# Starting Soon:
# ITRC 1,4-Dioxane Training – Six (6) Part Modular Training

- 1,4 Dioxane Online Guidance Document, https://14d-1.itrcweb.org/.
- Download PowerPoint slides
  - CLU-IN training page at https://clu-in.org/conf/itrc/14D-1/. Under "Download Training Materials."

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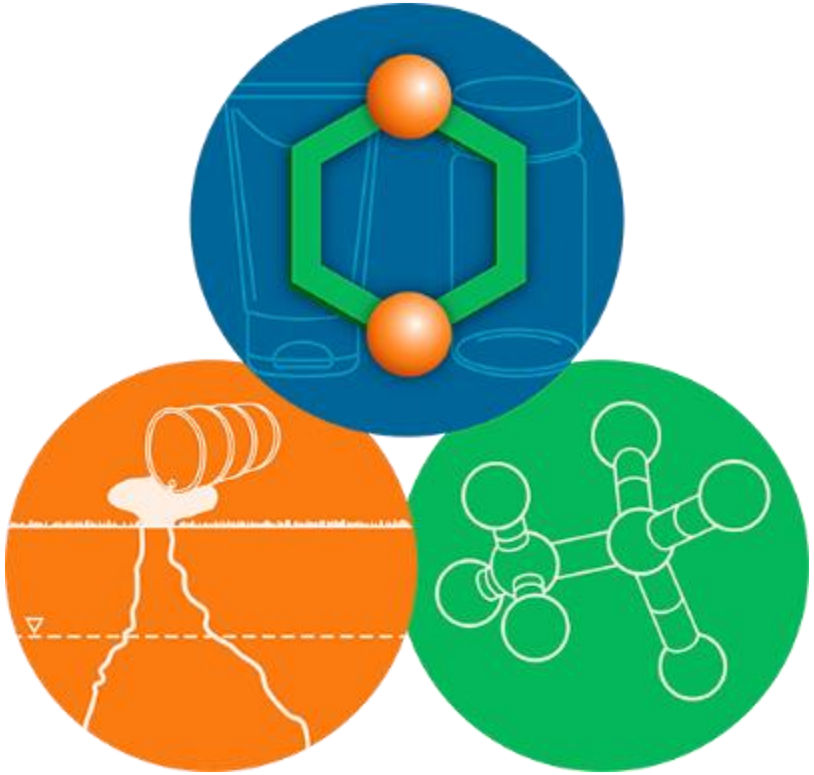
Advancing
Environmental
Solutions

# ITRC 1,4-Dioxane:

## Science, Characterization & Analysis, and Remediation



# Housekeeping

## Course time is 2 hours and 15 minutes

- This event is being recorded
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  - Fill out the feedback form and check box for confirmation email and certificate (only available for full 1,4D-1 Training)

# ITRC – Shaping the Future of Regulatory Acceptance

- Host organization – Environmental Council of States (ECOS)
- Network
  - State regulators
    - All 50 states, PR, DC
  - Federal partners
  - ITRC Industry Affiliates Program
  - Academia
  - Community stakeholders
- Follow ITRC

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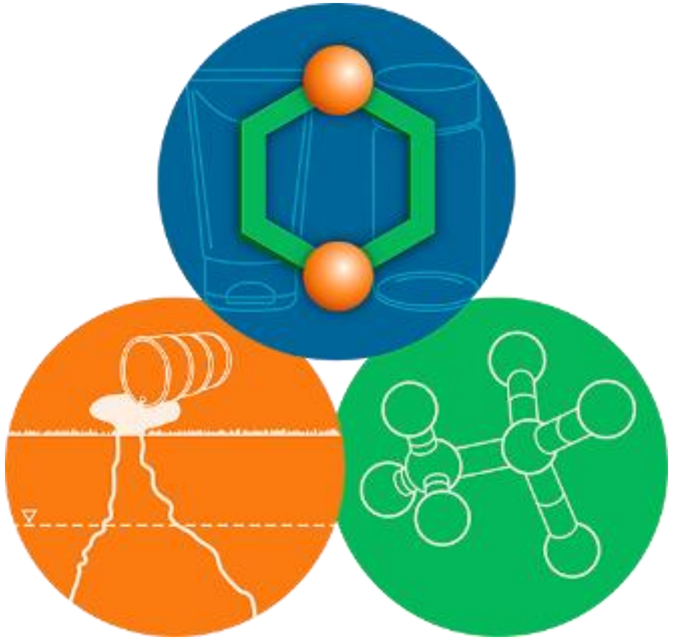
  - More…

# 1,4-Dioxane: Introduction



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Advancing Environmental Solutions

Based on ITRC Guidance Document and Fact Sheets:
ITRC 1,4-Dioxane Products (14d-1, February 2021)

## 6-Part Modular Training Series:
## 1,4-Dioxane: Science, Characterization, Analysis, and Remediation

**Module 1:** History of Use & Potential Sources

**Module 2:** Regulatory Framework

**Module 3:** Environmental Fate, Transport, & Investigation Strategies

**Module 4:** Sampling & Analysis

**Module 5:** Toxicity & Risk Assessment

**Module 6:** Remediation &Treatment Technologies

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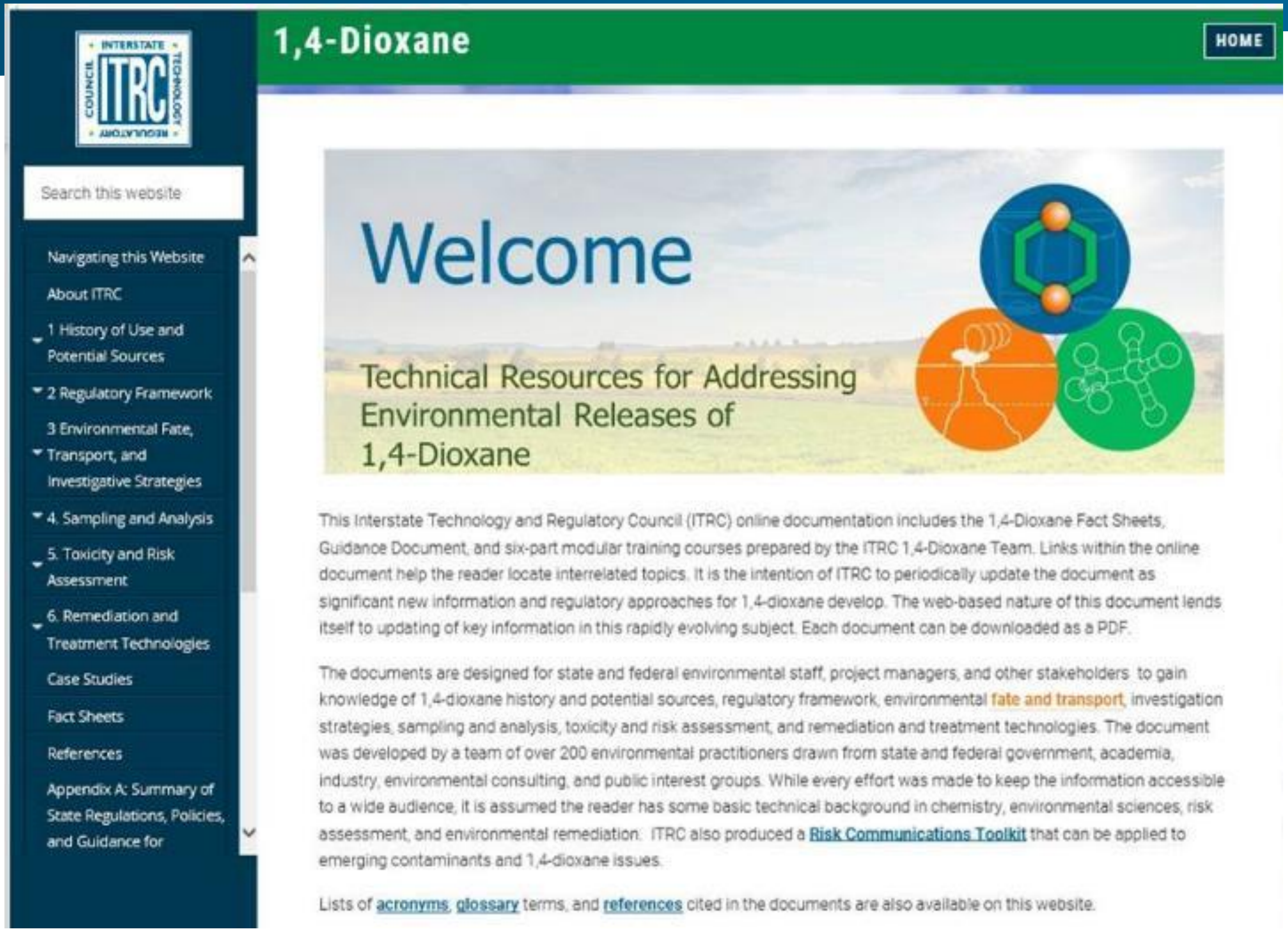
Hosted by: USEPA Clean Up Information Network (www.clu-in.org)

# Online Documents and Accessing the Training Modules



1,4-Dioxane

HOME

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3 Environmental Fate, Transport, and Investigative Strategies
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5. Toxicity and Risk Assessment
6. Remediation and Treatment Technologies
Case Studies
Fact Sheets
References
Appendix A: Summary of State Regulations, Policies, and Guidance for

Welcome

Technical Resources for Addressing Environmental Releases of 1,4-Dioxane

This Interstate Technology and Regulatory Council (ITRC) online documentation includes the 1,4-Dioxane Fact Sheets, Guidance Document, and six-part modular training courses prepared by the ITRC 1,4-Dioxane Team. Links within the online document help the reader locate interrelated topics. It is the intention of ITRC to periodically update the document as significant new information and regulatory approaches for 1,4-dioxane develop. The web-based nature of this document lends itself to updating of key information in this rapidly evolving subject. Each document can be downloaded as a PDF.

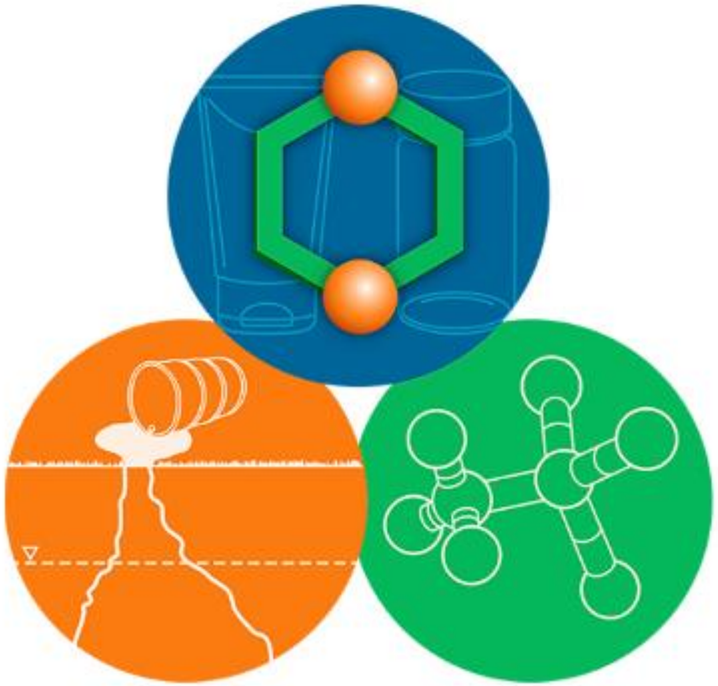
The documents are designed for state and federal environmental staff, project managers, and other stakeholders to gain knowledge of 1,4-dioxane history and potential sources, regulatory framework, environmental fate and transport, investigation strategies, sampling and analysis, toxicity and risk assessment, and remediation and treatment technologies. The document was developed by a team of over 200 environmental practitioners drawn from state and federal government, academia, industry, environmental consulting, and public interest groups. While every effort was made to keep the information accessible to a wide audience, it is assumed the reader has some basic technical background in chemistry, environmental sciences, risk assessment, and environmental remediation. ITRC also produced a Risk Communications Toolkit that can be applied to emerging contaminants and 1,4-dioxane issues.

Lists of acronyms, glossary terms, and references cited in the documents are also available on this website.

# ITRC 1,4-Dioxane Products and Focus?

- **Series of 1,4-Dioxane Fact Sheets** (https://14d-1.itrcweb.org/fact-sheets/) – Provide easy to access information about 1,4-Dioxane to answer immediate questions.
    - **Toxicity and Risk Assessment Fact Sheet** provides a summary of frequently asked questions regarding the potential human and ecological risks.
- **1,4-Dioxane Guidance Document** (https://14d-1.itrcweb.org/) – Provides an in-depth review and technical information that will assist the environmental community with 1,4-dioxane site management and cleanup.

# Our Focus is on 1,4-Dioxane



- What is 1,4-Dioxane?
- Why Do We Care About 1,4-Dioxane?
  - 1,4-Dioxane Concerns
  - We are still learning about 1,4-Dioxane
- Use 1,4-Dioxane information and science to your advantage and apply best practices at your sites

# Module 1: History of Use & Potential Sources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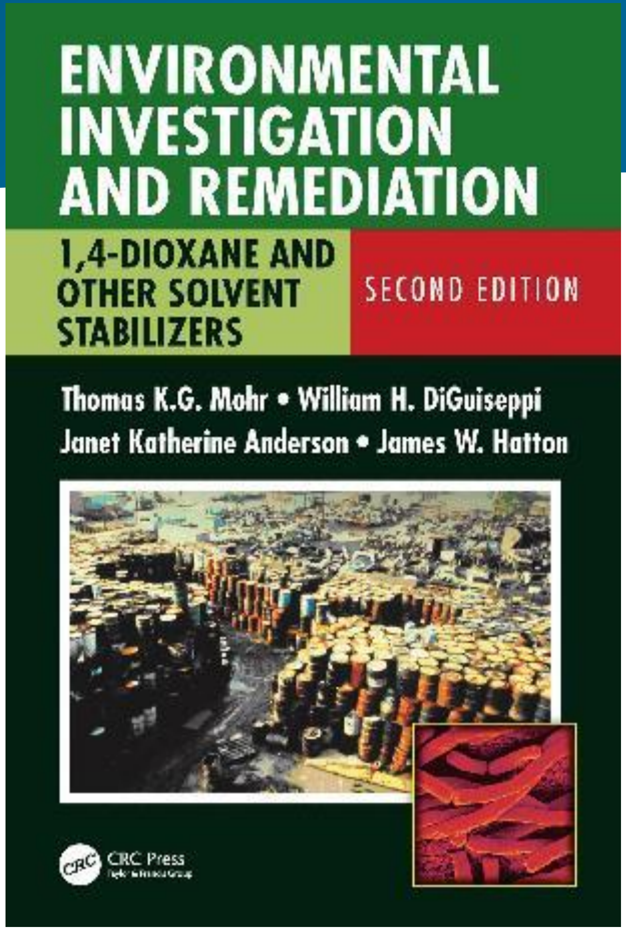
# Learning Objectives

- Provide an overview of uses and potential sources of 1,4-dioxane to the environment
- Provide an understanding of the history of 1,4-dioxane manufacturing and usage
- Provide case study of "typical" 1,4-dioxane and chlorinated volatile organic compound (CVOC) impacted site


http://clipart-library.com/clipart/1875703.htm

# 1,4-Dioxane Uses

- Solvent stabilizers (90% of usage)
- Medical, pharmaceutical, and biotechnical
- Rubber and plastics, especially polyester manufacturing
- Inks, paints, and coatings
- Adhesives
- Automotive and aircraft fluids
- Many other uses




- 1,4-Dioxane manufacture, usage and release tied inextricably to 1,1,1-trichloroethane (1,1,1-TCA)
- Understanding that relationship/history helps understand where 1,4-dioxane is likely to be found

See Section 1.2 for additional information

Image courtesy of Bill DiGuiseppi, Jacobs. Used with permission

# Why is 1,4-Dioxane Needed to Stabilize Solvents?

- Acids are formed as the solvent decomposes
- Reactions occur between the acids formed and the metals being degreased/plated, so stabilizers address acids:
  - Acid inhibitors – prevent the formation of acids in the first place
  - Acid acceptors – neutralize the acids that form
  - Metal inhibitors – deactivate catalytic properties of metal surfaces and complex metal salts
- 1,4-Dioxane is dominantly used as a metal inhibitor

See Section 1.2.1 for additional information

# Was 1,4-Dioxane a Stabilizer in Trichloroethene?

- Trichloroethene (TCE) has been stabilized for vapor degreasing applications since 1940s, but 1,4-dioxane is not documented as the stabilizer used
- Extensive documentation (Mohr et al 2020) for 1,4-dioxane as a stabilizer for 1,1,1-TCA, but scant documentation for TCE
- Vague early patent literature describing TCE formulations
- TCE is substantially more stable than 1,1,1-TCA

May not matter because of association between TCE and 1,1,1-TCA



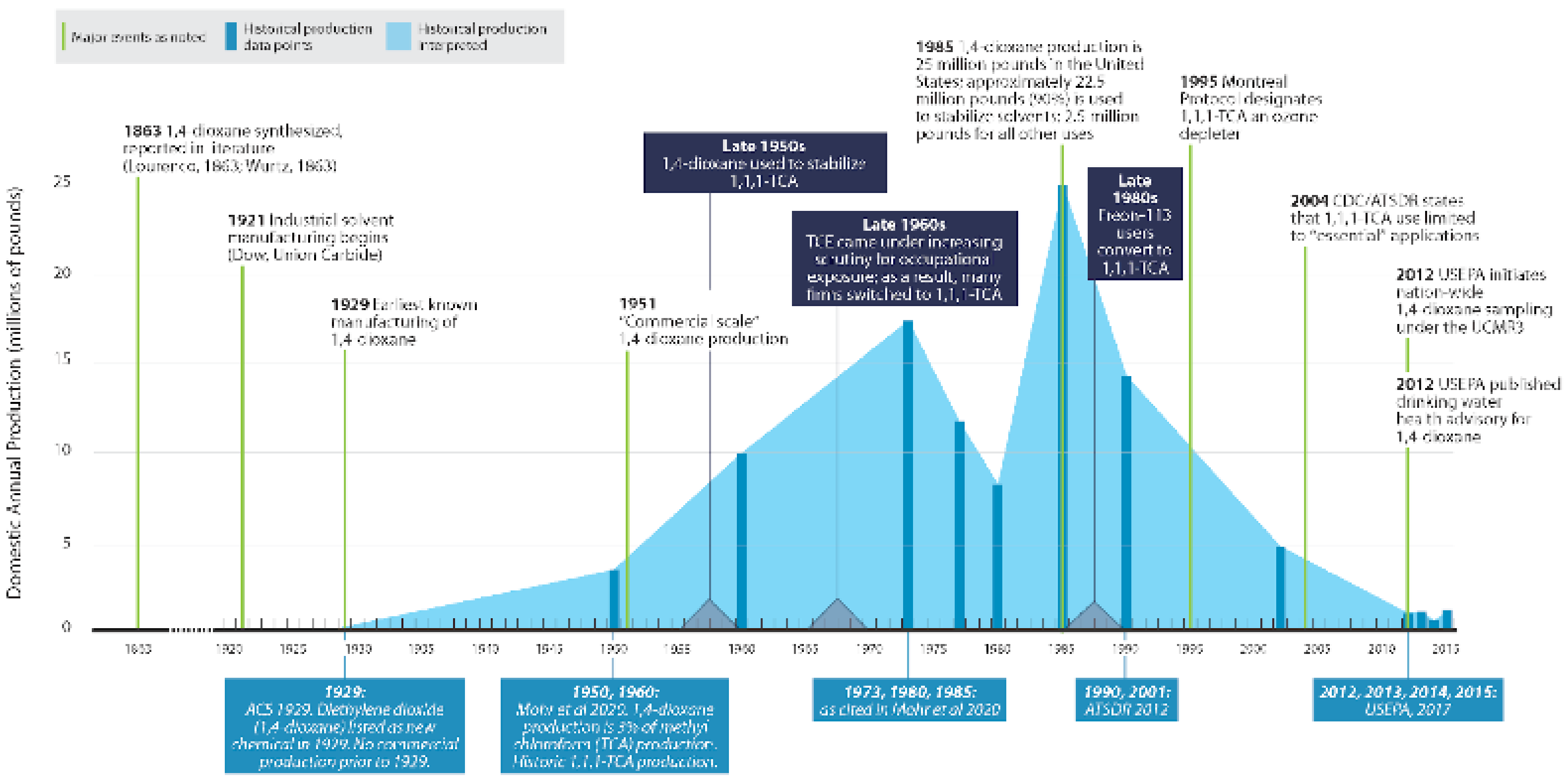
See Section 1.2.1 for additional information

# Production History

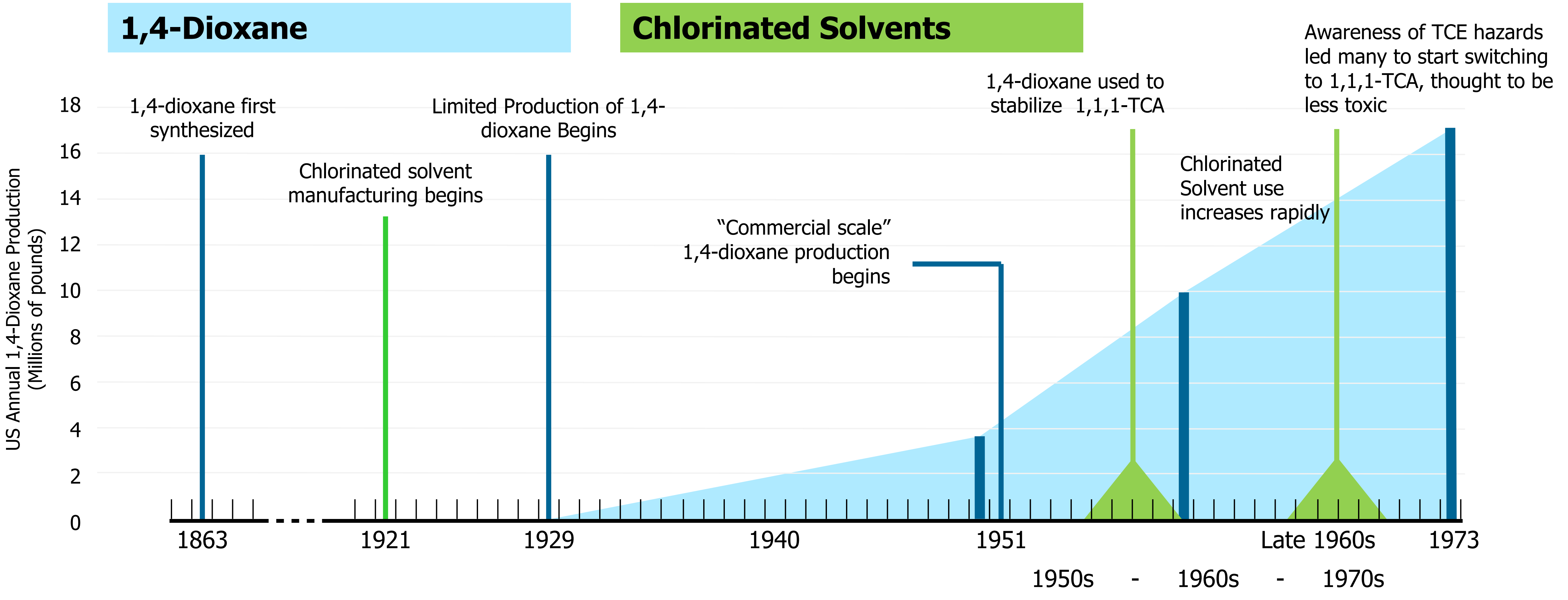
Discussed in time segments:

- ▶ Synthesis through 1973
- ▶ 1973-1990
- ▶ Post 1990

**1,4-DIOXANE TIMELINE AND HISTORICAL PRODUCTION**

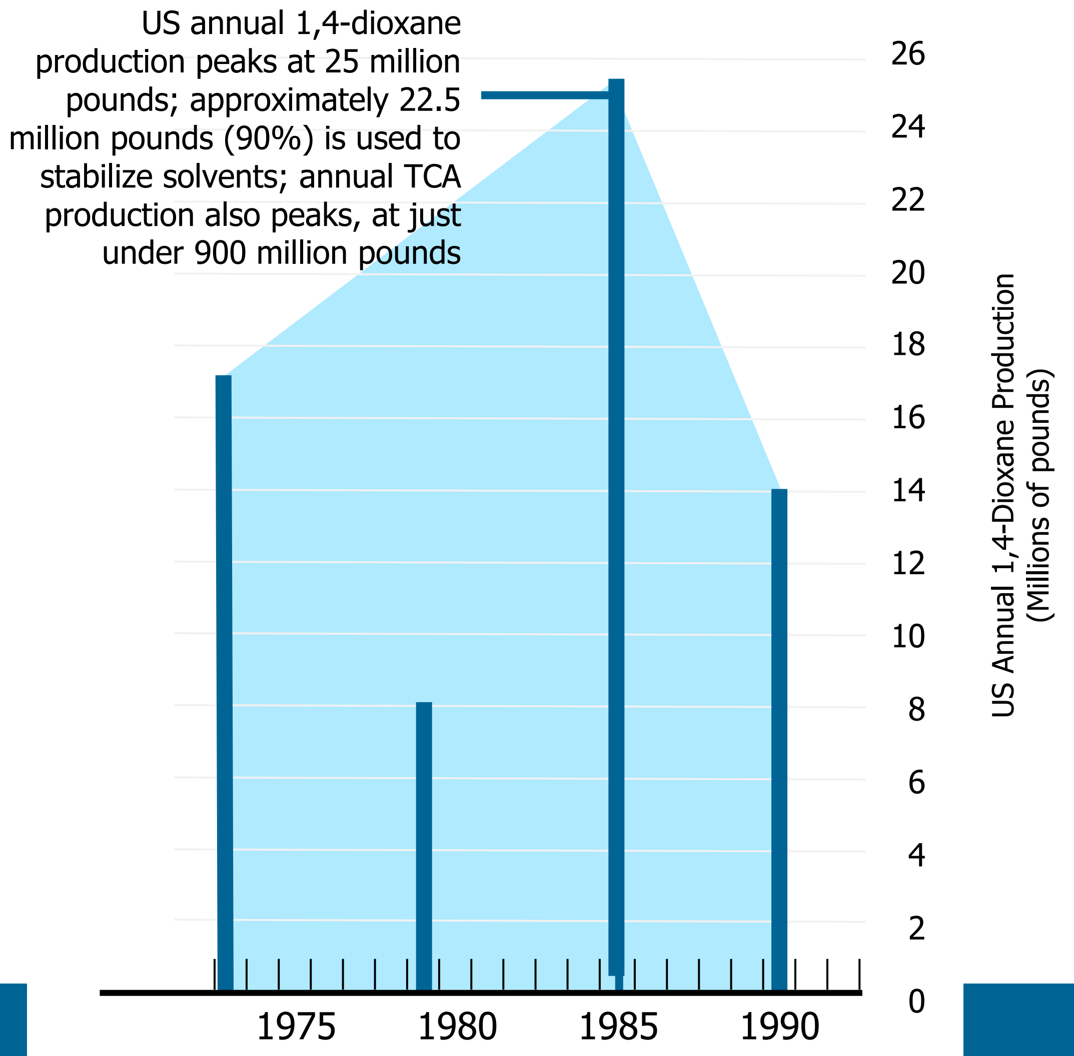


# Invention, Discovery and Growth (1863 – 1973)



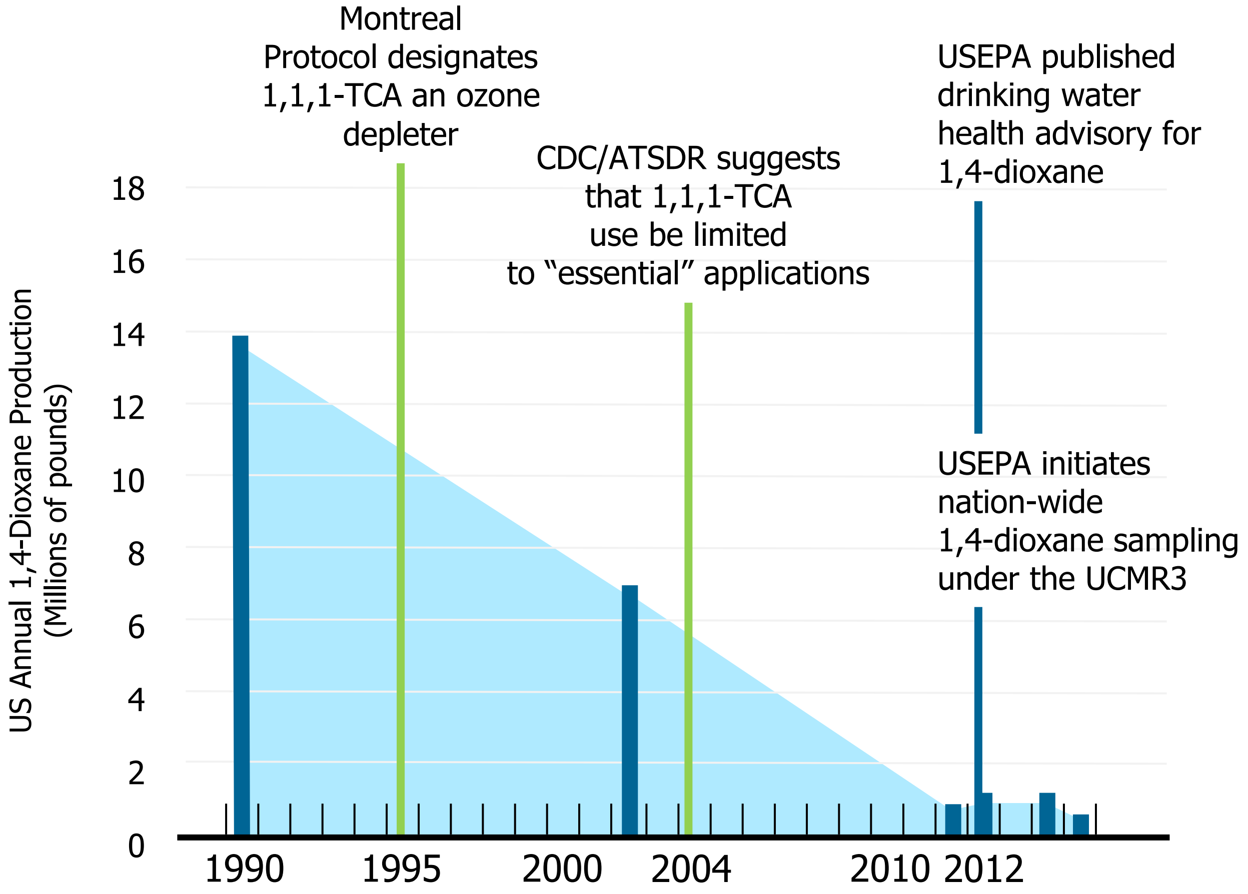
# 1973-1990

- Limited data available
- Shows variability over time (may be an artifact of data)
- Overall decline from early 1970s to 1990s due to industry reducing solvent usage overall
- 1985 data point valuable in that 90% of 1,4-dioxane in the United States was used for solvent stabilizing



# Post-1990

- Decline from 1990 from overall decline in chlorinated solvent usage in US and abroad
- 1995 Montreal Protocol designates 1,1,1-TCA as ozone depleting, driving widespread phase out
- By 2012, production falls to less than 1 million pounds/year



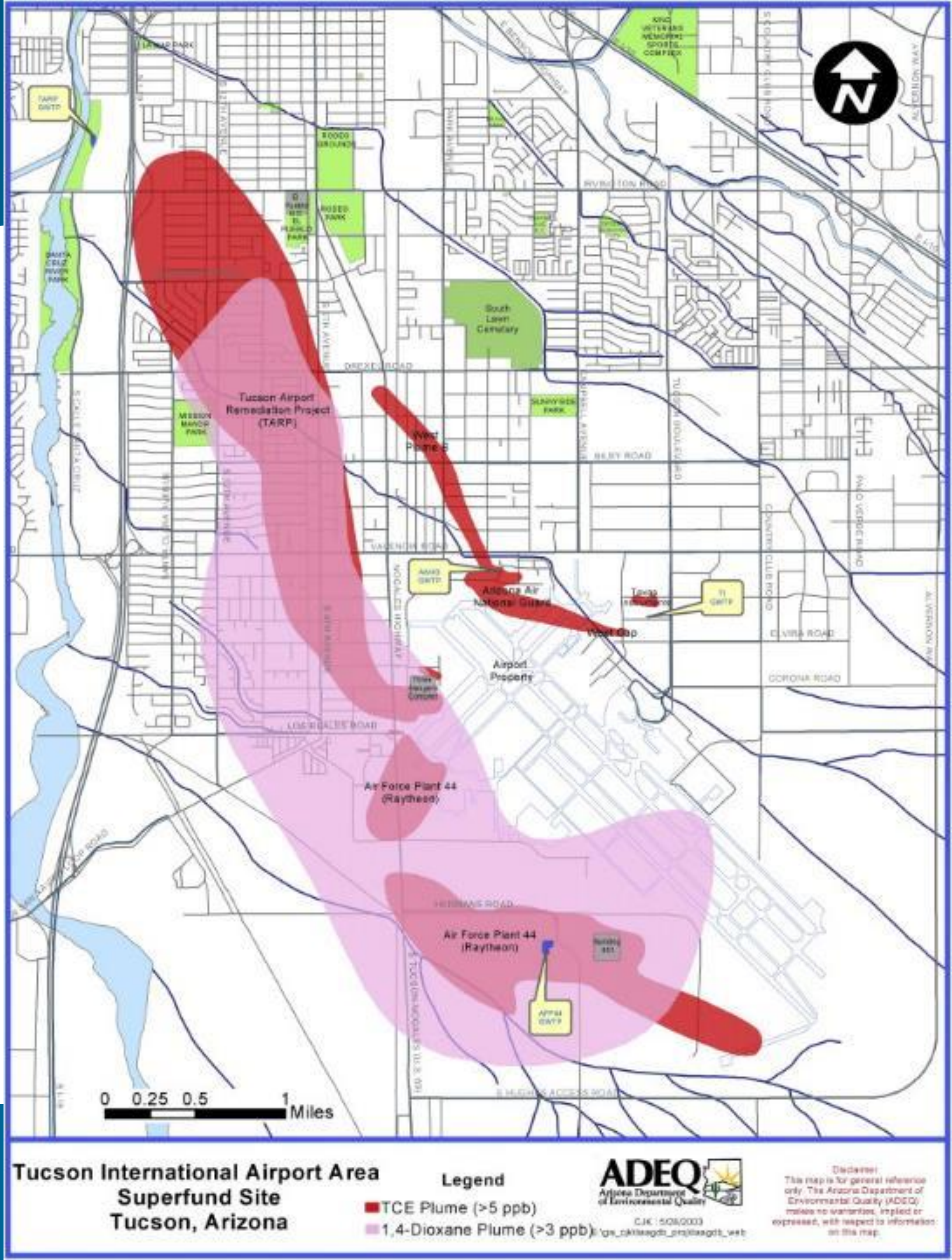

US EPA - U.S. Environmental Protection Agency
UCMR3 – Unregulated Contaminant Monitoring Rule #3

# History of Use Case Study – Air Force Plant 44 (AFP44)

- Missile Manufacturing Plant in Tucson, Arizona
- Used TCE from 1950s – present (minor uses)
- Dominantly switched to 1,1,1-TCA from 1974 through the early 1980s
- Site 3 – Operated 1966 - 1977, disposed vapor degreaser solvent waste in unlined lagoons
- Site 5 – Operated early 1960s until 1977, disposed wastewater and metal sludge from nearby plating shop with solvent degreasers
- Groundwater extraction and reinjection system operated 1987 - present

# AFP44 Plume Map

- 1,4-Dioxane plume confirms relationship with chlorinated solvents, specifically TCE
- AFP44 is one of several sources in the Tucson International Airport Area Superfund Site
- Main TCE plume disconnected by pump and treat activities since 1987
- 1,4-Dioxane plume wider at time of discovery, due to reinjection of treated (air stripper) water
- Plume has narrowed dramatically with elimination of reinjection on sides of the plume




From Brusseau, Hatton and DiGuiseppi, 2011
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# Takeaways

- 1,4-Dioxane is used in many industries, but primarily used in stabilizing 1,1,1-TCA
- 1,4-Dioxane manufacture over time is tied to 1,1,1-TCA manufacture and use
- May have been present in TCE but there's little direct evidence; there is, however an empirical association
- 1,4-Dioxane co-location with chlorinated solvents is common, at similar order of magnitude


http://clipart-library.com/image_gallery/311049.jpg

# Module 2: Regulatory Framework

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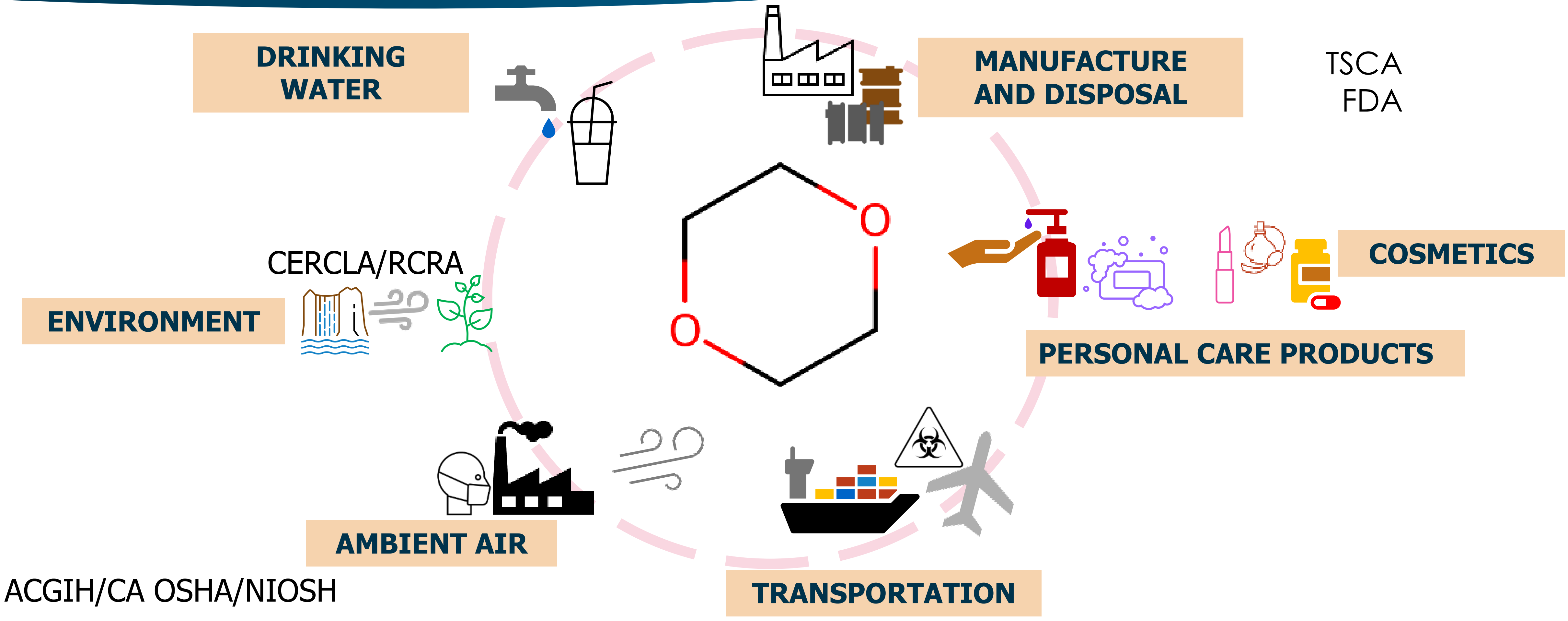
# Learning Objectives

- ▶ Understand the primary state and U.S. federal regulatory programs of relevance to 1,4-dioxane
- ▶ Recognize the current U.S. regulatory and guidance values for 1,4-dioxane in groundwater, drinking water, soil, and air


**Figure 2-1. 1,4-Dioxane State Regulatory Values for Drinking Water and Groundwater (µg/L)**

*Data as of 2/3/2021*

# Regulatory Framework & Landscape



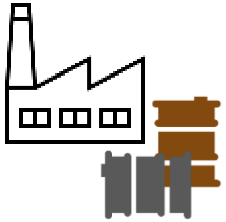



See Section 2 for additional information

# Manufacture
# (Import, Processing, Distribution, Use and Disposal)

<u>U.S. EPA Toxic Substances Control Act (TSCA):</u>

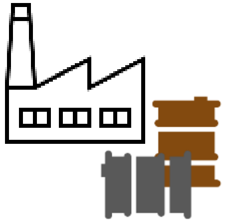
- Priority chemical - risk evaluation DRAFT issued June 2019
- Evaluation of risk to workers and occupational non-users
  - During "industrial and commercial conditions of use such as manufacturing, processing, distribution, use, and disposal"
  - Excludes unintentional occurrence in consumer products



# Manufacture
# (Import, Processing, Distribution, Use and Disposal)

## U.S. EPA Toxic Substances Control Act (TSCA):

- FINALIZED Dec 31, 2020
- Includes Supplemental Risk Evaluations released NOVEMBER 2020
- New evaluation of risk to general public:
  - as a byproducts in consumer products
  - surface water exposure (swimming and fish consumption) via released from manufacturing plants
  - Does NOT evaluate risk from drinking water exposure



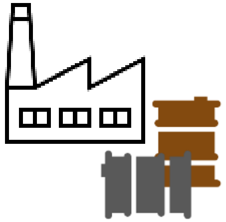
# Manufacture
# (Import, Processing, Distribution, Use and Disposal)

## U.S. EPA Toxic Substances Control Act (TSCA):

Final Conclusions

- No unreasonable risk to occupational non-users or to the environment
- No unreasonable risk to the general public from exposure to consumer products

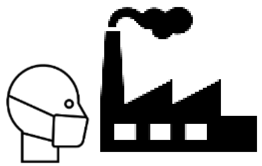
- No unreasonable risk to the general public from dermal or incidental ingestion of surface water, or from fish consumption
- Unreasonable risk to workers in domestic manufacturing, processing, industrial use and disposal



# Current Occupational Standards – Air

- American Conference of Governmental Industrial Hygienists (ACGIH)
  - 20 ppm as an 8-hour threshold limit value
- California Occupational Safety and Health Administration (CA OSHA)
  - 0.28 ppm as an 8-hour time weighted average
- National Institute of Occupational Safety and Health Administration (NIOSH)
  - 1 ppm as a 30-minute ceiling recommended exposure limit for a lifetime
  - 500 ppm immediately dangerous to life and health


Image purchased from Shutterstock

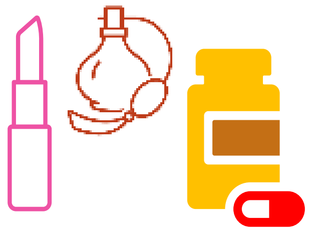


*See Section 2.1 ITRC Guidance Document for more detailed information*
*See Section 5.2 for inhalation toxicity values*

# Cosmetics and Pharmaceuticals

<u>U.S. Food and Drug Administration (FDA)</u>

- No limits in cosmetic products
  - Recommends maximum of 10,000 µg/L in product
- No limits in pharmaceuticals
  - Recommendation as Class 2 solvent that daily exposure should not exceed 3.8 mg/day



# Personal Care Products

- Federal: NEW EPA TSCA conclusion of no unreasonable risks (Dec 2020)
- States: Product Labeling and Consumer Products Laws:
  - California Safe Drinking Water and Toxic Enforcement Act – Prop 65
    - listed as a chemical known to cause cancer
    - requires manufacturers, distributors, and retailers to provide warning labels on products containing concentrations that would result in exposure >30 µg/day
  - California Cleaning Products Right to Know Act
    - requires that manufacturers disclose as an ingredient in cleaning products if present at or above 0.001% or 10,000 µg/L

# Personal Care Products - continued

- New York Cleaning and Personal Care Products
- Prohibits the sale of personal care and cleaning products with concentrations:

    > 2 ppm - after December 31, 2022

    > 1 ppm - after December 31, 2023

Thresholds will be re-evaluated every 5-years.

- Oregon Toxic-Free Kids Act
- Vermont State's List of Chemicals of High Concern to Children
- Washington State's Children's Safe Products Law
    - Requires manufacturers to report if >1 ppm in a product

# Surface Water

U.S. EPA Office of Water – Clean Water Act:

- No surface water quality criteria
  - EPA's Enforcement and Compliance History Online Database ("ECHO") lists numerous National Pollutant Discharge Elimination System (NPDES) permits with monitoring requirements for 1,4-dioxane

States:

- Surface water quality standards (e.g., Colorado and Michigan)
- Wastewater discharge requirements

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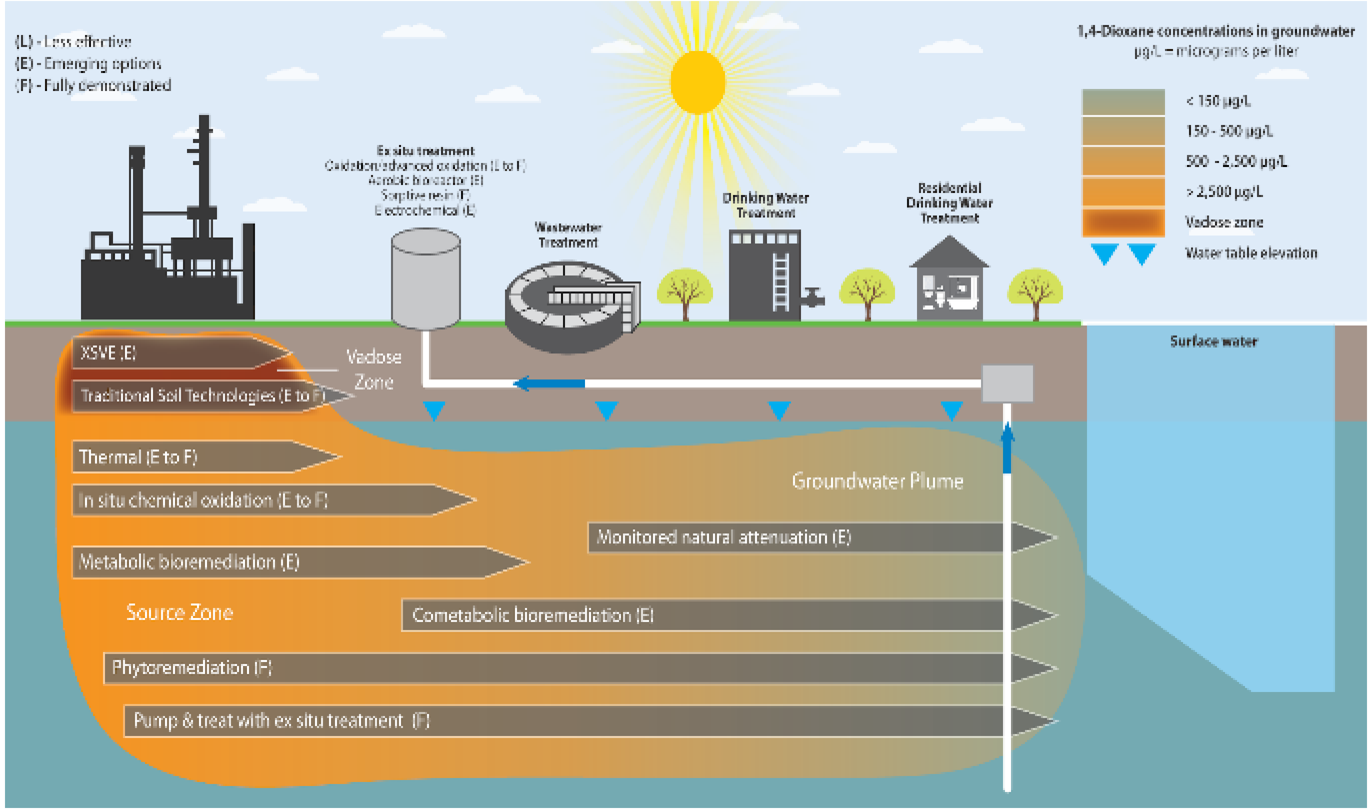
*See Section 2.1.1.1.2 ITRC Guidance Document for more detailed information*

# Environmental Cleanup Programs: Federal

- Hazardous Substance under CERCLA/RCRA
- CERCLA
  - screening levels* used for screening and informing cleanup goals
  - RSL** = 0.46 µg/L groundwater

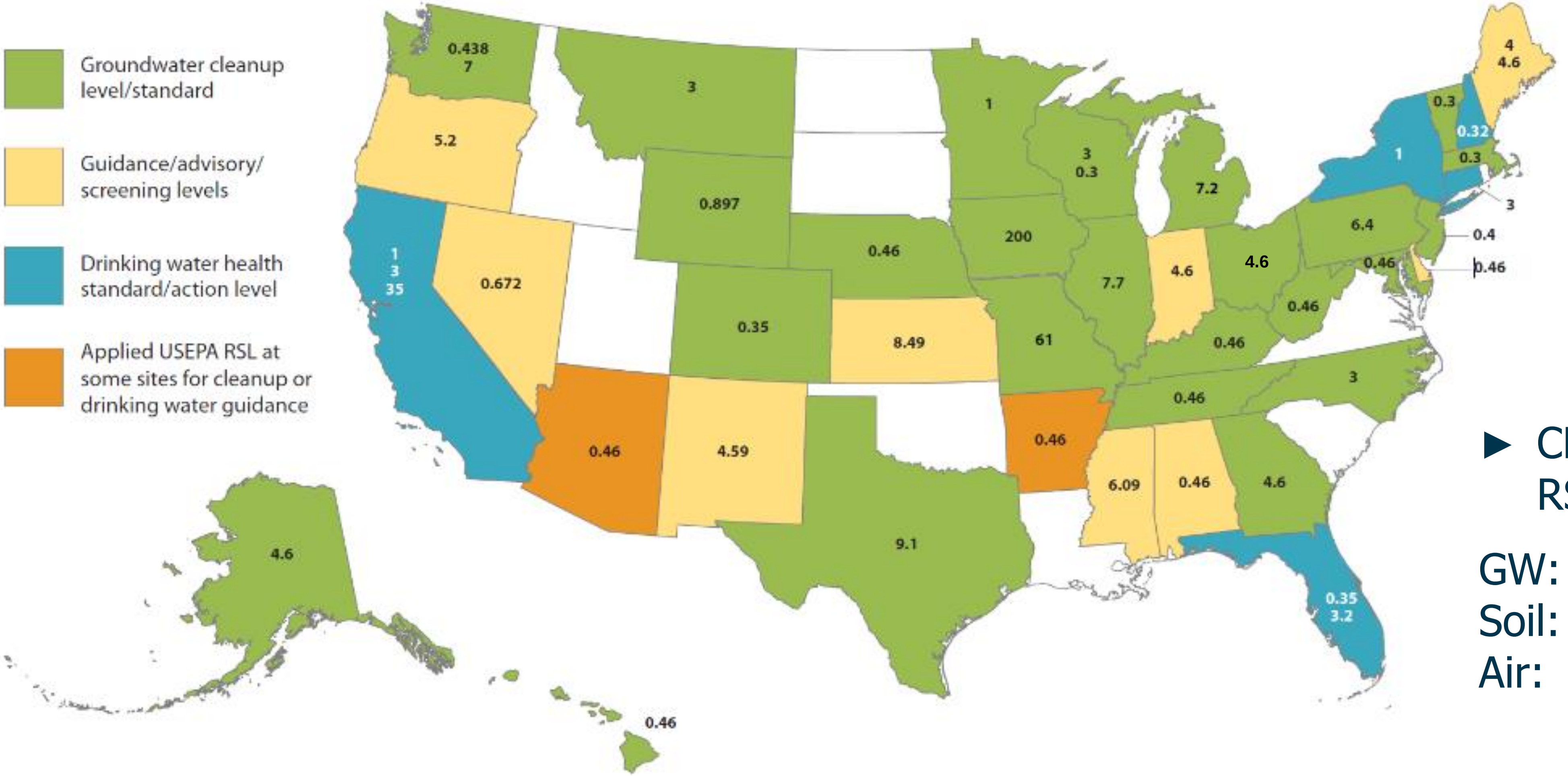
    = 5.3 mg/kg soil

    = 0.56 µg/m3 (0.16 ppm) air




*screening levels – not cleanup standards
** Regional Screening Levels (RSL) shown at $10^{-6}$ cancer risk level for residential exposure

# Environmental Cleanup Programs




- GW values range 0.3 to 200 µg/L
- Most recent: ~ 4 to 9 µg/L Reflecting $10^{-5}$ cancer risk level
- CERCLA Residential RSLs:

GW: 0.46 – 46 µg/L
Soil: 5.3 mg/kg
Air: 0.56 µg/m$^3$ (0.16 ppm)

Note: Some states may not be represented. Map based on best available information as of Feb 2021. States without an entry may apply the EPA RSL and/or HA

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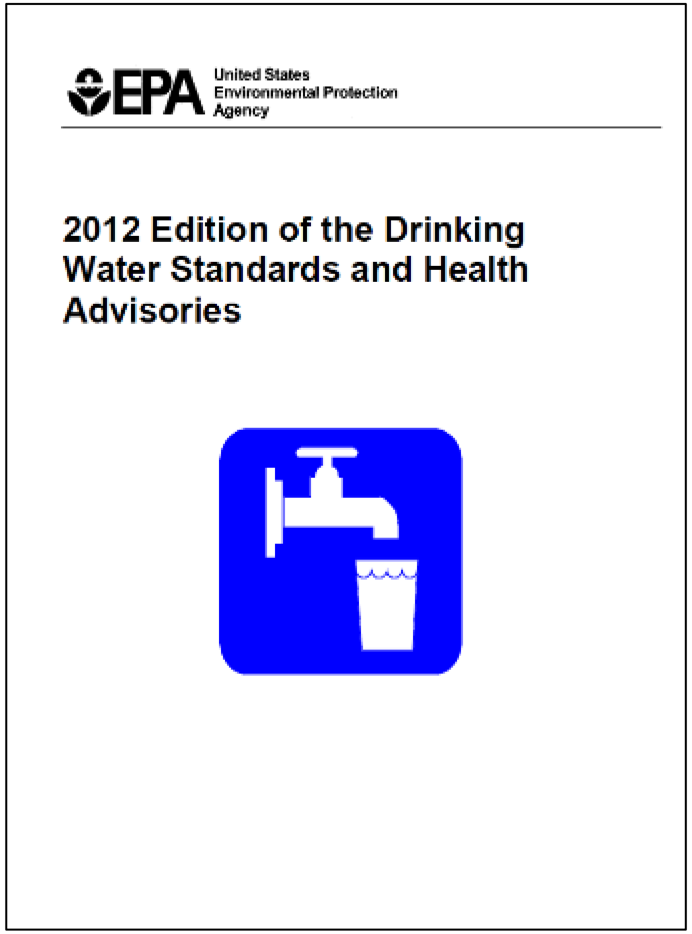
*See Appendix A and Figure 2-1 ITRC Guidance Document for more detailed information*

# Drinking Water - Safe Drinking Water Act (SDWA)

## U.S. EPA Office of Water – Safe Drinking Water Act:

- Standards for drinking water quality and monitoring requirements for public water systems
  - No maximum contaminant level (MCL)
- Identified as a chemical known to occur in public drinking water systems and may require regulation
  - Candidate Contaminant List (CCL) since 2008
- March 2021, EPA "has not determined whether there is a meaningful opportunity for public health risk reduction" (FRN, 86.40)
  - Continuing to evaluate for MCL

# Drinking Water - Health Advisory - Guidance

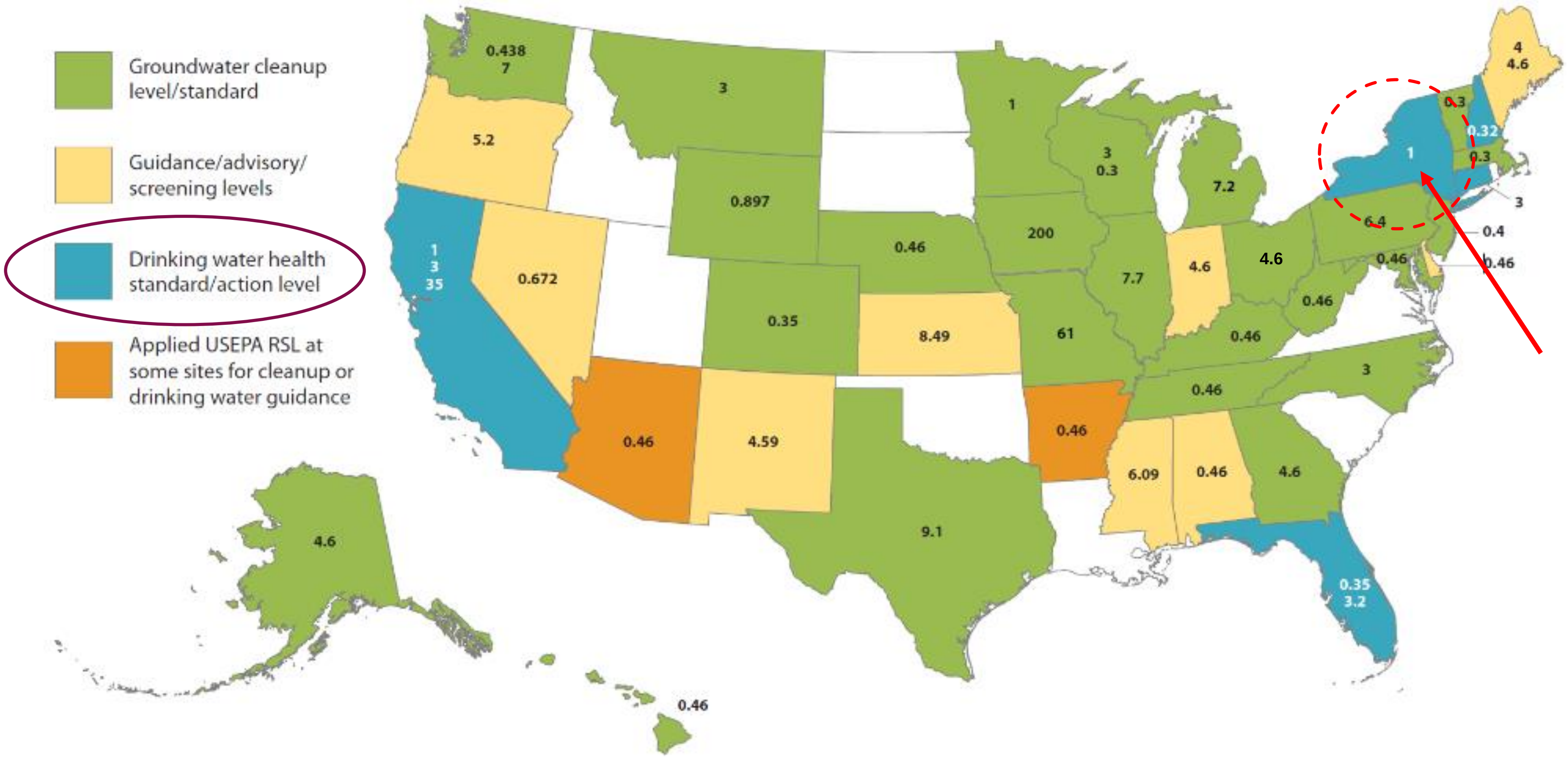

United States Environmental Protection Agency

2012 Edition of the Drinking Water Standards and Health Advisories

- Provide information for drinking water contaminants that can / are known to / anticipated to cause human health effects
- Issued when an enforceable drinking water standard has not been established
- Lifetime cancer risk level of **35 µg/L** (10-4 cancer risk)

*See Section 5 ITRC Guidance Document for more detailed information*

# Drinking Water – HA & State Regulation




Lifetime cancer risk level of **35 µg/L**

*($10^{-4}$ cancer risk)*

New York 2020 MCL of **1 µg/L** is first in the US

New Jersey proposed MCL of **0.33 µg/L**

Health Canada MAC of **50 µg/L**

*See Appendix A and Figure 2-1 ITRC Guidance Document for more detailed information*

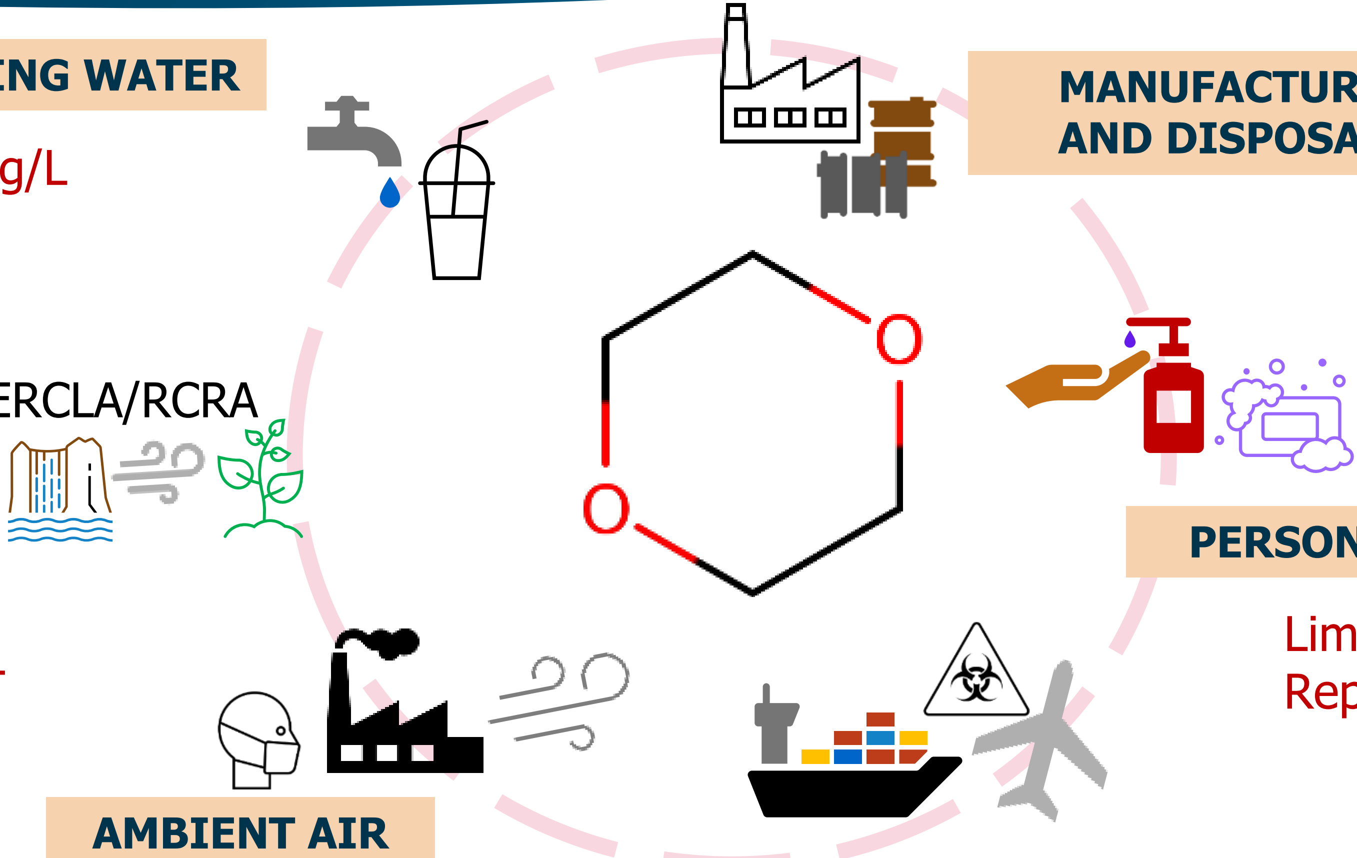
# Regulatory Framework & Landscape - Conclusion

**DRINKING WATER**

0.33 – 50 µg/L

**MANUFACTURE AND DISPOSAL**

TSCA evaluation




**COSMETICS**

**PERSONAL CARE PRODUCTS**

Limits of 10,000 µg/L (10 ppm)
Reporting if >1ppm

CERCLA/RCRA

**ENVIRONMENT**

Residential RSLs:

GW: 0.35 – ~9 µg/L
Soil: 5.3 mg/kg
Air: 0.56 µg/m$^3$ (0.16 ppm)

**AMBIENT AIR**

**TRANSPORTATION**

# Module 3: Environmental Fate, Transport and Investigation Strategies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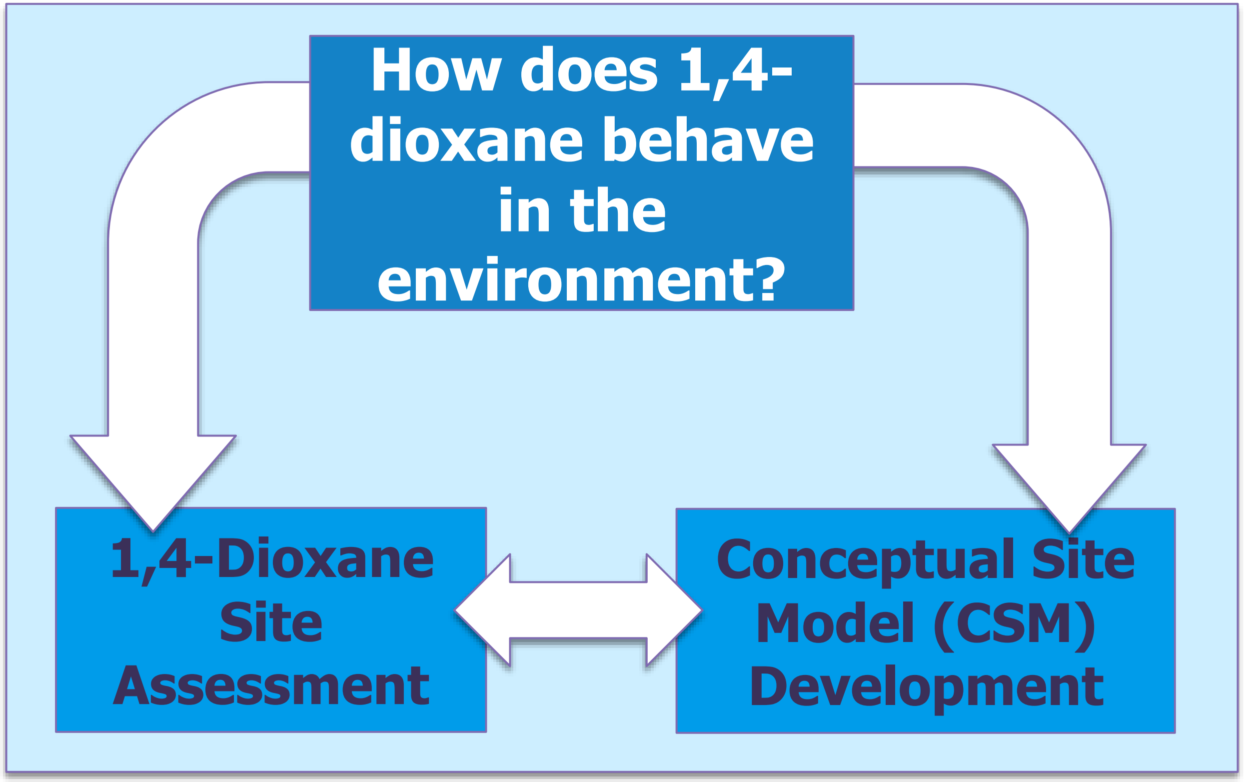
# Learning Objectives

- Understand key physical/chemical properties
- Identify fate and transport processes that are relevant for 1,4-D
- Develop a general conceptual site model for 1,4-D
- Establish an informed site assessment strategy

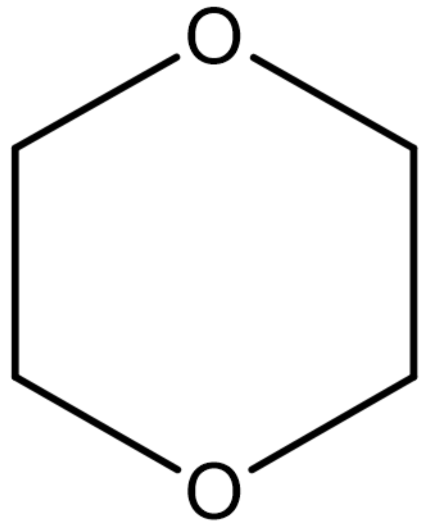
# Fate and Transport of 1,4-Dioxane – Why is this Important?

- Behavior in the environment helps us answer key questions about where to look for 1,4-dioxane, potential for risk, and how it might be treated
- Function of 1,4-dioxane's physical-chemical properties and site characteristics
- Still evolving!



# Fate and Transport of 1,4-Dioxane – Critical Characteristics

- Low organic carbon partitioning coefficient, so it does not bind strongly to soils and readily leaches to groundwater
- Miscible in water
- Common co-contaminant with chlorinated solvents
- Low Henry's constant relative to common co-contaminants
- Known degradation pathways involve oxidation



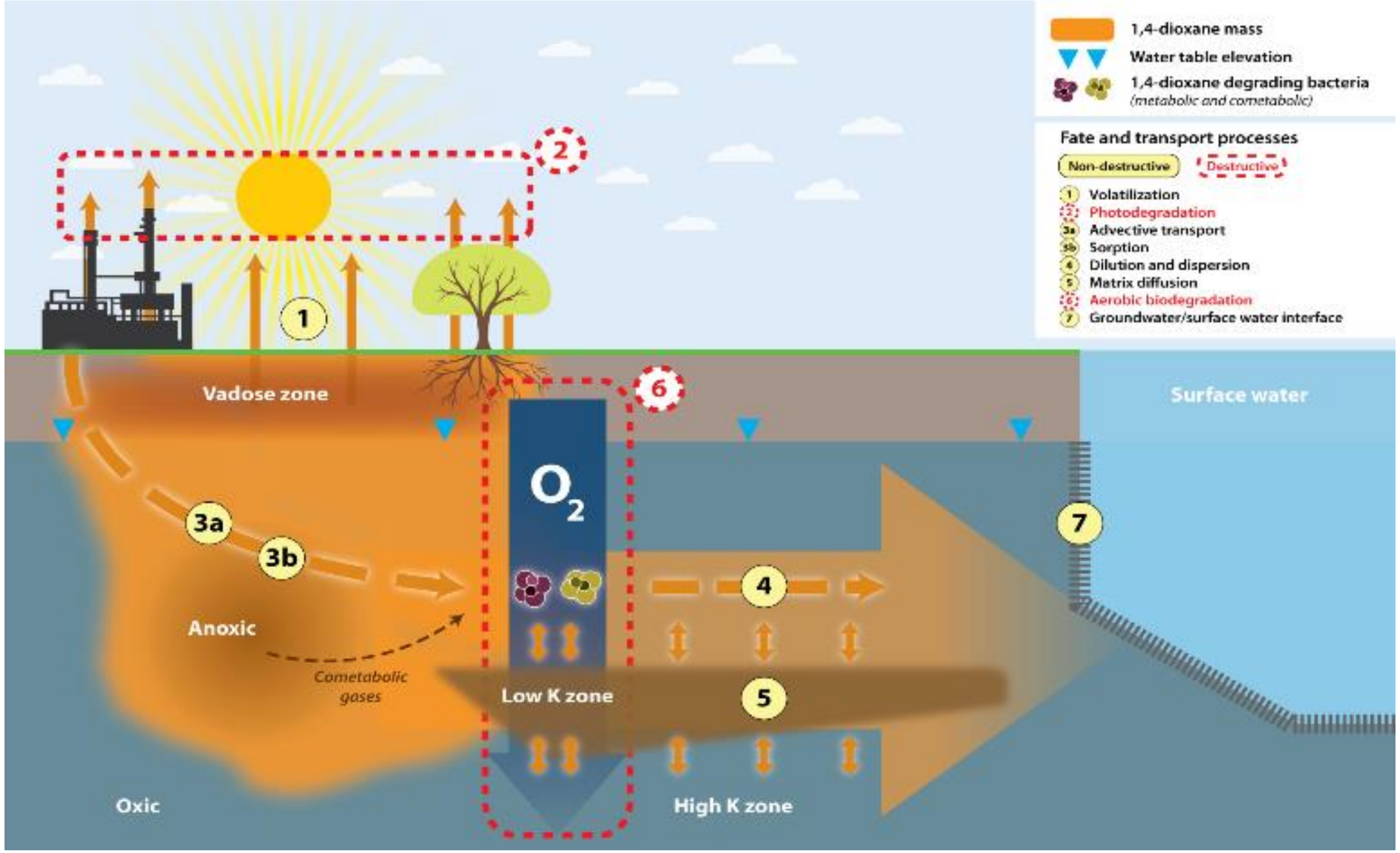

*1,4-Dioxane*

# Fate and Transport of 1,4-Dioxane – Critical Characteristics

| Property | Units | 1,4-D | Benzene | TCE | 1,1,1-TCA | 1,1-DCA | 1,1-DCE |
|---|---|---|---|---|---|---|---|
| **Water solubility** | g/L | 1000 | 1.8 | 1.1 | 0.91 | 5.04 | 5.06 |
| **Vapor pressure** | mm Hg (at 25°C) | 23.8 | 95.2 | 72.6 | 124 | 227 | 234 |
| **Henry's Law constant** | atm-m3/mol (at 25°C) | $4.8 \times 10^{-6}$ | $5.48 \times 10^{-3}$ | $9.1 \times 10^{-3}$ | $1.6 \times 10^{-2}$ | $5.62 \times 10^{-3}$ | $5.8 \times 10^{-3}$ |
| **Log $K_{oc}$** | Dimension-less | 0.54 | 1.92 | 1.81 | 2.18 | 1.55 | 1.48 |
| **Boiling point** | °C | 101 | 80 | 87 | 74 | 57.4 | 32 |

*See Table 3.1 in ITRC Guidance Document for complete table with additional parameters*

# Conceptual Site Model for 1,4-Dioxane



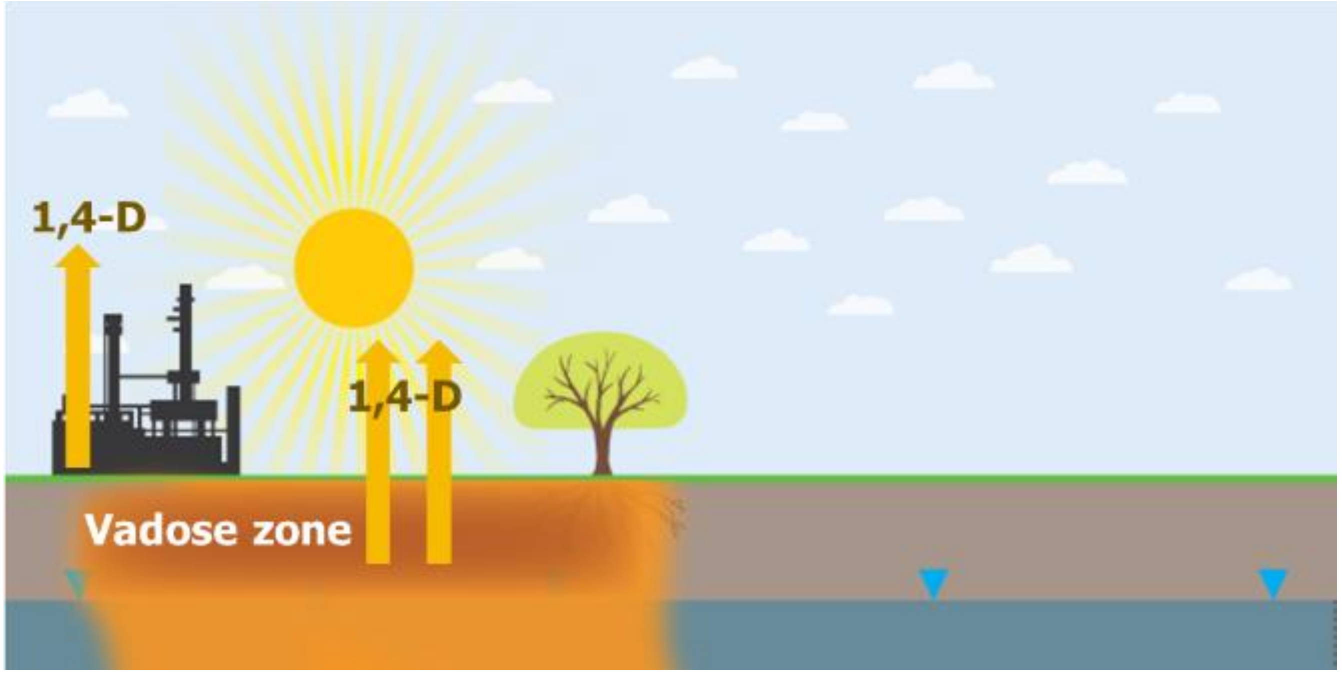

- Let's go through these processes individually

*See Figure 3-3 in ITRC Guidance Document for complete figure with additional details*

***DISCLAIMER:*** *CSM is an example and may not be applicable to all release types or settings*

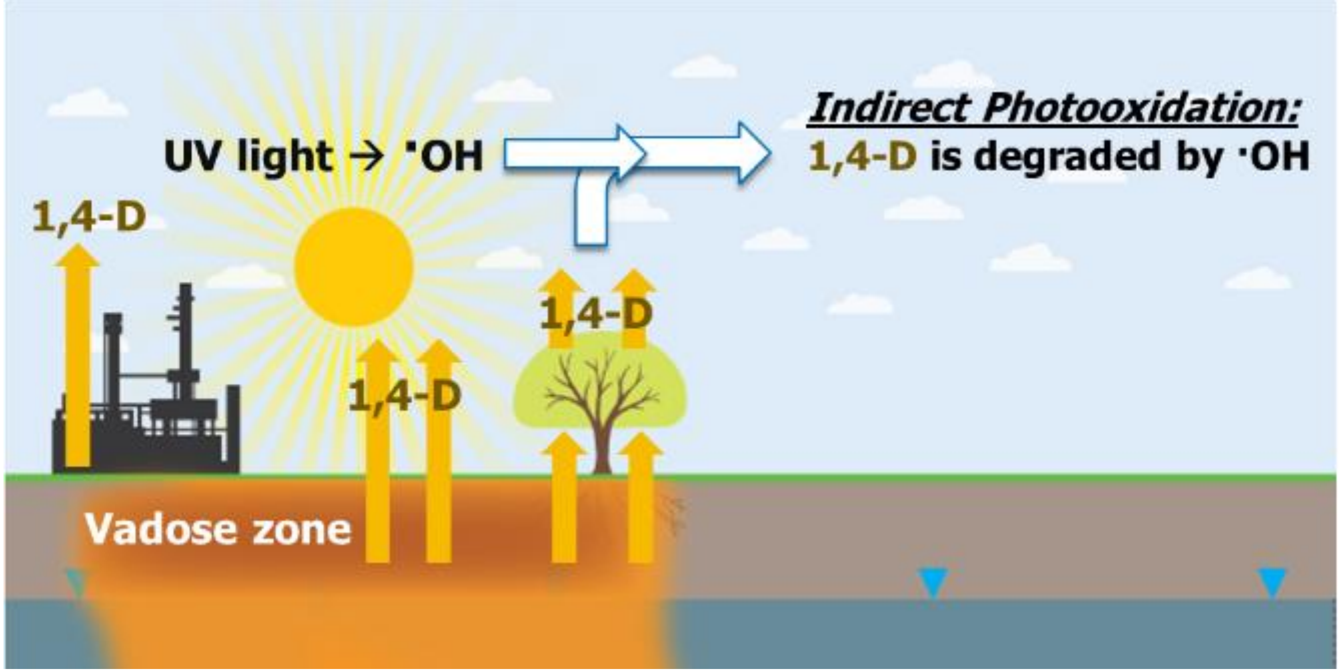
# Volatilization

- Transfer from liquid phase to gas phase is primarily a concern for releases from dry surfaces or releases of pure phase (i.e., absence of water)
- Volatilization of 1,4-dioxane once dissolved in groundwater is limited due to low Henry's Law constant (several orders of magnitude lower than values for TCE and 1,1,1-TCA)
- Non-destructive process



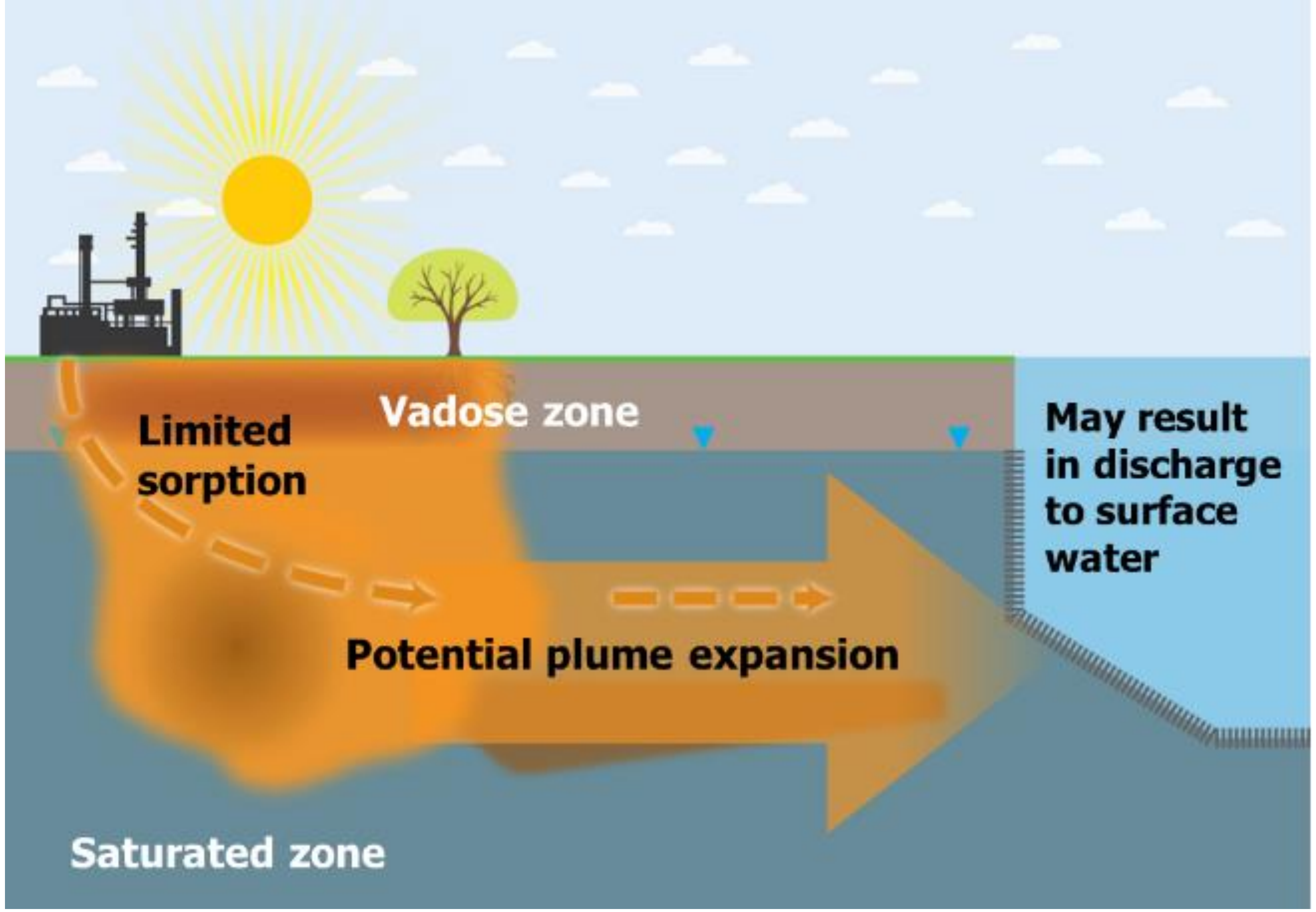
# Photodegradation

- Low organic carbon
- 1,4-dioxane is photodegradable once it is in the atmosphere – indirect photolysis via hydroxyl radicals
  - Destructive process
  - Half-life of a few hours to days
- Plant uptake has also been demonstrated
  - Leads to transfer from subsurface to atmosphere (where it is subject to photodegradation)



# Advection-Dispersion-Dilution

- Low organic carbon
- Advection is a major concern due to limited capacity to sorb to aquifer solids
  - Non-destructive process
- Potential for migration at similar velocity as groundwater
- High solubility (essentially miscible), though dilution and dispersion may affect concentrations during groundwater transport



# Advection Example: Hypothetical Release of Chlorinated Solvents and 1,4-Dioxane

- **Question:** How would 1,4-dioxane be expected to migrate in groundwater relative to other contaminants (e.g., chlorinated solvents) that may have been released?

- **Key Considerations:**
  (1) Physical-chemical characteristics of co-occurring contaminants
  (2) Hydrogeologic characteristics of aquifer
  (3) Timing of release(s)

# Advection Example: Hypothetical Release of Chlorinated Solvents and 1,4-Dioxane

## *1955 Release*

**TCE** (R = 1.1 – 1.7)

**1,1-DCE** (R = 1.0 – 1.3)

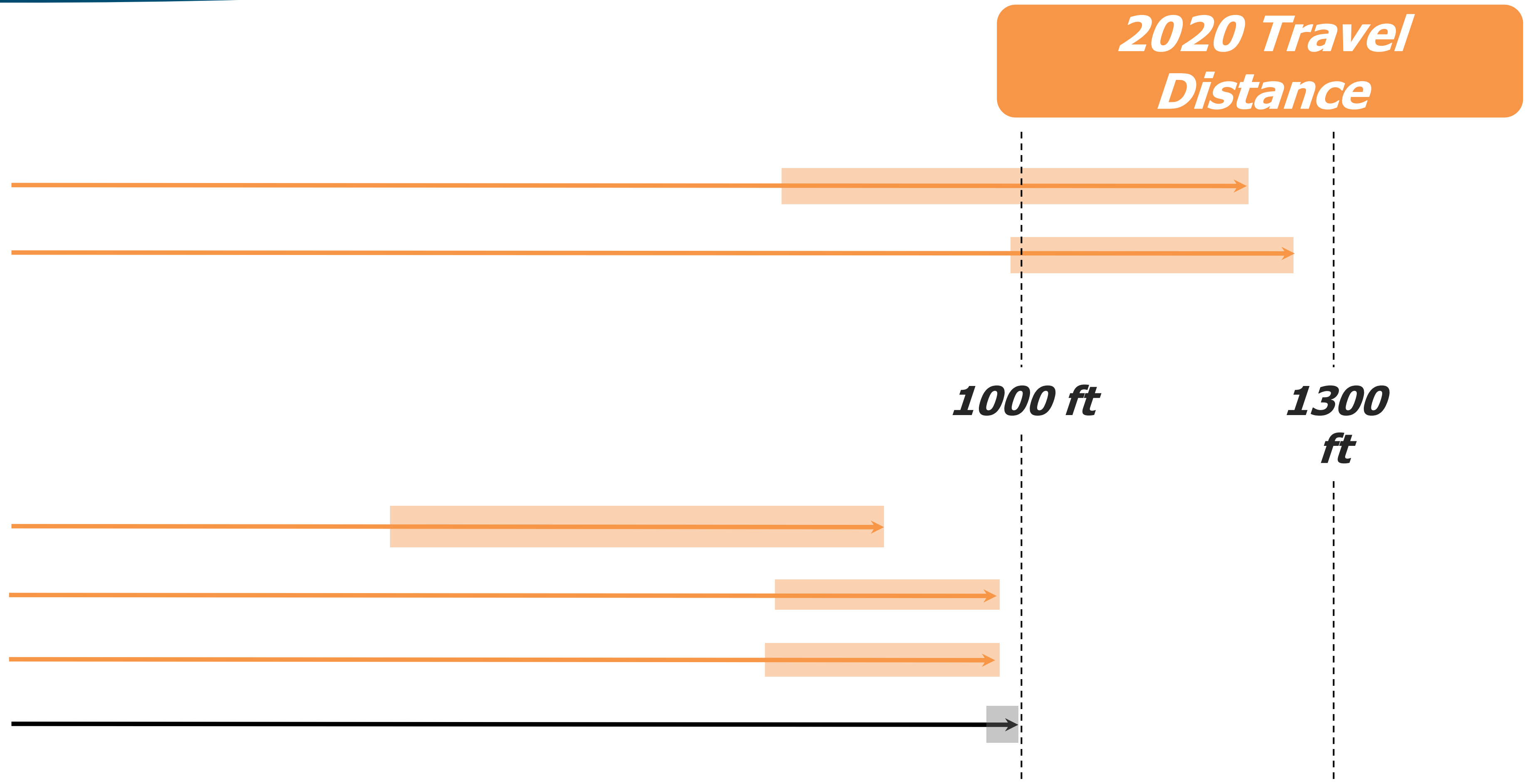
## *1970 Release (at the same site)*

**1,1,1-TCA** (R = 1.2 - 2.7)

**1,1-DCE** (R = 1.0 – 1.3)

**1,1-DCA** (R = 1.0 - 1.4)

**1,4-Dioxane** (R = 1.0 – 1.03)

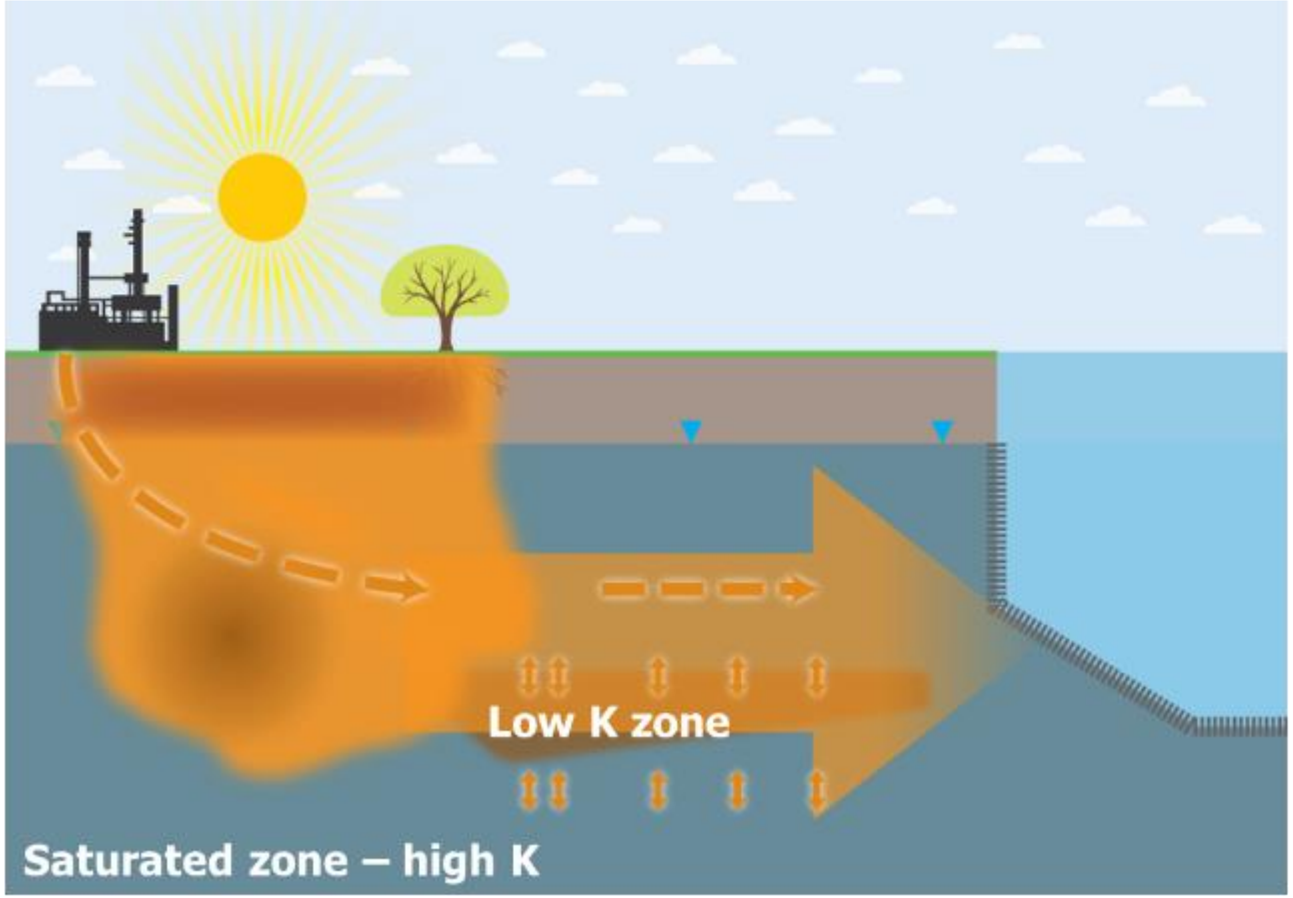



R = Retardation Factor with range based on $f_{oc}$ = 0.001 – 0.0001
GW seepage velocity = 20 ft/yr

***Figure 3-1.*** *ITRC 1,4-Dioxane Team, 2020*

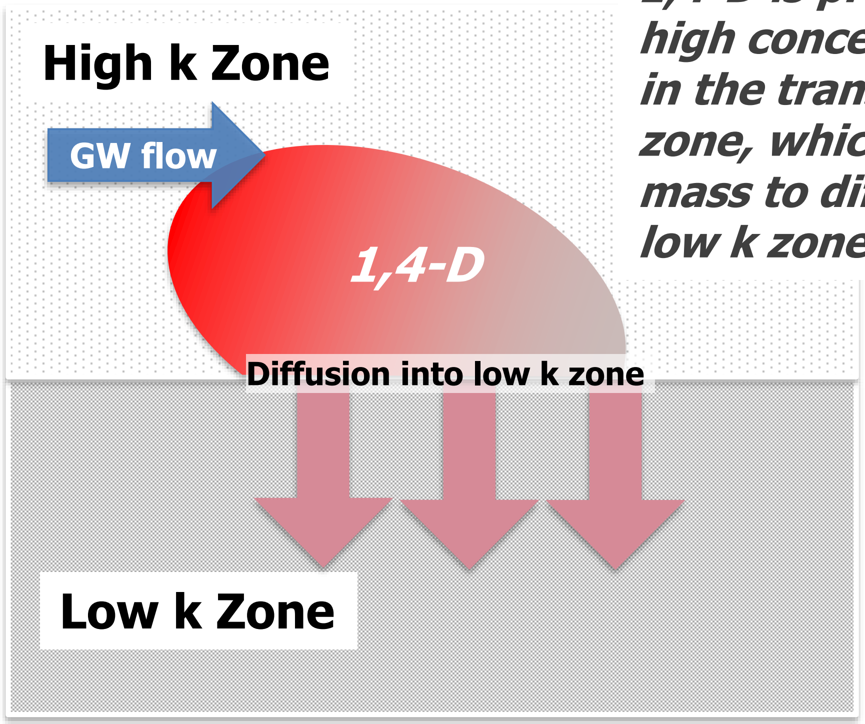
# Matrix Diffusion

- Diffusion of dissolved 1,4-dioxane mass into low-permeability (low K) zones (e.g., clays, silts, rock) within or adjacent to aquifer
  - Non-destructive process
- Storage of mass w/in low K zones could contribute to persistence
- Poses additional challenges for remediation



# Matrix Diffusion: Influences Over Time

## EARLY STAGES (After Release)

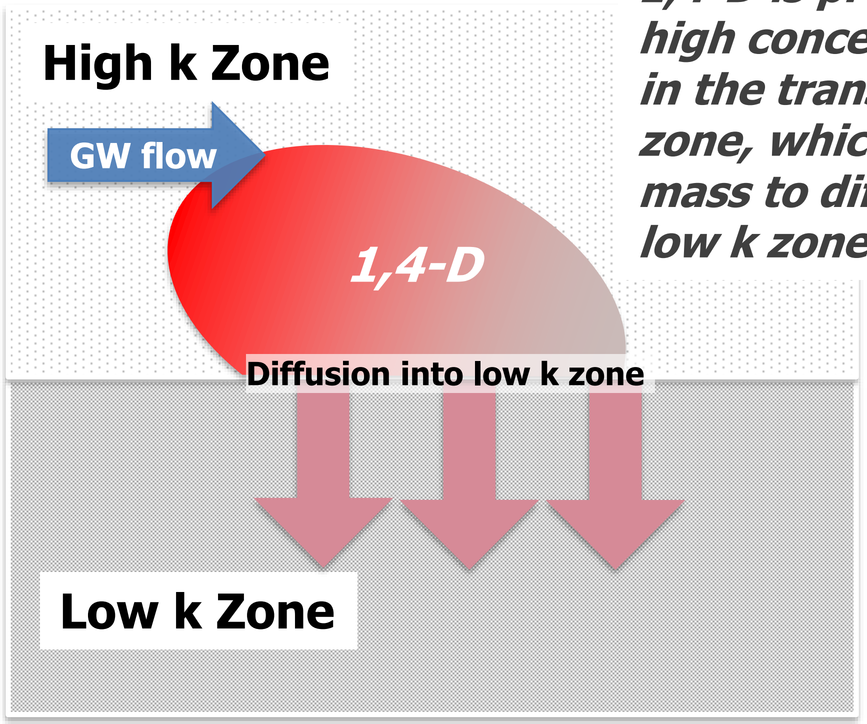



***1,4-D is present in high concentrations in the transmissive zone, which causes mass to diffuse into low k zone***

***Figure 3-2. Overview of Matrix Diffusion Process for 1,4-Dioxane.***
*ITRC 1,4-Dioxane Team, 2020.*

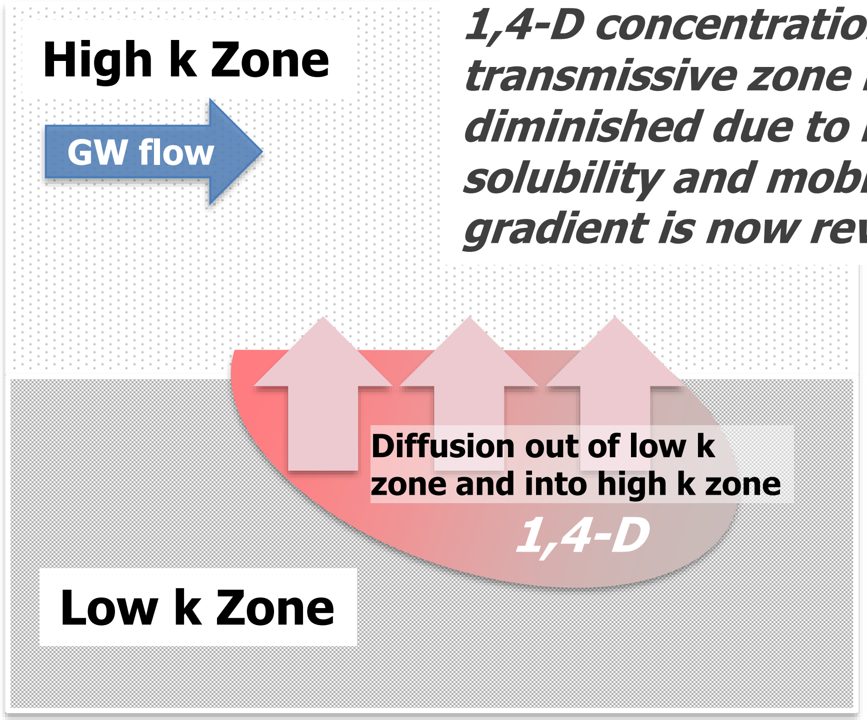
# Matrix Diffusion: Influences Over Time

## EARLY STAGES (After Release)




***1,4-D is present in high concentrations in the transmissive zone, which causes mass to diffuse into low k zone***

## LATER STAGES (During Site Investigation)

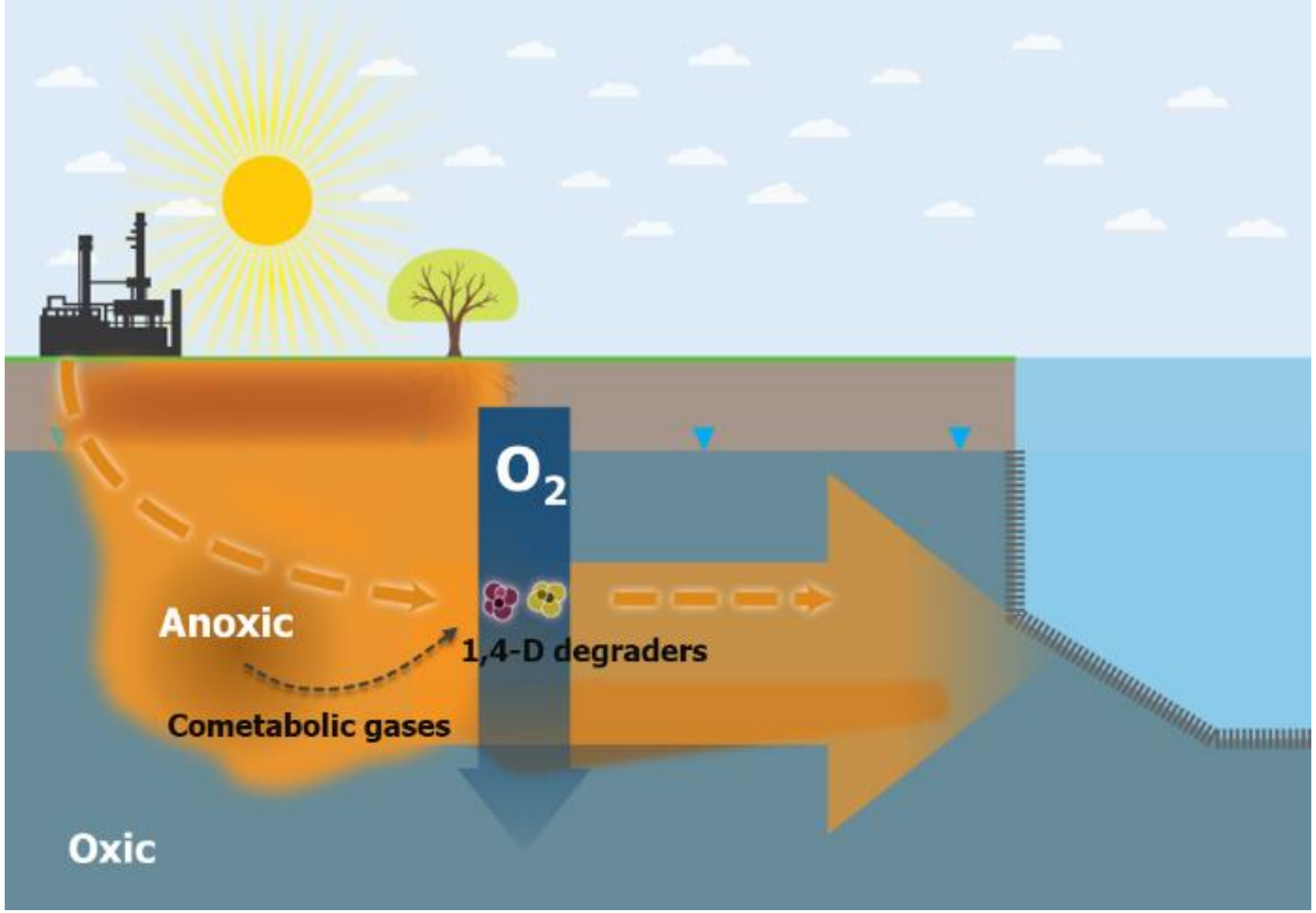



***1,4-D concentrations in transmissive zone have diminished due to high solubility and mobility - gradient is now reversed***

***Figure 3-2. Overview of Matrix Diffusion Process for 1,4-Dioxane.***
*ITRC 1,4-Dioxane Team, 2020.*

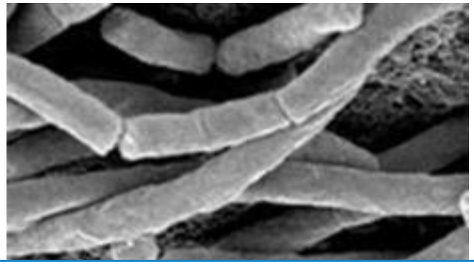
# Biodegradation

- 1,4-dioxane previously not considered to be biodegradable
- Now understood that 1,4-dioxane can be biologically oxidized
  - Destructive process
- Several different microorganisms have been identified (and more are likely)
- Relies on availability of dissolved $O_2$ in groundwater
  - Very limited evidence for anaerobic pathway for 1,4-dioxane



# Biodegradation

- **Metabolic** and **cometabolic** biodegradation pathways have been identified
  - **Metabolic:** 1,4-dioxane used by microbes as source of carbon and energy
  - **Cometabolic:** 1,4-dioxane is degraded by enzymes that lack specificity. This is side effect of degradation of primary substrates



**CB1190** - most widely studied degrader of 1,4-D via metabolic pathway

**Primary substrates**

**THF**
**isobutane**
**propane**
**ethane**
**toluene**
**isopentane**
**n-pentane**
**n-butane**

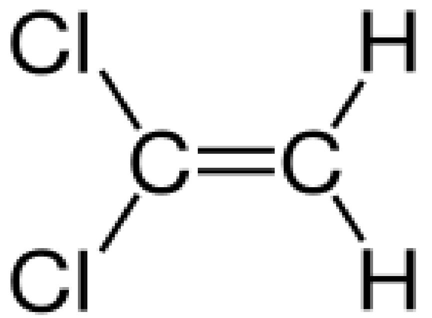
**Cometabolic target**

**1,4-D**

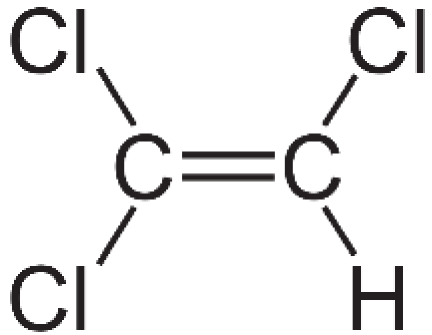
ITRC Interstate Technology Regulatory Council
ECOS
ERIS Environmental Research Institute of the States

# Biodegradation

- **Inhibition** is a potential concern for both types of 1,4-dioxane biodegradation processes
  - co-occurring chlorinated solvents (e.g., 1,1-DCE, TCE)
  - some metals (e.g., $Cu^{+2}$)

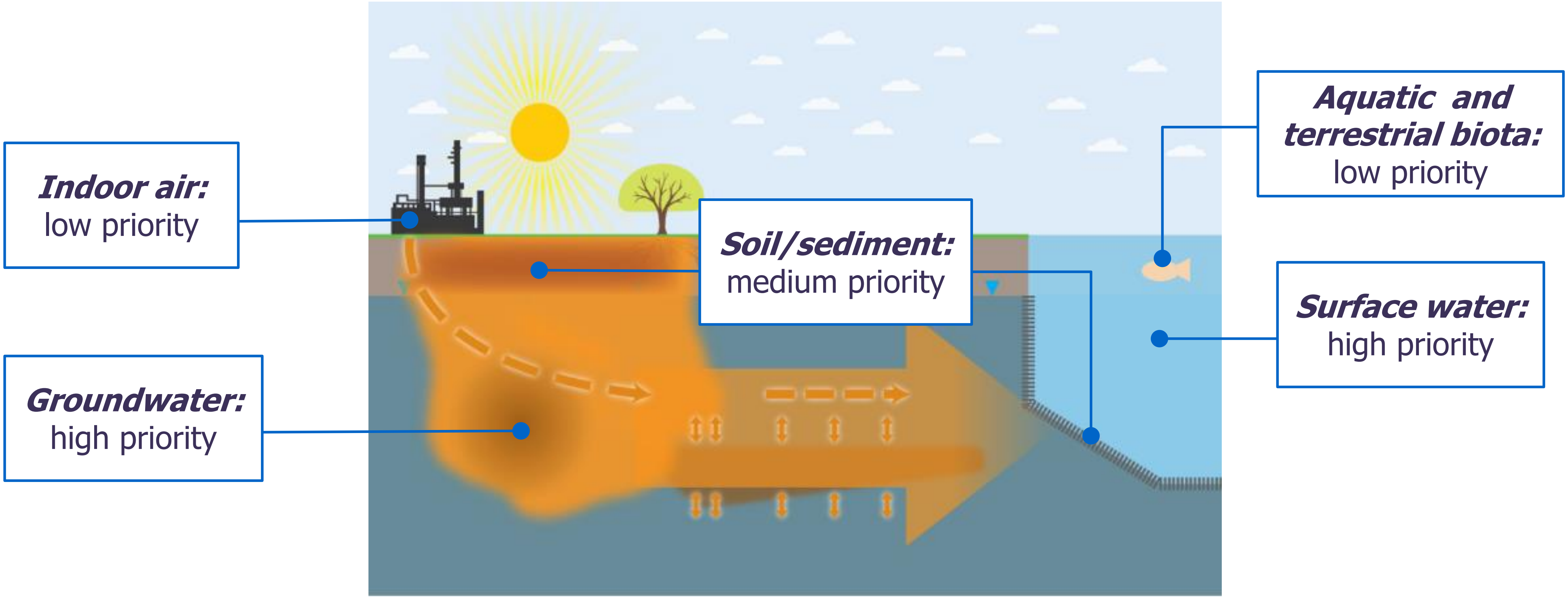



1,1-DCE



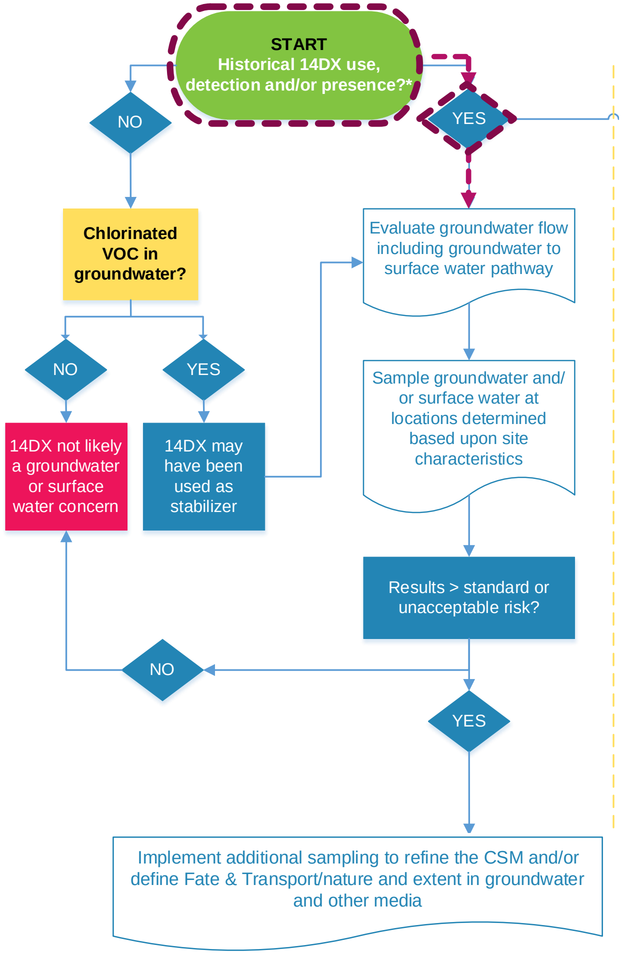

TCE

# What Media Are Likely To Be Important?




*See Table 3.4 in ITRC Guidance Document for tabulated summary of media considerations*

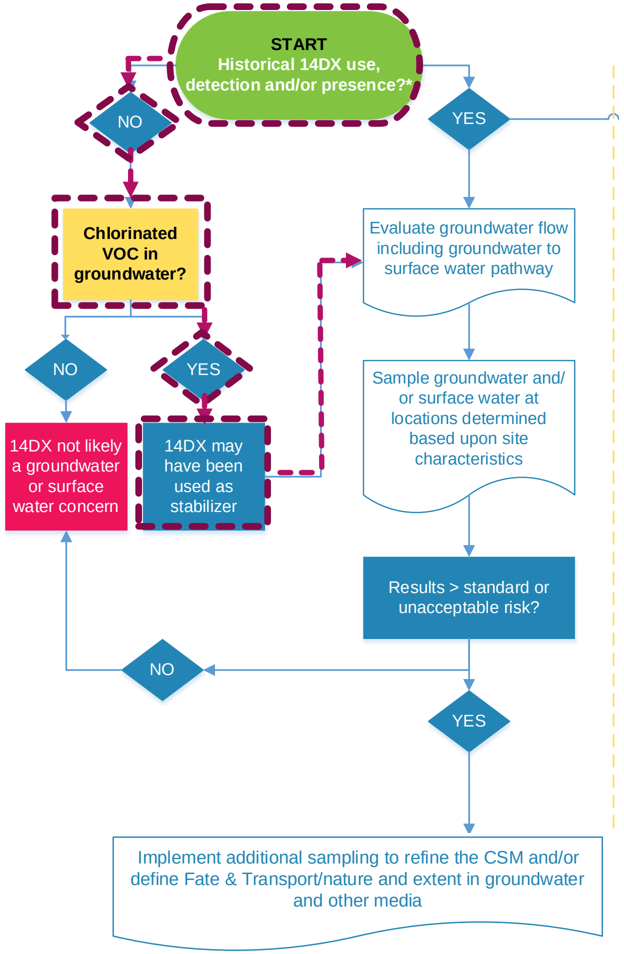
# Guidance for 1,4-Dioxane Site Assessment




## PRIORITIES:

- Sites where historical 1,4-dioxane use has been established and/or 1,4-dioxane has been detected

# Guidance for 1,4-Dioxane Site Assessment



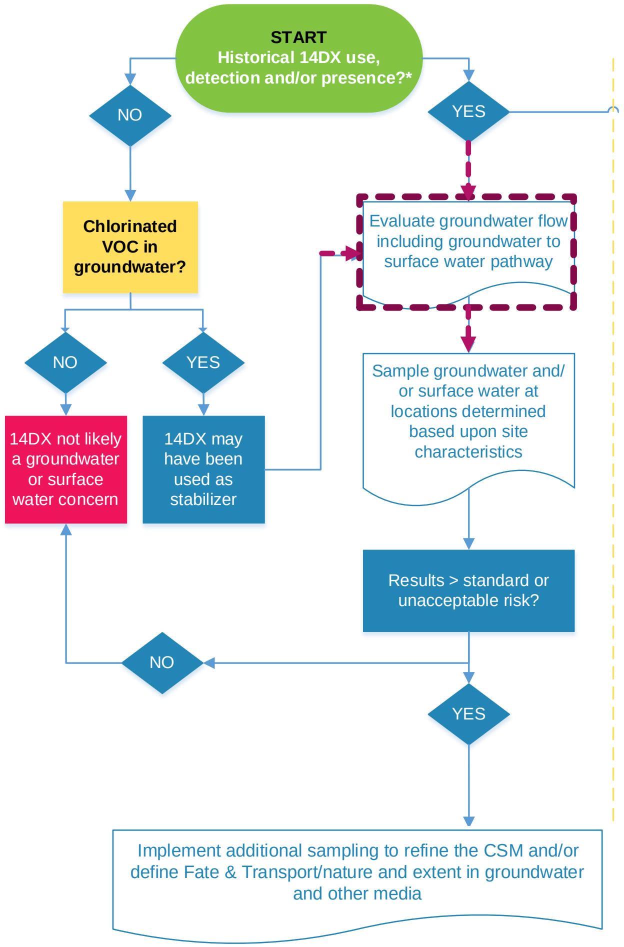

## PRIORITIES:

- Sites where historical 1,4-dioxane use has been established and/or 1,4-dioxane has been detected
- Site with chlorinated solvents



*See Figure 3-4 in ITRC Guidance Document for complete flowchart*

# Guidance for 1,4-Dioxane Site Assessment

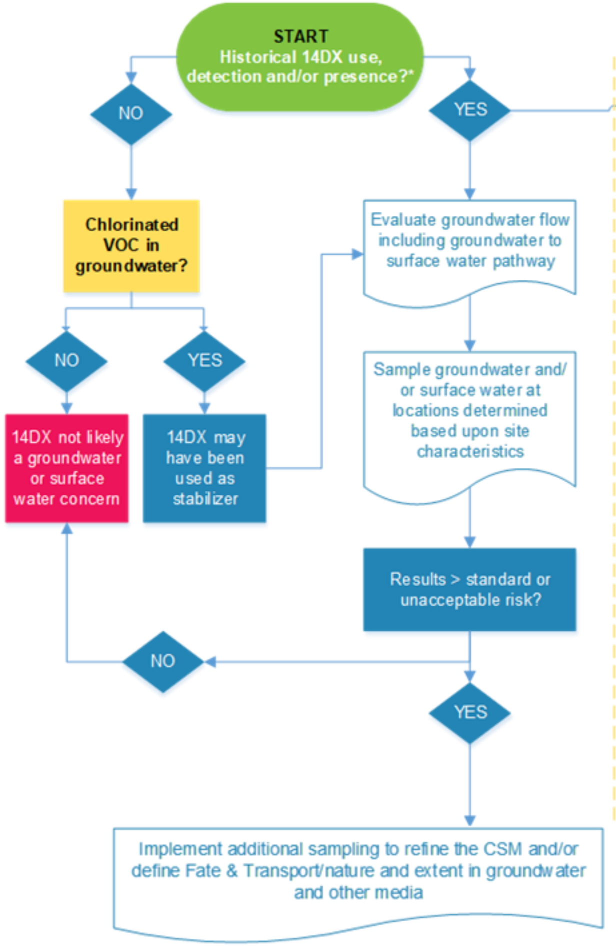



**PRIORITIES:**

- Sites where historical 1,4-dioxane use has been established and/or 1,4-dioxane has been detected
- Site with chlorinated solvents
- Groundwater first, but evaluate possible discharge to surface water (if applicable)

*See Figure 3-4 in ITRC Guidance Document for complete flowchart*

# Guidance for 1,4-Dioxane Site Assessment




**ALSO CONSIDER**

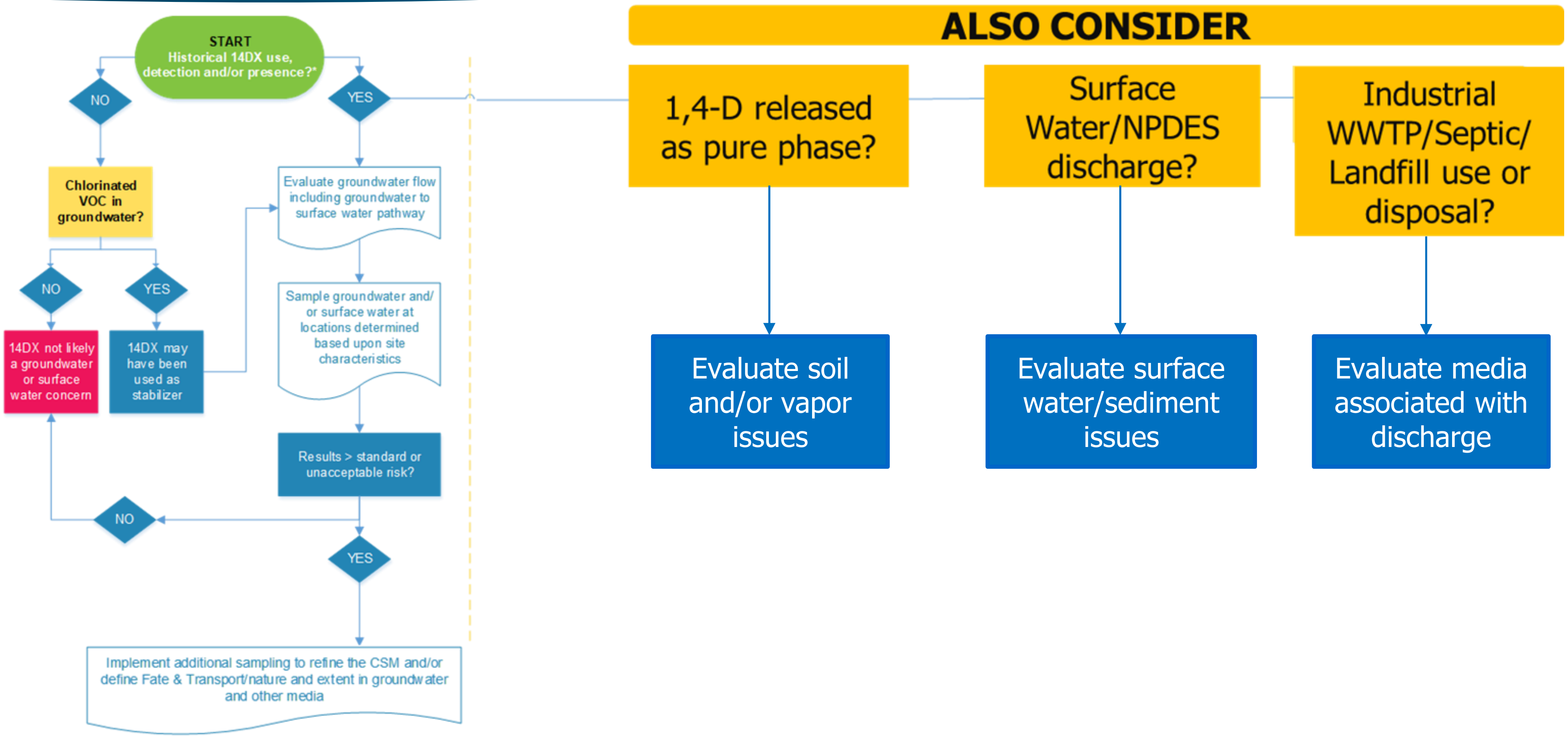
1,4-D released as pure phase?

Surface Water/NPDES discharge?

Industrial WWTP/Septic/ Landfill use or disposal?

*See Figure 3-4 in ITRC Guidance Document for complete flowchart*

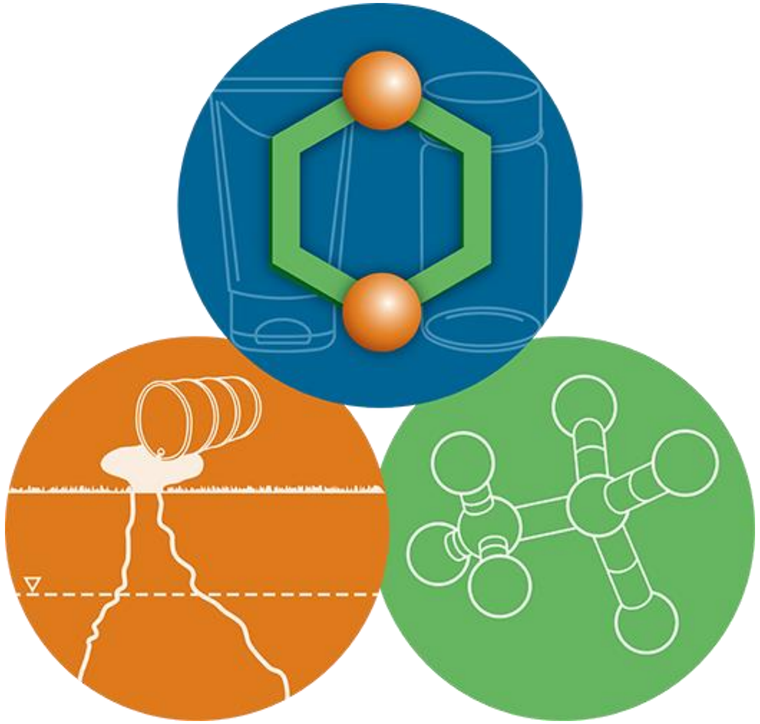
# Guidance for 1,4-Dioxane Site Assessment




*See Figure 3-4 in ITRC Guidance Document for complete flowchart*

# Take Home Messages

- Understand key physical/chemical properties
  - Low organic carbon partitioning coefficient and Henry's constant; high solubility
- Identify fate and transport processes that are relevant for 1,4-dioxane
  - Advection with limited sorption in subsurface
  - Photodegradation in atmosphere; biodegradation in water is possible but requires oxygen
- Develop a general conceptual site model for 1,4-dioxane
  - Must reflect site-specific conditions (e.g., low permeability zones in aquifer may promote matrix diffusion)
- Establish an informed site assessment strategy
  - Existing characterization data for chlorinated solvents can help guide, but recognize potential differences for 1,4-dioxane
  - Decisions about sampling other media if dictated by site-specific considerations, including potential sources, release histories, and hydrogeologic setting



# Question Break

# Module 4: Sampling & Analysis

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# Learning Objectives

- Highlight potential sampling precautions
- Explain different holding times, containers, and preservation techniques
- Identify the common analytical methods available for 1,4-dioxane in different matrices, with a focus on water
- Understand the benefits and limitations of the available analytical methods

# Sampling Precautions

- Groundwater Precautions
- Soil Precautions
- Decontamination

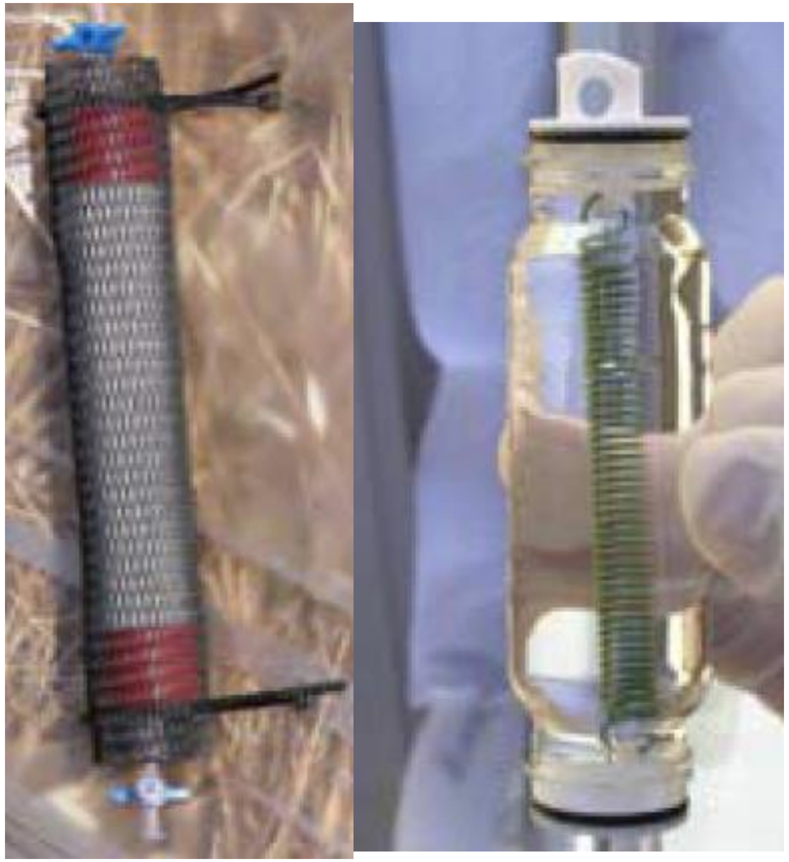
*Picture courtesy of TRC*

# Sampling Precautions - Groundwater

- Conventional Sampling acceptable;
  however, if passive diffusion sampling performed …
  - Low density polyethylene membrane in standard PDB:
    NOT suitable for 1,4-Dioxane
  - Need to use different membrane materials or pore sizes that facilitate diffusion of 1,4-Dioxane into the sampler.

Hydrasleeve
ITRC Technology Overview of Passive Sampler Technologies, March 2006

- Rigid Porous Polyethylene (RPP) sampler
- Dual Membrane PDB (DMPDB) sampler
- Snap Sampler®
- HydraSleeve™



**Left: RPP Sampler; Right: Snap Sampler**
**ITRC Technology Overview of Passive Sampler Technologies, March 2006**

- Low yield wells



*PDB: Passive diffusion bag*

# Sampling Precautions - Soil

- Conventional sampling acceptable; however, if samples have very low moisture content
  - Very dry (desert) climate
  - Local dry microclimate (e.g., under building)

The Terra Core® Sampler

Source: www.ennovativetech.com

***Expect more volatilization: use VOC soil collection method***

*VOC: Volatile organic compound*

# Sampling Precautions – Equipment Decontamination

- 1,4-Dioxane common impurity in detergents
- Need to prevent detergents from remaining on equipment
- Use of disposable equipment or passive samplers eliminates need for decontamination

TechNotes
critical cleaning advice from Alconox Inc.

Industry » Detergents »

*Categorized* | **Alconox, Environmental, Laboratory, Liquinox**

**Does Alconox or Liquinox contain 1,4-Dioxane?**

Posted on 07 March 2014. Tags: 1-4 Dioxane


Q. Does Alconox or Liquinox contain 1,4-Dioxane?

A. Nonionic Liquinox likely contains extremely trace levels 1,4-Dioxane, but anionic Alconox is very unlikely to contain 1-4 dioxane. Sometimes people inadvertently refer to Liquinox as Alconox because it is made by Alconox, inc.

Liquinox is a nonionic detergent and does contain extreme trace levels of 1,4-Dioxane. In general most detergents with nonionic surfactant ingredients will have trace 1,4 Dioxane as a trace impurity from the ethylene oxide condensed polymers that are part of most nonionic surfactants.

The trace contaminant 1,4-Dioxane is found in nonionic detergents. Most nonionic surfactants are derived from alkyl groups with condensed polymers of ethylene oxide attached. The ethylene oxide polymerization process during the manufacture of the nonionic surfactant results in traces of 1,4-Dioxane being formed.

The trace contaminant 1-4 dioxane is volatile. The concentration will diminish with time. In Liquinox the concentration would be well below tens or hundreds of ug/L. The residue potential in a detergent used at a 1% dilution that is thoroughly rinsed would be well below single digit nanograms/L in sampling equipment; very thorough rinsing can reduce that to tenths or hundredths of nanograms/L. Labs should do equipment blanks to assure that thorough rinsing has been done whenever any nonionic detergent such as Liquinox is used.

To ask another Technical Cleaning question from our experts please visit **Ask Alconox** at www.alconox.com. You can also find Liquinox and Alconox detergent **technical bulletins** and **MSDSs**.

INTERSTATE TECHNOLOGY REGULATORY COUNCIL ITRC
ECOS
ERIS ENVIRONMENTAL RESEARCH INSTITUTE OF THE STATES

# Holding Times, Containers, & Preservation

Dependent on analytical method and matrix

| Matrix | Method | Container | Preservation | Holding Time |
|---|---|---|---|---|
| **Aqueous** | SW-846 8260 | 3 40-mL VOA vials | HCl to pH <2; Cool 0-6°C | 14 days to analysis |
| | SW-846 8270 | 2 1-L amber glass | Cool 0-6°C | 7 days to extraction; 40 days from extraction to analysis |
| **Solid** | SW-846 8260 | 3 40-mL VOA vials or 3 EnCore™ samplers | Vials: low-level (water) and high-level (MeOH)<br>Cool 0-6°C | **Low-level:** 48 hours to freezer; 14 days to analysis<br>**High-level:** 14 days to analysis<br>EnCore™ samplers: 48 hours to preservation; 14 days to analysis |
| | SW-846 8270 | 1 4-oz glass jar | Cool 0-6°C | 14 days to extraction; 40 days from extraction to analysis |
| **Air** | EPA TO-15 | 1 canister | None | 30 days to analysis |
| | EPA TO-17 | 2 sorbent tubes | Cool <4°C | 30 days to analysis |

*HCl: Hydrochloric acid*
*MeOH: Methanol*
*VOA: Volatile organic analyte*

# VOC or SVOC: Why Does it Matter?

- VOC or SVOC Methods
- Modifications needed to typical VOC or SVOC methods
- Dependent upon required sensitivity
- Dependent upon other contaminants of concern in sample
- Regulatory agency requirements/certification



*SVOC: Semivolatile organic compound*
*VOC: Volatile organic compound*

# Analytical Methods

| Method | Technique | RLs | Comments |
|---|---|---|---|
| **8260 (VOC): Aqueous** | Ambient P&T with full scan GC/MS | 200-500 µg/L | 1,4-dioxane-d8 IS |
| | **Heated P&T with SIM GC/MS** | **2-5 µg/L** | **1,4-dioxane-d8 IS<br>Prone to interferences** |
| **8270 (SVOC): Aqueous** | Full scan GC/MS | 5-10 µg/L | Poor extraction efficiency |
| | **Isotope dilution with SIM GC/MS** | **0.15-0.4 µg/L** | **1,4-dioxane-d8 IS<br>Improved precision & accuracy** |
| **8260 (VOC): Solid** | Ambient P&T with full scan GC/MS | 0.2-0.5 mg/kg | 1,4-dioxane-d8 IS |
| | Heated P&T with SIM GC/MS | 0.002-0.005 mg/kg | 1,4-dioxane-d8 IS<br>Not routinely needed |
| **8270 (SVOC): Solid** | Full scan GC/MS | 0.05-0.2 mg/kg | Poor extraction efficiency |
| | Isotope dilution with SIM GC/MS | 0.00067 mg/kg | 1,4-dioxane-d8 IS<br>Improved precision & accuracy |
| **522: Drinking Water** | SIM GC/MS | 0.05-0.1 µg/L | Solid phase extraction |
| **TO-15 (Air)** | Full scan GC/MS | 0.7-1.0 µg/m$^3$ | |
| **TO-17 (Air)** | Full scan GC/MS | 1.1-11 ng/tube | |

*GC/MS = Gas chromatography/mass spectrometry*
*IS = Internal standard*

*P&T = Purge & trap*
*SIM = Selective ion monitoring*

# What to Know About Methods

- Use of 1,4-dioxane-d8 as internal standard: why critical?
- Why is 8260 analysis more prone to interferences?
- Why does isotope dilution improve precision & accuracy of results?

**Sample spiked with KNOWN amount of isotope (1,4-dioxane-d8)**

**1,4-dioxane result corrected by proportional amount based on isotope**

**BENEFITS**:

- Corrects for analytical error associated with matrix
- Corrects for matrix interferences

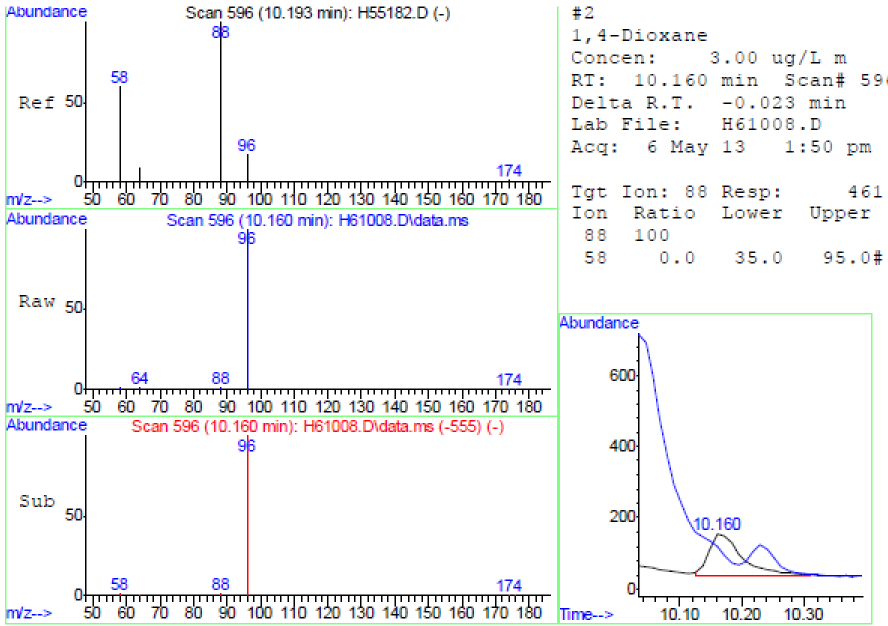
$$\text{Concentration 1,4D} = \frac{\text{1,4D Area} * \text{True Concentration 1,4-dioxane-d8}}{\text{Area 1,4-dioxane-d8} * \text{Response Factor}}$$

# 1,4-Dioxane 8260/SIM: Surrogate Recovery

```
      Compound                          R.T. QIon  Response  Conc Units Dev(Min)
-----------------------------------------------------------------------------------
Internal Standards
  1) 4-bromofluorobenzene             14.121  174     1760      1.00 ug/L    -0.01

System Monitoring Compounds
  3) 1,4-DIOXANE-D8                   10.033   96   959711   8777.13 ug/L    -0.10
  Spiked Amount      10.000     Range  60           Recovery    = 87771.30%#

Target Compounds                                                        Qvalue
  2) 1,4-Dioxane                      10.160   88      461m     3.00 ug/L
-----------------------------------------------------------------------------------
```



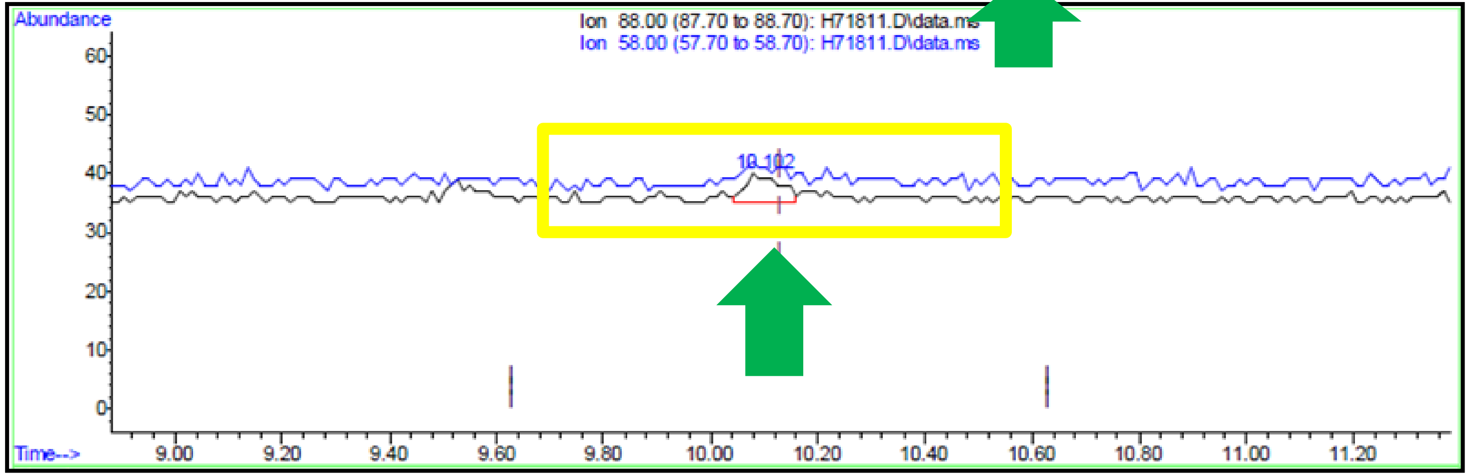

| | Concentration in sample | Primary Qions |
|---|---|---|
| Cis-1,2-Dichloroethene | 665 µg/L | 61, 96 |
| Trichloroethene | 8,290 µg/L | 95, 96 |
| 1,4-Dioxane-d8 | 10 µg/L | 96 |

***8260/SIM not as reliable when elevated levels of chlorinated VOCs present.***

*SIM = Selective ion monitoring*
*VOC = Volatile organic compound*

# 1,4-Dioxane 8260/SIM: 0.2 ug/L standard

| Compound | R.T. | QIon | Response | Conc Units | Dev(Min) |
|---|---|---|---|---|---|
| **Internal Standards** | | | | | |
| 1) 4-bromofluorobenzene | 14.085 | 174 | 1202 | 1.00 ug/L | 0.00 |
| **System Monitoring Compounds** | | | | | |
| 3) 1,4-DIOXANE-D8 | 10.090 | 96 | 475 | 8.45 ug/L | 0.03 |
| Spiked Amount 10.000 | Range 60 - 140 | | Recovery = 84.50% | | |
| **Target Compounds** | | | | | Qvalue |
| 2) 1,4-Dioxane | 10.102 | 88 | 22m | 0.31 ug/L | |




**Primary quantitation ion:**
m/z 88

**Secondary ion:**
m/z 58 (~60% of m/z 88)

**8260/SIM not as reliable at RLs below 5 µg/L due to extremely poor response (area counts) at lower concentrations**

*m/z = Mass to charge ratio*
*RL = Reporting limit*
*SIM = Selective ion monitoring*

| Method | Average Costs |
| --- | --- |
| SW-846 8260C (full scan) | $100 |
| SW-846 8260C (SIM) | $50-100 |
| SW-846 8270D (full scan) | $100-200 |
| SW-846 8270D (SIM) | $100-200 |
| EPA 522 | $150 |

*SIM = Selective ion monitoring*

Depends on other contaminants present at your site and project objectives

# Which Analytical Method Should I Use?

Depends on how low your reporting limits need to be

- 8270 with SIM more sensitive than 8260 with SIM

Safe to use 8270 with SIM and isotope dilution

- Does require larger sampling volume

If elevated concentrations of VOCs (> 200 µg/L), use one of the 8270 methods because 8260 won't work well

- If VOCs >200 µg/L, lab will need to perform dilution on 8260 SIM analysis to prevent contamination/saturation of trap during analysis
- If CVOCs >200 µg/L, same issue plus significant interference with 1,4-dioxane surrogate (1,4-dioxane-d8) with cis-1,2-dichloroethene (same quantitation ion)

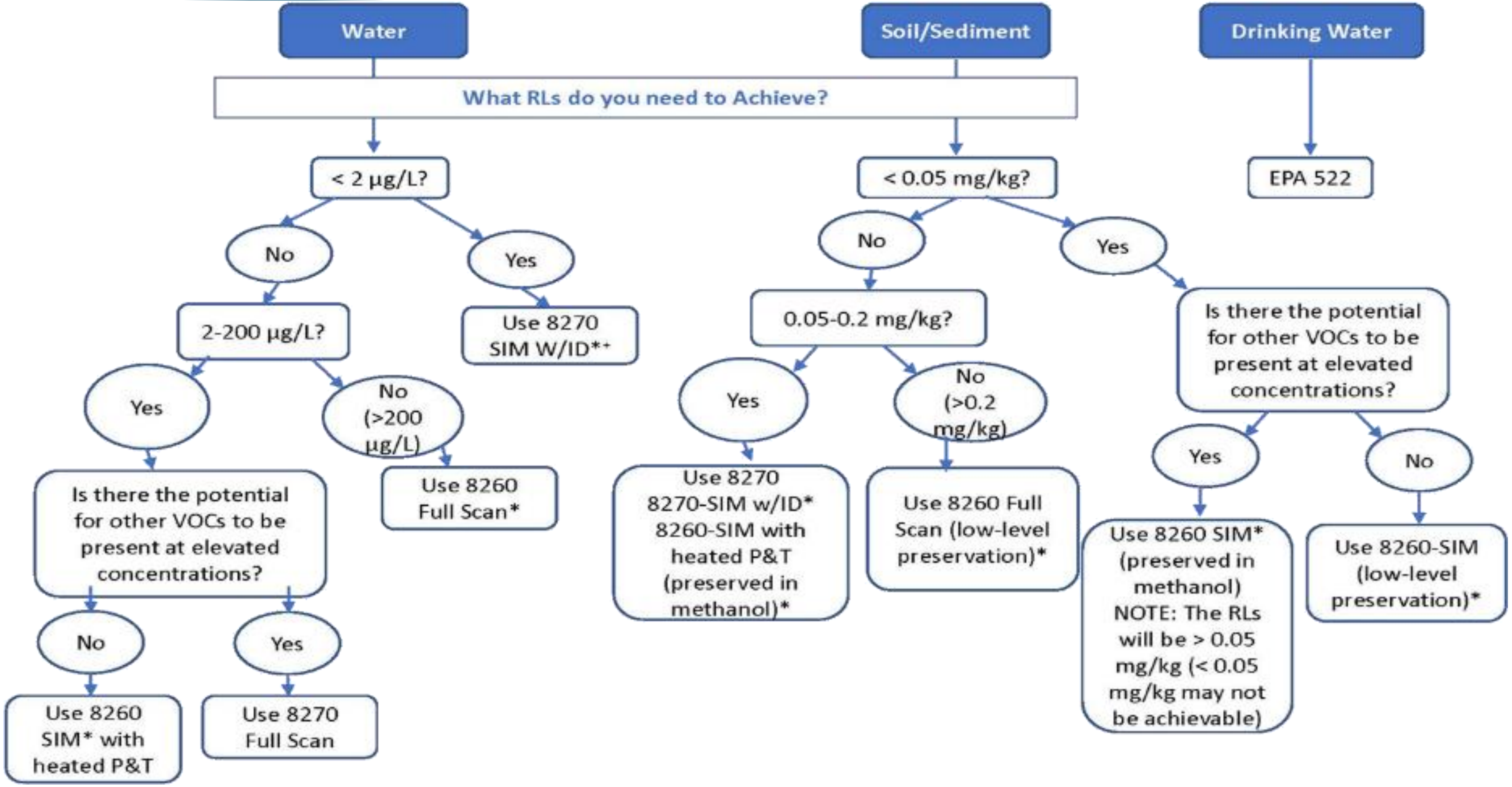
Check with the regulatory agency

- NYSDEC preferred method: 8270 with SIM

*CVOC = Chlorinated VOC*
*NYSDEC = New York State Department of Environmental Conservation*

*SIM = Selective ion monitoring*
*VOC = Volatile organic compound*

# Figure 4-2 in Tech Reg: Flow Chart for Selecting Method for 1,4-Dioxane



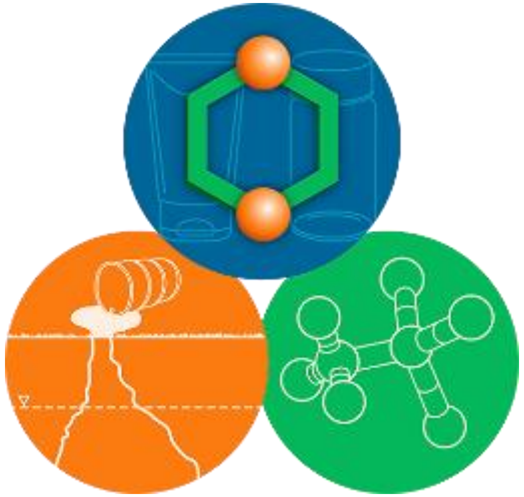
# Knowledge Check

Poll Question

You are sampling groundwater for 1,4-dioxane and need to meet the regulatory screening criteria of 0.3 ug/L. Prior rounds of sampling detected elevated concentrations of some chlorinated VOCs (e.g., cis-1,2-dichloroethene). Which analytical method will you likely need to use, in the absence of any regulatory requirement?

A. SW-846 8260 (VOC) with SIM
B. SW-846 8260 (VOC) without SIM
C. SW-846 8270 (SVOC) with SIM/isotope dilution

# Module 5: Toxicity and Risk Assessment



Janet K. Anderson, PhD, DABT
GSI Environmental Inc.
Austin, TX
513-226-6528
jkanderson@gsienv.com

# Learning Objectives

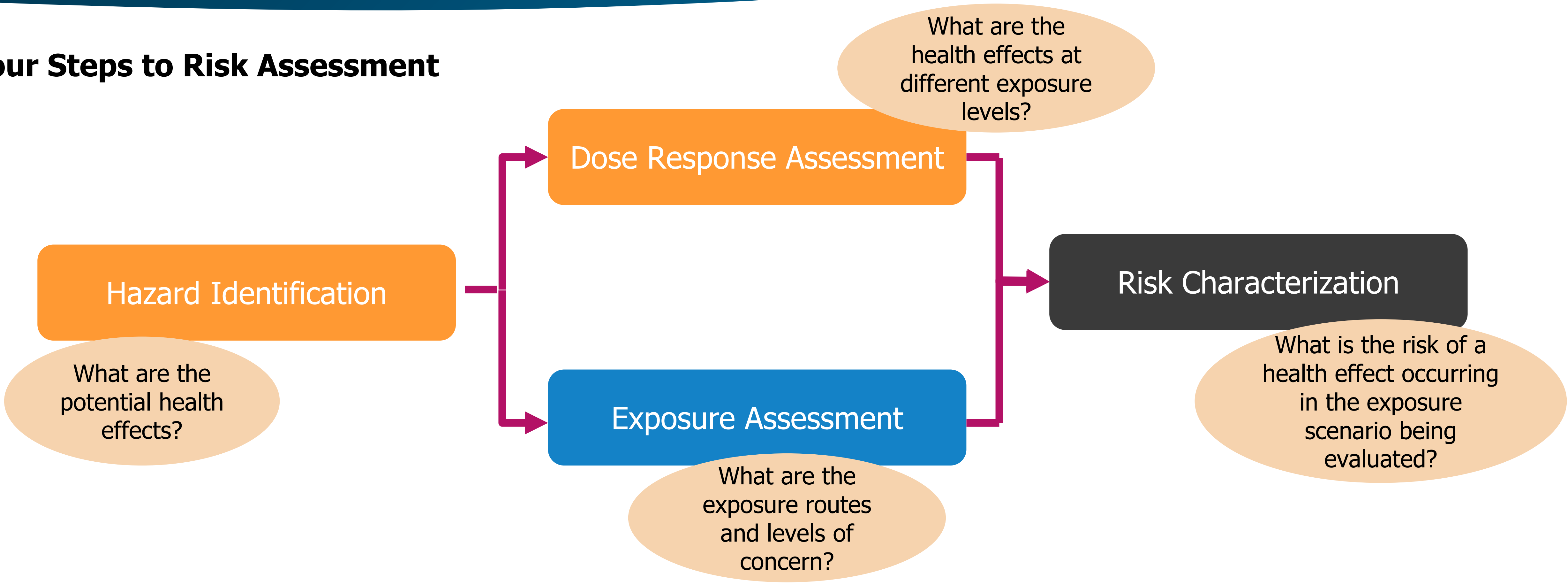
- Understand the risk drivers for human health and how ecological risk compares
- Become aware of the evolving science on how 1,4-dioxane causes cancer and how that impacts risk assessment decisions
- Risk Communication toolkit application to 1,4-dioxane

# 1,4-Dioxane - Toxicity and Risk Assessment Human Health

Image purchased from Shutter Stock

# Human Health

**Four Steps to Risk Assessment**




Adapted from the National Research Council's Risk Assessment in the Federal Government: Managing the Process, 1983

# Human Health – Hazard ID and Dose Response

What are the potential health effects?

Hazard Identification

What are the health effects at different exposure levels?

Dose Response Assessment

# Human Health – Hazard Identification

What are the potential health effects?

Hazard Identification

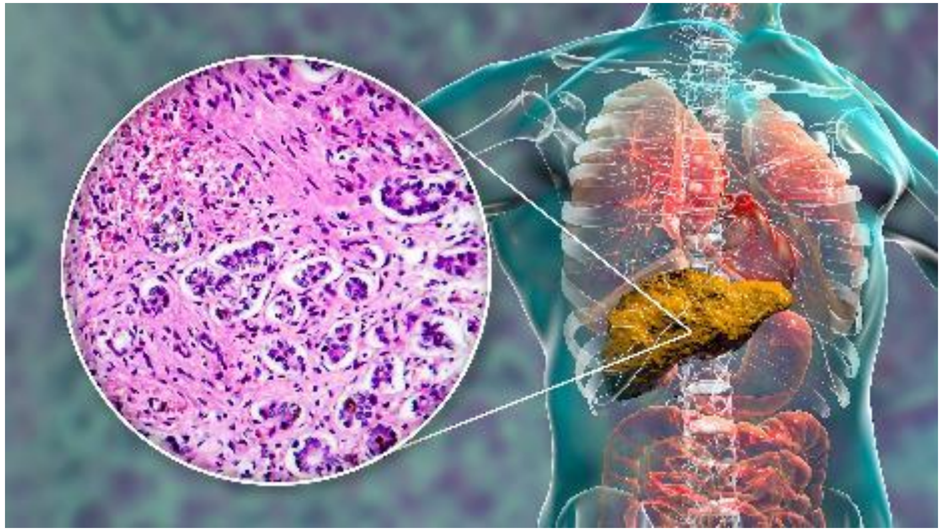
- Non cancer effects
  - Oral: Liver and kidney
  - Inhalation: Eye and respiratory
- **Cancer**
  - **"possibly carcinogenic" (IARC)**
  - **"likely to be carcinogenic" (EPA)**

Graphic art purchased from Shutter Stock

IARC = International Agency for Research on Cancer

# Cancer Risk/Toxicity Values Depend on MOA

- Rodent tumors
  - Liver, kidney, nasal, peritoneum, mammary gland…
- Generally, will be risk driver for human health
- HOWEVER, experts have different interpretations on cancer risk
  - Cancer Mode of Action (MOA)
    - USEPA
    - Health Canada (and others)



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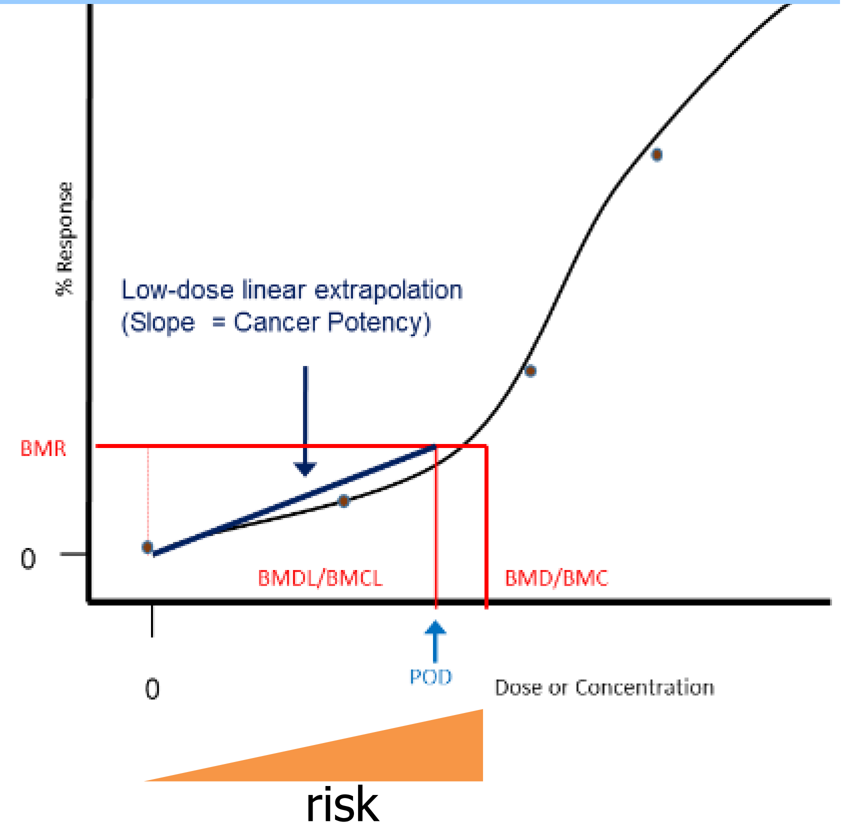
# USEPA = MOA is Unknown

- 2 USEPA Assessments
  - 2013 Integrated Risk Information System (IRIS)
  - 2020 Toxic Substances Control Act (TSCA)
- Mode of Action conclusions

"The available evidence is inadequate to establish a mode of action (MOA) by which 1,4-dioxane induces liver tumors in rats and mice." (USEPA 2013)

Default dose response model = any increase in exposure, increases risk

**= DW threshold of 0.35 – 35 µg/L for $10^{-6}$ to $10^{-4}$ cancer risk**



# Health Canada = MOA is Non-Genotoxic and Threshold

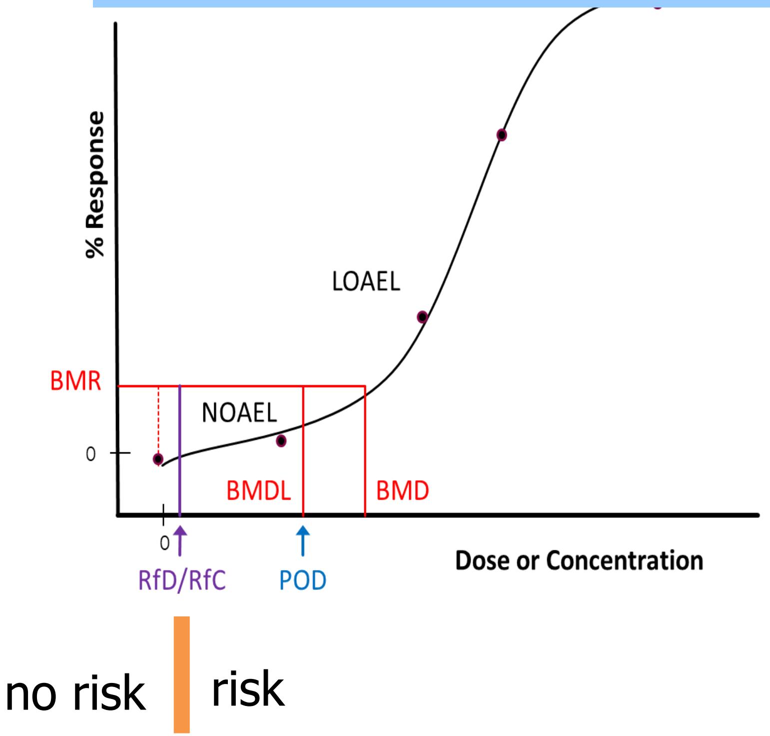
## Health Canada 2018 Mode of Action conclusions

"Using a MOA analysis, the weight of evidence supports a non-genotoxic MOA, with 1,4-dioxane inducing liver tumours through a regenerative proliferation-induced MOA."

- and is reasonable for other human-relevant tumor types
- also adopted by WHO and other international agencies
- and supported by recent publications

Threshold MOA = there is only risk above a certain threshold level of exposure

**= DW threshold of <u>50 µg/L</u> no concern if exposure is below threshold**



# Use of Best Professional Judgement Hierarchy of Toxicity Values

**Tier 1**

EPA Integrated Risk Information System (IRIS)

**Tier 2**

EPA Peer-Reviewed Provisional Toxicity Values (PPRTV)

**Tier 3**

- Agency for Toxic Substances and Disease Registry
- Other EPA offices (e.g., Office of Water)
- States, International Agencies, etc.

**CONSIDERATIONS**

- ☑ State-of-science methods, consistent with EPA
- ☑ Transparent
- ☑ **Best available information**
- ☑ Peer-reviewed



*See Section 5.2 .1 for policy and guidance for selection of tox values*
*See Tables 5.2-5.5 for Toxicity Values*

# Human Health – Cancer Risk/Toxicity Values Summary

- Choice of cancer toxicity value has a significant impact of drinking water/ groundwater screening level
  - ~ 0.33 to 50 µg/L (part per billion)
- Risk assessors should pay attention to the latest science and regulatory determinations
  - On-going research from academia, industry, etc. – watch for new science!
- Professional judgement on best toxicity value for human health risk assessment

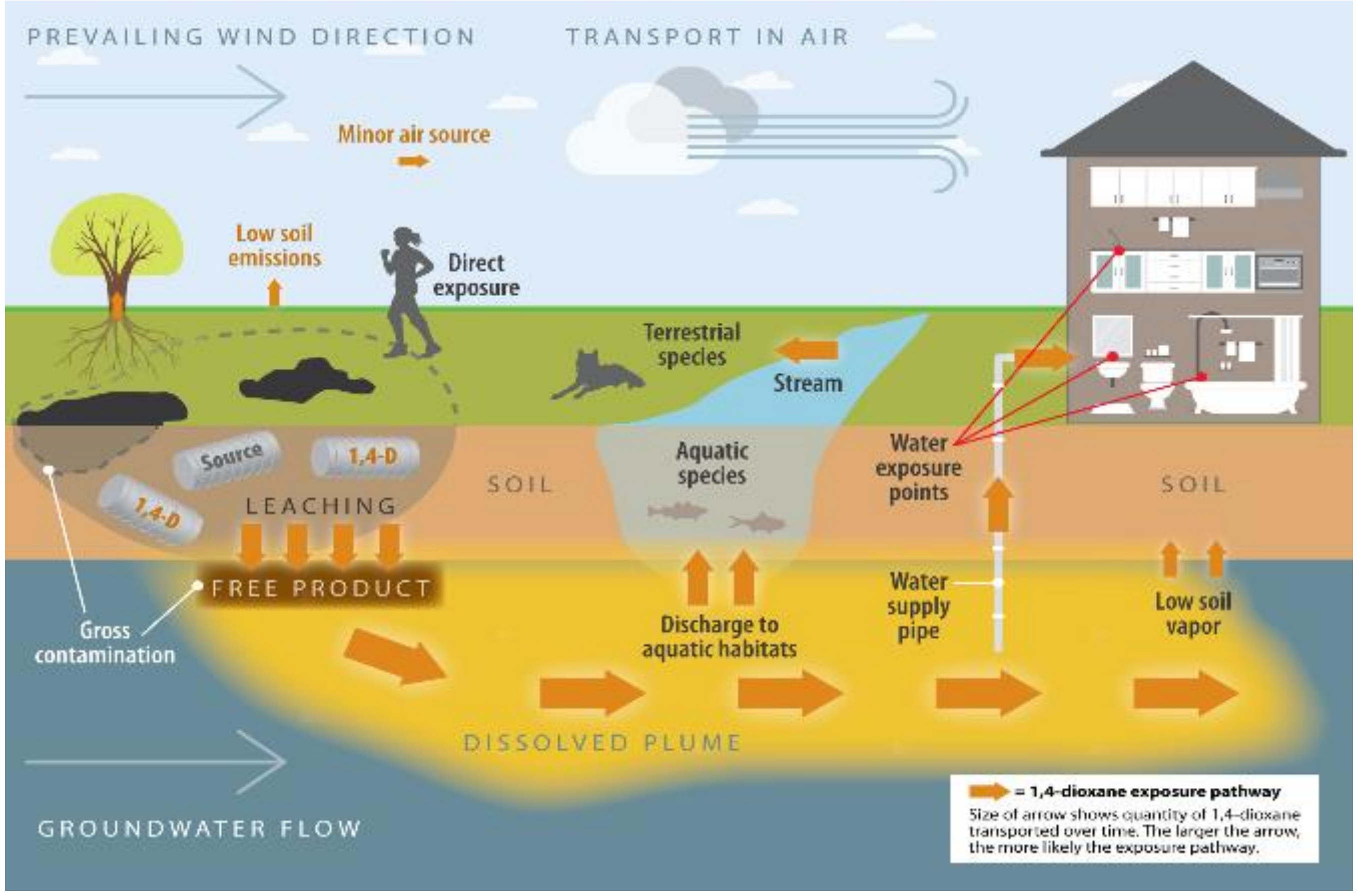
# Human Health – Exposure

Exposure Assessment

What are the exposure routes and levels of concern?

- Why estimate exposure?
  - Estimate the intake (dose) of the chemical for each exposure route
- Involves characterizing the:
  - Exposure setting,
  - Relevant exposure pathways, and
  - Magnitude, frequency, and duration of potential exposure
- Will be site specific

# Human Health – Exposure Routes




**ITRC Guidance Document Figure 5.1**

- Drinking water ingestion primary concern
- Not likely to remain in surface soil
- Low dermal absorption
- Unlikely to volatilize out of water

Consider Site Assessment guidance from Fate and Transport Section

*See Table 5.1 Examples of Potential Human Exposure Routes, ITRC Guidance Document*

# Risk Characterization and Sources of Uncertainty-Variability

- Describe the areas of uncertainty and variability within:
  - Toxicity evaluation
  - Derivation of toxicity value(s)
  - Exposure assumptions

- Important uncertainty = the cancer mode of action and quantitative impact it has on the risk assessment

# Ecological

Graphic art purchased from Shutter Stock

# Ecological – Hazard Identification

Hazard Identification

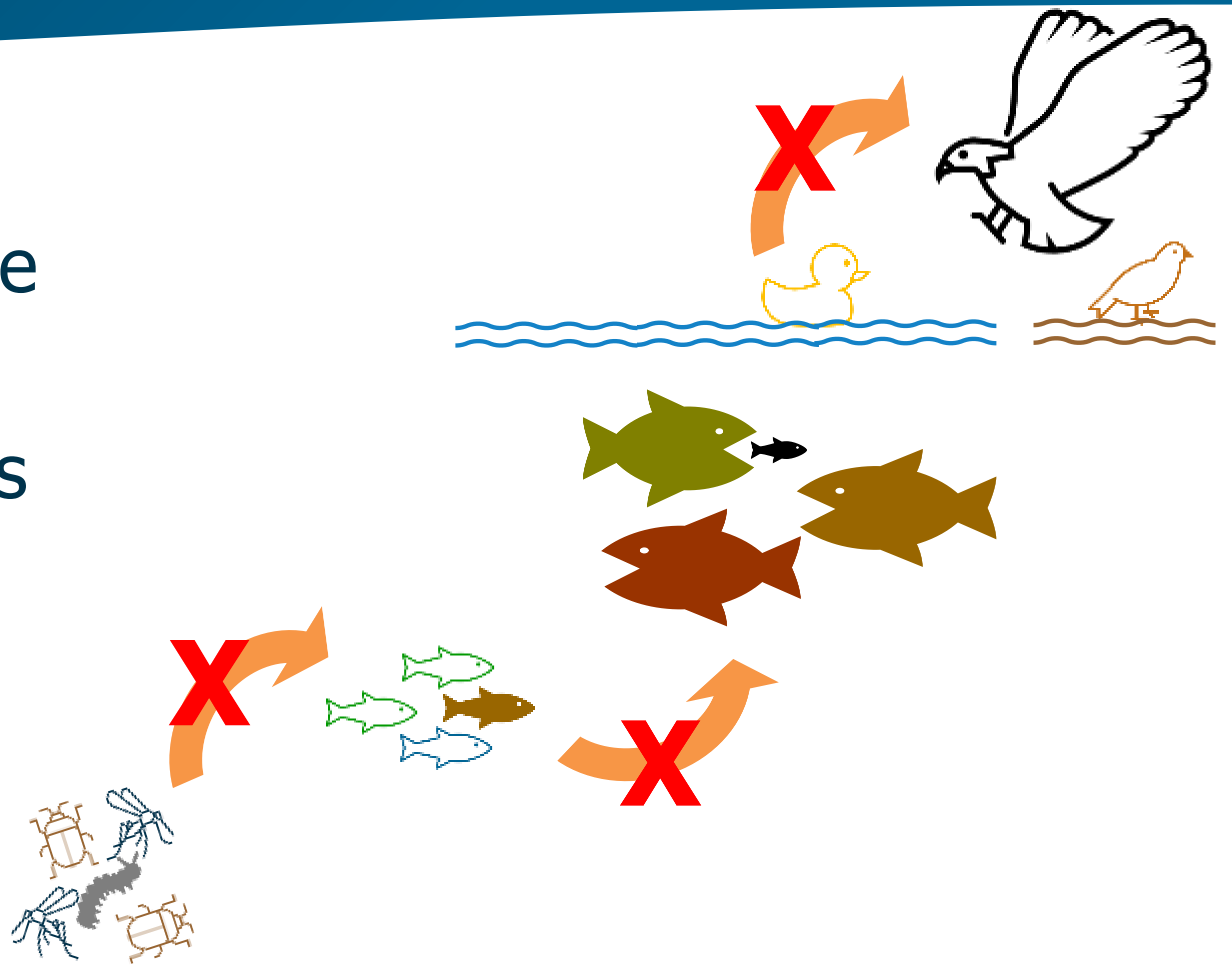
What are the potential health effects?

- Generally, not very toxic to ecological receptors
- Fish are the most sensitive aquatic receptors
- In mammals, effects likely only at high levels (in the 100s to 1000s mg/L)
- Generally, not toxic to plants; can be taken up from roots, but then volatilizes from foliage

Image purchased from Shutter Stock

# 1,4-Dioxane Does Not Bioconcentrate

- ▶ 1,4-Dioxane does not bioaccumulate or bioconcentrate
- ▶ Trophic-level secondary poisoning is not expected



# Ecological Screening Levels

| Medium | Concentration | Type/Media | Reference |
|---|---|---|---|
| Surface Water (freshwater) | **15 mg/L** | Chronic COC | EPA 2018 |
| | **57.5 mg/L** | PNEC-water | ECB 2002 |
| | **10 mg/L** | PNEC-water | ECHA 2014 |
| | **201 mg/L** | ChV-algae | EPA 2019 |
| Sediment | **43.3 mg/kg (ww)** | PNEC-sed | ECB 2002 |
| | **37 mg/kg (dw)** | PNEC-sed | ECHA 2014 |
| Soil | **14 mg/kg** | PNEC-soil | ECB 2002 |

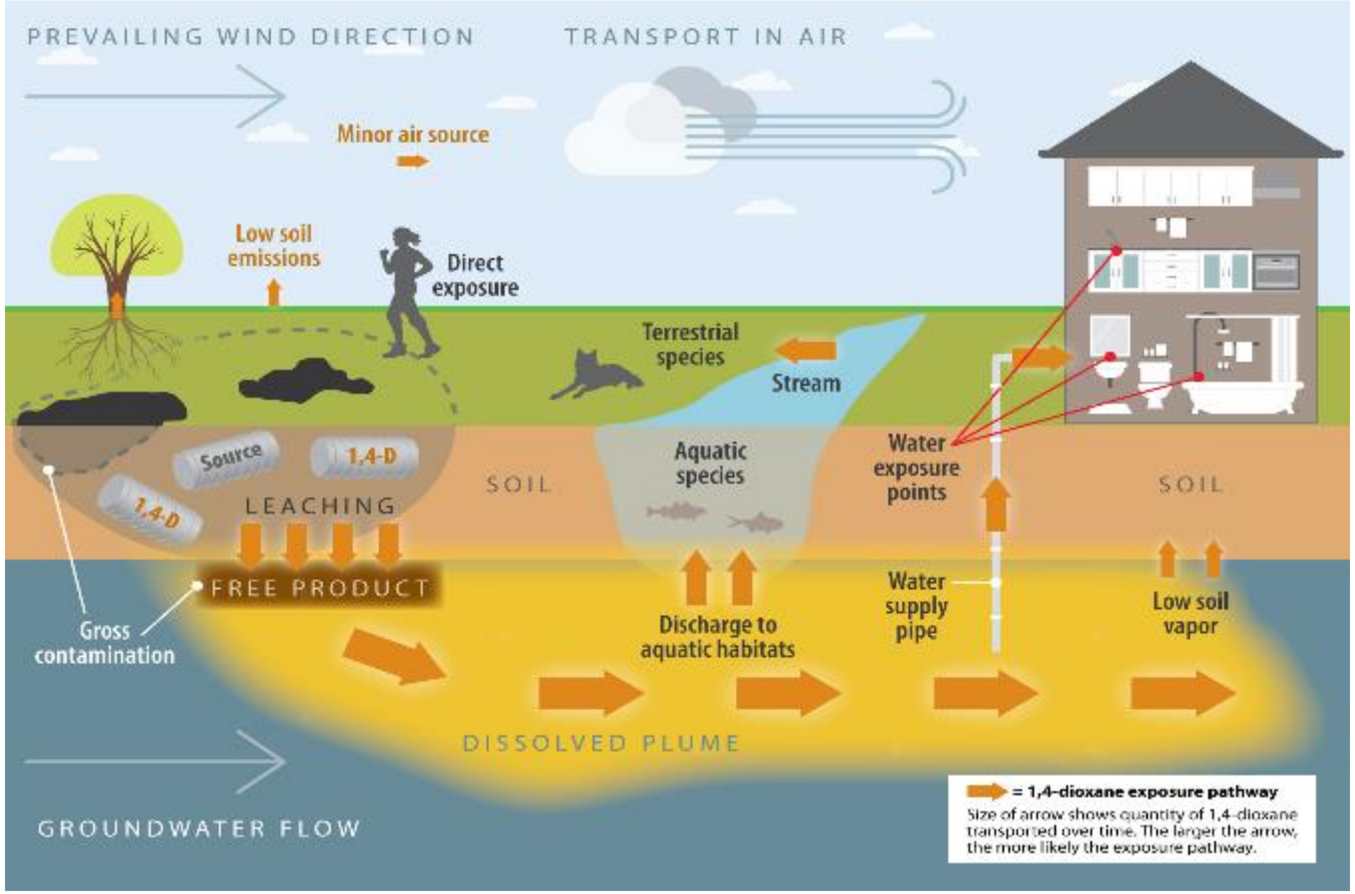
*See Table 5.6 Ecological Screening Levels ITRC Guidance Document for more information*

# Ecological Exposure Assessment

Exposure Assessment

What are the exposure routes and levels of concern?

- Primarily through ingestion and direct contact pathways
- Most likely through aquatic routes




**ITRC Guidance Document Figure 5.1**

*See Section 5.3 ITRC Guidance Document for more information*

# Ecological Risk Characterization

Risk Characterization

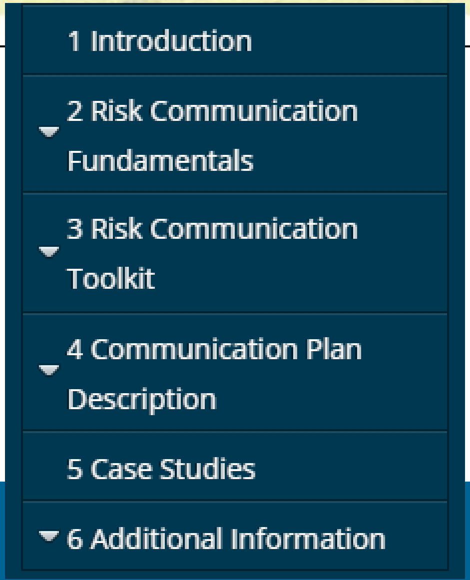
What is the risk of a health effect occurring in the exposure scenario being evaluated?

- Generally, will only require screening level risk assessment to determine if ecological risk is likely

# 1,4-Dioxane - Risk Communication

- Purpose:
  - Assist in understanding risk assessment
  - Assist in forming perceptions of the potential hazards
  - Assist in making decisions about risk management
- Can be difficult for emerging contaminants, like 1,4-dioxane, with evolving scientific data


https://rct-1.itrcweb.org/



# 1,4-Dioxane - Toxicity and Risk Assessment

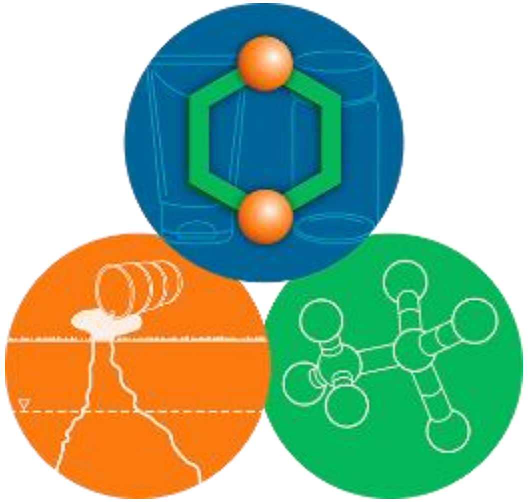
## Conclusions

- The ecotoxicity of 1,4-dioxane is low and not likely a risk driver compared to human health toxicity
- Cancer risk is the primary concern for human health and long-term exposures

**MOA**

- Science is still evolving regarding how 1,4-dioxane causes cancer
- Selected toxicity value(s) should be consistent with established guidance and policies, well justified
- Uncertainties and limitations fully communicated

# Module 6: Remediation & Treatment Technologies

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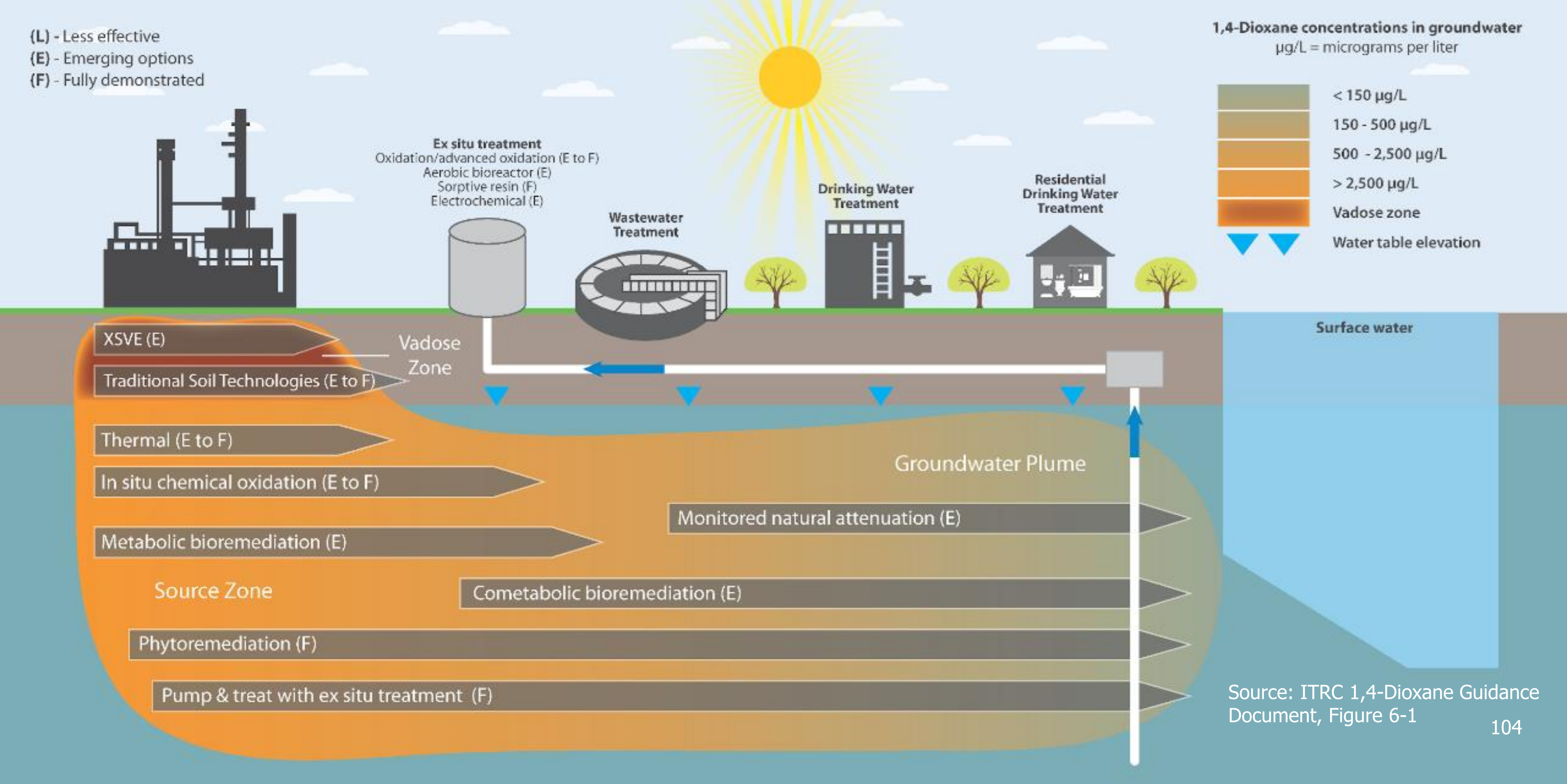
Read trainer bios at: https://clu-in.org/conf/itrc/14d-1/

# Learning Objectives

- Understand how/when/why different treatment technologies are appropriate
- Recall various soil, groundwater, drinking water, and wastewater treatment technologies for 1,4-dioxane
- Appreciate the design considerations for well-established treatment technologies
- Identify when certain technologies aren't appropriate for 1,4-dioxane treatment

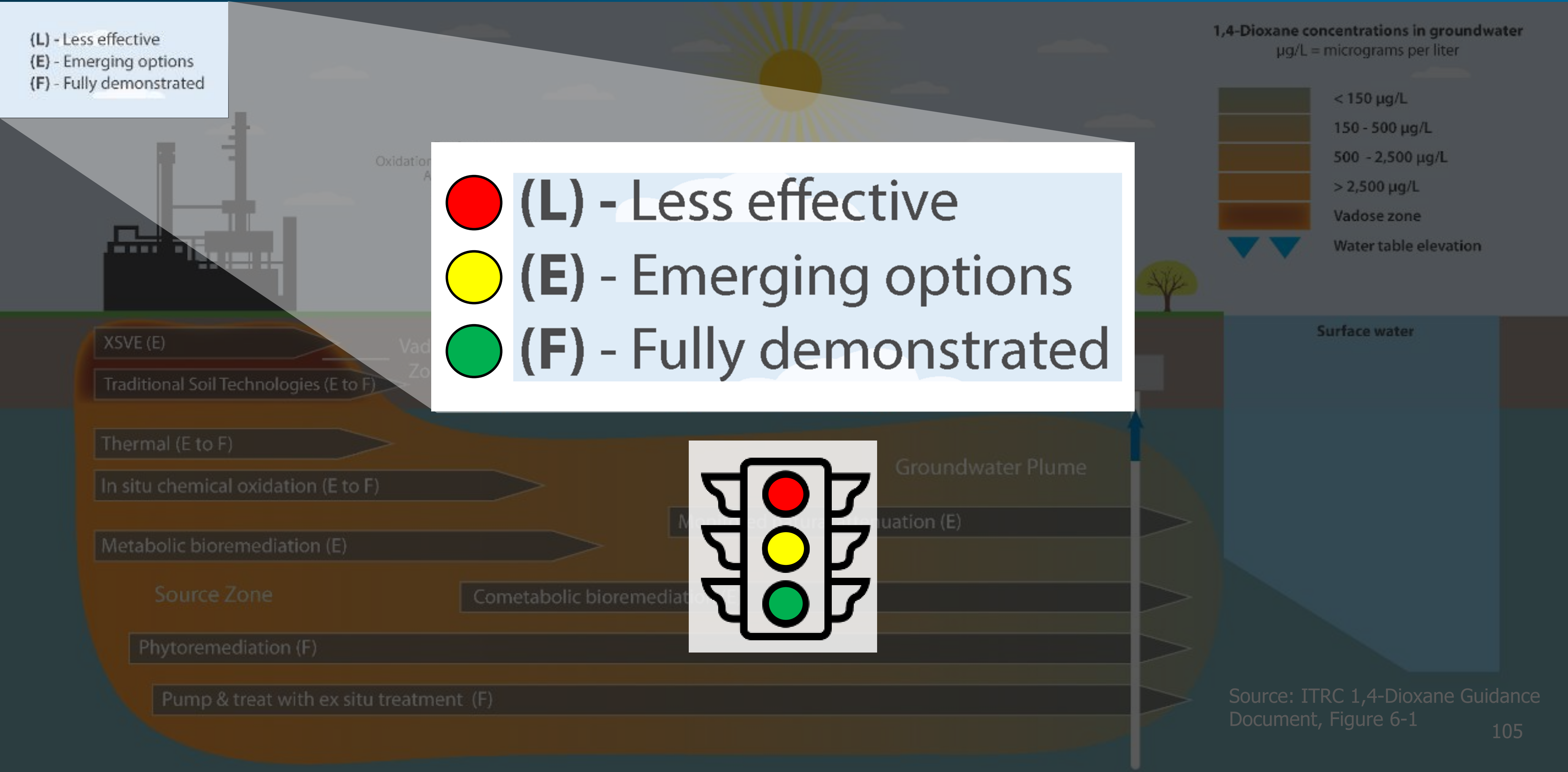
# Remediation and Treatment Technologies




Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

# Remediation and Treatment Technologies

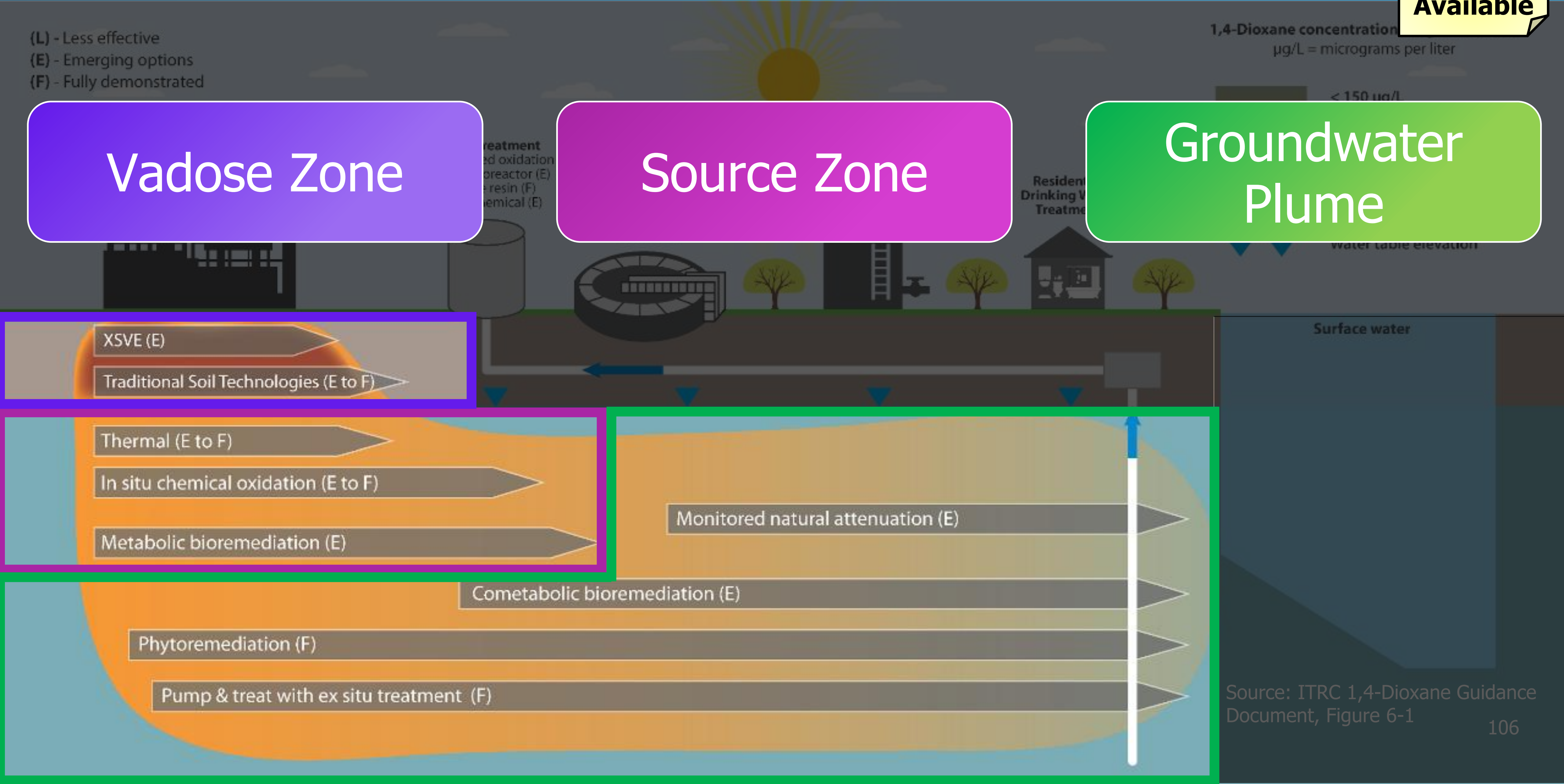
(L) - Less effective
(E) - Emerging options
(F) - Fully demonstrated




Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

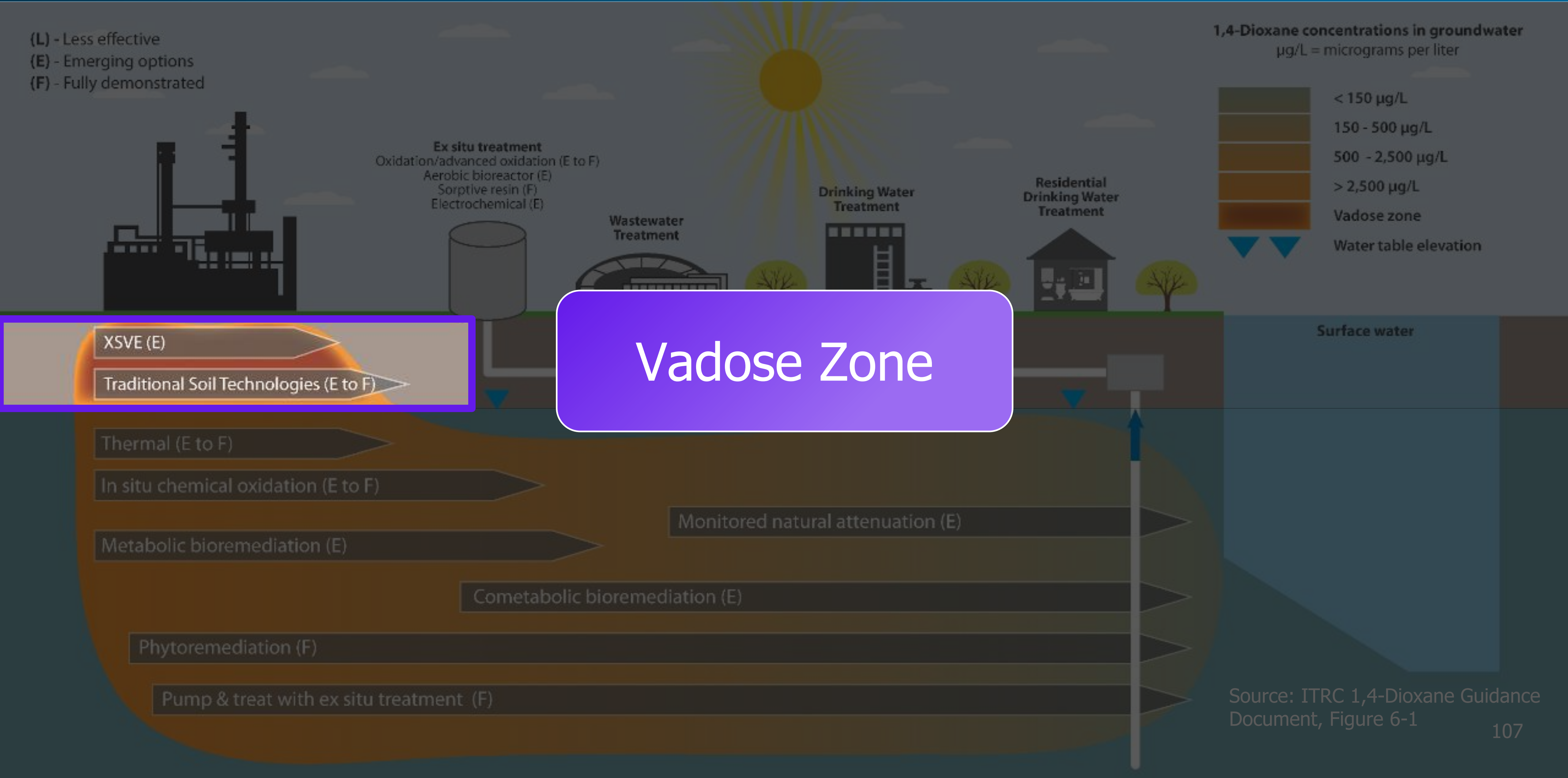
# Remediation and Treatment Technologies

**Case Study Available**



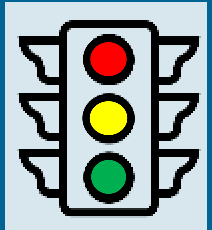

Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

# Vadose Zone Treatment



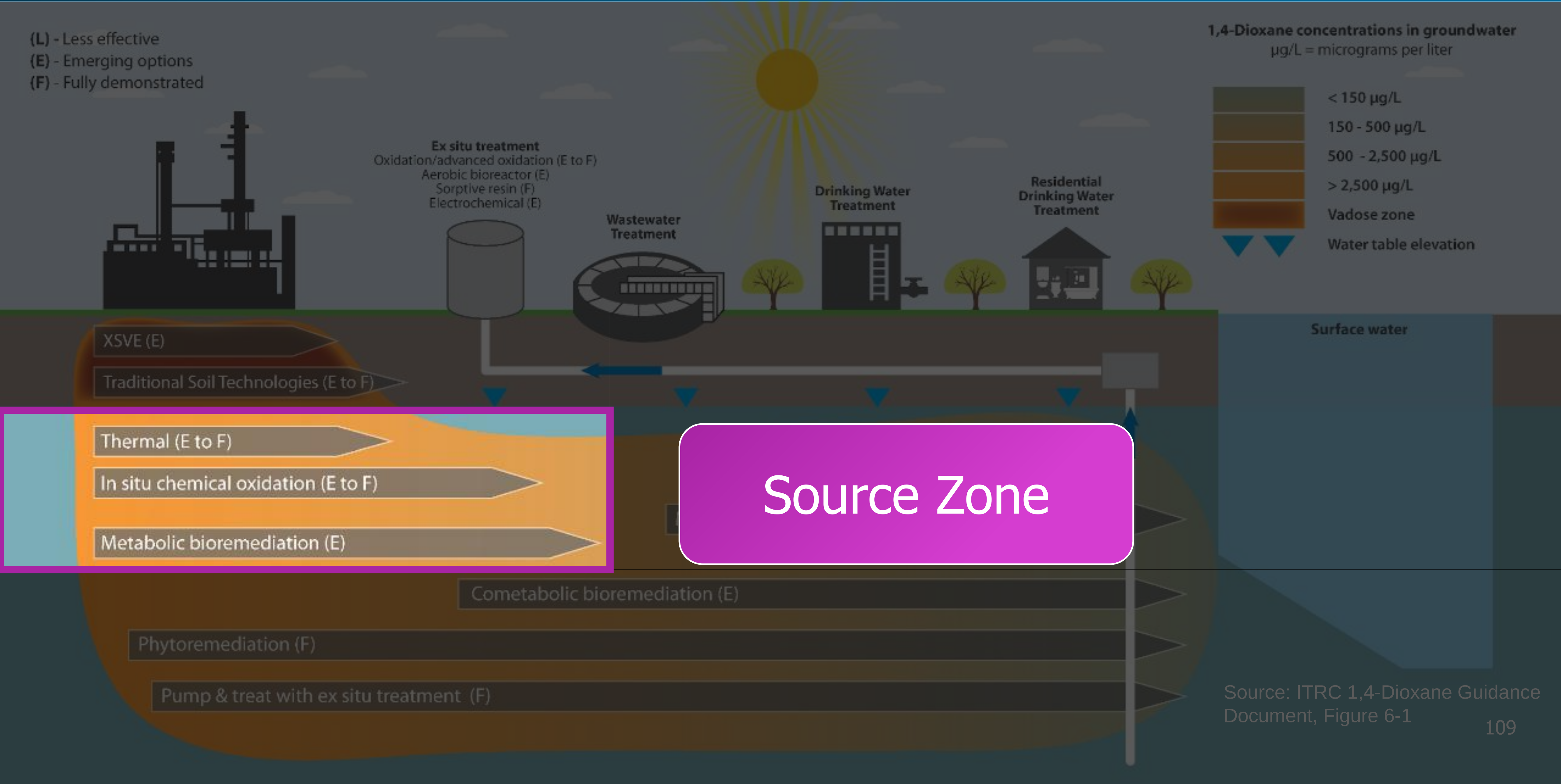

Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

# Vadose Zone Treatment



| Fully Demonstrated | Emerging Options | Less Effective |
| --- | --- | --- |
| • Excavation<br>• Thermal Desorption<br>• Solidification/ Stabilization | • Oxidant Soil Blending<br>• Extreme Soil Vapor Extraction | • Conventional Soil Vapor Extraction<br>• Bioventing<br>• Bio-piles |

# Source/Saturated Zone Remediation




Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

# In Situ Thermal Treatment

- Boiling point is 101.5°C, but is less when mixed with water
- Volatility can increase with heating
- Treatment zone heated and vapors captured
- Three types: ERH; TCH; and SEE
- Benefits: High mass removal
- Challenges: High cost, vapor removal affected by heterogeneity

| | ERH | TCH | SEE |
|---|---|---|---|
| Heating Mechanism | Electrodes | Heaters | Steam Injection |
| Maximum temperature | ~100°C | ~300°C | ~100°C |
| Heating affected by heterogeneity | No | No | Yes |

Electrical Resistive Heating (ERH); Thermal Conductive Heating (TCH); Steam Enhanced Extraction (SEE)

# In Situ Chemical Oxidation Reagents

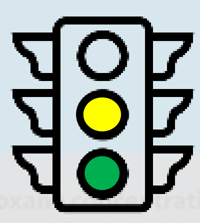
**Case Study Available**

| REAGENT | PHYSICAL STATE | ACTIVATOR | LONGEVITY | DELIVERY APPROACH | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Direct Push | Fixed Well | Gas Injection | Slurry | Cylinder |
| Persulfate | liquid solution (sodium persulfate); solid (potassium persulfate) | Heat | weeks to months | ✓ | ✓ | - | - | - |
| | | Hydrogen Peroxide | weeks to months | ✓ | ✓ | - | - | - |
| | | Alkaline | liquid: weeks to months<br>solid: months | ✓ | ✓ | - | ✓ | ✓ |
| | | Chelated Iron | weeks to months | ✓ | ✓ | - | - | - |
| | | ZVI | months | - | - | - | ✓ | ✓ |
| | | Natural Mineral Activation | months | ✓ | ✓ | - | ✓ | - |
| Ozone | gas | - | 30 minutes in water | - | - | ✓ | - | - |
| Peroxone | liquid solution (hydrogen peroxide); gas phase ozone | - | ozone as above; hydrogen peroxide: weeks | ✓ | ✓ | ✓ | - | - |
| Modified Fenton's Reagent | liquid solution (hydrogen peroxide) | Ferrous Iron | weeks | ✓ | ✓ | - | - | - |
| Permanganate | liquid solution (sodium permanganate); solid/dilute solution (potassium permanganate) | - | liquid: months<br>solid: months to years | ✓ | ✓ | - | ✓ | ✓ |

| Chemical Species | Standard Oxidation Potential |
|---|---|
| Hydroxyl radical (OH-•) | 2.8 |
| Sulfate radical (SO4-•) | 2.5 |
| Ozone | 2.1 |
| Sodium persulfate | 2.0 |
| Hydrogen peroxide | 1.8 |
| Permanganate | 1.7 |
| Chlorine | 1.4 |
| Oxygen | 1.2 |
| Superoxide ion (O-•) | -2.4 |

Source: Siegrist et al. 2001

# ISCO and 1,4-Dioxane



Case Study Available

Reagents yielding free radicals with higher oxidation/ reduction potential will degrade 1,4-dioxane more rapidly

- Hydroxyl radical
- Sulfate radical

Co-contaminants sometimes also treated

- Chlorinated ethenes – yes
- Chlorinated ethanes (1,1,1-TCA; 1,1-DCA; 1,2-DCA) not always treated

Source area versus plume remediation

- Injections versus permeable reactive barrier

Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

# ISCO – Other Considerations

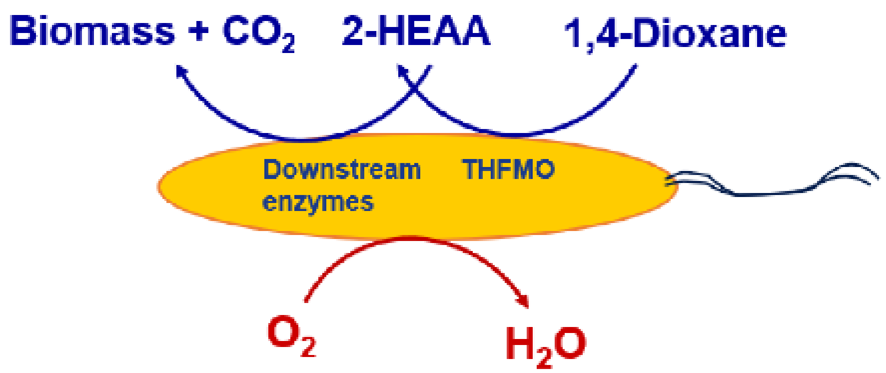
Case Study Available

| Design Considerations | Water Quality Issues | Byproducts |
| --- | --- | --- |
| • Optimizing contact (longevity, permeability, etc.)<br>• Matrix diffusion | • Reagent scavengers/matrix demand<br>• Temporary metals mobilization<br>• Bench testing recommended | • Bromate formation (ozone/$H_2O_2$)<br>• Sulfate<br>• Gases: $CO_2$, $O_2$<br>• Ions ($K^+$, $Na^+$)<br>• pH change |

# In Situ Metabolic Bioremediation

Check out the Fate & Transport Training, too

- 1,4-Dioxane used as carbon and energy source by bacteria
- End products are biomass and carbon dioxide ($CO_2$)
  - Lower biomass yield and rates than other metabolic processes (TCE/hydrocarbons)
  - Suitable for higher 1,4-dioxane concentrations
  - Requires oxygen to be present



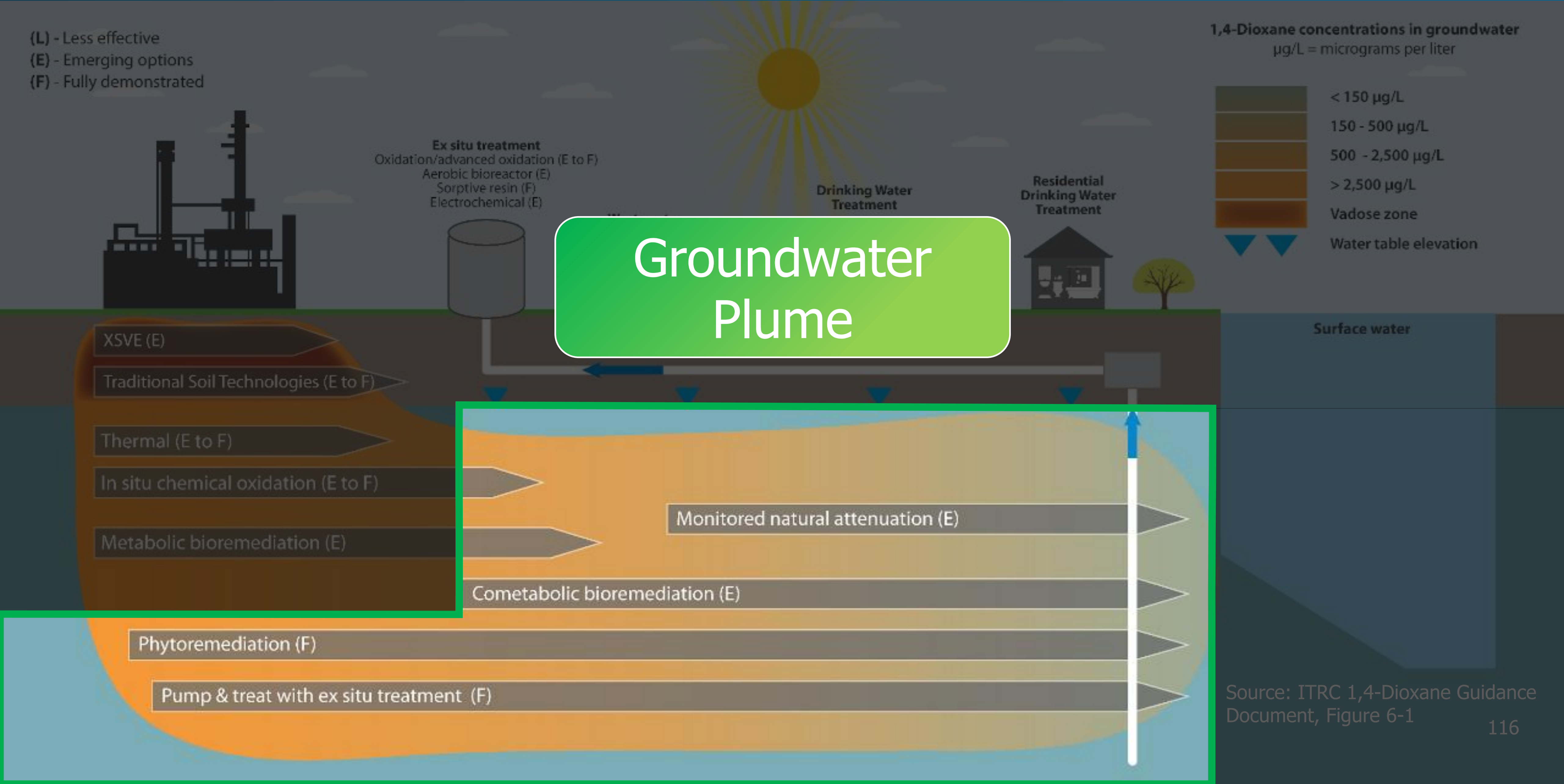

Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-4

# In Situ Metabolic Bioremediation

| Key Design Parameters | Effectiveness | Advantages | Disadvantages |
|---|---|---|---|
| Initial 1,4-dioxane concentration<br><br>Oxygen delivery<br><br>Initial bacteria culture mass present or injected | Degrades 1,4-dioxane at high starting concentrations<br><br>Low concentrations may not stimulate growth. | Effective for source areas<br><br>Does not require injection of a primary substrate | Bioaugmentation may be required, and limited microbial transport may be a concern<br><br>Technology requires maintenance of aerobic conditions, and chlorinated compounds/metals may inhibit biodegradation |

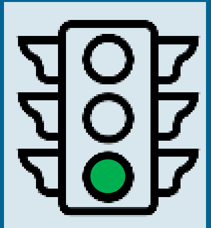
Source: ITRC 1,4-Dioxane Fact Sheet, Table 2

# Groundwater Plume Remediation

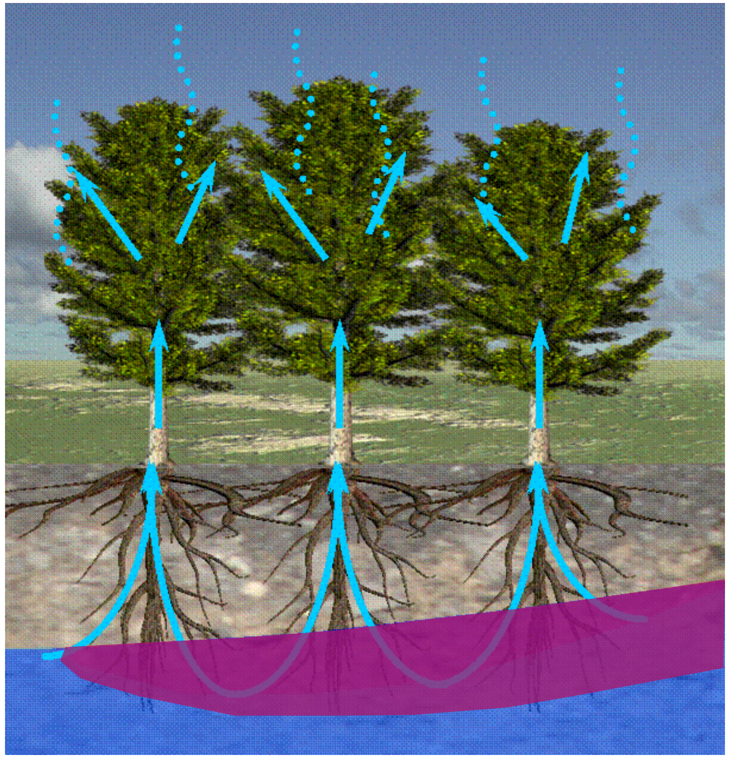



Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

# Phytoremediation



Case Study Available

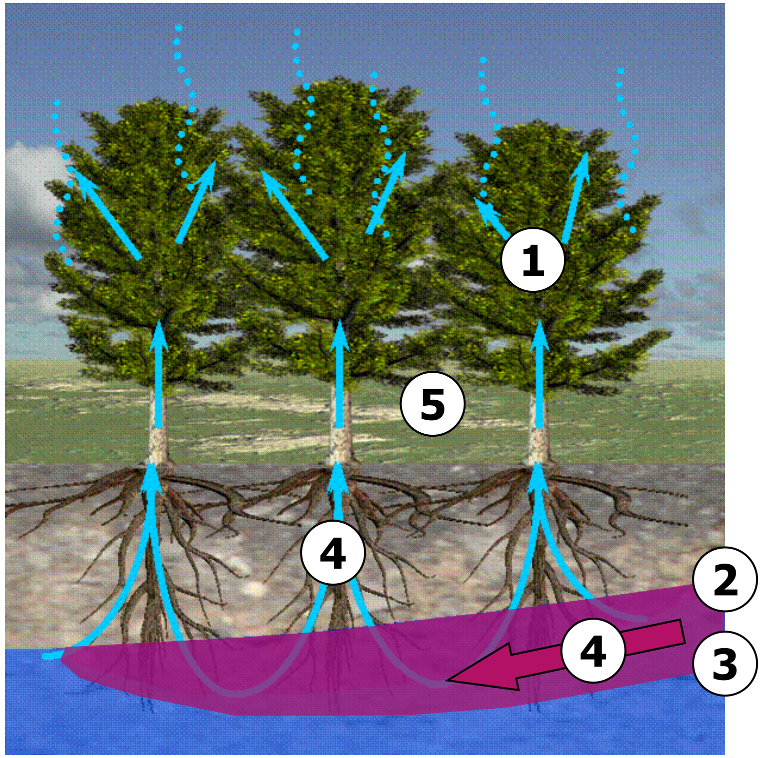


Source: Graphic modified from ITRC Phyto-2 2009

- Mechanism for treatment is "phyto-extraction"
  - Pull 1,4-dioxane in through roots, up xylem, out to atmosphere
- Benefits
  - Semi-passive
  - Leverages properties of 1,4-dioxane
- Challenges
  - Longer timeframe
  - Deep groundwater requires certain design

# Phytoremediation

Case Study Available




Source: Graphic modified from ITRC Phyto-2 2009

## DESIGN CONSIDERATIONS

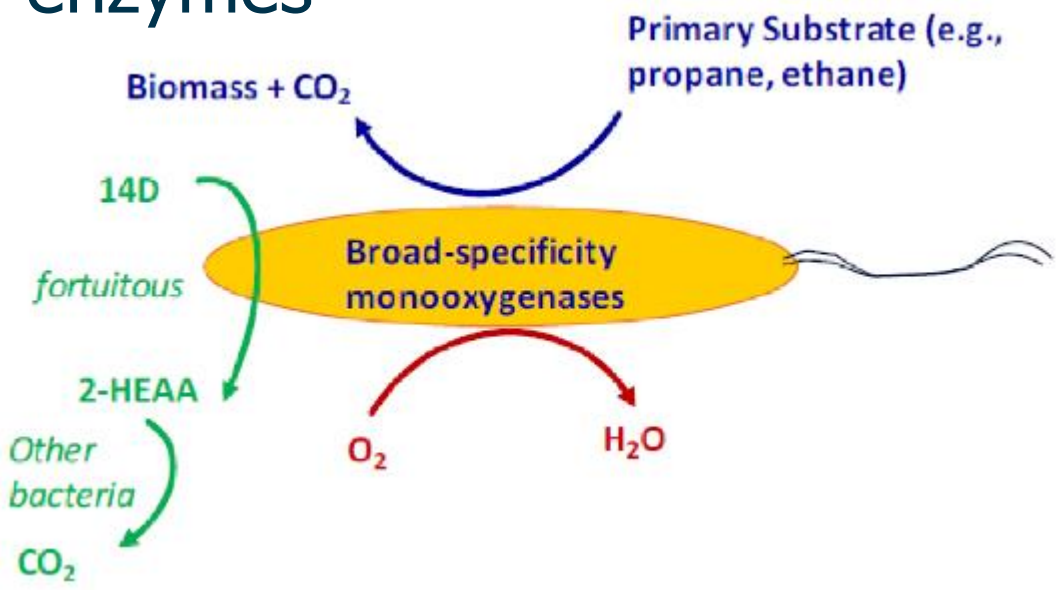
1. Use correct plant(s) for region
2. Depth of groundwater: 10-15 ft bgs optimal, 25 ft bgs maximum
3. Depth of 1,4-dioxane impacts: Within top 5 ft of groundwater is optimal
4. Water budget: Compare groundwater flux in versus estimated tree transpiration
5. Number of trees and spacing

# In Situ Cometabolic Bioremediation

Case Study Available

Check out the Fate & Transport Training, too

- Bacteria uses a primary growth substrate to sustain activity
- 1,4-Dioxane biodegraded fortuitously by enzymes generated from bacteria activity
  - Can also degrade other constituents of concern
  - Suitable for high or low 1,4-dioxane concentrations
  - Requires oxygen to be present




Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-2

# In Situ Cometabolic Bioremediation

**Case Study Available**

| Key Design Parameters | Effectiveness | Advantages | Disadvantages |
| --- | --- | --- | --- |
| Oxygen delivery<br><br>Initial bacteria culture mass present or injected<br><br>Primary substrate delivery and nutrients | Degrades 1,4-dioxane to <1 µg/L<br><br>A treatment option for low starting concentrations | Can degrade both chlorinated compounds and 1,4-dioxane<br><br>Several viable primary substrates<br><br>Applicable to dilute plumes<br><br>Independent of 1,4-dioxane concentration | Bioaugmentation may be required<br><br>Flammable gases are typically applied as primary substrate<br><br>Technology requires maintenance of aerobic conditions, and chlorinated compounds/metals may inhibit biodegradation |

Source: ITRC 1,4-Dioxane Fact Sheet, Table 2

# In Situ Monitored Natural Attenuation

*MNA programs generally include assessing the favorability of attenuation under site-specific conditions as part of a multiple lines of evidence approach.*

**Important Properties**

- Low Henry's law constant means low volatility
- Low organic carbon partition coefficient means low sorption

**Relevant Attenuation Mechanisms**

- Dilution
- Diffusion
- Biodegradation

**Biodegradation Considerations**

- Indigenous microbes
- Oxygen availability
- Primary substrate availability
- Inhibitors

# In Situ Monitored Natural Attenuation

- Analytical methods – need to take into account project-specific reporting limits
  - **Geochemical parameters – associated with aerobic/cometabolic conditions**
  - **Microbiological analyses – direct and indirect biomarkers (DXMO, ALDH vs other monooxygenases)**
  - **CSIA – isotopic enrichment provides evidence of degradation, limited by analytical detection limits**

*Note that these are evolving analytical techniques and the industry is still learning how to best apply them.*

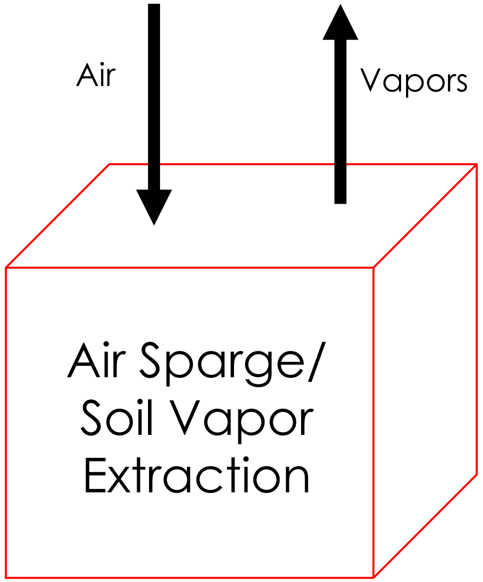
# 1,4-Dioxane Critical Characteristics

| Property | Units | 1,4-Dioxane | Benzene | TCE | 1,1,1-TCA | 1,1-DCA | 1,1-DCE |
|---|---|---|---|---|---|---|---|
| **Water solubility** | g/L | 1,000 | 1.8 | 1.1 | 0.91 | 5.04 | 5.06 |
| **Vapor pressure** | mm Hg (at 25°C) | 23.8 | 95.2 | 72.6 | 124 | 227 | 234 |
| **Henry's Law constant** | atm-$m^3$/mol (at 25°C) | $4.8 \times 10^{-6}$ | $5.48 \times 10^{-3}$ | $9.1 \times 10^{-3}$ | $1.6 \times 10^{-2}$ | $5.62 \times 10^{-3}$ | $5.8 \times 10^{-3}$ |
| **Log $K_{oc}$** | Dimension-less | 0.54 | 1.92 | 1.81 | 2.18 | 1.55 | 1.48 |
| **Boiling point** | °C | 101 | 80 | 87 | 74 | 57.4 | 32 |

*See Table 3.1 in ITRC Guidance Document for complete table with additional parameters*

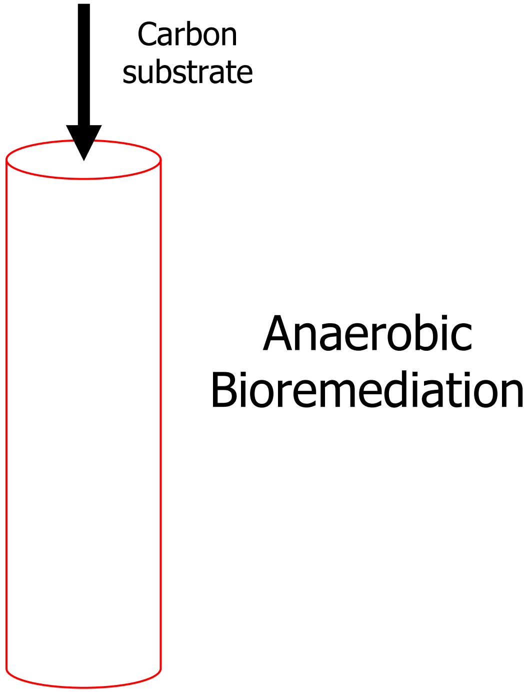
# Less Effective In Situ Technologies

Note that less effective technologies may still impart *some* benefit, but may not reach targets




*Low Henry's law coefficient makes this less efficient*


*Slow reaction times make this less appealing*




*Oxygen needed for biodegradation*

# Ex Situ AOPs and 1,4-Dioxane

Case Study Available

| METHOD TO CREATE HYDROXYL RADICALS | EFFECTIVENESS | | | GROUNDWATER TREATMENT APPROACHES | |
|---|---|---|---|---|---|
| | 1,4-DIOXANE | CO-CONTAMINANTS | | | |
| | | CHLORINATED ETHENES | CHLORINATED ETHANES | PUMP AND TREAT | DYNAMIC GROUNDWATER RECIRCULATION |
| UV/hydrogen peroxide | ✓ | ✓ | - | ✓ | ✓ |
| Ozone/hydrogen peroxide | ✓ | ✓ | TCA yes; DCA reluctant | ✓ | ✓ |
| UV/titanium dioxide catalyst/oxidant | ✓ | ✓ | - | ✓ | ✓ |
| UV/hypochlorite | ✓ | ✓ | - | ✓ | ✓ |
| UV/ozone/hydrogen peroxide | ✓ | ✓ | ✓ (multiple oxidants) | ✓ | ✓ |

| Chemical Species | Standard Oxidation Potential |
|---|---|
| *exited electron + electron gap | 3.18 - 4.8 |
| Hydroxyl radical (OH-•) | 2.8 |
| Sulfate radical (SO4-•) | 2.5 |
| Ozone | 2.1 |
| Sodium persulfate | 2.0 |
| Hydrogen peroxide | 1.8 |
| Permanganate | 1.7 |
| Chlorine | 1.4 |
| Oxygen | 1.2 |
| Superoxide ion (O-•) | -2.4 |

Source: Siegrist et al. 2001

# Ex Situ AOP – Other Considerations

Case Study Available

## Design Considerations

- Electrical/chemical usage
- Matrix diffusion

## Water Quality Issues

- Influent water quality (e.g., iron)
- Effectiveness in low pH water (UV/hypochlorite)
- Reagent scavengers
- Bench testing recommended

## Byproducts

- Bromate formation (ozone/$H_2O_2$)
- Gases: $CO_2$, $O_2$
- Free radicals (ozone/$H_2O_2$)
- pH change

# Ex Situ Bioreactors

- Metabolic Bioreactors
  - Laboratory fluidized bed reactor for high concentrations
  - Multi-stage aerobic system
  - Bio-GAC
  - No full-scale applications
- Cometabolic Bioreactors
  - Early studies showed that cometabolic bioreactors can be effective for treating wastewater with both 1,4-dioxane and tetrahydrofuran (cometabolic substrate)
    - Lab-scale trickling filter
    - Lab-scale reactors fed propane or ethane (fluidized bed reactor, membrane biofilm reactor)
    - Full-scale moving bed bioreactor (MBBR; Lowry Landfill)

MBBR at Lowry Landfill

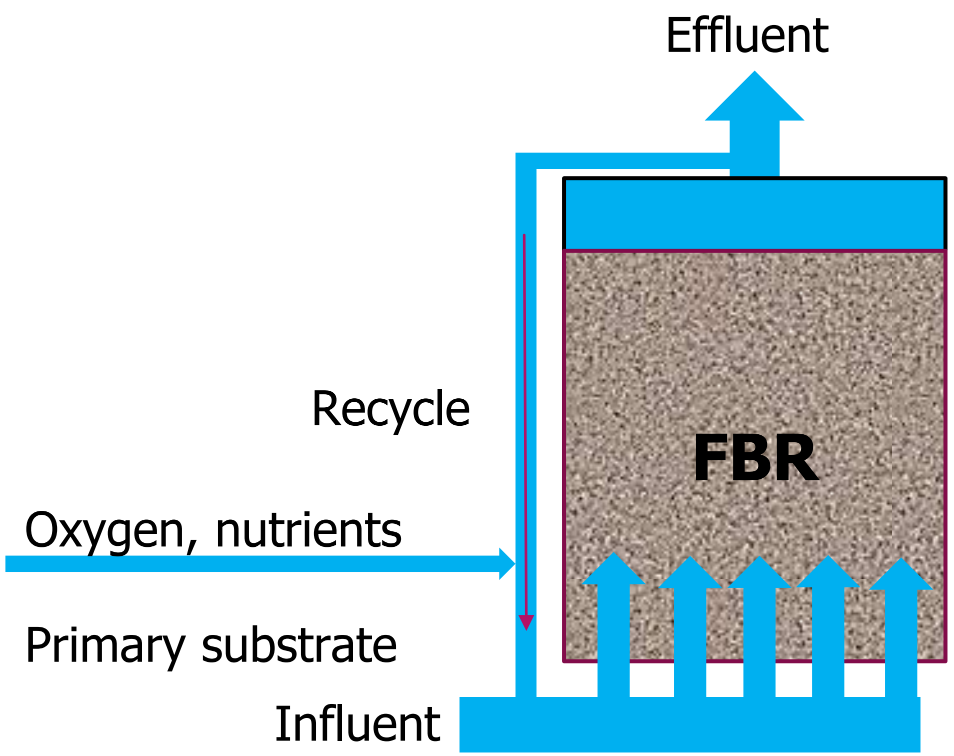


Photo source: Cordone, L., Carlson, C., Plaehn, W., Shangraw, T. and Wilmoth, D. (2016), Case Study and Retrospective: Aerobic Fixed Film Biological Treatment Process for 1,4-Dioxane at the Lowry Landfill Superfund Site. Remediation, 27: 159-172. https://doi.org/10.1002/rem.21502

# Ex Situ Bioreactors

- Design Considerations
  - Concentration of 1,4-dioxane
  - Effluent requirements
  - Co-contaminants
  - Metabolic vs cometabolic
  - Flow rate
  - Hydraulic retention time
  - Oxygen and inorganic nutrients
  - Primary substrate (cometabolic)
  - Microbial culture(s)

**Fluidized Bed Bioreactor (FBR)**

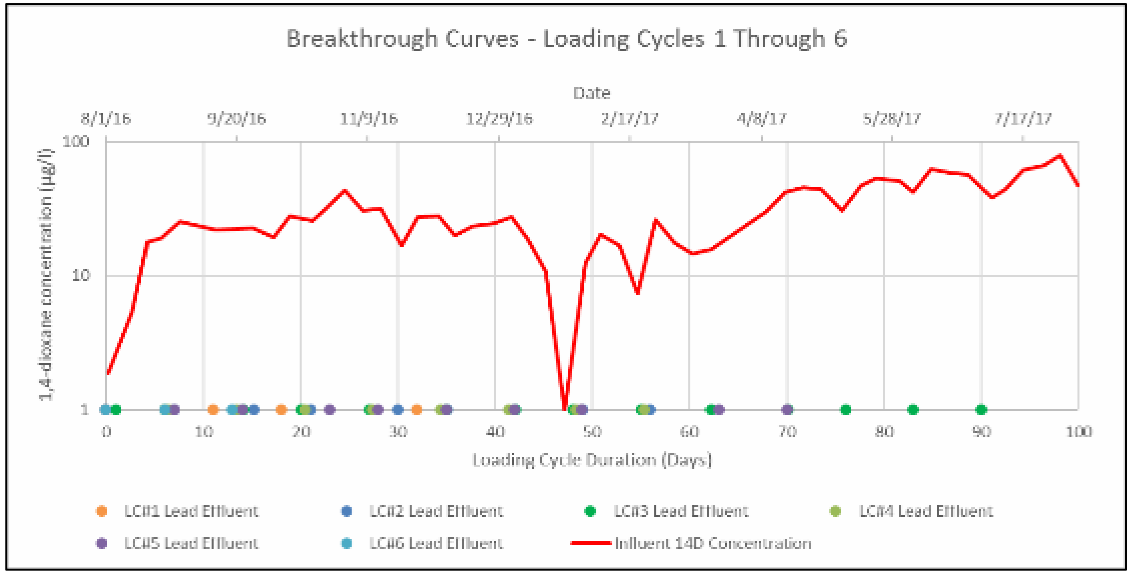


# Ex Situ Sorptive Resin

Case Study Available

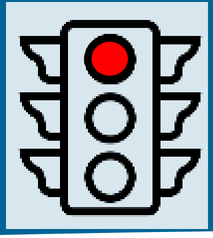
- Many sorbents are ineffective for treating 1,4-dioxane (e.g., GAC, IX)
- Synthetic AMBERSORB™ 560 resin has been applied at full-scale
  - Typically a lead-lag configuration
  - Steam regeneration
  - 1,4-Dioxane treatment of regenerant necessary

AMBERSORB™ treatment of 1,4-dioxane




Source: ITRC 1,4-Dioxane Guidance Document, Case Study

# Less Effective Ex Situ Technologies



Note that less effective technologies may still impart *some* benefit, but may not reach targets

Air Stripper

*Low Henry's law coefficient makes this less efficient*

Reverse Osmosis/Nanofiltration

*Small molecular weight makes these less efficient*

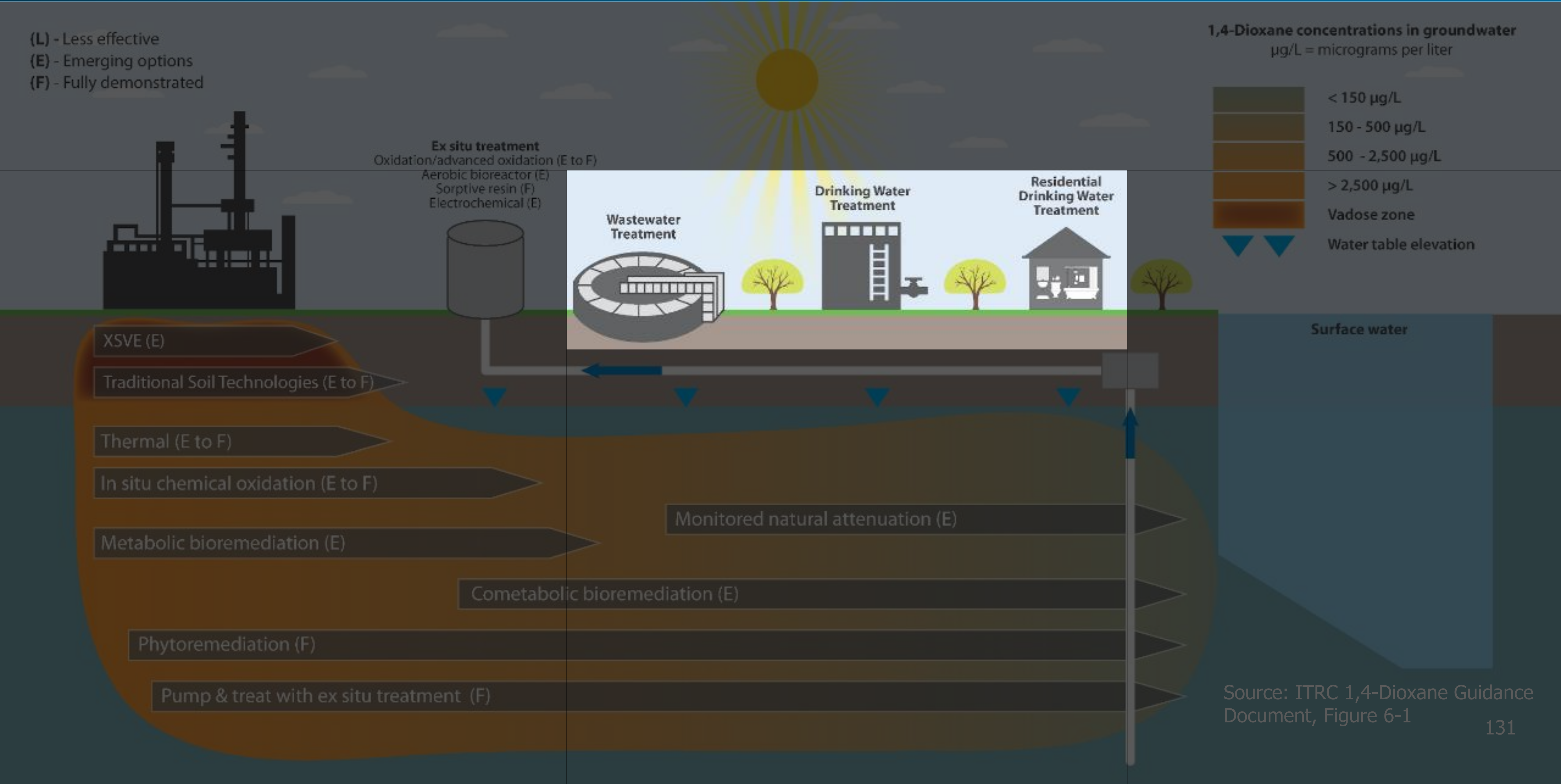
Ion Exchange

*Non-ionic nature cannot be exchanged*

Liquid-Phase Granular Activated Carbon

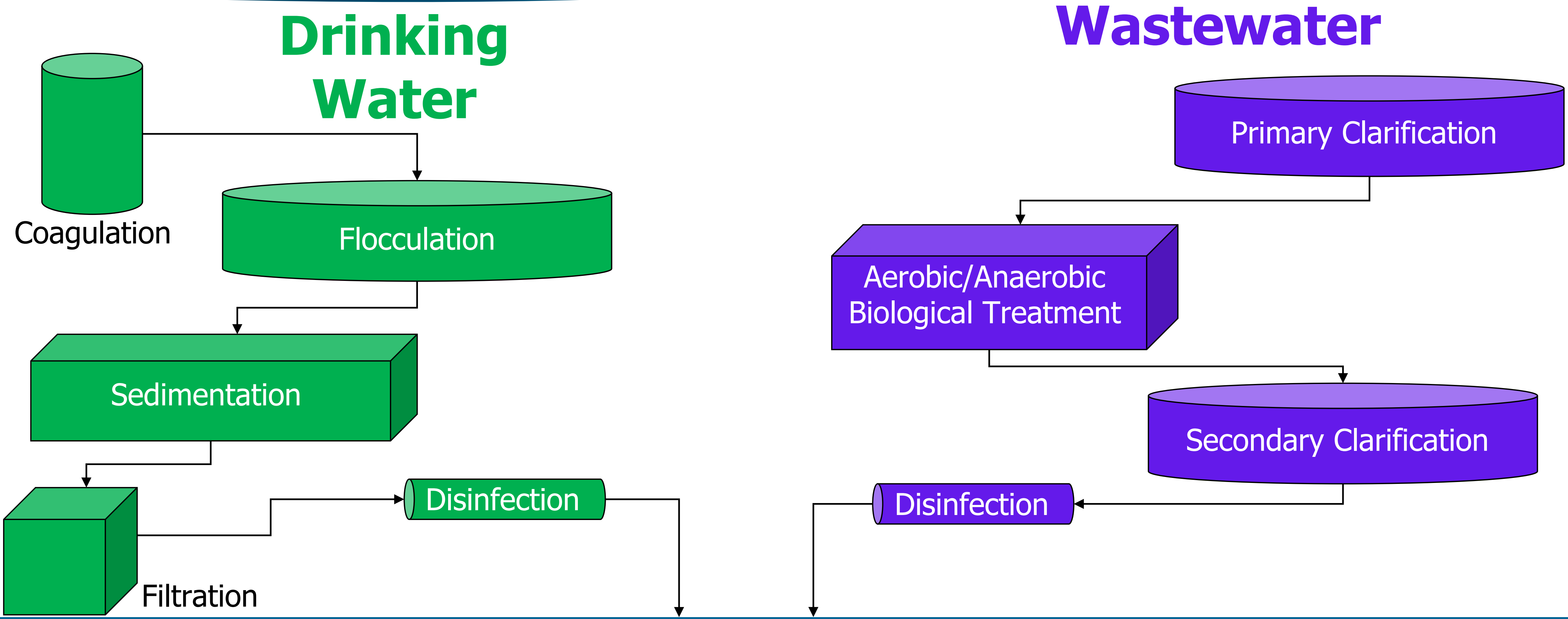
*Low sorption coefficient makes LGAC inefficient. May not be feasible/economical for drinking water, wastewater, and high-flow groundwater systems. May be applied to low-flow groundwater or residential treatment.*

# Drinking Water and Wastewater Treatment

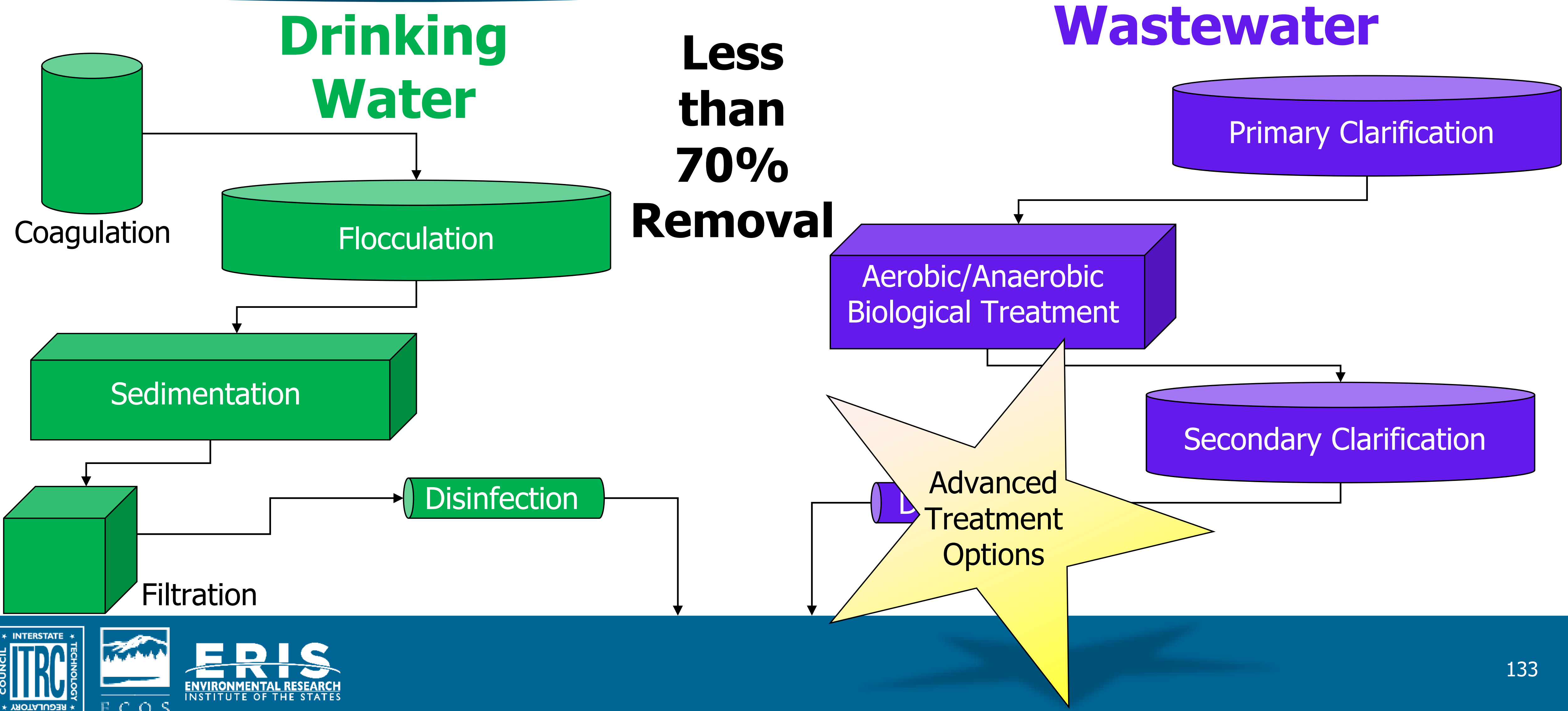



Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

# Conventional DW/WW Treatment

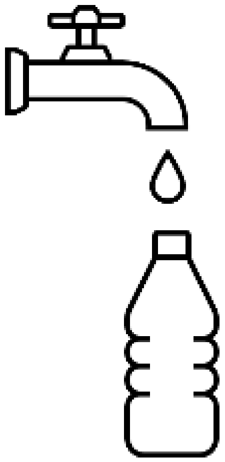


# Conventional DW/WW Treatment



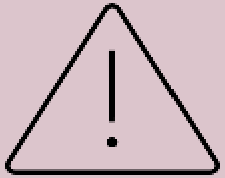
# Residential DW Treatment

**Case Study Available**



## Common Residential Water Treatment

- Less effective
  - Particulate filters
  - Water softening
  - UV disinfection
  - Pitcher/faucet filters



- Activated carbon (i.e., LGAC) can be used if designed properly

# Remediation and Treatment Technologies

- Many options for 1,4-dioxane treatment

- Best option will vary from site to site

- Be mindful of existing remediation approaches that might not be the best for 1,4-dioxane

Source: ITRC 1,4-Dioxane Guidance Document, Figure 6-1

# Thank you for attending! Questions & Answers?

- 1,4-Dioxane Modules will be hosted for separate viewing On Demand
- Questions? itrc@itrcweb.org
- Want more? For additional training on 1,4-Dioxane, visit https://clu-in.org/conf/itrc/14d/

**1,4-Dioxane Modules**

**Module 1:** History of Use (Sect 1)
**Module 2:** Regulatory Framework (Sect 2)
**Module 3:** Fate and Transport (Sect 3)
**Module 4:** Sampling and Analysis (Sect 4)
**Module 5:** Toxicity and Risk (Sect 5)
**Module 6:** Remediation Technologies (Sect 6)

Feedback Form (to receive a certificate of completion – for attending the full 1,4D training): https://clu-in.org/conf/itrc/14D-1/default.cfm#tabs-5