Implications of 1,4-Dioxane Source Attenuation and Plume Biodegradation on Its Behavior at Groundwater Sites

GSI ENVIRONMENTAL

Battelle Bioremediation Symposium 2023

11 May 2023

David T. Adamson, P.E., PhD

AGENDA / ACKNOWLEDGEMENTS

- Problem Statement
- Relevant Attenuation Processes
- Summary of Empirical Rate Data for 1,4-Dioxane
- Scenario Modeling
- When is a 1,4-Dioxane Source "Persistent"?

Maile Smith
GSI Environmental

Phil de Blanc
GSI Environmental

Tony Danko
NAVFAC EXWC

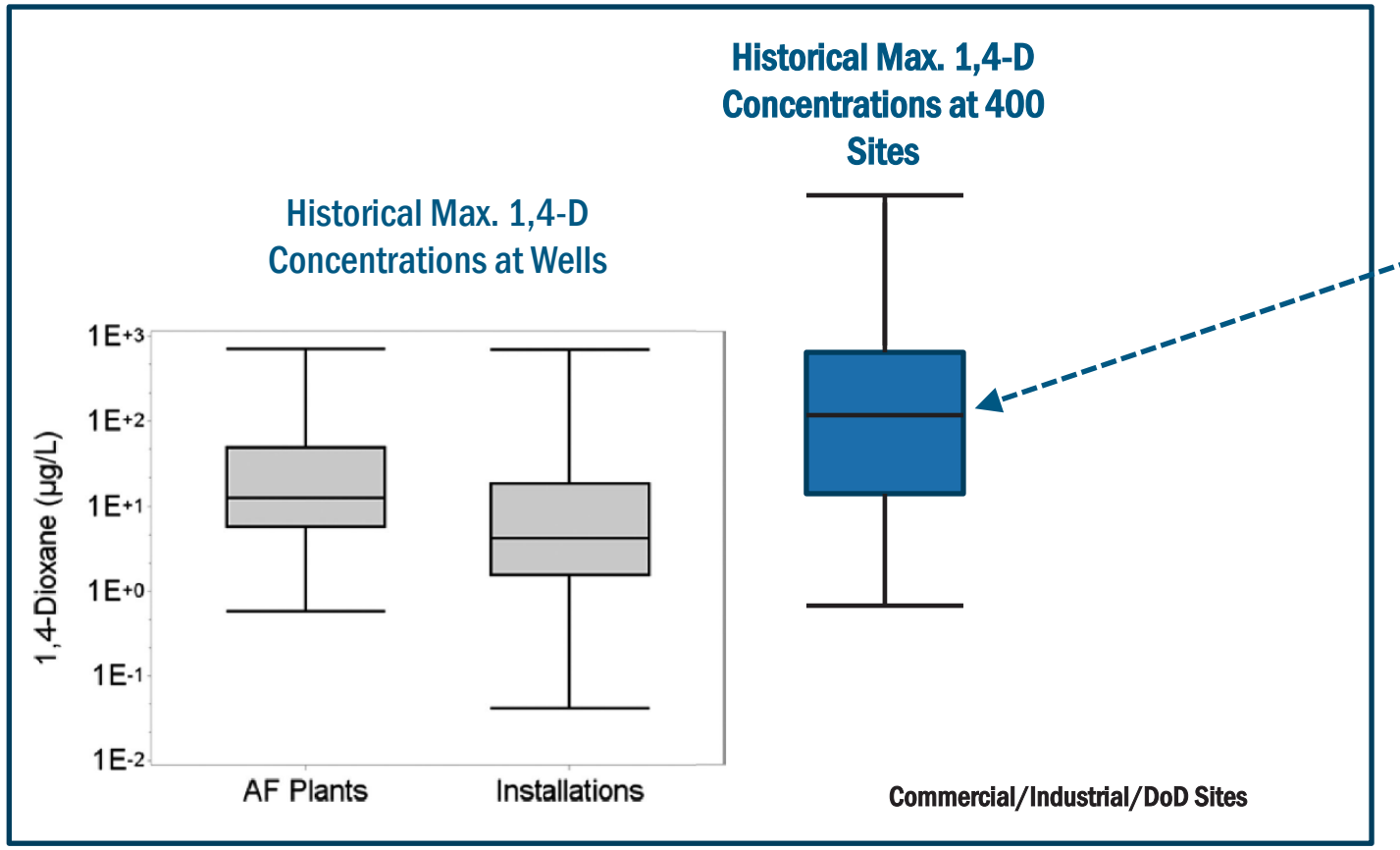
David Freedman and Angel Ramos García
Clemson University

John Wilson and Barbara Wilson
Scissortail

ESTCP ER-201730
Project Completed in 2022

Problem Statement:

1,4-Dioxane Sites are Challenging to Manage



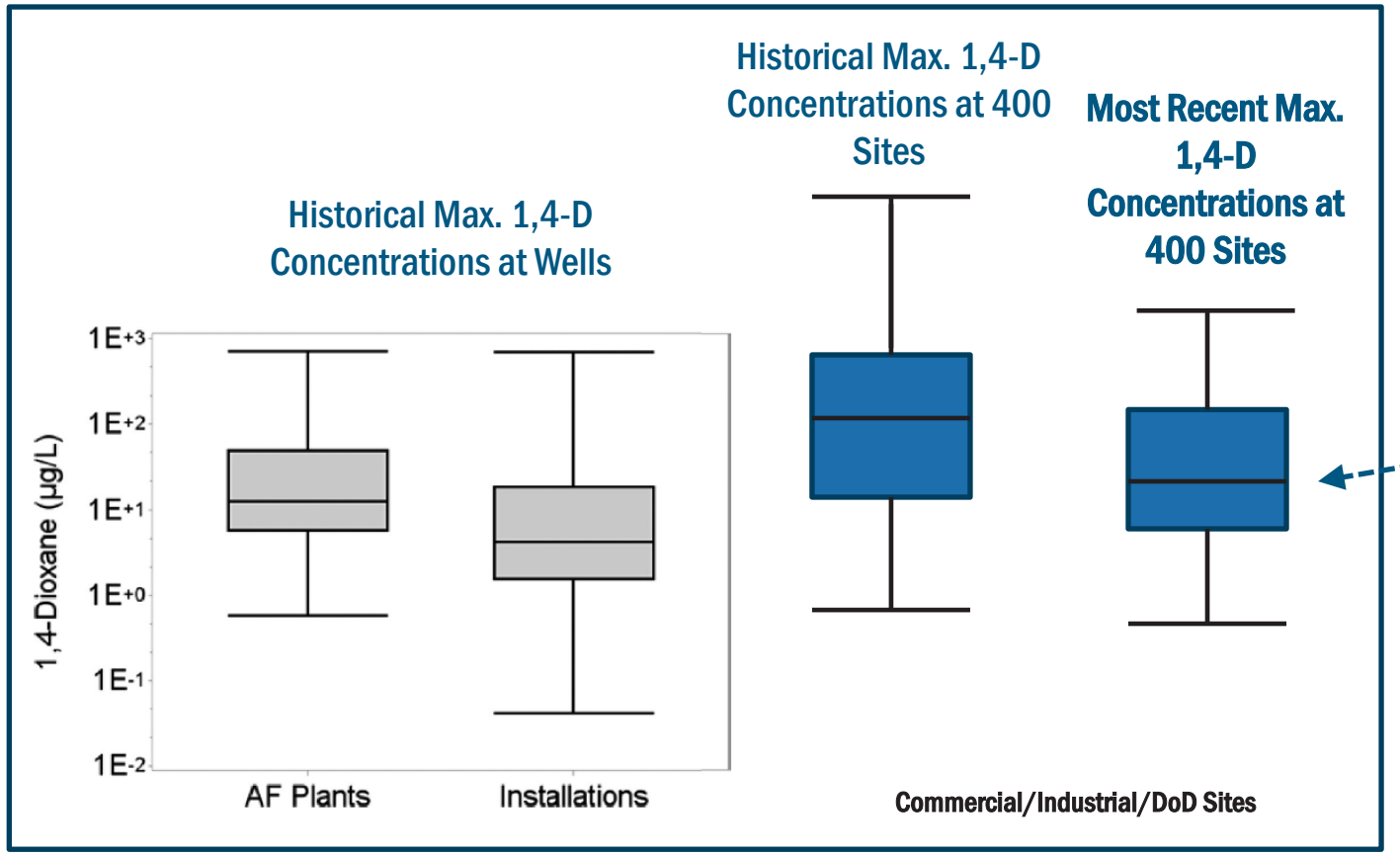
Source: Chiang, Anderson, Wilken, and Walecka-Hutchison, 2016, *Remediation*

Source: Adamson et al., 2015, *ES&T;* updated 2023 *(unpublished)*

- **1,4-D plumes are generally dilute**
  - Key concern at DoD sites
  - Recent survey of 400 primarily commercial/industrial sites: median site had historical max. concentration of **110 µg/L**
- **1,4-D plumes are often diffuse with poorly defined "source areas"**
  - Similar concentrations throughout much of plume

Problem Statement:

1,4-Dioxane Sites are Challenging to Manage



Source: Chiang, Anderson, Wilken, and Walecka-Hutchison, 2016, *Remediation*

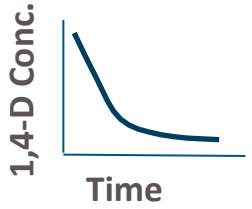
Source: Adamson et al., 2015, *ES&T;* updated 2023 *(unpublished)*

- **Long-term management using Monitored Natural Attenuation (MNA) may be an option**
  - Requires understanding of relevant attenuation processes and associated rates
  - Median of the most recent max. detections at these same sites is **17 µg/L** (decreased from 110 µg/L historical max.)
  - "Attenuation" is likely occurring, but what type?

What Processes Can Contribute to Dilute/Diffuse 1,4-Dioxane Plumes?

GSI ENVIRONMENTAL

1 ***Source depletion***

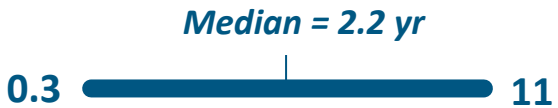


3 ***Plume biodegradation***

2 ***Migration (advection)***

- **Other considerations**
  - Low source strength?
  - Multiple and/or on-going sources?
  - Matrix diffusion?

Summary of Empirical Rate Data for 1,4-Dioxane

	Range of 1,4-D Half-Lives (yr) *(log-scale)*
1,4-D Degrading Pure Cultures *(Ramos-Garcia, Danko et al., 2022)*	
Source Attenuation Rates *(n = 22 sites + 131 wells; Adamson et al., 2015)*	
Site-Wide Biodegradation Rates *(n = 9 sites; Adamson et al., 2022)*	
Well-Specific Biodegradation Rates *(n=26 wells; Adamson et al., 2022)*	

KEY POINTS:

- 1,4-D source decay can be rapid
- 1,4-D is biodegradable, but rates can be slow and activity is location-specific

Using Rates to Model Natural Attenuation Scenarios

GSI ENVIRONMENTAL

SERDP ESTCP

Development of a Quantitative Framework for Evaluating Natural Attenuation of 1,1,1-TCA, 1,1-DCA, 1,1-DCE, and 1,4-Dioxane in Groundwater

ER-201730

POINT OF CONTACT

Anthony Danko, Ph.D.
Principal Investigator
NAVFAC EXWC
Phone: (805) 982-4805
anthony.s.danko.civ@us.navy.mil

PRODUCTS

Final Report

ER-201730 Final Report.pdf

12/8/2022

Executive Summary

ER-201730 Executive Summary.pdf

5/4/2022

User's Guide

BioPIC User's Guide and Tool

ER-201730 BioPIC User's Guide and Tool.zip

1/16/2023

User's Guide

MNA Rate Constant Estimator User's Guide and Tool

ER-201730 MNA Rate Constant Estimator User's Guide and Tool.zip

1/16/2023

Free Excel-based modeling tool:
"MNA Rate Constant Estimator"

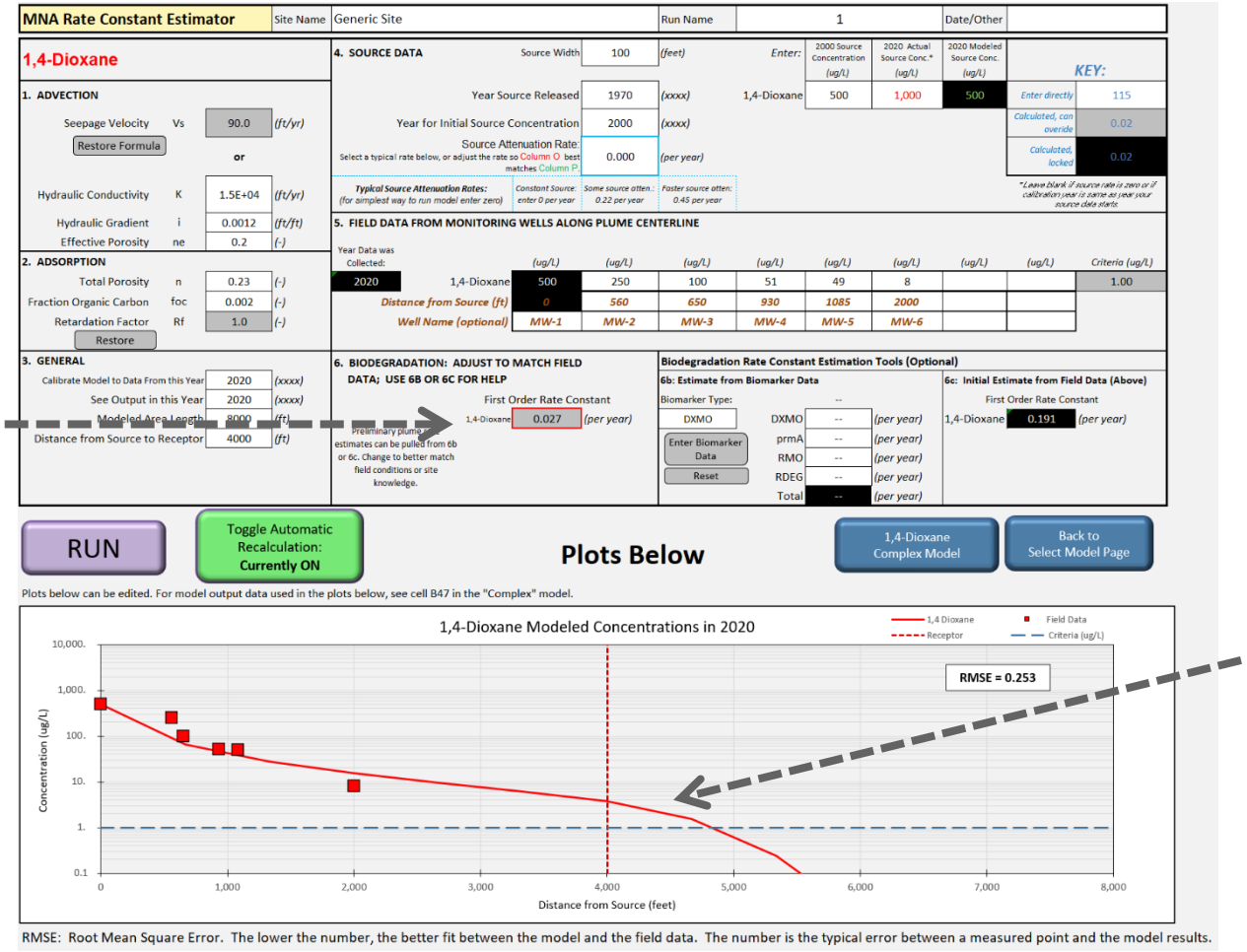
https://www.serdp-estcp.org/projects/details/bd9c56ae-002e-40fc-88cf-4a9c8566de93/er-201730-project-overview

Using Rates to Model Natural Attenuation Scenarios

GSI ENVIRONMENTAL

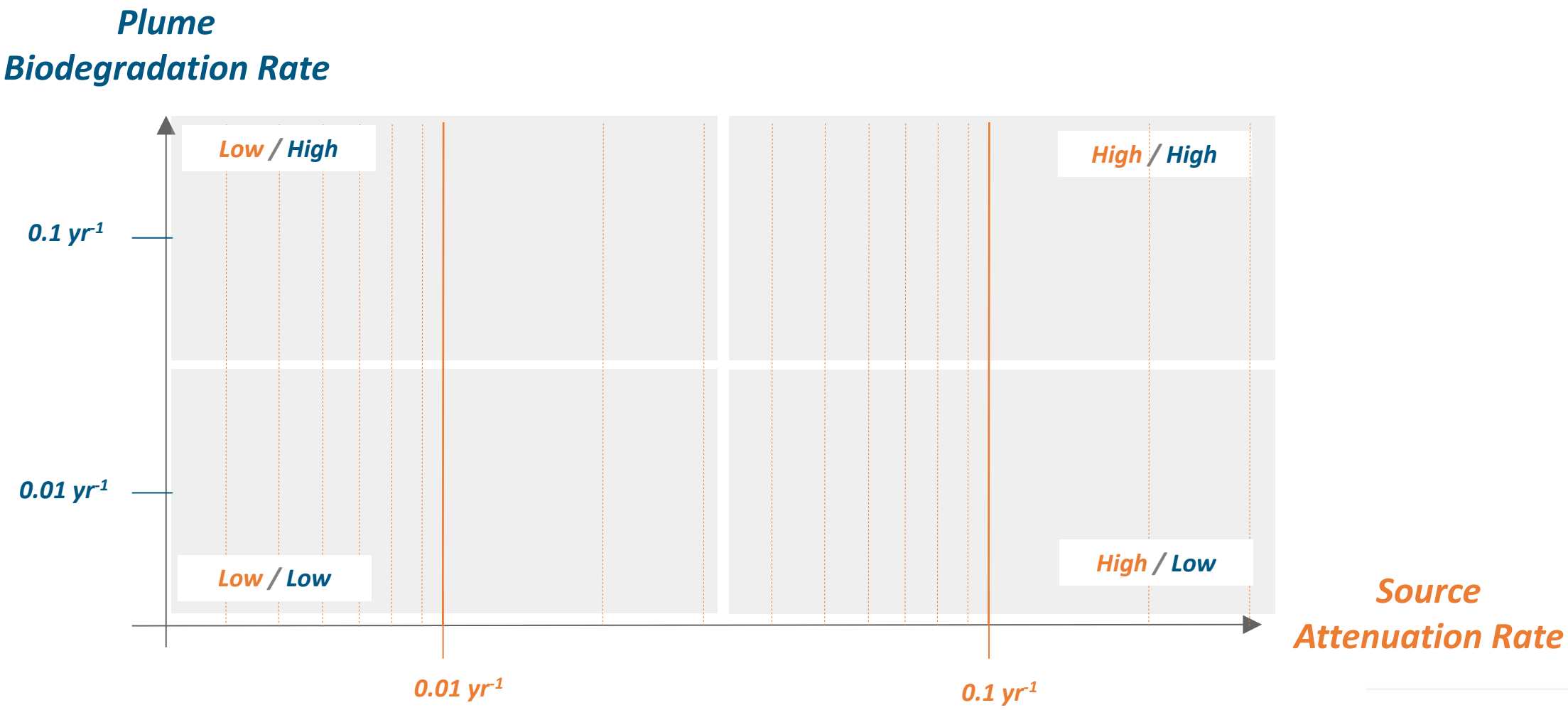
MNA Rate Constant Estimator

Intended Use #1:
Determine appropriate rate constants for relevant natural degradation processes (by calibrating model with C vs d data)

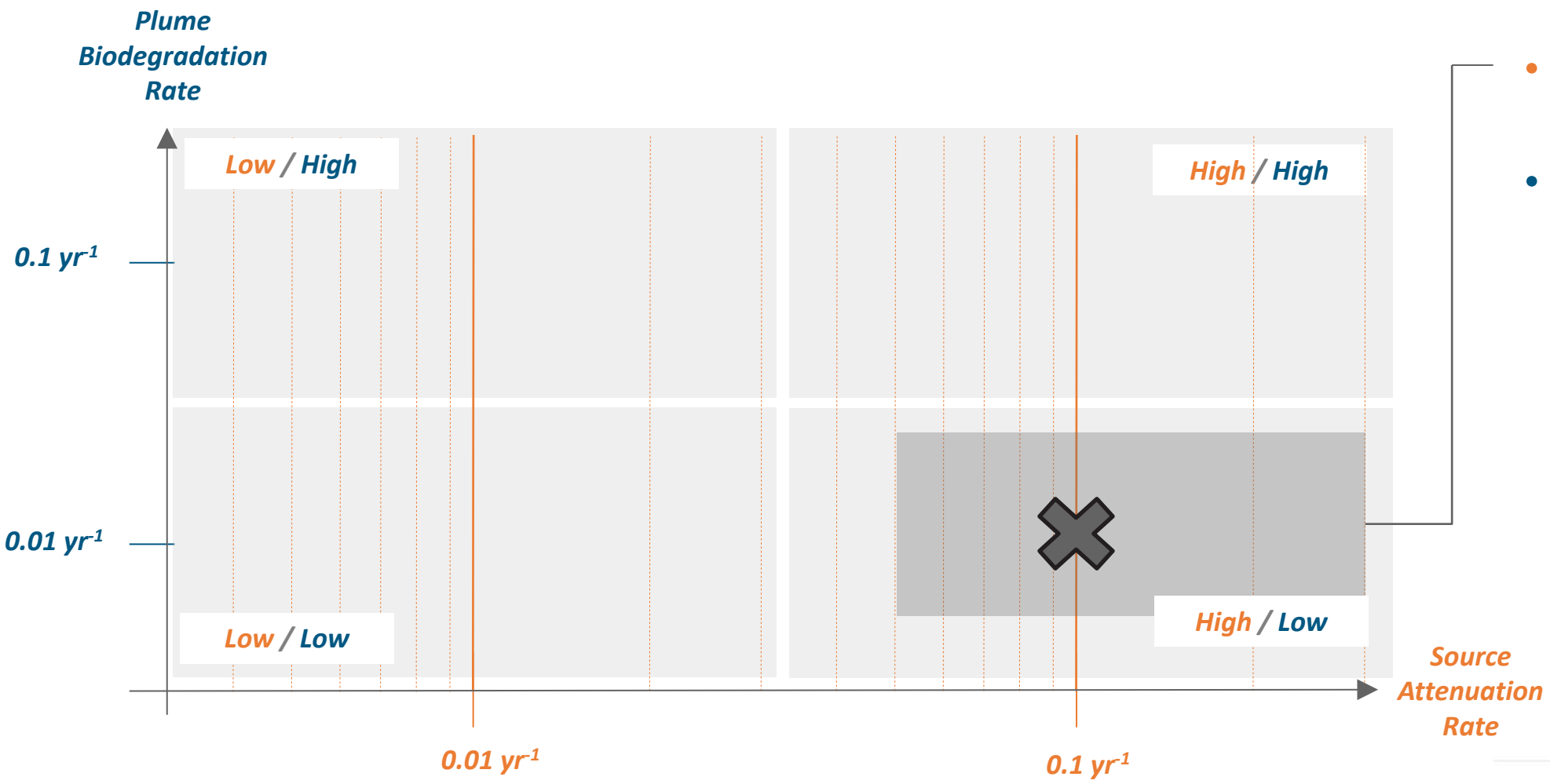


Intended Use #2:
Evaluate how far a dissolved plume will extend under natural attenuation scenario

Using Rates to Model Natural Attenuation Scenarios



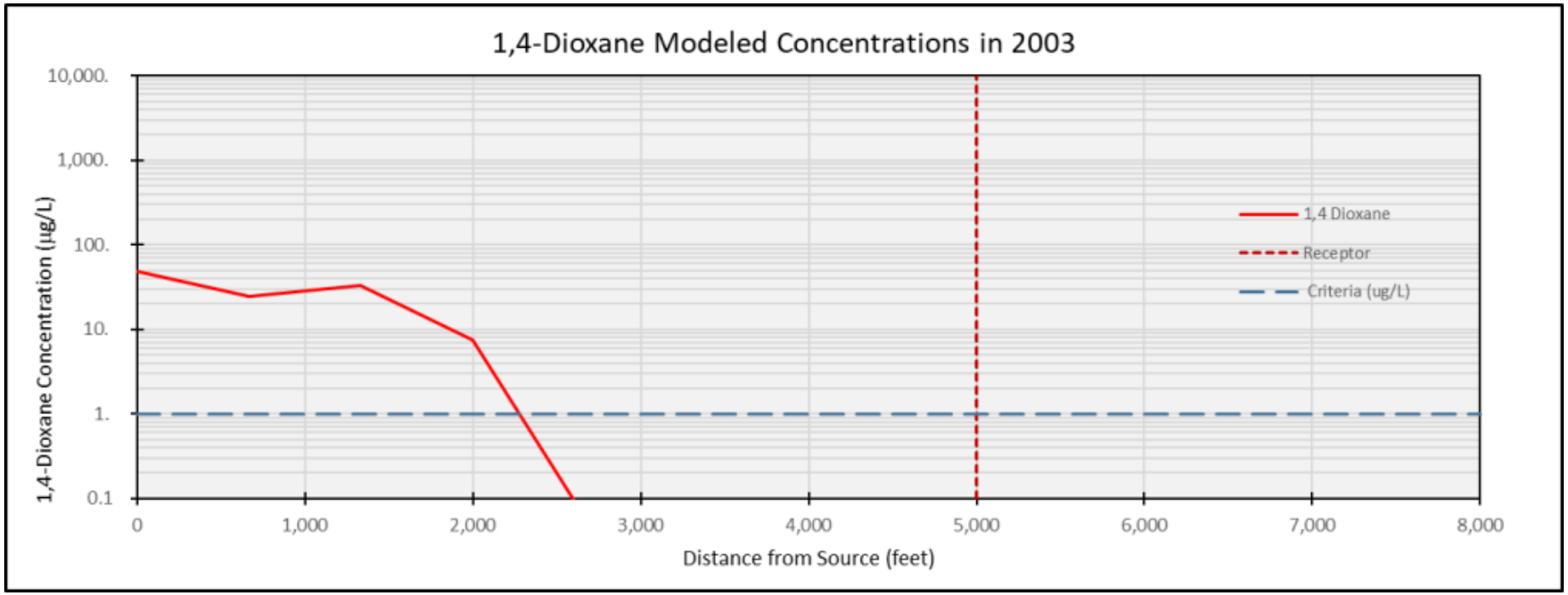
Scenario #1: "Typical" Rates for 1,4-Dioxane Based on Multi-Site Data



- High source attenuation
- Low plume biodegradation

Scenario #1: *"Typical" Rates for 1,4-Dioxane Based on Multi-Site Data*

GSI ENVIRONMENTAL



2003

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

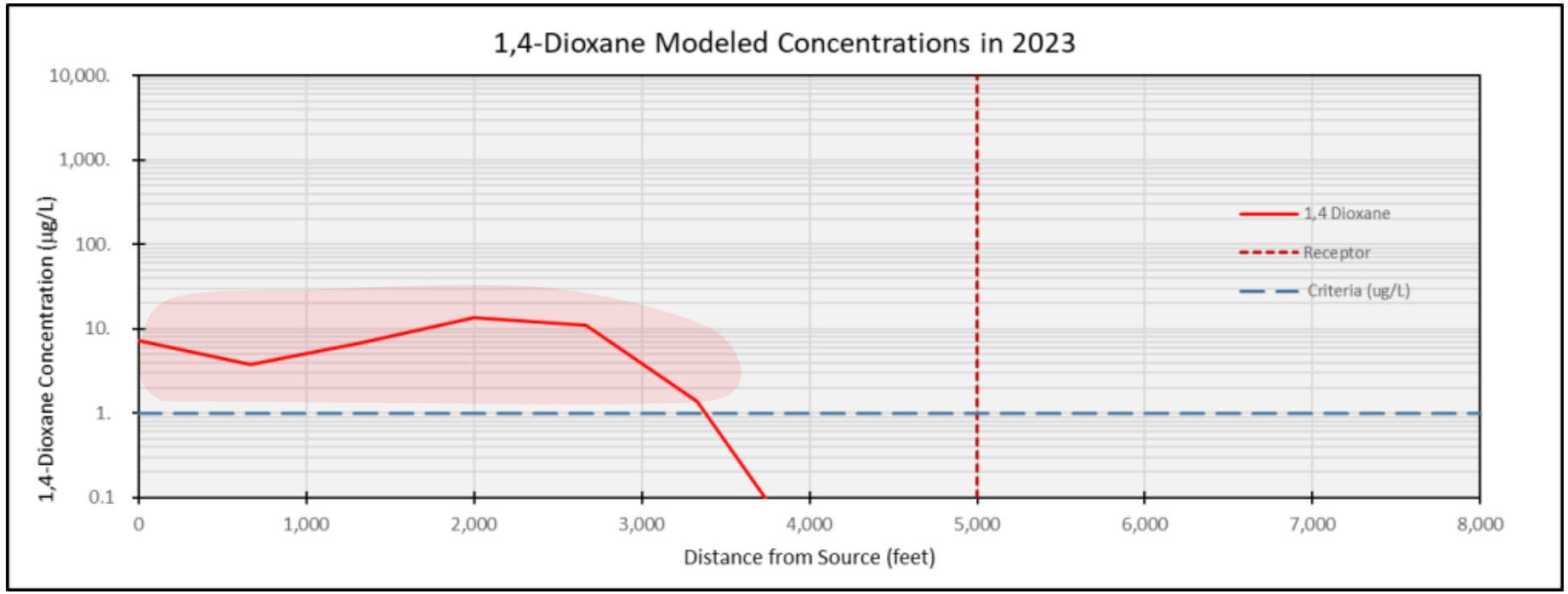
Seepage velocity = 50 ft/yr

Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.1 yr^{-1}

1,4-D plume rate = 0.01 yr^{-1}

Scenario #1: *"Typical" Rates for 1,4-Dioxane Based on Multi-Site Data*



2023

- **Dilute** ✓
  - Max concentration ~ 10 µg/L
- **Diffuse** ✓
  - Similar concentrations throughout majority of plume length (1 – 10 µg/L)

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

Seepage velocity = 50 ft/yr

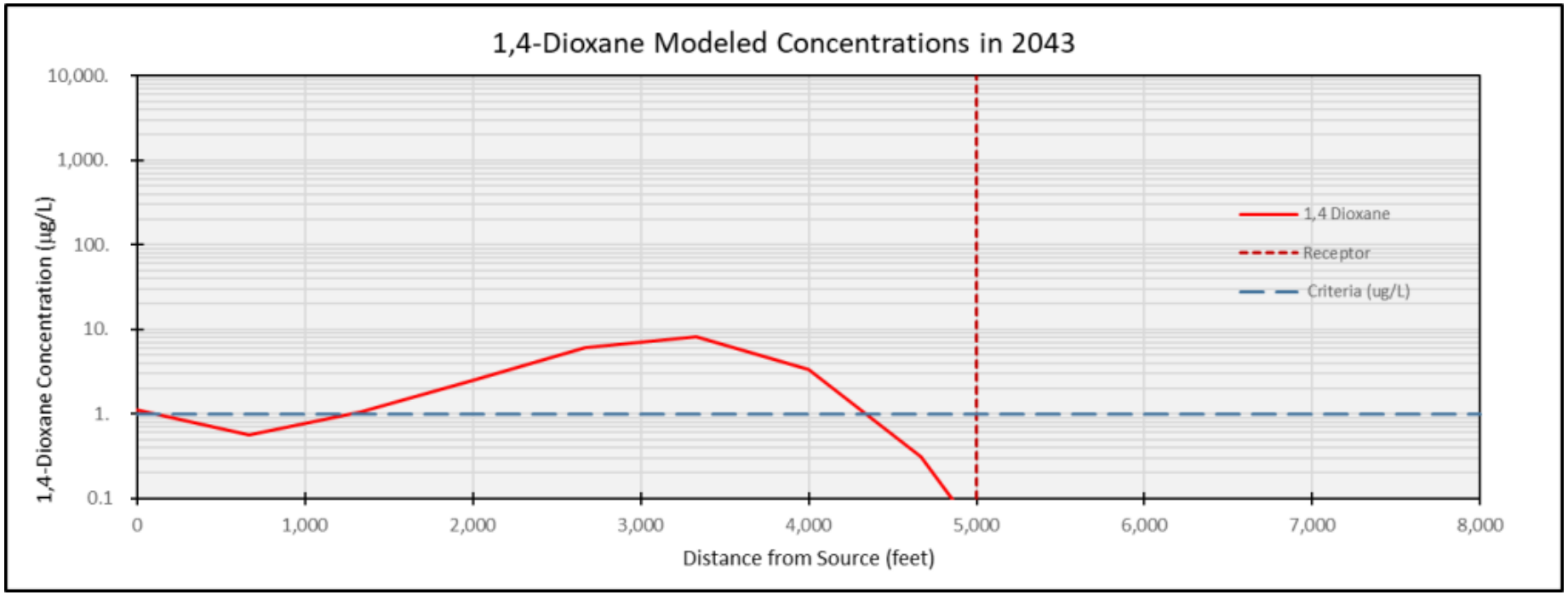
Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.1 yr^{-1}

1,4-D plume rate = 0.01 yr^{-1}

Scenario #1: *"Typical" Rates for 1,4-Dioxane Based on Multi-Site Data*

GSI ENVIRONMENTAL



2043

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

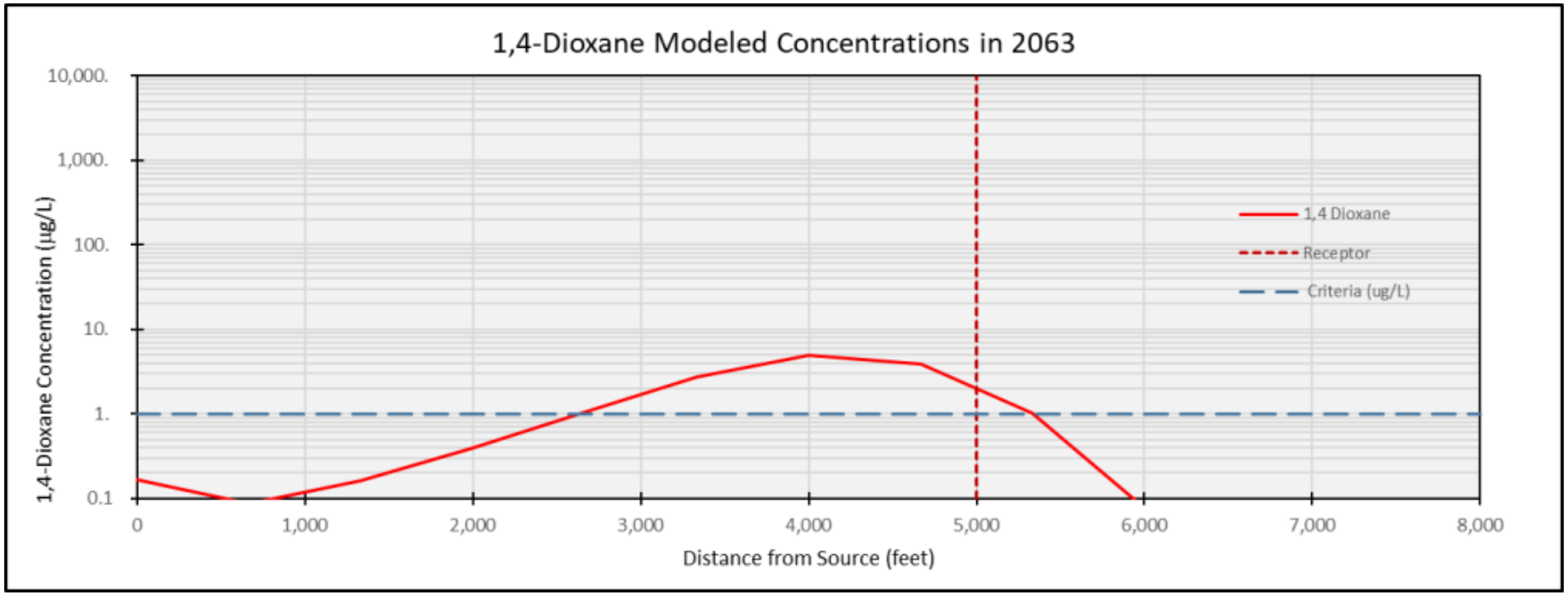
Seepage velocity = 50 ft/yr

Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.1 yr^{-1}

1,4-D plume rate = 0.01 yr^{-1}

Scenario #1: *"Typical" Rates for 1,4-Dioxane Based on Multi-Site Data*



2063

- **Dilute** ✓
  - Max concentration < 10 µg/L
- **Diffuse** ✓
  - Plume does not stabilize
  - Semi-detached

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

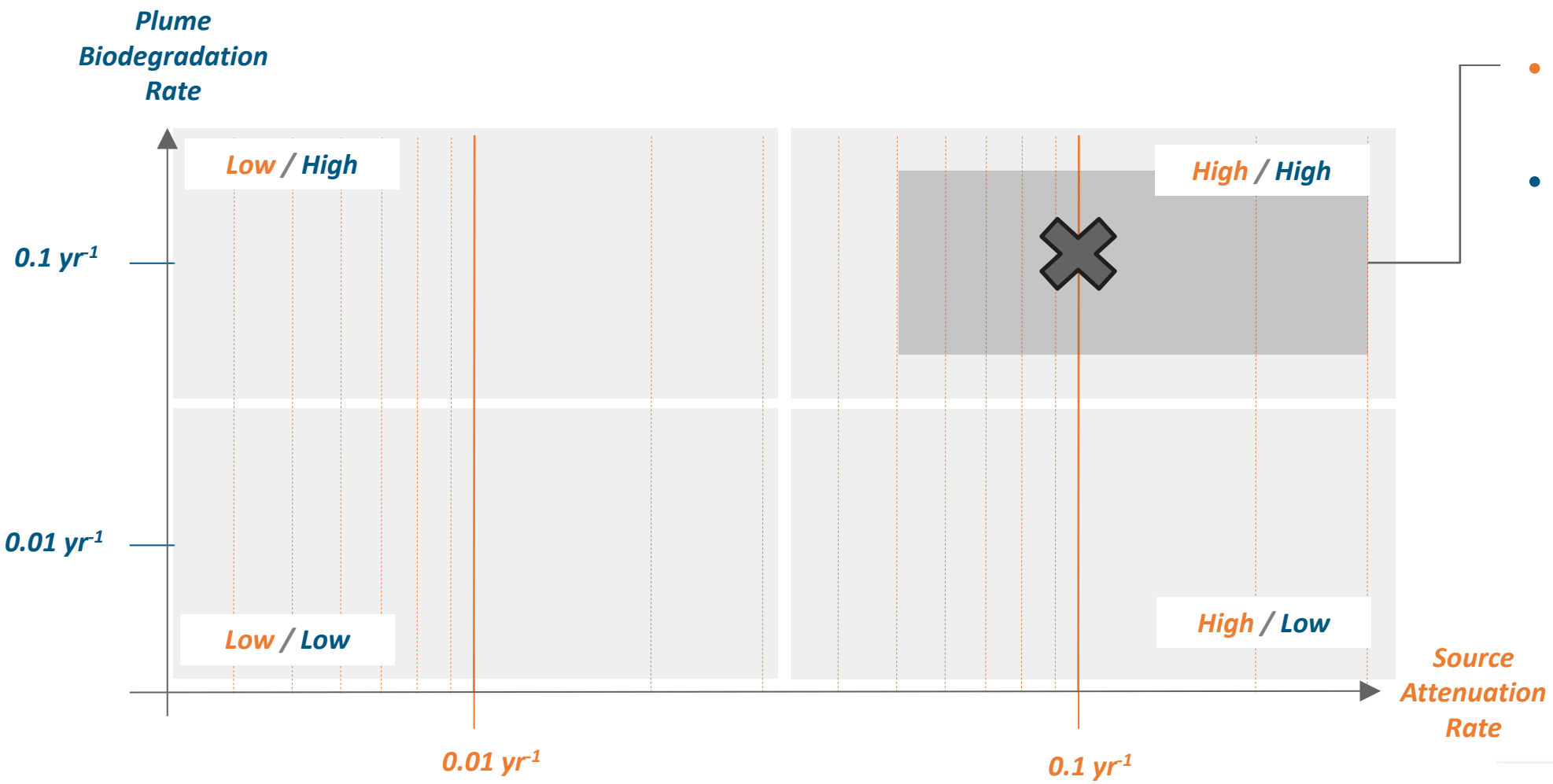
Seepage velocity = 50 ft/yr

Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.1 yr^{-1}

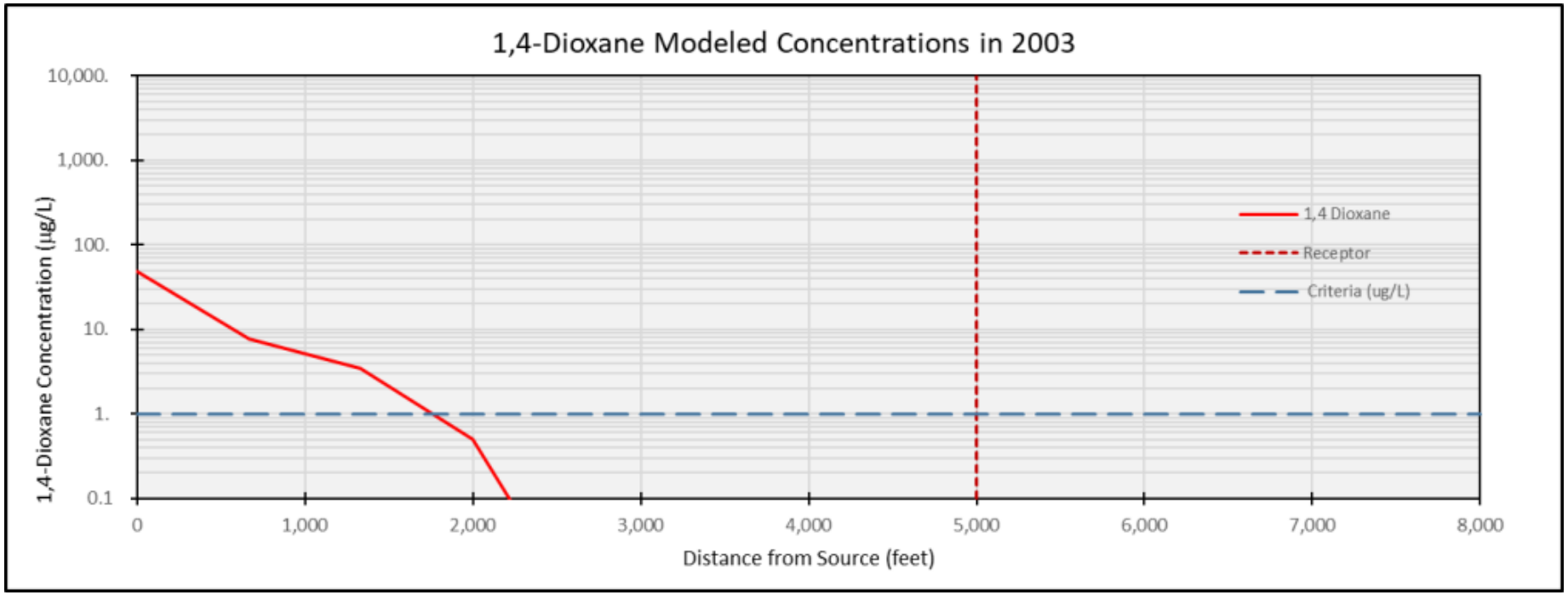
1,4-D plume rate = 0.01 yr^{-1}

Scenario #2: *Conditions Very Favorable for 1,4-Dioxane Biodegradation*



- High source attenuation
- High plume biodegradation

Scenario #2: *Conditions Very Favorable for 1,4-Dioxane Biodegradation*



2003

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

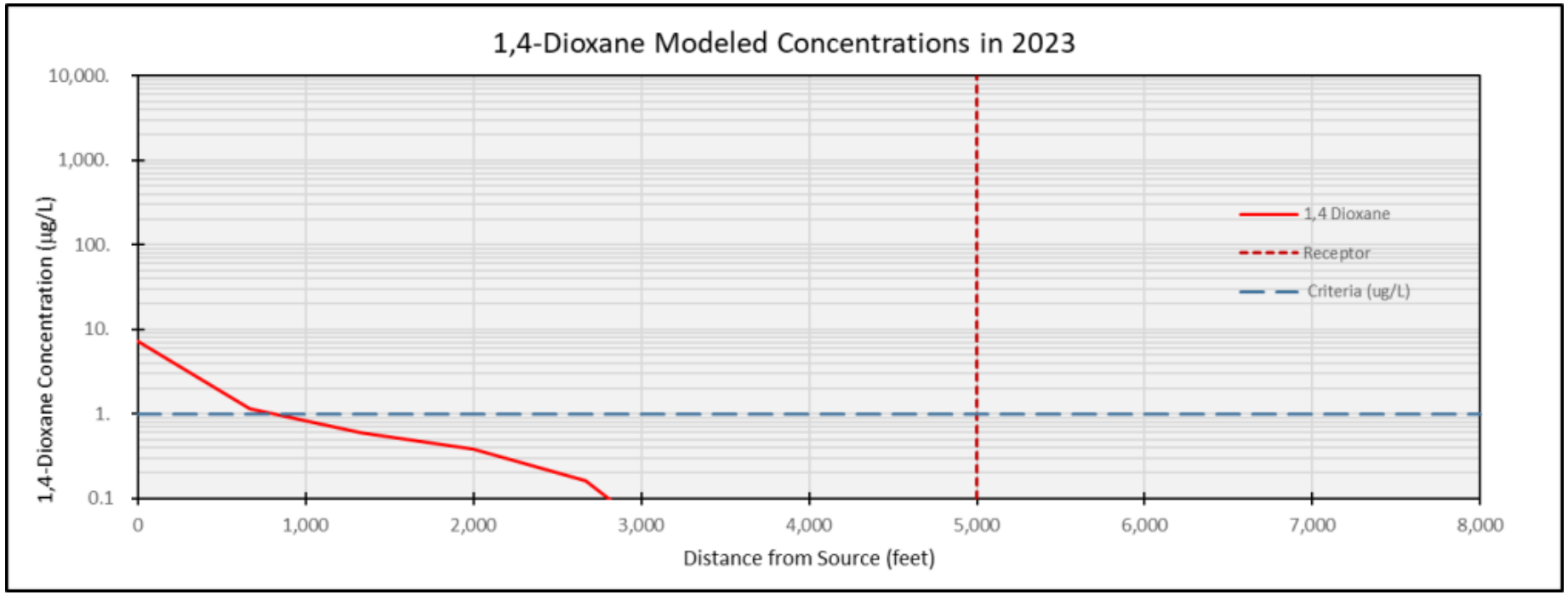
Seepage velocity = 50 ft/yr

Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.1 yr^{-1}

1,4-D plume rate = 0.1 yr^{-1}

Scenario #2: *Conditions Very Favorable for 1,4-Dioxane Biodegradation*



2023

- **Dilute** ✓
  - Max concentration < 10 µg/L
- **Diffuse?**
  - Concentrations vary by ~ 2 orders of magnitude within plume (0.1 – 10 µg/L)

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

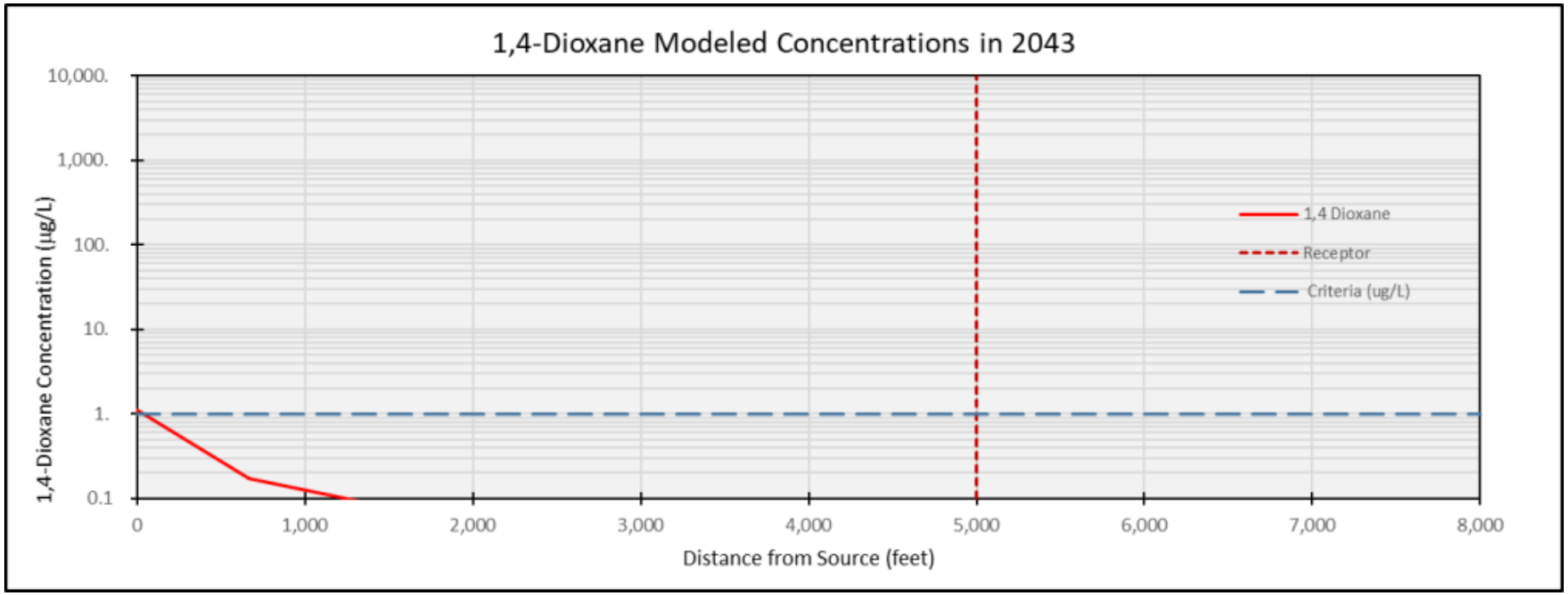
Seepage velocity = 50 ft/yr

Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.1 yr^{-1}

1,4-D plume rate = 0.1 yr^{-1}

Scenario #2: *Conditions Very Favorable for 1,4-Dioxane Biodegradation*



2043

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

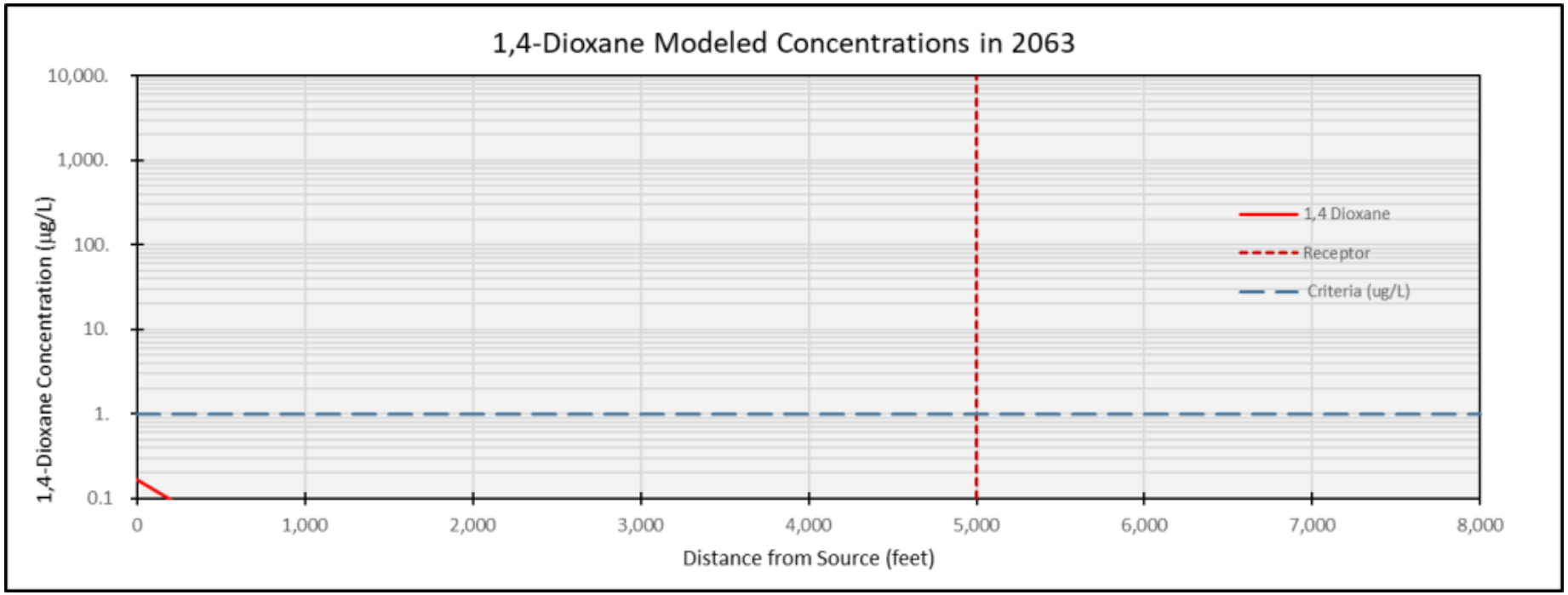
Seepage velocity = 50 ft/yr

Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.1 yr^{-1}

1,4-D plume rate = 0.1 yr^{-1}

Scenario #2: *Conditions Very Favorable for 1,4-Dioxane Biodegradation*



2063

- **Dilute** ✓
  - Max concentration < 1 µg/L
- **Diffuse** ✓
  - Plume is shrinking

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

Seepage velocity = 50 ft/yr

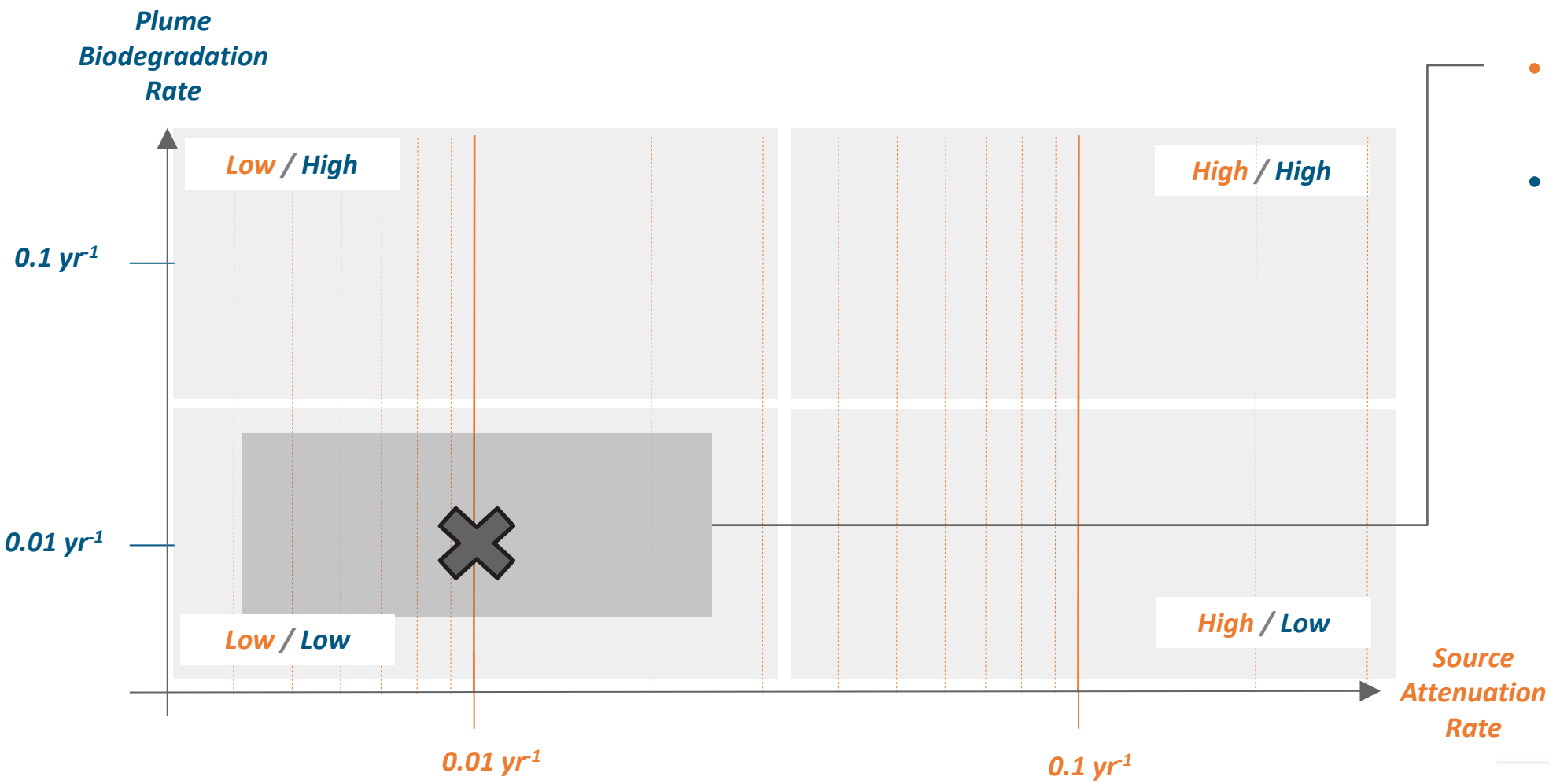
Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.1 yr^{-1}

1,4-D plume rate = 0.1 yr^{-1}

Scenario #3:

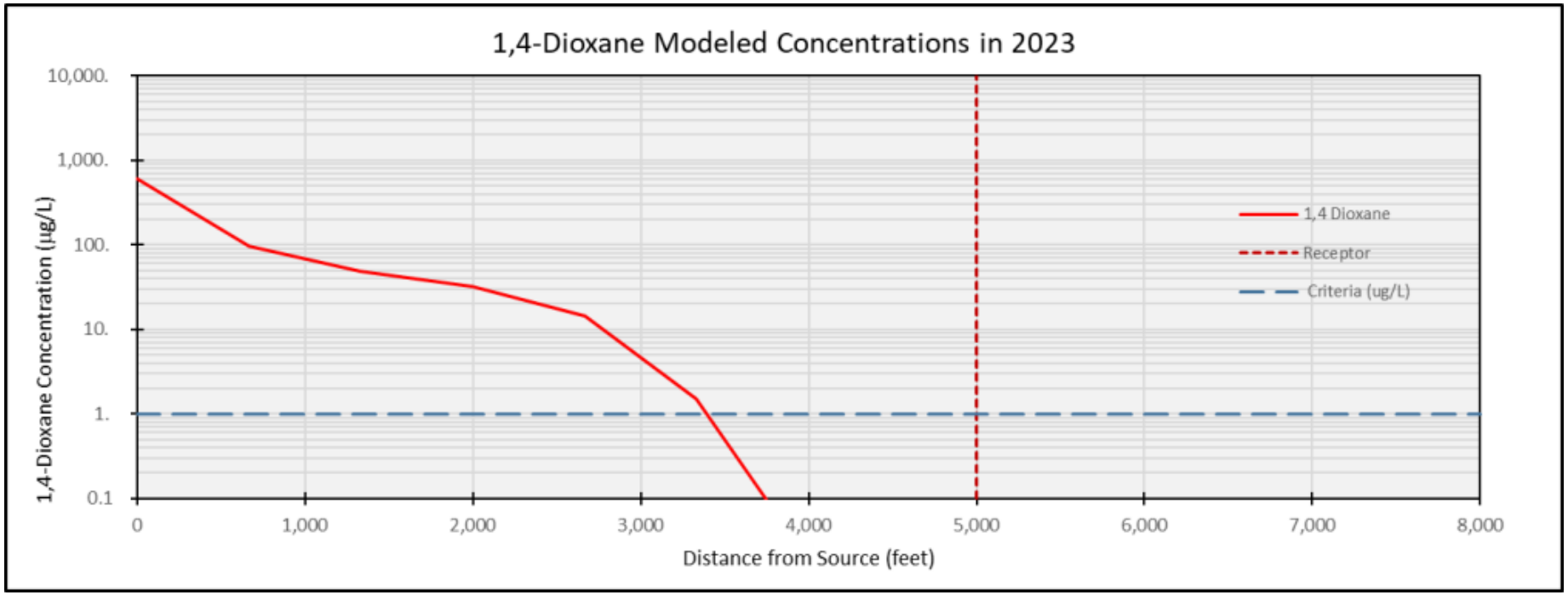
Persistent 1,4-Dioxane Source



- Low source attenuation
- Low plume biodegradation

Scenario #3:

Persistent 1,4-Dioxane Source



2023

- **Not Dilute**
  - Max concentration ~ 600 µg/L
- **Not Diffuse**
  - Concentrations vary by ~ 3 orders of magnitude within most of plume

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

Seepage velocity = 50 ft/yr

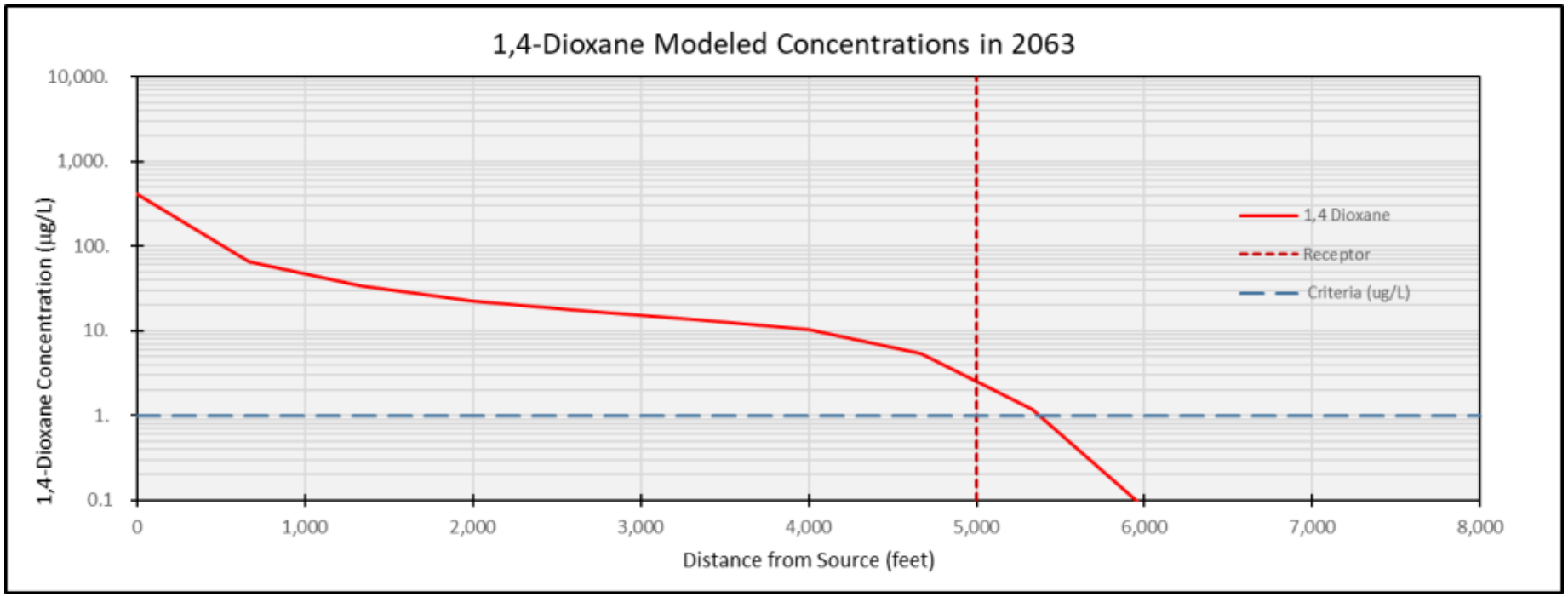
Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.01 yr^{-1}

1,4-D plume rate = 0.01 yr^{-1}

Scenario #3:

Persistent 1,4-Dioxane Source



2063

- **Not Dilute**
  - Max concentration ~ 400 µg/L
- **Diffuse?**
  - Concentrations vary by ~ 2 orders of magnitude within most of plume

INPUT VALUES:

1,4-D release date = 1970

1,4-D initial concentration = 1000 µg/L

Seepage velocity = 50 ft/yr

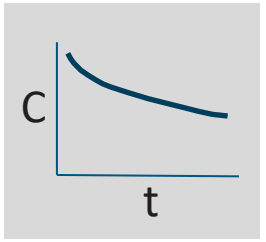
Regulatory criterion = 1.0 µg/L

1,4-D source rate = 0.01 yr^{-1}

1,4-D plume rate = 0.01 yr^{-1}

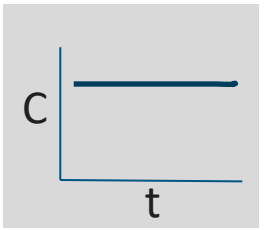
When is a 1,4-Dioxane Source "Persistent"?

- Source is in vadose zone with limited recharge
- Source is in saturated zone with poor flushing and/or slow dissolution
- Source is in low-permeability zone (matrix diffusion)



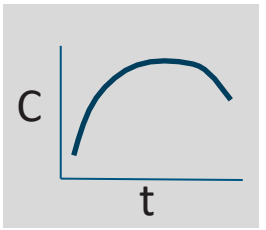
Concentrations will still decrease (slowly) at most/all locations over time

- Source is continuing to be released to the subsurface



Concentrations may plateau over time

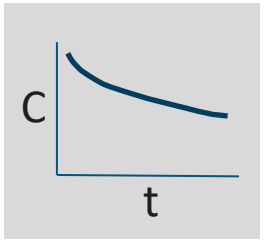
- Points of compliance (or other monitoring locations) are distant from source



Concentrations could still increase over time

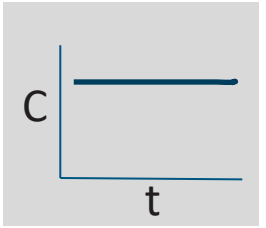
When is a 1,4-Dioxane Source "Persistent"?

- Source is in vadose zone with limited recharge
- Source is in saturated zone with poor flushing and/or slow dissolution

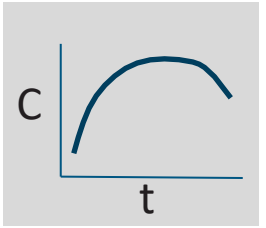


Concentrations will still decrease (slowly) at most/all locations over time

- Source is in low-permeability zone (matrix diffusion)
- Source is continuing to be released to the subsurface
- Points of compliance (or other monitoring locations) are distant from source



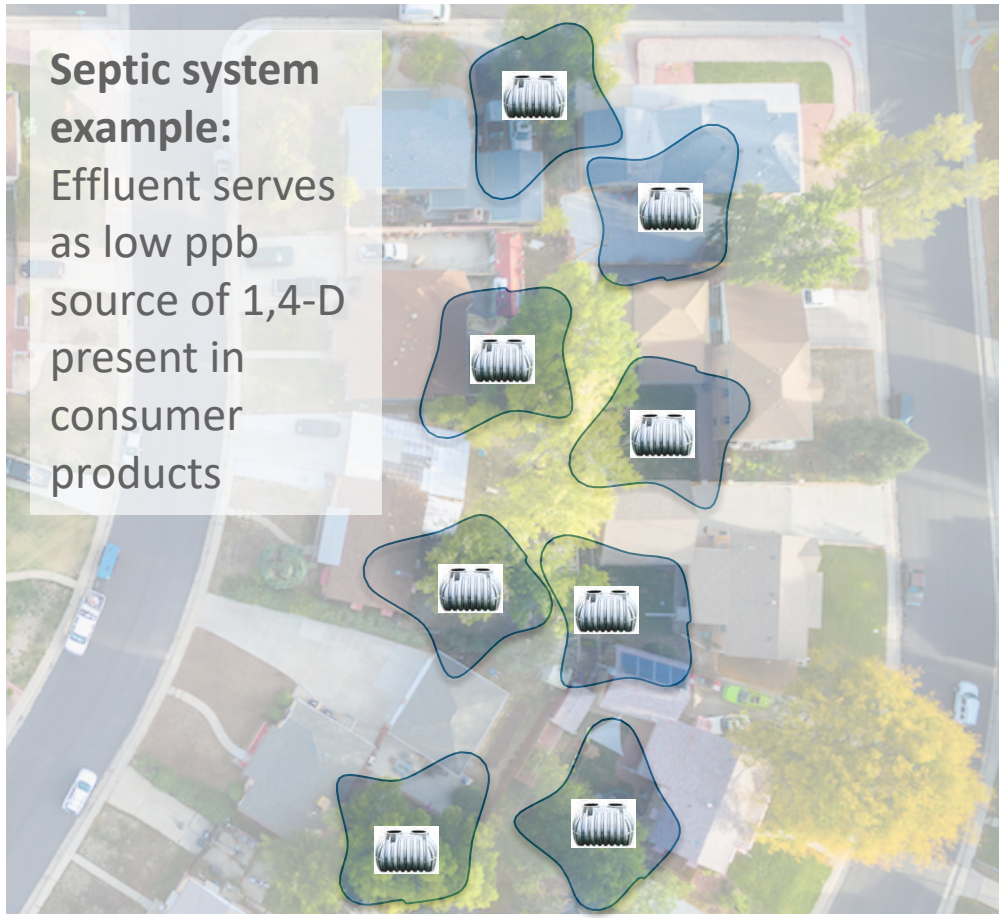
Concentrations may plateau over time



Concentrations could still increase over time

KEY POINT: **Each of these cases could also result in dilute, diffuse plumes.**

SUMMARY AND IMPLICATIONS

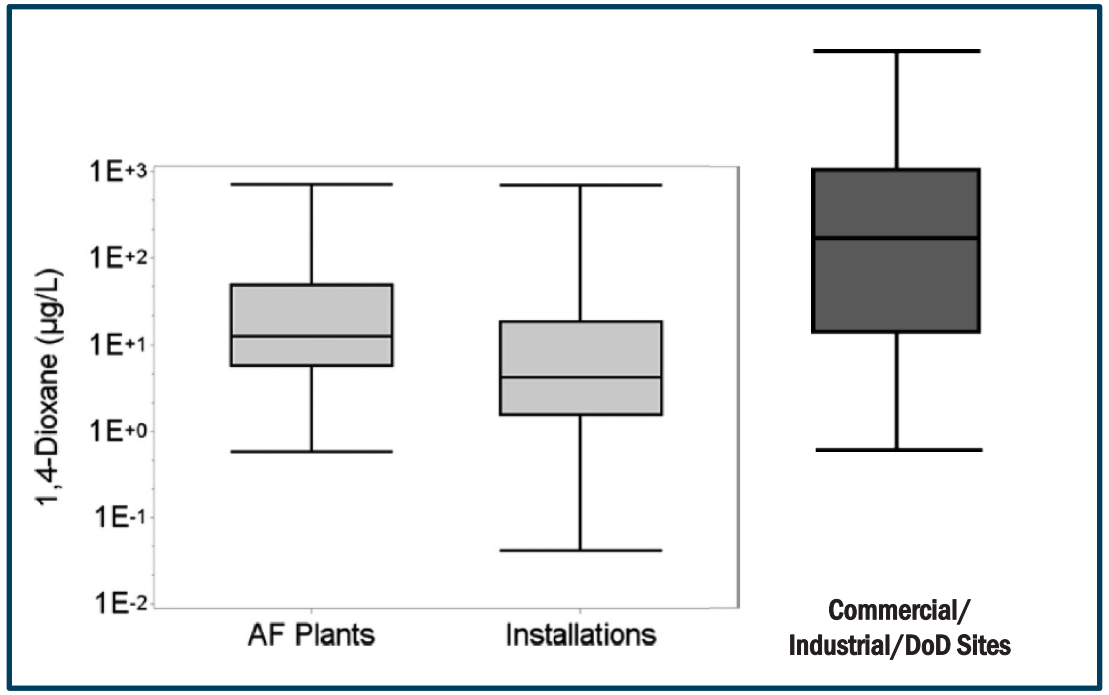


- **Dilute and diffuse plumes of 1,4-D can originate from common fate and transport processes**
  - High source decay rates + low plume biodegradation rates
  - Location of max. concentration may shift over time
  - Multiple sources may be present
- **Prevalence of dilute and diffuse 1,4-D plumes suggests that empirically derived rates are reasonable**
  - Attenuation is likely occurring - driven by source decay
- **Persistent 1,4-D sources are still possible in some cases**

Problem Statement:

1,4-Dioxane Sites are Challenging to Manage

Distribution of Historical Maximum 1,4-D Concentrations



Source: Chiang, Anderson, Wilken, and Walecka-Hutchison, 2016, *Remediation*

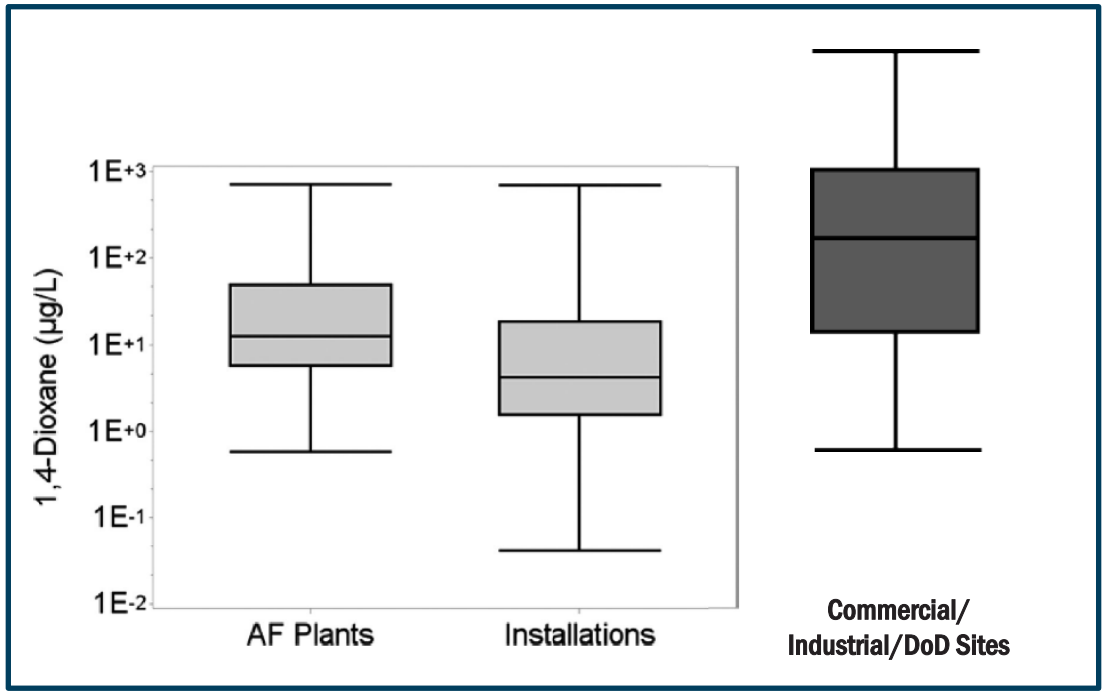
Source: Adamson, Anderson, Mahendra, et al., 2015, *ES&T*

- **Typical in situ treatment strategies may be ineffective and/or costly**
- **Long-term management using Monitored Natural Attenuation (MNA) may be an option**
  - Requires understanding of relevant attenuation processes and associated rates
  - "Attenuation" is likely occurring, but what type?

Problem Statement:

1,4-Dioxane Sites are Challenging to Manage

Distribution of Historical Maximum 1,4-D Concentrations



Source: Chiang, Anderson, Wilken, and Walecka-Hutchison, 2016, *Remediation*

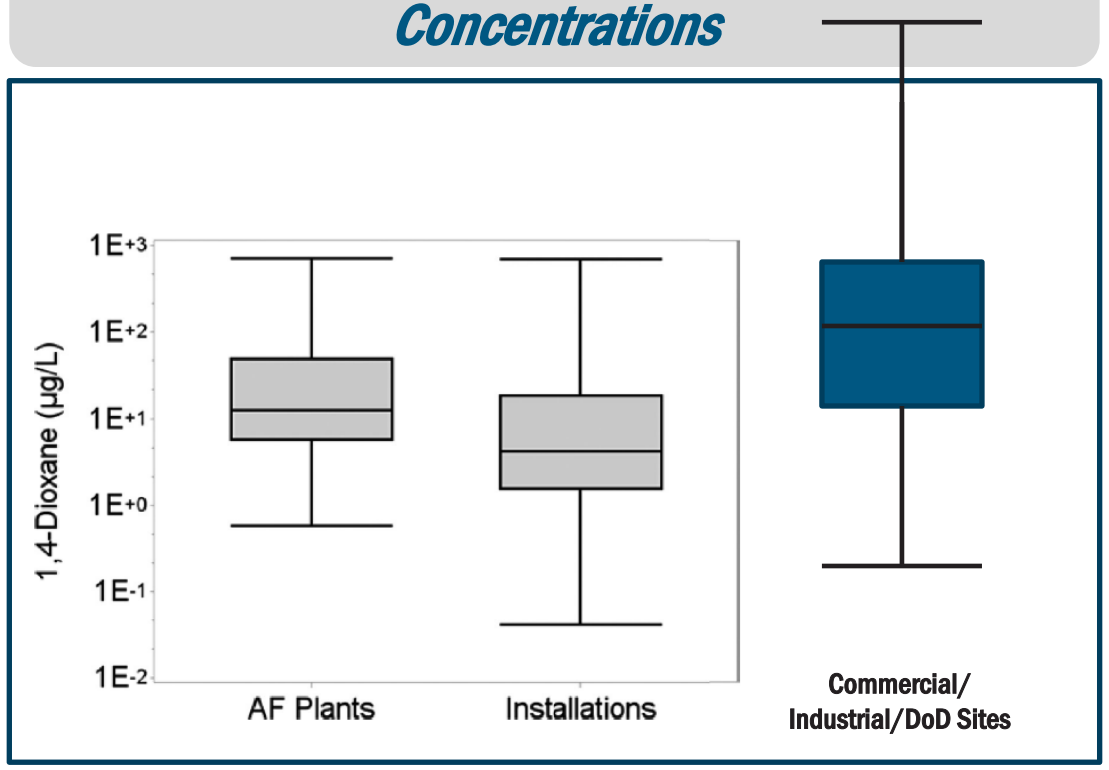
Source: Adamson, Anderson, Mahendra, et al., 2015, *ES&T*

- **1,4-D plumes are generally dilute**
  - Key concern at DoD sites (see chart)
  - Recent survey of 400 primarily commercial/industrial sites shows that median site had historical maximum concentration of 110 µg/L
- **1,4-D plumes are often diffuse with poorly defined "source areas"**
  - Similar concentrations throughout much of plume

Problem Statement:

1,4-Dioxane Sites are Challenging to Manage

Distribution of Historical Maximum 1,4-D Concentrations



Source: Chiang, Anderson, Wilken, and Walecka-Hutchison, 2016, *Remediation*

Source: Adamson et al., 2015, *ES&T;* updated 2023 *(unpublished)*

- **Typical in situ treatment strategies may be ineffective and/or costly**
- **Long-term management using Monitored Natural Attenuation (MNA) may be an option**
  - Requires understanding of relevant attenuation processes and associated rates
  - Median of the most recent maximum detections at these same sites is 17 ug/L (decreased from 110 ug/L historical maximum)
  - "Attenuation" is likely occurring, but what type?