Monitored Natural Attenuation (MNA) Rate Constant Estimator

USER'S GUIDE
ER-201730

October 2021

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
June 9, 2021

2. REPORT TYPE
ESTCP User's Guide

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Monitored Natural Attenuation (MNA) Rate Constant Estimator

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER ER-201730

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

ER-201730

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
ESTCP
4800 Mark Center Drive, Suite 16F16
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)

ESTCP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
ER-201730

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

The MNA Rate Constant Estimator is a screening model that simulates natural attenuation of dissolved compounds in groundwater. The software has been programmed using the Microsoft Excel platform and has the ability to simulate 3-D solute transport that incorporates advection-dispersion, linear adsorption, and various transformation processes using a modification of the analytical solutions developed by Wexler (1992). It includes three different modules:
1. Solute transport of 1,4-dioxane with biotransformation via an oxidative pathway
2. Solute transport of chlorinated ethenes (PCE, TCE, cis-1,2-DCE, and VC) with biotransformation modeled as a sequential first-order reductive dechlorination process
3. Solute transport of chlorinated ethanes (1,1,1-TCA, 1,1-DCA) and 1,1-DCE with two degradation pathways: i) biotransformation modeled as a sequential first-order reductive dechlorination; ii) abiotic hydrolysis/dehydrohalogenation of 1,1,1-TCA
GSI Environmental Inc. (GSI) developed the software for the Environmental Security Technology Certification Program (ESTCP) as part of Project Number ER-201730. It is designed to support an evaluation of MNA using BioPIC, but it also functions effectively as a standalone tool.

15. SUBJECT TERMS
1,4-dioxane, attenuation, model, MNA, biodegradation, chlorinated solvents, 1,1-DCE, 1,1,1-TCA, 1,1-DCA

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Anthony Danko
a. REPORT UNCLASS	**b. ABSTRACT** UNCLASS	**c. THIS PAGE** UNCLASS	UNCLASS	28	**19b. TELEPHONE NUMBER** *(include area code)* 805-982-4805

MONITORED NATURAL ATTENUATION (MNA) RATE CONSTANT ESTIMATOR

WHAT THIS SOFTWARE TOOL DOES

- Estimates degradation rate constants for multiple different types of contaminants based on field data (e.g., concentration vs. distance, biomarker abundance correlations) using a simple groundwater fate and transport model
- Generates lines of evidence to support a site-specific evaluation of monitored natural attenuation (MNA)

DISCLAIMER

The MNA Rate Constant Estimator is available "as is". Considerable care has been exercised in preparing this manual and software product; however, no party, including without limitation the United States Government, GSI Environmental Inc., the authors and reviewers, make any representation or warranty regarding the accuracy, correctness, or completeness of the information contained herein, and no such party shall be liable for any direct, indirect, consequential, incidental or other damages resulting from the use of this product or the information contained herein. Information in this publication is subject to change without notice. Implementation of the tool and interpretation of the predictions of the models are the sole responsibility of the user.

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ACKNOWLEDGEMENTS

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HOW TO CITE:

MNA Rate Constant Estimator, 2021:
C.J. Newell, A. Zaleski, B.A. Strasert, P.C. deBlanc, Wilson, J.T., and D.T. Adamson. Project ER-201730, Environmental Security and Technology Certification Program (ESTCP), Arlington, Virginia. April 2021. www.serdp-estcp.org

Final Project Report:
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201730

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OVERVIEW

The MNA Rate Constant Estimator is a screening model that simulates natural attenuation of dissolved compounds in groundwater. The software has been programmed using the Microsoft Excel platform and has the ability to simulate 3-D solute transport that incorporates advection-dispersion, linear adsorption, and various transformation processes using a modification of the analytical solutions developed by Wexler (1992). It includes three different modules:

1. Solute transport of ***1,4-dioxane*** with biotransformation via an oxidative pathway
2. Solute transport of ***chlorinated ethenes*** (PCE, TCE, cis-1,2-DCE, and VC) with biotransformation modeled as a sequential first-order reductive dechlorination process
3. Solute transport of ***chlorinated ethanes*** (1,1,1-TCA, 1,1-DCA) and 1,1-DCE with two degradation pathways: i) biotransformation modeled as a sequential first-order reductive dechlorination; ii) abiotic hydrolysis/dehydrohalogenation of 1,1,1-TCA

GSI Environmental Inc. (GSI) developed the software for the Environmental Security Technology Certification Program (ESTCP) as part of Project Number ER-201730. It is designed to support an evaluation of MNA using BioPIC, but it also functions effectively as a standalone tool.

INTENDED USES

This tool was designed to be similar to BIOCHLOR (USEPA) in terms of its design and application. BIOCHLOR was developed by GSI as a screening model for natural attenuation but focused primarily on chlorinated ethenes. The MNA Rate Constant Estimator has added features and increased functionality for newer versions of Excel, but it can be used to evaluate the same fundamental issues as BIOCHLOR:

Intended Use #1 - Evaluate how far a dissolved plume will extend under a natural attenuation scenario (i.e., if no engineered controls or source area reduction measures are implemented).

The tool uses an analytical solute transport model that includes options for multiple first-order degradation processes depending on the compound. The model will predict the extent of dissolved-phase plume migration over time, which may then be compared to the distance to potential points of compliance or points of exposure (e.g., drinking water wells, groundwater discharge areas, or property boundaries). Analytical ground-water transport models have seen wide application for this purpose (e.g., ASTM, 1995) and experience has shown such models can produce reliable results when site conditions in the plume area are relatively uniform. An evaluation of the plume extent requires an estimate of the rates at which compounds are being degraded, as described below.

Intended Use #2 -Determine appropriate rate constants for relevant degradation processes.

The tool provides a simple method to estimate site-specific degradation rate constants for individual compounds within a groundwater plume. It also allows users to simulate source decay to understand how plumes may expand or contract over time.

The use of an appropriate plume degradation rate constant is important because the model is typically sensitive to the magnitude of the rate constants. Although rate constants can be taken from the literature, the values reported for a given compound can vary by several orders of magnitude. Biotransformation rate constants are site-specific and will be dependent on the size of the microbial population, the availability of electron donors/acceptors/nutrients, and geochemical conditions. Many rate constants in the general literature are derived from laboratory microcosm studies under idealized conditions. Typically, these laboratory-derived values overestimate the rate of biotransformation seen in the field because of the difficulty in simulating field conditions in a laboratory environment (Aziz et al., 2000b).

The best approach for determining rate constants is to calibrate the model to field data for a given sampling event (see the **Instructions for Calibrating Model** section of this guide). Briefly, to estimate rate constants for a parent compound (e.g., PCE, 1,4-dioxane), change the rate constant for the compound until its predicted concentrations match the field data. The tool displays the Root Mean Square Error (RMSE) between the predicted concentrations and field-measured concentration, and this parameter can be used to optimize the fit. Next, change the rate constant for the next relevant daughter product until the predicted concentrations for that daughter product also match the field data. Continue estimating rate constants for the other constituents in the degradation pathway as needed. Using this approach, site-specific rate constants are estimated, and the model is then considered calibrated. Using the site-specific rate constants, predictive simulations can be conducted by increasing the simulation time to estimate future plume behavior.

To speed the calibration process for rate constants, the tool includes several options:

- Estimate rate constants based on the abundance of one or more qPCR-based biomarkers for degradation of individual compounds. These correlations have been developed using lab-based kinetic parameters and are designed to help calibrate the model. After the user chooses from a list of possible biomarkers and enters the measured abundance, the tool will generate a rate constant that can serve as a starting point for improving the fit between the actual field data and the model simulations.
- Estimate rate constants based on fitting the field concentration vs. distance data to a first order rate constant that lumps all processes. Although this has the potential to overestimate biotransformation rate constants by lumping the effects of multiple processes (including non-destructive processes), it quickly yields a reasonable first approximation of the rate constants. These rate constant estimates can be manually refined subsequently. This approach is most appropriate for parent constituents. Caution should be exercised in using this approach with daughter constituents, as daughter product generation is not accounted for in this method.

The user can also assume that the source is decaying via natural processes, including decreasing rates of dissolution from non-aqueous phase liquids, biotransformation, or any other degradation processes. Decay is modeled as a first order processes where the user estimates the date at which the release occurred, or alternatively the date when data from source area wells are first available. The user can then use the available source area data to estimate the first-order rate constant for source decay, or the user can enter their own estimates of the rate constant to help calibrate the plume data.

Intended Use #3 - Support a lines of evidence approach for evaluating MNA.

Based on existing USEPA and state protocols, establishing plume stability and documenting degradation processes and rates are key primary and secondary lines of evidence for selecting MNA as part of a site management strategy or remedy. The tool generates quantitative data that directly supports this type of approach. It was designed to be used in conjunction with BioPIC, which is another Excel-based tool that serves as a decision framework for MNA. BioPIC essentially provides a step-by-step roadmap for users to determine if MNA is appropriate for a particular site. The MNA Rate Constant Estimator provides key output data that helps answering several of the questions within BioPIC that require estimates of rates for compounds such as chlorinated ethenes, chlorinated ethanes, and 1,4-dioxane. However, the MNA Rate Constant Estimator also functions well as a standalone tool for evaluating fate and transport of these compounds.

MODEL BASIS

The model uses a modified version of the analytical solutions to 3-D solute transport equations presented in Wexler (1992). The solution assumes uniform flow within an aquifer of infinite width but finite height (to allow for reflection of dispersion at the upper and lower boundaries of the aquifer. It incorporates advection and hydrodynamic dispersion (with uniform constants), linear equilibrium adsorption, and chemical transformation (via first-order processes).

LIMITATIONS

This software tool has the following assumptions and limitations:

- As an analytical model, it assumes simple groundwater flow conditions. The model should not be applied where pumping systems create a complicated flow field. In addition, the model should not be applied where strong vertical flow gradients affect contaminant transport.
- The model assumes uniform hydrogeologic and biogeochemical conditions exist over the entire model area. Because it simplifies actual site conditions, the model should not be applied where extremely detailed, accurate results that closely match site conditions are required. More comprehensive numerical models should be applied in such cases.
- It is primarily designed for simulating the degradation of compounds via a first-order process where the rate does not change over time. This is a simplifying assumption in some cases but is generally reasonable for natural attenuation processes where concentrations are relatively dilute. In some cases, contaminants may be subject to metabolic biodegradation process in more upgradient portions of a plume where the concentration levels are high and subject to cometabolic biodegradation in more downgradient portion of the plume where the concentration levels are lower. Using a single first-order kinetic parameter to simulate the overall plume behavior in may be less accurate. In such cases, one can divide the plume into two portions and analyze them separately.
- It assumes the user is familiar with basic groundwater transport and mass balance concepts. It uses input parameters that should be easily estimated by this audience, although some guidance on parameter values is provided later in this guide.

NAVIGATION

On the home page for the MNA Rate Constant Estimator, the user can pick between several different models that are shown below in **Figure 1**. The user can select models using either the buttons or the tabs (both will lead to the same screen).

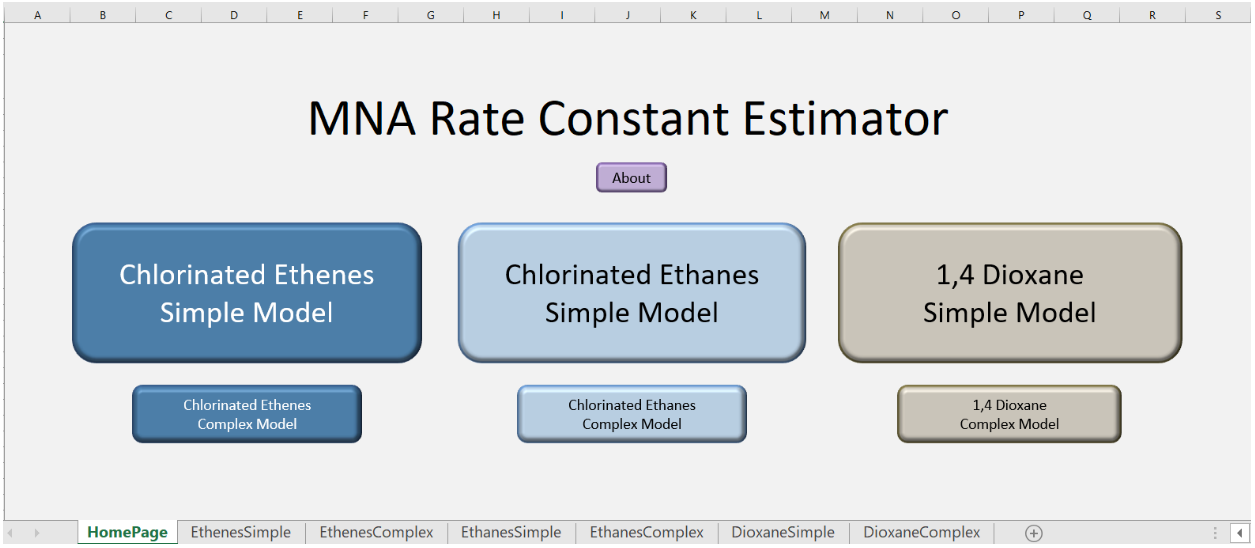


Figure 1. Home Page for MNA Rate Constant Estimator

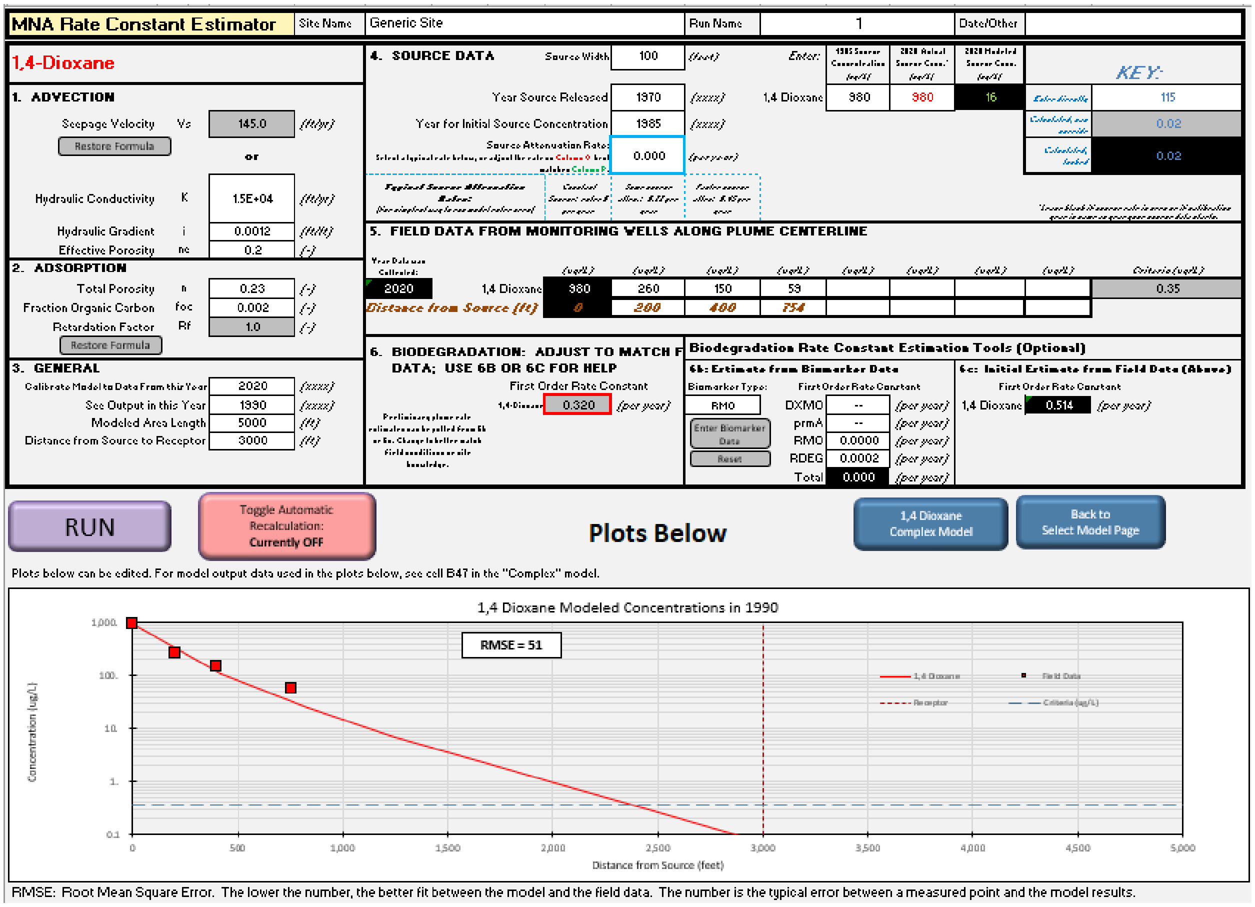
The user can evaluate chlorinated ethenes, chlorinated ethanes (plus 1,1-DCE), and 1,4-dioxane separately. There is a choice between “Simple” and “Complex” model for each set of compounds. The primary difference between the Simple and Complex models is the interface; the models themselves use the same fate and transport equations.

- Most users should choose the “Simple” models because the interface is more user-friendly and displays only the information needed to run the model. The rest of this User’s Guide focuses on how to use the “Simple” models.
- Users can choose the “Complex” model if they want more transparency on the input parameters and tabulations of various results.

DATA ENTRY (SIMPLE MODEL)

For each model, the interface is constructed so that all input and output data are shown on a single tab, although the user will need to scroll down to see the output data. Site-specific information is input on the top portion of the page in Boxes 1 – 6. In all cases, white cells represent parameters for which data can be entered directly, gray cells represent parameters for which values are calculated automatically by the tool but can be overridden, and black cells represent parameters with values that are locked (typically because they were already entered in a previous box).

The following set of screenshots from the 1,4-Dioxane Simple Model provides instructions on how data are entered. For more information on selecting parameter values, consult the Additional Help section of this User's Guide.



MNA Rate Constant Estimator

Site Name: Generic Site
Run Name: 1
Date/Other:

1,4-Dioxane

1. ADVECTION
Seepage Velocity Vs 145.0 (ft/yr)
or
Hydraulic Conductivity K 1.5E+04 (ft/yr)
Hydraulic Gradient i 0.0012 (ft/ft)
Effective Porosity ne 0.2 (-)

2. ADSORPTION
Total Porosity n 0.23 (-)
Fraction Organic Carbon foc 0.002 (-)
Retardation Factor Rf 1.0 (-)

3. GENERAL
Calibrate Model to Data From this Year 2020 (xxxx)
See Output in this Year 1990 (xxxx)
Modeled Area Length 5000 (ft)
Distance from Source to Receptor 3000 (ft)

4. SOURCE DATA
Source Width 100 (feet)
Year Source Released 1970 (xxxx)
Year for Initial Source Concentration 1985 (xxxx)
Source Attenuation Rate: 0.000 (per year)

Enter:	1985 Source Concentration (ug/L)	2020 Actual Source Conc. (ug/L)	2020 Modeled Source Conc. (ug/L)
1,4 Dioxane	980	980	16

KEY:	
Enter directly	115
Calculated, can override	0.02
Calculated, locked	0.02

5. FIELD DATA FROM MONITORING WELLS ALONG PLUME CENTERLINE

Year Data was Collected:		(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	Criteria (ug/L)
2020	1,4 Dioxane	980	260	150	59					0.35
Distance from Source (ft)		0	200	400	754					

6. BIODEGRADATION: ADJUST TO MATCH FIELD DATA; USE 6B OR 6C FOR HELP
First Order Rate Constant
1,4-Dioxane 0.320 (per year)

Biodegradation Rate Constant Estimation Tools (Optional)

6b: Estimate from Biomarker Data
Biomarker Type: RMO
First Order Rate Constant
DXMO -- (per year)
prmA -- (per year)
RMO 0.0000 (per year)
RDEG 0.0002 (per year)
Total 0.000 (per year)

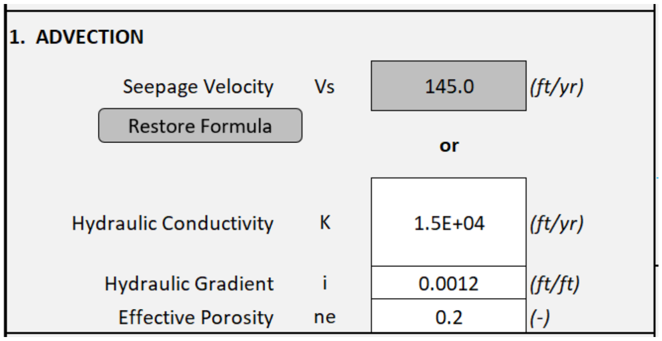
6c: Initial Estimate from Field Data (Above)
First Order Rate Constant
1,4 Dioxane 0.514 (per year)

Plots below can be edited. For model output data used in the plots below, see cell B47 in the "Complex" model.

RMSE: Root Mean Square Error. The lower the number, the better fit between the model and the field data. The number is the typical error between a measured point and the model results.

Figure 2. Interface for Simple 1,4-Dioxane Model.
Site specific data are entered in Boxes 1 – 6. Results are shown in plot at bottom of page.

Box 1 – Advection: Enter seepage velocity for groundwater directly into the grey box, if known. Alternatively, the user can enter the hydraulic conductivity, hydraulic gradient, and effective porosity, and the seepage velocity will be automatically calculated from these parameters. If the user has directly entered a seepage velocity into the gray box but would then like the tool to calculate based on the values for the other parameters, click the "Restore Formula" button. See the **Additional Help** section of this User's Guide for additional guidance on selecting appropriate parameter values.

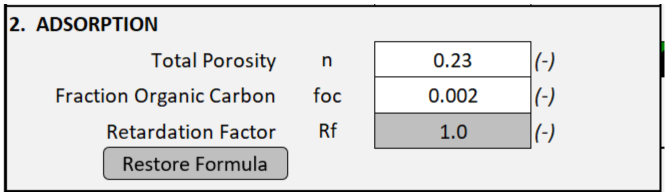


1. ADVECTION

Seepage Velocity	Vs	145.0	(ft/yr)
		or	
Hydraulic Conductivity	K	1.5E+04	(ft/yr)
Hydraulic Gradient	i	0.0012	(ft/ft)
Effective Porosity	ne	0.2	(-)

Figure 3. Box 1 Entry (Advection)

Box 2 – Adsorption: Enter the compound-specific retardation factor, if known. This reflects the ratio between the velocity of the contaminant in groundwater (which is influenced by adsorption to aquifer solids) and the groundwater seepage velocity Alternatively, the user can enter the total porosity and the fraction of organic carbon, and the tool will calculate the retardation factor based on stored K_{oc} values for the parent compound. See the **Additional Help** section of this User's Guide for additional guidance on selecting appropriate parameter values.

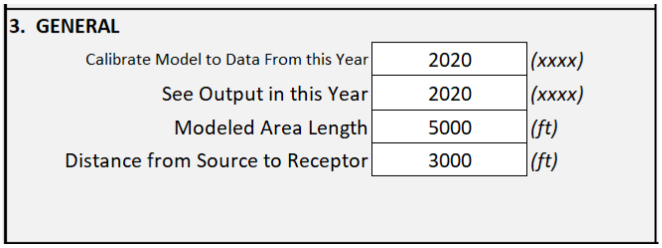


2. ADSORPTION

Total Porosity	n	0.23	(-)
Fraction Organic Carbon	foc	0.002	(-)
Retardation Factor	Rf	1.0	(-)

Figure 4. Box 2 Entry (Adsorption)

Box 3 – General: In the top row, enter the year that will be used to calibrate the model—this should correspond to one of the monitoring events with relevant data that will be entered in Box 5. In the second row, the user can select different years to show the historical plume extent or to see if the plume will expand in future years.



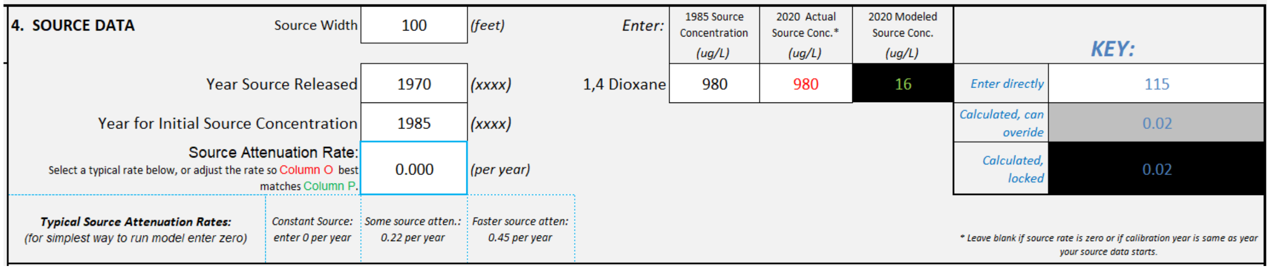
3. GENERAL

Calibrate Model to Data From this Year	2020	(xxxx)
See Output in this Year	2020	(xxxx)
Modeled Area Length	5000	(ft)
Distance from Source to Receptor	3000	(ft)

Figure 5. Box 3 Entry (General)

The user can also then specify the length of the modeled area, which should include the maximum downgradient distance that is relevant for evaluating the site (including receptors). The distance from source to receptor (or a Point of Compliance) can be entered in the final row as a visualization aid during plotting of the data.

Box 4 – Source Data: Enter relevant information for the source area. This includes the approximate width of the source and a best estimate of the year that the release occurred. The Year for Initial Source Concentration corresponds to the earliest date when concentration data are available for the monitoring location that is being designated as the source (e.g., 1985 in the screenshot above). The source concentration on that date is also entered, along with the source concentration on the date which will be used for model calibration (i.e., the date entered in the first row of Box 3).



4. SOURCE DATA

Source Width 100 *(feet)*

Year Source Released 1970 *(xxxx)*

Year for Initial Source Concentration 1985 *(xxxx)*

Source Attenuation Rate: 0.000 *(per year)*

Select a typical rate below, or adjust the rate so Column O best matches Column P.

Enter:	1985 Source Concentration *(ug/L)*	2020 Actual Source Conc.* *(ug/L)*	2020 Modeled Source Conc. *(ug/L)*
1,4 Dioxane	980	980	16

Typical Source Attenuation Rates: *(for simplest way to run model enter zero)*	*Constant Source: enter 0 per year*	*Some source atten.: 0.22 per year*	*Faster source atten: 0.45 per year*

KEY:

Enter directly	115
Calculated, can overide	0.02
Calculated, locked	0.02

** Leave blank if source rate is zero or if calibration year is same as year your source data starts.*

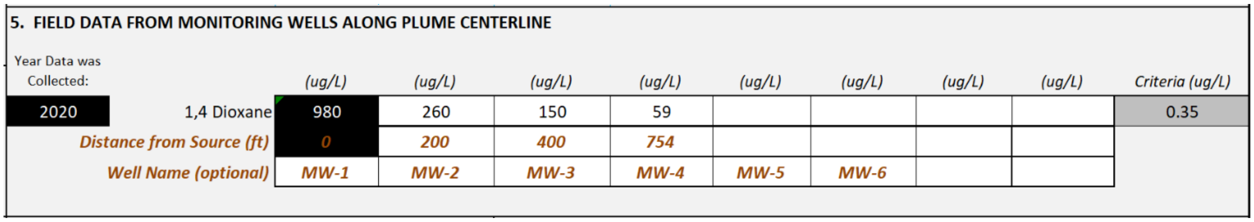
Figure 6. Box 4 Entry (Source Data)

The tool then uses these data to help determine an appropriate Source Attenuation Rate for the parent compound. The Source Attenuation Rate is based on an assumption of first-order decay, meaning that a starting point estimate of the rate can be made using the temporal and concentration data. This is done by manually adjusting the Source Attenuation Rate until the concentration in Column P (modeled source concentration) matches the concentration in Column O (actual source concentration based on field data). Note that this approach is optional; users do not have to enter values in these cells to proceed with the model. This would include cases where the Source Attenuation Rate is expected to be zero or if the calibration year is same as year as when your source data starts. However, if the modeled source concentration (Column P) is substantially different than the actual source concentration (Column O) for the year being simulated, then the calibration is less likely to be accurate.

Alternatively, the user can directly enter a Source Attenuation Rate based on a range of typical compound-specific values provided within Box 4 of the individual modules. For example, the range of Source Attenuation Rates for 1,4-dioxane span a range of 0 to 0.45 yr^{-1} based on the empirical data reported in Adamson et al. (2015).

As noted above, the user should check which of these approaches provide reasonable fit to the field data. In some cases, selecting zero for the Source Attenuation Rate may be appropriate. This would include sites where little change in the source concentration has been observed and/or the user wants to be conservative when estimating the possible extent of the plume.

Box 5 – Field Data from Monitoring Wells Along Plume Centerline: Enter the groundwater concentrations of relevant compounds in monitoring wells near the centerline of the plume. The relative distance of each monitoring location from the source well should also be entered. These data are used to help calibrate the model and are displayed with model results at the same locations.



5. FIELD DATA FROM MONITORING WELLS ALONG PLUME CENTERLINE

Year Data was Collected: 2020

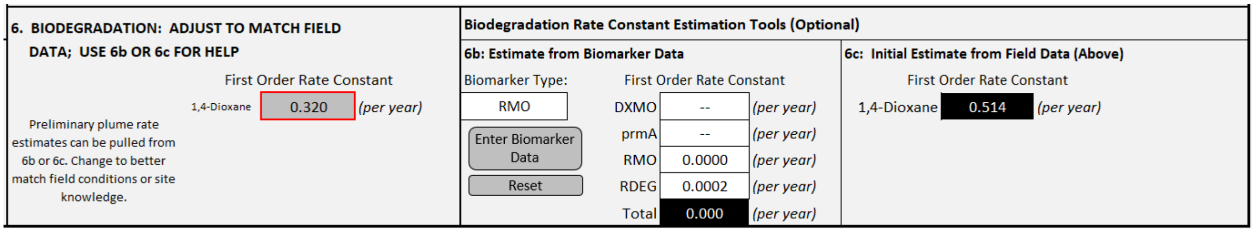
	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	Criteria (ug/L)
1,4 Dioxane	980	260	150	59					0.35
Distance from Source (ft)	*0*	*200*	*400*	*754*					
Well Name (optional)	*MW-1*	*MW-2*	*MW-3*	*MW-4*	*MW-5*	*MW-6*			

Figure 7. Box 5 Entry (Field Data)

Concentration and distance data from up to 8 wells can be entered. However, the tool can be used with data from less than 8 wells (generally 4 or more are recommended). To the extent practical, the user should enter data from a source area well (note that the tool will automatically enter the data that was used for the Source Data in Box 5) and data from a well located near the toe of the plume.

It is assumed that users will enter data that were all collected during a single monitoring event in Box 6. If users have access to data from multiple monitoring events, they can calibrate the model to obtain a biodegradation rate constant for each event, if desired (see Option 5 in the **Instructions for Calibrating Model** section).

Box 6 – Biodegradation: One of the primary uses of this tool is to estimate first-order biodegradation constant(s) that best match the observed site concentrations. The user may adopt a trial-and-error procedure to derive a best-fit decay coefficient for each contaminant by varying the decay coefficient until predicted concentrations match measured concentrations.



6. BIODEGRADATION: ADJUST TO MATCH FIELD DATA; USE 6b OR 6c FOR HELP

First Order Rate Constant

1,4-Dioxane 0.320 *(per year)*

Preliminary plume rate estimates can be pulled from 6b or 6c. Change to better match field conditions or site knowledge.

Biodegradation Rate Constant Estimation Tools (Optional)

6b: Estimate from Biomarker Data

Biomarker Type: RMO

	First Order Rate Constant	
DXMO	--	*(per year)*
prmA	--	*(per year)*
RMO	0.0000	*(per year)*
RDEG	0.0002	*(per year)*
Total	0.000	*(per year)*

6c: Initial Estimate from Field Data (Above)

First Order Rate Constant

1,4-Dioxane 0.514 *(per year)*

Figure 8. Box 6 Entry (Biodegradation)

The first order rate constant that the model uses to simulate concentration vs. distance data in highlighted in red in the main area on the left-hand side of Box 6. In other words, this rate constant (or rate constants for cases where daughter products are also considered) generates a dataset that can be used for calibration, and changes to these values are made to optimize the fit to the field data.

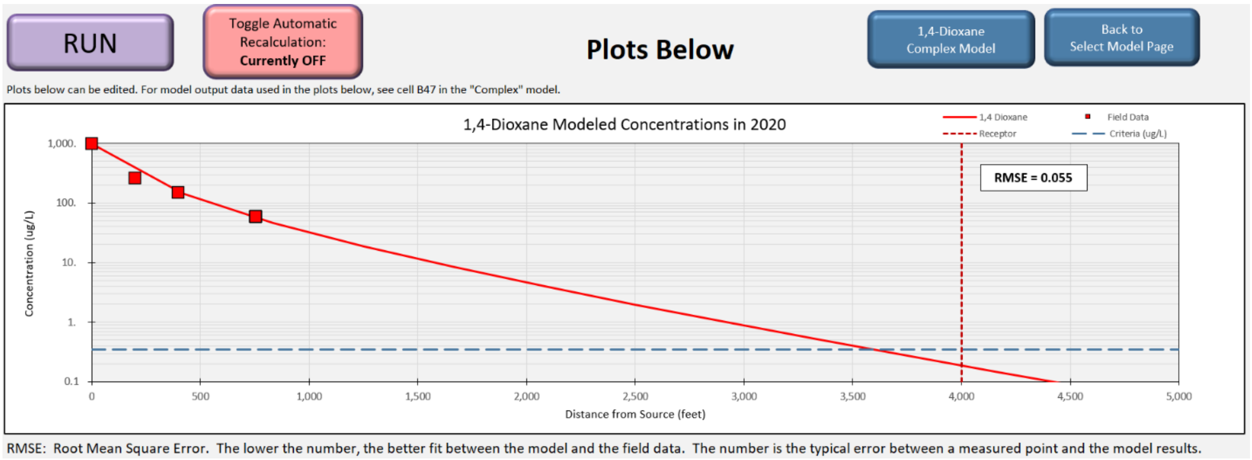
There are multiple different approaches that can be used to help estimate the rate constant(s), as discussed in the **Instructions for Calibrating Model** section. This includes entering Biomarker data in Box 6b for the compound of interest, as well as an "Initial Estimate" of the rate constant in Box 6c that is automatically generated from the user-provided field data.

OUTPUT DATA (SIMPLE MODEL)

The results of the model simulations are shown in one or more plots that can be found at the bottom of the interface page. These plots show:

1. The simulated concentration vs. distance data as a solid line.
2. The field-measured concentration at each location as a series of points.
3. The calculated RMSE, which is used as an optimization parameter.
4. The location of the receptor (or the point of compliance) as a vertical dashed line.
5. User-specified regulatory criteria (if applicable).

These plots allow the user the visualize the plume trends with respect to receptors and regulatory criteria. Importantly, they allow the user to visualize how well the simulated data (which are based on the user-inputted biodegradation rate constant from Box 6) fit the actual field-measured concentration vs. distance data.



Plots below can be edited. For model output data used in the plots below, see cell B47 in the "Complex" model.

RMSE: Root Mean Square Error. The lower the number, the better fit between the model and the field data. The number is the typical error between a measured point and the model results.

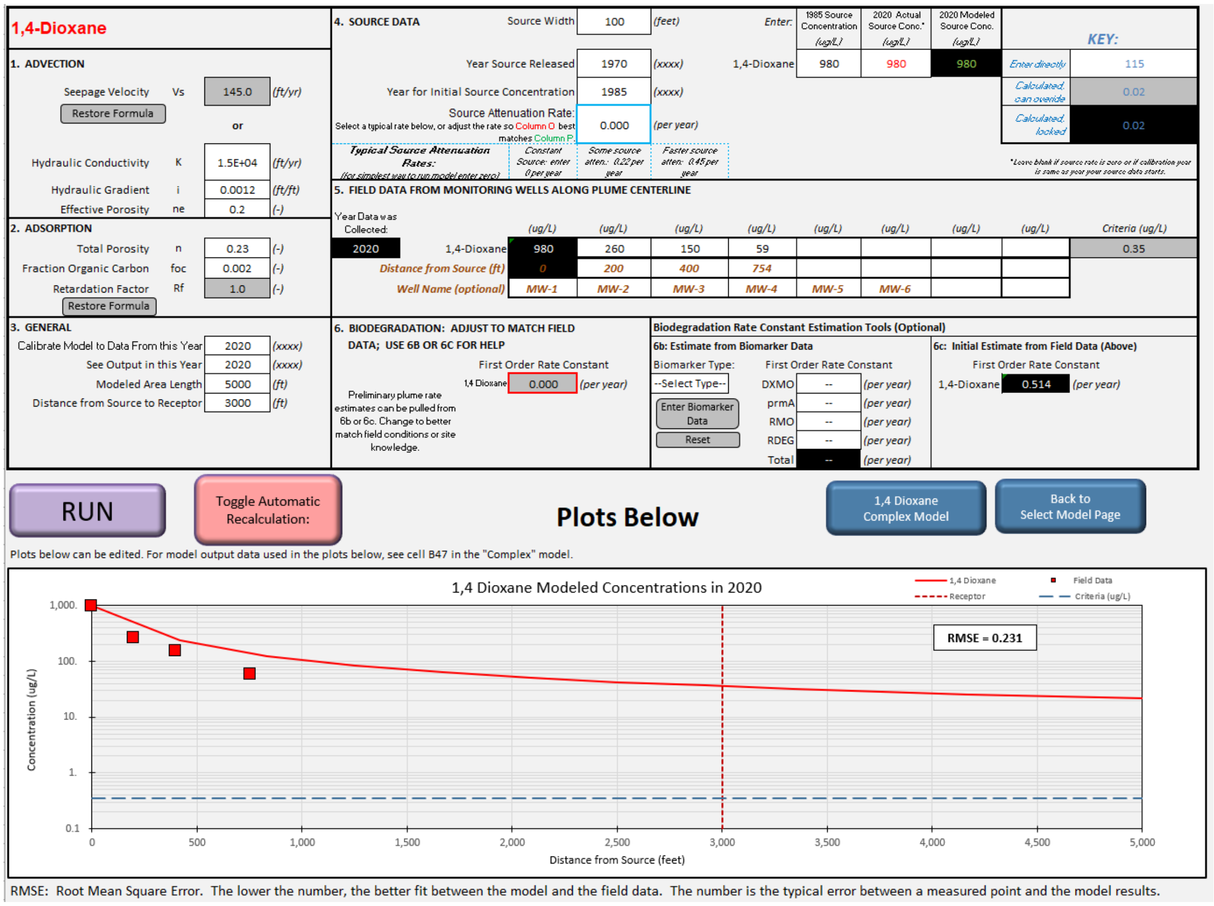
Figure 9. Output Data Plots. Concentration vs. distance are shown for a single year to allow for comparison between simulated data (solid red line) and field-measured data (square points).

The model results are also located in the “Complex Model” tab for each set of compounds (generally in Columns B through F at Rows 44 through 59). These data can be copied and pasted into other Excel spreadsheets or tables for other purposes (e.g., custom plots, reporting) as needed.

INSTRUCTIONS FOR CALIBRATING MODEL

Calibrating the model is based on optimizing the fit between the field data and the simulated concentration by adjusting the biodegradation rate constant. This can be accomplished iteratively using a few different approaches, as described below:

Option 1 – Simple Iteration: Prepare a new simulation where the rate constant for degradation of the parent compound (in Box 6) is set to zero. Compare the actual field-measured concentrations of the parent compound against the simulated concentrations. This can be done by visual inspection of the concentration vs. distance plots and recording the RMSE associated with this baseline case (i.e., the root mean square error between the field data and the concentrations predicted by the model). For example, in the simulation of 1,4-dioxane presented in Figure 10, the rate constant was initially set to zero. From visual inspection of the concentration vs. distance plot, it is clear that the simulated concentrations (the solid red line) are higher at each point along the groundwater flowpath than the field data. This means that the degree of attenuation is being underestimated. The RMSE for this baseline case (0.231) should be recorded and then compared to subsequent iterations, as described below.



1,4-Dioxane

1. ADVECTION

Seepage Velocity Vs 145.0 (ft/yr)

or

Hydraulic Conductivity K 1.5E+04 (ft/yr)

Hydraulic Gradient i 0.0012 (ft/ft)

Effective Porosity ne 0.2 (-)

2. ADSORPTION

Total Porosity n 0.23 (-)

Fraction Organic Carbon foc 0.002 (-)

Retardation Factor Rf 1.0 (-)

3. GENERAL

Calibrate Model to Data From this Year 2020 (xxxx)

See Output in this Year 2020 (xxxx)

Modeled Area Length 5000 (ft)

Distance from Source to Receptor 3000 (ft)

4. SOURCE DATA

Source Width 100 (feet)

Year Source Released 1970 (xxxx)

Year for Initial Source Concentration 1985 (xxxx)

Source Attenuation Rate: 0.000 (per year)

Select a typical rate below, or adjust the rate so Column O best matches Column P.

Enter:	1985 Source Concentration (ug/L)	2020 Actual Source Conc.* (ug/L)	2020 Modeled Source Conc. (ug/L)
1,4-Dioxane	980	980	980

Typical Source Attenuation Rates: (for simplest way to run model enter zero)	Constant Source: enter 0 per year	Some source atten.: 0.22 per year	Faster source atten.: 0.45 per year

KEY:	
Enter directly	115
Calculated, can override	0.02
Calculated, locked	0.02

*Leave blank if source rate is zero or if calibration year is same as year your source data starts.

5. FIELD DATA FROM MONITORING WELLS ALONG PLUME CENTERLINE

Year Data was Collected:		(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	Criteria (ug/L)
2020	1,4-Dioxane	980	260	150	59					0.35
	Distance from Source (ft)	0	200	400	754					
	Well Name (optional)	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6			

6. BIODEGRADATION: ADJUST TO MATCH FIELD DATA; USE 6B OR 6C FOR HELP

First Order Rate Constant

1,4 Dioxane 0.000 (per year)

Preliminary plume rate estimates can be pulled from 6b or 6c. Change to better match field conditions or site knowledge.

Biodegradation Rate Constant Estimation Tools (Optional)

6b: Estimate from Biomarker Data

Biomarker Type: --Select Type--

First Order Rate Constant		
DXMO	--	(per year)
prmA	--	(per year)
RMO	--	(per year)
RDEG	--	(per year)
Total	--	(per year)

6c: Initial Estimate from Field Data (Above)

First Order Rate Constant

1,4-Dioxane 0.514 (per year)

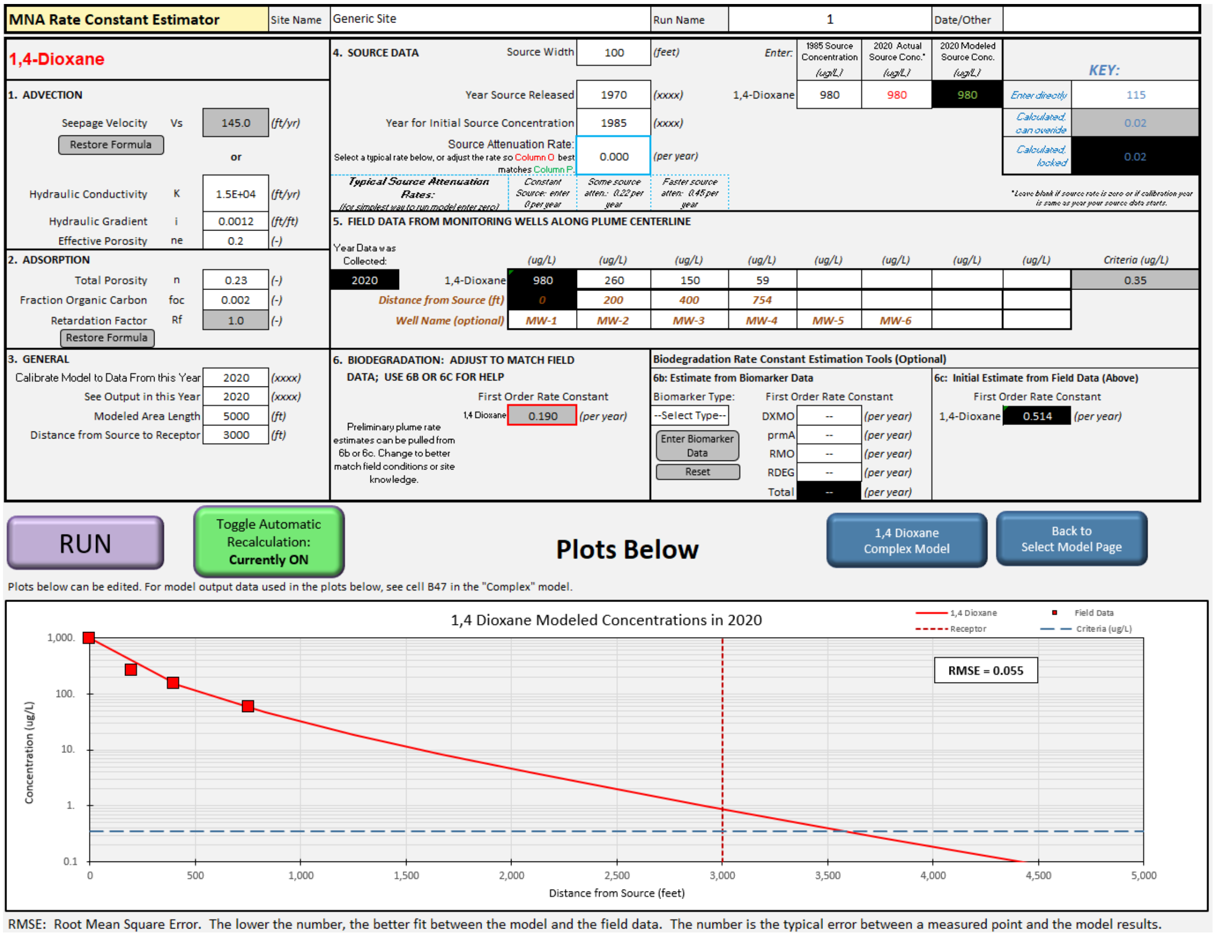
Plots Below

Plots below can be edited. For model output data used in the plots below, see cell B47 in the "Complex" model.

RMSE: Root Mean Square Error. The lower the number, the better fit between the model and the field data. The number is the typical error between a measured point and the model results.

Figure 10. Example Simulation with Assumption of No 1,4-Dioxane Biodegradation (Rate Constant = 0). Visual inspection of concentration vs. distance plot confirms that degradation is underestimated, such that model needs further calibrating.

Next, the user should enter new values for the biodegradation rate constant of the parent compound into Box 6 to determine if the resulting model projections provide a better fit to the actual field-measured concentrations. An initial guess for the rate constant can be entered manually or using one of the "starting point" guesses described in Option 2 or Option 3 below. A better fit is defined as having a lower value of RMSE. If rate constants greater than zero can be shown to provide a better fit, then the parent compound is degrading. Continue to adjust the rate constant until the RMSE is minimized. For example, Figure 11 shows the optimized rate constant (0.19 per year) for the same set of field data that was simulated in Figure 10 where it was assumed that no biodegradation was occurring. In this case, calibration resulted in an improved fit of the data, as confirmed by a significant reduction in the RSME (0.055 vs. 0.231). In this case, the degradation would be expected to reduce concentrations below the specified regulatory criteria (0.35 ug/L) by time the plume reaches the downgradient point of compliance.



MNA Rate Constant Estimator
Site Name: Generic Site
Run Name: 1
Date/Other:

1,4-Dioxane

1. ADVECTION
Seepage Velocity Vs 145.0 (ft/yr)
or
Hydraulic Conductivity K 1.5E+04 (ft/yr)
Hydraulic Gradient i 0.0012 (ft/ft)
Effective Porosity ne 0.2 (-)

2. ADSORPTION
Total Porosity n 0.23 (-)
Fraction Organic Carbon foc 0.002 (-)
Retardation Factor Rf 1.0 (-)

3. GENERAL
Calibrate Model to Data From this Year 2020 (xxxx)
See Output in this Year 2020 (xxxx)
Modeled Area Length 5000 (ft)
Distance from Source to Receptor 3000 (ft)

4. SOURCE DATA
Source Width 100 (feet)
Year Source Released 1970 (xxxx)
Year for Initial Source Concentration 1985 (xxxx)
Source Attenuation Rate: 0.000 (per year)
Select a typical rate below, or adjust the rate so Column O best matches Column P.

Typical Source Attenuation Rates: (for simplest way to run model enter zero)	Constant Source: enter 0 per year	Some source atten.: 0.22 per year	Faster source atten: 0.45 per year

Enter:	1985 Source Concentration (ug/L)	2020 Actual Source Conc.* (ug/L)	2020 Modeled Source Conc. (ug/L)
1,4-Dioxane	980	980	980

*Leave blank if source rate is zero or if calibration year is same as year your source data starts.

KEY:	
Enter directly	115
Calculated, can override	0.02
Calculated, locked	0.02

5. FIELD DATA FROM MONITORING WELLS ALONG PLUME CENTERLINE

Year Data was Collected:		(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	Criteria (ug/L)
2020	1,4-Dioxane	980	260	150	59					0.35
	Distance from Source (ft)	*0*	*200*	*400*	*754*					
	Well Name (optional)	*MW-1*	*MW-2*	*MW-3*	*MW-4*	*MW-5*	*MW-6*			

6. BIODEGRADATION: ADJUST TO MATCH FIELD DATA; USE 6B OR 6C FOR HELP
First Order Rate Constant
1,4 Dioxane 0.190 (per year)
Preliminary plume rate estimates can be pulled from 6b or 6c. Change to better match field conditions or site knowledge.

Biodegradation Rate Constant Estimation Tools (Optional)

6b: Estimate from Biomarker Data
Biomarker Type: --Select Type--
First Order Rate Constant
DXMO -- (per year)
prmA -- (per year)
RMO -- (per year)
RDEG -- (per year)
Total -- (per year)

6c: Initial Estimate from Field Data (Above)
First Order Rate Constant
1,4-Dioxane 0.514 (per year)

Plots below can be edited. For model output data used in the plots below, see cell B47 in the "Complex" model.

RMSE = 0.055

RMSE: Root Mean Square Error. The lower the number, the better fit between the model and the field data. The number is the typical error between a measured point and the model results.

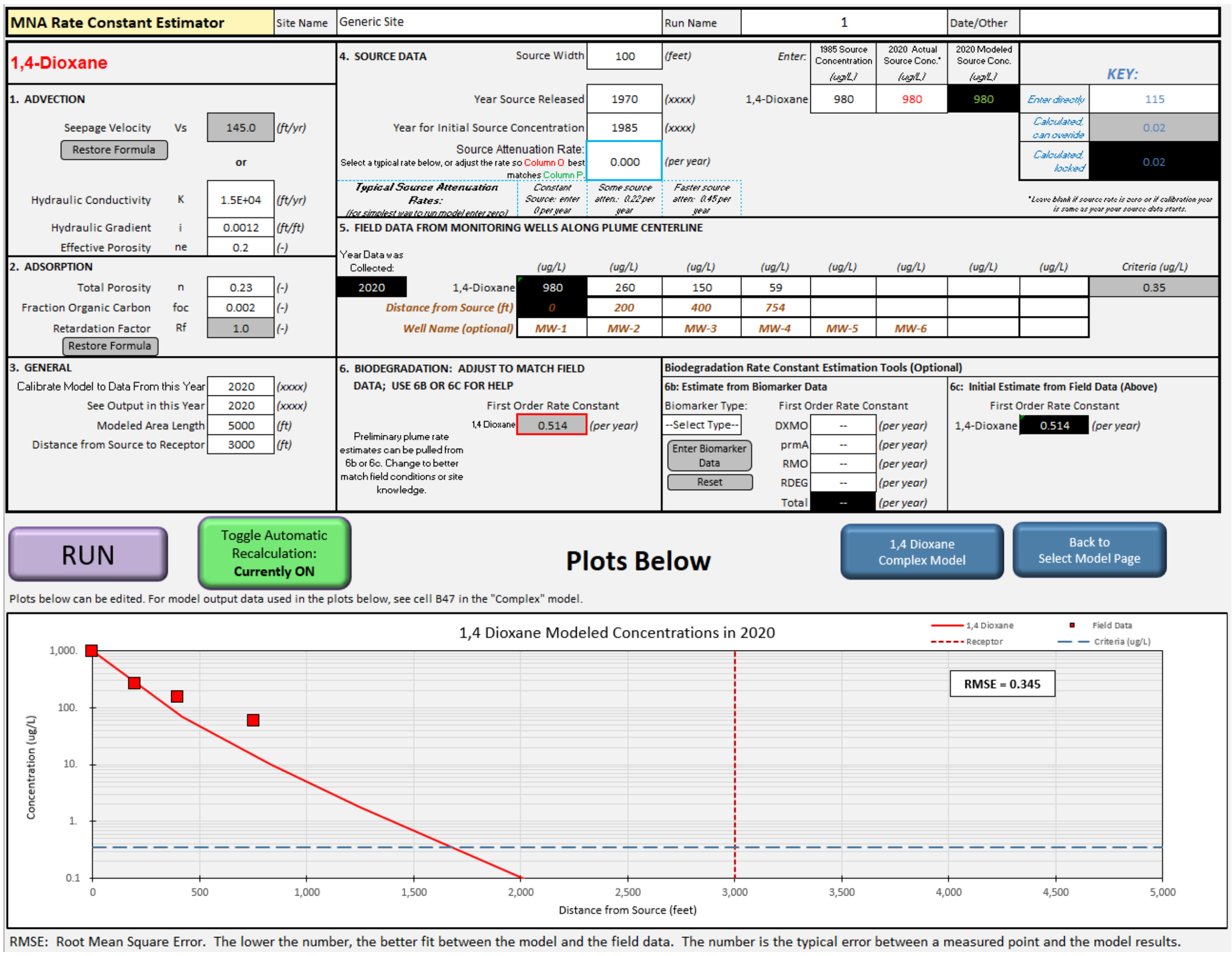
Figure 11. Example Simulation with Evidence of 1,4-Dioxane Biodegradation Based on Model Calibration (Rate Constant = 0.19 per year). Visual inspection of concentration vs. distance plot and low RMSE value confirms that model is calibrated.

For parent compounds that are degraded to daughter products that are also included in the model (e.g., TCE to cis-1,2-DCE), the next step is to change the rate constant for the next relevant daughter product until the predicted concentrations for that daughter product also match the field data. Continue estimating rate constants for the other constituents in the degradation pathway as needed. Using this approach, site-specific rate constants are estimated, and the model is then considered calibrated.

Option 1 is applicable to cases where it is (conservatively) assumed that the source is not decaying. For cases where source decay is assumed, see Option 4 below.

Option 2 – Use the "Initial Estimate" in Box 6c During Iteration: The tool automatically generates an "Initial Estimate" of the biodegradation rate constant in Box 6c from the user-provided field data. It is based on fitting the data to a first-order decay equation where the effects of processes other than biodegradation during transport are ignored. This initial estimate can be entered in Box 6 as a starting point for the iterative process of determining the rate constant that provides the best fit. The initial estimate is likely to be an upper bound estimate, such that the decreasing the rate constant should (at first) produce better RMSE values. As with Option 1, it is necessary to check all fits against the baseline case of no biodegradation (i.e., setting the rate constant of zero).

For example, Figure 12 shows the results of the simulation when the Initial Estimate (0.514 per year) was entered into Box 6. The RMSE value is higher than in the optimized case (Figure 11), and it is clear based on visual inspection that the rate constant is overestimating the extent of degradation, particularly in the far downgradient monitoring location. This suggests that the next iteration should use a lower value for the rate constant to improve the fit.



MNA Rate Constant Estimator

Site Name	Generic Site	Run Name	1	Date/Other	

1,4-Dioxane

1. ADVECTION

Seepage Velocity	Vs	145.0	(ft/yr)
or			
Hydraulic Conductivity	K	1.5E+04	(ft/yr)
Hydraulic Gradient	i	0.0012	(ft/ft)
Effective Porosity	ne	0.2	(-)

2. ADSORPTION

Total Porosity	n	0.23	(-)
Fraction Organic Carbon	foc	0.002	(-)
Retardation Factor	Rf	1.0	(-)

3. GENERAL

Calibrate Model to Data From this Year	2020	(xxxx)
See Output in this Year	2020	(xxxx)
Modeled Area Length	5000	(ft)
Distance from Source to Receptor	3000	(ft)

4. SOURCE DATA

Source Width	100	(feet)
Year Source Released	1970	(xxxx)
Year for Initial Source Concentration	1985	(xxxx)
Source Attenuation Rate: Select a typical rate below, or adjust the rate so Column O best matches Column P.	0.000	(per year)

Enter:	1985 Source Concentration (ug/L)	2020 Actual Source Conc.* (ug/L)	2020 Modeled Source Conc. (ug/L)
1,4-Dioxane	980	980	980

Typical Source Attenuation Rates: (for simplest way to run model enter zero)	Constant Source: enter 0 per year	Some source atten.: 0.22 per year	Faster source atten: 0.45 per year

KEY:

Enter directly	115
Calculated, can override	0.02
Calculated, locked	0.02

*Leave blank if source rate is zero or if calibration year is same as your your source data starts.

5. FIELD DATA FROM MONITORING WELLS ALONG PLUME CENTERLINE

Year Data was Collected:		(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	Criteria (ug/L)
2020	1,4-Dioxane	980	260	150	59					0.35
	Distance from Source (ft)	0	200	400	754					
	Well Name (optional)	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6			

6. BIODEGRADATION: ADJUST TO MATCH FIELD DATA; USE 6B OR 6C FOR HELP

First Order Rate Constant

1,4 Dioxane 0.514 (per year)

Preliminary plume rate estimates can be pulled from 6b or 6c. Change to better match field conditions or site knowledge.

Biodegradation Rate Constant Estimation Tools (Optional)

6b: Estimate from Biomarker Data

Biomarker Type: --Select Type--

First Order Rate Constant		
DXMO	--	(per year)
prmA	--	(per year)
RMO	--	(per year)
RDEG	--	(per year)
Total	--	(per year)

6c: Initial Estimate from Field Data (Above)

First Order Rate Constant

1,4-Dioxane 0.514 (per year)

Plots below can be edited. For model output data used in the plots below, see cell B47 in the "Complex" model.

RMSE: Root Mean Square Error. The lower the number, the better fit between the model and the field data. The number is the typical error between a measured point and the model results.

Figure 12. Example Simulation where Initial Estimate from Box 6c Used as Starting Point for 1,4-Dioxane Biodegradation (Rate Constant = 0.514 per year). Visual inspection of concentration vs. distance plot confirms that degradation is overestimated, such that model needs further calibrating.

Option 3 – Use the Biomarker Correlations in Box 6b During Iteration: The model an option to estimate rate constants based on the abundance of several different qPCR-based biomarkers for degradation. The resulting rate constant(s) are generated in Box 6c and are intended as a starting point for improving the fit between the actual field data and the model simulations. Since these correlations are designed to help calibrate the model, they should not be considered a true prediction of the actual degradation rate that is occurring at the site. This is because they are based on empirical data from other studies where conditions may be quite different than those observed at the site being evaluated.

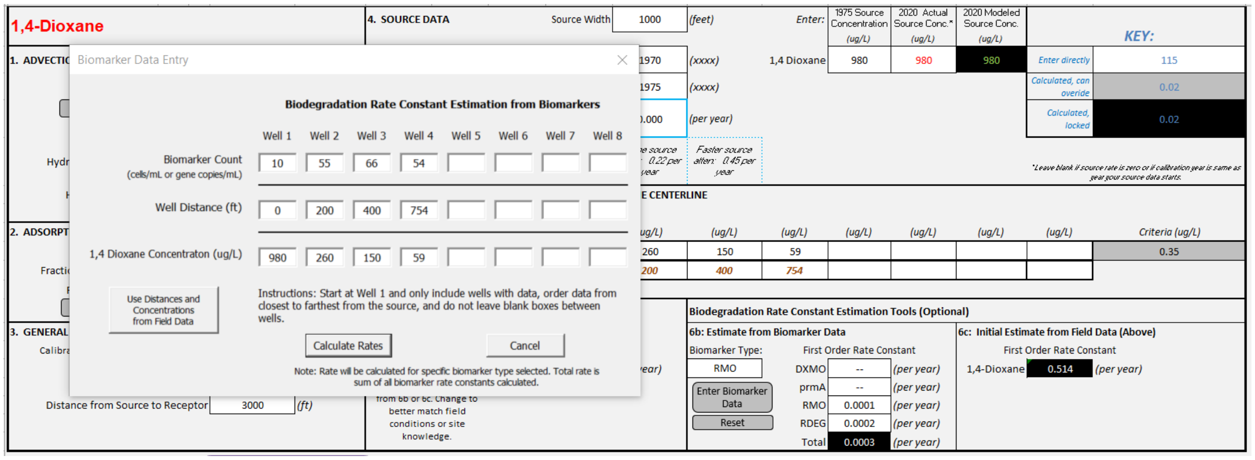
The following describes how to the biomarker correlations developed for 1,4-dioxane as part of this decision tool. A similar process can be followed for chlorinated ethenes and chlorinated ethanes using the biomarkers specific to those compounds (vcrA, Dhb).

1. In Box 6b, select a specific biomarker from the dropdown menu. For 1,4-dioxane, there is an option to enter the following biomarkers: DXMO, prmA, RDEG, and RMO. The DXMO biomarker (also known as THMXO) is associated with organisms that can grow by degrading 1,4-dioxane. The prmA biomarker (also known as PRM or PrMO) is associated with organisms that cometabolize 1,4-dioxane while growing on propane. The RDEG and RMO biomarkers are associated with organism that cometabolize 1,4-dioxane while growing on toluene, or native organic matter. Only 1 biomarker can be entered at a time; start with DXMO if available. Selecting a biomarker from the menu will launch a pop-up box where biomarker abundance data can be entered.
2. In the pop-up box, enter the abundance of the selected biomarker for those wells where data are available. The model will perform a spatial interpolation to estimate a representative biomarker abundance for the site (i.e., a single value that is weighted based on the distance between wells with biomarker data).
3. The rate constant associated with this biomarker abundance will then be automatically entered in the appropriate location in Box 6b.
4. Enter the rate constant from Box 6b into Box 6. This is the rate constant that is used for the model simulation (i.e., to generate a simulated concentration vs. distance curve).
5. The user should then evaluate the fit between the actual field data and the model simulation that is based on this estimated rate constant.
6. Manually adjust the rate constant in Box 6 until an optimal fit between the actual field data and the model simulation is obtained. Use the RMSE that is overlaid on the plot as a guide; lower RMSE values generally indicate a better fit. Record the rate constant that provided the optimal fit.
7. Return to Box 6b and repeat Steps 1 - 3 for all remaining biomarkers. In each case, record the rate constant that is generated in Box 6b (i.e., after the biomarker data are entered in the pop-up box).
8. Compare the recorded rate constants from the biomarker correlations with the “optimal” rate constant from Box 6. If the optimal rate constant from Box 6 is within a factor of 3 to 5 of one or more of the rate constants that were generated from the biomarker correlations, then this is considered reasonable evidence that this particular biodegradation process is contributing to the actual field trend in 1,4-dioxane concentrations.

9. The biomarkers target different genes in different organisms. Ideally, all the organisms could be present in the groundwater at the same time, and act on 1,4-dioxane concomitantly. Add all the rate constants associated with DXMO, prmA, RDEG, and RMO together, and if the optimal rate constant from Box 6 is within a factor of 3 to 5 of the sum of the rate constants that were generated from the biomarker correlations, then this is considered reasonable evidence that biodegradation processes are contributing to the actual field trend in 1,4-dioxane concentrations.

The derivation of these correlations is described in the project report. They are based on an assumption that aerobic biodegradation of 1,4-dioxane follows Michaelis-Menten (Haldane) kinetics (Mahendra and Alvarez-Cohen, 2006; Mahendra et al., 2013; Ye et al. 2017; Grostern et al., 2009; Parthasarathy et al., 2015). The rate equation for Michaelis-Menten kinetics can be rearranged to solve for a first-order rate constant that is a function of other kinetic parameters (specifically Km and Vmax expressed in terms of gene copies), the biomarker abundance (expressed in gene copies per mL) and the concentration of the organic chemical being degraded (in this case, 1,4-dioxane).

The calculations in the MNA rate constant estimator apply for biomarkers with known (published) kinetic parameters. Our work and the work of others shows that there are other enzyme systems that can degrade 1,4-dioxane in groundwater. However, the organisms that carry out this activity are not isolated, the enzyme systems are not characterized, and the kinetic parameters are not available. As a result, the calculations in the MNA Rate Constant Estimator based on the known biomarkers may underestimate the possible rate of biodegradation of 1,4-dioxane.



Biomarker Data Entry

Biodegradation Rate Constant Estimation from Biomarkers

	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7	Well 8
Biomarker Count (cells/mL or gene copies/mL)	10	55	66	54				
Well Distance (ft)	0	200	400	754				
1,4 Dioxane Concentraton (ug/L)	980	260	150	59				

Instructions: Start at Well 1 and only include wells with data, order data from closest to farthest from the source, and do not leave blank boxes between wells.

Note: Rate will be calculated for specific biomarker type selected. Total rate is sum of all biomarker rate constants calculated.

Source Width 1000 (feet)

Enter:	1975 Source Concentration (ug/L)	2020 Actual Source Conc.* (ug/L)	2020 Modeled Source Conc. (ug/L)
1,4 Dioxane	980	980	980

KEY:	
Enter directly	115
Calculated, can overide	0.02
Calculated, locked	0.02

*Leave blank if source rate is zero or if calibration year is same as year your source data starts.

Faster source after: 0.45 per year

(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	Criteria (ug/L)
260	150	59					0.35
200	400	754					

Distance from Source to Receptor 3000 (ft)

from 6b or 6c. Change to better match field conditions or site knowledge.

Biodegradation Rate Constant Estimation Tools (Optional)

6b: Estimate from Biomarker Data

Biomarker Type: RMO

First Order Rate Constant		
DXMO	--	(per year)
prmA	--	(per year)
RMO	0.0001	(per year)
RDEG	0.0002	(per year)
Total	0.0003	(per year)

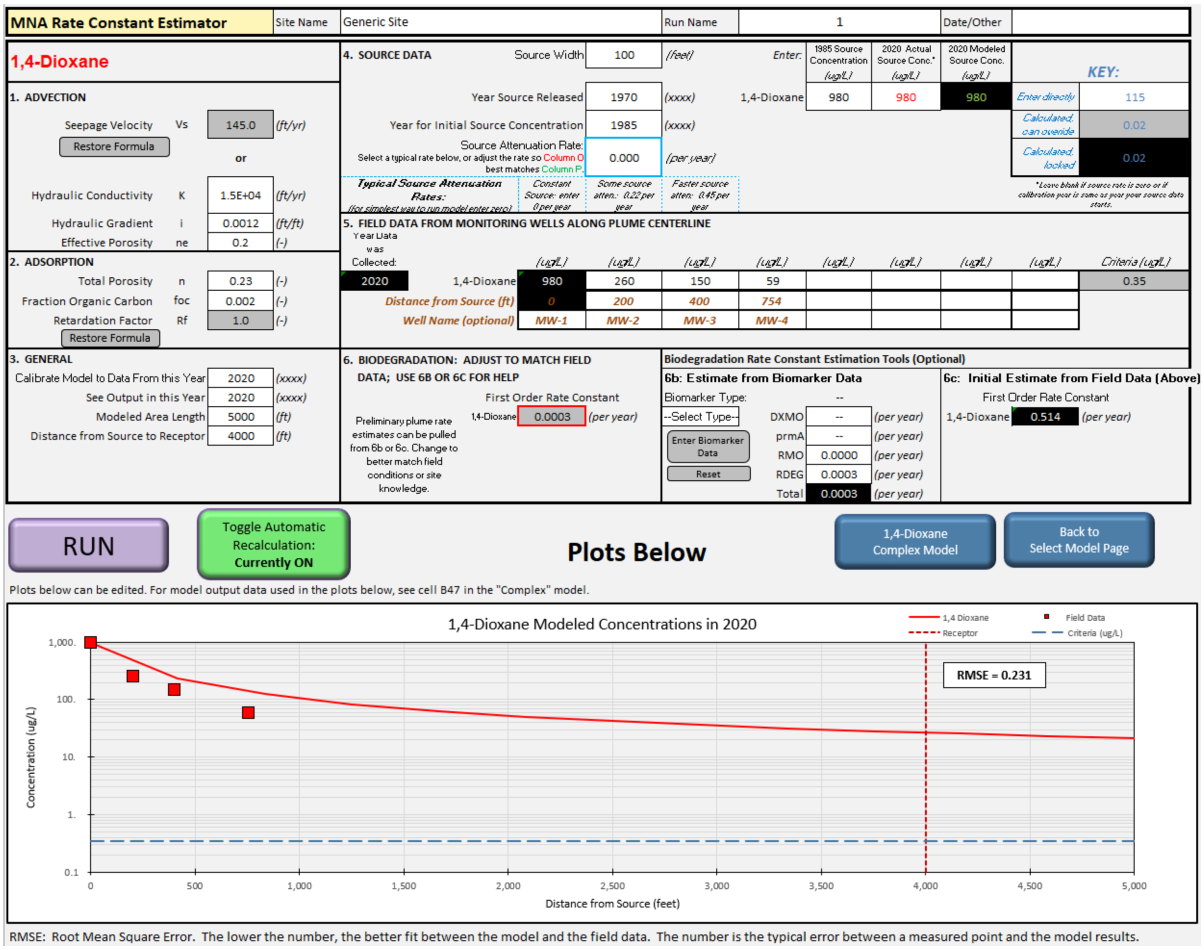
6c: Initial Estimate from Field Data (Above)

First Order Rate Constant

1,4-Dioxane 0.514 (per year)

Figure 13. Example Simulation Showing 1,4-Dioxane Biomarker Data Entry. Pop-up box for data entry is visible once the user selects the gray "Enter Biomarker Data" button in Box 6b. After entering the biomarker and 1,4-dioxane concentrations, the "Calculate Rate" button on the pop-up box will automatically enter the corresponding rate constant into Box 6b.

For example, Figure 14 shows the results of the simulation when the rate constant based on the biomarker correlations (0.0003 per year) was entered into Box 6. The RMSE value is very similar to the baseline "no biodegradation" case (Figure 10). Based on visual inspection of the concentration vs. distance data, the rate constant is clearly underestimating the extent of degradation, particularly in the far downgradient monitoring location. This suggests that the next iteration should use a higher value for the rate constant to improve the fit. Note that this finding does not mean that biodegradation is not occurring. Instead, it suggests that the correlations are not supportive for this particular case and/or that other (unquantified) enzymes are contributing to the observed biodegradation.



MNA Rate Constant Estimator | Site Name: Generic Site | Run Name: 1 | Date/Other:

1,4-Dioxane

1. ADVECTION

Seepage Velocity Vs 145.0 (ft/yr)

or

Hydraulic Conductivity K 1.5E+04 (ft/yr)

Hydraulic Gradient i 0.0012 (ft/ft)

Effective Porosity ne 0.2 (-)

2. ADSORPTION

Total Porosity n 0.23 (-)

Fraction Organic Carbon foc 0.002 (-)

Retardation Factor Rf 1.0 (-)

3. GENERAL

Calibrate Model to Data From this Year 2020 (xxxx)

See Output in this Year 2020 (xxxx)

Modeled Area Length 5000 (ft)

Distance from Source to Receptor 4000 (ft)

4. SOURCE DATA

Source Width 100 (feet)

Year Source Released 1970 (xxxx)

Year for Initial Source Concentration 1985 (xxxx)

Source Attenuation Rate: 0.000 (per year)

Select a typical rate below, or adjust the rate so Column O best matches Column P.

Typical Source Attenuation Rates: (for simplest way to run model enter zero) | Constant Source: enter 0 per year | Some source atten.: 0.22 per year | Faster source atten.: 0.45 per year

Enter:	1985 Source Concentration (ug/L)	2020 Actual Source Conc.* (ug/L)	2020 Modeled Source Conc. (ug/L)
1,4-Dioxane	980	980	980

*Leave blank if source rate is zero or if calibration year is same as year your source data starts.

KEY:	
Enter directly	115
Calculated, can override	0.02
Calculated, locked	0.02

5. FIELD DATA FROM MONITORING WELLS ALONG PLUME CENTERLINE

Year Data was Collected:		(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	Criteria (ug/L)
2020	1,4-Dioxane	980	260	150	59					0.35
	Distance from Source (ft)	0	200	400	754					
	Well Name (optional)	MW-1	MW-2	MW-3	MW-4					

6. BIODEGRADATION: ADJUST TO MATCH FIELD DATA; USE 6B OR 6C FOR HELP

First Order Rate Constant

1,4-Dioxane 0.0003 (per year)

Preliminary plume rate estimates can be pulled from 6b or 6c. Change to better match field conditions or site knowledge.

Biodegradation Rate Constant Estimation Tools (Optional)

6b: Estimate from Biomarker Data

Biomarker Type: --

--Select Type--

DXMO -- (per year)

prmA -- (per year)

RMO 0.0000 (per year)

RDEG 0.0003 (per year)

Total 0.0003 (per year)

6c: Initial Estimate from Field Data (Above)

First Order Rate Constant

1,4-Dioxane 0.514 (per year)

Plots below can be edited. For model output data used in the plots below, see cell B47 in the "Complex" model.

RMSE: Root Mean Square Error. The lower the number, the better fit between the model and the field data. The number is the typical error between a measured point and the model results.

Figure 14. Example Simulation where Biomarker Estimate from Box 6b Used as Starting Point for 1,4-Dioxane Biodegradation (Rate Constant = 0.0003 per year). Visual inspection of concentration vs. distance plot confirms that degradation is underestimated, such that model needs further calibrating.

Option 4 – Include Source Decay During Iteration: A first-order source decay assumption can be incorporated into the simulation using Box 4. This may be appropriate when the field-measured concentration in source area wells has been observed to decline during the available monitoring period. In these cases, a starting point estimate of the rate can be made using the temporal and concentration data by manually adjusting the Source Attenuation Rate until the concentration in Column P (modeled source concentration) matches the concentration in Column O (actual source concentration based on field data). Alternatively, the user can directly enter a Source Attenuation Rate based on a range of typical compound-specific values provided within Box 6 of the individual modules.

In either case, the user should first calibrate the model by entering a field-measured parent concentration for the source area well (i.e., Column J in Box 5) for the specific year that is being used for calibration (e.g., 2020). This will ensure that the biodegradation rate constant in Box 6 (which represents biodegradation in the plume) is properly calibrated. The user can then do further simulation where source decay is included to see how this parameter influences source and plume trends.

Option 5 – Simple Iterations Using Data from Multiple Events: In many cases, users may have access to data from multiple monitoring events. The user can choose to enter data from a single event and then calibrate the model to obtain a biodegradation rate constant for that event. The calibration process can then be repeated using data from other events, such that different rate constant estimates are generated for each event. The primary advantages of this approach include the following:

- The user can obtain a range of plausible rate constants.
- It helps quantify the variability (or uncertainty) associated with this process and can support statistical testing to confirm that the biodegradation rate constant is greater than zero
- It may help in evaluating if data from certain wells or events are outliers.

Alternatively, the user could convert data from multiple events into set of average values (e.g., arithmetic mean or geomean) for each well. This approach may be useful if the user is trying to identify a single biodegradation rate constant that could be considered representative for a certain time period. However, it may not be as applicable at sites where plumes are rapidly expanding or where other significant changes have been observed over that period. It is likely more applicable for data collected from closely spaced monitoring events (e.g., over the course of a few quarters or years) after the plume footprint has already been established.

EVALUTING PLUME EXTENT OVER TIME

The user can use this tool to simulate how the plume extent changes over time due to transport and degradation processes (including source decay). This is particularly useful for predicting how far a dissolved plume will extend under a natural attenuation scenario assuming no other remedies are implemented. This distance can then be compared to the distance where receptors or compliance points are located. It is also useful for determining if a plume is at steady state and/or expected to contract over time.

For example, the 1,4-dioxane simulation for the example site shown in Figures 10 – 14 was repeated using the calibrated biodegradation rate constant (0.19 per year) and no source decay. In this case, the plume extent was plotted in multiple different years by changing the "See Output in this Year" field in Box 3 of the model interface. Figure 15 shows the progression in the plume footprint in 10-year intervals between 1980 and 2020. These simulations predict that the plume is stable in 2020, and that it reached its maximum extent between 2010 and 2020. This outcome is the result of attenuation in the plume. Since source decay is neglected in the simulation, the plume extent would not be predicted to change over time. If modest source decay was incorporated into the simulation (Box 4), then the plume would be predicted to retreat over time.

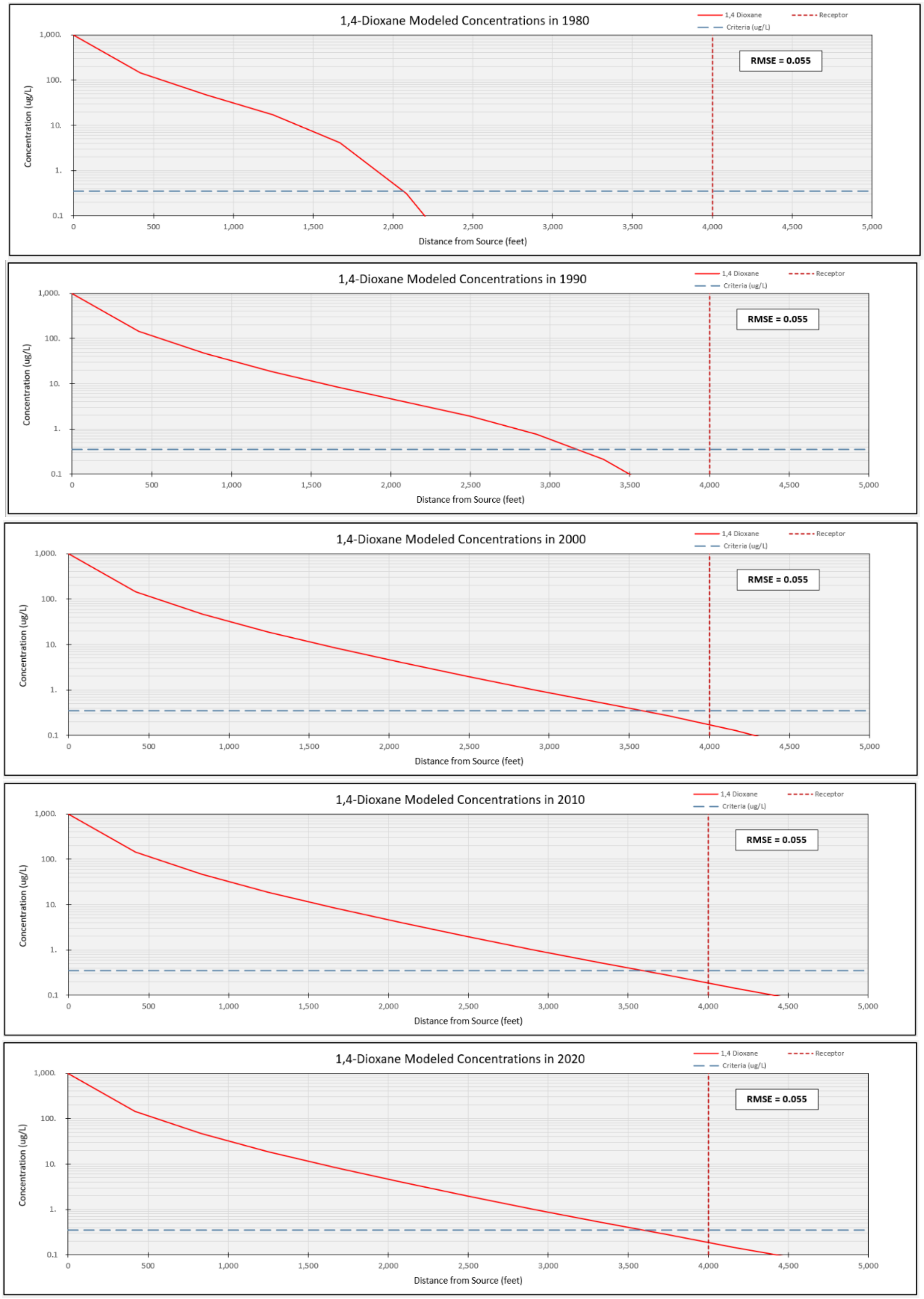


Figure 15. Example Simulation Showing 1,4-Dioxane Plume Extent Over Time (Rate Constant = 0.19 per year). Visual inspection of concentration vs. distance plots confirms that 1,4-dioxane plume would be predicted to stabilize between 2010 and 2020.

TIPS FOR TROUBLESHOOTING

- This software was developed to run on Microsoft Excel 2020. Some loss of functionality may be observed if earlier versions of Excel are used.
- Macros must be enabled for the tool to run properly. If macros are not already enabled by default, then the setting within Excel may need to be adjusted. The procedures for enabling macros will vary depending on the version of Excel that is being used to run the software. Users with security restrictions may need administrator support or approval to enable macros.
- Portions of the interface may not be visible on some screens without scrolling or adjusting the zoom level. The default zoom level was selected to accommodate most sc
- The tool was created in Excel and is not locked for editing. As a result, most features are customizable. This means that the user can adjust plot and cell dimensions based on individual preferences. In particular, the plots can be modified as needed for reporting purposes, and the data can be copied as transferred
- A “Run” button is provided for users who do not want the model to perform automatic calculations. This feature is included because calculation time(s) may take longer than a few seconds for some users, meaning that adjustments to parameter values may slow down the calibration process.
    - For users who do not want automatic calculations, they should first hit the “Toggle Automatic Recalculation” button so that it turns red and reads “Currently OFF”. Once this option is selected, no calculations will be performed unless the user hits the purple “Run” button. Both buttons are located in Rows 25 – 27 immediately above the plots.
    - For users who would prefer that simulations are updated automatically every time a parameter value is changed, they should hit the “Toggle Automatic Recalculation” once so that it reads “Currently ON” and turns green.
- In cases where the user has overridden automatic calculations of certain parameters, a “Restore Formula” button is provided so that the model will return to automatic calculations. These parameters are designated by gray cells in the interface, and they include the seepage velocity and the retardation factor. Once the formulas are restored, the parameters will again be calculated using the relevant input parameters (e.g., hydraulic conductivity, gradient, and effective porosity for the seepage velocity).

ADDITIONAL HELP

This section is primarily intended for users who want more information on selecting values for various parameters. Users should seek out additional resources as needed.

PARAMETER	**HYDRAULIC CONDUCTIVITY (K)**
Units	ft/yr
Description	Measure of the permeability of the aquifer. To characterize concentrations in the target 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 target layer should be obtained at one or more locations using appropriate slug test or pumping test methods (Newell et al., 2003).
Typical Values	*Horizontal K* Clay: $<1\times10^{-6}$ cm/s Fractured Sandstone: 1×10^{-6} - 1×10^{-2} cm/s Limestone: 1×10^{-7} - 1×10^{-4} cm/s Sandstone: 1×10^{-8} - 1×10^{-4} cm/s Shale: 1×10^{-11} - 1×10^{-7} cm/s Silt: 1×10^{-6} - 1×10^{-3} cm/s (Newell *et al*., 1996; Freeze and Cherry, 1979.)
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	Enter directly after converting to ft/yr units.

PARAMETER	**HYDRAULIC GRADIENT (i)**
Units	ft/ft
Description	The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table.
Typical Values	0.0001 – 0.05 ft/ft
Source of Data	Calculated by constructing potentiometric surface maps using static water level data from monitoring wells and estimating the slope of the potentiometric surface.
How to Enter Data	Enter directly.

PARAMETER	EFFECTIVE POROSITY (n_e)
Units	Unitless.
Description	Dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix. Note that “total porosity” is the ratio of all voids (included non-connected voids) to the bulk volume of the aquifer matrix. Differences between total and effective porosity reflect lithologic controls on pore structure. In unconsolidated sediments coarser than silt size, effective porosity can be less than total porosity by 2-5% (Smith and Wheatcraft, 1993).
Typical Values	Values for Effective Porosity: Clay 0.01 - 0.20 Sandstone 0.005 - 0.10 Silt 0.01 - 0.30 Unfractured Limestone 0.001 - 0.05 Fine Sand 0.10 - 0.30 Fractured Granite 0.00005 - 0.01 Medium Sand 0.15 - 0.30 Coarse Sand 0.20 - 0.35 Gravel 0.10 - 0.35 (From Wiedemeier et al., 1995; originally from Domenico and Schwartz, 1990 and Walton, 1988).
Source of Data	Typically estimated. One commonly used value for silts and sands is an effective porosity of 0.25. The ASTM RBCA Standard (ASTM, 1995) includes a default value of 0.38 (to be used primarily for unconsolidated deposits)
How to Enter Data	Enter directly.

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 for this parameter.
Typical Values	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.

PARAMETER	FRACTION ORGANIC CARBON (f_{oc})
Units	Unitless.
Description	Fraction of the aquifer soil matrix comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means more adsorption of organic constituents on the aquifer matrix.
Typical Values	0.0002 – 0.02
Source of Data	The organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated area and performing a laboratory analysis (e.g., ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.001 is often used (LaGrega et al., 1994).
How to Enter Data	Enter directly.

PARAMETER	RETARDATION FACTOR (R_f)
Units	Unitless.
Description	Adsorption to the soil matrix can reduce the concentration of dissolved contaminants moving through the ground water. The retardation factor is the ratio of the groundwater seepage velocity to the rate that organic chemicals migrate in the ground water. A retardation value of 2 indicates that if the ground-water seepage velocity is 100 ft/yr, then the organic chemicals migrate at approximately 50 ft/yr. The degree of retardation depends on both aquifer and constituent properties.
Typical Values	1 to 6
Source of Data	Typically estimated from soil and chemical data (using variables described below) with the following expression: $R = 1 + K_d * \rho_b / n_e$ where $K_d = K_{oc} * f_{oc}$, ρ_b = bulk density, n_e = effective porosity, K_{oc} = organic carbon-water partition coefficient, K_d = distribution coefficient, and f_{oc} = fraction organic carbon in soil When biotransformation rates are insignificant, the retardation factor can be estimated by comparing the plume length of an adsorbed compound to the plume length of a conservative (non-adsorbing) compound.
How to Enter Data	1) Enter directly; or 2) Allow the tool to calculate automatically using constituent parameter values stored in the “Complex Model” tabs

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