Closing the Mass Balance at Chlorinated Solvent Sites: Sources and Attenuation Processes

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Using detailed mass balance and simple analytical models, a spreadsheet-based application (BioBalance) was developed to equip decision makers with a predictive tool that can provide a semiquantitative projection of source-zone concentrations and provide insight into the long-term behavior of the associated chlorinated solvent plume. The various models were linked in a toolkit in order to predict the composite impacts of alternative source-zone remediation technologies and downgradient attenuation processes. Key outputs of BioBalance include estimates of maximum plume size, the time frame for plume stabilization, and an assessment of the sustainability of anaerobic natural attenuation processes. The toolkit also provides spatial and temporal projections of integrated contaminant flux and plume centerline concentrations.

Results from model runs of the toolkit indicate that, for sites trying to meet traditional, "final" remedial objectives (e.g., two to three orders of magnitude reduction in concentration with restoration to potable limits), "dispersive" mechanisms (e.g., heterogeneous flow and matrix diffusion) can extend remedial time frames and limit the benefits of source remediation in reducing plume sizes. In these cases, the removal of source mass does not result in a corresponding reduction in the time frame for source remediation or plume stabilization. However, this should not discourage practitioners from implementing source-depletion technologies, since results from the toolkit demonstrate a variety of measurable benefits of source remediation. Model runs suggest that alternative, "intermediate" performance metrics can improve and clarify source remediation objectives and better monitor and evaluate effectiveness. Suggested intermediate performance metrics include reduction in overall concentrations or mass within the plume, reduction of flux moving within a plume, and reduction in the potential for risk to a receptor or migration of a target concentration of contaminant beyond a site boundary.

This article describes the development of two key modules of the toolkit as well as illustrates the value of using intermediate performance metrics to evaluate the performance of a source-remediation technology. © 2010 Wiley Periodicals, Inc.

INTRODUCTION

Over the past decade, there has been an increased interest in using monitored natural attenuation (MNA) as a means of achieving remediation objectives at chlorinated solvent sites, either alone or as part of a treatment train. Most chlorinated volatile organic

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compounds (CVOCs) have been shown to be amenable to *in situ attenuation* processes such as dispersion, sorption, and biodegradation under certain conditions (Weidemeier et al., 1999). Like any remediation alternative, MNA is judged on key remediation metrics, such as risk reduction, exposure prevention, cost-effectiveness, regulatory considerations, and future land use. For MNA in particular, however, there is additional focus on considerations, such as the *stability* of the groundwater contaminant plume and its potential for migration, the *sustainability* of natural attenuation processes, and, perhaps most important, whether it is capable of achieving site-specific remedial goals within a *reasonable time frame* (National Research Council [NRC], 2000). MNA studies often entail more complex site characterization, extensive long-term monitoring of contaminant concentration trends within the plume, and development of analytical and numerical simulations of complex attenuation processes to support the occurrence of natural attenuation mechanisms.

MNA studies often entail more complex site characterization, extensive long-term monitoring of contaminant concentration trends within the plume, and development of analytical and numerical simulations of complex attenuation processes to support the occurrence of natural attenuation mechanisms.

MNA is more commonly used in conjunction or as a follow-up strategy to active source-remediation technologies (such as chemical oxidation, thermal oxidation, etc.) as opposed to being a sole remedy (McGuire et al., 2004). While source-depletion technologies are an attractive remedial action for sites with discrete source zones, the effectiveness and potential benefits of source depletion have been the subject of significant ongoing technical and policy debates. In 2003, the U.S. Environmental Protection Agency commissioned an Expert Panel on the remediation of dense nonaqueous-phase liquid (DNAPL) sites to evaluate major issues regarding implementation of source-depletion technologies at DNAPL sites (Kavanaugh et al., 2003). From a risk management perspective, source depletion can lead to reduced potential for migration of a DNAPL phase, reduction in source longevity and long-term management requirements, near-term enhancement of natural attenuation, near-term reduction in dissolved-phase loading to receptors, and near-term attainment of maximum contaminant levels (MCLs) established under the Safe Drinking Water Act. Nevertheless, the Expert Panel concluded that one of the major reasons for the reluctance of many site owners to undertake aggressive source-depletion technologies was due to the lack of reliable decision tools to predict the performance of DNAPL source-zone remediation technologies.

Consequently, in response to the requirements put forward by the Office of Solid Waste and Emergency Response (OSWER) MNA directive in 1999 (US EPA, 1999) and the conclusions of the US EPA DNAPL Expert Panel (Kavanaugh et al., 2003), researchers at the U.S. Department of Energy's (DOE's) Savannah River National Laboratory conceptualized new tools for evaluating and developing effective natural attenuation-based strategies for chlorinated solvent sites (Looney et al., 2006; Sink et al., 2004; Vangelas et al., 2006). Central to this project was the use of fundamental concepts such as *mass balance* and *enhanced attenuation*, which could be used to evaluate the efficacy of natural attenuation mechanisms at a site as well as to identify source-characterization and -depletion strategies to accelerate remediation projects. In this article, we describe the basis for the development of one of these mass-balance tools—namely, the *BioBalance Toolkit* (Kamath et al., 2007). The BioBalance Toolkit is a spreadsheet-based predictive tool that incorporates analytical solutions for source decay and plume migration, and integrates key mass balances on solvents, donors, and competing electron acceptors over the lifetime of the source to provide decision makers with a basis for preliminary management decisions related to the selection of remedial strategies at chlorinated solvent sites. The toolkit is structured to address the following key questions necessary for

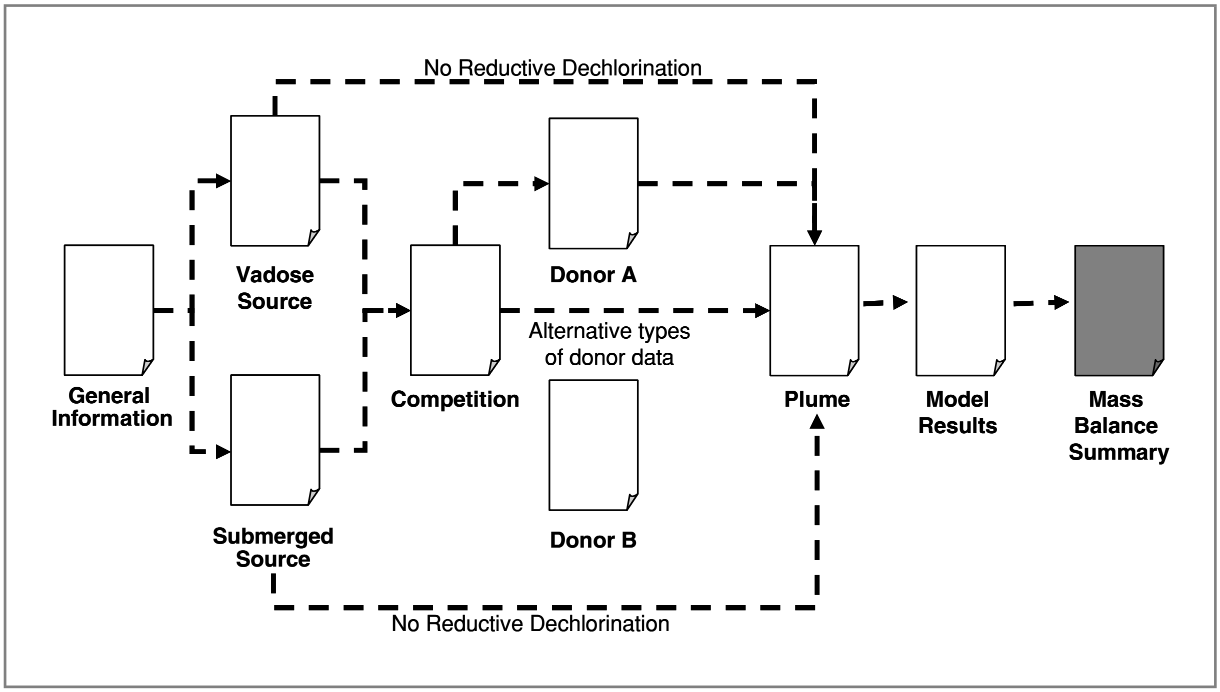

Exhibit 1. Architecture of the BioBalance Toolkit

selection of MNA at a chlorinated solvent site using a series of four separate software modules that can be used independently or in conjunction with each other (Exhibit 1):

a. *Source Remediation Time Frame (Source Module):* How long will it take to achieve groundwater objectives at a chlorinated solvent site using MNA as a sole remediation strategy? Can implementation of a source-depletion strategy reduce the overall remediation time frame?
b. *Plume Behavior (Plume Module):* How does the plume behavior change over time?
c. *Sustainability Within the Source Zone (Donor Module and Competition Module):* Are biological degradation reactions—specifically, reductive dechlorination—sustainable over the long term? Is there sufficient electron donor available to support complete reductive dechlorination *(Donor Module)* as well as to compensate for competing electron acceptor reactions *(Competition Module)* over the time frame of the project?

In the following discussion, the development and applicability of the modules on the source-remediation time frame and plume behavior are discussed. In general, the toolkit is intended to be used as (1) a screening tool to determine whether MNA is a feasible remediation approach at a chlorinated site and (2) a planning-level predictive tool to determine the potential impacts of source-depletion strategies on achieving plume management objectives. The toolkit is available for free on the GSI Web site at http://www.gsi-net.com/en/software/free-software.html.

DISCUSSION

Source-Zone Remediation

To apply the mass-balance concept to source remediation, two key variables are calculated: (1) *mass flux*, defined here as the mass per time leaving the source zone (this is also called *mass discharge* or *total mass discharge* by other researchers), and (2) *source mass*.

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Mass flux is a particularly valuable metric to practitioners involved in the selection of source-depletion strategies at a site. In fact, Einarson and Mackay (2001) presented a framework for predicting the severity of contamination at a site using a mass flux approach. They advocated the use of mass discharge/flux to identify high-risk sites that should be priorities for a greater degree of site investigation and corrective action. The US EPA Monitored Natural Attenuation Seminar, 1998 (US EPA, 1998) summarized the benefits of a mass flux approach to evaluate groundwater impacts as follows:

> *"The reduction in the flux along the flowpath is the best estimate of natural attenuation of the plume as a whole."*
>
> *"The flux is the best estimate of the amount of contaminant leaving the source area. This information would be needed to scale active remedy if necessary."*
>
> *"Flux estimate across the boundary to a receptor is the best estimate of loading to a receptor."*

As part of a Strategic Environmental Research and Development Program (SERDP)–funded project to create decision support systems for site management, Newell and Adamson (2005) recently developed a semi-analytical approach to help estimate the quantitative relationship between source depletion and the remediation time frame (RTF). The RTF was defined as the time required to reduce the initial mass (M_o) or mass flux (W_0) from the source zone to below a threshold mass (M_g) or mass flux goal (W_g). Two planning-level concentration vs. time models (First-Order Decay Model, Compound Model) were incorporated into the BioBalance Toolkit to estimate the remediation time frame.

A key simplifying assumption made during derivations of these empirical equations was that the change in mass discharge (i.e., flux) is directly proportional to the change in source mass (Stroo et al., 2003). In reality, the change in source mass and the source discharge term might not correspond to the 1:1 predicted relationship (Newell & Adamson, 2005; Stroo et al., 2003). Depending on the source architecture (i.e., distribution and geometry of DNAPL, and hydrogeologic and geochemical heterogeneities within the impacted zone), the relationship between mass flux and source mass can vary, as detailed in Stroo et al. (2003). However, the 1:1 assumption represents a "middle-of-the-road" approach and appears to be an acceptable solution for many sites based on a recent study by McGuire et al. (2006). In this compilation of the performance of source-depletion technologies, it was demonstrated that at 11 chlorinated solvent sites, the remaining fraction of DNAPL mass was within ± 0.3 units of a predicted 1:1 relationship with the remaining fraction of the groundwater concentration (and, therefore, source mass flux). Similarly, results from a DNAPL remediation survey (GeoSyntec, 2004) indicated that data from four of nine sites showed an approximately 1:1 relationship between source mass depletion and the resultant mass discharge. Finally, the RemCHLOR model (Falta et al., 2005a, 2005b; US EPA, 2007) presents a range for potential source architecture based on the "gamma" model so that the middle of this range represents the 1:1 mass flux:source mass assumption.

To account for the impact of source-depletion technologies on the source zone, Newell and Adamson (2005) incorporated a source reduction factor (RF) into their planning-level equations. The RF was defined as the fraction of total source mass remaining following active remediation, but this selection meant that a single term was used to describe the impact of the depletion technology on both the source mass and the mass discharge rate. However, it is understood that the change in source mass and the source discharge term immediately after the implementation of a remediation strategy may not be proportional in all cases, and that the relationship is highly dependent on the specific technology that is selected. For example, the implementation of a chemical oxidation strategy within the source zone would impact the source mass and the contaminant dissolution rate, but the installation of a horizontal barrier above a source located in the vadose zone would result in a decrease in the mass flux from the source into the plume while having no impact on the mass remaining in the source zone immediately following implementation.

Exploiting these differences in the posttreatment source characteristics could help better predict the impact on the source-depletion technologies on the remediation time frame of a subsequent MNA project. To do so, two RFs that define the posttreatment source zone were incorporated into the equations employed in the Source Module. They are defined as follows:

- Remaining Mass Factor (RF_M): The fraction of the original *mass* remaining after implementation of an active source-depletion technology ($0 < RF_M < 1.0$).
- Remaining Mass Flux (RF_W): The fraction of the original *mass flux* remaining after implementation of an active source-depletion technology ($0 < RF_W < 1.0$).

The simplest methods for incorporating source strength measurements into estimates of source lifetime rely on the intuitive assumption that the mass discharge rate from a source zone follows a linear or step-function pattern over time.

Based on the quantitative relationship between the RFs, remediation strategies can be grouped into four broad categories (Exhibit 2). For sites where the remediation time frame is the primary performance metric, these modified planning-level equations provide a tool for comparing the performance of different source-removal strategies and, therefore, selecting a site-specific remedial configuration.

In the BioBalance Toolkit, the First-Order Decay Model and the Compound Model developed by Newell and Adamson (2005) were incorporated as described in detail below.

1. ***First-Order Decay Model***: The simplest methods for incorporating source strength measurements into estimates of source lifetime rely on the intuitive assumption that the mass discharge rate from a source zone follows a linear or step-function pattern over time. However, recent research on complex mechanisms, such as matrix diffusion, linear desorption, desorption from fractions with different equilibrium kinetics, and dispersion, as well as field observations of a "tailing" effect within contaminant plumes, suggest that the first-order decay kinetics is an appropriate model for simulating source decay (Newell & Adamson, 2005). Given the assumption that the mass flux (W) from a source zone follows a first-order decay pattern, the source decay rate before

Exhibit 2. Classification of remediation strategies based on their impact on the source mass and mass flux

Characteristics of Remediation Strategy		Examples
Case 1: Reduction in source mass flux only. No impact on the source mass.	$RF_W < 1; RF_M = 1$	Physical barriers such as: a) Bentonite slurry wall upgradient of a groundwater source b) Horizontal cap installed on top of a vadose-zone source c) Hydraulic barrier that captures the plume leaving the source (without impacting the dissolution rate) d) *In situ* stabilization that binds or sorbs mass in the source zone
Case 2: Reduction in both source flux and mass (typical source-depletion scenario)	$RF_M < 1; RF_W < 1$	a) Complete excavation b) Enhanced bioremediation c) Chemical oxidation d) Thermal treatment e) Some pump-and-treat systems
Case 3: No impact on source mass or flux	$RF_M = RF_W = 1$	a) Permeable Reactive Barrier downgradient of a source zone b) Strategy involving no active source remediation
Case 4: Reduction in source mass only. No impact on mass flux (special source depletion)	$RF_M < 1; RF_W = 1$	a) Partial excavation of the top portion of a vadose-zone source b) Rebound in concentrations to the pretreatment concentrations

implementation of a source-depletion technology could be predicted by:

$$K_s = \frac{W_0}{M_s} \tag{1}$$

The time frame required to achieve remedial objectives at the site would be:

$$RTF_{MNA} = \frac{M_0}{W_0}\left(-Ln\left(\frac{W_g}{W_0}\right)\right) \tag{2}$$

Where:
K_s = source decay rate (per time)
W_0 = mass flux from source zone at $t = 0$ (prior to remediation) (mass per time)
W_g = mass flux calculated from the remedial concentration goal for the contaminant (mass per time)
M_0 = mass at source zone at $t = 0$ (prior to remediation) (mass)
RTF_{MNA} = remediation time frame for an MNA-only scenario (time)

After implementation of an active remediation technology, the modified source decay rate due to an alteration in the source mass and/or the mass flux would be:

$$K_{s-SD} = \frac{W_0}{M_s} \cdot \frac{RF_W}{RF_M} \tag{3}$$

And the impact of the altered decay rate on the time required to achieve a goal mass discharge rate could be predicted using:

$$RTF_{SD} = \frac{M_0}{W_0} \cdot \frac{RF_M}{RF_W}\left(-Ln\left(\frac{W_g}{W_0 \cdot RF_W}\right)\right) \tag{4}$$

where RTF_{SD} = remediation time frame for a source undergoing a remediation strategy (time).

Typical values for RF_W range between 0.01 and 0.4 for remediation technologies, such as enhanced bioremediation, chemical oxidation, thermal treatment, and surfactant/cosolvent addition (McGuire et al., 2006). The case studies in the following sections utilize this first-order decay model and illustrate the tailing behavior of both the mass and flux over time regardless of whether or not a source-remediation technology was implemented.

2. ***Compound Model***: The Compound Model assumes that over the lifetime of the source, half of the mass leaves the source zone at a constant concentration (and mass flux rate), and half leaves as the mass flux decays via a subsequent first-order decay process. This model is appropriate for heterogeneous sites where complex spatial distribution of the contaminants can result in complex mass discharge patterns. For example, mass discharge from a DNAPL ganglion will tend to remain independent of the contaminant mass. In this case, the mass discharge is solubility-limited and, therefore, will remain constant until the source reaches a critical mass. Given this, the remediation time frame for the source would be best described by

$$RTF_{MNA} = 0.5 \cdot \frac{M_0}{W_0}\left(1 - Ln\left(\frac{W_g}{W_0}\right)\right) \tag{5}$$

Upon implementation of a source-remediation technology, the remediation time frame would be described by:

$$RTF_{SD} = 0.5 \cdot \frac{M_0}{W_0} \cdot \frac{RF_M}{RF_W}\left(1 - Ln\left(\frac{W_g}{W_0 \cdot RF_W}\right)\right) \tag{6}$$

The Compound Model assumes that over the lifetime of the source, half of the mass leaves the source zone at a constant concentration (and mass flux rate), and half leaves as the mass flux decays via a subsequent first-order decay process.

Case Study

i. *Background*: A chlorinated solvent site with trichloroethene (TCE) and benzene in a submerged source zone (dimensions 25 feet by 25 feet) is located perpendicular to the flow of groundwater (seepage velocity, V_s = 103.8 ft/yr). The initial mass (M_o) of TCE in the source zone is estimated to be approximately 15 kg and, based on the average groundwater concentration in the source zone (5 mg/L) and the average soil concentration in the source (20 mg/kg), the original mass flux (W_o) is calculated to be approximately 3.22 kg/yr.

ii. *Traditional Performance Metric*: To achieve site closure, the decision maker would have to achieve a discharge goal (W_g) that is 0.1 percent of the original discharge rate (equivalent to decreasing the near-source groundwater concentration from 5 mg/L to 0.005 mg/L).

iii. *Toolkit Predictions*: Depending on the site heterogeneity and the complexity of the source zone, the site would require between 18 and 32 years (using both first-order decay kinetics and the Compound Model) to reach the discharge goal (RTF_{MNA}) if MNA were implemented as the sole remedy at the site. However, if 50 percent of the original source mass was excavated prior to implementing MNA, assuming a corresponding decrease in the source mass flux, the time required to reach this goal (RTF_{SD}) would be between 17 and 29 years. Thus, a 50 percent decrease in the source mass would result in a 9 to 10 percent decrease in the remedial life (i.e., monitoring phase) of the source zone. Alternatively, implementation of a hypothetical chemical oxidation technology with a predicted mass removal of 90 percent and a 90 percent mass flux reduction could result in a remediation time frame of 13 to 21 years for the source zone. Thus, a 90 percent reduction in the source mass and mass flux would only result in a 29 to 33 percent decrease in the remediation time frame. By contrast, installation of a barrier technology (e.g., a slurry wall upgradient of the source zone) that decreases the groundwater recharge rate to the source zone (but not the source mass) by 90 percent could extend the remediation time frame of the source zone to greater than 100 years (see Exhibit 3a).

Installation of a barrier technology (e.g., a slurry wall upgradient of the source zone) that decreases the groundwater recharge rate to the source zone (but not the source mass) by 90 percent could extend the remediation time frame of the source zone to greater than 100 years.

Simply put, these results indicate that removal of source mass often does not result in a corresponding reduction in the source-remediation time frame in most cases (i.e., not "equal benefit for equal work"). Furthermore, installation of barrier technologies (e.g., upgradient slurry walls) would increase the remediation time frame for the source zone.

These results, although discouraging at first glance, should not be taken at face value by practitioners. Traditional performance metrics, such as the source-remediation time frame, can be insensitive to the multitude of measurable benefits achieved during implementation of source-remediation technologies. Examples of these potential benefits include: reduced source loading (mass flux) to the plume, reduced potential for migration of a DNAPL phase, and/or reduced potential for environmental damage. In fact, these results demonstrate the need for more meaningful alternative, "intermediate," performance metrics that take into account the variety of benefits of source remediation. Instead of using a single metric (i.e., remediation time frame) to meet the groundwater concentration goal at the site, an appropriate intermediate goal for a site would be based on the remedial technology under evaluation and the remediation driver at the site. Alternate intermediate performance metrics include reduction in overall concentrations or mass within the plume, reduction of flux moving within a plume, and reduction in the potential for risk to a receptor or migration of a target concentration of contaminant beyond a site boundary (Sale et al., 2008).

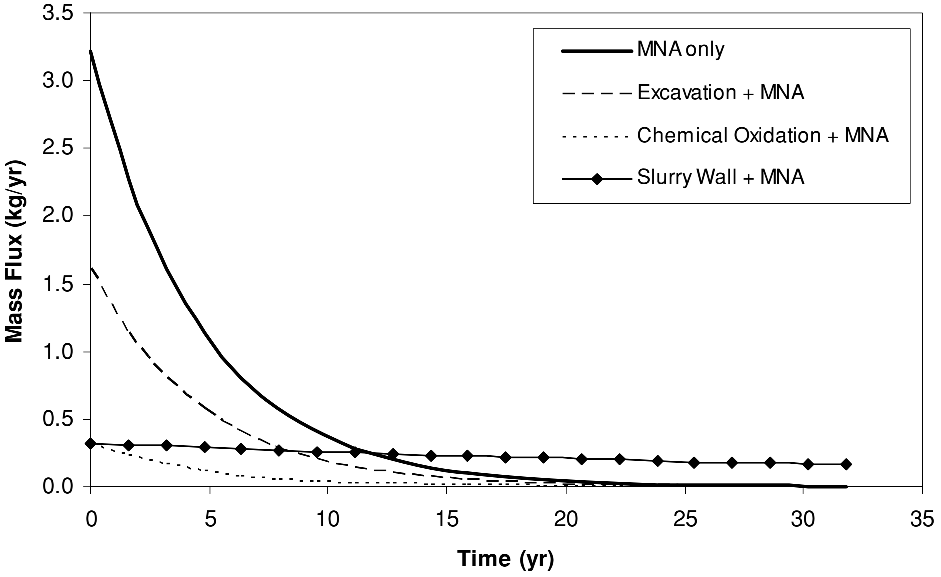
iv. *Suggested Intermediate Performance Metric:* For the case study described above, a decision maker could use the following two discharge goals ($W_{intermediategoal}$) as milestone markers for evaluating the three source-depletion technologies:

   a. *First milestone*: Time required to reduce the mass discharge from the source zone by 98 percent ($W_{intermediategoal\_1}$), which is equivalent to decreasing the overall near-source groundwater concentration from 5 mg/L to 0.1 mg/L.

   b. *Second milestone*: Time required to reduce the mass discharge from the source zone by 99.5 percent ($W_{intermediategoal\_2}$), which is equivalent to decreasing the overall near-source groundwater concentration from 5 mg/L to 0.025 mg/L.

v. *Toolkit Predictions*: The toolkit predicts that if MNA were implemented as the sole remedy at the site, the site would require between 11 and 18 years to reach the first milestone

a. Mass flux of TCE from the source zone



b. TCE concentration within the plume and stabilization distance from the source zone

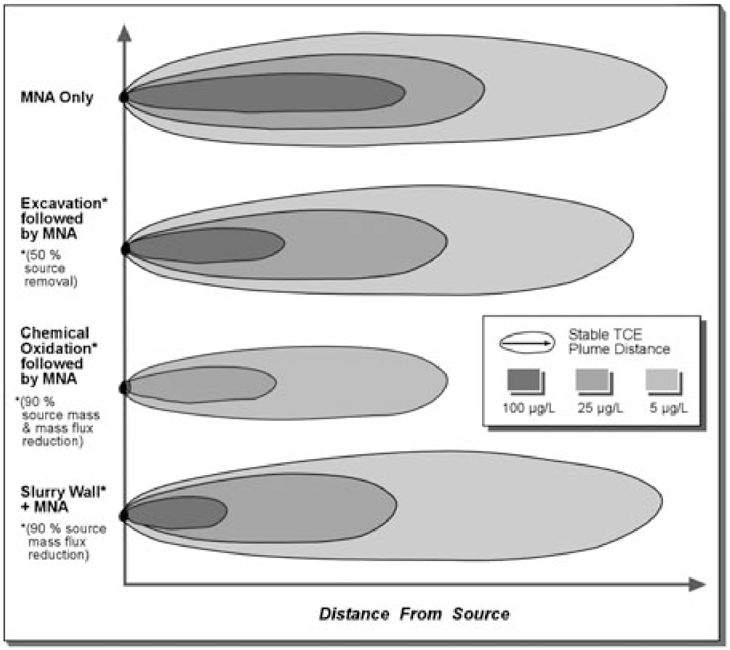


Exhibit 3. Impact of source remediation technologies on the distribution of TCE over time

(i.e., a groundwater concentration of 0.1 mg/L near the source) and between 15 and 24 years to reach the second milestone (i.e., a groundwater concentration of 0.025 mg/L near the source). However, if 50 percent of the original source mass was excavated prior to implementation of MNA, assuming a corresponding decrease in the source mass flux, the time required to reach the intermediate goals at the source zone would decrease by 10 to 17 percent. In the case of the hypothetical chemical oxidation technology with a predicted mass removal of 90 percent and a 90 percent mass flux reduction, the time frame to meet the milestones would decrease by 40 to 61 percent. Using the intermediate goals, therefore, provides results that better capture the impacts of the source-remediation technology. In the case of the barrier technology, evaluation of the performance in terms of the source remediation time frame is meaningless. Instead, an appropriate performance metric would be one that fully captures the impact of the slurry wall on reducing the overall mass and concentration of TCE within the plume such that the groundwater does not pose an unacceptable risk to the environment or human receptors. The case study described in the following section better illustrates the use of intermediate performance metrics in measuring the impact of these technologies on plume behavior.

The output from the Plume Module includes centerline CVOC concentrations as well as a breakdown of the relative contribution of different natural attenuation processes, such as advection, dispersion, sorption, and degradation, to temporal changes in the groundwater CVOC concentrations.

Understanding Plume Dynamics and Predicting Plume Stability

Establishing plume stability is an important line of evidence required by most states and the US EPA for selection of an MNA remedy. Furthermore, under certain conditions in some states, such as Texas, evidence of a stable petroleum hydrocarbon plume is sufficient to prove compliance with site-closure requirements. Thus, models that predict the plume-stabilization time and the maximum length of the plume could be useful to decision makers evaluating MNA.

The *Plume Module* of the BioBalance Toolkit helps predict the long-term behavior of a contaminant plume using iterative runs of a simple analytical model (i.e., the modified Domenico Analytical Solute Transport Model). The modified analytical model is designed to simulate groundwater flow considering a fully penetrating vertical plane source oriented perpendicular to groundwater flow, with contaminant transport subject to linear sorption and 3-D dispersion. It also assumes that the source strength degrades following first-order decay kinetics. Based on the rate of contaminant dissolution from the source zone and the rate of natural attenuation in the plume due to processes such as advection, desorption, dispersion, and biodegradation, tools such as BIOCHLOR (US EPA, 2000) can predict the migration of the contaminant over time and distance. In addition to this, the Plume Module can predict the maximum length (L_p) of the contaminant plume and the plume-stabilization time (i.e., the elapsed time before reaching L_p). For sites at which MNA follows an active remediation strategy, the module also predicts the maximum plume length (L_{pSD}) and the time taken to achieve this status for the altered source zone ($T_{MaxLength\_SD}$). An important feature of the toolkit is that it can simulate plumes originating from either vadose or submerged source zones.

The output from the Plume Module includes centerline CVOC concentrations as well as a breakdown of the relative contribution of different natural attenuation processes, such as advection, dispersion, sorption, and degradation, to temporal changes in the groundwater CVOC concentrations. Identifying the dominant natural attenuation mechanism is key to ensuring the future success and sustainability of these attenuation processes. In some states, such as Washington, the selection of MNA as a remedy at a site requires demonstration that destructive mechanisms—namely, biodegradation—will be more dominant compared to nondestructive attenuation mechanisms, such as sorption. Therefore, output from this module is well suited to making these types of predictions about the relative contributions of these processes for a given set of site-specific conditions.

Case Study

i. *Background:* At the site described in the previous section, the TCE biodegradation rate constant was calculated for the plume using time-series well concentrations and was estimated to be approximately 0.15 yr^{-1}.

ii. *Traditional Performance Metric*: To achieve site closure, the decision maker would have to demonstrate that the plume is stable or shrinking and achieve a discharge goal (W_g) that is 0.1 percent of the original discharge rate (equivalent to decreasing the near-source groundwater concentration from 5 mg/L to 0.005 mg/L).

iii. *Toolkit Predictions*: Implementation of MNA at the site would result in a plume (defined by a concentration isopleth of 5 μg/L-TCE) that would stabilize at a maximum distance of 1,500 feet downgradient from the source zone, 24 years after the release event. However, removal of 50 percent of the mass following a source-excavation program would result in the plume stabilizing at a distance 1,400 feet downgradient of the source zone, 24 years after the release event. This suggests that removal of 50 percent of source mass could result in an approximately 7 percent reduction in the maximum plume length but would not impact the plume-stabilization time. If a more aggressive technology were used (for example, if the source-zone mass and mass flux were reduced by 90 percent by implementing a hypothetical chemical oxidation program), the plume-stabilization distance and stabilization time for the 5-μg/L-TCE plume would decrease by 40 percent and 33 percent, respectively. In the case of the slurry wall, the maximum plume dimensions would ultimately be similar to the MNA-only scenario; however, it would take approximately 40 years (instead of 24 years) for the plume to stabilize at a distance of 1,500 feet from the source zone.

   Again, these results suggest that the maximum plume size and time frame, based on a traditional remedial objective, are relatively insensitive to source remediation. The results suggest the need for alternatives to the traditional metrics of plume-stabilization time and distance (defined by the 5 μg/L-TCE concentration isopleth).

iv. *Suggested Intermediate Performance Metric*: If the performance of remediation were measured in terms of the overall reduction in the mass and concentration of the parent CVOC within the plume, then the benefits of implementing partial source-depletion technologies become more apparent. For the case study described above, a decision maker could use the following two concentration goals as milestone markers for evaluating the three source-depletion technologies:

   a. *First milestone*: Time required to reduce the groundwater concentration within the plume from 5 mg/L to 0.1 mg/L.

   b. *Second milestone*: Time required to reduce the groundwater concentration within the plume from 5 mg/L to 0.025 mg/L.

v. *Toolkit Predictions*: Exhibit 3b illustrates the potential impact of a 50 percent and a 90 percent source mass depletion on the overall TCE concentration within the plume. In comparison to an MNA-only scenario, a realistically achievable 50 percent reduction in source mass by excavation can result in a CVOC footprint that has lower concentrations within the center of the plume. For example, under the excavation scenario discussed above, the model predicts that the plume as defined by the 100 μg/L-TCE concentration isopleth will stabilize at a distance that is 40 to 50 percent less than it would in the MNA-only scenario, thereby substantively reducing the overall environmental damage. In the case of the more aggressive hypothetical chemical oxidation, the benefits are more

> In comparison to an MNA-only scenario, a realistically achievable 50 percent reduction in source mass by excavation can result in a CVOC footprint that has lower concentrations within the center of the plume.

apparent. Under the 90 percent source-depletion scenario, the area impacted at TCE concentrations greater than 100 μg/L-TCE remains confined to within 4 feet of the source zone. In the case of the slurry wall example, the 100 μg/L-TCE concentration isopleth will stabilize at a distance that is more than 60 percent less than it would in the MNA-only scenario, thus possibly ensuring that the high concentrations of the contaminant remain confined within the boundaries of the site.

LIMITATIONS

The BioBalance Toolkit uses simple analytical models within the mass-balance framework to predict the complex behavior of sources and plumes. One of the known limitations of analytical models, such as the modified Domenico Analytical Transport Model, is that the solutions are derived using a number of simplified assumptions regarding groundwater flow (steady-state flow within uniform, homogeneous, and isotropic aquifer conditions). However, for the purposes of a preliminary screening-level toolkit, such as BioBalance, the use of this simplified model is appropriate since it is employed only to provide users with a semiquantitative estimate (i.e., a relative order-of-magnitude estimate of the impact of MNA and source-depletion technologies on plume length and stabilization time).

Another limitation of the plume transport model incorporated into the toolkit is that it assumes that the current conditions describe initial conditions $t = 0$ immediately after a release. Therefore, using the model to predict the impact of source-depletion technologies on future plume behavior can result in relative order-of-magnitude estimates at new release sites. However, at old sites with established plumes, the model could overpredict the impact of source-depletion technologies on the stabilization length.

> Using the model to predict the impact of source-depletion technologies on future plume behavior can result in relative order-of-magnitude estimates at new release sites. However, at old sites with established plumes, the model could overpredict the impact of source-depletion technologies on the stabilization length.

Furthermore, as a result of this limitation, calibration of the model with real site data has proved challenging. Most sites with new releases do not have sufficient long-term data to support results from the model. Other more recent toolkits, such as Remchlor, have managed to circumvent this problem by allowing the user to back-calculate source conditions immediately after the release based on current conditions and some knowledge of the original release.

CONCLUSIONS

BioBalance can be used by site managers and other decision makers to make preliminary assessments of the viability of natural attenuation as well as the potential benefits of implementing different source-remediation strategies. Specifically, it helps predict the feasibility of achieving remediation goals using a remediation time frame, sustainability, and plume stability as the primary measures of assessment. While final site-level management decisions should not be made based on the results of the BioBalance alone, the toolkit is designed to help make site management decisions during screening stages of a feasibility study. The development and application of the tool has resulted in the following general observations:

- Simple analytical models can be used to predict plume dynamics: length vs. time, attenuation process vs. distance.

- Removal of source mass does not result in a corresponding reduction in the source-remediation time frame in most cases. Complex mechanisms, such as matrix diffusion, linear desorption, desorption from fractions with different equilibrium kinetics, and dispersion, can result in long remediation time frames for sites undergoing MNA. This is especially the case for sites with stringent remedial objectives (i.e., remediation goals several orders of magnitude lower than current concentrations). As a result, using traditional performance metrics, such as the source-remediation time frame and plume-stabilization time and distance, at face value to help select remedial technologies for the site can obscure the true benefits of implementing a partial source-depletion technology.

Using performance metrics, such as reduction in the overall mass and concentration of the parent compounds, can provide the value addition necessary to encourage implementation of source-depletion technologies.

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