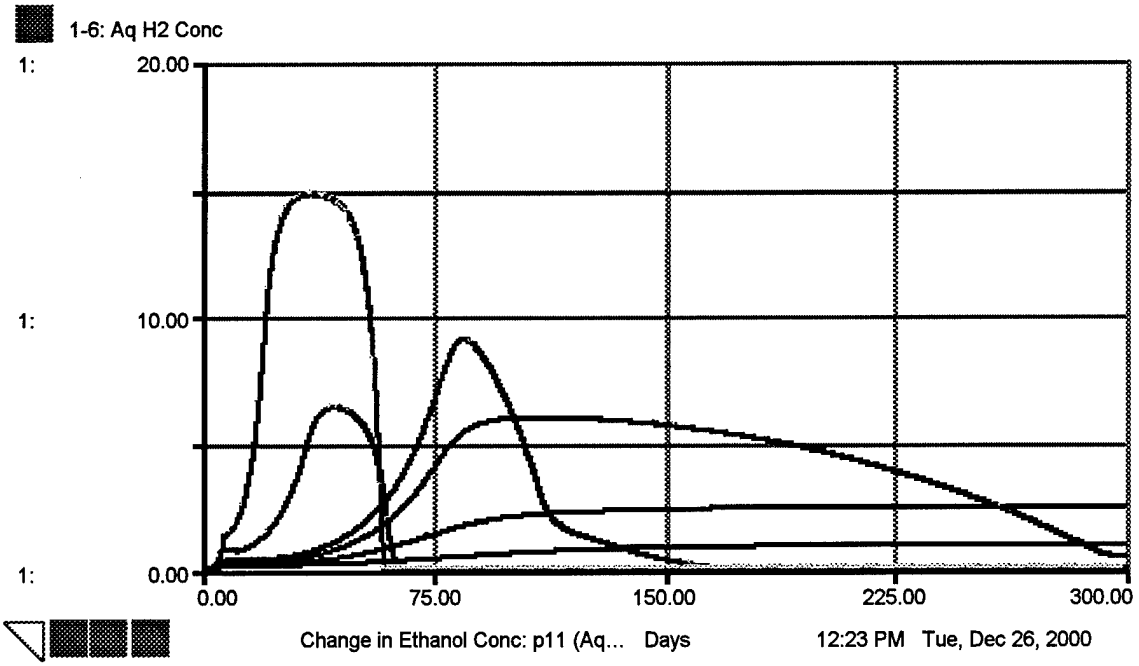
Simulation 17 Ethanol Concentration Changes

Run	Ethanol Concentration (mg)
1	0.1
2	0.6
3	2
4	5
5	20
6	50

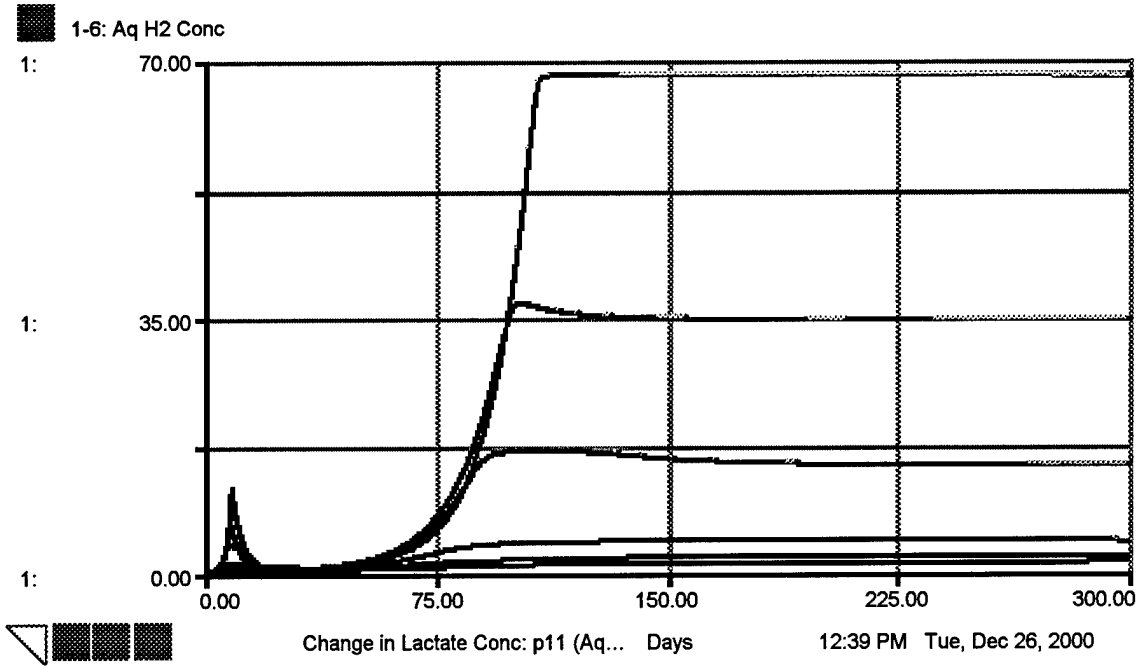


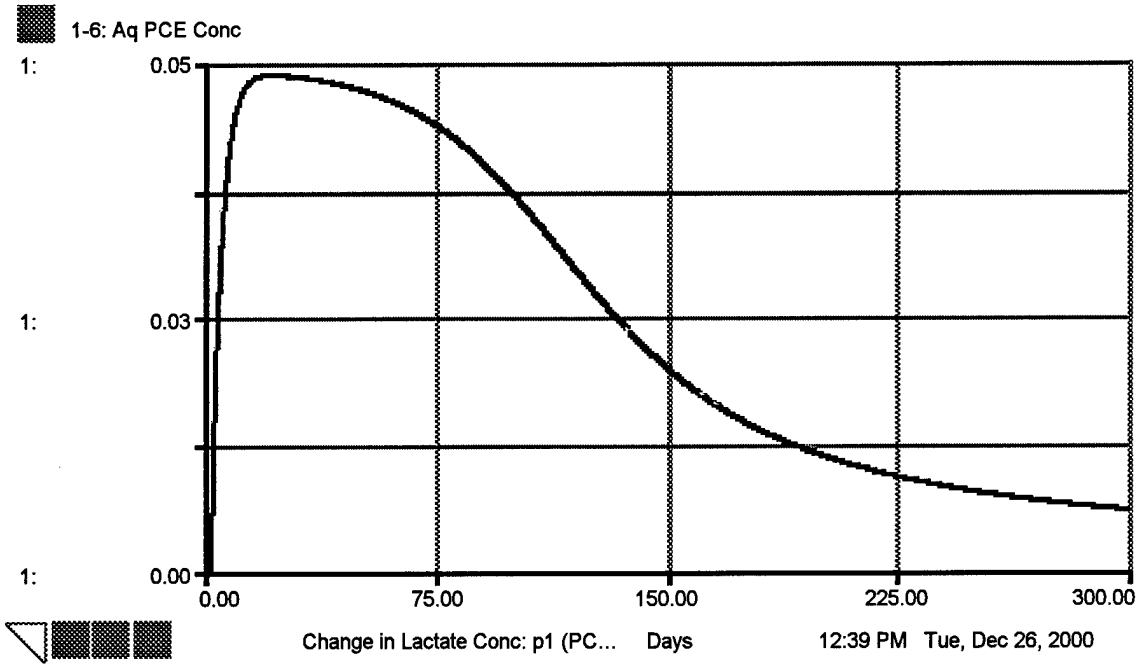



1-6: Hydrogentropic Biomass
1: 2.00e+008
1: 1.00e+008
1: 0.00
0.00
75.00
150.00
225.00
300.00
Change in Ethanol Conc: p10 (H... Days
12:23 PM Tue, Dec 26, 2000


1-6: Aq H2 Conc
1: 20.00
1: 10.00
1: 0.00
0.00
75.00
150.00
225.00
300.00
Change in Ethanol Conc: p11 (Aq... Days
12:23 PM Tue, Dec 26, 2000

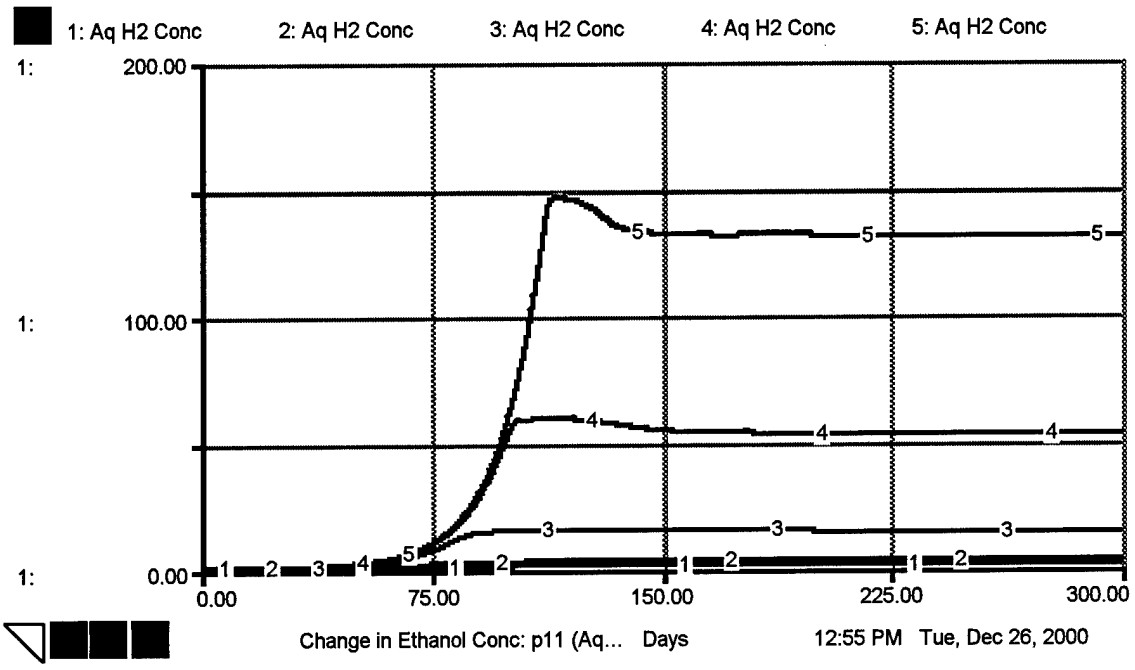
Simulation 18 Lactate Concentration Changes

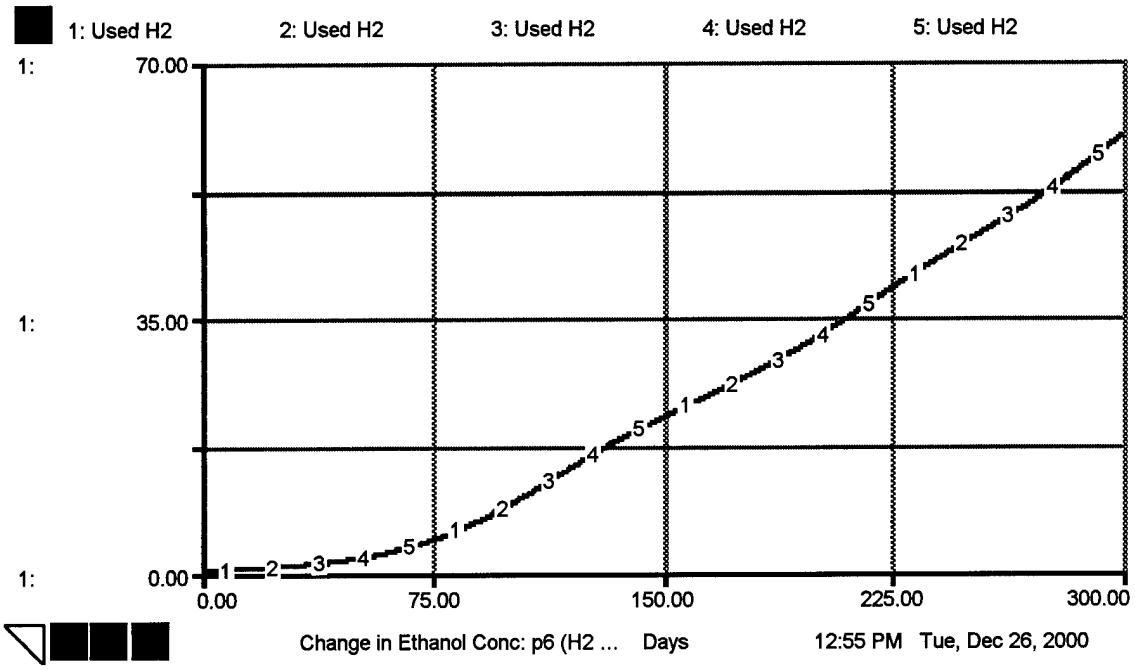


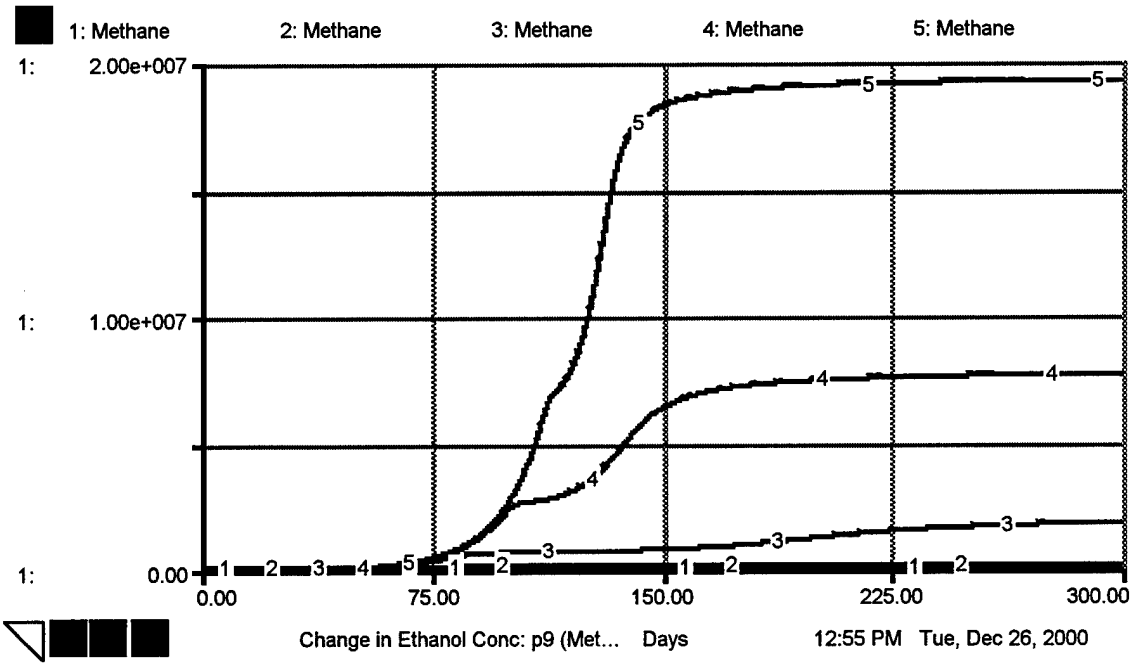


Simulation 19 Propionate Conc. Changes

Run	DCE half-velocity coefficient (Ks) (mg/L)
1	0.2
2	0.8
3	5
4	20
5	50




1: Used H2
2: Used H2
3: Used H2
4: Used H2
5: Used H2
1: 70.00
1: 35.00
1: 0.00
0.00
75.00
150.00
225.00
300.00
Change in Ethanol Conc: p6 (H2 ... Days
12:55 PM Tue, Dec 26, 2000


1: Methane
2: Methane
3: Methane
4: Methane
5: Methane
1: 2.00e+007
1: 1.00e+007
1: 0.00
0.00
75.00
150.00
225.00
300.00
Change in Ethanol Conc: p9 (Met... Days
12:55 PM Tue, Dec 26, 2000

Vita

Captain Randall L. Roberts graduated from Deer Park High School in Deer Park, Texas in May 1992. He entered undergraduate studies at the Unites States Air Force Academy in Colorado Springs, Colorado where he graduated with a Bachelor of Science Degree in Civil Engineering in May 1996. . He was commissioned on the same date and received a regular commission.

His first assignment was at Hanscom AFB as civil engineering officer in the 66th Civil Engineering squadron. While stationed at Hanscom, he deployed overseas in November 1998 to spend four months in Eskan Village Saudi Arabia. In August 2000, he entered the Graduate School of Engineering and Environmental Management, Air Force Institute of Technology. Upon graduation, he will be assigned to Elmendorf AFB, Alaska.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From – To)
03-20-2001	Master's Thesis	Aug 1999 – Mar 2001

4. TITLE AND SUBTITLE

MODELING CHLORINATED ETHENE REMOVAL IN THE METHANOGENIC ZONE OF CONSTRUCTED WETLANDS: A SYSTEM DYNAMICS APPROACH

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Roberts, Randall L., Captain, USAF

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(S)

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Graduate School of Engineering and Management (AFIT/EN)
2950 P Street, Building 640
WPAFB OH 45433-7765

8. PERFORMING ORGANIZATION REPORT NUMBER

AFIT/GEE/ENV/01M-17

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Dr. David Burris
Air Force Research Laboratory
Material Directorate
Environmental Quality Division
Tyndall AFB, FL

10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/MLQ

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The purpose of this study is to gain understanding of the dynamics of the processes that degrade Perchloroethene (PCE) to ethene, within the confines of the methanogenic zone of a constructed wetland. A system dynamics modeling approach is used. This model is focused on determining conditions that will enhance contaminant degradation.

The chemical and biological processes within the methanogenic zone of a wetland system are extremely complex and dynamic processes. The model is broken up into three simultaneous processes: dechlorination, methanogenesis, and fermentation. The system behavior of the methanogenic zone can be adequately described by the classical formulations of representative microbial reactions acting simultaneously within each process in response to substrate limitation. The zone is assumed to be homogeneous and well mixed.

This study provides a fundamental understanding of the complex interactions within the methanogenic zone of a constructed wetland and gives some insight for implementation. Testing identified flow rate, hydrogen concentration, and initial PCE biomass as specific parameters, which could be optimized to have the most effect on contaminant fate.

15. SUBJECT TERMS

dechlorination, wetlands, constructed wetlands, methanogenic, anaerobic, methanogenesis, tetrachloroethene, trichlororethene, PCE, TCE

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Michael L. Shelley, ENV
U	U	U	UU	185	19b. TELEPHONE NUMBER (Include area code) (937) 255-3636 ext. 4594

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

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OMB No. 074-0188