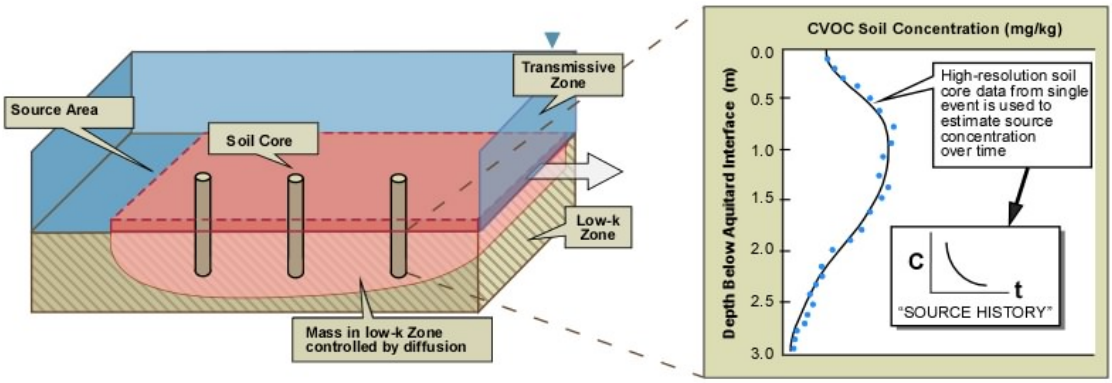
Source History Tool

USER'S MANUAL

Version 1.0
September 2013



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CITE USING

Farhat, S.K., P.C. de Blanc, C.J. Newell, and D.T. Adamson, 2013. Source History Tool, developed for the Environmental Security Technology Certification Program (ESTCP) by GSI Environmental Inc., Houston, Texas.

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SOURCE HISTORY TOOL

Environmental Security Technology Certification Program

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INTRODUCTION

One of the key constraints in the selection of remedies for closing sites contaminated by chlorinated solvents is that there is typically only a short time interval where monitoring data are available to assess trends. This problem is exacerbated in situations where source material is expected to be present because of uncertainty in plume stability versus source stability. In particular, this hinders an evaluation of monitored natural attenuation (MNA) as a remedy, despite the fact that recent historical surveys of MNA have determined that it was a feasible remedy in over 75% of the sites where it was included in the evaluation, either alone or in conjunction with an active treatment technology (McGuire et al., 2004; Newell, 2006). Often concentration trends are difficult to discern, even with the use of advanced statistical tools such as AFCEC's MAROS tool, such that insufficient evidence is available to demonstrate that natural attenuation is viable. This can delay the decision-making process until more data can be collected and evaluated, and any supplemental data is gathered to support a "lines of evidence" approach that is not necessarily definitive or reflective of long-term trends.

Furthermore, regulators frequently adhere to a conceptual model of an unchanging, non-attenuating source zone, and insist on source remediation projects to replace or augment natural attenuation. As a result, site managers often are faced with implementing a costly technology and demonstrating performance in terms of mass removal efficiency, even though estimates of the mass present or remaining in a source zone are typically difficult to make and are subject to significant uncertainty given the limitations in monitoring data and investigation resolution, especially as subsurface releases age over time.

To aid in the selection of MNA as a long-term remedy, the Environmental Security Technology Certification Program (ESTCP) of the U.S. Department of Defense (DoD) has funded the development of this Source History Tool (Toolkit).

Based on the Microsoft Excel® platform, the Toolkit is an easy-to-use, comprehensive, free software tool that can assist site personnel reconstruct long-term source histories that extend back to the beginning of the original source release. Methods developed by Parker et al. (2004, 2005, 2008), specifically, the collection of closely spaced soil concentration measurements at discrete depths in low permeability zones within and downgradient of source zones to provide insight into historic concentration trends at interfaces with the low permeability zones, provide a focused way to reconstruct long-term source histories that extend back to the beginning of the original source release.

The Source History Tool was developed for the ESTCP by GSI Environmental Inc., Houston, Texas.

INTENDED USES AND LIMITATIONS

The **Source History Tool** attempts to assist site managers and site consultants better understand and reconstruct long-term source histories. A long-term source history, from the beginning of releases at a site to present time, would help confirm a site conceptual model that shows attenuation is a significant process for both the source and the plume, and generate data that are well-suited for use in predicting future concentration and attenuation trends. Reducing the uncertainty associated with assessing long-term concentration trends before a remedy is selected and implemented, could assist site stakeholders select more appropriate remedies and improve effective risk communication with regulators and the public.

The Toolkit is intended to be used **as a screening level tool for reconstructing long-term source history effects.** The Toolkit brings key technical resources, an easy-to-use calculation worksheet, and case studies together into one easy-to-access platform.

In addition, the Toolkit provides a Monte Carlo-type approach to analyze uncertainty in the input parameters such as the porosity, apparent tortuosity factor exponent, fraction organic carbon/distribution coefficient, and constituent half-life. With this tool, groundwater practitioners can evaluate the accuracy of the hydrologic measurements that are being used for the reconstruction of source histories.

The Toolkit has the following assumptions and limitations:

- Assumes the User is familiar with basic groundwater transport and mass balance concepts.
- Assumes the presence of low permeability strata within or downgradient of the source zone.
- Assumes diffusion occurs only in the water phase.
- Requires presence and delineation of interface between two geologic strata with contrasting permeabilities.
- Collection of high-resolution data can be costly at sites with complex geology or deep contamination.
- Presence of multiple sources and/or commingled plumes can complicate analysis.
- Modeling may generate multiple “source histories” solutions, such that some User knowledge is required to narrow down solutions to most appropriate.
- Occurrence of reactions (abiotic or biotic), non-linear sorption, etc. within the low-k zones can complicate analysis.
- To run the Monte Carlo analysis, Users need to estimate what type of statistical distribution best fits the input data and what values best describe the distribution.

In many cases data will be unavailable to make these estimates, so the User may have to rely on scientific/engineering judgment to use the Monte Carlo analysis.

- The Monte Carlo analysis cannot account for plume data that are not part of the monitoring system. Actual concentration values can be outside the reported range of values from the Monte Carlo analysis (for example, if new data show high concentration zones that were not captured by the original monitoring network).

FREQUENTLY ASKED QUESTIONS

What is a low-k zone? Do I have these zones at my site?

Based on her research program at the University of Guelph, Dr. Beth Parker has a rule of thumb indicating that matrix diffusion can be an important process if there is a plume in a transmissive zone that is in contact with adjacent zones that have permeabilities lower than by a factor of 100 or more. In other words, if a contaminant plume moving in a 10^{-3} cm/sec sand is in contact with a 10^{-5} cm/sec silt, then the silt can be charged up with contaminants during a loading period (when concentrations in the sand are higher than the silt) and then slowly discharge contaminants into the sand via diffusion when the silt has higher concentrations than the sand.

What does the Source History Tool do?

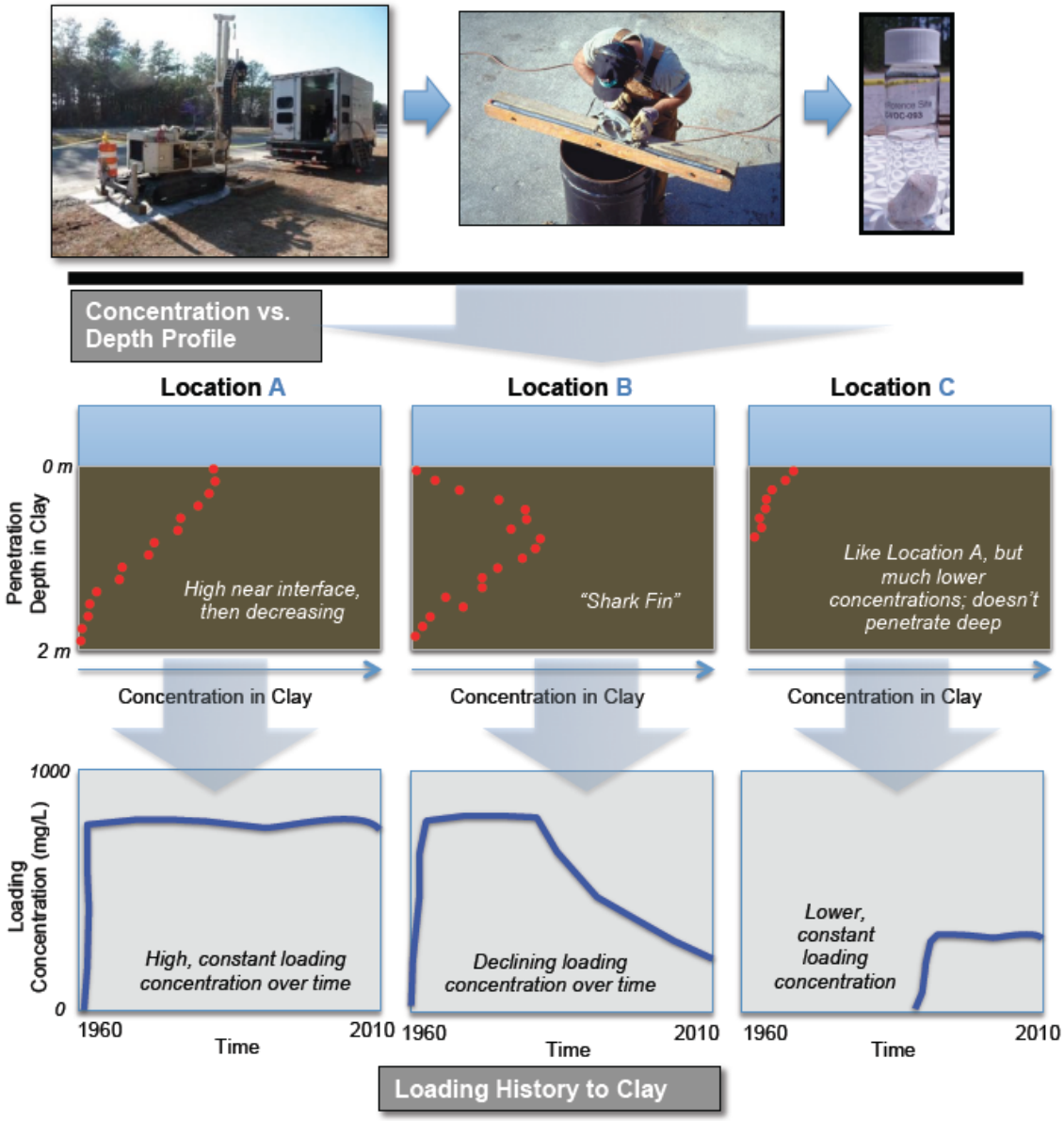
The Toolkit generates an estimate of the source concentration over time, i.e., a "source history", that can be used as a line of evidence for natural attenuation (see Exhibit 1 for Conceptual Example). At many sites, natural attenuation has been proposed, but not accepted by regulators due to concerns that the source is not being treated fast enough, or where routine monitoring data do not show definitive trends. A long-term source history, from the beginning of releases at a site to present time, would help confirm a site conceptual model that shows attenuation is a significant process for both the source and the plume, and generate data that are well-suited for use in predicting future concentration and attenuation trends. The Toolkit can assist site personnel reconstruct long-term source histories that extend back to the beginning of the original source release. Reducing the uncertainty associated with assessing long-term concentration trends before a remedy is selected and implemented, could assist site stakeholders select more appropriate remedies and improve effective risk communication with regulators and the public.

Do I need sampling data from the low-k zones to run the Toolkit?

Yes, you will need high-resolution, depth-discrete soil samples near geologic interfaces in contact with lower permeability zones, within or downgradient of the source, to generate a detailed contaminant profile with depth within these zones. These soil data are similar to a "tree ring" in that they provide historical information (even though they are collected at a single point in time).

EXHIBIT 1
Reconstructing Source Histories from High-Resolution Sampling of Low-k Zones: Conceptual Example

1. First collect high-resolution data to find the interfaces between contaminated transmissive zones and underlying/overlying low-k zones (typically clays or silts).
2. Then find the concentration vs. penetration depth profile in the low-k zone.
3. With this data, the general style of the long-term source history in the transmissive zone at the location the core was collected can be estimated.



What input data will I need?

The high-resolution soil contaminant profile with depth is the key input data, but there are a few other pieces of information that are important. Some of these input parameters are similar to what is used for existing solute transport models (e.g., Darcy groundwater velocity, size of the modeled area, information on when the source started, etc.) Other input data will look new to many Users, for example, you'll need to estimate the tortuosity of the low-k materials where matrix diffusion has occurred, diffusion coefficients, and fraction organic carbon of the clays and silts being modeled, etc. The Toolkit provides default values and advice on selecting representative values for your site conditions.

Does the Toolkit provide default values or guidance for input parameters?

Yes. The Toolkit asks you to provide these key input data:

1. What is your best estimate for the year the original release occurred? This is based on your understanding of site history.
2. What is your best guess for the concentration in the year of original release? It is rare to have monitoring data from the time of the release to now, so we've provided some guidance based on the maximum concentration ever observed (see Data Entry Step 3).
3. What is the **diffusion coefficient** for the contaminant of interest? The Toolkit provides a library of diffusion coefficients for the most common contaminants we deal with at sites.
4. What are the key transport properties of the clay: **tortuosity and retardation factor**? The Toolkit provides a calculator for you to estimate these parameters if you are not familiar with them.

What contaminants can be modeled with the Toolkit?

To date, most of the research involving matrix diffusion processes for low-k zones has focused on chlorinated solvents such as TCE (trichloroethene). However, in theory, the Toolkit should apply to almost any dissolved contaminant, including benzene and other aromatic compounds found in gasoline.

How does the Toolkit handle uncertainty?

The Toolkit utilizes a Monte Carlo-type approach to analyze uncertainty in the porosity, apparent tortuosity factor exponent, fraction organic carbon/distribution coefficient, and constituent half-life measurements. With this tool, groundwater practitioners can estimate 1) the accuracy of the hydrologic measurements being used for the source history reconstruction and 2) the sensitivity of the model to these parameters.

Of course, with more field data, the accuracy of the modeling results will increase.

How accurate are the Toolkit results?

Because of the simplifying assumptions in the model, and the early state of matrix diffusion modeling in general, we consider the Toolkit to be a screening level accuracy tool.

MODEL PROTOCOLS

Collection of High-Resolution Core Data

Application of the Source History Tool requires high-resolution characterization data collected from soil cores in the low-k zone. This is because the output of the model—the source concentration history over time—is based on fitting predictions of soil concentrations (based on the one-dimensional diffusion equation) to actual (measured) soil data. Consequently, the more comprehensive the dataset, the greater the confidence that the model is capturing the general "style" of source attenuation history at the site.

Based on this objective, the following recommendations are made with respect to collecting high-resolution data from soil cores (additional detail is provided in Appendix 1):

ISSUE	RECOMMENDATION
Identifying suitable locations for coring	• Use one (or more) of several commercially-available rapid data acquisition tools (e.g., MIP, Waterloo Profiler, Geoprobe HPT) that provide high-resolution hydrostratigraphic information. • Focus on establishing the permeability distribution, particularly depth(s) where the interface between high and low permeability units occurs.

Core collection methods	• Many suitable options, including:
	  • Direct-push (Geoprobe) methods (dual-tube or MacroCore).
	  • Sonic methods (including AquaLok).
	  • Auger-based methods.

Sampling frequency with depth	• 1 sample per vertical ft of core or less at a minimum. • 1 sample per 0.2 to 0.5 vertical ft of core is preferred within low-k zones. • Also should collect samples within transmissive zone (though lower frequency than in low-k is acceptable)
Sampling frequency with time	• Collecting core data during a single event is acceptable for using the Toolkit.
Number of coring locations per source area	• Small and/or well-delineated source area: 1 -2 borings. • Larger, heterogeneous, and/or poorly-delineated site: 3-4 borings. • Focus on collecting cores along transects or flowpath to evaluate/confirm trends.
Analytical data to be collected	• Soil VOC concentration. • Soil f_{oc} (selected depths to get representative value or distribution of values). • Optional (to evaluate degradation or other processes; some may require collection of groundwater samples): isotopes (e.g., ^{13}C), molecular biomarkers (e.g., *Dehalococcoides)*, sulfate, methane, etc.
Sample handling and analysis considerations	• Immediate methanol preservation in field is strongly recommended. • Consider using extended and/or enhanced extraction methods to improve recovery and detection limits within low-k matrices.

ISSUE	RECOMMENDATION
Groundwater data	• Not required for Toolkit, but is useful for calibrating and confirming model simulations. • Collected at same time as soil data: useful in confirming concentrations near interface are being accurately simulated. • Collected over several events (years) following coring: useful in confirming predicted source history trends are reasonable. • May also provide valuable information regarding degradation.

How to Use the Source History Tool

The Toolkit couples a detailed site characterization approach involving collection of high-resolution profiles of contaminant concentrations in lower permeability zones with transport modeling to reconstruct the source history at a site.

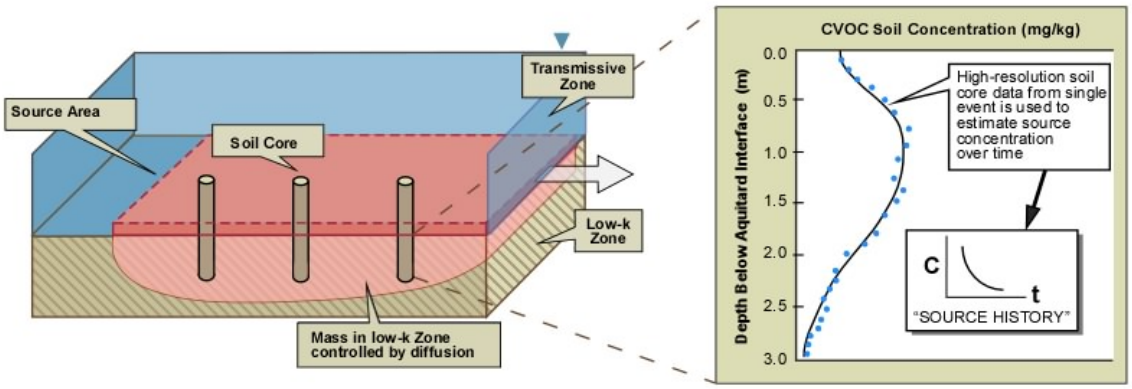


Figure 1: Conceptual model of the Source History Tool.

Governing equations and assumptions are provided in Appendix 2. Guidelines for selecting key input parameters for the model are outlined in Data Entry. For help on results, see Model Results.

Uncertainty Analysis

Similar to other modeling approaches, the level of uncertainty in the estimated source history reconstruction is a key issue. The Toolkit provides a Monte Carlo-type approach to analyze uncertainty in the porosity, apparent tortuosity factor exponent, fraction organic carbon/distribution coefficient, and constituent half-life measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements that are being used for the source history reconstruction.

Monte Carlo analysis is a method of analyzing and quantifying uncertainties in model outputs due to the uncertainties in the input parameters (Rong *et al.*, 1998). Monte Carlo analysis refers to a computer-based system that uses random numbers from a probability distribution to obtain an approximation for the parameter of interest (USEPA, 1997; Bergin and Milford, 2000).

In the standard Monte Carlo approach, simple random sampling and a large number of runs (typically 100 to 1000) are required to obtain a meaningful probability distribution for the parameter. For each run of the standard approach, a random number is generated for the porosity, apparent tortuosity factor exponent, fraction organic carbon/distribution coefficient, and constituent half-life entered by the User. This set of random inputs is then used to calculate concentration in the low-k unit. Repeating this procedure a large number times yields a probability distribution from which statistical characteristics such as mean, percentile, and variance can be obtained.

The Toolkit performs 253 iterations for the Monte Carlo approach (limited by the maximum number of lines that can be plotted in an Excel graph).

Guidelines for selecting key input parameters for the model are outlined in Uncertainty Analysis.

DATA ENTRY

Data Input Screen
Results
Uncertainty Analysis

Three important considerations regarding data input are:

1) To see the example dataset in the input screen of the software, click on the *Paste Example* button on the lower right portion of the input screen.
2) Because the Toolkit is based on an Excel® spreadsheet, you have to click outside of the cell where you just entered data or hit *Return* before any of the buttons will function. Additionally, **REMOVING OR ADDING** rows or columns in input screens may cause the program to crash.
3) Parameters used in the model are to be entered directly into the white/blue cells.

NOTE: Although literature values are provided, site-specific hydrogeologic, transport, and plume characteristic values will likely provide better results. If literature values are used and there is uncertainty in the value chosen, sensitivity analyses should be conducted to determine the effects of the uncertainty on model predictions.

Recommendations regarding calibrating (fitting) Toolkit to actual field data

The goal of this modeling approach is to match the ***style*** of the actual soil VOC concentration vs. depth data. The Toolkit generates a simulated soil VOC concentration profile (from the source concentration vs. time estimate) and the User attempts to match the shape of this profile to actual soil data.

After all input information has been entered, the initial model output is compared to high-resolution core data collected from the low-k unit. The initial run is based on a preliminary guess for the source concentration vs. time pattern (i.e., the source history). In most instances, this initial run will not produce modeled data that match field data. Considerations and recommended steps to improve the fit of simulated to field data are provided below.

In cases where a good comparison between field-measured vertical profiles of soil concentrations and model simulated concentrations can be made, the recommended sequence of model input values to change is:

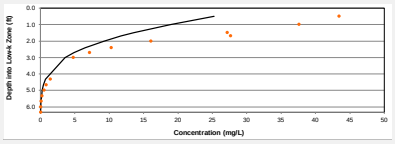
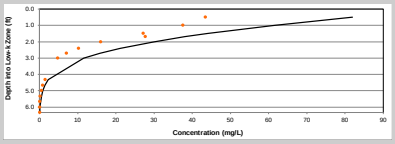
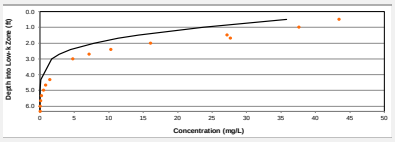
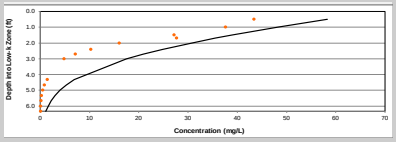
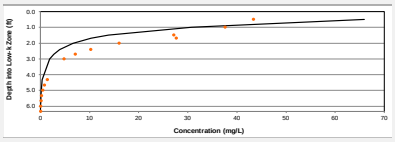
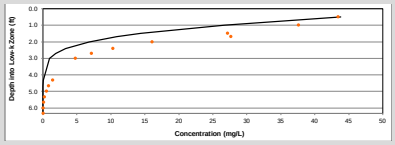
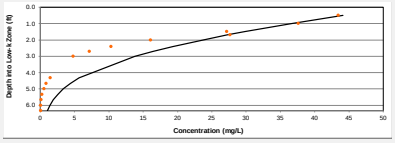
1. If the styles of the actual soil data and simulated soil data are significantly different, then the first step should be to simply select a different source concentration vs. time pattern (e.g., exponential decay instead of constant source). If there is no general improvement in the fit, then the User may wish to revert back to the initial guess for the pattern.

2. Next, change the "source concentration" (C_o). If the simulated concentrations (solid black line in the concentration vs. depth graph) are higher than observed concentrations, increase the concentration. Decrease the source concentration if simulated concentrations are lower than observed concentrations.
3. Fitting the data at the interface is easiest to achieve because it is highly dependent on the source concentration at the most recent timepoint. The latter should be adjusted until the condition is met.
4. The source concentration (C_o) can then be further adjusted as needed to match the peak concentration (either at the interface for constant source patterns, or at some depth below the interface for attenuating source patterns).
5. After choosing first-round guesses for the source concentration and the source concentration at the most recent timepoint, the source concentration at intermediate times can be adjusted as needed. Note that these values generally have limited impact on the extent that the target constituents penetrate to deeper intervals, but will influence the concentrations observed closer to the interface.
6. If it is still difficult to get a good fit, try changing the estimate for the original source release if there is some uncertainty on the exact year. To increase the simulated concentrations, move the start of the release period earlier in time. In other words, more time for diffusion into low-k zones during the source loading period will result in higher concentrations in the low-k zone.
7. To further improve the match, after working with the previous steps, consider changing some of the hydrogeologic and/or transport properties such as Darcy velocity (advection-diffusion dominated flow), tortuosity, and retardation factor. Other parameters in the model can also be changed to develop a better match.

Other helpful hints in achieving good results from the Toolkit are described below:

1. Clear evidence that the peak soil concentration occurs below the depth of the permeability interface (i.e., depth = 0) is indicative of a source concentration that has decreased over time. In such cases, exponential decay or linear decay patterns should be selected as a starting point and refinements made.
2. Conversely, a single depth-discrete sample with a high concentration from below the interface may be anomalous if this point is not consistent with the pattern of surrounding datapoints. In general, several points with high concentrations below the interface should be present before selecting an attenuation-based source concentration vs. time pattern.
3. The Root Mean Square (RMS) error and the Relative Error (RE) are suitable for evaluating the closeness of fit between actual and simulated data. However, neither should be considered an absolute optimization metric. Each can suffer from biases due to one or more datapoints that may (or may not) be representative of the entire dataset. In some cases, better (or more sensible) visual fits can be obtained even at higher RMS/RE error values.
4. The best fits occur when the following conditions are met and there is a close match between actual and simulated data: i) at the permeability interface; ii) at the depth where the peak concentration is encountered; and iii) at the deepest depth where the target constituent has been detected.

Additional guidance on obtaining good fits between actual and modeled data is provided in the following table:

PROBLEM IN MATCHING SOIL DATA	EXAMPLE (● = measured soil data) (— = simulated soil data)	POTENTIAL ADJUSTMENT(S) TO TRY TO IMPROVE MATCH
Measured concentration at interface is too low		• Increase source concentration at most recent timepoint • Increase initial source concentration (C_o) • Increase porosity
Measured concentration at interface is too high		• Decrease source concentration at most recent timepoint • Decrease initial source concentration (C_o) • Decrease porosity
Measured concentration is uniformly too low at most depths		• Increase source concentration at all timepoints • Increase initial source concentration (C_o) • Increase porosity
Measured concentration is uniformly too high at most depths		• Decrease source concentration at all timepoints • Decrease initial source concentration (C_o) • Decrease porosity
Measured concentration is overestimated at shallow intervals but underestimated at deeper intervals		• Decrease f_{oc}/K_d • Decrease initial source concentration (C_o) and/or source concentration at most recent timepoint, then increase source concentration at earlier timepoints
Measured concentration at interface shows good match but penetration to deeper intervals is insufficient		• Select earlier release date • Decrease foc/Kd • Increase source concentration at earlier timepoints • Increase tortuosity • Increase half-life in low k zone • Include vertical advection
Measured concentration at interface shows good match but excessive penetration to deeper intervals is observed		• Select later release date • Increase foc/Kd • Decrease source concentration at earlier timepoints • Decrease tortuosity • Decrease half-life in low k zone

It should be understood that the analysis can be complicated by the presence of multiple sources, commingled plumes, occurrence of reactions (abiotic or biotic), non-linear sorption, etc. within the low-k zones. The influence of degradation reactions can be accounted for in the Toolkit, but other factors that are not part of the model may be more difficult to incorporate. Because of the simplifying assumptions in the model, and the early state of matrix diffusion modeling in general, we consider the Toolkit to be a screening level accuracy tool.

Projected Modeled Parameter Sensitivity

To supplement the information provided in the previous sections, the following table summarizes how the individual input parameters influence the results. Specifically, it describes how an increase or a decrease in the value of these parameters can impact the simulated soil concentration vs. depth profile that is being fitted to the actual soil data.

PARAMETER	PRIMARY EFFECT OF INCREASING PARAMETER VALUE	PRIMARY EFFECT OF DECREASING PARAMETER VALUE
Diffusion Coefficient (D_o)	↑ penetration to deeper intervals	↓ penetration to deeper intervals
Porosity (n)	↓ penetration to deeper intervals	↑ penetration to deeper intervals
Soil bulk density (ρ_b)	↓ soil concentration ↓ penetration to deeper intervals	↑ soil concentration ↑ penetration to deeper intervals
f_{oc}/K_d	↑ soil concentration ↓ penetration to deeper intervals	↓ soil concentration ↑ penetration to deeper intervals
Half-life in low-k zone	↑ soil concentration ↑ penetration to deeper intervals	↓ soil concentration ↓ penetration to deeper intervals
Initial Source Concentration (C_o)	↑ soil concentration (particularly at interface) ↑ constituent penetration	↑ soil concentration (particularly at interface) ↑ penetration to deeper intervals
Release date (t_0)	↑ penetration to deeper intervals (from later dates)	↓ penetration to deeper intervals (from later dates)
Source Concentration at most recent timepoint	↑ soil concentration	↓ soil concentration
Source Concentrations at intermediate timepoints	↑ soil concentration	↓ soil concentration
OTHER INPUT INFORMATION		
Soil Type	Influences porosity and tortuosity	
Transport Type	Option to include vertical advection component	
Key Constituent	Influences diffusion coefficient and retardation factor	

Notes: (1) *Source concentration* refers to concentration of target constituent in the transmissive zone above low k zone; (2) *Soil concentration* refers to concentration of target constituent in the soil core collected from the low k zone; (3) *Penetration* refers to transport of detectable levels of the target constituent to deeper portions of the low k zone.

Data Input Screen:

Step 1: *Hydrogeology*

PARAMETER	TYPE OF MATERIAL IN LOW-k ZONE
Description	Description of the soil type in the low-k zone.
How to Enter Data	Choose from drop down list or enter directly. (Note that if using a Macintosh, the drop down options are accessed by pressing the mouse and clicking on the dropdown button.)

PARAMETER	TOTAL POROSITY (n)
Units	Unitless.
Description	Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix, but excluding secondary porosity (fractures, solution cavities, etc.). Total porosity is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Effective porosity and any porosity data with secondary porosity information should not be used.
Typical Values	The model input screen has these default values: Fine Sand: 0.40 (mid-range of values below) Silt: 0.48 (mid-range of values below) Clay: 0.47 (mid-range of values below) Sandstone/shale: 0.10 (Pankow and Cherry (1996), Table 12.2) Granite: 0.006 (Pankow and Cherry (1996), Table 12.2) Values for total porosity from Domenico and Schwartz (1990), in part from Davis (1969) and Johnson and Morris (1962), and as stated, Payne et al. (2008): **SEDIMENTARY** Porosity (-) Gravel, coarse: 0.24 - 0.36 Gravel, fine: 0.25 - 0.38 Sand, coarse: 0.31 - 0.46 Sand, fine: 0.26 - 0.53 (Payne et al., 2008, Table 2.3) Silt: 0.34 - 0.61 (Payne et al., 2008, Table 2.3) Clay: 0.34 - 0.60 (Payne et al., 2008, Table 2.3) **SEDIMENTARY ROCKS** Sandstone: 0.05 - 0.30 Siltstone: 0.21 - 0.41 Shale: 0 - 0.10 **CRYSTALLINE ROCKS** Dense crystalline rocks: 0 - 0.05 Koerner (1984) reports these values for unit weight for saturated soils (note no dry bulk density values are reported for these materials): Glacial till, very mixed grain: 0.20 Stiff glacial clay: 0.37 Soft very organic clay: 0.75 Soft glacial clay: 0.57 Soft slightly organic clay: 0.66 Soft bentonite: 0.84 One fractured microcrystalline limestone in Virginia had matrix porosities ranging from 0.0004 to 0.0065 (GSI Environmental).

Source of Data	Typically estimated. Occasionally obtained through physical property testing of site soil samples.
How to Enter Data	Enter directly. (Note that if the low-k zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.)

PARAMETER	TRANSPORT TYPE
Description	The Toolkit can use diffusion as the sole transport process for contaminants in the low-k zone, or it can include both diffusion plus vertical (1-D) advection as relevant transport processes.
How to Enter Data	Choose from drop down list. (Note that if using a Macintosh, the drop down options are accessed by pressing the mouse and clicking on the dropdown button.)

PARAMETER	HYDRAULIC CONDUCTIVITY (K)
Units	cm/sec, ft(or m)/day, ft(or m)/yr.
Description	Measure of the permeability of the low-k layer. To characterize concentrations in the low-k layer utilizing advection, representative measurements are required for both the hydraulic conductivity and the hydraulic flow gradient of the flow system. Representative measurements of the hydraulic conductivity of the low-k layer should be obtained at one or more locations using appropriate slug test or pumping test methods (Newell et al., 2003). Apply a correction for anisotropy as needed (e.g., vertical conductivity value may be less than horizontal conductivity value). Note that this parameter is required only if the advection option is included in the Transport Type.
Typical Values	*Horizontal K* Clay: $<1x10^{-6}$ cm/s Fractured Sandstone: $1x10^{-6}$ - $1x10^{-2}$ cm/s Limestone: $1x10^{-7}$ - $1x10^{-4}$ cm/s Sandstone: $1x10^{-8}$ - $1x10^{-4}$ cm/s Shale: $1x10^{-11}$ - $1x10^{-7}$ cm/s Silt: $1x10^{-6}$ - $1x10^{-3}$ cm/s (Newell *et al*., 1996; Freeze and Cherry, 1979.) Note, for vertical hydraulic conductivities, dividing horizontal K by a factor of 3 or less is common for homogenous aquifers while dividing by a factor of 10 or more may be appropriate for heterogeneous aquifers (Freeze and Cherry, 1979; Parker et al., 2004).
Source of Data	Pump tests or slug tests at the site. It is strongly recommended that actual site data be used for all evaluations.
How to Enter Data	1) Select units, and 2) Enter directly.

PARAMETER	VERTICAL HYDRAULIC GRADIENT (i)
Units	ft/ft (or m/m).
Description	The head difference between two adjacent well relative to the distance between the screened intervals of the wells. It defines the direction of groundwater flow (upward or downward) and is proportional to the magnitude of the flow. Note that this parameter is required only if the advection option is included in the Transport Type.
Typical Values	0.0001 - 0.1 ft/ft (0.0001 - 0.1 m/m).
Source of Data	Calculated using static water level data from monitoring wells installed at the same location but screened at different depths within the same formation. The gradient is calculated as the difference between the measured water levels in these wells divided by the difference in screen depth between the wells.
How to Enter Data	Enter directly.

Step 2: *Transport*

PARAMETER	KEY CONSTITUENT DIFFUSED IN LOW-k ZONE
Description	Constituent of interest.
How to Enter Data	Enter directly or choose from drop down list.

PARAMETER	MOLECULAR DIFFUSION COEFFICIENT IN FREE WATER (D_o)
Units	cm^2/sec, m^2/sec.
Description	A factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time.
Typical Values	Benzene: 9.8E-06 cm^2/s Ethylbenzene: 7.8E-06 cm^2/s Toluene: 8.6-06 cm^2/s Xylene: 8.5E-06 cm^2/s MTBE: 9.4E-05 cm^2/s Tetrachloroethene: 8.2E-06 cm^2/s Trichloroethene: 9.1E-06 cm^2/s cis-1,2-Dichloroethene: 1.1E-05 cm^2/s Vinyl Chloride: 1.2E-05 cm^2/s 1,1,1-Trichloroethane: 8.8E-06 cm^2/s (TRRP, 2008) (Note that there is a wide range of reported values; for example, Wiedemeier et al. (1999) report a D_o for benzene of 1.1E-05 cm^2/s.) For more information see Pankow and Cherry, 1996 (for solvents) and Wiedemeier et al., 1999 (variety of constituents).
Source of Data	Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier et al., 1999 (variety of constituents); or other references with chemical properties. Values for free water diffusion coefficients can also be found in a variety of other literature sources (e.g., Lyman et al., 1990; Mackay et al., 2006; Montgomery, 2007) or estimated

	from empirical correlations, (e.g. Wilke & Chang, 1955; Hayduk & Laudie, 1974). Grathwohl (1998) provides an overview of various estimation methods including example calculations. EPA also provides an on-line calculator for estimating free water diffusion coefficients based on Tucker & Nelken (1982): http://www.epa.gov/athens/learn2model/part-two/onsite/estdiffusion-ext.html. Note that free water diffusion coefficients vary as a function of temperature, which is mainly due to differences in water viscosity, which decreases with increasing temperature. This dependence is evident in the empirical correlation equations of Wilke & Chang (1955) (Equation 2-22 in Grathwohl, 1998) and Hayduk & Laudie (1974) (Equation 2-23 in Grathwohl, 1998).
How to Enter Data	1) Select units, and 2) Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a value for the parameter.)

PARAMETER	LOW-k ZONE APPARENT TORTUOSITY FACTOR EXPONENT (p)
Units	Unitless.
Description	The Apparent Tortuosity Factor (τ) relates the molecular diffusion coefficient in free water (D_o) of a constituent in a porous medium to its effective diffusion coefficient (D_e). Values of τ can range between 0 and 1. Estimations of τ can be obtained using the relationship: $$\frac{D_e}{D_o} = \tau \cong n^p$$ Where *n* is the porosity and *p* the Apparent Tortuosity Factor Exponent. Depending on the geologic medium, values for p can vary between 0.3 and 5.4 (Charbeneau, 2000; Pankow and Cherry, 1996; Dullien, 1992; Lerman, 1979; and Millington and Quirk, 1961; Parker et al., 1994). Note: Some of these references use a diffusion equation based on a different formulation of Fick's Law, where the effective diffusion coefficient is a function of porosity and frequently referred to as De. For this software tool, tortuosity is based on the effective diffusion coefficient De. Consequently, apparent tortuosity factor exponents have been adjusted where needed to reflect the De formulation used in the Toolkit.
Typical Values	Sand: 0.33 Silt: 1.1[a] (range of 0.33[b] to 2.0[a]) Clay: 1.1[a] (range of 0.33[b] to 2.0[a]) Sandstone/Shale: 1 (calculated from Pankow and Cherry (1996) Table 12.2). The apparent tortuosity factor exponent for sandstone/shale will likely be similar or smaller than silt or clay. Granite: 0.55 (calculated from Pankow and Cherry (1996) Table 12.2). The apparent tortuosity factor exponent for granite will likely be smaller than silt or clay. ([a]Parker et al., 2004; [b]Millington and Quirk, 1961.)
Source of Data	Literature.
How to Enter Data	Enter directly. (Note that if the low-k zone description is selected from the drop down list, the Toolkit provides a value for the parameter.)

PARAMETER	BULK DENSITY OF LOW-k ZONE (ρ_b)
Units	g/mL.
Description	Density of the saturated low-k zone (referred to as "soil"), excluding soil moisture.
Typical Values	Although this value can be measured in the lab, estimated values are used in most cases. A value of 1.7 g/mL is used frequently for unconsolidated media. Representative values in g/mL for specific geologic media are shown below (Lovanh et al., 2000; derived from Domenico and Schwartz, 1990). Clay: 1.0 - 2.4 Loess: 0.75 - 1.6 Sands: 1.6 - 2.68 Shale: 1.54 - 3.17 Limes: 1.74 - 2.79 Granite: 2.24 - 2.46 Basalt: 2 - 2.7 Medium Sand: 1.34 - 1.81 Koerner (1984) reports these values in g/mL for unit weight for saturated soils (note no dry bulk density values are reported for these materials): Glacial till, very mixed grain: 2.32 Soft glacial clay: 1.77 Stiff glacial clay: 2.07 Soft slightly organic clay: 1.58 Soft very organic clay: 1.43 Soft bentonite: 1.27
Source of Data	Either from an analysis of soil samples at a geotechnical lab or more commonly, application of estimated values. Note the Toolkit assumes that concentration data is being entered on a dry weight basis. If concentration data is only available on a wet weight basis, then an easy correction is to enter the wet bulk density instead of the dry bulk density. The wet bulk density can be calculated by multiplying the dry density by the following factor: 1+moisture content/100.
How to Enter Data	Enter directly.

PARAMETER	DISTRIBUTION COEFFICIENT (K_d)
Units	L/kg.
Description	The partition (or distribution) coefficient between the pore water (ground water) and the soil solids. Calculated as: $$K_d = f_{oc} K_{oc}$$ where f_{oc} is the fraction organic carbon in the low-k zone and K_{oc} the partitioning coefficient.
How to Enter Data	Enter directly.

PARAMETER	FRACTION ORGANIC CARBON IN LOW-k ZONE (f_{oc})
Units	Unitless (gram per gram).
Description	Fraction of the aquifer material comprised of natural organic carbon in uncontaminated areas. More natural organic carbon is associated with higher adsorption of organic constituents within the aquifer matrix.
Typical Values	Although based on limited data, 0.0002 - 0.10 for low-k zones is a likely range. But values for some sites may be higher or lower. Examples:

	At the Moffatt Field site, the foc of the clay fraction is about 0.0066 (Roberts et al., 1990). Domenico and Schwartz (1990) report these values: silt (Wildwood Ontario): 0.00102; from Oconee River sediment: coarse silt: 0.029; medium silt: 0.02; fine silt: 0.0226. Chapman and Parker (2005) report a f_{oc} of glaciolacustrine aquitard composed of varved silts and clays: 0.0024 to 0.00104 with an average of 0.00054. Adamson (2012) reports f_{oc} = 0.001 for a clay layer in Jacksonville, Florida and f_{oc} values for silts at the MMR site in Massachusetts ranging from <0.0005 to 0.0022 (median value = 0.0014) for one core using Leco carbon analyzer; a second core had foc values < 0.005 for 10 samples and two samples with 0.00067 and 0.00084 (gram per gram). Values for f_{oc} using Walkley-Black wet oxidation method were generally higher by a factor of 2 to 3. Values ranging from 0 to 0.078 have been reported for silts at the F.W. Warren site in Wyoming, with a median value of 0.
Source of Data	The fraction organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated saturated zone and performing a laboratory analysis (e.g., ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.002 should be used (twice the typical default of 0.001 value used for transmissive systems).
How to Enter Data	Enter directly.

PARAMETER	**ORGANIC CARBON PARTITIONING COEFFICIENT (K_{oc})**
Units	mL/g.
Description	Chemical-specific partition coefficient between soil organic carbon and the aqueous phase. Larger values indicate greater affinity of organic constituents for the organic carbon fraction of soil. This value is chemical specific and can be found in chemical reference books.
Typical Values	Tetrachloroethene: 155 mL/g; Benzene: 66 mL/g Trichloroethene: 93 mL/g; Ethylbenzene: 204 mL/g cis-1,2-Dichloroethene: 29 mL/g; Toluene: 140 mL/g Vinyl Chloride: 11 mL/g; Xylene: 240 mL/g 1,1,1-Trichloroethane: 110 mL/g; MTBE: 14 mL/g (TRRP, 2008.) (Note that there is a wide range of reported values; for example, Mercer and Cohen (1990) report a K_{oc} for benzene of 83 mL/g.) For more information, see Pankow and Cherry, 1996 (for solvents) and Wiedemeier et al., 1999 (variety of constituents).
Source of Data	Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier et al., 1999 (variety of constituents); or other references with chemical properties. Alternatively, one can use relationships between K_{oc} and solubility or K_{oc} and the octanol-water partition coefficient (K_{ow}) to determine K_{oc}. A collection of values is presented in the Chemical Parameter Database included in this manual.

How to Enter Data	Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a value for the parameter.)

PARAMETER	CONSTITUENT HALF-LIFE IN LOW-k ZONE ($t_{1/2}$)
Units	Days, years.
Description	Time for dissolved plume concentrations to decay by one half as contaminants migrate through the low-k zone. The amount of degradation that occurs is related to the number of degrading organisms that are present, the degradation rates of these organisms, and the residence time in the low k zone. If unknown, assume 1000 yrs.
Typical Values	Not well established; assume large value (1000 yrs) unless site-specific evidence suggests low values are appropriate Activity in low-k zones is generally thought to be minimal due to soil type constraints that limit microbial activity (e.g., pore size restrictions), but this is a subject of active research.
Source of Data	Typically obtained from microcosm studies. **Note that many references report the first-order decay coefficients (k); these values can be converted to half-lives ($t_{1/2}$) using $t_{1/2} = 0.693 / k$.** **From site studies:** Biodegradation rate constants can be obtained from calibrated groundwater models.
How to Enter Data	Enter directly.

Step 3: *General*

PARAMETER	YEAR CORE SAMPLE COLLECTED FROM LOW-k ZONE (t_1)
Units	Year (yyyy).
Description	Year high-resolution core data was collected.
How to Enter Data	Enter directly.

PARAMETER	ENTER BEST GUESS FOR CONCENTRATION (C_0)
Units	mg/L.
Description	Representative historical loading concentration of the modeled area. If unknown, assume 10% of plume phase solubility. This value is a key parameter that can be changed during the calibration process to increase or decrease the simulated mass discharge, concentration, or mass to better match field data (see the beginning of this section).
Typical Values	0.0001 – 20,000 mg/L.

Source of Data	*Data Source 1. Site History or Process Information:* For example, the effective solubility of a constituent in a known DNAPL pool in the source could be used when modeling the source zone, or if the DNAPL in the pool was comprised of 50% Trichloroethene (TCE), a concentration of 550 mg/L (50% of TCE solubility of 1100 mg/L) could be used. Alternatively, one could use an estimate of the average historical concentration from the time the source started to the end of the loading period; sometimes a groundwater model with a source decay term (such as REMChlor (Falta et al., 2007)) can be used to estimate historical groundwater concentrations in the early period of a plume's life cycle. *Data Source 2. 10% of Solubility:* More commonly, good Data Source 1 information will not be available. In that case, we recommend using 10% of the plume phase solubility.
How to Enter Data	Enter directly.

Step 4: *High-Resolution Core Data*

PARAMETER	UNITS FOR DEPTH
Units	ft or m.
How to Enter Data	Select from drop down list.

PARAMETER	DEPTH INTO LOW-k ZONE
Units	ft or m.
Description	Vertical depth of the low-k zone from which high-resolution core data are collected.
How to Enter Data	Enter directly. Up to 500 discrete depth intervals can be entered into the Toolkit.

PARAMETER	SOIL CONCENTRATION
Units	mg/kg.
Description	Soil concentration in the low-k zone. These data are converted to equivalent groundwater (porewater) concentrations and displayed on the Concentration vs. Depth graph along with the simulated concentrations.
Source of Data	High-resolution vertical sampling in the area of interest.
How to Enter Data	Enter directly. Up to 500 discrete depth intervals can be entered into the Toolkit.

PARAMETER	IMPORT SOIL DATA
Description	High-resolution core data can be imported into the Toolkit. For this purpose, data must be a tab-delimited text file and follow the format: Depth Conc

	0.05 28.96 1.00 25.07 Where the first row contains labels, the first column contains depth information, and the second column contains concentration information. Up to 500 discrete depth intervals can be entered into the Toolkit.

PARAMETER	VIEW ALL SOIL DATA
Description	All high-resolution core data can be viewed at once. On this screen data can be entered directly and/or edited.

Step 5: *Check Data (Optional)*

PARAMETER	CHECK INPUT DATA
Description	A check is performed to look for missing data. Users are prompted if input data are missing or appear unreasonable.

Step 6: *Match Data*

PARAMETER	STEP 1. BEST ESTIMATE FOR YEAR OF ORIGINAL RELEASE
Units	Year (yyyy).
Description	Year source loading started. Estimated from site historical records and is usually from the 1950s, 1960s, 1970s, or early 1980s. If the release was over a long period of time, it is usually better to enter the earliest year. For chlorinated solvents, it is almost always from the 1950s, 1960s, 1970s, or early 1980s based on common uses for these compounds. This can be used as a calibration parameter (see the beginning of this section).
How to Enter Data	Enter directly.

PARAMETER	STEP 2. SELECT GENERAL FIRST-ROUND CONCENTRATION VS. TIME PATTERN
Description	An initial guess for the pattern in source strength concentration over time. The Toolkit provides three options: constant source, linear decaying source, and exponentially-decaying source. The latter two options are based on evidence that source strength may decrease over time as natural processes deplete mass from the source zone (Newell et al., 2006, Zhu and Sykes, 2004; Parker and Park, 2004; Falta et al., 2005; Falta, 2008; Basu et al., 2008). The behavior of source material (i.e., DNAPL) following release is also strongly influenced by heterogeneities in subsurface environments.
How to Enter Data	Select radio button.

PARAMETER	STEP 3. ADJUST CONCENTRATIONS IN HISTOGRAM MANUALLY
Description	Vertical concentration profiles within the low-k zone are employed to establish the interface concentration vs. time pattern that would best represent this profile. This is done by systematically adjusting the interface concentration

	(C_o) at various time intervals (t) until a representative "best" fit is obtained Adjust the concentrations in the histogram manually, using the up/down buttons, to try and get the black line (the model prediction) to match the actual data (orange dots). Use Root Mean Square (RMS) error and Relative Error as guidelines for better/worse matches.
How to Enter Data	Enter directly or use up/down buttons.

PARAMETER	UNCERTAINTY ANALYSIS
Description	Uncertainty in parameter estimates is a key issue in evaluating source attenuation effects. The Toolkit also utilizes a Monte Carlo-type approach to analyze uncertainty in the porosity, apparent tortuosity factor exponent, fraction organic carbon/distribution coefficient, and constituent half-life measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements that are being used for the source history reconstruction.

PARAMETER	PASTE EXAMPLE
Description	Clears **ALL** data related to the model in the Toolkit memory banks and pastes an example dataset.

PARAMETER	PRINT/EXPORT
Description	Prints the screen and graphs shown on the screen on the default printer. To print on a different printer, select the printer in the "Print" options in Excel® and then press the "Print" button. Exports the data shown on the Concentration vs. Depth graph as a text file for use in other programs.

Model Results

PARAMETER	TIME VS. CONCENTRATION AT TRANSMISSIVE ZONE-LOW-K ZONE INTERFACE GRAPH
Description	Graph of the concentration at the transmissive zone-low-k zone interface over time. The Toolkit assumes 10 time intervals for plotting the graph. The User may use the Log ←→ Linear button to see the results on a semi-log plot.

PARAMETER	CONCENTRATION VS. DEPTH INTO LOW-K ZONE GRAPH
Description	Graph of concentration vs. depth into low-k zone. Orange dots represent the actual high-resolution concentration data obtained from the soil core. The solid black line represents the Toolkit-simulated concentrations.

PARAMETER	RMS ERROR
Description	Root mean square (RMS) error is a commonly-used measurement employed by groundwater professionals. Second-order statistics, such as the RMS error, provide an indication of overall model calibration and an indication of the goodness-of-fit to the measured data because they are based on the absolute value of the residuals so that negative and positive values do not cancel each other out. RMS errors are calculated as follows: $$RMS = \sqrt{\frac{\sum_{i=1}^{n}(x_i - y_i)^2}{n}}$$ Where x_i is the simulated value, y_i is the observed value, and n is the total number of values. An RMS error of 0 indicates a perfect match between predicted and measured values, and increasing values of RMS indicate an increasingly poor match of predicted to measured data.

PARAMETER	RELATIVE ERROR
Description	Relative error is the difference between simulated and observed values divided by the observed value. The Toolkit displays the *average* relative error. Relative error approaching 0 indicates a better match between simulated and measured values, and increasing values indicate an increasingly poor match of simulated to measured data.

Uncertainty Analysis: Data Entry

Uncertainty in parameter estimates is a key issue in reconstructing source history. The Toolkit utilizes a Monte Carlo-type approach to analyze uncertainty in the porosity, apparent tortuosity factor exponent, fraction organic carbon/distribution coefficient, and constituent half-life measurements. With this tool, groundwater practitioners can estimate the accuracy of the hydrologic measurements that are being used for the source history reconstruction.

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PARAMETER	UNCERTAINTY ANALYSIS (EVALUATE HOW UNCERTAINTY IN INPUT DATA AFFECTS SOURCE HISTORY RECONSTRUCTION)
Description	This module uses the Monte Carlo approach to analyze uncertainty in the actual porosity, apparent tortuosity factor exponent, fraction organic carbon/distribution coefficient, and constituent half-life measurements. In the Monte Carlo-type approach, a random number is generated for every value of actual porosity, apparent tortuosity factor exponent, fraction organic carbon/distribution coefficient, and constituent half-life entered by the User. This set of random inputs is then used to calculate concentration in the low-k unit. Repeating this procedure a large number times yields a probability distribution from which statistical characteristics such as mean, percentile, and variance can be obtained. The Toolkit performs 253 iterations for the Monte Carlo approach (limited by the maximum number of lines that can be plotted in an Excel graph).
How to Enter Data	1) Select the parameters to use in the uncertainty analysis. Individual or multiple parameters can be included. 2) Specify a probability distribution for each parameter (see Appendix A.3 of the User's Manual for details on probability distributions). The Toolkit assumes that the values entered in the Input screen are the mean values. 3) For the normal distribution, specify the standard deviation as a percent of the mean. For lognormal distributions, specify the error factor, EF; (the ratio of the 95th percentile to the median of the lognormal data or the ratio of the median to the 5th percentile). (NOTE: the error factor MUST be greater than one). For uniform distribution, specify the lower and upper limits as percentages of the mean (i.e., ± 10%). 4) Perform Input Uncertainty Analysis.

Uncertainty Analysis: Results

PARAMETER	CONCENTRATION VS. DEPTH INTO LOW-K ZONE GRAPH
Description	Graph of concentration vs. depth into low-k zone. Orange dots represent the actual high-resolution core data concentration. The solid black line represents the Toolkit simulated concentration based on the data provided on the main Input screen. Solid blue lines represent the Monte Carlo realizations.

PARAMETER	PRINT GRAPH
Description	Prints the screen and graphs shown on the screen on the default printer. To print on a different printer, select the printer in the “Print” options in Excel® and then press the “Print” button.

CHEMICAL PARAMETER DATABASE

Chemical Name	Organic Carbon Petitioning Coefficient[1] (log (K_{oc}) @20-25 °C)) (log (1/kg))*	Solubility (@20-25 °C) (mg/L)*
Acetone	-0.24	1.00×10^{6}
Acenaphthene	3.85	3.93×10^{0}
Acenaphthylene	4.00	3.93×10^{0}
Anthracene	4.15	4.50×10^{-2}
Benzene	1.58	1.75×10^{3}
Benzoic acid	1.83	6.22×10^{4}
Benzo (a) Anthracene	6.14	5.70×10^{-3}
Benzo (b) Fluoranthane	5.74	1.47×10^{-2}
Benzo (k) Fluoranthene	5.74	4.30×10^{-3}
Benzo (g,h,i) Perylene	6.20	7.00×10^{-4}
Benzo (a) Pyrene	5.59	1.20×10^{-3}
Bromodichloromethane	1.85	6.22×10^{1}
Butanol, n-	0.74	7.70×10^{4}
Carbon disulfide	2.47	2.30×10^{3}
Carbon tetrachloride	2.67	7.62×10^{2}
Chlorobenzene	2.46	4.45×10^{2}
Chloroethane	1.25	2.00×10^{4}
Chloroform	1.93	9.64×10^{3}
Chloromethane	1.40	4.00×10^{-3}
Chlorophenol, 2-	2.11	2.85×10^{4}
Chrysene	5.30	1.80×10^{-3}
Dibenzo (a,h) Anthracene	5.87	5.00×10^{-4}
Dibromochloromethane	2.05	5.25×10^{3}
Dichlorobenzene, (1,2) (-o)	3.32	1.50×10^{2}
Dichlorobenzene, (1,4) (-p)	3.33	1.45×10^{2}
Dichlorodifluoromethane	2.12	1.98×10^{3}
Dichloroethane, 1,1-	1.76	5.00×10^{3}
Dichloroethane, 1,2-	1.76	8.69×10^{3}
Dichloroethene, cis1,2-	1.38	8.00×10^{2}

Chemical Name	Organic Carbon Petitioning Coefficient[1] (log (Koc) @20-25 °C)) (log (1/kg))	Solubility (@20-25 °C) (mg/L)*
Dichloroethene, trans1,2-	1.46	1.75×10^{3}
Ethylbenzene	1.98	6.00×10^{2}
Ethylene glycol	-0.90	1.00×10^{6}
Fluoranthene	4.58	2.06×10^{-1}
Fluorene	3.86	1.69×10^{0}
Hexane, n-	2.68	1.30×10^{1}
Indeno (1,2,3,c,d) Pyrene	7.53	7.17×10^{2}
Methanol	-0.69	1.00×10^{6}
Methylene chloride	1.23	1.54×10^{4}
Methyl ethyl ketone	0.28	2.18×10^{5}
Methyl t-Butyl Ether	1.08	4.80×10^{4}
Naphthalene	3.11	3.29×10^{1}
Phenanthrene	4.15	1.60×10^{0}
Phenol	1.44	9.30×10^{4}
Pyrene	4.58	1.60×10^{-1}
Tetrachloroethane 1,1,2,2-	0.00	7.18×10^{2}
Tetrachloroethene	2.43	1.43×10^{2}
Toluene	2.13	5.15×10^{2}
Trichlorobenzene	3.91	3.03×10^{1}
Trichloroethane 1,1,1-	2.45	1.26×10^{3}
Trichloroethane 1,1,2-	1.75	5.93×10^{3}
Trichloroethene	1.26	1.00×10^{3}
Trichlorofluoromethane	2.49	2.47×10^{3}
Vinyl Chloride	0.39	2.54×10^{3}
Xylene (mixed isomers)	2.38	1.98×10^{2}
Xylene, m-	3.20	1.58×10^{2}
Xylene, o-	2.11	1.75×10^{2}

Notes:

1. Values obtained from “Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface” by Wiedemeier *et al*., 1999, Appendix B.

GEOLOGIC PARAMETER DATABASE

Parameter	Value	Units
Hydraulic Conductivity[1]		
Clean sands	0.001 - 1	cm/s
Clays	$<1 \times 10^{-6}$	cm/s
Gravels	>1	cm/s
Silts	1×10^{-6} - 1×10^{-3}	cm/s
Silty sands	1×10^{-5} - 1×10^{-1}	cm/s
Total Porosity[2]		
Basalt	0.03 - 0.35	(-)
Clay	0.34 - 0.60	(-)
Coarse Gravel	0.24 - 0.36	(-)
Fine Gravel	0.25 - 0.38	(-)
Fine Sand	0.26 - 0.53	(-)
Coarse Sand	0.31 - 0.46	(-)
Limestone	0.0 - 0.5	(-)
Sandstone	0.05 - 0.30	(-)
Shale	0.0 - 0.10	(-)
Silt	0.34 - 0.61	(-)
Siltstone	0.21 - 0.41	(-)
Effective Porosity[3]		
Clay	0.01 - 0.20	(-)
Fine Gravel	0.2 - 0.35	(-)
Medium Gravel	0.15 - 0.25	(-)
Coarse Gravel	0.1 - 0.25	(-)
Sandy Clay	0.03 - 0.2	(-)
Loess	0.15 - 0.35	(-)
Peat	0.3 - 0.5	(-)
Silt	0.01 - 0.3	(-)
Gravely Sand	0.2 - 0.35	(-)
Fine Sand	0.10 - 0.30	(-)
Medium Sand	0.15 - 0.30	(-)
Coarse Sand	0.20 - 0.35	(-)

Parameter	Value	Units
Effective Porosity[3]		
Glacial Sediments	0.05 - 0.2	(-)
Limestone	0.01 - 0.24	(-)
Unfractured Limestone	0.001 - 0.05	(-)
Sandstone	0.1 - 0.4	(-)
Siltstone	0.01 - 0.35	(-)
Fractured Granite	0.00005 - 0.01	(-)
Volcanic Tuff	0.02 - 0.35	(-)
Dry Bulk Density[2]		
Clay	1.00 - 2.40	(g/cm^3)
Silt	-	(g/cm^3)
Granite	2.24 - 2.46	(g/cm^3)
Fine Sand	1.37 - 1.81	(g/cm^3)
Medium Sand	1.37 - 1.81	(g/cm^3)
Coarse Sand	1.37 - 1.81	(g/cm^3)
Sandstone	1.60 - 2.68	(g/cm^3)
Gravel	1.36 - 2.19	(g/cm^3)
Limestone	1.74 - 2.79	(g/cm^3)

Notes:
1. From Newell *et al*., 1996.
2. From Wiedemeier *et al*., 1995.
3. From Wiedemeier *et al*., 1999 (originally from Domenico and Schwartz, 1990 and Walton, 1988).

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SOURCE HISTORY TOOL TROUBLESHOOTING TIPS

Minimum System Requirements

The Source History Tool requires a computer system capable of running Microsoft© Excel® (2007 or 2010) for Windows. Operation requires an IBM-compatible PC equipped with a Pentium or later processor running at a minimum of 450 MHz. A minimum of 256 MB of system memory (RAM) is strongly recommended. The Toolkit can also be run on a Macintosh capable of running Office 2011. Computers not meeting these recommendations will experience slow running times and/or problems with memory.

Installation and Start-Up

The software is installed by unzipping the Toolkit model file (SourceHistoryTool.zip) and keeping all the unzipped files in the same folder on your computer hard drive. To use the software, start Excel® and load the SourceHistoryTool.xlsm model file from the File / Open menu. If you are using Excel® 2010, you may see a message box that asks you whether you want to disable or enable the macros. For the Toolkit to operate effectively, you must *enable* the macros.

Spreadsheet-Related Problems

Backspace doesn't clear cell. Use the delete key on the keyboard or the mouse to clear data.

The buttons won't work. The Toolkit is built in the Excel® spreadsheet environment, and to enter data one must click anywhere outside the cell where data was just entered. If you can see the numbers you just entered in the data entry part of Excel® above the spreadsheet, the data have not yet been entered. Click on another cell to enter the data.

is displayed in a number box. The cell format is not compatible with the value (e.g., the number is too big to fit into the window). To fix this, select the cell, pull down the format menu, select *Format Cells* and click on the *Number* tab. Change the format of the cell until the value is visible. If the values still cannot be read, select the format menu, select *Cells,* and click on the *Font* tab. Reduce the font size until the value can be read.

***#DIV/0!* is displayed in a number box.** The most common cause of this problem is that some input data are missing. In some cases, entering a zero in a box will cause this problem. Double check to make certain that data required for your run have been entered in all of the input cells.

***#VALUE!* is displayed in a number box.** The most common cause of this problem is that some input data are missing. Double check to make certain that data required for your run have been entered in all of the input cells and all options have been selected.

Common Error Messages

Unable to Load Help File: The most common error message encountered with the Toolkit is the message 'Unable to Open Help File' after clicking on a *Help* button. Depending on the version of Windows® you are using, you may get an Excel® Dialog Box, a Windows® Dialog Box, or you may see Windows® Help load and display the error. This problem is related to the ease with which the Windows® Help Engine can find the data file, SourceHistoryTool.chm. Here are some suggestions (in decreasing order of preference) for helping WinHelp find it:

- If you are asked to find the requested file, do so. The file is called SourceHistoryTool.chm, and it was installed in the same directory/folder as the Source History Tool model file (SourceHistoryTool.xlsm).

- Use the File/Open menus from within Excel® instead of double-clicking on the filename or Program Manager icon to open the Source History Tool model file. This sets the *current directory* to the directory containing the Excel® file you just opened.

- If you are using a Macintosh, you will have to download a program able to read Microsoft® compiled HTML files, e.g., Chmox (free), xCHM (free), iCHM (free), etc.

ACKNOWLEDGEMENTS

The Source History Tool was developed for the Environmental Security Technology Certification Program (ESTCP) of the U.S. Department of Defense by GSI Environmental Inc., Houston, Texas.

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APPENDICES

APPENDIX 1. RECOMMENDATIONS FOR COLLECTING HIGH-RESOLUTION FIELD DATA

Application of the Source History Tool requires high-resolution characterization data collected from soil cores in the low-k zone. This is because the output of the model—the source concentration history over time—is based on fitting predictions of soil concentrations (based on the one-dimensional diffusion equation) to actual (measured) soil data. Consequently, the more comprehensive the dataset, the greater the confidence that the model is capturing the general "style" of source attenuation history at the site.

Based on this objective, the following recommendations are made with respect to collecting high-resolution data from soil cores:

Identify Suitable Coring Locations Using Rapid Data Acquisition Tools

An initial objective should be to obtain sufficient high-resolution characterization data to ensure a proper site conceptual is in place and locations for subsequent soil coring can be selected with confidence. To this end, methods should focus on seeking out and identifying permeability interfaces, as well as a better understanding of the relative contaminant distribution. There are several different commercially-available investigative tools that allow for rapid collection of quantitative information on stratigraphy and/or (to a more limited extent) relative contaminant levels. This includes systems such as the Membrane Interface Probe (MIP), Waterloo$^{APS\ TM}$, and Geoprobe HPT® that have been shown to provide direct or complimentary hydrostratigraphic data within low-k zones (Adamson et al., 2013). These subsurface tools can be advanced using direct-push equipment at drive rates favorable to recording large amounts of data in short periods of time; characterization of several hundred vertical feet per day is not uncommon. They provide a more comprehensive picture of site geologic heterogeneities, with data displayed real-time for on-site interpretation of results and adjustment of sampling intervals. These screening-level data can be used to focus coring efforts on locations and depths where low-k layers are indicated.

Core Collection Methods

Obtaining high-quality cores for high-resolution soil sub-sampling is a key goal for implementing this approach. There are a variety of readily-available and effective methods for collecting cores in unconsolidated sediments, and a few are highlighted below. Ultimately, the choice may depend on site conditions and User preferences.

- **Geoprobe Methods.** Direct-push techniques are very commonly used in relatively shallow unconsolidated units and tend to be viewed favorably due to flexibility and cost. Both the Macro-Core and dual-tube sampler methods are capable of obtaining quality cores from fine-grained units. The former is a piston-type system where a center rod holds the piston in place during advancement. The center rod is removed at the top of the sampling interval of interest and the tool string advanced and then retracted to collect the core. This system is effective in areas with heaving sands, however, a major limitation is that it is not

designed to prevent cross contamination between intervals. The dual-tube method prevents cross contamination because it consists of an outer casing around the inner casing that holds the sample liner. Further, its design allows for continuous coring. The primary disadvantage is that in sands, it may be difficult to avoid heaving and poor recovery may occur.

- **Sonic Methods.** Sonic rigs use physical vibration to advance to depths that are often not achievable using direct push methods. This approach makes it more successful in areas with very coarse unconsolidated soils, and also allows for faster drilling than other methods. A core barrel is advanced ahead of an outer casing, and cores collected either in a plastic sleeve or split barrel with a rigid plastic liner. This method allows for continuous coring. Primary disadvantages of the sonic methods are: 1) the costs are generally higher per vertical foot (which may not negatively impact overall costs due to the inherently faster drill rates); 2) increased disturbance of core samples and possible redistribution of pore fluids may contribute to loss of volatiles; and 3) heating of cores may occur and further contribute to loss of volatiles (this has been known to impact its regulatory acceptance in certain situations).

- **Auger Methods**. Hollow-stem augers (HSA) are commonly used for installing monitoring wells and can be suitable for environmental coring. They can utilize a split barrel that is advanced inside of the auger or a thin-wall Shelby tube. HSA does not require drilling fluids, and is an easy and reasonably fast approach that works well in shallow unconsolidated formations without significant coarse-grained sediments (i.e., boulders). Their primary disadvantages for coring relative to other options are the generation of cuttings and the inability to prevent cross contamination.

Other promising methods for collecting cores within low-k zones are currently in development, including the use of cryogenic freezing techniques during drilling to maintain core integrity and improve recovery.

Sampling Frequency with Depth

Increasing the number of samples per location essentially increases the level of confidence that an accurate soil VOC profile has been obtained. Consequently, the greater the confidence that the style of source history can be estimated using the Toolkit. Since the incremental costs of higher sampling frequencies are relatively modest, it is recommended that sampling programs use as high a frequency as project budgets reasonably permit. Because diffusion-dominated penetration into low-k units generally occurs within the first 5 to 10 ft, it is recommended that sampling frequencies of no more than 1 sample per ft be used to implement this approach. Further, sampling frequencies of 1 sample per 0.2 to 0.5 ft are highly preferable within the low-k zones.

It is highly recommended that sampling should be completed within the overlying and/or underlying higher permeability zones as well. Data from these zones can help establish vertical contaminant distribution and degradation patterns. Relative to the low-k zones, a lower sampling frequency with depth within these more transmissive zones is likely to be appropriate.

Sampling Frequency with Time

The objective of these methods is to collect core(s) at a single point in time. Therefore, repeated coring efforts over time are not required.

Number of Locations per Source Area

The number of locations per source area is a site-specific decision that should be based on the scale of the source area, level of heterogeneity, and uncertainty in the existing conceptual model. For a site where the source area is small and well-delineated (e.g., a single storage tank), one or two borings within the area of highest concentration may be sufficient to establish trends. However, larger sites or sites where there is greater heterogeneity and/or uncertainty may require several additional borings to adequately characterize the source area. Another option involves collecting cores from locations that are farther downgradient of the source area. These can be used to confirm the source history within the source area, but also to demonstrate attenuation along the plume flowpath.

Analytical Data to be Collected

At a minimum, volatile organic compound (VOC) analyses should be completed for all soil sub-samples from the low-k zone; soil VOC concentrations with depth are primary input data for the Toolkit. On a select number of samples (10 to 50%), analyses for the fraction of organic carbon should be performed. To the extent that the information is not already available, the porosity of the low-k zone soils should also be established through lab analyses. Both porosity and organic carbon are input parameters for the Toolkit. Grain size analyses should also be considered if there is a question about soil classification. Analyses that support an assessment of degradation (e.g., isotopes, biomarkers) may also be valuable in calibrating the model. Finally, core material can be collected for a site-specific assessment of diffusion coefficient, but this type of service is not commercially available and would require specific User expertise.

Sampling Handling and Analysis Considerations

To ensure high-quality data, it is critical to use methods that accurately characterize contaminants in low-k soils. Commercially-available protocols are aimed at complying with EPA Method 5035/5035A for preparing samples for VOC analysis by Method 8260 (or equivalent purge-and-trap gas chromatograph (GC) method). This method requires methanol preservation or freezing within 48 hours of sample collection. For samples that are expected to be high in concentration (> 250 μg/kg), options include: 1) soil sampled into a vial with methanol; or 2) soil collected in an EnCore sampler and shipped to a laboratory immediately (to ensure methanol preservation within 48 hours). For samples that are expected to be low in concentration (5 to 500 μg/kg), options include 1) soil sampled into vials with sodium bisulfate and methanol as a preservative; 2) soil collected in an EnCore sampler and shipped to a laboratory immediately (to ensure methanol preservation within 48 hours); and 3) soil sampled into vials containing water or methanol and shipped to a laboratory immediately (to ensure samples are frozen within 48 hours).

Regardless of the expected concentration, ***we strongly recommend methods that use methanol preservation in the field*** to eliminate the potential for contaminant losses during sampling handling and shipping. Data from ESTCP ER-201032 established that VOC concentrations in soils collected using EnCore samplers and sent to a commercial lab without field preservation were significantly biased relative to field-preserved samples (32% lower based on the slope of the regression line). Delaying the methanol preservation step until samples arrived at the laboratory was not sufficient for eliminating losses.

Key objectives in evaluating low-k soils are ensuring the extraction techniques are sufficient to overcome limitations in diffusion-dominated transport from these soils and analysis techniques are able to quantify trace contaminant levels. Options specifically aimed at meeting these data quality objectives include: 1) rapid field extraction (approximately 2 hr) using a combination of sonification and vigorous shaking; 2) extended extraction (several weeks) using continuous shaking with an option to enhance extraction using microwave-based techniques; and 3) direct (on-column) injection of methanol extracts (Dincutoiu et al., 2001; Dincutoiu et al., 2003; Górecka et al., 2001).

Collection of Groundwater Data

Groundwater concentration data are not used as input for the Toolkit. In other words, results can be obtained without collecting groundwater data from the site. However, groundwater data can be a valuable component to the source history approach in two ways, one short-term and one long-term:

1. ***Information at the interface can help calibrate the model.*** Groundwater data collected at a single timepoint provides supplemental information for understanding contaminant distribution. In particular, the groundwater concentration from a sample collected in the transmissive zone as close as possible to the interface with the low-k zone can be used to calibrate the modeled concentration at the interface. The latter value is converted from a soil concentration to an equivalent porewater concentration, such that direct comparison to an actual groundwater concentration is useful in confirming the assumptions involved in this conversion are reasonable. A close fit between actual and modeled data at the interface is key in ensuring that the fit across the entire interval is also close and that the style of the source history is being captured. Groundwater samples can also provide other valuable information that might otherwise be difficult to obtain with soil cores. This includes geochemical and dissolved gas concentration data that serve as lines of evidence for attenuation.

   There are several methods for collecting groundwater data quickly and efficiently within more transmissive zones. For high-resolution characterization purposes, it is very important that the samples are collected from relatively short intervals. This reduces the flow-weighting that occurs when collecting groundwater across conventional (10-ft) monitoring well screens, and ensures that representative, depth-discrete data are being generated. Methods that utilize this approach without relying on monitoring well installation include the Waterloo$^{APS\ TM}$ and the Geoprobe HPT-GWS. Both of these use very short screens (< 1 ft) to generate high-resolution groundwater data. In addition, they also generate real-time

information on the permeability distribution so that low-k interfaces can be more accurately targeted.

2. ***Temporal groundwater data can help confirm that the model-predicted trends in groundwater concentration are reasonable.*** Groundwater data collected over a longer time period can be compared to model predictions to determine if the trends are consistent. The focus should be on transmissive zones near the low-k zone interface since the Toolkit provides estimates of concentration within the transmissive zone. Groundwater samples can be collected in a variety of ways, but multi-level systems (e.g., Solinst Model 403 CMT®) may provide the most relevant information. Because collecting these data requires a more significant investment in terms of time and money, they would likely be a component of a long-term monitoring program after remedy selection (MNA) had been completed, although it is possible that it could be part of the remedial investigation/ feasibility study (RI/FS) stage.

It is important to note that collecting groundwater data from the low-k zone itself can be difficult, regardless of the method employed. This is largely the result of flow limitations within fine-grained media. In zones with even a modest level of heterogeneity, any groundwater that is collected may be largely from those sub-layers of highest permeability. This reduces confidence in how representative these data may be. Consequently, soil cores should always be the primary method for obtaining input data for the Toolkit.

APPENDIX 2. ESTIMATION OF AQUEOUS CONCENTRATION IN LOW-k ZONE

Purpose:
Determine the aqueous concentration in the low-k zone.

Given:
There is source material in a transmissive zone that loads up a source area or downgradient low-k zone before the source is removed.

Assumptions:
The Toolkit uses a simplified conceptual model of a two-layer aquifer system (a transmissive layer and a low-k layer) and assumes:

1. A loading period where there is a constant concentration of contaminants in the transmissive zone that drives contaminants into the low-k zone.
2. There is no DNAPL phase.
3. Diffusion occurs only in the water phase.

Summary:

Diffusion Dominated Transport

For diffusion dominated transport, aqueous concentrations in the low-k zone at a given time and depth can be estimated using (Carslaw and Jaeger, 1959):

$$C_{lk} = \sum \frac{1}{2}\left(I_j - I_{j+1}\right)\left\{\begin{array}{l} \exp\left(-x\sqrt{\frac{k}{D_{sT}}}\right) erfc\left[\left(\frac{x}{\sqrt{4D_{sT}t}}\right) - \sqrt{kt}\right] \\ + \exp\left(x\sqrt{\frac{k}{D_{sT}}}\right) erfc\left[\left(\frac{x}{\sqrt{4D_{sT}t}}\right) + \sqrt{kt}\right] \end{array}\right\} \qquad (1)$$

with I_j, k, and D_{sT} defined as:

$$I_j = \left(Source\ Concentration\ at\ t_j\right)\left(n + \rho_b K_d\right) \qquad (2)$$

$$k = \left(\frac{\ln(2)}{t_{1/2}}\right)\frac{n}{n + \rho_b K_d} \qquad (3)$$

$$D_{sT} = \frac{D_o n^{1+p}}{n + \rho_b K_d} \qquad (4)$$

Where:

C_{l_k} = Concentration in the low-k zone (ML^{-1});
x = Depth into low-k zone (L);
t = Time increment (T);
I_j = Interfacial concentration at time t_1 given by (ML^{-1});
j = Time interval (T);
$t_{1/2}$ = Constituent Half-Life in Low-k Zone (T^{-1});
n = Porosity of low-k zone (unitless);
ρ_b = Bulk density of low-k zone (M/L^3);
K_d = Soil/water partitioning coefficient (L^3/M);
= $f_{oc}.K_{oc}$;
f_{oc} = Fraction organic carbon of the low-k layer (unitless);
K_{oc} = Organic carbon partitioning coefficient (L^3/M).
D_o = Molecular diffusion coefficient in free water (L^2/T); and
p = Low-k Zone Apparent Tortuosity Factor Exponent (unitless).

Advection and Diffusion Dominated Transport

Aqueous concentrations in the low-k zone for advection and diffusion dominated transport can be estimated using:

$$C_{lk} = \sum \left(I_j - I_{j+1}\right) C(x,t,v,D_{sT},k) \qquad (5)$$

For slow degradation in the low-k zone (i.e., $k < 2\text{x}10^{-7}$ day^{-1}):

$$C(x,t,v,D_{sT},k) = \frac{1}{2} erfc\left(\frac{x-vt}{\sqrt{4D_{sT}t}}\right) + \sqrt{\frac{v^2 t}{\pi D_{sT}}} \exp\left(-\frac{(x-vt)^2}{4D_{sT}t}\right) - \frac{1}{2}\left(1 + \frac{vx}{D_{sT}} + \frac{v^2 t}{D_{sT}}\right) \exp\left(\frac{vx}{D_{sT}}\right) erfc\left(\frac{x+vt}{\sqrt{4D_{sT}t}}\right) \qquad (6)$$

With v defined as:

$$v = \frac{K.i}{n + \rho_b K_d} \qquad (7)$$

where

K = Hydraulic conductivity (L/T); and
i = Vertical hydraulic gradient (unitless)

For $k \geq 2\text{x}10^{-7}$ day^{-1}:

$$C(x,t,v,D_{sT},k) = \frac{v}{v+u}\exp\left[\frac{(v-u)x}{2D_{sT}}\right]erfc\left(\frac{x-ut}{4D_{sT}t}\right) + \frac{v}{v-u}\exp\left[\frac{(v+u)x}{2D_{sT}}\right] erfc\left(\frac{x+ut}{\sqrt{4D_{sT}t}}\right) + \frac{v^2}{2kD_{sT}}\exp\left(\frac{vx}{D_{sT}-kt}\right)erfc\left(\frac{x+vt}{\sqrt{4D_{sT}t}}\right) \quad (8)$$

With u defined as:

$$u = v + \sqrt{1 + \frac{4kD_{sT}}{v^2}} \quad (9)$$

Conversion of Soil Concentration to Aqueous Concentration

Assuming equilibrium chemical partitioning between the solid phase and pore water, and that no NAPL phase is present, total soil concentration can be converted to aqueous concentration using:

$$C_w = \frac{C_s \rho_b}{Rn} \quad (10)$$

With R defined as:

$$R = 1 + \frac{\rho_b K_d}{n} \quad (11)$$

Where:

- C_w = Pore water concentration in the low-k zone (ML^{-1});
- C_s = Soil concentration in the low-k zone (MM^{-1});
- ρ_b = Bulk density of low-k zone (M/L^3);
- R = Retardation factor (unitless);
- n = Porosity of low-k zone (unitless);
- K_d = Soil/water partitioning coefficient (L^3/M);
  = $f_{oc}.K_{oc}$;
- f_{oc} = Fraction organic carbon of the low-k layer (unitless); and
- K_{oc} = Organic carbon partitioning coefficient (L^3/M).

Note the Toolkit assumes that concentration data is being entered on a dry weight basis. If concentration data is only available on a wet weight basis, then an easy correction is to enter the wet bulk density instead of the dry bulk density. The wet bulk density can be calculated by multiplying the dry density by the following factor: 1+moisture content/100.

APPENDIX 3. PROBABILITY DISTRIBUTIONS

This section describes in greater detail the probability distributions employed in the Monte Carlo analysis. The Source History Tool offers the User three distribution options: normal, lognormal, and uniform.

Normal Distributions

Normal distributions are defined by the density function:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\left(\frac{(x-\mu)^2}{2\sigma^2}\right)} \qquad -\infty < x < \infty$$

where, σ is the standard deviation and μ the mean of the distribution. The Toolkit assumes that the values entered in the main input screen are the means. The uncertainty analysis requires the User to specify a σ as a percentage of the mean.

Lognormal Distributions

A lognormal distribution is a distribution whose logarithms are normally distributed. The lognormal density function is:

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} e^{-\left(\frac{(\ln(x)-\mu)^2}{2\sigma^2}\right)} \qquad x, \sigma > 0$$

where, σ is the standard deviation and μ the mean of the underlying normal distribution.

Lognormal distributions are typically specified in two ways throughout literature (Swiler and Wyss, 2004). One way, as described above, is to use the mean and standard deviation of the underlying normal distribution. The other way is to use the mean of the lognormal distribution (α) and a term called the "Error Factor." For a lognormal distribution, the error factor is the ratio of the 95th percentile to the median, or equivalently, the ratio of the median to the 5th percentile. Therefore, the error factor represents the width of a 90% confidence interval around the median.

In terms of the error factor, the relationship between the underlying normal distribution and the lognormal distribution can be described by:

$$\sigma = \ln(\text{error factor})/1.645$$

and

$$\mu = \ln(\alpha) - \frac{\sigma^2}{2}$$

where, α is the mean of the lognormal distribution, and σ and μ the standard deviation and mean of the underlying normal distribution, respectively.

The Toolkit describes the lognormal distribution using the error factor.

Uniform Distributions

A uniform distribution is specified over a particular interval and implies that all the points within that interval have equal probability of occurring. The uniform probability distribution function is:

$$f(x) = \frac{1}{B - A} \qquad A \le x \le B$$

where, A and B are the lower and upper bounds, respectively.

CASE STUDIES

CASE STUDY 1. NAS JACKSONVILLE, FLORIDA FORMER BUILDING 106

Overview:

The Source History Tool was used to estimate source loading history based on high-resolution sampling of low-k zones at the former Building 106 area in Operable Unit 3 (OU3), a former dry cleaner site, at Naval Air Station (NAS) Jacksonville, Florida. The high-resolution data was obtained by GSI Environmental and the University of Guelph as part of an ESTCP-sponsored project (ESTCP ER-201032). The site was studied using University of Guelph high-resolution core sampling techniques. Mr. Mike Singletary of the Naval Facilities Engineering Command was the Navy point of contact for this project.

This building was the former dry cleaner for the air station and is located in the north/northwest portion of OU3. It was operated as a dry cleaner beginning in 1962 and was believed to have used approximately 150 gallons of PCE per month until 1990 or so when dry cleaning operations were discontinued and the building was demolished shortly afterwards. Chlorinated ethenes have been detected in the soil and groundwater beneath the site, including in a lower permeability clay layer that is present within the sandy shallow aquifer.

The Toolkit was applied as follows:

- Step 1: Initial values of all parameters, site-specific or Toolkit default parameters, were entered into the model. Tetrachloroethene (PCE) is the dominant compound and was chosen as the constituent type.
- Step 2. Toolkit simulated concentrations in the low-k unit were compared to observed PCE soil concentrations at a location near the source area (location OU3-3 in Figure 1.1).
- Step 3. Input parameters were adjusted, as needed, to improve the comparison of simulated and observed PCE concentrations.

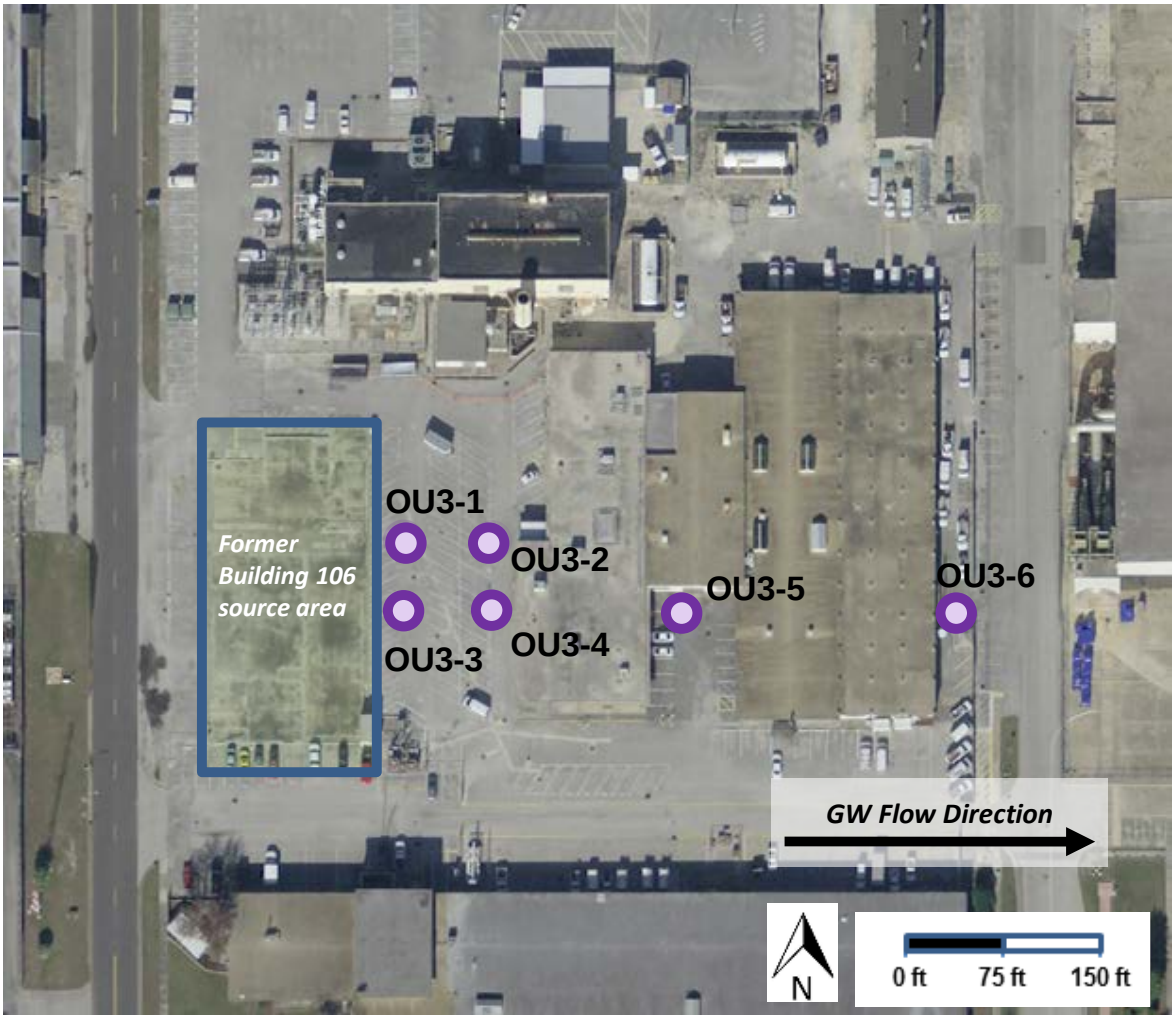

Figure 1.1. Site Layout. Building 106 in Operable Unit 3,
Naval Air Station, Jacksonville, Florida. Data from Location OU3-3 were used in Case Study 1.

Input Data:

Data Type	Parameter	Value	Source of Data
Hydrogeology	• Low-k zone material: • Low-k zone porosity: • Transport type:	Clay 0.38 (-) Diffusion only	• Site information • Site information • Site information
Transport	• Key constituent: • Molecular diffusion coefficient in free water: • Low-k. zone apparent tortuosity factor exponent: • Low-k zone bulk density: • Low-k. zone fraction organic carbon: • Organic carbon partitioning coefficient: • Constituent half-life in low-k zone:	PCE 8.2E-10 (m^2/sec) Initial: 1.1 (-) Calibrated: 1.33 (-) 1.5 (g/mL) 0.0018 (-) 155 (L/kg) 1000 (yr)	• Site information • Literature (Toolkit default) • Initial: Toolkit default • Site information • Site information • Literature (Toolkit default) • Estimated site information
General	• Year core sample collected: • Source concentration:	2011 Initial – 14.3 (mg/L) Calibrated - 71 (mg/L)	• Site information • Initial: Toolkit suggestion of 10% PCE solubility .
Match Data	• Source loading starts in year: • Source decay method:	1962 Constant	• Site information • Site information

High-Resolution Core Data Collected at OU3-3

Depth (ft)	0.5	1.0	1.5	1.7	2.0	2.4	2.7	3.0	4.33	4.67	5.0	5.33	5.67	6.0	6.33
PCE Conc (mg/L)	29.0	25.1	18.1	18.5	10.7	6.9	4.7	3.2	0.99	0.58	0.35	0.17	0.09	0.04	0.03

Model Summary:

- The Toolkit was used to reconstruct the source history based on PCE soil concentrations in the low-k zone at a former dry cleaner site (OU-3 Building 106) at Naval Air Station Jacksonville, Florida studied using University of Guelph high-resolution core sampling techniques. Mr. Mike Singletary of the Naval Facilities Engineering Command was the point of contact for this project.
- Toolkit default values were used as input parameters where necessary. Source concentration and year source release occurred were varied until a reasonable comparison between simulated and observed low-k zone concentrations was obtained.
- Toolkit inputs and outputs are shown on Figures 1.2 and 1.3 for the initial and calibrated models, respectively.
- To run the model, hydrogeological data were entered in Section 1, transport parameters in Section 2, general information in Section 3, high-resolution core data in Section 4, and data for matching in Section 6.

KEY POINT:

The Toolkit was able to reproduce observed low-k zone concentrations reasonably well at this location. Root mean square (RMS) and average relative errors of 2.9 mg/L and 0.16, respectively, were observed.

The initial site estimated source concentration and release date were unable to reproduce the observed concentrations in the low-k zone. A better comparison between simulated and observed concentrations was obtained by increasing the concentration and employing a larger tortuosity factor exponent. Based on the calibrated model, the Toolkit yielded a good comparison to soil core concentrations.

Note that although for this evaluation, only the source concentration and tortuosity factor exponent were used as calibration parameters, there could be other combinations of input parameters that could be adjusted to yield similar or better results.

The modeling demonstrated that the locations at this source area were characterized by relatively constant source histories, i.e., source loading that changed gradually over time. The soil profiles generally exhibited decreasing concentration with depth, which is a distinguishing characteristic of continued loading over these low-k zones by a source strength that remains high relative to historical values. This is consistent with the assumption that the majority of degradation activity is occurring in the transmissive zones as opposed to in the low-k zones. Had degradation in the low permeability zones been occurring to a significant degree, then it would have been difficult to obtain similar source histories with the parent compound alone vs. the parent compound plus its degradation products.

The modeling suggests that an appreciable decline in the source strength cannot be verified. Consequently, monitored natural attenuation may not an appropriate site remedy if source control is a requirement. However, modeling results from downgradient locations (not shown) indicate that attenuation processes are clearly helping to maintain plume stability and reduce risk.

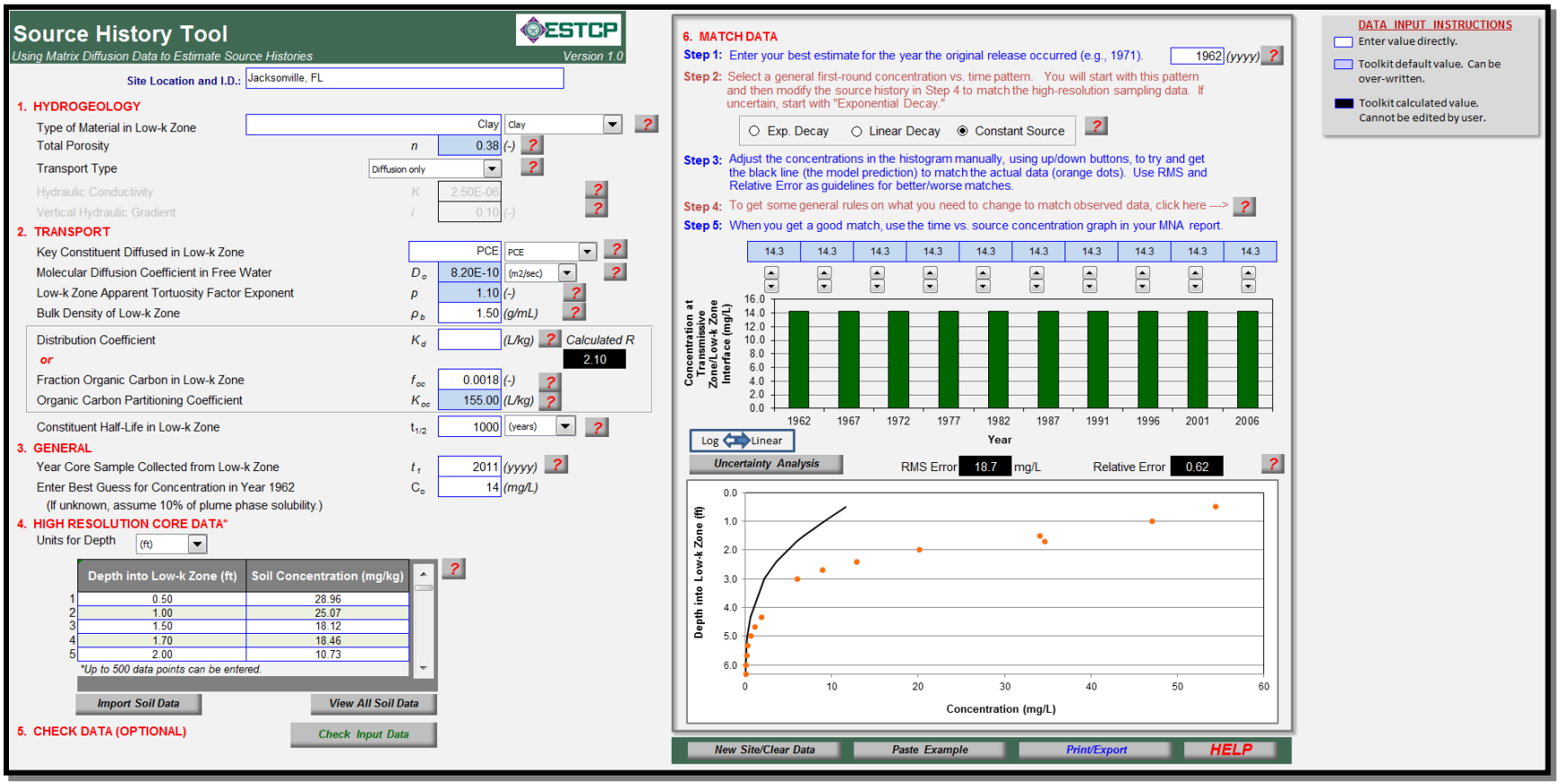

Figure 1.2. Initial Model for Case Study 1.

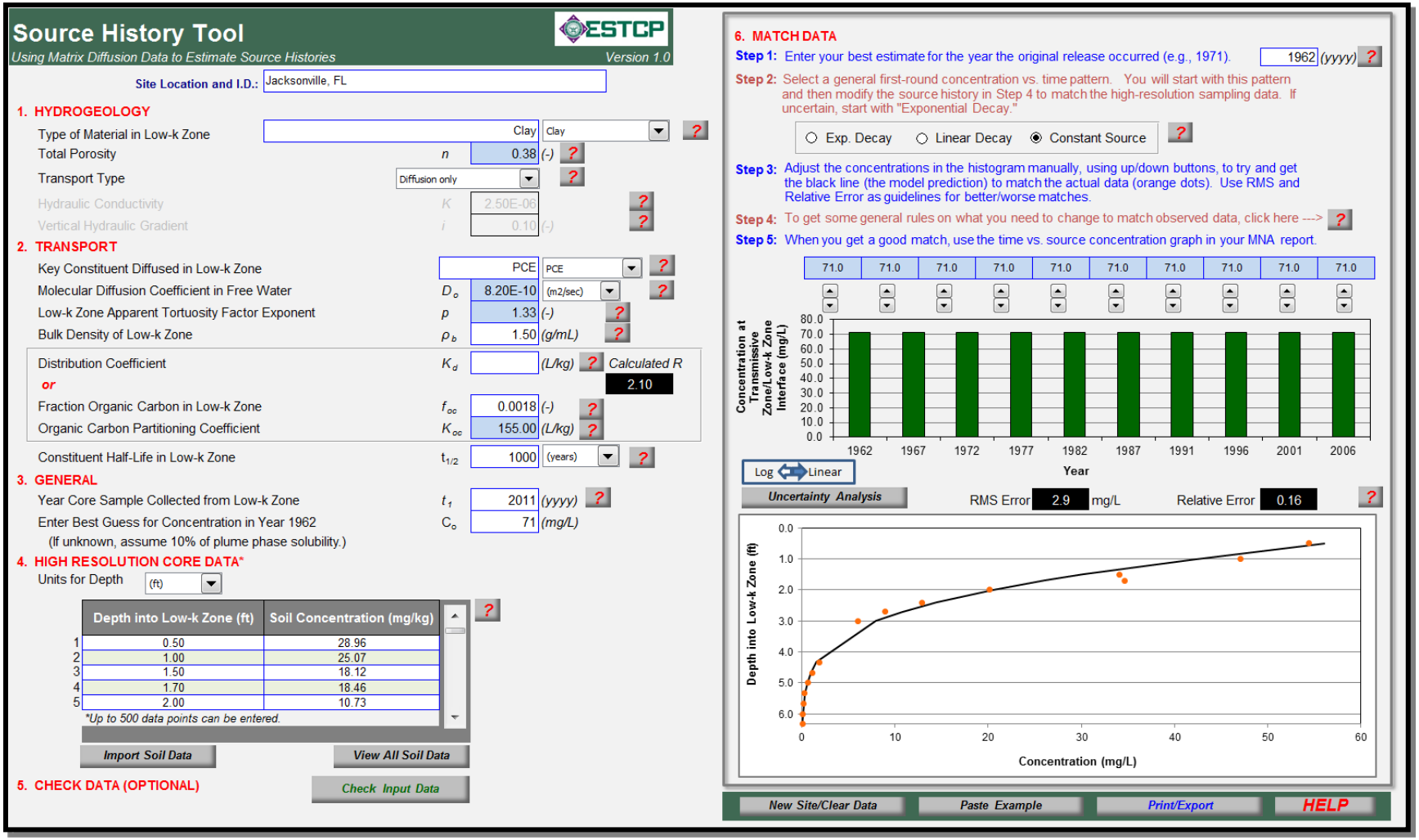

Figure 1.3. Calibrated Model for Case Study 1.

CASE STUDY 2. NAS JACKSONVILLE, FLORIDA BUILDING 780

Overview:

The Source History Tool was used to estimate source loading history based on high-resolution sampling of low-k zones at the Building 780 area in Operable Unit 3 (OU3) at Naval Air Station (NAS) Jacksonville, Florida. The high-resolution data was obtained by GSI Environmental and the University of Guelph as part of an ESTCP-sponsored project (ESTCP ER-201032). The site was studied using University of Guelph high-resolution core sampling techniques. Mr. Mike Singletary of the Naval Facilities Engineering Command was the Navy point of contact for this project.

This building housed a paint stripping and solvent recycling operation and currently is used as a general (non-hazardous) recycling facility and is located in the northern portion of OU3. The exact start date for solvent use is unknown, but it reportedly occurred throughout the 1970s and 1980s to strip paints from aircraft and parts (as well as disposal of spent jet fuels). Chlorinated solvents such as TCE and 1,1,1-TCA have been detected in the soil and groundwater beneath the site, including in a lower permeability clay layer that is present within the sandy shallow aquifer. In 1998, a soil-vapor extraction system and a groundwater pump-and-treat system were implemented at Building 780 to address contamination associated with this source as part of the Record of Decision. These systems were shut down following the 2004-2005 optimization review.

The Toolkit was applied as follows:

- Step 1: Initial values of all parameters, site-specific or Toolkit default parameters, were entered into the model. In this case, the parameters for cis-1,2-dichloroethene (cis-DCE) were used since it is the most prevalent compound detected in soil samples.
- Step 2. Toolkit simulated concentrations in the low-k unit were compared to observed soil concentrations (entered as total chlorinated ethenes) at a location near the presumed source (location OU3-9 in Figure 2.1).
- Step 3. Input parameters were adjusted, as needed, to improve the comparison of simulated and observed concentrations.

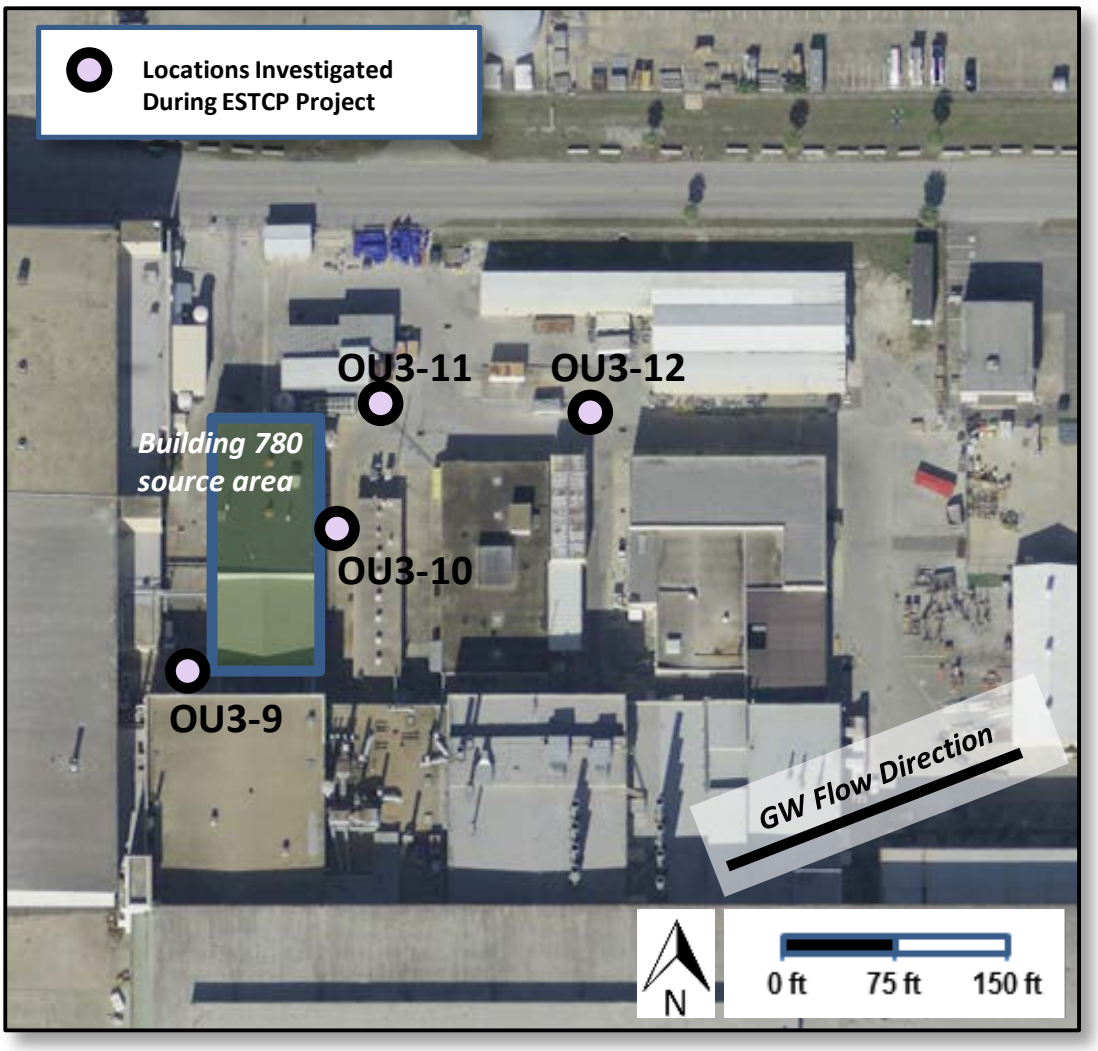

Figure 2.1. Site Layout. Building 780 in Operable Unit 3,
Naval Air Station, Jacksonville, Florida. Data from location OU3-9 were used in Case Study 2.

Input Data:

Data Type	Parameter	Value	Source of Data
Hydrogeology	• Low-k zone material: • Low-k zone porosity: • Transport type:	Clay 0.38 (-) Diffusion only	• Site information • Site information • Site information
Transport	• Key constituent: • Molecular diffusion coefficient in free water: • Low-k. zone apparent tortuosity factor exponent: • Low-k zone bulk density: • Low-k. zone fraction organic carbon: • Organic carbon partitioning coefficient: • Constituent half-life in low-k zone:	Cis-DCE 1.13E-9 (m^2/sec) Initial - 1.1 (-) Calibrated – 1.00 (-) 1.5 (g/mL) 0.0018 (-) 29 (L/kg) 1000 (yr)	• Site information • Literature (Toolkit default) • Literature (Toolkit default) • Site information • Site information • Literature (Toolkit default) • Estimated site information
General	• Year core sample collected: • Source concentration:	2011 Initial – 80 (mg/L) Calibrated - 150 (mg/L)	• Site information • Initial: Toolkit suggestion of 10% cis-DCE solubility .
Match Data	• Source loading starts in year: • Source decay method:	Initial - 1975 Calibrated – 1971 Linear decay Calibrated - histogram concentrations adjusted manually.	• Initial - median date of solvent use Calibrated - within range of estimated site values • Site information

High-Resolution Core Data Collected at OU3-9

Depth (ft)	0.1	0.9	1.3	1.8	2.3	2.8	3.3	3.8	4.3	4.8	5.3	5.9
Cis-DCE Conc (mg/L)	4.84	5.55	6.03	8.38	8.07	7.99	7.43	8.26	6.35	6.52	7.58	2.27

Model Summary:

- The Toolkit was used to reconstruct the source history based on cis-DCE soil concentrations in the low-k zone at a former solvent use site (OU-3 Building 780) at Naval Air Station Jacksonville, Florida studied using University of Guelph high-resolution core sampling techniques. Mr. Mike Singletary of the Naval Facilities Engineering Command was the point of contact for this project.
- Toolkit default values were used as input parameters where necessary. Source concentrations (both initial source concentration and histogram source concentrations), year source release occurred, and apparent tortuosity factor exponent were varied until a reasonable comparison between simulated and observed low-k zone concentrations was obtained.
- Toolkit inputs and outputs are shown on Figures 2.2 and 2.3 for the initial and calibrated models, respectively.
- To run the model, hydrogeological data were entered in Section 1, transport parameters in Section 2, general information in Section 3, high-resolution core data in Section 4, and data for matching in Section 6.0.

KEY POINT:

The Toolkit was able to reproduce observed low-k zone concentrations reasonably well at this location. Root mean square (RMS) and average relative errors of 5.9 mg/L and 0.2, respectively, were observed.

The initial site estimated source concentration, release date, and apparent tortuosity exponent factor were unable to reproduce the observed concentrations in the low-k zone. A better comparison between simulated and observed concentrations was obtained by increasing the release year concentration, varying the concentrations in the histogram, employing an earlier release date, and decreasing the apparent tortuosity exponent factor. Based on the calibrated model, the Toolkit yielded a reasonable comparison to soil core concentrations.

Note that although for this evaluation, only the source concentrations, release date, and apparent tortuosity exponent factor were used as calibration parameters, there could be other combinations of input parameters that could be adjusted to yield similar or better results.

The modeling demonstrated that the locations at this source area were characterized by declining source histories for total chlorinated ethenes, i.e., source loading that changed gradually over time. Soil profiles generally exhibited a maximum concentration at some distance (1 to 4 ft) into the low-k clay, with lower concentrations measured near the interface. This pattern is a distinguishing characteristic of a declining source strength over time, such that the diffusion out of the low-k zone (due to a change in the concentration gradient) has decreased concentrations near the low-k interface.

The modeling suggests that an appreciable decline in the source strength has occurred over time as a result of significant attenuation at this location. Consequently, monitored natural attenuation may be an appropriate site remedy.

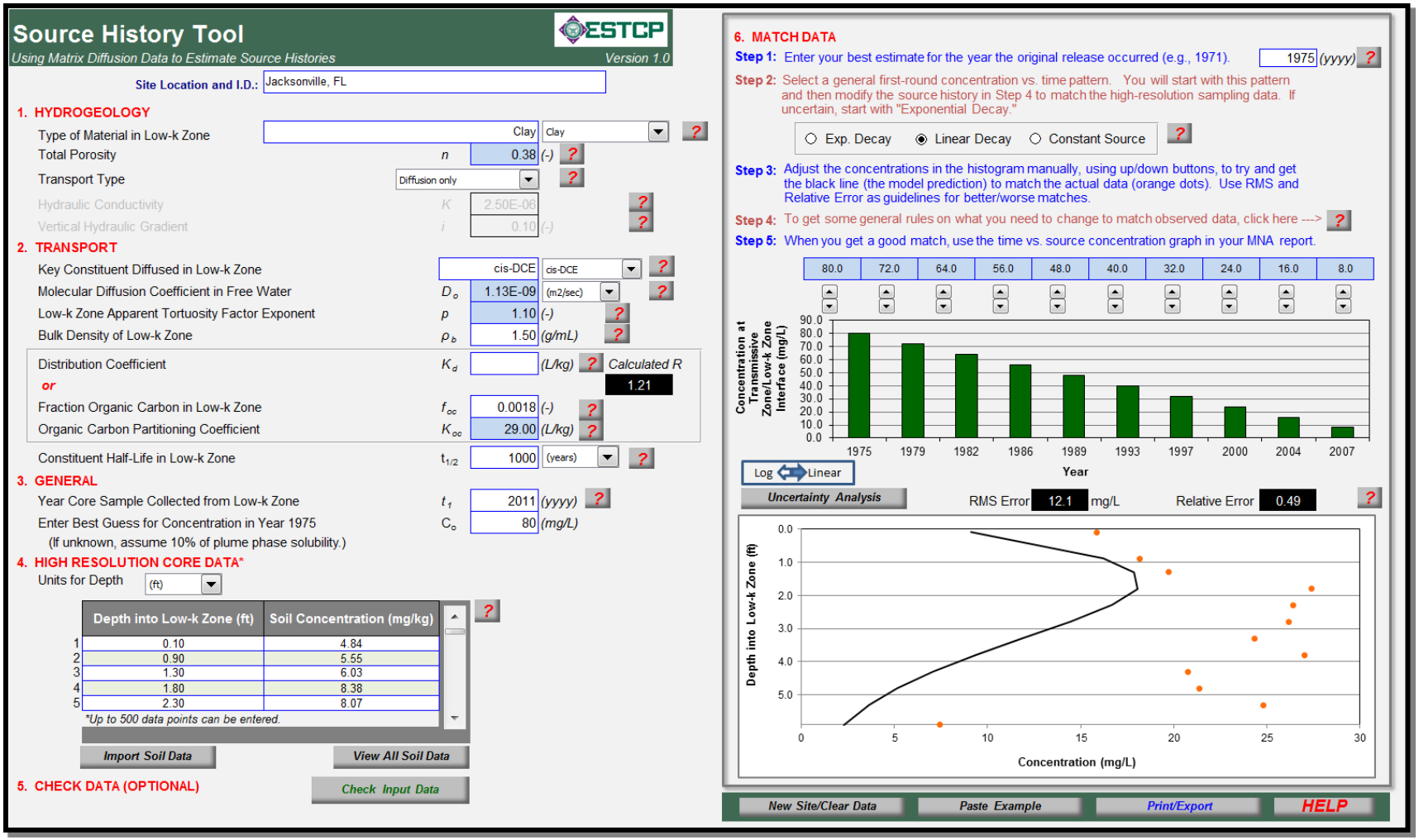

Figure 2.2. Initial Model for Case Study 2.

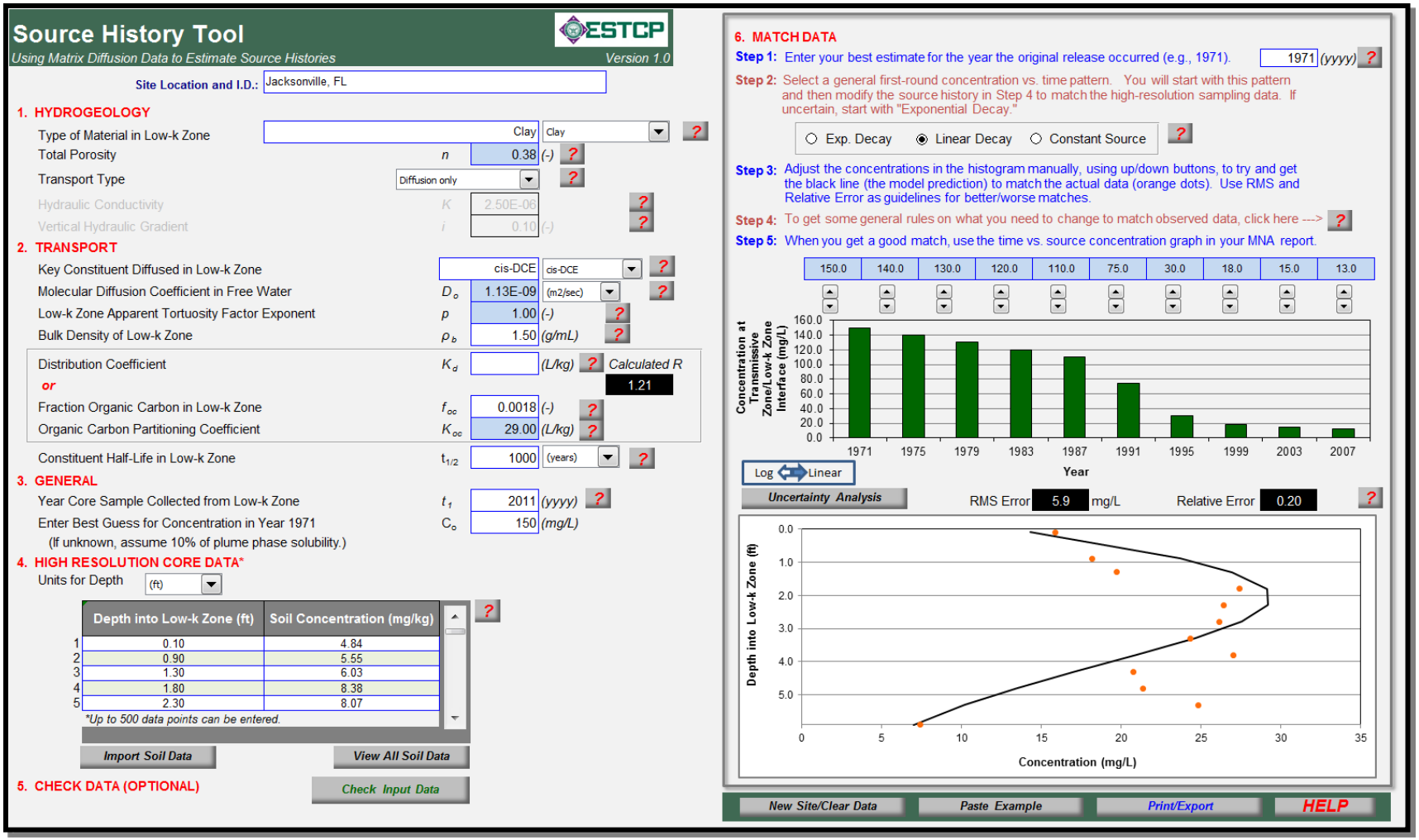

Figure 2.3. Calibrated Model for Case Study 2.

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