

Considerations for the Design of Organic Mulch Permeable Reactive Barriers

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Organic mulch consists of insoluble carbon biopolymers that are enzymatically hydrolyzed during decomposition to release aqueous total organic carbon (TOC). The released TOC is utilized by microorganisms as an electron donor to transform electrophilic contaminants via reductive pathways. Over the last decade, organic mulch permeable reactive barriers (PRBs), or biowalls, have received increased interest as a relatively inexpensive slow-release electron donor technology for addressing contaminated groundwater. To date, biowalls have been installed to enhance the passive bioremediation of groundwater contaminated with a variety of electrophilic compounds, including chlorinated solvents, explosives, and perchlorate. In addition, several mulch biowall projects are currently under way at several U.S. Department of Defense facilities. However, at the present time, the guidelines available for the design of mulch PRBs are limited to a few case studies published in the technical literature. A biowall design, construction, and operation protocol document is expected to be issued by the Air Force Center for Environmental Excellence in 2007. In this publication, three technical considerations that can have a significant impact on the design and performance of mulch PRBs are presented and discussed. These technical considerations are: (1) hydraulic characteristics of the mulch bed; (2) biochemical characteristics of different types of organic amendments used as mulch PRB fill materials; and (3) a transport model that can be used to estimate the required PRB thickness to attain cleanup standards. © 2007 Wiley Periodicals, Inc.

INTRODUCTION

Permeable reactive barrier (PRB) technology is a low-maintenance remediation technology that has the distinct advantage of cutting across geologic heterogeneities present in an aquifer. Typically, PRBs are emplaced downgradient of dissolved contamination, and the technology relies on the natural groundwater gradient to transport the contaminant(s) through the PRB where treatment occurs. PRBs are engineered to have a higher permeability than the surrounding formation by controlling the particle size of the fill material. This helps to induce preferential flow of contaminated groundwater through the PRB.

Among the various reactive fill materials available for PRBs, organic mulch is perhaps the alternative with the lowest cost. Organic mulch is a complex (i.e., insoluble) carbon source that is naturally populated with a consortium of microorganisms. Organisms in the mulch hydrolyze the complex carbonaceous material to slowly release smaller, soluble, and more readily fermentable molecules. These molecules are utilized by microorganisms

to treat chlorinated aliphatic contamination via biologically catalyzed reductive transformation pathways. Because dissolved organic carbon is released by mulch biowalls, an additional treatment zone is created immediately downgradient of the mulch PRB, or “biowall.” Therefore, besides being the lower-cost PRB remedial alternative, a mulch biowall offers a larger treatment zone than other PRBs, such as a zero-valent iron (ZVI) PRBs.

Mulch biowalls have a proven performance record for treating nitrate (Robertson & Anderson, 1999; Robertson & Cherry, 1995; Robertson et al., 2000), acid mine drainage (Benner et al., 1997, 1999), chlorinated solvent (Aziz et al., 2001; Haas et al., 2000; Henry et al., 2003), explosives (Ahmad et al., 2006), and perchlorate (Xu et al., 2003) contamination. Several mulch biowall projects are currently under way at multiple U.S. Department of Defense (DOD) facilities. At present, there is no guidance available for the design and installation of mulch PRBs; however, a guidance document is under development by the Air Force Center for Environmental Excellence (AFCEE). In this article, we present key technical considerations (i.e., hydraulic characteristics, fill selection, and modeling) that should be taken into account when designing mulch biowalls. These technical considerations are based on lessons learned while participating in four different mulch biowall projects. The projects include the design and installation of pilot- and full-scale biowalls for treating chlorinated solvent contamination at Offutt Air Force Base (AFB), the pilot-scale biowall for treating munitions contamination at the Pueblo Chemical Depot, and two full-scale biowalls for treating chlorinated solvent contamination at a U.S. Army facility (ongoing project).

At present, there is no guidance available for the design and installation of mulch PRBs; however, a guidance document is under development by the Air Force Center for Environmental Excellence (AFCEE).

HYDRAULIC CHARACTERISTICS OF MULCH-PACKED BEDS

PRB technology is a passive *in situ* groundwater remediation technology. Because PRBs require trenching for installation, it is more typically applied to sites where the groundwater contamination is relatively shallow (i.e., 35 to 45 feet below ground surface). A PRB is emplaced downgradient of dissolved contamination, and the technology relies on the natural groundwater gradient to provide a steady flux of the target contaminant(s) on its upgradient face. The contamination is subsequently treated by the reactive fill material as it traverses the thickness of the PRB. Generally, a PRB is engineered to be more permeable than the surrounding formation by controlling the particle size of the inert fill material that is mixed with the mulch. This allows for preferential flow of contaminated groundwater to occur through the PRB. Furthermore, this measure reduces the seepage velocity of the contaminated groundwater, thereby allowing longer “contact time” available to the contaminant for reaction. Hence, the key parameters in PRB design are its thickness and the seepage velocity through the PRB, which together control the treatment contact time.

Although the design of mulch PRBs follows the same principles as other types of PRBs, there are some characteristics of the mulch-packed bed that make the hydraulics through mulch PRBs unique. As mentioned earlier, the seepage velocity through the PRB is largely controlled by the particle size of the inert material. However, in mulch beds, the contaminant flow path is determined not only by the pore spaces between particles, but also by the permeability through the organic material itself. It has been widely reported in the literature that the lignin fraction of sapwood is highly permeable because of its

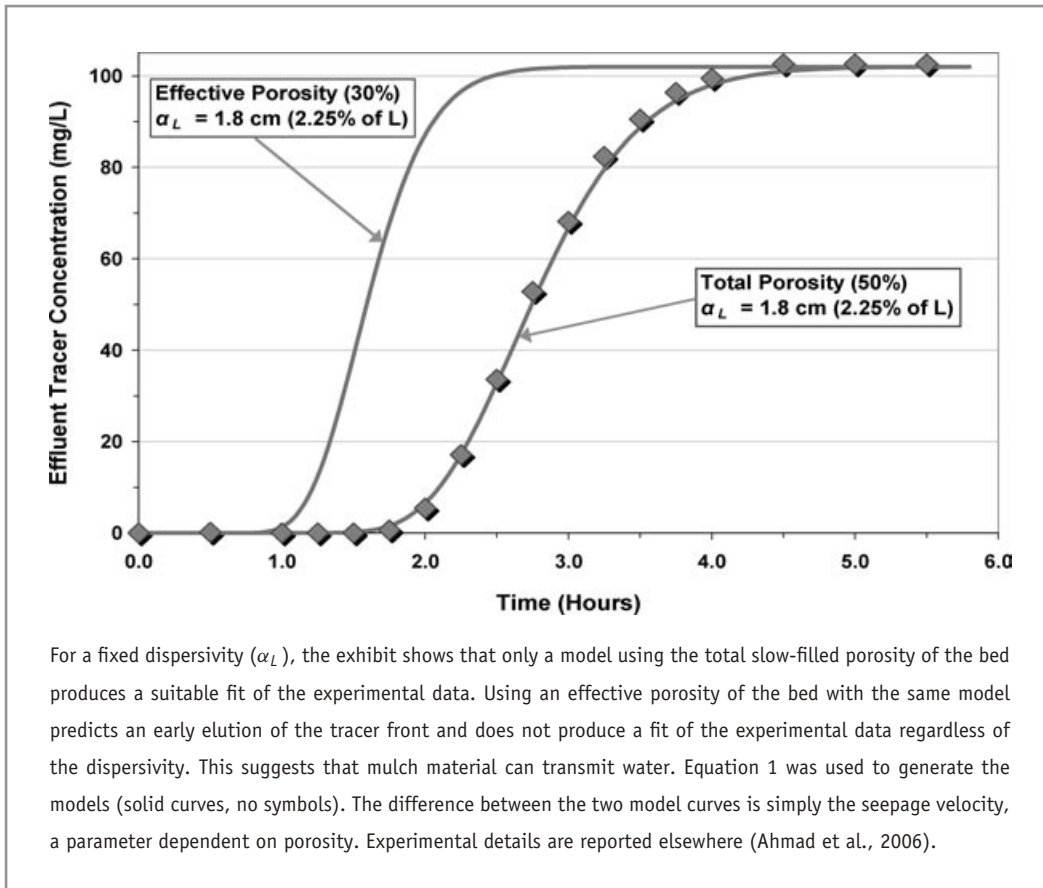


Exhibit 1. A step-change chloride tracer test (influent concentration = 102 mg/L) performed on a column with a 70 percent:30 percent mulch (pine+pine bark):pea gravel (Vol.:Vol.) packing (experimental data shown as pink diamond symbols)

association with highly lignified vascular cells (e.g., xylem tracheids in gymnosperms) prevalent in trees. The permeability of mulch is further evidenced in results of tracer tests conducted through mulch-/gravel-/sand-packed beds. Solutions to the advection-dispersion equation for conservative materials based on air-filled effective porosity are unable to fit experimental data. Conversely, solutions using a porosity determined by slowly filling the packed bed, so as to allow for complete mulch and pore-space hydration, fit the experimental data exceptionally well (Exhibit 1).

Water transmission through mulch complicates the control of porosity and permeability by the simple manipulation of the average particle size and volumetric content of the inert material (e.g., pea gravel or sand) in the biowall mulch bed. This phenomenon has the effect of buffering porosity values against drastic change by allowing additional paths to groundwater flow through the lignin channels. Exhibit 2 shows the effect of varying the volumetric content of the inert material (i.e., pea gravel) in a mulch-pea gravel-packed bed. Increasing the volumetric content of inert material from 30 to 50 percent is offset by the decreasing lignin content, resulting in an overall stabilization of the total available porosity.

Exhibit 2. Porosity and lignin content variation with volumetric content of inert material (i.e., sub-1/4" pea gravel) in a mulch bed

PARAMETER	Gravel, 0% (by Vol.)	Gravel, 30% (by Vol.)	Gravel, 50% (by Vol.)
Total Porosity (% Bulk Volume)	75.3	48.1	47.6
Effective (Air-Filled) Porosity (% Bulk Volume)	49.1	29.2	37.0
Relative Bed Lignin Content (% Bulk Volume, assuming constant mulch density)	52.6	36.8	26.3

Notes:

1. Porosity measurements completed using American Petroleum Institute (API) RP40 procedures.
2. Lignin content measured using National Forage Testing Association (NFTA) procedures.

The second hydraulic condition to take into consideration is the dispersivity through the mulch PRB. Since mulch PRBs are packed under controlled conditions with specific well-mixed materials, these PRBs tend to display a dispersivity that is relatively smaller and more consistent than dispersivities observed in heterogeneous groundwater-bearing units (GWBUs) surrounding the PRB. Tracer tests conducted as part of a bench-scale column study yielded an average longitudinal dispersivity value of 3.6 percent of bed-length, with a range of 2.3 to 5.8 percent of bed-length (Ahmad et al., 2006). The 3.6 percent longitudinal dispersivity is significantly smaller than the typical 10 percent default value utilized in groundwater transport models.

SELECTION OF ORGANIC FILL MATERIALS

Over the past decade, a variety of organic mulch materials have been used as a carbon source in the installation of mulch biowalls. These materials range from various types of hardwoods (angiosperms) and softwoods (gymnosperms) to different types of compost. No clear consensus exists on the selection criteria for organic mulch materials. Hence, in this section, a brief review of the structural chemistry of plant and tree fiber, as well as key factors that facilitate or hinder this material’s biological decomposition, are presented. The goal of this section is to provide sufficient technical background to demonstrate how simple indicators can be employed to: (1) rank available mulch materials by their likely anaerobic degradability and (2) match organic mulches used in laboratory tests to those that will be used in the field in order to generate similar contaminant degradation rates.

Mulch Structure and Decomposition

Organic mulch is composed of lignocellulosic materials. These materials are lignin, a three-dimensional biopolymer with a high degree of aromaticity, and complex carbohydrates (i.e., polysaccharides). Carbohydrates in mulch consist of glucans and glycans, of which cellulose and xylans are the most prevalent, respectively. Note that glycans are also known as hemicelluloses. In wood-based mulches, the amount of each of these three components on a dry weight basis ranges from 15 to 40 percent for lignin, 35

to 55 percent for cellulose, and 5 to 25 percent for hemicellulose. Detailed wood fiber compositions on a species-specific basis for most North American tree species have been published elsewhere (Pettersson, 1984).

The overall structure of a plant is strengthened primarily by its cell walls. Cellulose and hemicelluloses are the dominant components of plant cell walls. Cell walls also contain lignin, which begins to deposit once the plant begins its maturation process (Jung, 1997). Microscopic examination of a mature tree cell shows that its walls are further divided into three subwalls (Jung, 1997). These are the primary wall, the middle lamella, and the secondary wall. The primary or outermost wall contains all three biopolymers (i.e., lignin, cellulose, and hemicellulose). But this wall is often heavily lignified, leading to a disproportionate amount of lignin being present within this wall as compared to the other biopolymers. The middle lamella is the main location of lignin deposition during plant maturation. Therefore, in mature plants and trees it is almost entirely composed of lignin. Finally, the innermost or secondary wall is rich in cellulose and hemicellulose, and contains three layers (referred to as S1, S2, and S3), each of which possesses a different orientation of cellulose fibers than its adjacent layer (Rowell, 1995). Typically, the S2 layer within the secondary wall is the richest in cellulose. However, cellulose in all three layers has lignin embedded in it with the help of “cross-linking” provided by hemicelluloses.

Cellulose is capable of forming distinct crystalline structures that are somewhat recalcitrant to decomposition (Lynd et al., 2002) because these regions allow little or no penetration of water. However, cellulose structure in plants is not purely crystalline. Deposited cellulose has amorphous regions that are more accessible to water and, consequently, to extracellular enzymes. Elementary- or proto-fibrils of cellulose (i.e., approximately 30 monomers long) are packed into larger units called microfibrils. Microfibrils, in turn, arrange themselves into sheets that overlie each other, being held together with hydrogen bonding and Van der Waals forces. In addition, cellulose microfibrils are cross-linked to each other and to lignin with hemicellulose residues. The exact nature of this cross-linking (i.e., covalent or intermolecular bonding) at the cellulose end is unclear. However, hemicelluloses are known to be covalently bound to lignin (Winandy & Lebow, 2001).

In addition to overcoming mass transfer limitations posed by the arrangement of cellulose and other biopolymers in wood, the biological decomposition of wood must overcome biochemical challenges arising from the recalcitrant chemical structure of the different biopolymers. During the aging and (slow) decomposition of wood, the decomposition order followed is hemicelluloses, then cellulose (amorphous before crystalline), and finally lignin (Winandy & Lebow, 2001). This degradation order is also evident in composted wood, where the hemicellulose content is negligible, making the cellulose more available for decomposition (see Exhibit 3). As a result, biowalls using only compost tend to initially release a much higher total organic carbon (TOC) level in water than wood chips, followed by a sharp drop-off. Note that a similar effect is produced when vegetable oils are used in small quantities as amendments to mulch instead of compost. The decomposition order in organic mulch materials is influenced not only by the arrangement of the carbon biopolymers in wood, but also by the actual chemical structure of the biopolymer.

As far as recalcitrant chemical structure is concerned, the high aromatic content of lignin offers the most formidable challenge. The lignin content of forage is often used as an

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Exhibit 3. Variation in biopolymer content in wood and compost in samples collected from NE Texas in July 2006 for a potential biowall installation

SAMPLE	DESCRIPTION	Lignin (%)	Cellulose (%)	Hemicellulose (%)
<i>Pine 1 (Bark Free)</i>	Wood Mulch	19.87	54.30	14.54
<i>Pine 2 (Bark Free)</i>	Wood Mulch	21.82	53.24	13.87
<i>Pine Bark</i>	Wood Mulch	37.84	38.05	4.13
<i>Oak</i>	Wood Mulch	22.31	51.99	14.94
<i>Cedar</i>	Wood Mulch	23.16	45.71	9.01
<i>Pine Compost</i>	Compost	37.32	30.32	0.00
<i>Pot Ash</i>	Compost	49.55	40.14	1.43
<i>Mushroom Compost</i>	Compost	9.60	70.47	2.24

Note that a high cellulose content is favorable to mulch biowall applications, whereas a high lignin content is not. Hemicellulose content indicates the degree of cross-linking between cellulose and lignin and, consequently, affects the slow-TOC-release or leaching properties of the organic material.

indicator of whether it is digestible by herbivores (Duryea et al., 1999; Kirk & Cowling, 1984). Lignin is degraded only by nonspecific extracellular oxidative enzymes found in soil (Kirk & Cowling, 1984). These enzymes are secreted most commonly by fungi, and work via free radical-mediated mechanisms (e.g., lignin peroxidase). Because of these constraints, lignin decomposition always requires aerobic conditions.

The decomposition of cellulose requires the hydrolytic cleavage of β -1,4-glycosidic bonds between the glucose monomers (Pettersen, 1984) and can occur under both aerobic and anaerobic conditions (Lynd et al., 2002). Enzymes that decompose cellulose are broadly grouped under the name “cellulases.” The complete decomposition of cellulose requires the activity of three classes of cellulases (Kirk & Cowling, 1984; Lynd et al., 2002). Readers interested in biochemical and enzymatic basis of cellulose decomposition are directed to review articles on this topic available in the scientific literature (Leschine, 2005; Lynd et al., 2002).

The last of the three biopolymers, hemicelluloses (or glycans), are planar molecules that serve as cross-linking agents within cellulose and between cellulose and lignin (Winandy & Lebow, 2001). In the decomposition of wood, hemicelluloses are the first to break down, rendering the cellulose more “available” in the lignocellulosic matrix (Winandy & Lebow, 2001). Many cellulolytic organisms can also break down hemicelluloses (Leschine, 2005; Lynd et al., 2002). However, such organisms are rarely ever able to utilize the decomposition products of glycans as an electron donor (Lynd et al., 2002). In such cases, mixed cultures become more important as they allow noncellulolytic organisms to utilize not only the leftover cellulose breakdown products, but also products of hemicellulose decomposition.

Tests for Analyzing Organic Mulch

A variety of tests can be utilized for the analysis of mulch. Most of these tests fall either under the category of fiber or forage analysis, or under elemental analysis. All test results

are reported on a dry weight basis, necessitating the determination of moisture content as the first step of mulch analysis.

Fiber analysis methods are primarily used to analyze forage feed for livestock. These methods allow the determination of total fiber content and type, providing average composition values for cell walls. Most forage laboratories adhere to methods standardized by the National Forage Testing Association (NFTA; Undersander et al., 1993). Fiber analysis methodology involves chemical extraction with a detergent under reflux, followed by gravimetric determination of the fiber residue (Jung, 1997). The pH of the detergent and other extraction conditions determine the type of biopolymer extracted. The full suite of fiber analysis includes neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL). The NDF method extracts all three forms of fiber—namely, cellulose, hemicellulose, and lignin. The ADF method also extracts all three forms of fiber; however, the acidic conditions hydrolyze hemicellulose, leaving only cellulose and lignin as filtered residue during the gravimetric phase of the test. Finally, the ADL method is specific to lignin, using permanganate to solubilize lignin in the ADF extract. Note that an alternative method for determining lignin content is the Klason lignin method, but this method tends to overestimate the lignin content. Cellulose (ADF-ADL) and hemicellulose (NDF-ADF) content can be determined by subtraction between different fiber analysis results.

In addition to fiber analysis, elemental analysis of mulch can also yield useful results. Common elements analyzed include total carbon (C), total nitrogen (N), total phosphorus (P), total potassium (K), total calcium (Ca), total magnesium (Mg), and total sulfur (S). Furthermore, total nitrogen speciation into ammonia- and nitrate-nitrogen is also a beneficial analysis.

Evaluation of Test Results

Although significant additional research is warranted to study the transient TOC release from different types of mulch under conditions representative of mulch PRBs, some simple predictions of relative mulch decomposition rates can be made based on the material presented earlier in this article. The first set of parameters includes individual fiber components cellulose and lignin. This set of results is concerned with the total carbon source available for contaminant reduction, and the ratio of biochemically beneficial to less beneficial carbon sources. As discussed earlier, cellulose and hemicellulose can be enzymatically hydrolyzed by both aerobic and anaerobic organisms. On the other hand, lignin can be hydrolyzed only by aerobic organisms, and, in general, it is considered to be recalcitrant even under aerobic conditions (Duryea et al., 1999). So, a high cellulose content is favorable to mulch biowall applications, whereas a high lignin content is not. Alternatively, results can be arranged into different forms such as (1) the total polysaccharide content ($[(\% \text{Cellulose} + \% \text{Hemicellulose})/100] \times \text{mass of dry sample}$) and (2) the cellulose/lignin ratio.

The second set of parameters is concerned with the sustainable release of carbon under anaerobic conditions. For this set, the hemicellulose content is significant because it acts as the cross-linking agent between the cellulose and lignin. Material with a higher percentage of hemicellulose (e.g., wood chips) is likely to release aqueous TOC at a slow and sustained level. Subsequently, such material would also have to be supplemented with other materials that can release high concentrations of TOC rapidly (e.g., compost) so

Some simple predictions of relative mulch decomposition rates can be made based on the material presented earlier in this article.

that oxygen could be scavenged out of the system shortly after startup. Lignin-to-total nitrogen ratios, with lower ratios favoring faster decomposition, have also been used in the past to predict relative mulch decomposition rates (Duryea et al., 1999).

Finally, for supplemental carbon evaluation, parameters used for aerobic mulch decomposition can be utilized because the supplemental carbon is used to provide an initial TOC boost to drive the system anoxic via aerobic reactions. To this end, compost, vegetable oil, and plant mulch have all been used successfully in the past (Henry et al., 2003; Perlmutter et al., 2000). For compost and plant mulch, a low hemicellulose content, a C:N ratio in the range of 25:1 to 40:1 (for cured compost [Cooperbrand, 2002]), and low salt content (nitrate and chloride) are favorable.

For supplemental carbon evaluation, parameters used for aerobic mulch decomposition can be utilized because the supplemental carbon is used to provide an initial TOC boost to drive the system anoxic via aerobic reactions.

An important point to remember is that the extent and rate of mulch decomposition does not necessarily shed any light on the aqueous TOC level that will be required to sustain the degradation reaction of a particular target contaminant. This critical TOC level is not only a function of the type of mulch materials used, but also a function of target contaminant structure, level and type of competing electron acceptors (e.g., mixed contaminants and inorganic anions, such as nitrate and sulfate), and other site-specific conditions. However, all mulch PRBs installed to date still exhibit strong and sustained removal efficiencies.

USING ANALYTICAL MODELS TO DESIGN A MULCH PRB

Analytical solutions to the advection-dispersion equation for a substance undergoing first-order decay can be used (a) to mine past field data for effective first-order decay constants and (b) to predict the required PRB thickness for achieving a desired contaminant removal once a first-order degradation rate is known. Mathematical solutions can vary depending on the type of target contaminant involved. A simple steady-state bed-profile solution can be utilized in the case of contaminants whose first-order decay constant represents a direct degradation to innocuous products. An example of this type of contaminant is RDX, which is believed to rapidly undergo ring cleavage to innocuous products in the environment after initial reductive reactions (Ahmad et al., 2006; Hawari, 2000; McCormick et al., 1981). When the target contaminant is part of a more complicated degradation reaction scheme, such as a reaction in a series, a more sophisticated model must be employed.

A Simple Steady-State Analytical Model for PRB Design

The steady-state operation of a PRB can be described mathematically by the steady-state bed-profile solution to the reactive advection-dispersion equation developed by Van Genuchten and Alves (1982). This equation describes the flow of contamination from a continuous source, undergoing first-order decay within the PRB, with negligible diffusion and no sorption:

$$\frac{C}{C_0} = \exp \left[\left(\frac{L}{2\alpha_L v_x} \right) \left(v_x - \sqrt{v_x^2 + 4k\alpha_L v_x} \right) \right] \quad (1)$$

where

Boundary Conditions: $C (@ x = 0) = C_0$; $dC/dx (@ x = \infty) = 0$

- C_0 = concentration of target contaminant entering PRB
- C = concentration of target contaminant leaving PRB
- L = PRB thickness (x , if variable)
- α_L = longitudinal dispersivity through the PRB
- v_x = seepage velocity through the PRB
- k = pseudo-first-order decay rate constant

A simple material balance on water (incompressible fluid) at the upgradient formation-PRB interface leads to the following expression:

$$v_f A = v_x \eta_p A \tag{2}$$

where

- v_f = specific discharge or Darcy velocity of the formation = $K (dh/dL)$
- η_p = PRB porosity
- A = cross-sectional area at the interface

Substituting Equation 2 into Equation 1 yields the final steady-state PRB design equation:

$$\frac{C}{C_0} = \exp \left[\left(\frac{L \eta_p}{2 \alpha_L v_f} \right) \left((v_f / \eta_p) - \sqrt{(v_f / \eta_p)^2 + 4k \alpha_L (v_f / \eta_p)} \right) \right] \tag{3}$$

In terms of fractional contaminant removal (R) Equation 3 can be written as:

$$R = 1 - \frac{C}{C_0} = 1 - \exp \left[\left(\frac{L \eta_p}{2 \alpha_L v_f} \right) \left((v_f / \eta_p) - \sqrt{(v_f / \eta_p)^2 + 4k \alpha_L (v_f / \eta_p)} \right) \right] \tag{4}$$

Equations 3 and 4 can be used to predict the post-treatment effluent concentration and contaminant removal, respectively, from a PRB of a fixed thickness (L). They can also be used iteratively to determine the pseudo-first-order decay constant. Alternatively, Equation 3 can be solved for L to give an expression that can be utilized for determining the PRB design thickness required to treat inflowing contamination at concentration C_0 to an effluent regulatory standard, C :

$$L = \left[(2 \alpha_L v_f / \eta_p) \ln \left(\frac{C}{C_0} \right) / \left((v_f / \eta_p) - \sqrt{(v_f / \eta_p)^2 + 4k \alpha_L (v_f / \eta_p)} \right) \right] \tag{5}$$

The porosity of the biowall (η_p) is dependent on the mulch content of the fill material, largely because of high water permeability through hydrated mulch.

The formation Darcy velocity or specific discharge (v_f) in Equations 3, 4, and 5 can be estimated by the product of the site hydraulic conductivity and the hydraulic gradient in the vicinity of the location selected for biowall installation. As discussed earlier in the hydraulic characteristics section, the porosity of the biowall (η_p) is dependent on the mulch content of the fill material, largely because of high water permeability through hydrated mulch. This value can be determined experimentally using API Method RP40. Since biowall fill materials are typically mixed in a 50:50 mulch:inert material (V:V) mixture, the porosity of the biowall is somewhat predictable, falling in the range of 40 to 50 percent. The dispersivity through the biowall (α_L) is small (less than 5 percent of the biowall thickness) because the fill consists of engineered materials that are thoroughly mixed prior to installation. By using conservative estimates of biowall porosity and dispersivity, and by assuming biowall installation thicknesses of 2 feet and 1 feet, Equation 4 can be used to generate nomographs demonstrating the contaminant removal

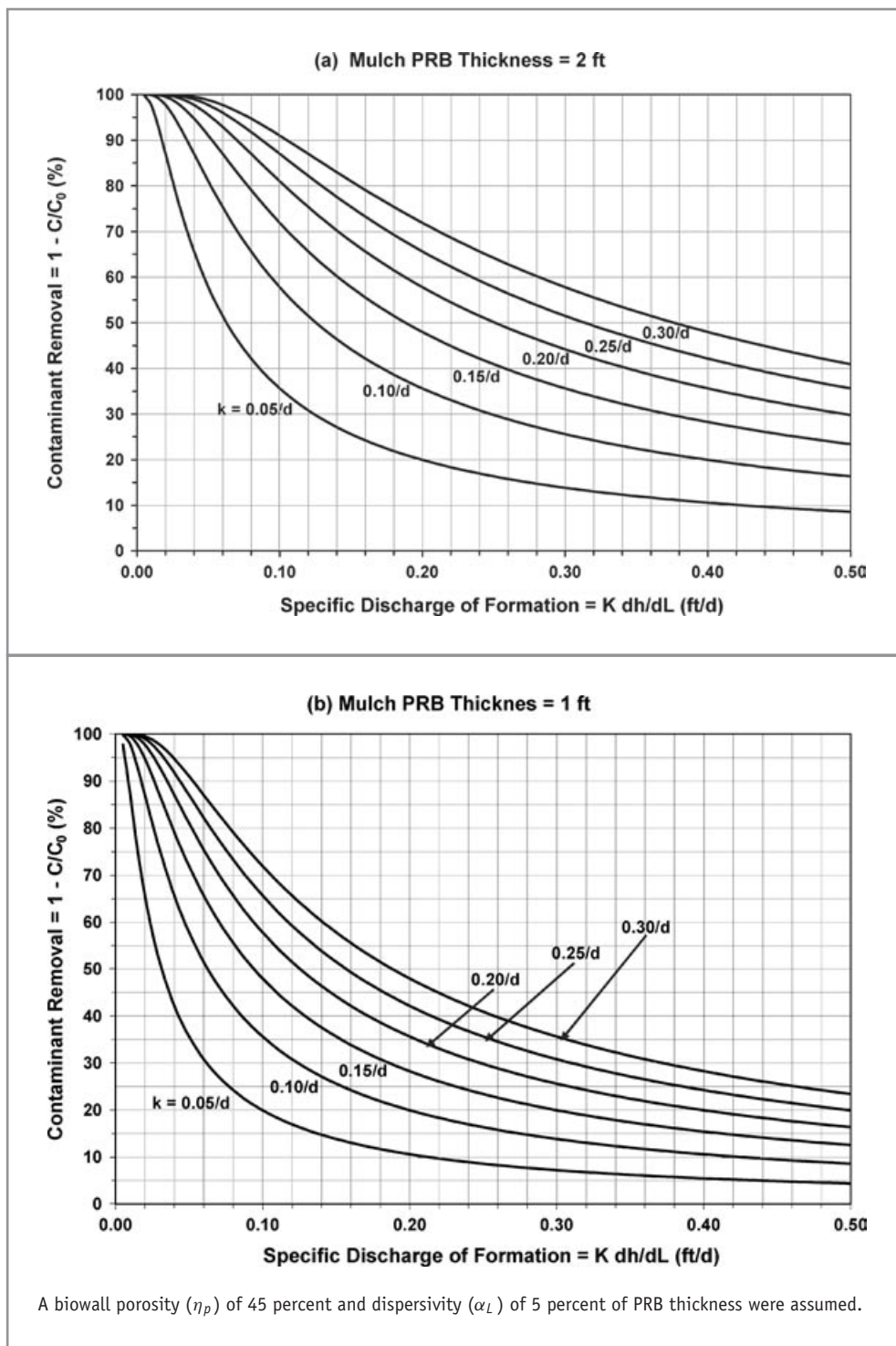


Exhibit 4. Nomographs of Equation 4 for (a) two-foot- and (b) one-foot-thick mulch PRBs or biowalls showing the relationship between percent contaminant removal, the formation specific discharge, and incremental values of the first-order contaminant decay constant

Exhibit 5. Calculated TCE first-order decay constant (*k*) from data for past mulch PRB studies published in technical literature (GSI, 2001, 2004; Henry et al., 2003) using Equation 4

Site	K (ft/d)	dh/dL	Ave. TCE Removal Reported (%)	C/Co	Biowall Thickness (L, ft)	k (day ⁻¹)	Reference
Altus AFB (Full-Scale)	14.2	0.003	95.3%	0.047	1.5	0.230	Henry et al., 2003
Offutt AFB (Pilot-Scale)	3.5	0.01	73.0%	0.270	1.0	0.114	GSI, 2001
Offutt AFB (Full-Scale)	3.5	0.01	95.0%	0.050	1.5	0.185	GSI, 2004

In these cases, influent PCE concentrations were negligible, if present at all. Hydrodynamic constants used were the same as Exhibit 4. Average removals reported were used to extract *k* values.

(*R*) as a function of the formation specific discharge and first-order rate constant, *k* (see Exhibit 4).

The biowall thicknesses in Exhibits 4a and 4b are the discrete thicknesses at which biowalls are typically installed using the one-pass trenching technique. One-pass trenching is the preferred method for installing PRBs because of its speed and cost-effectiveness. All mulch biowalls implemented to date have been installed using one-pass trenching, with backfilling accomplished by either an in-line hopper or with the use of earth-moving equipment. A three-foot thickness is also possible with one-pass trenching; however, the mobilization costs for the commercial trenching machine capable of such an installation are prohibitively expensive.

In most practical cases involving stable plumes, both the specific discharge and the required contaminant removal become defined once the location of the biowall is selected with respect to the plume. The only critical unknown is the first-order decay constant, *k*. If time permits, this can be determined using a continuous-flow packed-column study (Ahmad et al., 2006). Alternatively, it can be estimated from past studies, provided rate constants for the target contaminant have been published. Exhibit 5 presents field *k* values calculated for three past mulch biowall studies by iteratively solving Equation 4. Data utilized from past studies assumed steady-state conditions by the last monitoring round reported.

It must be noted that Equations 3, 4, and 5 only address steady-state performance of the biowall. Since the time to steady-state is both a function of hydrodynamics and biological growth rates, it is difficult to predict. However, the time to steady-state cannot be less than the time to displace readily available inert (i.e., conservative) material. If the available TOC is assumed to be present freely in solution, then the minimum time to steady-state would be the time required to displace approximately two pore volumes of the wall, or the time required for a constant (influent) concentration tracer front to pass through the mulch PRB.

Since Equations 3, 4, and 5 only address steady-state performance of the biowall, they are more suitable for use as planning-level design estimates. Furthermore, a large variety

of biogeochemical complicating factors, beneficial or nonbeneficial to biowall performance, preclude the use of these equations for a long-term performance evaluation. These factors can include inorganic precipitation within the PRB and reduction in the enzymatic hydrolysis rates for the mulch due to changes in upgradient conditions or due to changes in bioactivity (e.g., biomass concentrations and contaminant biodegradation rates).

An item not discussed in the article so far is the design of biowalls for mixed target contaminants present at a site. For such a site, an additive approach can be utilized, using individual contaminants to generate required biowall thicknesses and then summing these thicknesses to get an overall thickness for the biowall to be installed at the site.

CONCLUSIONS

Three technical considerations that can impact the design and performance of mulch PRBs were presented and discussed. These technical considerations were: (1) hydraulic characteristics of the mulch bed; (2) characteristics of different types of organic amendments used as mulch PRB fill materials; and (3) transport models that can be used to estimate the required PRB thickness to attain cleanup standards. For the first technical consideration, it was shown that mulch materials can transmit water once hydrated. It was also discussed that dispersivities through mulch PRBs tend to be fairly small (less than 5 percent of thickness). For the second technical consideration, a brief review of materials was presented to illustrate that the structure and arrangement of the biopolymers in mulch control its extent and rate of decomposition. The decomposition in mulch tends to occur in the following preferential order: hemicellulose > amorphous cellulose > crystalline cellulose > lignin. As part of this technical consideration, tests that can be used to compare different organic amendment materials were described. It was also emphasized that a substantial amount of additional work is warranted before mulch decomposition and TOC release can be correlated with the degradation of particular contaminants. Finally, two transport models and procedures for their use were presented to estimate the thickness of a mulch PRB. The first model described the steady-state behavior of a target contaminant undergoing first-order decay to innocuous products.

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