



Report on:

**Hydrogeological Assessment Tools
to Determine the Rate of Biodegradation
for Organic Contaminants in Groundwater**

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**Submitted by:
Science Advisory Board
for Contaminated Sites in British Columbia**

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Submitted to
The Science Advisory Board for Contaminated Sites
in British Columbia

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EXECUTIVE SUMMARY

King Groundwater Science, Inc. was retained by the Science Advisory Board for Contaminated Sites in British Columbia to identify scientifically defensible methods that can be used to determine biodegradation rate constants for organic compounds in shallow groundwater. The purpose of this work is to identify methods which can be incorporated into the Screening Level Risk Assessment 2 process risk assessment process for transport of groundwater contaminants at contaminated sites in British Columbia. A key challenge in development of a risk management strategy for a contaminated site is to be able to collect the appropriate evidence to support or reject a hypothesis that biodegradation is occurring at a rate that is sufficiently protective.

A fundamental concept that must be considered when determining biodegradation rate constants is the need to differentiate the effects of degradation (or transformation) from other attenuation processes such as dispersion. Transformation of a particular contaminant typically requires specific geochemical conditions that may not be present at all sites or within the aquifer everywhere at a particular site. In addition, subsurface flow and chemical heterogeneity can affect the mixing of contaminant and reactants required for the reaction. Quantification of biodegradation requires recognition of process-related characterization issues that may affect the result and therefore the ultimate prediction of future behaviour. Items such as where samples should be collected, the number of monitor wells, the analytes to be tested, and distribution of the plume may affect how the results will be interpreted

Many of the methods used to calculate biodegradation rates in groundwater, assume a first-order rate constant. This is often because of a lack of sufficient data points at the groundwater plume scale and the ease with which these values can be calculated. But, use of the first- and zero-order approximations may lead to inaccurate model predictions if the relative magnitudes of the substrate concentration and the half-saturation constant are not within appropriate ranges. Therefore, there is a challenge in appreciating where and how biodegradation processes occur in a plume and how that might affect data collection efforts and interpretation of attenuation caused by biodegradation.

Several general factors affect the application of biodegradation rates in groundwater systems, such as some degrading species produce toxic degradation products which must be accounted for in a risk assessment, biodegradation rates can be spatially variable, rates are site-specific, sources and plumes may be variable, vertical and horizontal discretization is important, and the groundwater-surface water transition zone can play an important role since the active processes may occur within a short travel zone rather than within the aquifer or plume itself. Correct determination and use of a biodegradation rate constant requires an understanding of the different processes that affect biodegradation

Methods to estimate biodegradation rate constants can be grouped into three general categories: Laboratory, Field and Modelling Techniques. Laboratory methods discussed in the report include microcosm and columns studies. Field techniques include push-pull tracer tests, well to well injection tests, biotracer tests, circulating well test, and in situ testing devices. Evaluation of field data through modelling can extract a biodegradation rate.

Estimation of a first-order rate model from field data requires several assumptions: a steady-state plume, a uniform groundwater flow field, contaminant concentration data collected along the plume centerline, constant source strength through time and negligible volatilization of the contaminant. Methods to determine rates from characterization data include: plume stability tests, mass flux estimates (from transects, pumping wells, or passive flux meter), compound specific isotope

analysis, mass balances, regression or conservative tracers, and the use of more complex models (analytical, numerical, coupled reactive transport).

The characterization of the magnitude and rate of biodegradation at a field site is a challenging task. The complexity of a typical field site makes it difficult to separate the effects of biodegradation from other processes that affect contaminant concentration. Some methods may not be practical, cost-effective, or appropriate, depending on site constraints. For the particular needs of a screening level risk assessment where a contaminated site may be screened out, there must be confidence that the contaminants will continue to degrade in the future at a rate that is protective

A fundamental concept of SLRA-2 is the objective of screening low-risk sites out of the regulatory process while ensuring that no moderate-risk sites are inadvertently screened out. Conservatism in the process is necessary and intentional, as one potential outcome is that contaminants which exceed numerical standards will be left in the subsurface in perpetuity without remediation. Therefore, biodegradation rates determined for use in SLRA-2 must not only be conservative, but must also be sustainable. A number of restrictive assumptions and precluding conditions are part of the SLRA-2 process. If a site is not appropriate for SLRA-2, then a detailed risk assessment (DRA) may be undertaken which does not have the restrictive assumptions of SLRA-2.

The screening process described in this report is based on the following fundamental points:

- A conservative approach is inherent.
- Evidence that biodegradation is occurring must be provided.
- It applies only to contaminants where there is a high level of understanding of the biodegradation processes, and there is a high likelihood that biodegradation will be effective in reducing concentrations to acceptable levels (BTEX, Gasoline, fuel oil, naphthalene, low-molecular weight alcohols, ketones and esters).
- Site hydrogeologic conditions must be simple and reasonably well characterized.
- The biodegradation processes must be sustainable.
- Degradation products must be of low concern.

The screening steps involve: 1) Development of a conceptual model, 2) Screening decisions (for appropriate compounds, occurrence of biodegradation, plume stability, naturally aerobic aquifer), 3) Estimation of biodegradation rate, and 4) Application of rate in groundwater module.

The following conclusions are drawn regarding hydrogeological assessment tools for determining the biodegradation rate constants for organic compounds in groundwater.

Scientifically-defensible tools are available to determine biodegradation rate constants for organic contaminants at contaminated sites. The challenge is to understand site conditions well enough to interpret the data in order to determine biodegradation rate(s), their variability in space and time, and to distinguish biodegradation from other attenuation processes and uncertainty contributed by hydrogeologic complexity.

Biodegradation rate constants are not necessarily transferable between sites.

Proper application of any of the tools described herein requires the user to understand site-specific complexity involved with subsurface biodegradation processes in groundwater and to develop an appropriate site-specific conceptual model.

Each tool has assumptions and limitations which must be appropriate for the site and fit within the conceptual framework for use of the resulting degradation rate constant.

A screening procedure has been developed for addressing the biodegradation component of the Groundwater Module of SLRA-2. This procedure is conservative and is restrictive as to the organic compounds and conditions under which it should be applied.

Based on these conclusions, the following recommendations are offered:

Risk assessment modelling that involves biodegradation in groundwater should utilize a site-specific rate constant(s). All model assumptions should be appropriate for the site and the level of uncertainty acceptable for decision making.

The selection of a tool(s) to determine a site-specific biodegradation rate constant should be made by contaminated site professionals, based on site-specific knowledge.

Site specific rates of biodegradation for use in risk assessment modelling should be supported by well-developed conceptual models, collection of site characterization data that indicates biodegradation is a meaningful process, and appropriate sensitivity analysis to address uncertainty as part of the decision making process.

There is one policy issue associated with the biodegradation aspects of SLRA-2 screening that should be considered by BC MOE. The SLRA-2 screen will result in contaminated groundwater left in the subsurface at concentrations above standards which will be left to degrade without monitoring. Such contaminants could be slow moving as well as slow degrading. Ensuring that conditions remain the same in the future as determined at the time of screening is important to avoid inadvertent disruption of biodegradation processes or new receptor exposure through a change in land use or aquifer development. An appropriate tracking mechanism should be considered.

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1 Introduction

King Groundwater Science, Inc. was retained by the Science Advisory Board for Contaminated Sites in British Columbia to identify scientifically defensible methods that can be used to determine biodegradation rate constants for organic compounds in shallow groundwater. The purpose of this work is to identify methods which can be incorporated into the risk assessment process for transport of groundwater contaminants at contaminated sites in British Columbia. The methods are intended to provide a good scientific basis for use in quantitative risk assessment and predictive modelling, and to also have practical utility. The ultimate goal will be to provide assessment tools for practitioners in BC to determine a biodegradation rate for use in the soil/groundwater module of Screening Level Risk Assessment Level 2 (SLRA-2). In addition, the methods could also be used as part of detailed risk assessments (DRA)¹ to predict the concentration of a contaminant traveling through a groundwater system at more complex sites.

There is considerable scientific literature available that has addressed biodegradation of organic compounds in groundwater through the implementation of natural attenuation initiatives at contaminated sites throughout the world (Rugner and Teutsch, 2001; United Kingdom Environment Agency, 2000; USEPA, 1999; Western Australia Department of Environment, 2004). Although abiotic reactions are significant for a very few organic contaminants, biotransformation reactions are significant for a much broader spectrum of regulated compounds and are the most important transformation process for many of the most commonly detected organic pollutants in groundwater (e.g. BTEX, chlorinated ethenes, and phenolic compounds). Monitored natural attenuation has been accepted as a remediation technology in the US with specific procedures and requirements (National Research Council, 2000; USEPA, 1999), but is not yet formalized in British Columbia (Morrow Environmental Consultants Inc., 2004). The National Research Council evaluated the scientific basis of 14 published natural attenuation protocols in their 2000 report (National Research Council, 2000). In addition to biodegradation, the fate and transport of an organic compound in groundwater is affected by advection, dispersion, sorption, and volatilization (National Research Council, 2000). All of these processes affect contaminant concentration.

A fundamental concept that must be considered when determining biodegradation rate constants is the need to differentiate the effects of degradation (or transformation) from other attenuation processes such as dispersion. Many methods in the natural attenuation literature are actually “attenuation rates” which address the bulk behaviour of a plume, and include biodegradation and dispersion. This report is focused on the biodegradation rate only.

Transformation of a particular contaminant typically requires specific geochemical conditions that may not be present at all sites or within the aquifer everywhere at a particular site. In addition, subsurface flow and chemical heterogeneity can affect the mixing of contaminant and reactants required for the reaction. Therefore, a thorough understanding of the hydrogeological and geochemical conditions at a contaminated site are required before identifying one or more appropriate rate constant(s) and applying it (them).

¹ For the purposes of this document, a DRA refers hydrogeologic assessments of the groundwater pathway at contaminated sites which are more complex than those that would pass the SLRA-2 screening. Such detailed assessments would likely require specialized hydrogeologic knowledge.

2 Important Considerations

2.1 Overview

A key challenge in development of a risk management strategy for a contaminated site is to be able to collect the appropriate evidence to support or reject a hypothesis that biodegradation is occurring at a rate that is sufficiently protective. Due consideration must be given to the processes which affect biodegradation. This includes how it is to be measured, the choice of tool to be used, and how to implement that tool.

Quantification of biodegradation requires recognition of process-related characterization issues that may affect the result and therefore the ultimate prediction of future behaviour. Items such as where samples should be collected, the number of monitor wells, the analytes to be tested, and distribution of the plume may affect how the results will be interpreted. Every assessment tool has assumptions and limitations.

Estimation of biodegradation rate in groundwater can be complicated by many factors ranging from the delivery of reactants, presence/absence of appropriate microbes, subsurface heterogeneity, reactions in the transition zone to surface water, or variability of the source distribution and concentration.

2.2 Introduction to Biodegradation Rate Estimates

What is a Biodegradation Rate Constant?

For the purposes of this report, where methods to estimate rate constants are described, it is important to understand what a biodegradation rate constant represents and how it is applied to the contaminated groundwater setting.

Simply defined, a biodegradation rate is the rate of change of contaminant concentration through time as a consequence of a biologically mediated reaction. In biologic systems, microbes generate energy for growth through the catalyzing of redox reactions resulting in the transfer of electrons for electron-rich chemicals (donors) to electron-poor chemicals (acceptors). Microorganisms require a source of carbon (substrate) that can be oxidized, releasing electrons and a molecule to accept the electron. Typical electron acceptors in groundwater include oxygen, nitrate, manganese (IV), iron (III), sulphate and carbon dioxide (in order of decreasing energy derived). Sequential redox zones have been observed in plumes that develop as electron acceptors are used up and microbes adapt and take advantage of the electron donors and acceptors that are available (Chapelle et al., 2002)

Biologic activity has the ability to greatly affect groundwater chemistry, and activity will occur as long as the environmental conditions remain suitable for microbes to mediate reactions. The rate of reaction, or kinetics, will be dependent on the environmental conditions and the availability and concentration of the substrate and electron acceptors. The rate-controlling step in biodegradation is often the transfer of electron acceptors which is related to transport controls of mixing of groundwater and solute.

The most common way to describe biodegradation reactions is the Monod equation and its first- or zero-order approximations. Since biodegradation can be limited by the concentrations of all substance that participate in the reaction, the Monod equation is usually simplified to indicate the concentration of two solutes, substrate and electron acceptor, in a dual Monod equation.

$$\frac{dS}{dt} = - \left[\frac{V_{\max}MS}{K_s + S} \right] \left[\frac{E}{E + K_E} \right] \quad (1)$$

where V_{\max} is the maximum utilization rate (T^{-1})
 M is the equivalent biomass expressed as the equivalent concentration of substrate required to produce a given biomass ($M L^{-3}$)
 S is the substrate concentration ($M L^{-3}$)
 K_S is substrate half saturation constant ($M L^{-3}$)
 E is the electron acceptor concentration ($M L^{-3}$)
 K_E is the electron acceptor half saturation constant ($M L^{-3}$)

If degradation is not limited by electron acceptor availability, the second term can be ignored, and the equation reduces to a single Monod expression. The half-saturation constant is the substrate concentration at which the transformation rate is half the maximum value, and will be site and contaminant variable. At low concentrations of substrate when $S \ll K_S$, the equation can be approximated as a first-order reaction:

$$\frac{dS}{dt} = - \left[\frac{V_{\max}M}{K_s} \right] S = -k_1 S \quad (2)$$

In this case, the first-order rate constant, k_1 , is equal to $V_{\max}M/K_S$. The rate of transformation is dependent on the substrate concentrations (S). When written in a more useful form relating initial substrate concentration (S_0) with later concentration, it is also evident how first order equations can be used to calculate half-lives ($t_{1/2}$) of a contaminant.

$$k_1 = \frac{\ln\left(\frac{S_0}{S}\right)}{t} \quad (3)$$

$$t_{1/2} = \frac{\ln 2}{k_1} \quad (4)$$

A zero-order rate constant is calculated when the substrate concentration is much greater than the half-saturation constant, i.e. $S \gg K_S$. In this case the form of the equation reduces to:

$$\frac{dS}{dt} = -V_{\max}M = -k_0 \quad (5)$$

$$k_0 = \frac{S_0 - S}{t} \quad (6)$$

In this case, the rate of biodegradation is not affected as the substrate is consumed and remains constant. The rate constant equals the rate of substrate consumption.

As noted in this report, many methods used to calculate biodegradation rates in groundwater, assume a first-order rate constant. This is often because of a lack of sufficient data points at the groundwater plume scale and the ease with which these values can be calculated (Aronson et al., 1999). Bekins et al.(1998) showed that automatic use of first-order rate constants without first verifying that the substrate concentration is less than the half-saturation constant may lead to incorrect model predictions. This is particularly important when biodegradation is the predominant factor in natural attenuation.

How are biodegradation rate constants used?

Rate constants are used in solute transport models to characterize the effect of biodegradation or contaminant migration. In the context of this report, rate constants would be used in models to simulate the concentration at a receptor located downgradient of a contaminated site. The time of arrival and the concentration would be used to evaluate whether contaminated groundwater at a site would be acceptable or not.

Use of the first- and zero-order approximations may lead to inaccurate model predictions if the relative magnitudes of the substrate concentration and the half-saturation constant are not within appropriate ranges (Bekins et al., 1998; Schreiber and Bahr, 2002). The first-order and zero-order approximations are applicable only at low and high values of the substrate concentration relative to half saturation coefficient ratio (Goudar and Strevett, 2000). To avoid misusing first-order rate based models, several procedures were proposed by Bekins et al.(1998), and indicates that a check of field data as to appropriateness of the biodegradation rate constant should be a necessary step in natural attenuation and risk assessments.

Biodegradation can be spatially variable

Field studies have shown that the attenuation of phenolics (Thornton et al., 2001), some aromatic hydrocarbons and fuel oxygenates (Landmeyer et al., 2001) is dominated by aerobic and nitrate reduction at the plume fringes. These fringes may be thin and have strong concentration gradients of electron acceptors and donors (Cozzarelli et al., 2001; Davis et al., 1999). The opposite is also observed for reductive dechlorination of halogenated solvents which require the presence of hydrogen, typically found in the strongly anaerobic core of commingled hydrocarbon and solvent plumes. Thus there is a challenge in appreciating where and how biodegradation processes occur in a plume and how that might affect data collection efforts and interpretation of attenuation caused by biodegradation.

In a sequence of redox zones, biodegradation would differ for each zone in which degradation was occurring. The availability of electron acceptors or nutrients (Allen-King et al., 1994) or the presence of toxic substrate concentrations could conceivably lead to a heterogeneous spatial distribution of where biodegradation occurs and hence nonuniform biodegradation rates. Scholl (2000) used models to assess the effect of assuming aquifer homogeneity on rate calculations for a homogenous aquifer. Homogenous models generally overestimated remediation rate (underestimating time for remediation) due to the effects of low hydraulic conductivity zones. Therefore, the role of biologic, geochemical and hydrogeologic heterogeneity in the subsurface should be considered when addressing biodegradation rates.

Production of toxic degradation products

For some degrading species, (e.g. chlorinated ethenes, chlorinated ethanes) the production of toxic degradation products (e.g. vinyl chloride) must also be accounted for in a risk assessment. The kinetics of transformation for each parent and daughters in the decay chain must be known for a reasonable assessment of risk. Two significant difficulties in addressing this issue in transport models are: the identification of transport parameters; and the estimation of multidimensional reaction rates under advection and dispersion conditions (Suna et al., 2001).

Rates are site-specific

Several studies have compiled published biodegradation rates for many compounds (Aronson et al., 1999; Aronson and Howard, 1997; Wiedemeier et al., 1999). Although care was taken to consider site conditions of each plume, these compilations show that the apparent biodegradation rate constant for BTEX compounds in groundwater can vary over four orders of magnitude and one to two orders of magnitude for TCE and degradation products (Aziz et al., 2000). Given the site-specific properties that can affect the apparent plume-scale degradation rates, there can be little confidence that applying tabulated published rate constants to a risk assessment would yield valid site-specific results.

Sources and plumes may be variable

Usually the historical release of contaminants at a contaminated site is poorly known, if known at all. Temporal or spatially variable releases, preferential flowpaths and other heterogeneity may result in variability in the distribution of contaminants in a groundwater plume (Wilson et al., 2004). Seasonal variation in recharge and groundwater flow can also affect plume distribution and biodegradation (Davis et al., 1999; Schirmer et al., 2001). An important long-term consideration is whether the supply of electron acceptors will last as long as the source of contamination. This is one of the key conclusions from the investigation of the Bemidji crude oil spill research site (Cozzarelli et al., 2001).

The state of plume development is also important. It can be expected that if biodegradation is a significant process at a site, then the mass flux loss due to biodegradation (and dispersion) should be equal to, or exceed, the mass flux released from the site leading to a steady-state plume.

Vertical and horizontal discretization is important

In addition to the usual need to delineate contaminated groundwater, the number and screen length of monitor wells can influence interpretations. Long-screened wells may cross multiple electron acceptor zones and theoretically incompatible electron acceptors may overlap (Schreiber et al., 2004) and be found within the same zone. Biodegradation rates can be overestimated if sufficient vertical delineation is not conducted (Wilson et al., 2004).

The role of groundwater-surface water interaction

The hyporheic zone is an area beneath and adjacent to a stream that contains some portion of channel water or has been altered by surface water. This zone has been found to enhance some microbially mediated reactions and may play an important role in reducing concentrations in groundwater before they discharge to surface water (Conant et al., 2004; Harvey and Fuller, 1998). Rivers and streambeds (and presumably foreshore areas) may have geochemically and microbially active sediment surfaces. As contaminated groundwater with relatively lower pH and dissolved oxygen passes through the transition from groundwater to surface water, hyporheic sediments containing organic carbon and relatively higher dissolved oxygen may increase the potential for microbially-mediated oxidation reactions to occur. Conversely, Conant et al. (2004) documented anaerobic biodegradation of an apparently recalcitrant PCE plume within the top 2.5 m of streambed sediments containing extensive organic carbon. Therefore, rapid changes in plume chemistry can occur due to either aerobic or anaerobic processes. Due to the close proximity of many contaminated sites to surface water bodies in British Columbia, the role of the transition zone between groundwater and surface water in attenuation processes may be important in estimating risk to aquatic receptors. However, it is MOE policy not to include attenuation within the transition zone in screening risk assessments.

3 Assessment Tools

Methods to estimate biodegradation rate constants have been grouped into general categories: Conceptual Model, Laboratory, Field and Fitting Techniques. It is anticipated that some of these methods or combinations could be used in a pathway screening or detailed risk assessment phase following a detailed site investigation. Others may be too new or impractical to implement.

A comparison of aspects of the assessment tools, such as stage of development, applicability to field conditions, practicality and relative cost, are compiled in Table 1. A qualitative comparison of aspects which might affect implementability is shown in Table 2.

3.1 Conceptual Model Development

Correct determination and use of a biodegradation rate constant (or multiple constants for different biogeochemical conditions) requires an understanding of the different processes that affect biodegradation. Although development of a conceptual model through site characterization will not produce a rate constant, it is a necessary step in the process of estimating one. Alternatively, the conceptual model may lead to the conclusion that biodegradation is not a significant or useful process for the specific site conditions.

Following the site characterization process and development of a hydrogeologic site conceptual model, the risk management process may require the collection of additional data specific to the biodegradation rate issue. Such data collection may include geochemical or microbiologic sampling, specific laboratory tests, or additional field experimentation and/or characterization. Then, the conceptual model can be refined to incorporate biodegradation, and will provide the appropriate information to any rate determinations.

3.2 Laboratory Techniques

3.2.1 Microcosms

Laboratory microcosm studies are a well-known and useful method of assessing biodegradation. Usually consisting of a small volume of aquifer or site soils (< 1 kg) contained in a sealed flask with groundwater, substrate and electron acceptors or donors as the study requires. Periodic sampling of the contaminant substrate through time indicates the loss of a contaminant. A rate can be determined by curve-fitting to the concentration versus time relation developed by sampling. Microcosms can be designed to examine aerobic, anaerobic, specific microbial consortia or substrate-limited conditions (Landmeyer et al., 2001; Landmeyer et al., 1998).

Advantages of laboratory microcosms are that techniques are well-established, and can be completed within a reasonable period of time depending on the compound involved. They are very useful in demonstrating the feasibility of biodegradation under specific conditions, stoichiometric mass balances (Brauner and Widdowson, 2001; Brauner et al., 2002) or demonstrating degradation pathways. A microcosm study will provide a direct measurement of an intrinsic biodegradation rate for the compound, microbial consortia and conditions tested. Disadvantages are that microcosms are static closed systems and may not be comparable to an aquifer setting if mixing of microorganisms, electron acceptors and donors is important. It is generally accepted that laboratory microcosm

experiments do not provide a biodegradation rate constant that is directly applicable to field conditions.

3.2.2 Column studies

Column studies can be used to provide estimates of contaminant behaviour and biodegradation using site aquifer materials and groundwater. One advantage of column studies over microcosms is that the results reflect a dynamic test with advection of water and other solutes through the column. The procedure to calculate biodegradation rate constants involves observation and interpretation of breakthrough curves for the contaminant, conservative tracers and other geochemical indicators. One-dimensional analytical or numerical solutions of the advection dispersion equation are fitted to the data, first to determine best-fit transport parameters, then for biodegradation. In cases where the start of biologic activity is delayed, the lag time is often ignored in the data fitting.

3.3 Field Experiment Techniques

3.3.1 Push-pull tracer test

A “push-pull” test can be used in single wells to assess site-specific biodegradation and transport behavior of a contaminant. In these tests, a test solution is prepared that contains the contaminant of interest and a conservative non-reactive tracer. The solution is injected (“pushed”) into the groundwater zone and then, extracted (“pulled”) from the same well. Analysis of samples from the solution as it is extracted from the aquifer produces a breakthrough curve which can then be interpreted with regard to transformation and dispersion of the compound. Comparison with the conservative tracer and use of mathematical models can separate the effects of dilution and sorption from degradation. Depending on the length of time that the solution is left in the subsurface and the rate of transformation, a rate can be calculated from dilution-adjusted recovery curves (concentration versus time).

Surrogate compounds can be used to determine the transformation rates of trichloroethene and degradation products (Hageman et al., 2001).

3.3.2 Well to well injection tests

Tracer tests are valuable tools for aiding in estimation of biodegradation rates, and transport parameters over the scale of a contaminant plume. Essentially, a solution containing degradable and non-reactive compounds are injected in one well and their arrival is monitored at a downgradient well. Loss of mass due to biodegradation can be distinguished from dispersive effects and degradation rate can be derived from the mass loss and travel time in the aquifer. This type of test provides a site-specific rate for the portion of the aquifer contacted. Care is also required with the injected solution to maintain near-natural aquifer conditions within the test zone. This technique is considered to require considerable effort and skill in design and execution and would not likely be appropriate for a screening level assessment.

3.3.3 Biotracer tests

Sandrin et al.(2004) describe the use of biotracer as a means to characterize the in situ biodegradation potential for field-scale systems. Compounds are selected that are biodegradable,

have low volatilities, large aqueous solubilities and minimal sorption and not subject to abiotic transformation. Compounds that are structurally similar to specific contaminants may indicate potential rate of transformation of contaminants. The reactive tracer was injected with a non-reactive tracer at a well and recovered from a downgradient well. Breakthrough curves were analyzed using mathematical models to evaluate the advection-dispersion transport. Non-reactive tracer data was used to calibrate numerical models which were then used to interpret the effects of biodegradation and biodegradation rate through curve-fitting. The use of many wells under the controlled injection experiment allowed an assessment of spatial variability of the biodegradation potential and rate.

3.3.4 Circulating well test

A groundwater circulation well system is used to create vertical circulation flow cell in the aquifer. Groundwater circulation wells extract groundwater from one zone of the aquifer and re-inject it above or below the extraction zone. Addition of a conservative tracer with a biodegradable compound of interest to the injected solution allows monitoring of concentration changes due to biodegradation in comparison to the conservative compound.

Such systems are best suited for homogenous aquifers with minor horizontal stratification so that vertical flow can be induced. Proper design is necessary to maintain control over the circulating solution.

3.3.5 In situ Testers

In situ microcosms have been developed that are designed to isolate a small portion of an aquifer and make measurements directly in the field (Agertved et al., 1992; Gillham et al., 1990). These devices can be installed using standard drilling equipment. The concept is that site groundwater enters the tester through a screened opening, is pumped to the surface, spiked with nutrients, electron acceptors or other compounds of interest and then reinjected into the test chamber to react with the in situ solids and microbial consortia. The test cell is isolated from the effects of groundwater advection and dispersion and can be sampled through time. Degradation rates are calculated in the same manner as for laboratory microcosms where loss of contaminant with time is monitored.

3.4 Field Characterization and Modelling Methods

This group of techniques involves the process of evaluating field data. For adequate application, it is assumed that a detailed site characterization has already been performed and areas of contaminated groundwater and associated biogeochemical and hydrogeological conditions have been delineated. This includes any necessary geochemical or biological characterization so that the biodegradation can be properly evaluated within the context of the site conceptual model.

Many field techniques assume that biodegradation rates follow a first order approximation. But extracting first order rate information from field data may be subject to error due to uncertainties in monitoring well placement, variations in groundwater flow, and fluctuations in plume movement. Use of first order rate models assumes:

- a steady-state plume
- a uniform groundwater flow field
- contaminant concentration data are collected along the plume centerline

- a constant source strength with time (i.e., dissolution from the source is not a function of time)
- volatilization of the contaminant is negligible

3.4.1 Plume Stability Test

A steady state plume condition is necessary for application of some of the rate assessment tools described below. It is also a valuable line of evidence in assessing the natural attenuation of the plume as a whole. At steady-state, the mass of contamination released from the source is balanced by the loss of mass due to downgradient attenuation processes. There are several methods that can be applied to determine plume stability through visual or statistical means. A multi-method approach may be useful because of the fullness of understanding offered by the partially overlapping results (Gibbs et al., 2002).

Visual methods for assessing plume stability include isopleth maps constructed for a series of sampling events, and plotting concentration versus time for individual monitoring wells (Wiedemeier et al., 1999), plots of dissolved mass over time, and estimating the center of mass (Gibbs et al., 2002). Statistical methods include trend analysis such as Mann-Whitney U test used in New Jersey over eight consecutive quarters of monitoring data (Wiedemeier et al., 1999), Mann-Kendall test on concentration trends at individual wells, applying a student's t-test on the slope of a regression line for concentration versus time to test for zero slope. Alternatively a prescriptive test may be appropriate such as used in Iowa where "*the three most recent consecutive groundwater samples from all monitoring wells must not increase more than 20 percent from the first of the three samples to the third sample; samples cannot increase more than 20 percent of the previous sample; and samples must be separated by at least six months*" (Lovannah et al., 2000). Gibbs et al.(2002) found that statistical methods confirmed qualitative visual changes in an MTBE plume, but could distinguish subtle behaviour better.

In some cases, different portions of a plume may be stable or unstable. At the Bemidji MN crude oil spill site the distribution of BTEX concentrations within the plume increased as electron acceptors were depleted, and the interior became more reducing even though the overall extent of the plume appeared unchanged (Bekins et al., 2001; Cozzarelli et al., 2001). Recognition of subtle patterns in concentration changes was important.

3.4.2 Mass Flux Estimates

The estimation of mass flux may be a practical method to assess natural attenuation or the performance of other remediation technologies (Einarson and Mackay, 2001). These methods can also be used to assess non-aqueous phase liquids (NAPL) source areas (Pankow and Cherry, 1996). In the broader context of a contaminant plume, the reduction in mass flux along a flowpath is an estimate of the natural attenuation of the plume as a whole. The American Petroleum Institute addresses the mass flux issue in the natural attenuation context in their "Groundwater Remediation Strategies Tool" (API, 2003). However, it is important to note that in order to distinguish the mass loss due to biodegradation, the effects of dispersion must be accounted for.

The mass loss rates derived from this method are "apparent field scale natural attenuation rates" based on all processes which cause mass reduction between the control planes such as dispersion. Therefore, these rates are not "biodegradation rates" which are often used in solute transport models.

The same assumptions that apply to all first order decay models apply to decay calculated using the mass flux method. Mass flux methods assume the concentration associated with each sampling point is constant over the area represented by the sampling point. A greater distance between monitoring wells (as well as the downgradient distance between the control planes) results in a greater uncertainty in the estimates of both the contaminant (and hence mass) and the travel time. Three methods to estimate mass flux are described below.

3.4.2.1 Transect Method

In this approach, concentration data from monitoring wells oriented along a hypothetical plane transverse to groundwater flow can be integrated to estimate the mass discharge of contaminants or electron acceptors across the plane. The comparison of mass flux loss across successive transects indicates mass loss due to natural attenuation. Methodologies are described by (Wiedemeier et al., 1999) and (API, 2003). For best results, such a method requires substantial investment in multi-level monitoring at small vertical and horizontal intervals in order to adequately delineate the cross-sectional area of the plume and reduce uncertainty in the result. This may be economically feasible for small plume widths but may not be for larger plumes (Bockelmann et al., 2003). The technique is susceptible to uncertainty in site characterization of the spatial distribution of all electron acceptors and donors (Wilson et al., 2004) and effects of temporal variability in the source or flow direction.

Flux values can be used to estimate degradation rates in the same way as concentration profiles to calculate pseudo-first order rate constants (Devlin et al., 2002). The approach of Devlin et al. (2002) also provide rates that are averaged over longer time periods than based on “snapshot” concentration profiles, emphasizing the need to know if a plume has stabilized or not. When compared to other estimates of degradation rate, the mass flux calculations in Devlin et al. (2002) were considered to be the most “robust”. In that case, dispersion was not a significant factor, but at other sites the effects of dispersion or other processes would need to be separated from the effects of biodegradation.

3.4.2.2 Pumping Wells

At the field scale, there are inherent difficulties in precisely delineating the distribution of contaminants particularly at heterogeneous sites. To overcome these difficulties an integral method was developed (Rugner and Teutsch, 2001) based on the in situ quantification of contaminant mass fluxes across predefined control planes situated perpendicular to groundwater flow. It is based on large sampling volumes obtained by pumping. When pumping the wells, the concentration of the contaminant is monitored as a function of time and interpreted using an analytical solution. The concentration-time series data represent an estimation of the mobile contaminant mass flux crossing a defined control plane. The mass flux of electron acceptors can also be quantified. The shape of the C versus t curve is indicative of possible plume position and concentration relative to the location of the pumping well. (Bockelmann et al., 2001) applied the method at a former gasworks site and (Bockelmann et al., 2003) applied the method at a site with a limited number of monitoring wells and obtained good agreement (within 10 %) with results from a center-plume approach using the sparse monitor well network. In both cases, effective “natural attenuation” rates were estimated.

3.4.2.3 Passive Flux Meter

A recent technologic development has created the potential to monitor the contaminant flux occurring at discrete well locations in aquifers. As described by Hatfield et al (2004), permeable sorbents are placed in well screens and contain known amounts of water soluble resident tracers. As the tracers are dissolved at a rate proportional to groundwater flow, cumulative groundwater flux can

be calculated. The sorption of contaminant mass to the sorbent can also be used to calculate a cumulative mass flux arriving at the meter. This technique is recent, is still undergoing application trials and should be considered to be a research-level tool at this time.

The main advantages of this technique are that both groundwater flux and mass flux can be estimated at discrete locations within a contaminant plume to assess spatial and temporal variability.

3.4.3 Compound Specific Isotope Analysis

Recent advances in compound specific isotope analysis has produced a technique for direct monitoring of biodegradation of aromatic hydrocarbons and chlorinated ethenes in groundwater. Isotopic measurements have the potential to differentiate between concentration decreases due to degradative and non-degradative processes and therefore to verify biodegradation. The naturally present stable isotopes of carbon (^{12}C and ^{13}C) and hydrogen (^1H and ^2H) react at different rates during reactions where bonds are broken. In biodegradation, bonds containing lighter isotopes are preferentially broken leading to the remaining compound to be enriched in the heavier isotope. This is important where the bond containing the element of interest is broken or formed is the rate-limiting step, and therefore can aid distinguishing mass loss due to biodegradation from physical processes (Mancini et al., 2003). Various studies have identified biodegradation of chlorinated ethenes (Hunkeler et al., 1999; Morrill et al., 2005; Sherwood-Lollar et al., 1999; Slater et al., 2001) and petroleum hydrocarbons in groundwater (Mancini et al., 2003). For chlorinated ethenes, enriched isotopic values of transformation products can be used to monitor the last two steps of reductive chlorination, cisDCE and VC (Hunkeler et al., 1999)

Morrill et al. (2005) calculated biodegradation rate constants for cisDCE using isotope data and found them to be lower than, but within a factor of 2-4 of rate constants calculated from concentration data in a separate study (Major et al., 2002). The methodology used to estimate a degradation rate relies on Rayleigh fractionation factors and knowledge of enrichment factors for various reactions, usually derived from specific laboratory microcosm studies. For chlorinated ethenes, a variety of studies have shown that fractionation factors are reproducible for a range of microbial consortia and microcosms, and fall within a narrow range. Rate constants can be derived for the ^{12}C and ^{13}C bond-breaking reactions (^{12}k and ^{13}k) assuming first order degradation and $\delta^{13}\text{C}$ value. Since 98.9% of all carbon is ^{12}C , the contribution of ^{13}k to the overall reaction is minimal and the only rate constant of interest is ^{12}k .

$$\left(\frac{\delta^{13}\text{C}}{1000} + 1 \right) = \left(\frac{\delta^{13}\text{C}_0}{1000} + 1 \right) \exp\left[^{12}k(1-\alpha)t \right] \quad (7)$$

where $\delta^{13}\text{C}$ is the carbon isotope ratio at a downgradient location
 $\delta^{13}\text{C}_0$ is initial carbon isotope ratio
 α is the enrichment factor
 t is time
 ^{12}k is the reaction rate constant for the ^{12}C -containing bonds

Solving for ^{12}k yields a rate constant that is solely due to biodegradation.

Compound specific isotopic analyses can be used to verify and monitor biodegradation processes, distinguish between degradative and non-degradative processes and to derive rate constants.

3.4.4 Mass Balances

Contaminant mass loss due to biodegradation is indicated by the presence of reaction products, and related changes in groundwater geochemistry. Nearly all field studies documenting natural attenuation involve well-developed plumes that may extend hundreds of meters in length but defined by relatively small number of monitoring wells constructed with long screens (Devlin et al., 2002). Estimating a plume scale biodegradation rate using such a network through a plume mass balance for either electron acceptor or contaminant loss is likely to be highly uncertain.

A method to conduct a material balance for benzene in a plume was presented by Chiang et al. (1989). A series of mathematical expressions was used to describe the mass balance of benzene which exhibited first-order attenuation in a shallow aquifer. Calculation of the benzene mass in the plume was made for several sampling periods. Lovannh et al. (2000) mathematically describe the rate relationship as the relative mass depleted per period of time.

$$k_{mb} = [(M_0 - M) / M_0] / \Delta t \quad (8)$$

where

- k_{mb} is biodegradation rate constant (T^{-1})
- M_0 is initial contaminant mass at time $t=0$ (M)
- M is contaminant mass remaining at time t (M), and
- Δt is elapsed time (T^{-1}).

Thornton et al.(2001) describe a methodology to perform plume-scale electron and carbon balances for a phenolics plume in sandstone. Their framework used mass inputs from the plume source, background groundwater and plume residuals in a simple box model to give global mass balances for the plume. Calculation of the electron balance assumes that steady-state conditions exist for the source term and hydrogeological regime over the reference period of the plume. A Monte Carlo approach was used to include parameter variability. Detailed geochemical analyses and modelling were used to determine contaminant mass loss over a 47 year time period and a first-order, plume-averaged half-life was calculated (Mayer et al., 2001).

3.4.5 Regression

The technique described in this section was derived by Buschek and Alcantar (1995) and allows calculation of an approximate biodegradation rate constant along a plume flowpath. This method should only be applied when a contaminant plume has reached a steady-state condition. The method involves regression of a semi-log plot of contaminant concentration versus distance along the plume centerline and coupling this with an analytical solution for one-dimensional transport including advection, dispersion, sorption and biodegradation.

For a steady-state plume, the first-order decay rate is given as:

$$\lambda = \frac{v_c}{4\alpha_x} \left(\left[1 + 2\alpha_x \left(\frac{k}{v_x} \right) \right]^2 - 1 \right) \quad (9)$$

- where λ is the approximate first-order biodegradation rate constant
- v_c is retarded contaminant velocity
- α_x is longitudinal dispersivity

k/v_x is slope of linear regression of log-linear plot of contaminant concentration vs. distance

This method assumes that dispersivity is also one-dimensional. Therefore, transverse dispersion is neglected. If it is assumed that biodegradation only occurs in the dissolved phase, then v_c should be replaced by the groundwater velocity, v . The entire plume is fit with one rate constant, therefore this method does not account for any heterogeneity in biogeochemical or physical conditions.

Chapelle et al.(1996) describe a similar method as well as compare results of several field and laboratory methods for petroleum hydrocarbon plume.

The center line plume regression techniques assume that:

- Monitor wells are on the plume center line
- Plume is at steady-state
- Flow field is homogeneous
- Degradation is first-order
- Degradation occurs in one redox zone
- Geochemical conditions are maintained as long as source is present.

Careful attention should be paid to these assumptions when applying this method to a particular site.

3.4.6 Conservative Tracers and “Process Probes”

The observed mass loss of a degrading compound compared to a non-degrading compound in the same aquifer can provide quantitative insights on the rate of biodegradation. This method assumes that for two compounds with similar transport behaviour, a decline in concentration of the non-reactive tracer between any two points is due to the effects of dispersion and sorption and not biodegradation. Normalization of a contaminant’s concentration to the conservative tracer may then permit approximation of a first-order biodegradation rate using a log-linear plot of corrected concentration versus downgradient travel time.

Wiedemeier et al. (1996) describe a method for monoaromatic hydrocarbons (i.e. BTEX) using a tracer commonly found with petroleum hydrocarbon fuel mixtures 1,3,5-trimethylbenzene (TMB). Other compounds may be used as tracers such as chloride (Wilson et al., 2004), or benzene in an anaerobic plume (Davis et al., 1999) . Bekins et al. (1998) note that this method of removing the effects of dispersions are accurate for first-order rates, but not for Monod degradation kinetics. For petroleum hydrocarbon plumes with a NAPL source, the depletion of the NAPL and its effect on source longevity and composition may need to be taken into account.

The degree of TMB recalcitrance to biodegradation is site specific and must be evaluated for each site. The method used to correct the compound of interest concentration is given by:

$$C_{B,Corr} = C_B \left(\frac{TMB_A}{TMB_B} \right) \quad (10)$$

where $C_{B,Corr}$ is corrected concentration of compound of interest at Point B
 C_B is measured concentration of compound of interest at Point B
 TMB_A is measured concentration of TMB at Point A, a point upgradient
 TMB_B is measured concentration of TMB at Point B

If the contaminant distribution approximates a first-order distribution, then the decay relationship can be written as:

$$C_{B,Corr} = C_A e^{-kt} \quad (11)$$

where C_A is the measured contaminant concentration at upgradient point A
k is approximate first-order biodegradation constant
t is travel time between points A and B for the contaminant

Eganhouse et al. (2001) used pairs of alkyl-benzene isomers to probe the processes responsible for the observed attenuation of VOC in the anoxic core of a landfill plume in Norman, OK. The basis for this was that compounds having identical or closely similar physical-chemical properties should have the same distribution within the plume. By selecting pairs of xylene isomers in the leachate that had identical, or systematically different properties, and examining the distribution of concentration ratios, they evaluated the relative importance of volatilization, sorption and biodegradation processes. This method assumes concentrations in a plume do not increase over time and was considered to be ancillary evidence for proof of natural attenuation. Rates were not calculated in this study, but in theory could in a similar manner as above.

3.4.7 Evaluation Using More Complex Models

The use of mathematical models may be one of the most effective methods of estimating a biodegradation reaction rate from field characterization data. Computer models have the ability to include the processes that affect contaminant fate and transport in detail, including heterogeneity and the development of redox zones with different transformation rate constants. Through comparison to field data, calibration, inverse modelling and/or sensitivity analyses, the appropriate parameter values can be determined. The process may be an iterative one, testing a series of hypotheses based on the site conceptual model to determine the most reasonable outcome. The more sophisticated the model used (e.g. the more processes or heterogeneity represented), the greater the need becomes for more extensive field characterization data to obtain calibration for the multiple parameters required to represent the variety of processes.

There are many types of mathematical models and the selection of the appropriate equation or computer code must be based on satisfying the purpose of the modelling and be representative of the conceptual model. Models may describe biodegradation processes with a rate constant (commonly a first-order constant, or half-life) or determine them through more fundamental process-oriented calculations. Complexity of models vary and may be analytical, numerical or a hybrid of each. All models require assumptions and simplifications in order to represent natural systems and it is important that the selected model has a formulation that is appropriate for the problem it is intended to solve. For example, analytical solutions typically assume homogenous and isotropic aquifers which would not be appropriate for a multi-layered aquifer system. Numerical models can accommodate more complex heterogeneous systems with distributed, non-uniform properties and irregular geometry. Reliable estimates of dispersion coefficients are necessary to obtain reasonable estimates of the degradation rate (Stenback et al., 2004).

Additional information concerning the application of models can be found in ASTM (1998).

3.4.7.4 Analytical models

Screening level models are available which are programmed in the Microsoft Excel spreadsheet environment and solve an analytical solute transport model. These models are easy to use with graphical output and can be used to compare the effects of decay or no decay. A biodegradation rate can be determined using these models in a trial and error mode to inverse match site data. Once site hydrogeologic parameter values are entered, site concentration data along a plume length can also be included for comparison to modeled results. By varying the input rate constant until model results match the field data, judgments can be made as to the significance of biodegradation and the likely value of the rate constant. These models should only be used when site conditions are similar to the model assumptions.

Selected examples of available models:

BIOSCREEN is an easy-to-use screening model which simulates remediation through natural attenuation of dissolved hydrocarbons at petroleum fuel release sites. The software has the ability to simulate advection, dispersion, adsorption, and aerobic decay as well as anaerobic reactions that have been shown to be the dominant biodegradation processes at many petroleum release sites. BIOSCREEN includes three different model types: solute transport without decay, solute transport with biodegradation modeled as a first order decay process (simple, lumped-parameter approach), solute transport with biodegradation modeled as an "instantaneous" biodegradation reaction. The model is designed to simulate biodegradation by both aerobic and anaerobic reactions.

BIOCHLOR is similar to BIOSCREEN and intended for use as a screening-level model to assess natural attenuation of chlorinated ethenes. This code is capable of modelling the first-order degradation of chlorinated ethenes and the production and decay of daughter products. It assumes simple homogenous hydrogeology one-dimensional advection, with three-dimensional dispersion, linear adsorption and biodegradation by reductive dechlorination.

AT123D is an analytical groundwater transport model which accounts for advection, dispersion, adsorption and decay of a single component. AT123D computes the spatial-temporal concentration distribution of wastes in the aquifer system and predicts the transient spread of a contaminant plume in an aquifer.

3.4.7.5 Numerical Models

In a similar method as the simple models above can be used to estimate a biodegradation rate through matching model results to field data, the following models can also be applied. The numerical codes listed here are much more complicated to apply, but they are also much more capable of simulating complicated hydrogeology or specific biodegradation reactions.

Selected examples of available models:

BIOPLUME III is a two-dimensional model that simulates the transport and biodegradation of organic contaminants using a number of aerobic and anaerobic electron acceptors: oxygen, nitrate, iron (III), sulfate and carbon dioxide. It requires a first-order decay rate.

RT3D (Reactive Transport in 3 Dimensions) is a FORTRAN 90-based model for simulating 3D multi-species, reactive transport in groundwater. This model is based on the 1997 version of MT3D (DOD Version 1.5), but has several extended reaction capabilities. RT3D can

accommodate multiple sorbed and aqueous phase species with any reaction framework that the user needs to define. The RT3D computer code was developed by the researchers at the Battelle Pacific Northwest National Laboratory. A variety of pre-programmed reaction packages are already provided and the user has the ability to specify their own reaction kinetic expressions.

BIOMOC is a two-dimensional model that can simulate the transport and biotransformation of multiple reaction solutes. Biotransformation rates include single, multiple and minimum Monod kinetics and competitive, noncompetitive and Haldane inhibition. Kinetic rates can be formulated to first-order or zero-order approximations.

EPACMTP is a simulation model for subsurface fate and transport of contaminants released from land disposal sites created by USEPA. The model was applied to support development of regulations for management and disposal of hazardous wastes. It was designed for generic nationwide assessments and uses Monte Carlo simulation techniques. It would need to be modified for site-specific application. The model takes into account chain decay reactions and transport of daughter and granddaughter products, effects of water table mounding on flow and contaminant migration, finite or continuous source function.

3.4.7.6 Coupled Multicomponent Reactive Transport Models

MIN3P The model includes advective-dispersive transport in the water phase and diffusive gas transport and allows the analysis of problems involving inorganic and organic chemicals. Geochemical reactions considered are hydrolysis, complexation, oxidation-reduction, ion exchange, gas dissolution-exsolution and dissolution-precipitation reactions. A general kinetic formulation is included for intra-aqueous and dissolution-precipitation reactions. Microbially mediated reactions can be described using a multiplicative Monod formulation. The model is based on a partial equilibrium formulation and employs a global implicit solution method. The geochemical reaction network, including the reaction parameters for all kinetic reactions, can be specified in a database. The resulting model is versatile and can be used for the investigation of a wide variety of reactive transport problems in saturated and unsaturated porous media in one, two and three dimensions (Mayer et al., 2002).

PHT3D The PHT3D model couples the three dimensional transport simulator (MT3DMS) with the geochemical model PHREEQC-2. PHREEQC-2 is capable of solving simultaneously both equilibrium and kinetically controlled reactions, the coupled model can address a wide range of mixed equilibrium and /or kinetic reactive transport problems (Prommer et al., 2003).

PHAST The computer program PHAST is a public domain model developed by the United States Geological Survey. It simulates multi-component, reactive solute transport in three-dimensional saturated ground-water flow systems. PHAST has capabilities to model a wide range of equilibrium and kinetic geochemical reactions. The flow and transport calculations are based on a modified version of HST3D that is restricted to constant fluid density and constant temperature. The geochemical reactions are simulated with the geochemical model PHREEQC, which is embedded in PHAST (Parkhurst et al., 2004).

4 Application of Methods

A qualitative comparison of the applicability of each tool, along with a summary of advantages and limitations, is provided in Table 2.

The characterization of the magnitude and rate of biodegradation at a field site is a challenging task. The complexity of a typical field site makes it difficult to separate the effects of biodegradation from other processes that affect contaminant concentration. At many sites the initial mass of contaminants released to the subsurface is unknown and may have been variable through time thus affecting spatial contaminant concentration data.

It has been assumed for this report, that the need to determine site-specific biodegradation rate constants is most applicable at those sites which might have the following general characteristics:

- contain biodegradable constituents,
- have biodegradation as the principle attenuating mechanism,
- are located at a sufficiently large distance, or travel-time from receptors to allow biodegradation to be effective,
- contain an appropriate supply of electron acceptors and donors to sustain reactions into the future
- are easily monitored to evaluate performance, and benefit from the effort to collect the appropriate information to document biodegradation.

All methods require an understanding of site biogeochemical conditions and processes. Selection of the tool to use for the calculation of biodegradation rate constants will also depend on the purpose and intended use of the rate. Some methods may not be practical, cost-effective, or appropriate, depending on site constraints. For the particular needs of a screening level risk assessment where a contaminated site may be screened out, there must be confidence that the contaminants will continue to degrade in the future at a rate that is protective.

Sustainability is affected by the rate at which contaminants are transferred from the source area and whether the degrading reactions are “renewable” or “non-renewable”. For example, a supply of electron acceptors in upgradient groundwater (i.e. oxygen or nitrate) may be steady and predictable whereas, soil minerals which may act as electron acceptors, sorption sites or pH buffers have a limited supply and are non-renewable. A high release rate from the source (i.e. large source area, high concentration) could overwhelm the attenuating mechanisms leading to a non-protective condition. Estimating the sustainability of biodegradation requires identifying the reactions, distinguishing the nonrenewable from renewable reactants and comparing the release rates with the rates of biodegradation. A mass budget analysis of a plume will assist in assessing sustainability, but because of inherent uncertainty, monitoring may be necessary at some site to ensure protectiveness (National Research Council, 2000). The SLRA-2 process addresses sustainability through

conservative assumptions, but once a site is screened out, there are no requirements for long-term monitoring.²

If it appears that a risk assessment hinges on the degradation rate estimate such that a need to reduce uncertainty is required, a detailed assessment approach with application of a combination of methods or methods in sequence may be appropriate. For example, a regression of center-line plume data followed by use of a simple screening model to make a preliminary evaluation that biodegradation is a significant process, may lead to additional data collection to support development of a detailed numerical model capable of simulating site-specific conditions.

Some specific issues which may be of concern at contaminated sites in British Columbia due to their potential influence on biodegradation reactions and which may need to be addressed during site characterization include:

- proximity to waterways and aquatic receptors (this is addressed in the precluding factors of SLRA-2)
- role of groundwater-surface water transition zone and plume fringe reactions (In some cases, the biodegradation reactions occur at the plume edges rather than throughout the plume. A detailed risk assessment may be appropriate to address this issue if it is significant to plume migration.)
- landfilling with hogfuel and other wood waste affecting local geochemical redox conditions (the presence of organic matter would likely drive the groundwater to an anaerobic redox condition which may be unfavourable for some biodegradation processes).
- heterogeneous fill used in water lot development making groundwater flowpaths or velocity estimates difficult to characterize
- plumes containing mixed contaminants where one contaminant may be necessary to sustain degradation reactions of the other (For example, biodegradation of chlorinated solvents in the presence of hydrocarbon fuels may stop once the hydrocarbon has been consumed. Due to sustainability concerns and complexity, such situations should be addressed through a DRA)
- reductive dissolution of iron hydroxide coatings due to biodegradation activity releasing secondary contaminants (For example, adsorbed metals such as naturally occurring arsenic are commonly released when biodegradation of a petroleum hydrocarbon plume causes the plume to go to an iron-reducing redox state.)

4.1 Application to the SLRA-2 Protocol

A qualitative screening level risk assessment protocol for contaminants in soil and groundwater has been proposed for British Columbia (SABCS, 2004). The SLRA-2 is designed to evaluate the soil-to-groundwater transport pathways for the purposes of screening out sites which pose an acceptable risk to the receptor. Acceptable risk is defined to mean that either i) contaminants in soil are not

² The SLRA-2 screening procedure assumes that a contaminant plume that is “screened out” will continue under conditions that remain unchanged into the future. A potential issue of concern is that a property containing a screened out plume or a nearby property may be redeveloped in some way that changes the conditions in the aquifer affecting biodegradation or migration of the plume. A solution to this issue is beyond the scope of this document.

expected to result in groundwater concentrations in excess of applicable standards, or ii) concentrations of contaminants in groundwater at the receiving environment are not expected to exceed applicable standards. Some of the assessment tools described in this document are applicable to the biodegradation aspect of the SLRA-2 “Groundwater Module” and others may be more appropriate for detailed assessments.

A fundamental concept of SLRA-2 is the objective of screening low-risk sites out of the regulatory process while ensuring that no moderate-risk sites are inadvertently screened out. Conservatism in the process is necessary and intentional, as one potential outcome is that contaminants which exceed numerical standards will be left in the subsurface in perpetuity without remediation. Therefore, biodegradation rates determined for use in SLRA-2 must not only be conservative, but must also be sustainable. A number of restrictive assumptions and precluding conditions are part of the SLRA-2 process. If a site is not appropriate for SLRA-2, then a detailed risk assessment (DRA) may be undertaken which does not have the restrictive assumptions of SLRA-2.

As described above in Section 2.2, there are numerous complexities concerning biodegradation processes in the subsurface and in determining a rate constant. In order to be applicable to SLRA-2, the determination of a biodegradation rate constant for inclusion in the Groundwater Module model should be straightforward to estimate, conservative, reliable and supported by evidence that biodegradation is actually occurring at the site.

If a site is screened out by the SLRA-2 process, then no further action is required. If a site is not screened out by SLRA-2, then further assessment of remediation would be required.

4.2 Proposed SLRA-2 Biodegradation Screen

This screening process is appropriate for identifying a biodegradation rate constant at sites where biodegradation is a significant attenuating process and the likelihood of long-term success is good.

This screening process is based on the following fundamental points:

1. A conservative approach is inherent.
2. Evidence that biodegradation is occurring must be provided.
3. It applies only to contaminants where there is a high level of understanding of the biodegradation processes, and there is a high likelihood that biodegradation will be effective in reducing concentrations to acceptable levels.
4. Site hydrogeologic conditions must be simple and reasonably well characterized.
5. The biodegradation processes must be sustainable.
6. Degradation products must be of low concern.

A process flow chart indicating the steps involved in the screening is shown in Figure 1. Each step is described below.

Step 1. Develop Conceptual Model.

This is fundamental to any site characterization and evaluation, but is included here for emphasis of its critical nature. A proponent should show a good understanding of site subsurface conditions, the presence and spatial distribution of contaminants of concern, and have analyzed the site data for evidence of biodegradation. Until a natural attenuation protocol is developed for British Columbia, it is recommended that evidence of biodegradation be presented using techniques and lines of evidence as described in an existing, peer-reviewed document such as ASTM (1997).

Step 2. Screening Decisions

1. *Are constituents appropriate?* For the purpose of SLRA-2 screening, only a limited suite of constituents will be considered to be appropriate for screening. These constituents are those which have simple, well-understood biodegradation reactions, and have high likelihood for effective biodegradation. For example, the lighter fraction of petroleum hydrocarbons (i.e. monoaromatics, such as Benzene, Toluene, Ethylbenzene, Xylene) have been well-studied for many years and will readily degrade in most shallow groundwater aquifers which are aerobic. These compounds are the primary source of carbon and energy in the reactions, and only require the presence of electron acceptors. Appropriate degrader microbes have been found to be ubiquitous. Therefore, SLRA-2 screening would certainly be appropriate for these compounds.

Other biodegradable compounds can have more complex biodegradation requirements than BTEX. The gasoline additive MTBE is often found with BTEX plumes but is generally more mobile and recalcitrant under the same conditions. Technical protocols are available for the natural attenuation of chlorinated solvents, but the required environmental conditions are more constraining and may be more difficult to sustain in the long-term. In addition, chlorinated ethenes can degrade to more toxic products which require different conditions for their biodegradation (e.g. vinyl chloride). Creosote, coal tar or other heavy hydrocarbon mixtures containing polycyclic aromatic hydrocarbons (PAH) may have a recalcitrant heavy fraction, but may release naphthalene and phenolics which are soluble, mobile and do have a high likelihood of biodegradation success. Therefore, it is considered that some classes of organic compounds, or fractions of mixtures are unsuitable to be included in SLRA-2, which is intended to be simple and final.

According to National Research Council (2000), classes of organic compounds which have both a high or moderate level of understanding and a high or moderate likelihood of biodegradation success include: BTEX; gasoline and fuel oil; and low-molecular weight alcohols, ketones, and esters.

Therefore, it is proposed that only the compounds listed below be included in the SLRA-2 screening:

- BTEX
- Gasoline, fuel oil
- Low-molecular weight alcohols, ketones, esters
- Naphthalene

Contaminant plumes which contain significant concentrations of other organic compounds of concern (singly or mixtures) should be addressed in a DRA. The list of appropriate compounds could be revised in the future as the level of process understanding improves or regulatory requirements change.

2. *Is biodegradation occurring?* With the aid of the conceptual model and lines of evidence gathered in Step1, this question can be assessed. If biodegradation is not occurring or the evidence is indeterminate, then further assessment or remediation is required. Otherwise, proceed with the screening.
3. *Is the plume stable or shrinking?* As described in Section 3.4.1, knowledge of whether a plume is growing, stable or shrinking is very useful when making decisions regarding plume management. For this task, a statistical method should be used to assess plume stability.

For example, a Mann-Kendall t test (Gilbert, 1987) on eight consecutive quarters of monitoring data should be performed to assess the plume. If the plume is expanding or cannot be shown to be stable, further assessment or remediation is required. Otherwise, proceed with screening.

4. *Is aquifer naturally aerobic?* This question is included as one way of indirectly dealing with the sustainability of the biodegradation reactions for the compounds of concern. It is recognized that the presence of oxygen will result in rapid hydrocarbon degradation. However, most biodegradation in a plume usually occurs under anaerobic conditions (iron or sulphate reducing) within the plume. The presence of oxygen in the groundwater upgradient and surrounding the plume provides additional capability to degrade hydrocarbons than may be occurring within a plume. When coupled with the plume stability question, it is considered to be a reasonable assumption that biodegradation will likely continue into the foreseeable future if oxygen is present in the aquifer around a stable plume. For the purpose of this screening, a field-measured dissolved oxygen concentration greater than 3 mg/L in the upgradient groundwater is necessary for an aquifer to be considered to be aerobic. If the aquifer is not aerobic, further assessment or remediation is required. Otherwise, proceed with screening.

Step 3. Estimate Biodegradation Rate

For the purpose of SLRA-2, the Groundwater Module requires a first-order rate constant. In this step, a rate shall be estimated for each contaminant of concern using two techniques described in Section 3 of this report. This will provide an indication of variability among estimates and among different compounds. The two rate estimates shall be made using methods from the following short-list of methods which are considered to be practical, implementable and reasonable cost:

- Mass flux transects (Section 3.4.2)
- Regression along plume centerline (Section 3.4.5)
- Conservative tracer (Section 3.4.6)
- Compound specific isotope analyses
- Data matching with mathematical model (Section 3.4.7)

The limitations and assumptions in each method and how they affect the result must be addressed by the proponent. In order to be conservative, the minimum rate determined shall be called the “worst-case” and the average of the two rate estimates shall be called the “best-estimate” for use in the Groundwater Module.

Step 4. Apply Rate to Groundwater Module

The minimum rate constant derived in Step 3 is used in the SLRA-2 Groundwater Module to predict concentration at the receptor. This rate should also be used to calculate the two dimensionless factors, S_I and S_{II} , for use in the cross-plot and sensitivity steps of SLRA-2 (Science Advisory Board on Contaminated Sites for British Columbia, 2004).

The proposed screening described above, when included with the other conservative assumptions inherent in SLRA-2, is intended to provide a conservative estimate of biodegradation rates for simple plumes composed of easily degradable compounds in simple hydrogeologic settings. By necessity some restrictive assumptions have been made. For those plumes where this approach is not appropriate a detailed risk assessment should be undertaken.

5 Conclusions and Recommendations

The following conclusions are drawn regarding hydrogeological assessment tools for determining the biodegradation rate constants for organic compounds in groundwater at high risk sites.

1. Scientifically-defensible tools are available to determine biodegradation rate constants for organic contaminants at contaminated sites. The challenge is to understand site conditions well enough to interpret the data in order to determine biodegradation rate(s), their variability in space and time, and to distinguish biodegradation from other attenuation processes and uncertainty contributed by hydrogeologic complexity.
2. Biodegradation rate constants are not necessarily transferable between sites.
3. Proper application of any of the tools described herein requires the user to understand site-specific complexity involved with subsurface biodegradation processes in groundwater and to develop an appropriate site-specific conceptual model.
4. Each tool has assumptions and limitations which must be appropriate for the site and fit within the conceptual framework for use of the resulting degradation rate constant.
5. A screening procedure has been developed for addressing the biodegradation component of the Groundwater Module of SLRA-2. This procedure is conservative and is restrictive as to the organic compounds and conditions under which it should be applied.

Based on these conclusions, the following recommendations are offered:

1. Risk assessment modelling that involves biodegradation in groundwater should utilize a site-specific rate constant(s). All model assumptions should be appropriate for the site and the level of uncertainty acceptable for decision making.
2. The selection of a tool(s) to determine a site-specific biodegradation rate constant should be made by contaminated site professionals, based on site-specific knowledge.
3. Site specific rates of biodegradation for use in risk assessment modelling should be supported by well-developed conceptual models, collection of site characterization data that indicates biodegradation is a meaningful process, and appropriate sensitivity analysis to address uncertainty as part of the decision making process.
4. There is one policy issue associated with the biodegradation aspects of SLRA-2 screening that should be considered by BC MOE. The SLRA-2 screen will result in contaminated groundwater left in the subsurface at concentrations above standards which will be left to degrade without monitoring. Such contaminants could be slow moving as well as slow degrading. Ensuring that conditions remain the same in the future as determined at the time of screening is important to avoid inadvertent disruption of biodegradation processes or new receptor exposure through a change in land use or aquifer development. An appropriate tracking mechanism should be considered.

6 Closure

This report is intended for the use of the Science Advisory Board for Contaminated Sites in British Columbia, and has taken a technical approach to the issue. It is recognized that portions of this document may be used to develop guidance, as appropriate, by the Ministry of Environment for use at contaminated sites in British Columbia.

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KING GROUNDWATER SCIENCE, INC.

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Table 1 Assessment tools for determining biodegradation rates - Laboratory

TYPE	ASSESSMENT TOOL	APPLICATION	ADVANTAGES	LIMITATIONS
Laboratory Techniques	Microcosms	<ul style="list-style-type: none"> • Confirmation of biodegradation for test conditions • Identification of pathways • Provides a rate for conditions tested 	<ul style="list-style-type: none"> • Uses site microbial consortia, soil, groundwater • procedures well-known • confirms reactions 	<ul style="list-style-type: none"> • Rate may not be applicable to field behaviour • Does not take into account advective or dispersive effects • small sample of soil used
	Column Studies	<ul style="list-style-type: none"> • Confirmation of biodegradation for test conditions • Identification of pathways • Provides a rate for conditions tested 	<ul style="list-style-type: none"> • Uses site microbial consortia, soil, groundwater • procedures well-known • confirms reactions • uses larger volume of site soil • includes advective and dispersive effects 	<ul style="list-style-type: none"> • Rate may not be applicable to field behaviour • Does not take into account advective or dispersive effects • Time and analytically intensive

Table 2 Assessment tools for assessing biodegradation - Field

TYPE	ASSESSMENT TOOL	APPLICATION	ADVANTAGES	LIMITATIONS
Field Techniques	Push-Pull tracer test	<ul style="list-style-type: none"> • injection of water containing reactive and non-reactive tracers • best results if site groundwater used • provides indication of biodegradation and rate in aquifer 	<ul style="list-style-type: none"> • derive a field scale rate • test a large volume of aquifer • use site groundwater to prepare solution • can assess the effects of dispersion 	<ul style="list-style-type: none"> • aquifer heterogeneity may limit/confine spread of tracer • potential mass loss of tracer due to poor recovery • solution chemistry may be altered prior to injection • time and analytically intensive to monitor breakthrough
	Well to Well injection	<ul style="list-style-type: none"> • can use either natural-gradient or forced-gradient conditions • provides indication of biodegradation and rate derived from breakthrough curve analysis • provide indication of biodegradation in aquifer 	<ul style="list-style-type: none"> • derive a field scale rate • test a large volume of aquifer • can control flow field and injection 	<ul style="list-style-type: none"> • natural gradient test needs extensive monitor well control • aquifer heterogeneity must be well understood • potential alteration of aquifer conditions by injected solution • time and analytically intensive to monitor breakthrough
	Biotracer	<ul style="list-style-type: none"> • injection of appropriate reactive and non-reactive compounds provides indication of biodegradation and rate • applied in well to well type setup 	<ul style="list-style-type: none"> • biotracers are structurally similar to compounds of interest • can be used to assess spatial variability of processes 	<ul style="list-style-type: none"> • need to be low toxicity • need appropriate physicochemical properties • time and analytically intensive to monitor breakthrough • recently developed technique
	Circulating Well injection	<ul style="list-style-type: none"> • controlled vertical circulation of a solution around one well • injection of a reactive and non-reactive tracer provides indication of biodegradation and rate 	<ul style="list-style-type: none"> • derive a field scale rate • test a large volume of aquifer • can control flow field and injection 	<ul style="list-style-type: none"> • aquifer heterogeneity affects vertical circulation effectiveness • possible loss of tracer due to incomplete capture • potential alteration of aquifer condition by injected solution • time and analytically intensive to monitor breakthrough
Field Techniques	Mass Flux Estimates a) Transect	<ul style="list-style-type: none"> • Concentration data from wells along a transverse plane to estimate mass discharge • Reduction in mass flux between 	<ul style="list-style-type: none"> • can provide rates over longer time periods • can produce a first-order rate 	<ul style="list-style-type: none"> • must distinguish biodegradation from dispersion • better result with increased horizontal and vertical discretization which may be

TYPE	ASSESSMENT TOOL	APPLICATION	ADVANTAGES	LIMITATIONS
		transects in a plume will reflect attenuation processes		costly • plume must be stable • susceptible to uncertainty in spatial distribution of plume
	Mass Flux Estimates b) Pumping Wells	<ul style="list-style-type: none"> • Pumping well captures a plume at series of “control planes” • Concentration vs. time relationship can be related to plume geometry 	<ul style="list-style-type: none"> • may overcomes effects of heterogeneity and plume spatial variability • less plume discretization may be required • based on large sampling volumes 	<ul style="list-style-type: none"> • rates are apparent field scale natural attenuation rates, not biodegradation rates •
	Mass Flux Estimates c) Passive Flux meter	<ul style="list-style-type: none"> • Permeable sorbent devices placed in monitor wells • Loss of tracer sorbent and sorption of contaminant mass indicate mass flux 	<ul style="list-style-type: none"> • Both groundwater and mass flux can be determined • Easily installed and used in existing monitor wells 	<ul style="list-style-type: none"> • still in developmental research phase • sorbed tracers and sorbents may need to be tailored to a particular site
	Compound Specific Isotope Analysis	<ul style="list-style-type: none"> • compound specific isotope analysis directly measure the isotopic fractionation of remaining contaminant as degradation proceeds 	<ul style="list-style-type: none"> • verification of field biodegradation rate • helps differentiates between degradative and non-degradative processes 	<ul style="list-style-type: none"> • not useful for all compounds • fractionation must be significant
	In Situ Microcosm Testers	<ul style="list-style-type: none"> • an isolated test microcosm is created in the subsurface • reactions occur in contact with relatively undisturbed native soil and microbes in the field 	<ul style="list-style-type: none"> • easily installed using drilling technology • simple design and easy to operate • requires less time and equipment than larger-scale tracer test • effects of advection and dispersion are removed. 	<ul style="list-style-type: none"> • need long time period to equilibrate with surrounding aquifer • withdrawing and injecting water is necessary • requires reasonably permeable geologic materials • some physical disturbance of aquifer may occur

Table 3 Assessment tools for determining biodegradation rates - Data techniques

TYPE	ASSESSMENT TOOL	APPLICATION	ADVANTAGES	LIMITATIONS
Data Analysis and Fitting Techniques	Mass Balance	<ul style="list-style-type: none"> • changes in mass over time are calculated • mass loss per time is the rate 	<ul style="list-style-type: none"> • direct measurement of biodegradation (e.g. Thornton method) 	<ul style="list-style-type: none"> • requires extensive monitoring well network • sensitive to effects of dispersion • requires monitoring over time • not appropriate for steady-state plumes (Chiang method) • interpolation is required
	Regression (Buschek and Alcantar 1999)	<ul style="list-style-type: none"> • Linear regression of concentration versus distance downgradient along central plume axis 	<ul style="list-style-type: none"> • easily applied simple analysis • does not require long term monitoring data 	<ul style="list-style-type: none"> • requires steady-state plume • data from wells must be along plume centerline • requires knowledge of dispersivity and retarded velocity • neglects horizontal and transverse dispersivity • first-order kinetics is assumed
	Conservative Tracers	<ul style="list-style-type: none"> • compares mass loss between degrading and non-degrading compounds and normalizes concentration to remove effects of dispersion and sorption • linear regression of concentration versus distance downgradient along central plume axis 	<ul style="list-style-type: none"> • easily applied • sorption or degradation of TMB tracer leads to more conservative estimate 	<ul style="list-style-type: none"> • accurate for first-order kinetics • tracer may not behave as expected • assumes constant plume concentrations over time • assumes wells located along same flow line • groundwater velocity must be known
	Mathematical Models Analytical	<ul style="list-style-type: none"> • method to obtain best match with field data by varying parameter value 	<ul style="list-style-type: none"> • easily applied to quickly develop insight • some operate in spreadsheet environment • numerically stable • effective screening tool 	<ul style="list-style-type: none"> • assumes simple hydrogeology and regular geometry • assumes steady state source and plume
Data Analysis and Fitting Techniques	Mathematical Models Numerical	<ul style="list-style-type: none"> • method to obtain best match with field data by varying parameter value • some are process-oriented on specific reactions 	<ul style="list-style-type: none"> • simulate more complex physical systems • multi-dimensional systems • complex boundary conditions • spatial variability of input parameters • accommodate steady-state or transient conditions 	<ul style="list-style-type: none"> • more development time compared to analytical models • more data requirements • numerical dispersion may occur

TYPE	ASSESSMENT TOOL	APPLICATION	ADVANTAGES	LIMITATIONS
	Mathematical Models Coupled Multicomponent Reactive Transport	<ul style="list-style-type: none"> • Process-oriented modeling using specified reactions and detailed biogeochemical data 	<ul style="list-style-type: none"> • can include fundamental reactions • multiple components • simulate more complex physical systems • multi-dimensional systems • complex boundary conditions • spatial variability of input parameters • accommodate steady-state or transient conditions 	<ul style="list-style-type: none"> • most development time compared to other models • more data requirements • numerical dispersion may occur

Table 4 Comparative Summary of Assessment Tools

Assessment Tool	Stage Of Development	Training Requirements	Applicability To Field Conditions	Practicality	Relative Cost
Microcosm	Established	Specialized Usually subcontracted to specialized laboratory	Low	Low	Moderate
Column Studies	Established	Specialized Usually subcontracted to specialized laboratory	Low	Low	Moderate
Push-Pull tracer test	Established	Advanced hydrogeologic skills Knowledge of tracers	High	Moderate	Moderate
Well to Well injection	Established	Advanced hydrogeologic skills Knowledge of tracers	High	Low - Moderate	High
Biotracer	Early (Research level)	Advanced hydrogeologic skills Knowledge of tracers	High	High potential	Moderate
Circulating Well injection	Early	Advanced hydrogeologic skills Knowledge of tracers	High	Moderate	Moderate
Mass Flux Estimates Transect	Moderate	Moderate	High	High	Low – High Affected by number of monitoring locations needed
Mass Flux Estimates Pumping Wells	Early	Advanced hydrogeologic skills	High	Low	Moderate Affected by treatment requirements for pumped groundwater
Mass Flux Estimates Passive Flux meter	Early (Research level)	Moderate Easily installed with standard procedures	High	High	Unknown
In Situ Microcosm Testers	Established	Advanced skills required to design and conduct experiments	Moderate	Low Requires long time periods	Moderate

Assessment Tool	Stage Of Development	Training Requirements	Applicability To Field Conditions	Practicality	Relative Cost
Compound Specific Isotope Analysis	Moderate (< 10 years)	Normal sampling procedures Subcontracted to specialized laboratory Advanced skills to interpret	High	High	Low
Mass Balance	Moderate	Moderate	Moderate	Low - moderate	Moderate The quality of the result depends on the level of site characterization
Regression	Established	Moderate	Low-Moderate	High	Low
Conservative Tracers	Established	Moderate	Moderate	Moderate - High	Low
Mathematical Models Analytical	Established	Moderate	Moderate	High	Low
Mathematical Models Numerical	Advanced	Advanced	High	High	Moderate- High
Mathematical Models Coupled Multicomponent Reactive Transport	Moderate	Advanced	High	Low – Moderate High degree of specific data must be collected	Moderate-High Time and data intensive

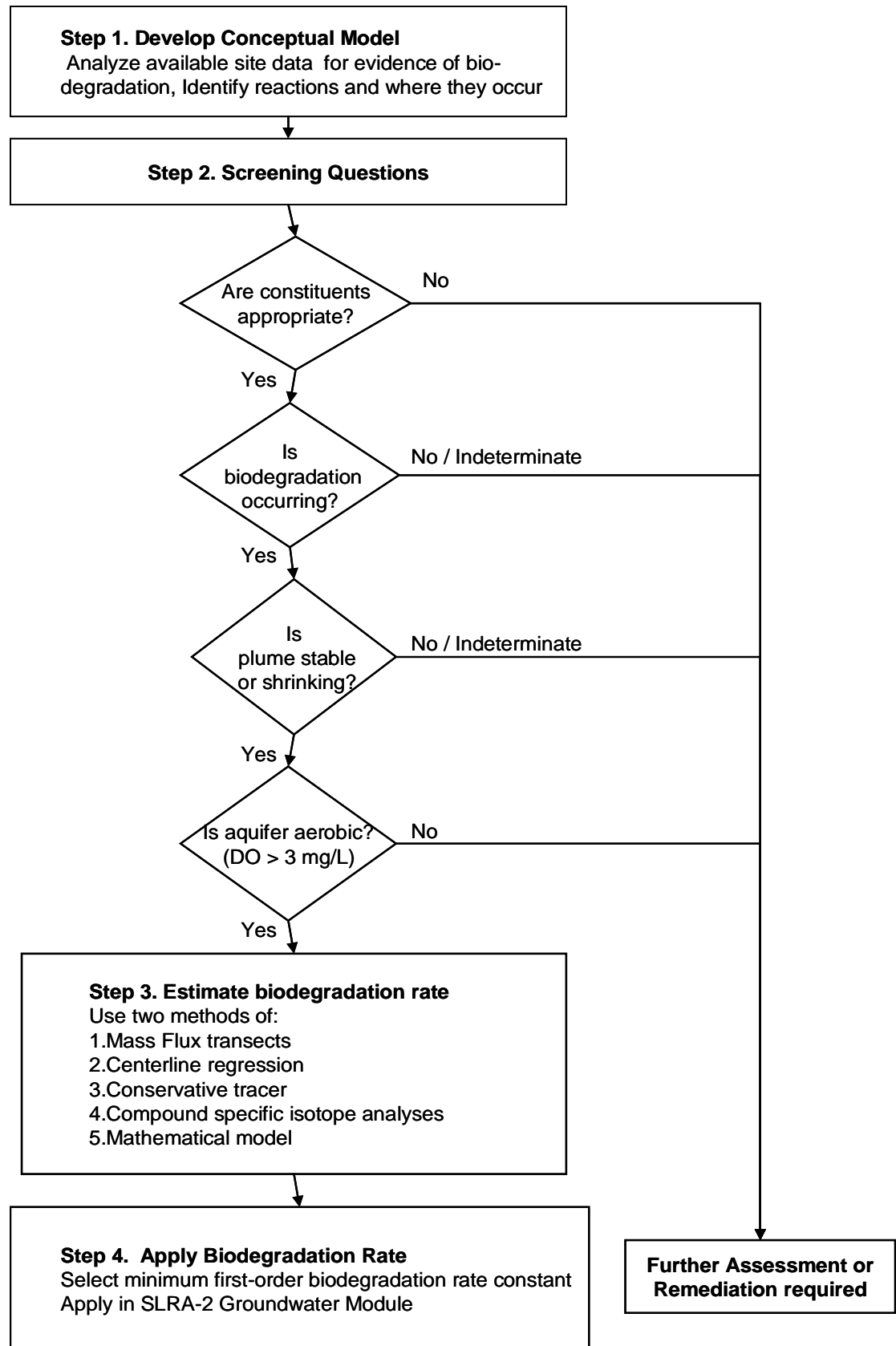


Figure 1 Screening process for biodegradation rate estimate in SLRA-2 Groundwater module