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

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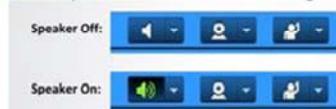
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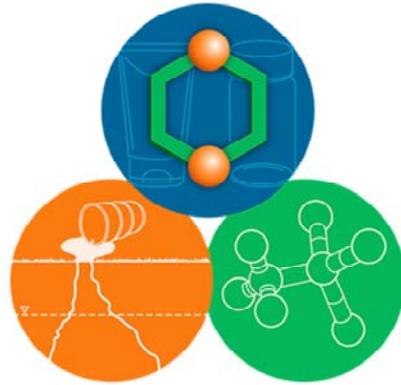
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Poll Question

## ITRC 1,4-Dioxane: Science, Characterization & Analysis, and Remediation



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Guidance Document: <https://14d-1.itrcweb.org/>

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### POLL Question:

What is your role in 1,4-Dioxane Site Management? (Select all that apply)

- A. State or Federal Regulator
- B. Consultant
- C. Policy maker
- D. Site Owner
- E. Technology Vendor
- F. Community Stakeholder
- G. Other

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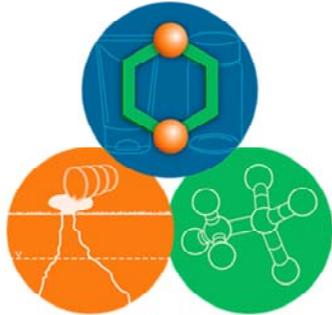
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# 1,4-Dioxane: Introduction



**Heather Barbare**  
Colorado Department of Public  
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Read trainer bios at: <https://clu-in.org/conf/itrc/14d-1/>

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Welcome to Heather Barbare with the CO Dept of Public Health and Environment. She was a co-team leader for the ITRC 1,4-Dioxane team and will serve as the moderator for the 1,4-Dioxane Training Modular Series.

\*\*\*\*\*

**Heather Barbare** is an engineer with the Colorado Department of Public Health and Environment. Heather has worked for the CDPHE since 2015 and manages solid waste permitting projects. Prior to her work for the CDPHE, from 2014 to 2015, Heather worked for a local government managing solid waste projects and as an environmental planner. From 2005 to 2014, Heather worked as an environmental consultant specializing in remediation and environmental compliance. Heather earned a bachelor's degree in chemistry from the Colorado School of Mines and a master's of engineering degree from the University of Wisconsin – Madison. Heather is a professional engineer and a Certified Hazardous Materials Manager.



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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](http://www.clu-in.org))

Today's training is based on the ITRC 1,4-dioxane team products. We have developed six fact sheets and the 2021 guidance document. These will be referred to during the training and are available on the ITRC 1,4-dioxane website.

The training modules are based on the fact sheets and sections of the guidance document.

This training is a 6-part modular series focused on:

- history of use and potential sources;
- regulatory framework;
- environmental fate, transport and investigation strategies;
- sampling and analysis;
- toxicity and risk assessment; and
- remediation and treatment technologies.

The training is being recorded and will be available as individual modules or a full training session.

# Online Documents and Accessing the Training Modules

**ITRC 1,4-Dioxane Website**

*Guidance Document*

*Fact Sheets*

*Training Modules*

1,4-Dioxane

HOME

Search this website

Navigating this Website

About ITRC

1 History of Use and Potential Sources

2 Regulatory Framework

3 Environmental Fate, Transport, and Investigative Strategies

4 Sampling and Analysis

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.

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Guidance Document: <https://14d-1.itrcweb.org/>

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A link to the ITRC 1,4-Dioxane website is available at the bottom of this slide. Here you will find the fact sheets, guidance document, and access to this modular training.

## ITRC 1,4-Dioxane Products and Focus?

- ▶ **Series of 1,4-Dioxane 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** – Provides an in-depth review and technical information that will assist the environmental community with 1,4-dioxane site management and cleanup.



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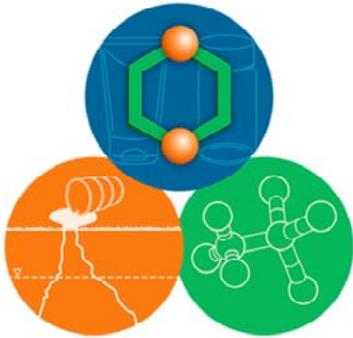
Our team has developed the fact sheets and guidance document to address questions and guide practitioners in best management practices when managing sites where 1,4-dioxane is present. We have developed the tools for multiple user groups, including the public. In particular, the toxicity and risk assessment fact sheet was created to address common questions the public has about 1,4-dioxane and its risks.

**Series of 1,4-Dioxane Fact Sheets** (<https://14d-1.itrcweb.org/>) – 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



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As a starting point and for background, 1,4 dioxane has been used as a solvent stabilizer since the 1950s. The widespread use of solvents through the 80s suggests it's presence at thousands of solvent sites in the US; however, it has not always been a standard compound in typical analytical suites so it has been often overlooked in the past.

The EPA has classified 1,4-dioxane as "likely to be carcinogenic to humans." Some states have devised standards or regulatory guidelines for drinking water and groundwater and these are often sub-part per billion values. These low values present challenges for analysis, characterization and remediation of 1,4-dioxane, so our team has created multiple tools and documents that provide information to assist all interested stakeholders in understanding this contaminate and for making informed, educated decisions.

If you have questions, please place these in the chat box and we will discuss them during the question and answer session.

ITRC initiated the 1,4-Dioxane team in 2018 to review the information and science of 1,4-Dioxane.

1,4-dioxane has seen widespread use as a solvent stabilizer since the 1950s. The widespread use of solvents through the 80s suggests it's presence at thousands of solvent sites in the US; however, it has not always been a standard compound in typical analytical suites run at hazardous waste sites so it has been often overlooked in the past.

The U.S. EPA has classified 1,4-dioxane as "likely to be carcinogenic to humans." Some states have devised health standards or regulatory guidelines for drinking water and groundwater standards and these are often sub-part per billion values. These low standards present challenges for analysis, characterization and remediation of 1,4-dioxane so our team has created multiple tools and documents that provide information to assist all interested stakeholders in understanding this contaminate and for making informed, educated decisions.

We encourage you to use the ITRC 1,4-Dioxane products and these training modules to learn about 1,4-Dioxane and how you can apply these best practices at your sites.

## Module 1: History of Use & Potential Sources



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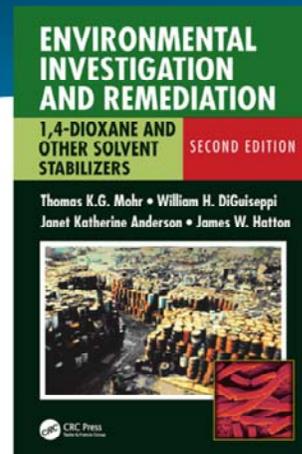
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I'm Bill DiGuseppi, a principal hydrogeologist at Jacobs with more than 30 years experience overall, and 20 years dealing with 1,4-dioxane.



## 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



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See [Section 1.2](#) for additional information

Image courtesy of Bill DiGiuseppi,  
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There are 100's of different applications for 1,4-dioxane, including but not limited to those listed here. For a more comprehensive listing, see Section 1.2 of the ITRC guidance document, as well as the comprehensive compilation of uses in Tom Mohr's 1,4-dioxane book.

The primary application of 1,4-dioxane was in stabilizing chlorinated solvents, especially 1,1,1-trichloroethane or TCA, so the history of DX is intertwined with the history of TCA usage in the US.

Understanding that key relationship helps in identification of potential 1,4-dioxane release locations.

## 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



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See [Section 1.2.1](#) for additional information

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One question you might ask is: why is 1,4-Dioxane needed to stabilize solvents?

Well, when chlorinated solvents break down during vapor degreaser operations used in metal plating, various acids are formed which are detrimental to the metal plating process.

Stabilizers address these acids one of 3 ways: acid inhibitors, which prevent formation of acids, acid acceptors, which neutralize the acids that DO form, and metal-inhibitors, which deactivate the properties of metal surfaces that make them susceptible to acid impacts.

1,4-dioxane is primarily a metal inhibitor.

## 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



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See [Section 1.2.1](#) for additional information

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Another question that comes up frequently is whether 1,4-dioxane was a stabilizer for Trichloroethene or TCE.

While there is evidence that TCE was stabilized, 1,4-dioxane has not been identified in any documentation as that stabilizing agent.

On the other hand, there is extensive evidence of DX being a stabilizer in TCA, but Tom Mohr in his decades of searching patents and other literature, found no documentation of DX in TCE. It is possible DX was used in early TCE formulations, but early patent literature is vague.

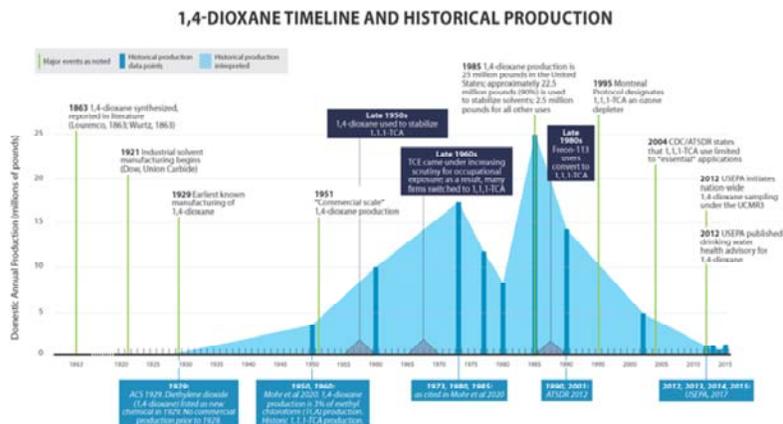
Lastly, since TCE is more stable and less susceptible to degradation during usage than TCA, DX may not have been needed.

Regardless, an empirical association exists between TCE and DX, as will be detailed in the fate and transport module, so it may not matter whether DX was IN TCE itself, TCE presence is still a good indicator of the possibility of DX being present..

# Production History

Discussed in time segments:

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

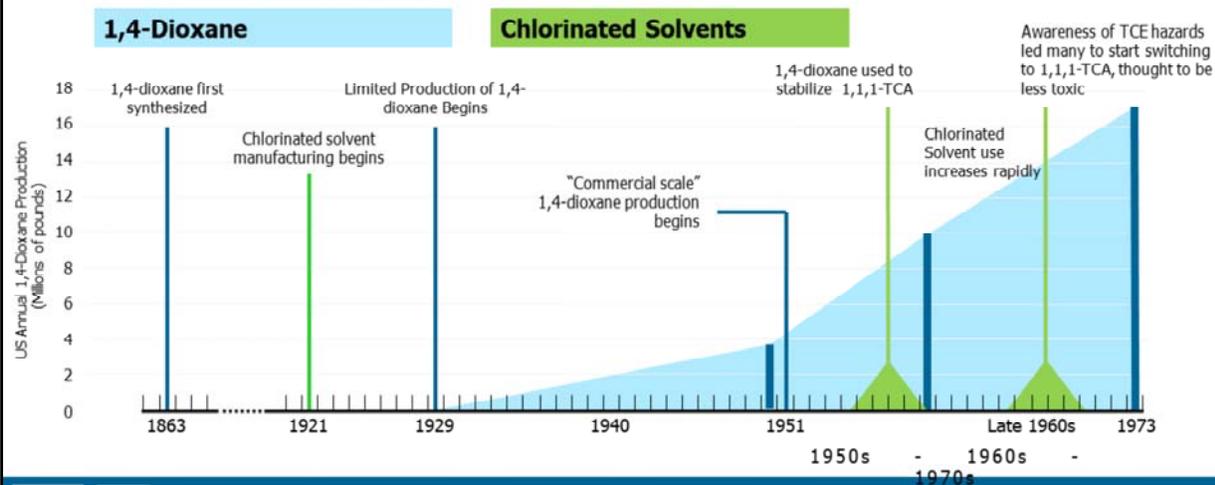


See [Section 1.1](#) for additional information

Now we want to talk about the history of production of 1,4-dioxane in the US, and especially in relation to production history of chlorinated solvents, specifically TCA.

We'll cover that history in 3 big time blocks.

## Invention, Discovery and Growth (1863 – 1973)



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1,4-DX was first synthesized in 1863, but was not put into production until 1929, and even then it was limited.

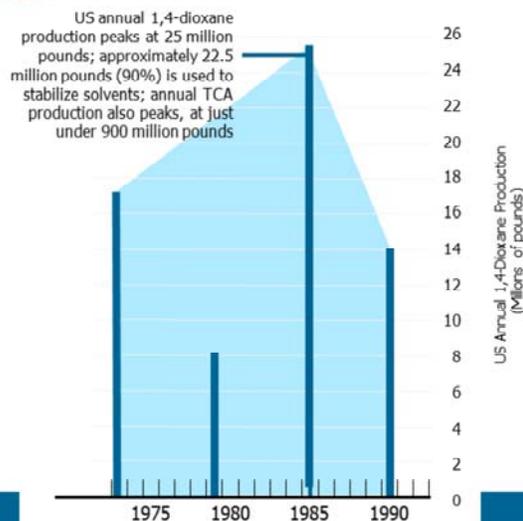
Commercial scale production began in 1951, and ramped up through the 50s, 60s, and 70s.

Chlorinated solvent manufacture began in 1921, and the first documented evidence of DX use in TCA was in the late 1950's. Chlorinated solvent use in the US ALSO ramped up dramatically in the 50s, 60s, and 70s.

In the late 1960's and early 1970's awareness of toxic effects of exposure to TCE caused some users to switch from TCE to TCA because the latter was thought to be less toxic.

## 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

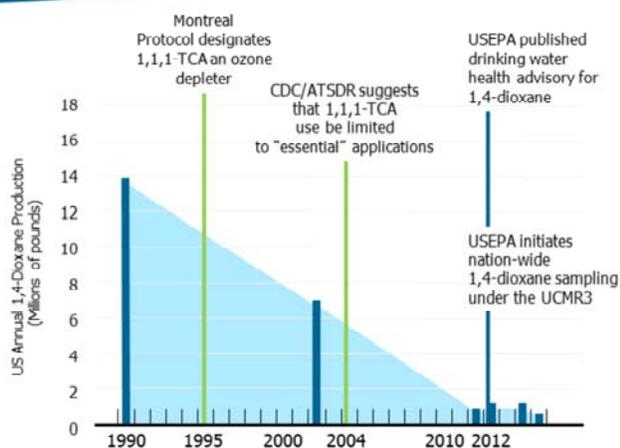


During the 1970's and 1980's, 1,4-DX usage increased with the increase in TCA usage, although these data suggest some variability over that time period.

One data point that is important, is that in 1985, US 1,4-dioxane production reached a peak of 25 million pounds per year and 90% of that went into TCA, who's production also peaked in 1985 at almost 900 million pounds annually.

## 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



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

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1,4-dioxane production declined steadily in the 90's, aughts, and 20tens, to less than 1 million pounds per year. Most of this decline was driven by awareness and regulation of the hazards of TCA, which was designated an ozone depleter in 1995, and in 2004 the CDC/ATSDR suggested that TCA usage be limited to only "essential" applications.

US EPA published a drinking water health advisory for 1,4-dioxane in 2012, around the same time they required sampling in drinking water supplies across the US as part of the Unregulated Contaminant Monitoring Rule (UCMR3).

## 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



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Now we'll briefly go through a case study with a fairly typical pattern of chlorinated solvent and 1,4-dioxane usage, in this case for Air Force Plant 44, which is part of the Tucson International Airport Area Superfund site.

This was a missile manufacturing plant, with TCE used from the 1950's through today, albeit at minor levels since the 1980's.

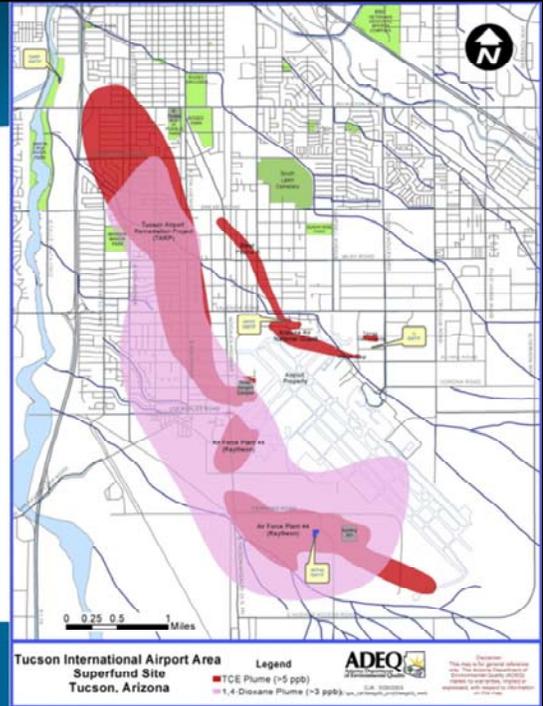
In 1974, there was a documented switch from TCE to TCA in vapor degreasers used to support metal plating operations.

Two sites are of interest for evaluating 1,4-dioxane: Site 3 – which was an unlined solvent waste lagoon operating from 1966-1977, and Site 5 – which was a metal plating wastewater and sludge disposal area that operated from the early 1960s through 1977.

A groundwater extraction and reinjection system has operated since the late 1980s to treat the chlorinated solvent plume.

## 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



Looking at the 1,4-dioxane plume confirms the relationship between the chlorinated solvents and DX.

The red on the map is the TCE plume and you can see that the plume represents a number of sources, beyond AFP44 which is located at the bottom of the map.

The main TCE plume is discontinuous due to 40 years of pumping at a couple of key locations. But the purple DX plume is co-located with the TCE plume for the most part.

The dioxane plume was wider at the time of discovery because the groundwater system extracted from the center of the plume and re-injected on the outside of the plume. At the time of discovery, DX was being injected at about 10 ug/L.

The plume has subsequently narrowed dramatically as reinjection was changed to be upgradient of the plumes instead of cross-gradient.

## 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://dpart-library.com/image\\_gallery/311049.jpg](http://dpart-library.com/image_gallery/311049.jpg)



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The takeaways from this discussion are that 1,4-DX is widely used in a variety of industries, but the primary use was in TCA.

DX manufacture over time is tied to the manufacture and use of TCA.

DX may have been present in TCE, but there is little direct evidence of this. However, the empirical association between TCE and DX is well documented, so it really doesn't matter.

And lastly, DX is found co-located with chlorinated solvents at many sites, and at about the same order of magnitude.

## Module 2: Regulatory Framework



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

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Welcome to Module 2 of the ITRC 1,4-Dioxane Training Series. During this module we will provide a discussion on the regulatory framework of 1,4-Dioxane. **Dr. Janet Anderson** is a Principal Toxicologist with GSI Environmental Inc. with 15 years of experience providing toxicology and risk management strategies to federal agencies, private industry, and municipal clients.

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**Dr. Janet Anderson** is a Principal Toxicologist with GSI Environmental Inc. with 15 years of experience providing toxicology and risk management strategies to federal agencies, private industry, and municipal clients. She also provides litigation consulting and expert services and is a Diplomate of the American Board of Toxicology. Dr. Anderson specializes in communicating the key findings from toxicology studies used to inform state and federal regulatory policy and public health decisions, and helping stakeholders understand the sometimes-disparate interpretations. She is a recognized leader in unregulated and emerging chemicals, such as per- and polyfluoroalkyl substances (PFAS), 1,4-dioxane, and 1,2,3-trichloropropane. She has developed strategies to mitigate human health risks and address environmental liability associated with unregulated and emerging chemicals for both private and public sector clients. She has extensive experience developing risk communication and risk management strategies for multi-stakeholder groups. Dr. Anderson received her Ph.D. in Molecular and Cancer Biology from the University of Cincinnati, completed a post-doctoral fellowship with the U.S. Environmental Protection Agency, and as a civilian government employee, led the U.S. Air Forces Emerging Contaminants program and advised the Department of Defense on matters related to toxicology and environmental restoration. A skilled communicator, Dr. Anderson is often an invited speaker and panelist at high-level scientific conferences, regulatory and industry meetings, law seminars, technical webinars and workshops, and community stakeholder meetings.

## 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

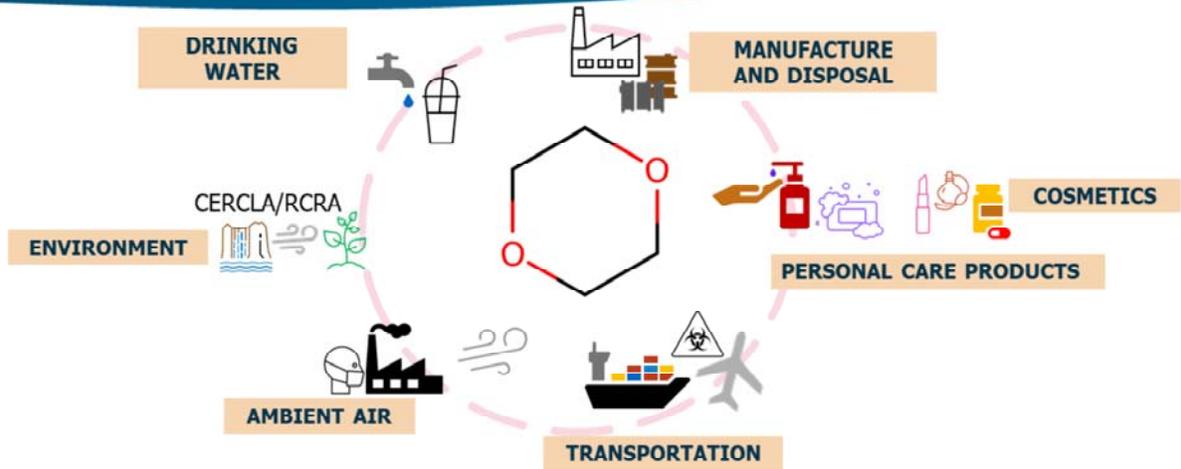


**Figure 2-1. 1,4-Dioxane State Regulatory Values for Drinking Water and Groundwater (µg/L)**

*Data as of 2/3/2021*

Objectives?

# Regulatory Framework & Landscape



- For an emerging contaminant 1,4-DX actually regulated across a wide array of programs at both federal and state level – shown here
- High-lighting only a few in this training. More details can be found in Section 2 of Guidance Doc

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

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

- ▶ 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



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- In the US, the EPA TSCA program, amended in 2016, evaluates potential risks from new and existing chemicals during manufacture, import, distribution, use and end of life disposal
- 1,4-DX was identified as one of the top 10 priority chemicals under the amended TSCA program
- Initial draft risk evaluated issued for public comment in June 2019
- This evaluation was for risk to workers and occupational non-users during industrial conditions of use only

## 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



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- However, in November of 2020, a supplemental risk evaluation was released for public comment that included new evaluation of risk to the general public under conditions including as a byproduct in consumer products and related to surface water exposure (both direct contact and incidental ingestion during swimming and fish consumption from surface water bodies near manufacturing facilities)
- The TSCA risk evaluation does not include potential exposures that fall under the purview of other EPA programs, including risks from potential drinking water exposure
- The risk evaluation was finalized on Dec 31, 2020

# 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



Final conclusions are: (summarize bullets)

## 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



See [Section 2.1 ITRC Guidance Document](#) for more detailed information  
See [Section 5.2](#) for inhalation toxicity values

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- So what are the current existing regulations for protecting occupational workers?
- 1,4-DX is regulated in the occupational setting under some relatively outdated air exposure guidance.
- Both ACGIH and CA OSHA have 8-hr time weighted average limits
- NIOSH also has ceiling limits and an acute “immediately dangerous to life and health” limit

## Cosmetics and Pharmaceuticals

### U.S. Food and Drug Administration (FDA)



- ▶ 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



See [Section 2.1 ITRC Guidance Document](#) for more detailed information

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- In the U.S. the FDA regulates compounds in cosmetics and pharmaceuticals
- Currently there is no formal regulation for 1,4-DX under FDA, however, FDA recommends a maximum of 10,000 µg/L in any finished cosmetic product and has a daily exposure maximum recommendation for pharmaceuticals

## 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  $>30 \mu\text{g}/\text{day}$
  - ▶ **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  $\mu\text{g}/\text{L}$



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- Although EPA determine that there is currently no unreasonable risk to the general public associated with 1,4-DX present in personal care products, several states have issued their own product labeling and limit requirements
- For example, California.... (summarize bullets)

## 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
- ▶ 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



Thresholds will be re-evaluated every 5-years.



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See [Section 2.2.2 ITRC Guidance Document](#) for more detailed information

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- And NY recently passed legislation prohibiting the sale of personal care products with these threshold limits, which will be re-evaluated every 5 years.
- Several other states also have similar labeling and reporting rules, and for more information see Section 2.2 in the Guidance document

## 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

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- Surface water is regulated by the EPA pursuant to the Clean Water Act and although there are currently no surface water quality criteria, there are numerous National Pollutant Discharge Elimination System permits with requirements for 1,4-DX monitoring
- Several states have issued their own surface water quality standards and wastewater discharge requirements

# Environmental Cleanup Programs: Federal

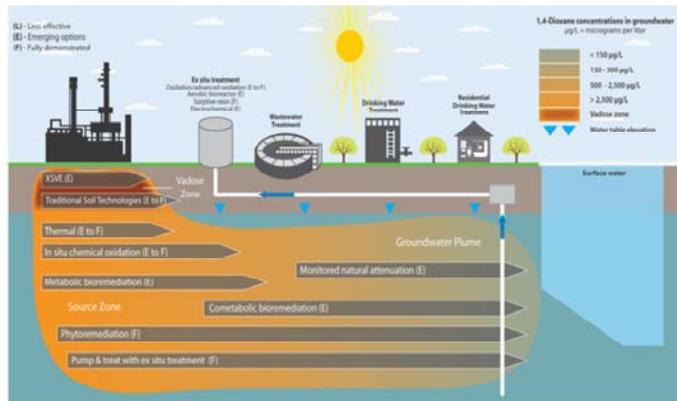
## ▶ Hazardous Substance under CERCLA/RCRA

### ▶ CERCLA

- ▶ screening levels\* used for screening and informing cleanup goals
- ▶ RSL\*\* = 0.46 µg/L groundwater  
= 5.3 mg/kg soil  
= 0.56 µg/m<sup>3</sup> (0.16 ppm) air

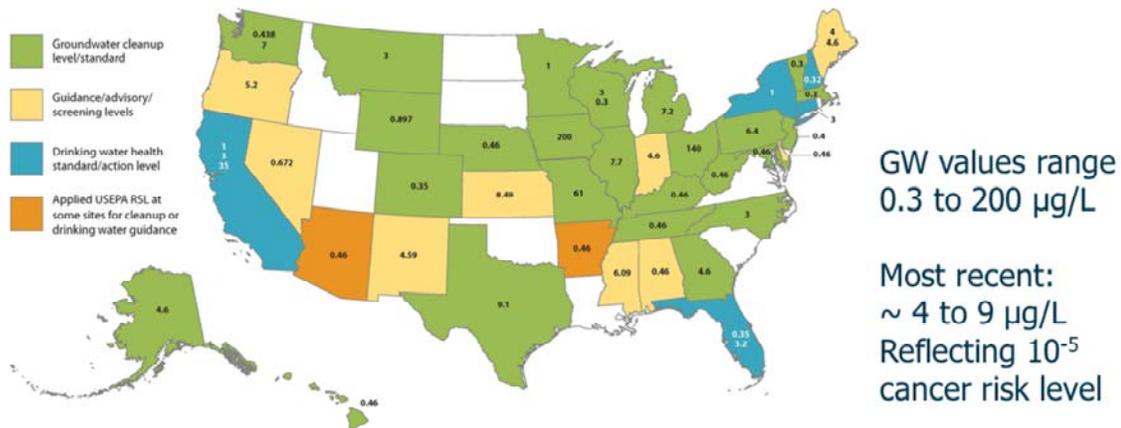
\*screening levels – not cleanup standards

\*\* Regional Screening Levels (RSL) shown at 10<sup>-6</sup> cancer risk level for residential exposure



- 1,4-Dx is considered a hazardous substance under CERCLA/RCRA
- There are screening levels available for Superfund sites from the EPA Regional Screening Levels – shown here are the levels for the residential exposure scenarios at the 10<sup>-6</sup> cancer risk level.

## Environmental Cleanup Programs: States



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 [Figure 2-1 ITRC Guidance Document](#) for more detailed information

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- Numerous states also have cleanup standards or guidance.
- Shown here is an image of a hyperlinked map that is available online as part of the Guidance document.
- If you click on a certain state, links will take you to additional information for each state.
- States shown here in green, yellow and orange have either standards or guidance values for groundwater cleanup, based on the team's best attempt to identify and summarize this information as of Feb. 2021.
- Although values range from 0.3 to 200 µg/L, some of the most recent promulgated values fall around 4 to 9 ppb, reflecting the 10<sup>-5</sup> risk level based on the USEPA toxicity assessment from 2013.
- Additional information can be found in Section 2 and Appendix A.

# 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
- ▶ January 2021, EPA "has not determined whether there is a meaningful opportunity for public health risk reduction"
  - ▶ Continuing to evaluate for MCL

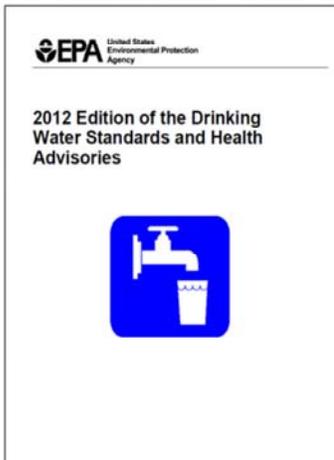


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- 1,4-DX is not regulated in drinking water at the federal level
- However, as of January 2021, EPA has listed 1,4-DX on the candidate contaminant list and is still determining whether there is a meaningful opportunity for public health risk reduction

# Drinking Water - Health Advisory - Guidance



- ▶ 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)



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See [Section 5 ITRC Guidance Document](#) for more detailed information

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- EPA does have a drinking water lifetime health advisory for drinking water systems at 35 ug/L – this is a guidance value that provides risk management guidance for municipal drinking water systems
- Section 5 and the toxicity component of the guidance document provides additional information on how this value was derived

## Drinking Water - State Regulation



Note: Map based on best available information as of February 2021. States without an entry may apply the EPA HA.



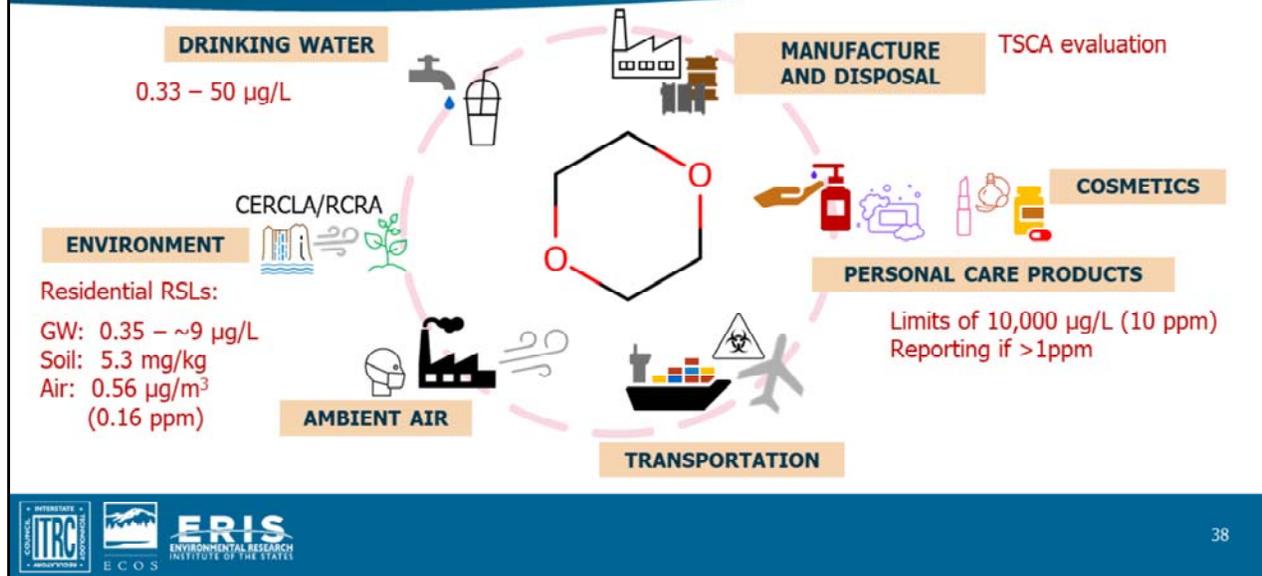
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See [Appendix A](#) and [Figure 2-1](#) ITRC Guidance Document for more detailed information

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- Shown in blue are some of the states that also have their own drinking water guidance.
- NY was the first state to issue to issue a formal promulgated standard, set at 1 ppb in 2020
- NJ has a recommended MCL from their advisory board at 0.33 ppb
- And Health Canada has had a proposed maximum allowable concentration, their version of the federal MCL, of 50 ppb that was issued in 2018.
- The technical reasons behind the difference in these values is discussed in the toxicology portion of this training and of the guidance document

## Regulatory Framework & Landscape - Conclusion



- To summarize, 1,4-DX is regulated across a variety of state and federal programs.
- EPA's recent TSCA evaluation is final and suggests only a concern for some occupational settings.
- States in particular have reporting, labeling and limit requirements in personal care products
- Screening levels are available for CERCLA
- And although not yet regulated at the federal level, there is a range of 0.33 to 50 ppb in proposed agency drinking water standards and we will likely continue to see states finalize drinking water regulations in the near future.

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



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

## 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



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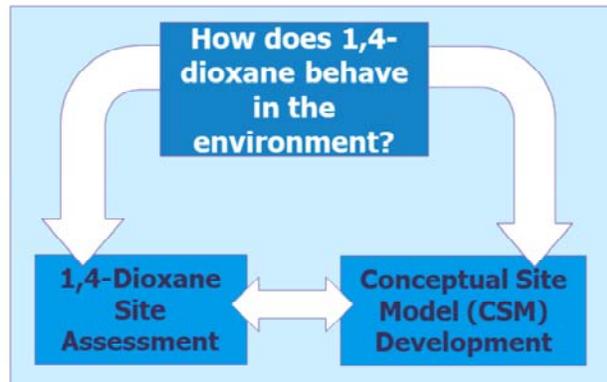
Thanks Heather. I'm going to start off then pass it on to Monica later in this session.

Here are the learning objectives, which serve also serve as a good general road map for what we'll be covering. At the end of this session, these are what we want people to take away.

First, what are the key physical and chemical properties that distinguish 1,4-dioxane?  
Second, what F&T processes are most likely to be relevant for 1,4-dioxane.  
This serves as a basis for developing a conceptual site model, or CSM, for 1,4-dioxane.  
And finally, we'd like people to come away with a more information to guide site assessment. This ITRC team doesn't have a separate site characterization section, but we think it fits in well here in the F&T section.

## 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!



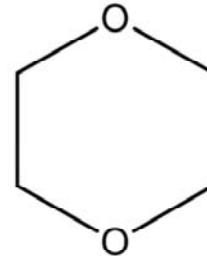
To start off, why is fate and transport important? What we're really talking about when we say fate and transport is "how does 1,4-D move in the environment?" And what happens to it while it's moving? This provides the real technical basis for making decisions about 1,4-D. Like where to look for 1,4-D when doing site assessment, how to evaluate the potential for risk, and the basis for making treatment decisions about 1,4-D. That last point is discussed in detail in the Remediation and Treatment training module.

The characteristics can be placed into two broad categories: (1) the physical-chemical properties of 1,4-dioxane itself, like solubility; and (2) the characteristics of the site where it was released, for example the groundwater velocity or the dissolved oxygen levels.

These are components of any CSM for 1,4-dioxane. We've learned a lot about 1,4-dioxane in the past few years, but our knowledge is still evolving. What's presented here and in the ITRC guidance is based on the current state of the science, with the understanding that we're still learning.

## 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***

So what are some of those critical characteristics? The ITRC Guidance Doc has a few tables that compile all the physical chemical properties of 1,4-dioxane, and they're a good reference. The next couple slides highlight the big important properties as a reminder that they are the ones that really dictate the fate and transport of 1,4-D and how we have to manage it. So if you remember anything, remember these!

[READ bullets]

## 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-m <sup>3</sup> /mol (at 25°C)	4.8 x 10 <sup>-6</sup>	5.48 x 10 <sup>-3</sup>	9.1 x 10 <sup>-3</sup>	1.6 x 10 <sup>-2</sup>	5.62 x 10 <sup>-3</sup>	5.8 x 10 <sup>-3</sup>
Log K <sub>oc</sub>	Dimensionless	0.54	1.92	1.81	2.18	1.55	1.48
Boiling point	°C	101	80	87	74	57.4	32



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

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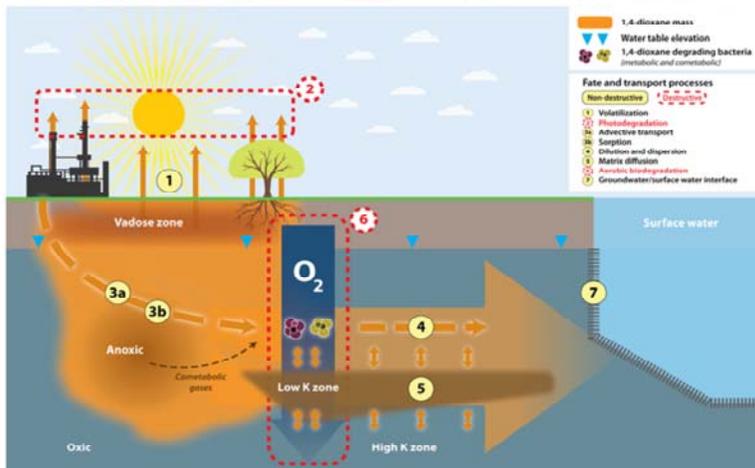
Another useful way to think about 1,4-dioxane is to directly compare the values of several key physical-chemical parameters against other common contaminants. 1,4-D is this first column highlighted in red, and in the rows are the values for the parameters.

So for example, 1,4-Dioxane is a miscible compound, that translates to a solubility of 1000 g/L in the first, a value that that's around 3 orders of magnitude higher than co-occurring compounds like the chlorinated solvents.

Similarly, it's Henry's Law constant, which describes its tendency to partition to air AFTER it is dissolved in water, is generally at least 3 OoMs LESS than these other compounds. It's vapor pressure, on the other hand, is lower but not that much different. We'll talk more about this in a few slides when we discuss volatilization.

It's also worth pointing out the reported Koc values for 1,4-dioxane vs. the other compounds. These are log values, so a log Koc of 0.54 for 1,4-dioxane means that it's more than 1 OoM different than most of these other compounds. Remember that Koc is a measure of the relative proportions that would be associated with the soil vs. water phase (normalized by organic carbon content), having such a low value is another reflection of just how much 1,4-dioxane would prefer to stay in the water.

# 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

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Next, let's look at a basic conceptual site model for 1,4-D releases to the environment. For any contaminant, we typically use the conceptual site model to lay out the relationships between sources and receptors based on possible migration and exposure pathways.

This figure is in the Guidance Document (it's Figure 3-3), and it's nice to use for training because we can use as a starting point for discussing various fate and transport processes.

It doesn't necessarily cover all release scenarios or all processes that might occur, but it covers what the ITRC team considers the most relevant for evaluating 1,4-D.

## 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



First we start with volatilization, which is the transfer of a contaminant from a liquid phase to a gas phase. It's inherently a non-destructive process—it just describes the transfer between two different types of media.

EPA has two criteria for establishing if a compound is volatile, and 1,4-D meets the one based on vapor pressure since it has a VP of 24 mm Hg. But its Henry's Law Constant ( $4.6 \times 10^{-6}$  atm-m<sup>3</sup>/mole) is below the EPA threshold ( $1 \times 10^{-5}$  atm-m<sup>3</sup>/mole) and lower than chlorinated solvents.

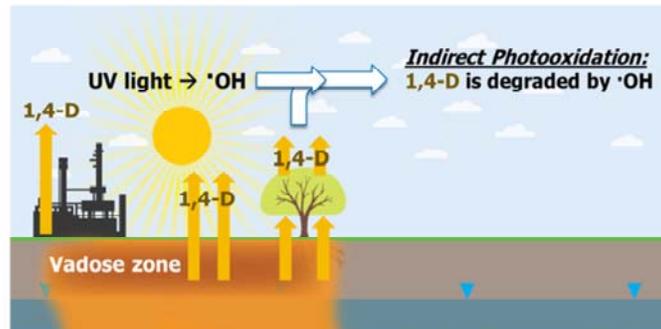
So based to this combination, transfer to vapor could be an issue in situations where there is a lack of water to partition into, such as a pure phase or dry surface soils. In this case, 1,4-D's vapor pressure becomes relevant.

However, that's probably pretty rare since water is likely to be present in most settings. If water is present, the low Henry's Law constant dictates that concentrations in the liquid phase are going to be much higher than the vapor phase because 1,4-dioxane doesn't like to partition to air once it is dissolved.

OPTIONAL: Similarly, VI concern in dry soils and with pure phase presence. Obviously, you would also need to have these conditions in a setting where the vapor would be entering a building as well. Other CVOCs are more likely to be VI risk drivers.

# 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)



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The next process is photodegradation, which is a catch-all term for destructive processes that occur in due to the presence of light. So this might include contaminants that have been released to the atmosphere.

1,4-D can undergo photodegradation, but it's not a direct reaction because 1,4-D is a weak absorber of UV light, as the compound lacks chromophores or functional groups that absorb the longer wavelength, higher-energy UV.

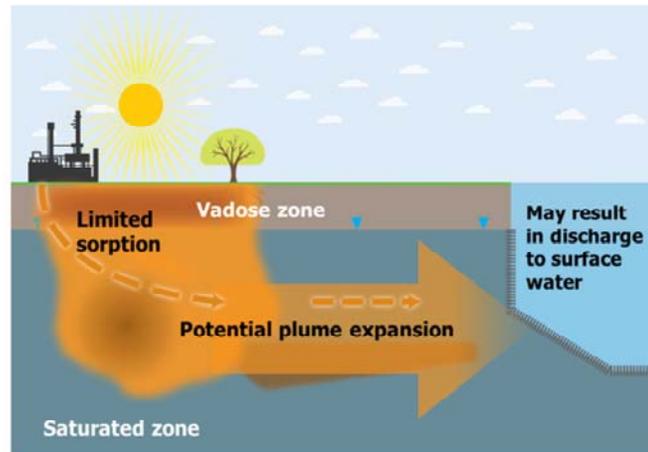
Instead, 1,4-D undergoes what is called indirect photolysis, which occurs when hydroxyl radicals, that's the OH with the little dot symbol, are produced naturally in the presence of sunlight. This is a radical oxygen species that reacts with 1,4-dioxane. The reaction rate exhibits a first-order dependence on the relative concentration of OH radical, so the reaction will be faster if there are high levels of the radical and slower if not. Based on literature reports and expected range for OH radical concentrations, you might expect 1,4-dioxane photodegradation rates on the order of a few hours to days in the atmosphere.

Plant uptake is also noted on this slide, and that is a potentially relevant process given that plants can take up a lot of water and 1,4-D likes water. This has led to interest in the use of phytoremediation as a remedy for 1,4-D. It's also worth noting that this could promote release of 1,4-D to the atmosphere through evapotranspiration, where the 1,4-D would be subject to photodegradation.

Note that photodegradation is not anticipated to occur in surface water, or least there are no direct reports of it being relevant.

## 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 is the movement of a compound due to the bulk movement of a fluid. So a typical example that's represented in this figure is 1,4-dioxane transport in groundwater that is moving in response to a hydraulic gradient. Advection is a particularly important consideration for 1,4-D due to the compound's relatively limited ability to partition to soil. This means that sorption doesn't provide much resistance to 1,4-D transport, and the compound has the potential to migrate at similar velocities as groundwater.

If a 1,4-D plume is expanding due to advection, dilution and dispersion can occur and can reduce concentration. However, dispersion in GW tends to be pretty minor, and it's probably more of a consideration if the plume expands to the point where it is discharging to a surface water body. Discharge to surface water can be a concern given 1,4-dioxane mobility.

## 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)



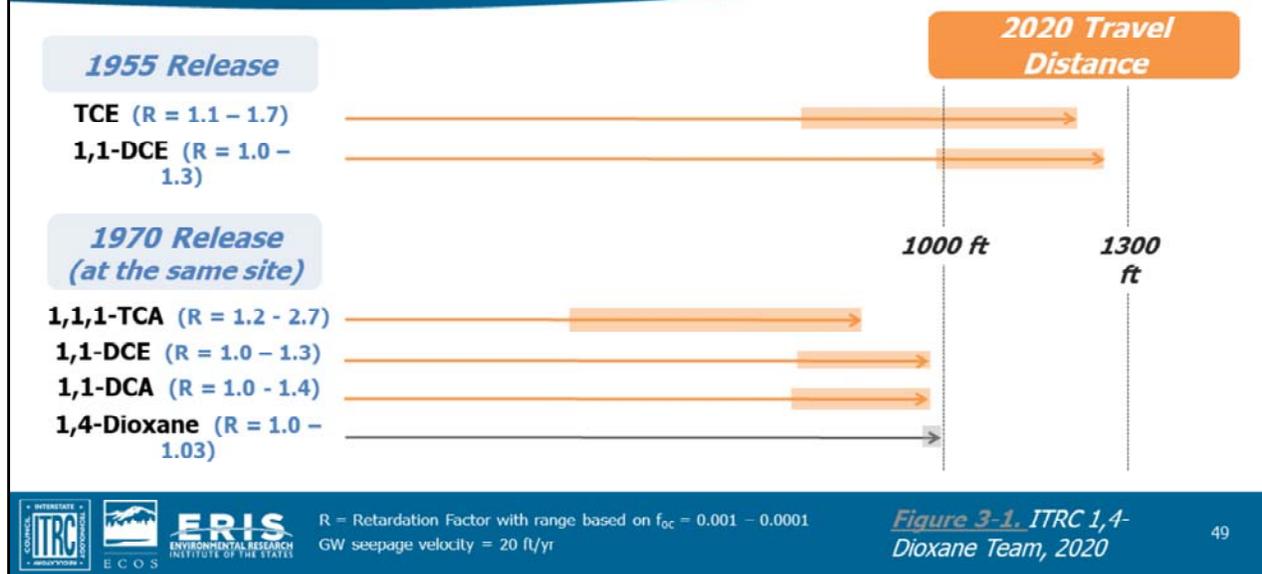
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Now, when we're talking about 1,4-dioxane's mobility and potential for plume expansion, it should be placed in context. The next couple slides go through a theoretical example that to answer the question "how far would 1,4-D be expected to migrate in GW relative to chlorinated solvents that may have been released at this same site?"

The key considerations in answering this question are:

1. The physical chemical characteristics of the contaminants.
2. The characteristics of the aquifer, like how much organic carbon is present, and finally
3. The timing is the real key here, since 1,4-dioxane may have been released with some of these compounds, but the use and release of chlorinated solvents that **weren't** stabilized with 1,4-dioxane may have also occurred earlier.

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



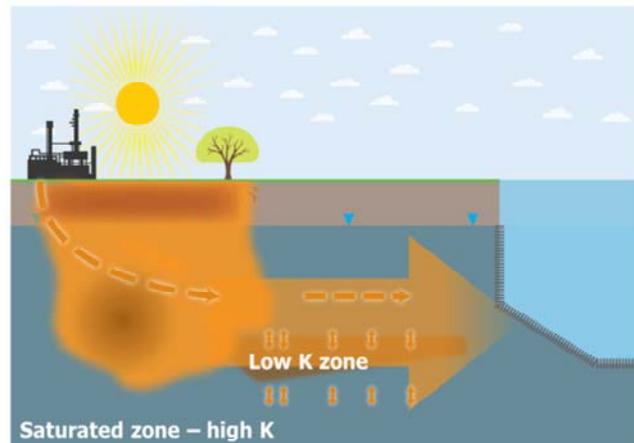
Let's consider possible plume sizes at a site where TCE was released in 1955 and 1,1,1-TCA with 1,4-dioxane was released later in 1970. In this case we'll assume a groundwater velocity, and then apply a simple 1-D transport calculation where we conservatively assume no degradation is occurring in the plume. Then will give us an estimate how far each compound would be expected to travel by 2020. We can also look at a range of  $f_{oc}$  values in the aquifer to show how this influences the retardation factors for each compound—that's reflected by the R values in parentheses behind each compound name.

For the early release, you can see that the maximum travel distance is out near 1300 ft, particularly for 1,1-DCE in aquifers with low  $f_{oc}$  since that degradation product is pretty mobile. The shaded bar represents the range of distances based on the range of  $f_{oc}$  values, so naturally the travel distance is less when higher  $f_{oc}$  is available to promote sorption.

Now let's look at the distances for the later release. 1,4-dioxane transport isn't that dependent on  $f_{oc}$  since it's not sorbed, so the travel distance of 1000 ft really just reflects the groundwater velocity. But you'll see that that distance is pretty similar to the distance that solvents from the earlier release may have traveled, in part because they've been in the aquifer 15 years longer. And the 1,4-dioxane travel distance may not be that dissimilar to solvents that were part of the 1970 release with 1,4-dioxane, in part because many of those solvents are fairly mobile in low  $f_{oc}$  environments.

## 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



Let talk now about matrix diffusion, which is sort of a new topic for 1,4-D. Matrix diffusion describes the movement of dissolved 1,4-D from permeable soils within an aquifer (like sands) into less permeable (also called low K) soils (like silts and clays) via diffusion. Diffusion occurs naturally in response to a concentration gradient. That's shown on in the plume portion of the figure where the double sided arrows indicate that the contaminants can move in and out of these low k zones depending on the concentration gradient.

Once the contaminant has diffused into these lower k soils, it can be hard to get out, and it can contribute to longer-term persistence of a contaminant. It can also make it harder to treat, especially if you're relying on injection-based technologies. (To be discussed later in more detail.)

## Matrix Diffusion: Influences Over Time

### EARLY STAGES (After Release)

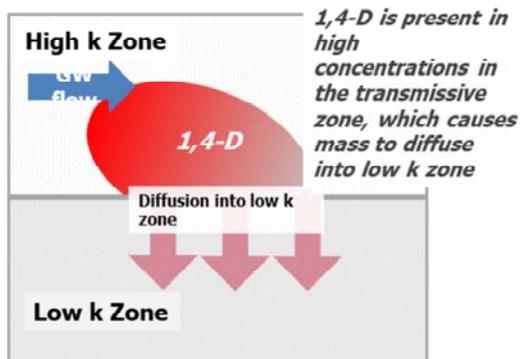


Figure 3-2. Overview of Matrix Diffusion Process for 1,4-Dioxane.  
ITRC 1,4-Dioxane Team, 2020.

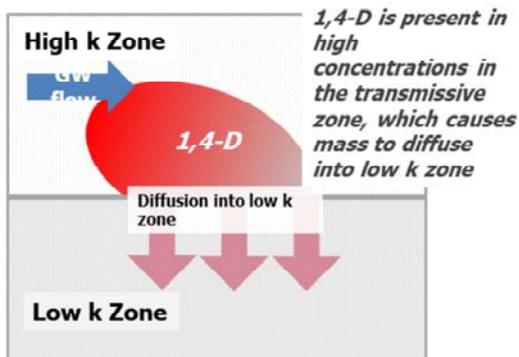
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The graphics on the next couple slides help illustrate how matrix diffusion can influence where the mass is located over time.

Imagine in the early stages after release, the 1,4-dioxane mass is mostly in the higher permeability (high K) zones, as shown by this red blob. But since the concentration can be pretty high at first due to 1,4-dioxane's solubility, you start with this high initial concentration gradient that drives 1,4-dioxane into the lower-k zone via diffusion, the process shown in these red arrows. Once it's in the low-k zone, advection rates are slow, so the mass isn't going to get flushed out very quickly. It's essentially getting stored up over time.

## Matrix Diffusion: Influences Over Time

### EARLY STAGES (After Release)



### LATER STAGES (During Site Investigation)

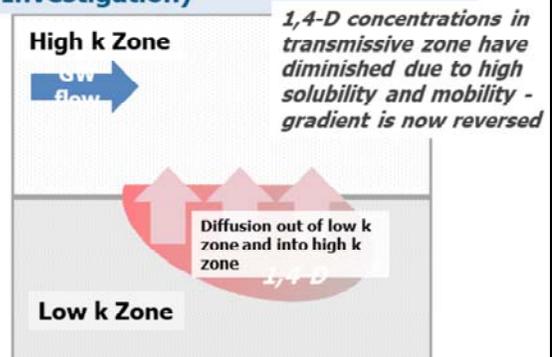


Figure 3-2. Overview of Matrix Diffusion Process for 1,4-Dioxane.  
ITRC 1,4-Dioxane Team, 2020.

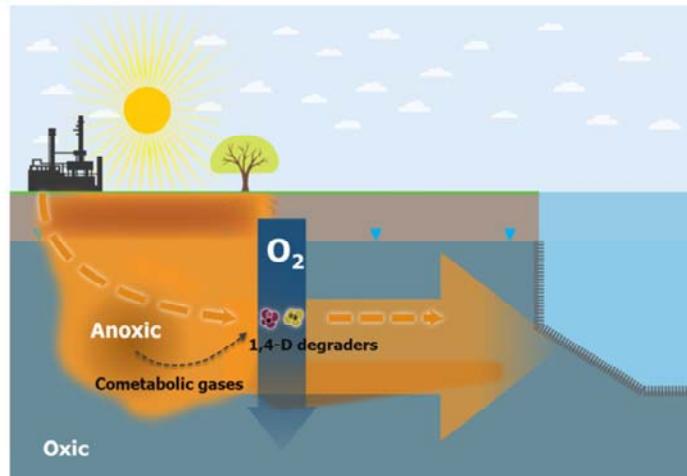
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Later as time has passed, and maybe someone has finally gotten around to realizing that 1,4-dioxane may be a problem that needs to be investigated, we've got a different situation, as shown in the right-hand panel. Now, the concentration in the overlying transmissive zone (the high k zone) has probably diminished because 1,4-D is so soluble and mobile. That means the concentration gradient is now reversed, and the 1,4-D that had diffused into the low-k zones can diffuse back out into the aquifer. But it's going to be slow because diffusion is a slow process.

Because of this, back diffusion from these low k zones may serve as a long-term secondary source of 1,4-D contamination, particularly at sites with lots of heterogeneity ~~or where you have these interfaces between zones with really different permeabilities~~. It can also make identification, delineation, and treatment of 1,4-D sources more difficult.

# 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



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Next up is biodegradation. This is a process where there has been a substantial shift in understanding over the past decade because 1,4-D was historically perceived as resistant to biodegradation but we now know that biodegradation is possible under the right environmental conditions.

This is important because biodegradation is a destructive process, so 1,4-D is not necessarily going to persist forever once it is released to the environment if conditions are favorable for biodegradation. Importantly, as discussed further in the remediation training section, favorable conditions for biodegradation can be engineered if not present.

As Dave mentioned earlier, 1,4-dioxane is biodegraded via oxidation. This process is mediated by a variety of organisms that have been identified and further identification of relevant organisms is likely in the coming years.

This last point regarding the availability of oxygen is key. While some compounds may be biodegraded via oxidation using either oxygen or alternative terminal electron acceptors, each of the currently characterized pathways for 1,4-D biodegradation is dependent on monooxygenase enzymes, which require dissolved oxygen.

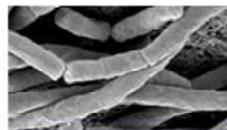
Importantly, this means that conditions that are suitable for 1,4-D biodegradation are different from the strongly reducing conditions that are suitable for biodegradation of the primary chlorinated solvents that 1,4-dioxane is associated with at many sites. As such, understanding redox boundaries is important in:

- Predicting where these different biodegradation processes are likely to occur,
- Understanding 1,4-D fate and transport in the context of mixed plumes, and
- Characterizing natural attenuation or designing other remediation strategies, as discussed further in the remediation training section.

# 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



While each known 1,4-dioxane biodegradation pathway is mediated by monooxygenase enzymes and requires oxygen in the first degradation step both metabolic and cometabolic degradation are possible.

When the transformation of a constituent results in carbon and/or energy yield to the microorganism, the process is termed metabolic biodegradation. Metabolic degradation is dependent on the 14DX concentration in that concentrations must be high enough to meet the microorganisms demands for energy and growth. Concentrations that are likely to support metabolic degradation are on the order of hundreds of micrograms to milligrams per liter in groundwater. As illustrated here, an organism called CB1190 is the most widely studied organism capable of metabolic 1,4-dioxane biodegradation.

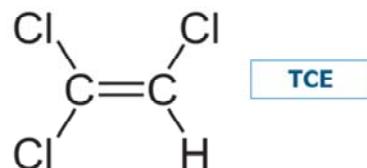
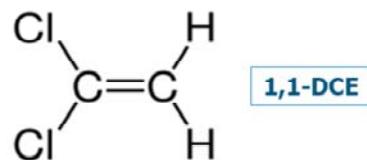
Microorganisms may also degrade 14DX, as a side-effect of targeted degradation of a different constituent and as a result of low specificity of some monooxygenase enzymes for their primary substrates, this process is termed cometabolism.

Cometabolic biodegradation of 1,4-dioxane has been documented with degradation of primary substrates that include Tetrahydrofuran (THF), propane, toluene, butane, and ethane have been identified as primary substrates that can support 14DX cometabolism. Ethane is a particularly interesting cometabolic substrate because it is a product of complete reductive dechlorination of some of the chlorinated solvents that 1,4-dioxane is like to occur with.

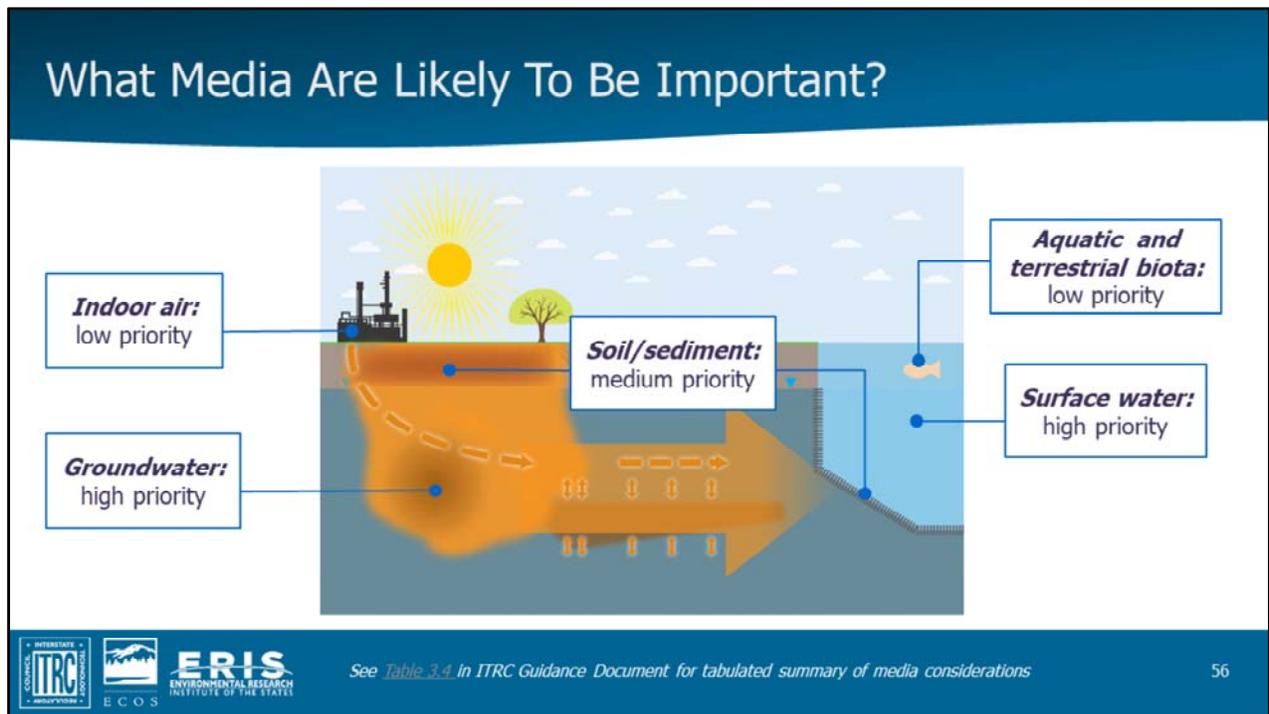
Notably, in the cometabolic case, since 1,4-dioxane is not acting as a carbon or energy source the rate and extent of degradation is largely controlled by the presence and concentrations of the primary substrates rather than by the concentration of 14DX.

## 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.,  $\text{Cu}^{+2}$ )



Finally, on the topic of 1,4-dioxane biodegradation, it is notable that microbial inhibition is a potential concern. Co-occurring chlorinated solvents and metals (for example copper) have been demonstrated to be inhibitory under some conditions. There are multiple inhibition mechanisms hypothesized for these constituents, as described in greater detail in the guidance document, and this is certainly still an area of active research. At this time, our advise is to consider the potential for inhibition on a site specific basis and to keep up on scientific advances in our understanding of this process.



Moving on from fate and transport processes, the next topic on this module is media.

This graphic summarizes the primary media as well as the relative priority of each based on where one would expect to find 1,4-D and (to a certain extent) what might be risk drivers. Let me reemphasize that these are “relative” priorities, and some sites are obviously going to differ. The Guidance Doc has a table that provides further detail and rationale on this prioritization.

Based on what we’ve talked about thus far, it shouldn’t be a surprise that Groundwater is a high priority given 1,4-D’s properties.

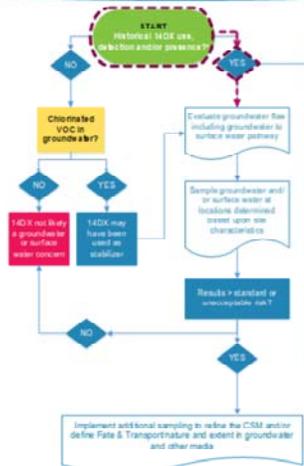
Surface water is also considered a high priority because of the potential for discharge from groundwater and also because there are cases where direct discharge to 1,4-D from wastewater treatment plants or other sources might occur. This is a potential concern if that surface water is used as a source of drinking water.

Soil and sediment are ranked as having a medium priority. This is because sorption of 1,4-D is generally limited and therefore it is not expected to persist in these media. However, since 1,4-D may come into direct contact with these media during release or after discharge, there is some potential for 1,4-D to be present, and should be considered on a site specific basis.

Indoor air and aquatic and terrestrial biota, on the other hand, are ranked as a low priority. As we mentioned before, it would require fairly specific set of circumstances, including elevated concentrations and complete vapor intrusion pathway to drive risk in this media. Risk to aquatic and terrestrial biota is considered to be low based on a lack of evidence for bioaccumulation and other toxicity drivers. This topic is discussed in detail in the training modules on Toxicology and Risk Assessment.

Based on this understanding of prioritization of media, we have developed a framework to support decision making for 1,4-dioxane site assessment.

## 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



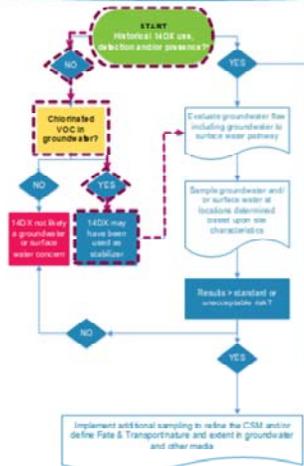
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See Figure 3-4 in ITRC Guidance Document for complete flowchart

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I want to start by noting that the flowchart presented here is an abbreviated version from that in the guidance document, and I encourage you to review that document for additional supporting details. Here we want to start by emphasizing the highest priorities for site investigation and that starts with the simple question: Was 1,4-dioxane historically used or detected at the site?

# Guidance for 1,4-Dioxane Site Assessment

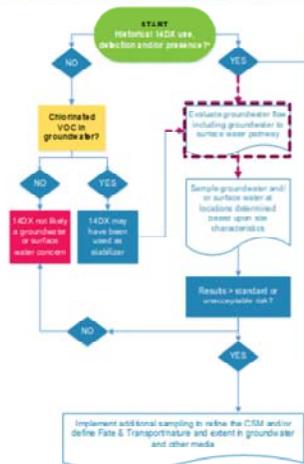


## PRIORITIES:

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

If the answer to the question on 1,4-dioxane use or presence is no or unknown, then the next relevant question is: Were chlorinated solvents historically used or detected at the site? As mentioned in the History of Use module, one of the primary historical uses of 1,4-dioxane was as a stabilizer in chlorinated solvents. Therefore, where these constituents are present or suspected, additional investigation of 1,4-dioxane is warranted.

# 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)



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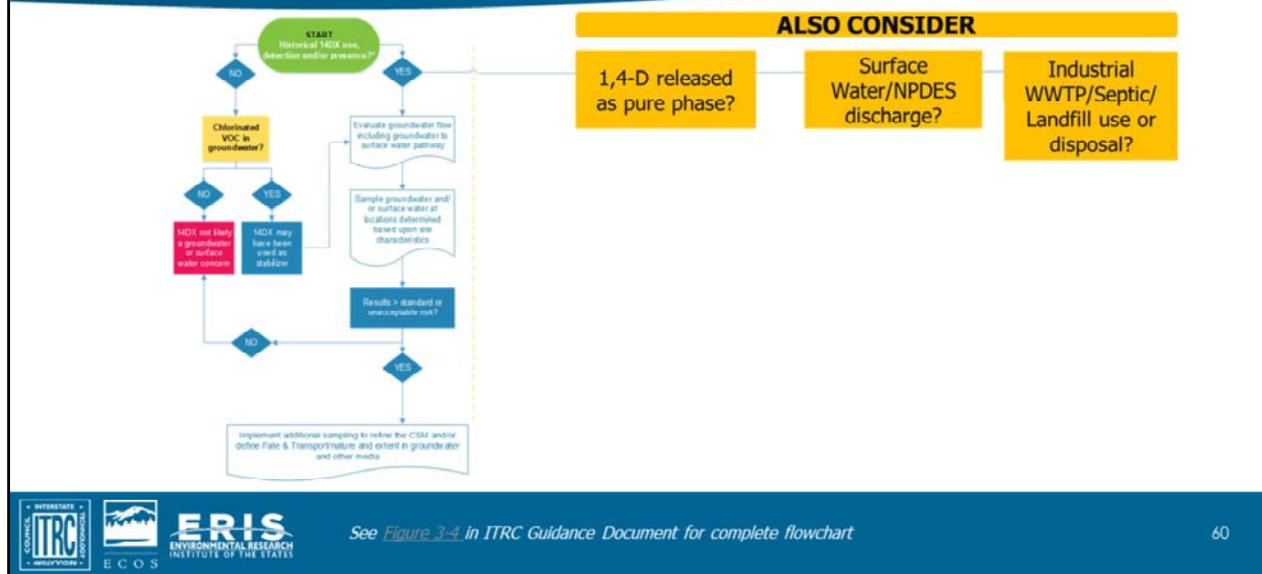
See Figure 3-4 in ITRC Guidance Document for complete flowchart

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If the answer to either of these initial questions is yes, then site investigation should likely proceed to development of a CSM for 1,4-dioxane in groundwater, considering first where water is expected to travel and then sampling at appropriate locations.

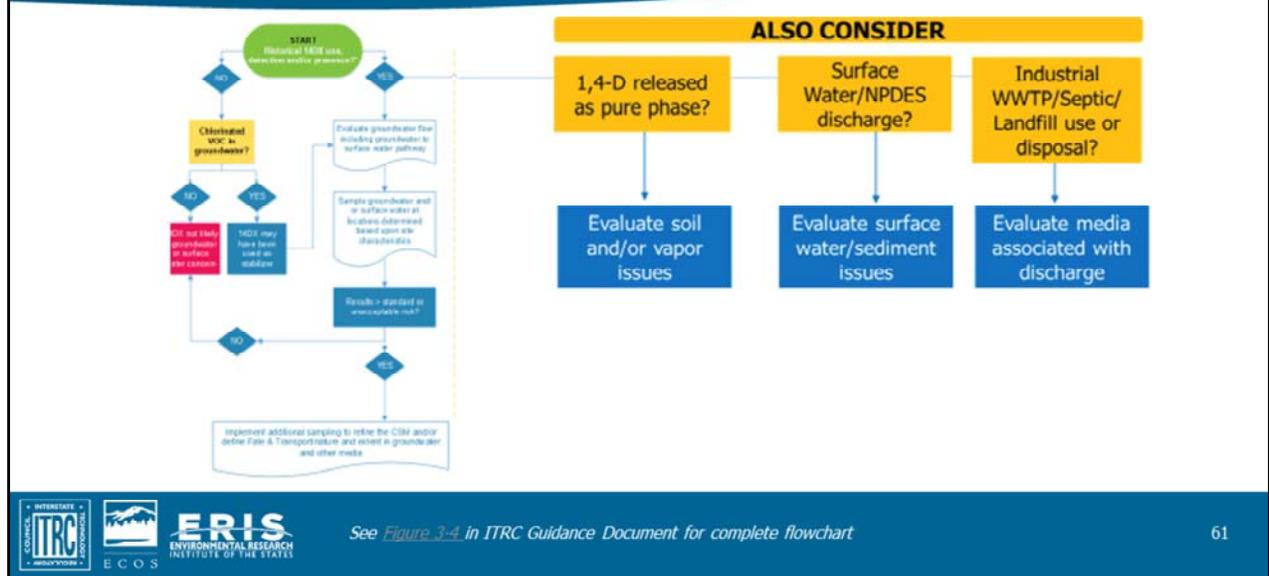
Concentrations of 1,4-dioxane in groundwater should then be compared to relevant standards or site-specific risk thresholds. If 1,4-dioxane concentrations in groundwater are not greater than the relevant criteria then 1,4-dioxane is likely not a groundwater or surface water concern. If 1,4-dioxane does exceed these standards, then the next step is to implement additional sampling to refine the CSM and/or understanding of site-specific 1,4-dioxane fate and transport and the nature and extent of 1,4-dioxane concentrations.

## Guidance for 1,4-Dioxane Site Assessment



As mentioned in the discussion of media, groundwater and surface water are the primary concerns for 1,4-dioxane. However, we also want to take a few minutes to highlight other key considerations, specifically cases where 1,4-dioxane was or may have been released as a pure phase, cases where there is a surface water or NPDES discharge, and cases with industrial WWTP, Septic, or landfill disposal.

## Guidance for 1,4-Dioxane Site Assessment



As shown, in these cases other media may need additional investigation, including:

- soil and or vapor where pure phase may be present,
- surface water or sediment in the case of surface water or NPDES discharge, and
- any other potentially relevant media associated with industrial WWTP, septic, or landfill disposal.

## Take Home Messages

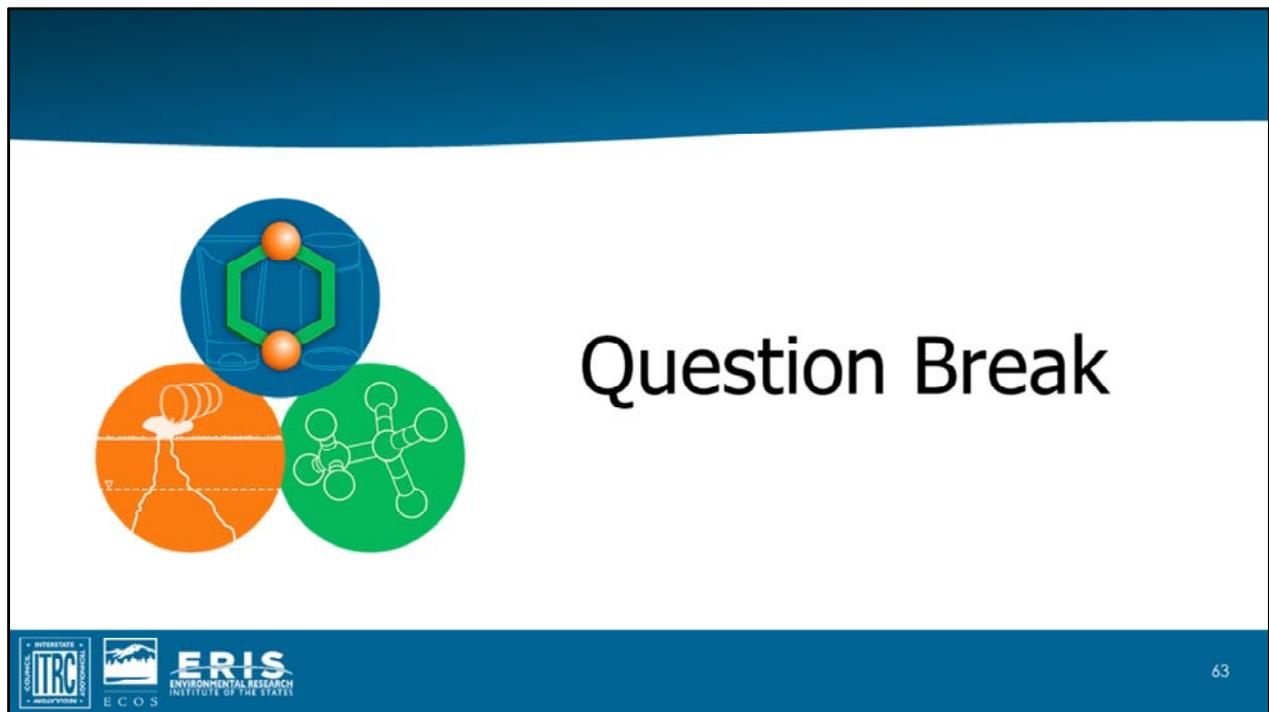
- ▶ Understand key physical/chemical properties
  - ▶ Low organic carbon partitioning coefficient and Henry's constant; high solubility
- ▶ Identify fate and transport processes that are relevant for 1,4-dioxane
  - ▶ Advection with limited sorption in subsurface
  - ▶ Photodegradation in atmosphere; 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



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*Just use text on slide*

That concludes Module 3 of the ITRC 1,4-Dioxane Training Series. Thank you!"



Thank you, **[Speaker Name]**.

At this time we will open the questions and answers portion of our training. At any time you can type in your question in the Q&A pod in the bottom right corner of your screen. We will try to get through as many of those questions as we can.

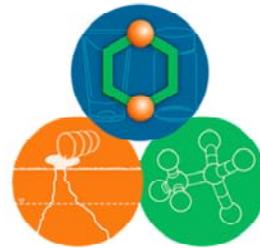
Let's go to our phone lines - if you would like to ask a question out loud this is your opportunity to do so. It's Pound 6 to unmute.

Then read questions from the Q&A Pod.

## Module 4: Sampling & Analysis



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

## 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



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E C O S

# 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™

▶ Low yield wells



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



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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.innovativetech.com](http://www.innovativetech.com)

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



VOC: Volatile organic compound

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Just focus on issue with very dry soils

If soil has moisture, then sample can be treated as a SVOC; otherwise, collect and analyze as a VOC

# 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



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 of 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 randomized 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 decrease 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](#).



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# 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) Cool 0-6° C	<b>Low-level:</b> 48 hours to freezer; 14 days to analysis <b>High-level:</b> 14 days to analysis 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



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*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 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 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 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 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 <sup>3</sup>	
TO-17 (Air)	Full scan GC/MS	1.1-11 ng/tube	



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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



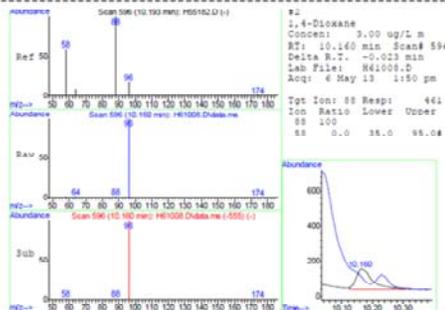
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$$\text{Concentration 1,4D} = \frac{\text{1,4D Area} * \text{True Concentration 1,4-dioxane-d8}}{\text{Area 1,4-dioxane-d8} * \text{Response Factor}}$$

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# 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
Method Calibration Compounds						
3) 1,4-DIOXANE-D8	10.033	96	959711	8777.13	ug/L	-0.10
Spiked Amount	10.000	Range	40	1000	Recovery	= 87771.305%
Target Compounds						
2) 1,4-Dioxane	10.160	88	441m	3.00	ug/L	Qvalue



	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

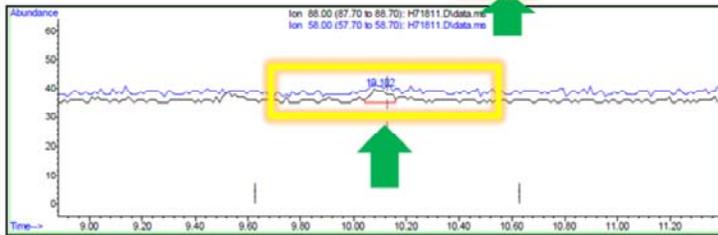
**8260/SIM not as reliable when elevated levels of chlorinated VOCs present.**

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

Compound	R.T.	QIon	Response	Conc	Units	Dev(Min)
<b>Internal Standards</b>						
1) 4-bromofluorobenzene	14.085	174	1202	1.00	ug/L	0.00
<b>System Monitoring Compounds</b>						
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%
<b>Target Compounds</b>						
2) 1,4-Dioxane	10.102	88	22m	0.31	ug/L	Qvalue

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

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

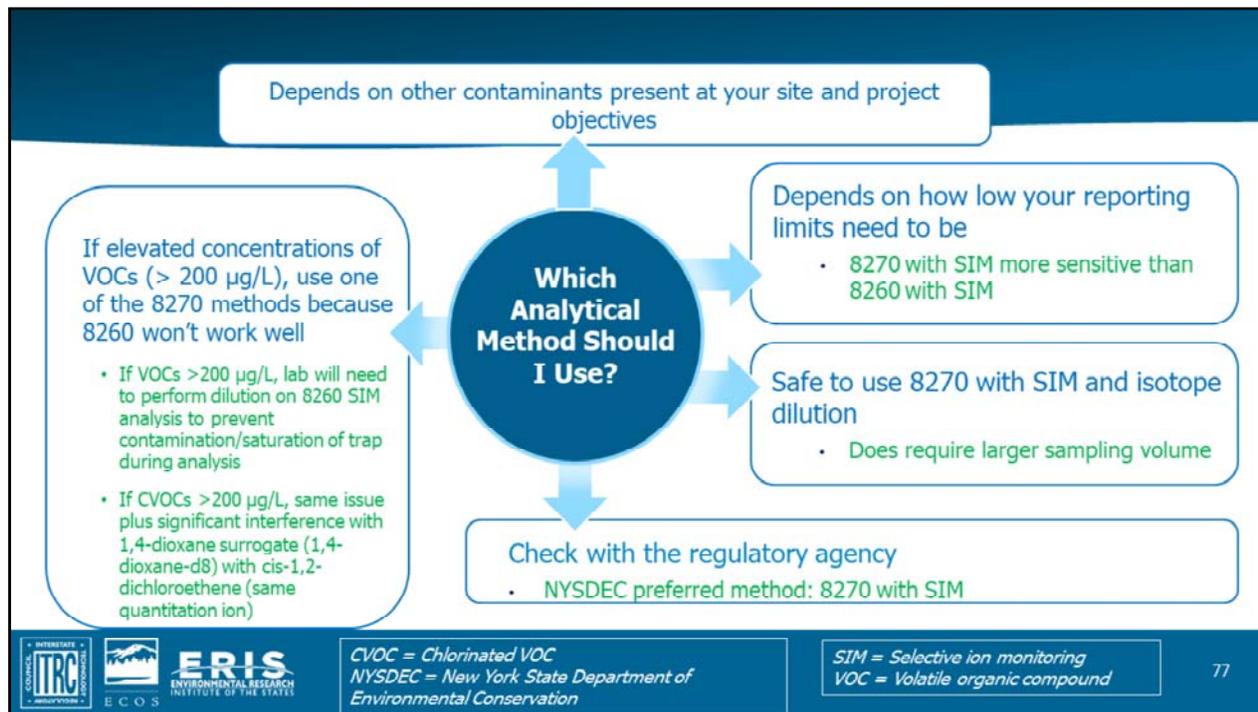


**8260/SIM not as reliable at RLs below 5 µg/L due to extremely poor response (area counts) at lower concentrations**

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

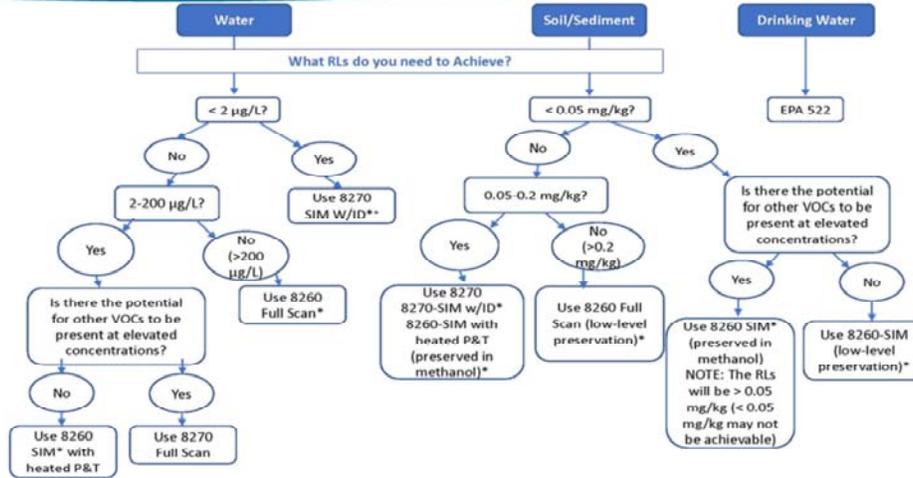



SIM = Selective ion monitoring
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Is there any way to present this graphically using some kind of Smart Art?

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



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jkanderson@gsienv.com



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

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We will discuss toxicity and risk assessment of 1,4-Dioxane during Module 5.

**Dr. Janet Anderson** will be the trainer for this module. Janet is a Principal Toxicologist with GSI Environmental Inc. with 15 years of experience providing toxicology and risk management strategies to federal agencies, private industry, and municipal clients. She also covers Module 2 for this training series.

\*\*\*\*\*

**Dr. Janet Anderson** is a Principal Toxicologist with GSI Environmental Inc. with 15 years of experience providing toxicology and risk management strategies to federal agencies, private industry, and municipal clients. She also provides litigation consulting and expert services and is a Diplomate of the American Board of Toxicology. Dr. Anderson specializes in communicating the key findings from toxicology studies used to inform state and federal regulatory policy and public health decisions, and helping stakeholders understand the sometimes-disparate interpretations. She is a recognized leader in unregulated and emerging chemicals, such as per- and polyfluoroalkyl substances (PFAS), 1,4-dioxane, and 1,2,3-trichloropropane. She has developed strategies to mitigate human health risks and address environmental liability associated with unregulated and emerging chemicals for both private and public sector clients. She has extensive experience developing risk communication and risk management strategies for multi-stakeholder groups. Dr. Anderson received her Ph.D. in Molecular and Cancer Biology from the University of Cincinnati, completed a post-doctoral fellowship with the U.S. Environmental Protection Agency, and as a civilian government employee, led the U.S. Air Forces Emerging Contaminants program and advised the Department of Defense on matters related to toxicology and environmental restoration. A skilled communicator, Dr. Anderson is often an invited speaker and panelist at high-level scientific conferences, regulatory and industry meetings, law seminars, technical webinars and workshops, and community stakeholder meetings.

## 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

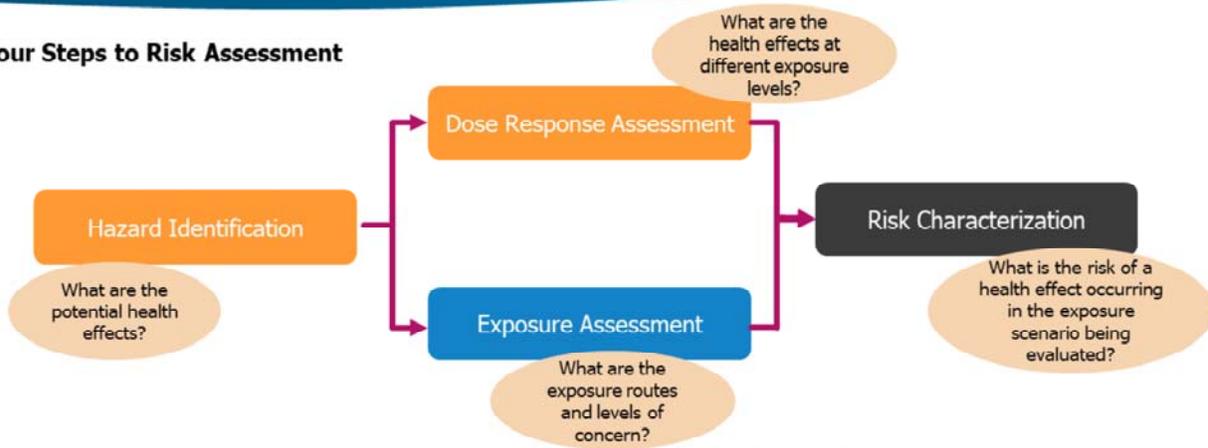


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Start with human health



## Four Steps to Risk Assessment



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



There are four general steps used for HHRA.

The toxicology component consists of the HI – figuring out what the potential health effects might be anticipated following human exposure; and the DR – at what levels do those different health effects occur. Combined with an exposure assessment, which is either default generic exposure assumptions or is a site-specific analysis of what exposure routes and levels of concern might be for a given site. Combining those aspects together results in the risk characterization, which helps the risk assessor understand what the risk is of a given health effect under the exposure scenario in question.

This next portion of slides will present information for 1,4-DX along these steps.

# Human Health – Hazard ID and Dose Response



Starting with potential health effects and how those are assessment across a range of doses.

# 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)

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IARC = International Agency for Research on Cancer

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Those designations are based on rodent tumors seen following chronic high dose exposure – tumors developed in the liver, kidney, nasal cavity, etc.

Generally, all experts agree that cancer risk is the risk driver and concern for human health

However, importantly, experts currently have different opinions on how exactly 1,4-DX may cause cancer. There is pretty significant controversy over what is called the 1,4-dx carcinogenic mode of action. Here, we will quickly summarize the opposing opinions offered by USEPA and Health Canada

## 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)

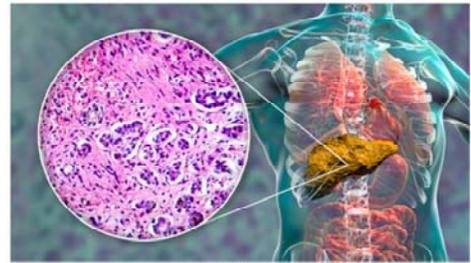


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Generally, all experts agree that cancer risk is the risk driver and concern for human health

However, importantly, experts currently have different opinions on how exactly 1,4-DX may cause cancer. There is pretty significant controversy over what is called the 1,4-dx carcinogenic mode of action. Here, we will quickly summarize the opposing opinions offered by USEPA and Health Canada

# USEPA = MOA is Unknown



## ▶ 2 USEPA Assessments

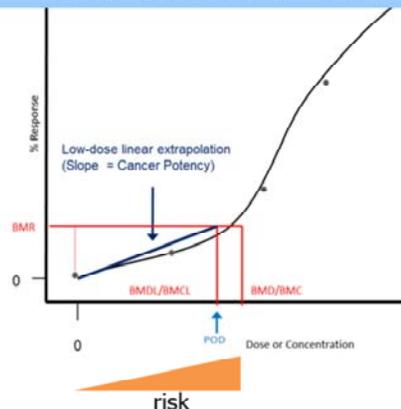
- ▶ 2013 Integrated Risk Information System (IRIS)
- ▶ 2020 Toxic Substances Control Act (TSCA)

## ▶ 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<sup>-6</sup> to 10<sup>-4</sup> cancer risk



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See Section 5.2 of ITRC Guidance Document for more detailed information

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USEPA’s decision regarding how 1,4-dioxane causes cancer is documented in the final IRIS assessment and in the recently finalized TSCA risk evaluation.

According to their interpretation of the data, the available evidence is “inadequate to established a mode of action” for how 1,4DX causes cancer.

When a MOA is not established, EPA’s policy is to use what is called low-dose linear extrapolation of the data, which means that any increase in exposure above zero increases cancer risk.

This results in drinking water threshold values that can represent different risk ranges, for example, the DW threshold of 0.35 to 35 ppb used by the office of water representing the 10<sup>-6</sup> and 10<sup>-4</sup> cancer risk level.

# Health Canada = MOA is Non-Genotoxic and Threshold



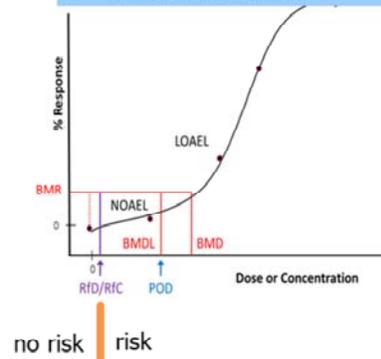
## Health Canada 2018 Mode of Action conclusions

"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  $50 \mu\text{g/L}$   
no concern if exposure is below threshold



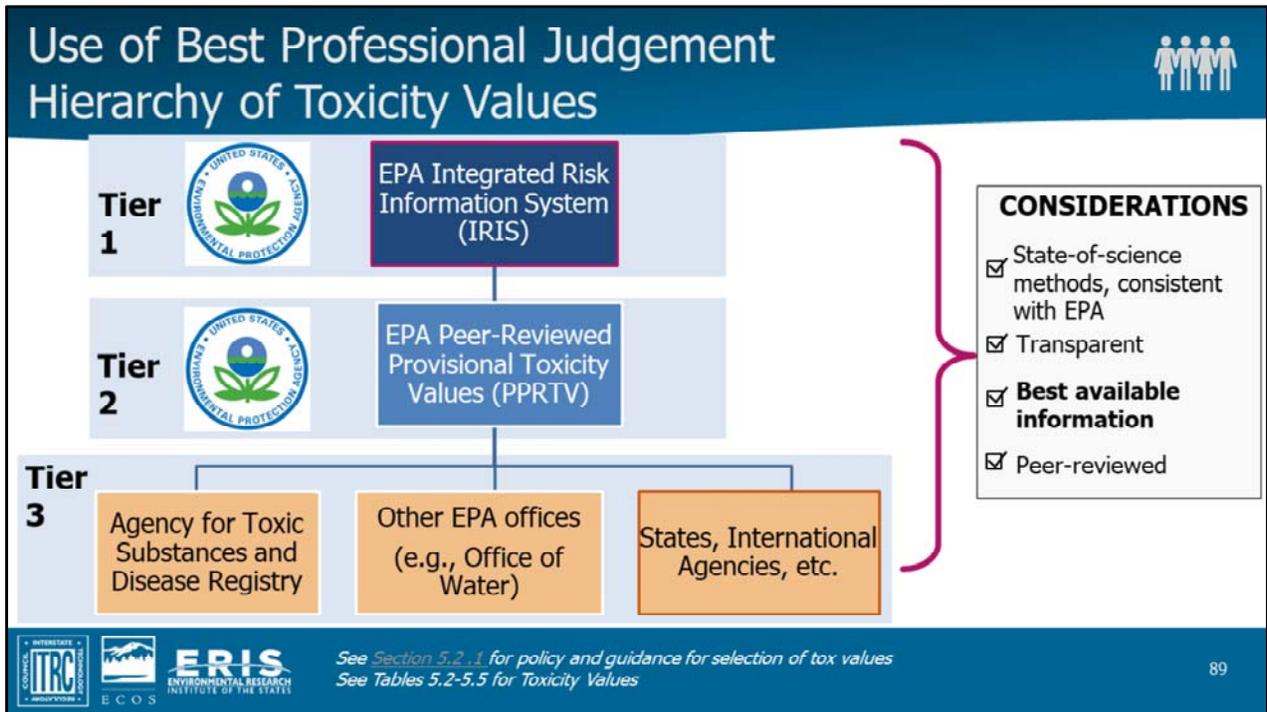
See Section 5.2 of ITRC Guidance Document for more detailed information

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In contrast, however, health Canada and several other international authorities have determined that data support a non-genotoxic mode of action, meaning that 1,4-dioxane causes cancer through uncontrolled cellular proliferation, only after an internal dose threshold is reached.

In other words, under this model, there are low doses of 1,4-DX exposure to which our bodies can respond through metabolism and then cellular repair, and it is only when that threshold exposure is exceeded, is there an increased risk in cancer.

This results in a single threshold value, set by Health Canada and other agencies at 50 µg/L or 50 ppb; so if exposures are lower than that, there is negligible risk.



Why is it important to understand the differences in opinion? Because it results in different toxicity criteria and depending on the regulatory and legal framework for your site, you may be in a situation where best professional judgement can be used to select toxicity criteria for a chemical.

Under the EPA superfund program and many state policies, risk assessors can choose from a hierarchy of toxicity values, with USEPA IRIS toxicity values being the preferred source, and state and international agencies being the third-tier choice. However, importantly, it is well recognized that EPA IRIS values may not exist or may not be based on the most recent science, and within EPA’s policy and guidance is the requirement to use the most current science information, as long as it is based on methods consistent with EPA and has been peer-reviewed.

Importantly, whatever toxicity criteria is selected for your situation should be based on your site’s requirements and best and most current information.

## 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



The choice of toxicity criteria for 1,4-DX can have a significant impact on the screening or risk level.

Risk assessors need to be aware of this ongoing debate and on-going research. New information from academic, industry, regulatory agencies, need to be evaluated if possible.

For example, in just the last few months, new scientific studies in rodents have come out on this topic.

Best professional judgement and well-supported decisions are important.



## 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



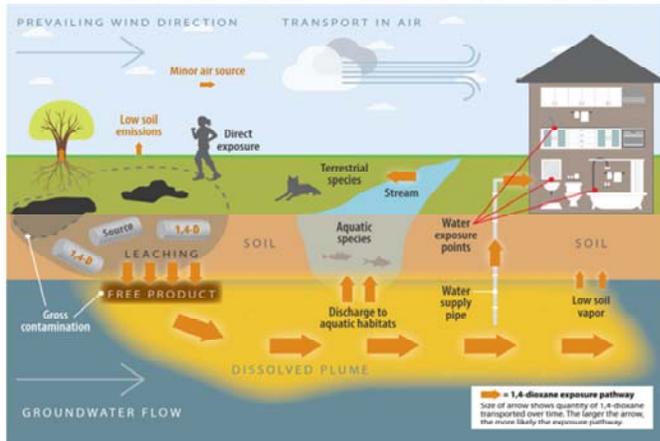
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E C O S

Exposure assessment for human health will be site specific

We estimate exposure to define the relevant pathways, magnitude, frequency and duration of exposure and help estimate the intake dose of 1,4-DX for each exposure route.

# Human Health – Exposure Routes



- ▶ 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

ITRC Guidance Document Figure 5.1



See [Table 5.1](#) Examples of Potential Human Exposure Routes, ITRC Guidance Document

For 1,4-DX drinking water ingestion will most likely be the primary pathway of concern.

As discussed in the fate and transport section, 1,4-DX is not likely to remain in the surface soil and not likely to volatilize.

## 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

When we combine the exposure information with toxicity information together, the risk characterization step will then help provide context for risk management decisions.

For risk managers, it will be critical that the uncertainty, including toxicity criteria and exposure assumptions, is well described.

As discussed, the cancer mode of action determination has a significant quantitative impact on risk, and therefore needs to be carefully and thoroughly justified.

# Ecological



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Moving to eco...

## 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



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See [Section 5.3 ITRC Guidance Document](#) for more information

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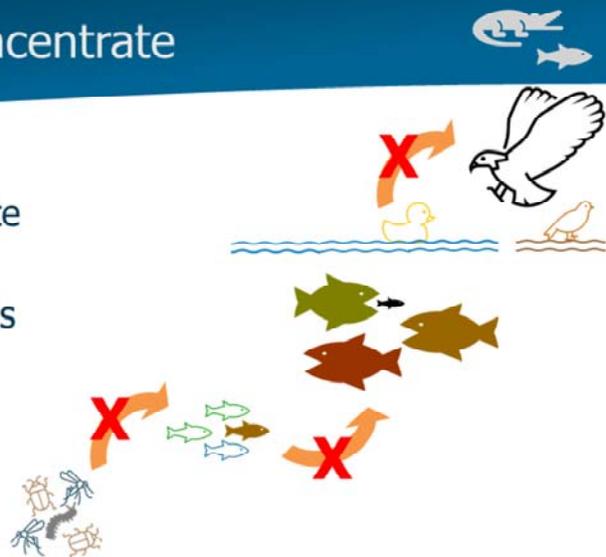
1,4-DX is not typically considered to be much of a concern for ecological risk

Fish are the most sensitive receptors, and for mammals that may be exposed via drinking water, we only see effects at the very high levels – in the 100s to 1000s mg/L

As mentioned in the fate and transport section, 1,4-DX can be taken up by plants, but generally is not toxic to plants at all.

## 1,4-Dioxane Does Not Bioconcentrate

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



Importantly, 1,4-DX does not bioaccumulate or bioconcentration, therefore, trophic level transfer and biomagnification is not a concern.

# 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



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See [Table 5.6 Ecological Screening Levels ITRC Guidance Document](#) for more information

Shown here are a few ecological screening values that have been derived for 1,4-DX. As you can see, no effect levels are in the ppb range. More information can be found in Section 5

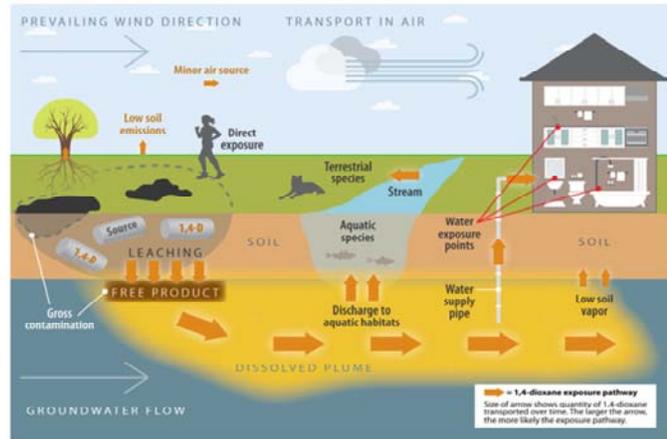
# Ecological Exposure Assessment



## 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



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See [Section 5.3](#) ITRC Guidance Document for more information

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Similar to human health, the primary concern for ecological receptors will be direct contact and ingestion of impacted water.

# 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

Generally, what we have seen thus far is that a screening level ecological risk assessment to just confirm that your concentrations are below screening levels will be sufficient at most sites.

# 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/>



Last, we wanted to reference ITRC’s risk communication tool kit. This tool kit can be very helpful for emerging contaminants and contaminants with different regulatory criteria and evolving science. The tool kit is available at the link shown here and if you are interested, there will be separate training sessions on risk communication available through ITRC, as well.

# 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

### MOA

- ▶ Cancer risk is the primary concern for human health and long-term exposures



- ▶ 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



To summarize:

- Ecotoxicity of 1,4-DX is low and will not likely require anything more than a SLERA
- Cancer risk is the primary concern for human health
- However, science is still evolving and there is controversy regarding exactly how 1,4-DX causes cancer, which has a significant quantitative impact on human health risk assessment
- Therefore, selected toxicity criteria should be consistent with your site's requirements and regulatory and legal frameworks, and need to be well-justified
- As with all chemicals, all uncertainties and limitations in the risk assessment needs to be transparent and fully communicated.

## Module 6: Remediation & Treatment Technologies



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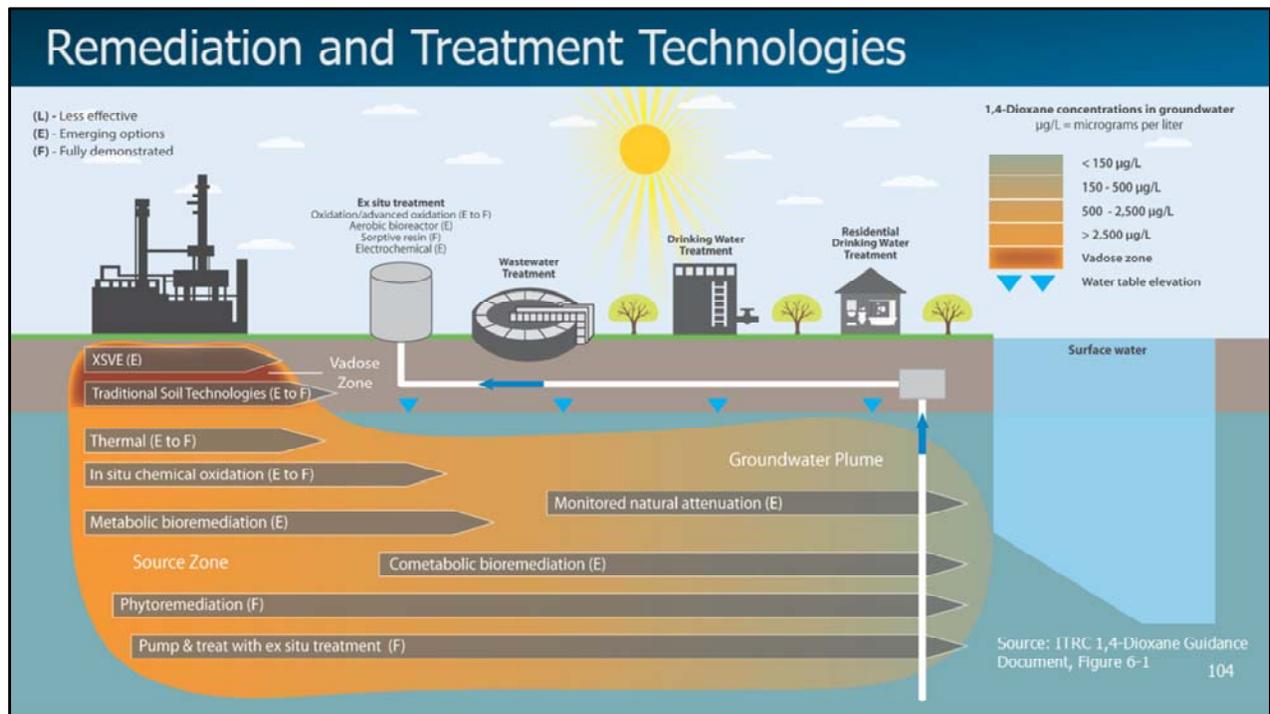
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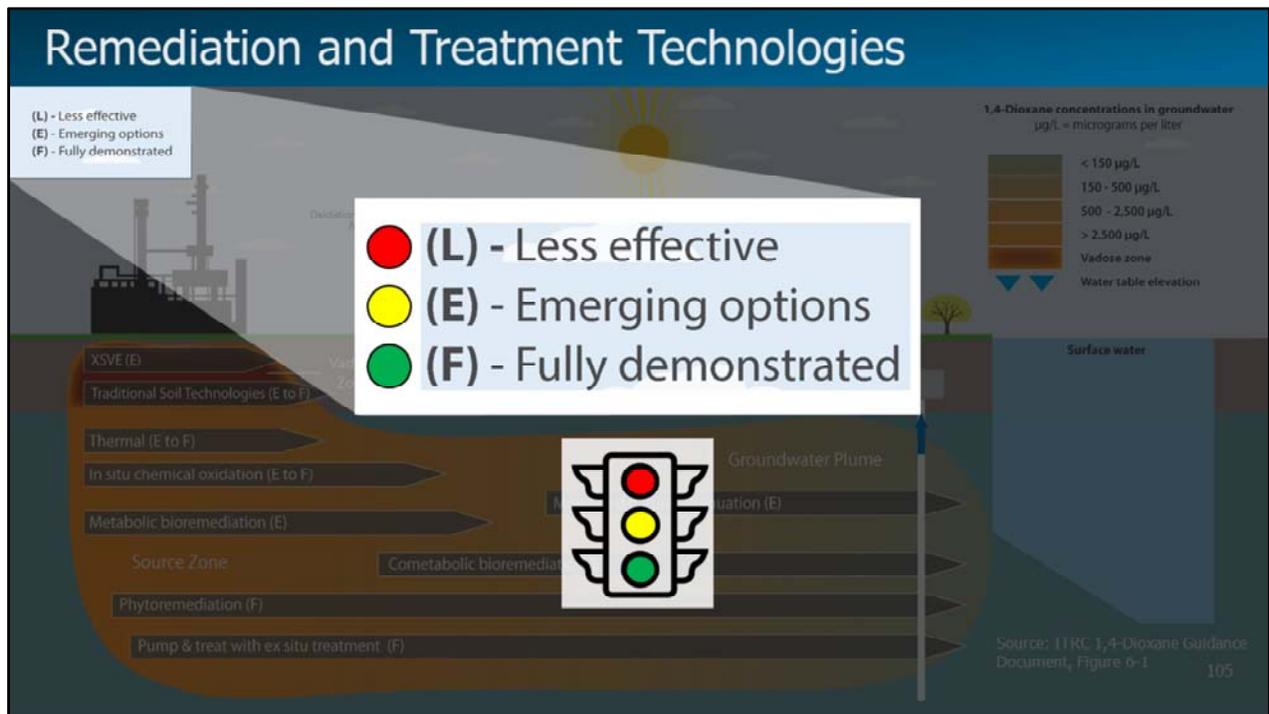
## Learning Objectives

- ▶ 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

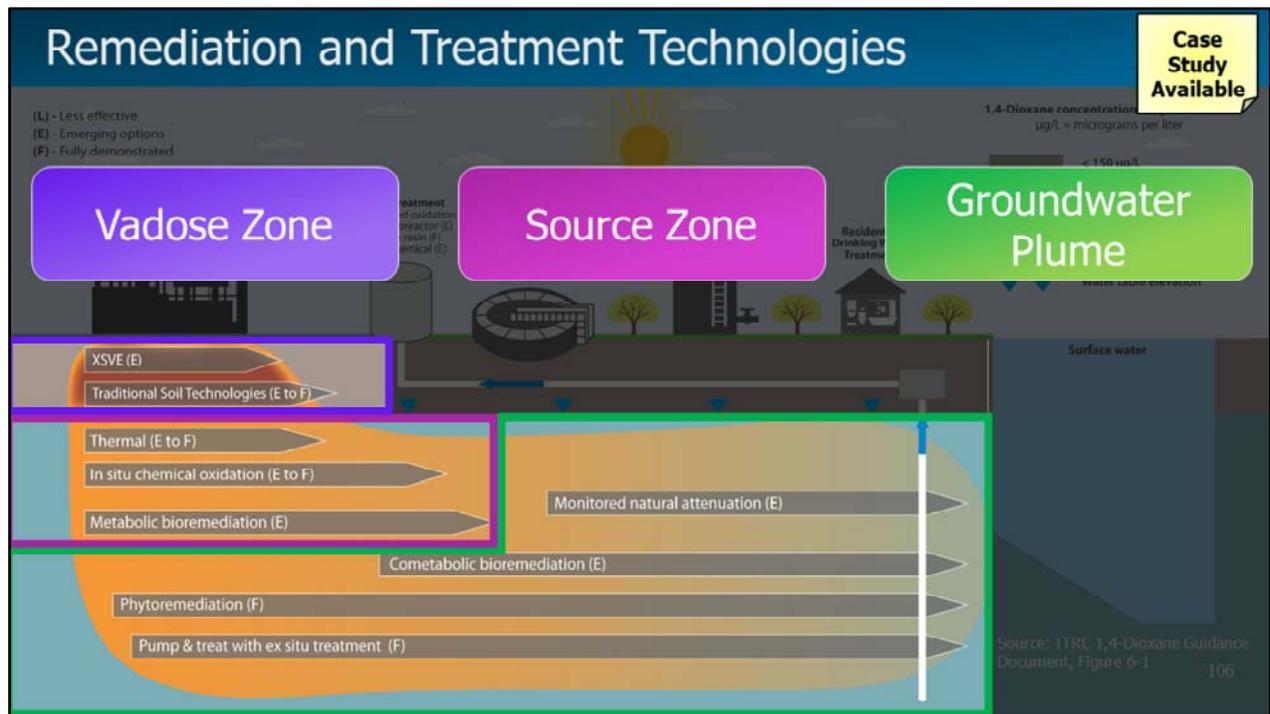
30 sec: Thank you. Let's start by looking at our learning objectives, these include...



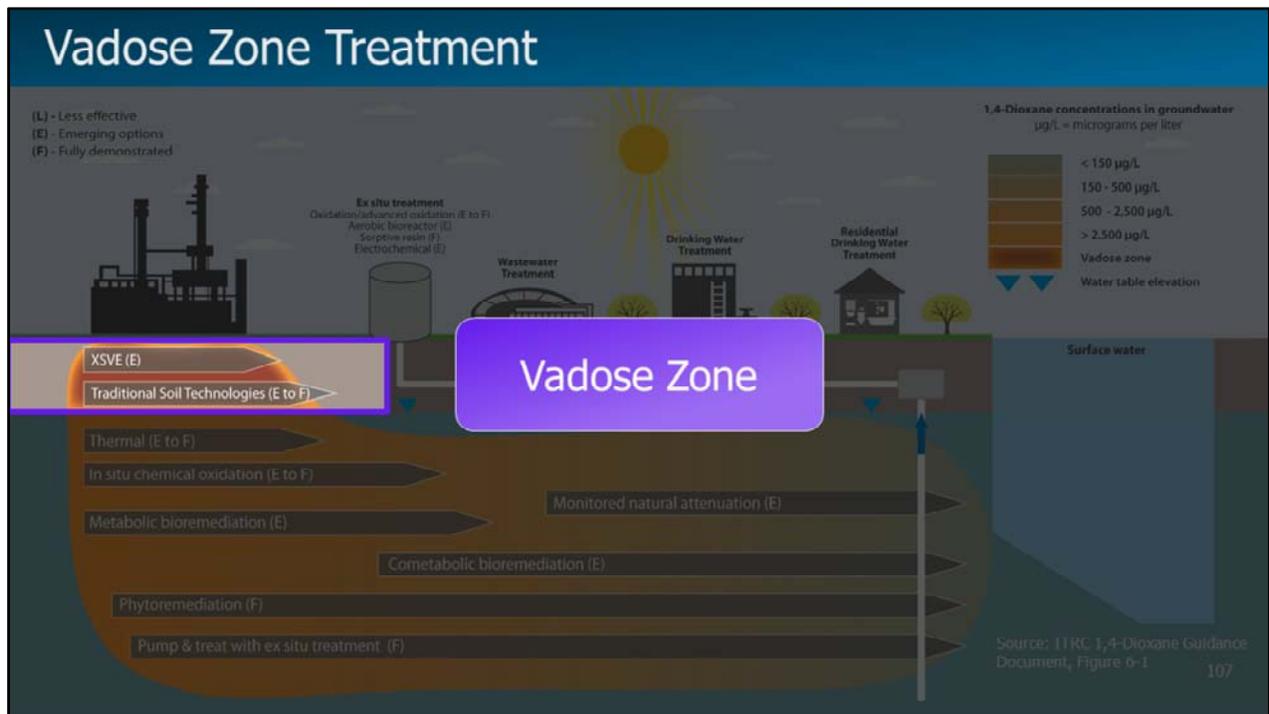
30 sec: We wanted to introduce this figure, which you'll see over and over again today. It's also a central part of the guidance document. You'll see that we have a 1,4-dioxane groundwater plume in orange with several in situ treatment technologies listed down there. We also have some ex situ treatment technologies listed alongside wastewater treatment and drinking water treatment. We'll touch on all of these today.



45 sec: Today we're using a red/yellow/green stoplight motif to help illustrate how we've categorized these technologies. Less effective technologies are those with negligible or limited capacity for 1,4-dioxane removal, either by demonstration or theoretical considerations. Emerging options may be partially demonstrated or researched. They may include technologies that have been implemented at the bench- or pilot-scale. Fully demonstrated technologies are those that have been implemented or demonstrated under full-scale situations. These typically include effective treatment technologies that are well documented. We'll focus on the fully demonstrated and emerging options, but will touch on some of the less effective technologies that could be potential pitfalls when 1,4-dioxane is present with CVOCs. You'll see this stoplight throughout the slides so you can quickly identify what category a technology falls into.



45 sec: We've also broken down the technologies down by where they may be best applied within the subsurface. The purple box shows the vadose zone that includes various soil and soil vapor treatment technologies. In the groundwater plume, we have the source zone in pink with higher concentrations of 1,4-dioxane. Then we show the downgradient groundwater plume in green. Note that each of these technologies can have application in different subsurface areas...this graphic isn't meant to be limiting. As we talk through the treatment technologies shown here, we'll briefly describe the technology, discuss how it applies to 1,4-dioxane, and identify special design considerations. We'll keep things at a high level for today, but the guidance document gets into more details. One last thing, the little post it note you see on the right of the slides today will help identify when we have a case study about a particular technology in the guidance document.



30 sec: We'll start with the vadose zone and soil or soil vapor treatment technologies. As you heard in the F&T training, we've seen that there are a limited number of instances where soil or soil vapor treatment is needed for 1,4-dioxane. Typically, the 1,4-dioxane will quickly be transported into groundwater, where it likes to remain. However, in instances where 1,4-dioxane was used directly or stored at a site, it's possible that it may remain in the vadose zone. Also, sites located in arid environments might have residual 1,4-dioxane in soil. This would be because there's not much precipitation to transport the 1,4-dioxane down to the groundwater, or because the groundwater may be very deep below ground surface.

# Vadose Zone Treatment



## Fully Demonstrated

- Excavation
- Thermal Desorption
- Solidification/  
Stabilization

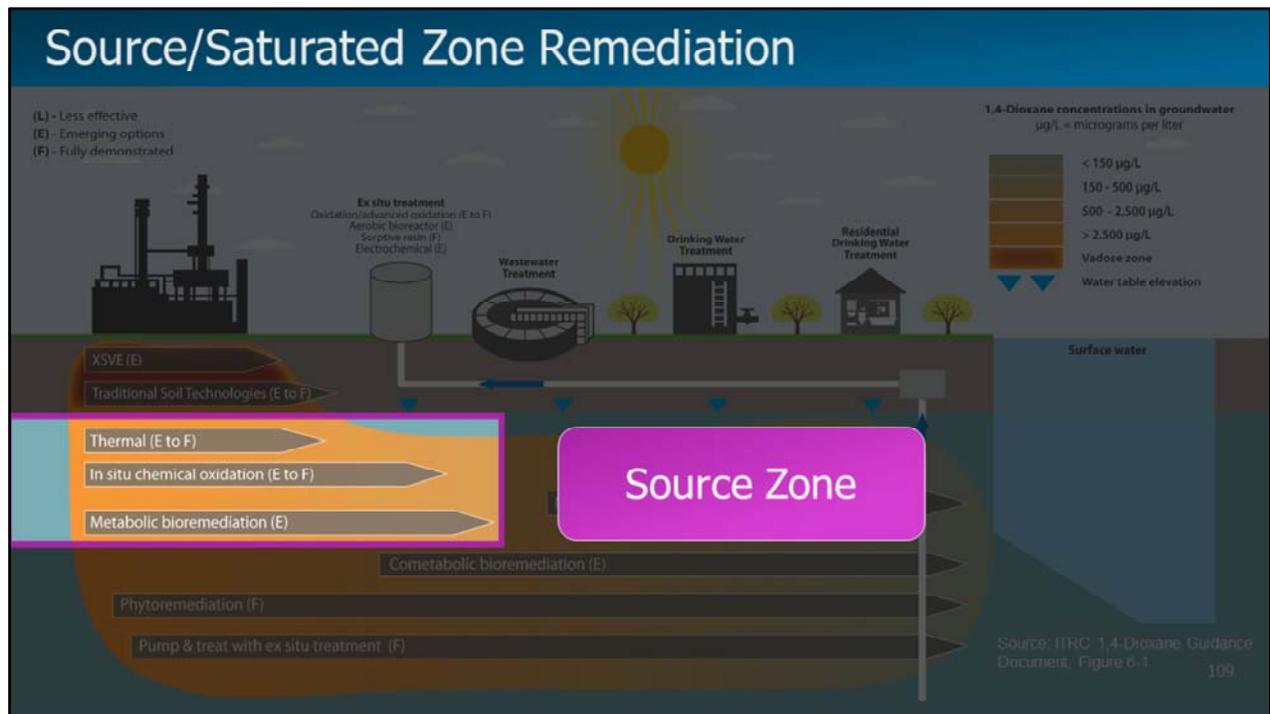
## Emerging Options

- Oxidant Soil Blending
- Extreme Soil Vapor  
Extraction

## Less Effective

- Conventional Soil Vapor  
Extraction
- Bioventing
- Bio-piles

30 sec: The vadose zone has fully demonstrated, emerging, and less effective treatment technologies. Note that many of the fully demonstrated traditional soil technologies listed here are standardized, regardless of whether it's 1,4-dioxane being removed, or another compound. These include excavation, thermal desorption, solidification, and stabilization. Both oxidant soil blending and extreme SVE are approaches identified as emerging options. Extreme SVE differs from conventional SVE in that it typically includes heating of the subsurface or higher pore volume exchange rates. There are a few less effective treatment technologies to mention here, including traditional SVE, bioventing, and biopiles. These aren't particularly effective due to the physical and chemical characteristics of 1,4-dioxane, as well as some of the limitations of most indigenous microorganisms.



30 sec: Now we switch gears into groundwater treatment. First we'll start in the source zone and talk about treatment technologies that can be applied there. Just a reminder that these technologies can also be applied in the downgradient portion of the plume; they aren't meant to be limited to source zone treatment only.

# 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)



1 min: In situ thermal treatment can be used for 1,4-dioxane, and may be particularly helpful when it's present in a chlorinated solvent source area. The boiling point of 1,4-dioxane is higher than the chlorinated solvents, and it doesn't volatilize as well at ambient temperatures. However, heating the subsurface can help increase 1,4-dioxane volatility and if heated enough, it will boil off. Different types of thermal treatment can be applied, including electrical resistive heating, thermal conductive heating, and steam enhanced extraction. Each of these have their benefits and challenges. The biggest benefit of thermal treatment is that a large amount of mass can be removed over a short period of time; that's why we're highlighting it for source area treatment.

# 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 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 solid: months to years	✓	✓	-	✓	✓

Chemical Species	Standard Oxidation Potential
Hydroxyl radical (OH•)	2.8
Sulfate radical (SO <sub>4</sub> •-)	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 <sup>•-</sup> )	-2.4

Source: Siegrist et al. 2001

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3 min: In situ chemical oxidation is another technology commonly considered for source area treatment. Different oxidants have varying strengths, as you can see from the list of standard oxidation potentials on the right-hand side. The larger table breaks down the common oxidants used to treat 1,4-dioxane, what their physical state typically is, how long they last in the subsurface, and their ability to be delivered to the subsurface via various methods. We've also tried to help identify which chemical species play a role in treatment for each chemical reagent using those very colorful shapes you see. Persulfate is a commonly used chemical oxidant for 1,4-dioxane treatment. It can be procured as a liquid sodium persulfate solution or as solid potassium persulfate. Persulfate requires an activation step to generate the most powerful reactive species, and the activator chosen will dictate what reactive species are generated. Common activators include heat, hydrogen peroxide, alkaline solution like NaOH, and various forms of iron. Depending on how it's being activated, persulfate can be delivered to the subsurface via direct push methods, permanent injection wells, a slurry injection, or slow-release cylinders. Once there, persulfate can remain active in the subsurface on the order of weeks to months. If we hop down to the bottom of the table, we see that using various forms of permanganate can be delivered to the subsurface in a similar manner and can also remain reactive for months. Moving up a row...Modified Fenton's reagent is a liquid injection that has a faster reaction timeframe than persulfate or permanganate. And lastly...Use of gas-phase oxidants, like ozone or perOXone also have shorter reaction timeframes, as well as different injection strategies since gas distribution is a key component.

Persulfate - The free radicals that are formed depend on the activation mechanism that is used, and can, include the sulfate radical (SO<sub>4</sub>•<sup>-</sup>, an oxidizing radical), the hydroxyl radical (OH•, an oxidizing radical), and in the case of alkaline-activated persulfate, the superoxide ion (O<sup>•-</sup>).

## ISCO and 1,4-Dioxane



Case  
Study  
Available

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

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

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

1min: One of the reasons why persulfate is used quite frequently for 1,4-dioxane treatment is because it can generate some very reactive species, like the hydroxyl radical as well as active sulfate radicals, both of which can react with 1,4-dioxane. Likewise, persulfate, as well as many of the other oxidants on the prior slide, can also degrade chlorinated ethenes and ethanes. Sometimes it's important to get the right oxidant dosing and activation method to get at those chlorinated ethanes. A lot of people start with bench testing for this reason. And just reminder that while ISCO is commonly chosen as a source area treatment, it can be applied further downgradient, perhaps in something like a permeable reactive barrier.

## ISCO – Other Considerations



Case Study Available

### Design Considerations

- Optimizing contact (longevity, permeability, etc.)
- Matrix diffusion

### Water Quality Issues

- Reagent scavengers/matrix demand
- Temporary metals mobilization
- Bench testing recommended

### Byproducts

- Bromate formation (ozone/H<sub>2</sub>O<sub>2</sub>)
- Sulfate
- Gases: CO<sub>2</sub>, O<sub>2</sub>
- Ions (K<sup>+</sup>, Na<sup>+</sup>)
- pH change

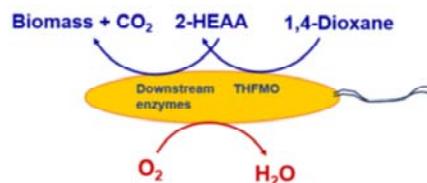
1 min: A few other things to consider with ISCO...it has been described as a contact sport. In order for it to work, the oxidant needs to come in contact with the contaminant. Depending on the subsurface conditions, you may want to choose an oxidant that will stick around for months, rather than weeks, and a delivery method that will get it where it needs to be in the subsurface. It's also important to understand the likelihood of the aquifer to back diffuse contaminants into groundwater after the oxidant has worn off. The natural water quality is also important to understand for ISCO. Natural organic matter in the subsurface can scavenge the oxidant, meaning that higher dosing than originally calculated may be needed. Delivery of oxidant into the subsurface will temporarily change the redox conditions, which can lead to metals mobilization. The type of oxidant used, and the inherent subsurface conditions mean that various byproducts could form, some of which are regulated themselves. These are just more reasons to conduct bench testing prior to field application. And before we get off this topic, I do want to point out that we have an ISCO case study in the guidance document, as you can see from that sticky note.

## In Situ Metabolic Bioremediation



- ▶ 1,4-Dioxane used as carbon and energy source by bacteria
- ▶ End products are biomass and carbon dioxide (CO<sub>2</sub>)
  - ▶ Lower biomass yield and rates than other metabolic processes (TCE/hydrocarbons)
  - ▶ Suitable for higher 1,4-dioxane concentrations
  - ▶ Requires oxygen to be present

Check out the Fate & Transport Training, too



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

1 min: In situ metabolic bioremediation can also be a useful tool in the toolbox, particularly for source area treatment. Typically, when we think of bioremediation, we're thinking about metabolic bioremediation. If we think about petroleum hydrocarbons for a second, those microorganisms use the hydrocarbons and oxygen to generate energy and new biomass. It's the same for 1,4-dioxane. There are a handful of microbes we know to date that will utilize 1,4-dioxane and oxygen to generate energy and new biomass while leaving only carbon dioxide behind. Based on our current understanding of the microbes able to metabolize 1,4-dioxane, they prefer to do this when high concentrations of 1,4-dioxane are present. That's why this approach may be of interest for source area remediation.

# In Situ Metabolic Bioremediation



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

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

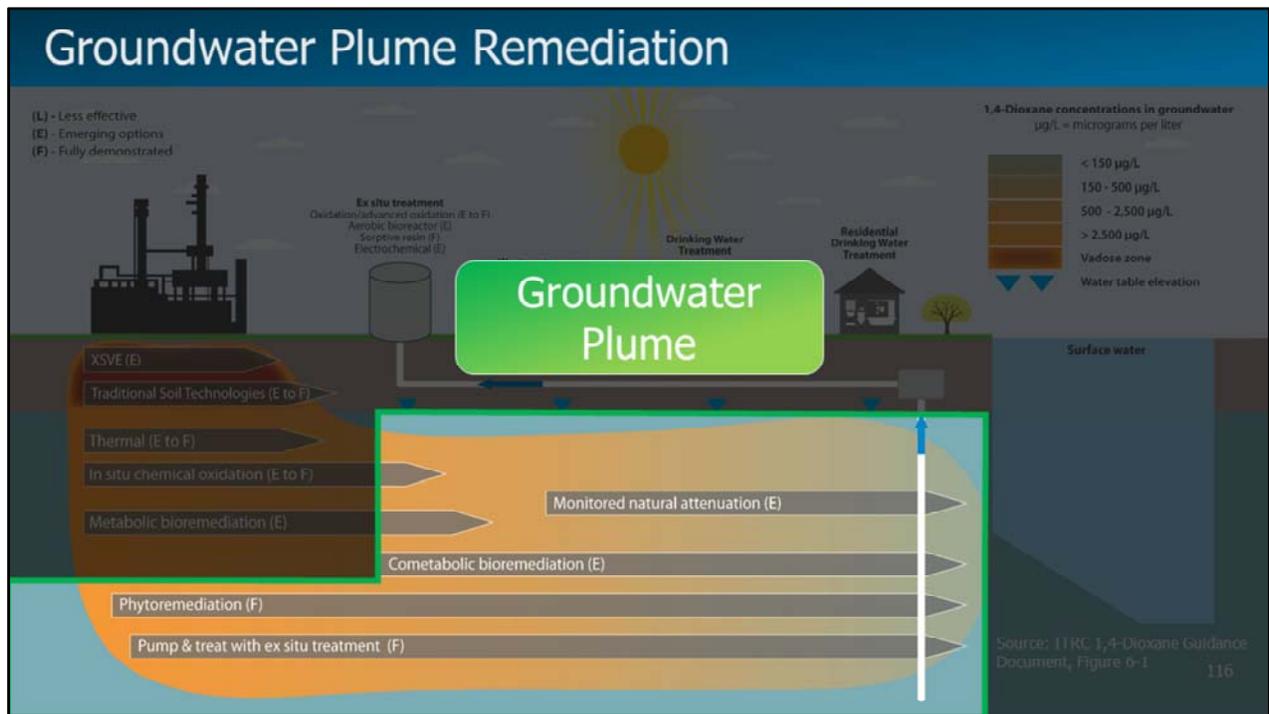


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1 min: Because 1,4-dioxane metabolizers prefer higher starting concentrations, it's important to understand whether there's enough 1,4-dioxane in the subsurface to support this type of treatment strategy. It may be tougher to implement at downgradient portions of the plume where 1,4-dioxane concentrations decrease. Additionally, oxygen needs to be present. So if it's not available naturally, then the treatment system will need to be engineered to deliver an adequate amount of oxygen into the groundwater. Like I mentioned before, we currently only know of a few types of microorganisms that can degrade 1,4-dioxane metabolically, so bioaugmentation may be necessary if those microbes aren't present in the subsurface already. The last word of caution with this approach is that high concentrations of some chlorinated solvents and some metals can inhibit the microbe's ability to degrade the 1,4-dioxane. TRANSITION TO SECOND SPEAKER.

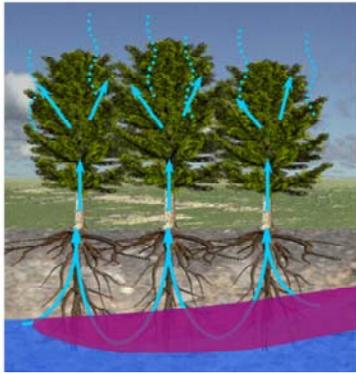


30 sec: Now we move into discussing treatment technologies that are more commonly applied to the downgradient portion of the groundwater plume. These include both in-situ and ex-situ treatment technologies. Just a reminder that these technologies can also be applied in other portions of the plume; they aren't meant to be limited to downgradient treatment only.

# 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

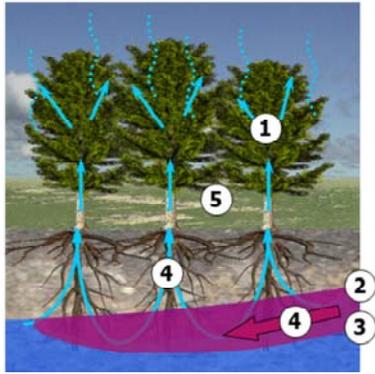
## ▶ Benefits

- ▶ Semi-passive
- ▶ Leverages properties of 1,4-dioxane

## ▶ Challenges

- ▶ Longer timeframe
- ▶ Deep groundwater requires certain design

1 min: With that we transition into some in situ treatment technologies. We start with phytoremediation which is a fully demonstrated treatment technology that we happen to have a case study about in the guidance document. While there are several treatment mechanisms for trees, phyto extraction is the dominant one at play for 1,4-dioxane. This is where the 1,4-dioxane is pulled up through the roots of the trees and transpired into the atmosphere where it can be destroyed via UV rays. Phytoremediation is attractive because it's a relatively hands off remedy, and it benefits from the high solubility of 1,4-dioxane in water. However, phytoremediation can take longer than some other in situ technologies and the presence of deeper groundwater requires special design considerations.



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

1 min: It's important to use the right plants for the region where the site is located. It's best employed when groundwater is less than 25 feet below ground surface and the 1,4-dioxane impacts are within the top 5 feet of groundwater. However, use of engineered phytoremediation systems, like TreeWells, can be used to help reach deeper groundwater. It's important to understand whether the transpiration rate of the trees will be enough to counter the groundwater flux into the treatment area. This may start to dictate the number of trees needed and the potential spacing.

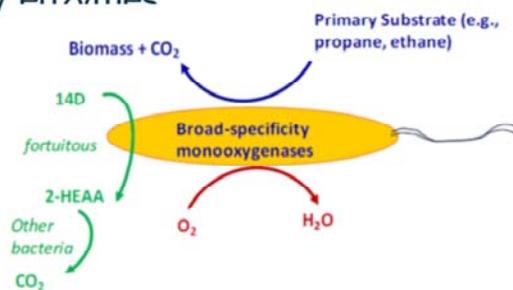
## In Situ Cometabolic Bioremediation



Case Study Available

- ▶ Bacteria uses a primary growth substrate to sustain activity
- ▶ 1,4-Dioxane biodegraded fortuitously by *ANZVMAE* 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

Check out the Fate & Transport Training, too



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



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1 min: We already talked about metabolic bioremediation in the context of source area treatment strategies. Now we'll get into cometabolic bioremediation as a strategy typically employed downgradient. In cometabolic bioremediation, the microorganisms does not gain energy from using the 1,4-dioxane. In fact, it doesn't use the 1,4-dioxane at all. It uses a primary substrate, coupled with oxygen, to generate energy and biomass. There are lots of primary substrates that can be used, including many of the alkane gases, like propane and ethane. Lucky for us, the enzymes that are produced as part of that process can also go on to degrade 1,4-dioxane – ultimately to carbon dioxide. They can also degrade other constituents of concern, like some chlorinated solvents. One nice thing about cometabolic bioremediation is that you don't have a concentration limitation like we talked about for metabolic bioremediation. All you need is to have enough oxygen around, along with the primary substrate, in the same place as the 1,4-dioxane.

# In Situ Cometabolic Bioremediation



Case Study Available

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

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



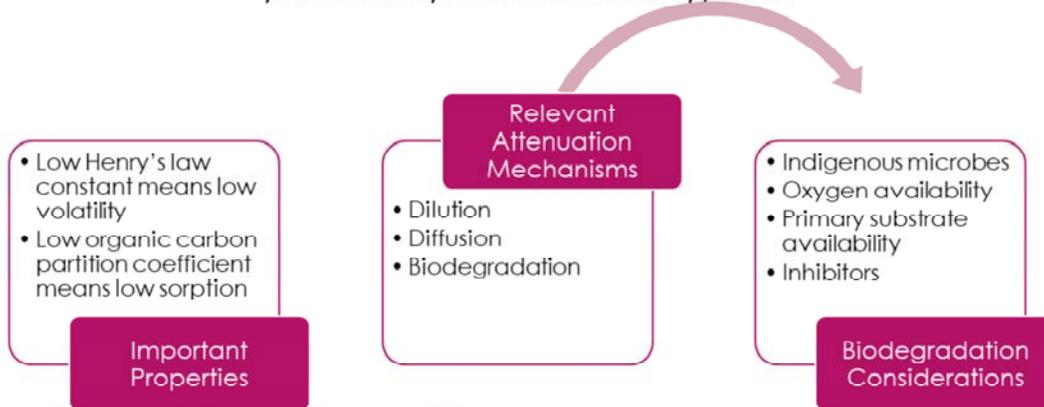
120

1 min: When engineering this type of treatment system there are a few moving parts to consider. For example, enough oxygen and primary substrate need to be delivered to the subsurface, typically through sparging or gas-saturated water. There is a catch 22 where we don't want to give them too much primary substrate, because then the enzymes won't have a chance to go on to degrade the 1,4-dioxane, so it's a bit of a balance. Also, many of these primary substrates are flammable gasses, so delivery systems need to be built with extra controls in place. The right microbes need to be present to do the work, and bioaugmentation may be needed. They also likely need some macronutrients, like nitrogen and phosphorous, so that will need to be delivered into the subsurface. Like I mentioned before, cometabolic biodegradation can work for any starting concentration of 1,4-dioxane and has been shown to decrease concentrations to below 1 ug/L. It can also be used to degrade chlorinated compounds, but there is a warning that high enough concentrations of some chlorinated compounds can actually inhibit biodegradation. We do have a fun case study that tracks this approach from bench-scale testing all the way to full-scale operation.

## 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.*



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1 min: When thinking about the attenuation processes relevant to 1,4-dioxane it's important to remind ourselves that it has a low Henry's law constant and low Koc value. That means that volatilization and sorption to soil may not be the dominant attenuation mechanisms. Really, the relevant attenuation mechanisms for 1,4-dioxane include dilution, diffusion, and biodegradation. We've talked a lot about biodegradation in engineered systems, but now we're talking about natural systems. Luckily, we have both the metabolic and cometabolic pathways available to us. In either case, the right microorganisms need to be present and oxygen needs to be present. If we're evaluating the cometabolic pathway, then a primary substrate also needs to be present. Likewise, we need to make sure there aren't levels of chlorinated solvents or metals present that could inhibit natural biodegradation. These are all the types of things we'll want to look for as part of a natural attenuation evaluation.

## 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.*



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1 min: Luckily, there is a growing arsenal of advanced analytical tools that we can use to evaluate natural attenuation mechanisms. These are similar to the tools we use for evaluating other compounds, like chlorinated solvents, but have been tailored to 1,4-dioxane. First up are the geochemical parameters. These can be used to confirm whether aerobic conditions are present and if primary substrates are present that could foster cometabolic biodegradation. Next we move onto the microbial analyses. These include things like genetic targets designed to evaluate metabolic biodegradation of 1,4-dioxane, as well as targets designed to evaluate cometabolic biodegradation. Last is compound specific isotope analysis. This is an analytical method that can demonstrate evidence of biodegradation, but it has limitations, particularly when lower concentrations of 1,4-dioxane are present. A word of warning, as an industry we are still developing these tools and learning how to best apply them to evaluating natural attenuation of 1,4-dioxane.

## 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 <sup>3</sup> /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 <sub>oc</sub>	Dimensionless	0.54	1.92	1.81	2.18	1.55	1.48
Boiling point	°C	101	80	87	74	57.4	32



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

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30 sec: Before we talk about some of the ex situ treatment technologies that are less effective against 1,4-dioxane, I wanted to remind folks about some of the critical characteristics of 1,4-dioxane. In particular, a reminder that 1,4-dioxane has a low Henry's law constant, so it doesn't volatilize from water very much. Also, it has a low K<sub>oc</sub> value, which means it doesn't readily sorb to carbon.

## Less Effective In Situ Technologies



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



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1min: Similar to the less effective ex-situ treatment technologies we touched on earlier, we wanted to mention some of the less effective in-situ treatment technologies. Again, it's important to note that these technologies may still result in some treatment of 1,4-dioxane, but they aren't expected to meet targets over reasonable timeframes. Similar to before, these technologies are commonly applied to chlorinated solvent plumes, so it's important to understand the limitations for 1,4-dioxane treatment. The low volatility of 1,4-dioxane makes air sparge/SVE approaches less effective. Zero valent iron may have some benefit in treating 1,4-dioxane, but studies conducted to date indicate that the timeframes for this may be longer than desired. We just spent some time talking about aerobic biodegradation of 1,4-dioxane. It's important to note that anaerobic bioremediation strategies have not been shown to have the same success. This is important because things like carbon substrate injection is very common for treatment of chlorinated solvents.

# Ex Situ AOPs and 1,4-Dioxane



Case Study Available

METHOD TO CREATE HYDROXYL RADICALS	EFFECTIVENESS		GROUNDWATER TREATMENT APPROACHES	
	1,4-DIOXANE	CO-CONTAMINANTS	PUMP AND TREAT	DYNAMIC GROUNDWATER RECIRCULATION
		CHLORINATED ETHENES	CHLORINATED ETHANES	
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
*excited 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



3 min: Similar to ISCO being a solid option for 1,4-dioxane treatment in situ, advanced oxidation processes – or AOPs – are a commonly implemented approach for ex situ treatment. Again, similar to ISCO, different oxidants used in AOPs have varying amounts of destructive capability. You’ll notice that most of the AOPs listed on this table utilize ultraviolet light in combination with various oxidants and/or catalysts to generate reactive species. All of these AOPs can effectively destroy 1,4-dioxane and chlorinated ethenes, however, those that use ozone and hydrogen peroxide can also destroy some of the chlorinated ethanes that may also be present. AOPs are typically used in conjunction with pump and treat systems. This can include groundwater extraction and treatment in the very classical sense, or in a more dynamic recirculation approach.

## 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<sub>2</sub>O<sub>2</sub>)
- Gases: CO<sub>2</sub>, O<sub>2</sub>
- Free radicals (ozone/H<sub>2</sub>O<sub>2</sub>)
- pH change

1 min: While some of the considerations for AOPs are similar to ISCO, some are different. AOPs are known for being energy intensive and may require a large use of chemical oxidants. Similar to ISCO, matrix diffusion can play a role in concentration rebound, particularly for more traditional P&T configurations. The characteristics of the influent water are also very important to understand. It may be necessary to include other treatment processes before or after the AOP system to address things like naturally occurring iron or generation of bromate. AOPs can readily scale up or down and can be retrofitted onto existing pump and treat systems if 1,4-dioxane is found to be present after initial design. We have a great case study in the guidance document about how impacted groundwater can lead drinking water providers augmenting existing systems with an AOP to treat 1,4-dioxane.

# 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>

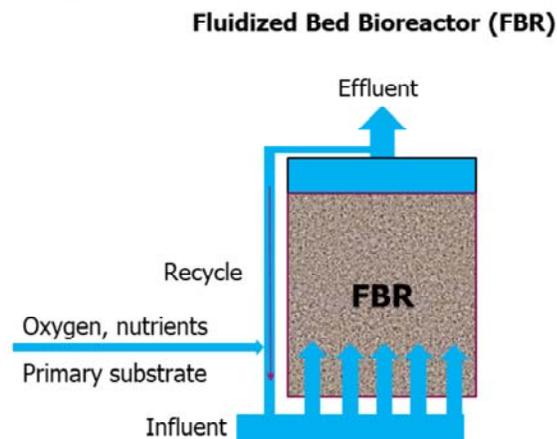
127

1 min: Bioreactors are an emerging option being considered for ex situ treatment. Metabolic bioreactors build off of the same process as we discussed for in situ metabolic bioremediation. They can be useful when 1,4-dioxane concentrations are high and require the presence of oxygen and the right microorganisms. While there have been lab- and pilot-scale demonstrations, our team wasn't aware of full-scale application of this type of approach. However, cometabolic bioreactors have been used at both the lab-scale and full-scale. We'll learn more about cometabolic bioremediation later, but in summary the microbes need another substrate provided in order to grow. The bioreactor treating landfill leachate at the Lowry Landfill is probably the longest running cometabolic bioreactor treating 1,4-dioxane in the presence of tetrahydrofuran.

## 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)



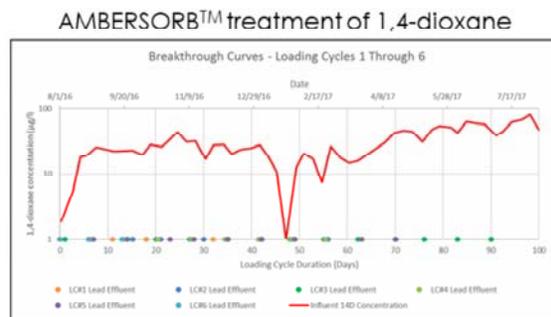
1 min: There are several things to consider when designing a bioreactor system to treat 1,4-dioxane. The concentration of 1,4-dioxane present, the effluent treatment requirements, and the potential presence of co-contaminants may guide the decision of whether to design a metabolic or cometabolic bioreactor. The necessary treatment flow rates and hydraulic retention time may dictate the type of bioreactor configuration chosen. It may be necessary to deliver oxygen, nutrients, or a primary substrate into the bioreactor. Lastly seeding with the right microbial community and establishment and proliferation of that community is key to maintaining the effectiveness of the bioreactor.

## 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



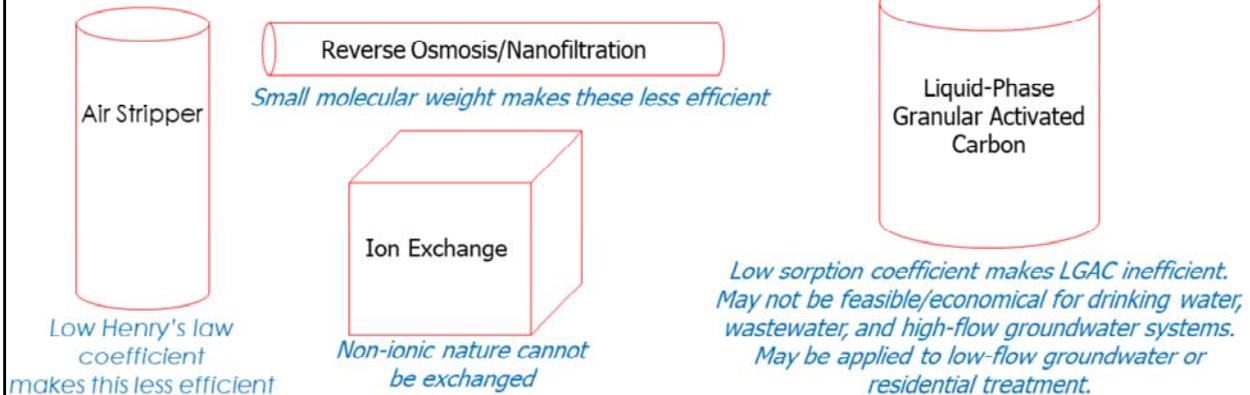
129

1 min: We've already learned that 1,4-dioxane has a low sorption coefficient. This means that under many circumstances, most sorbents are not particularly effective at removing 1,4-dioxane. However, there is a sorptive resin specifically designed to better remove 1,4-dioxane from water. Ambersorb has been applied at full scale, and we have a case study about that in the guidance document. As with any sorbent design, the size of the vessels, the number of vessels, the hydraulic retention time, and the breakthrough monitoring all need to be specifically designed to site conditions. One of the benefits of Ambersorb is that it can be regenerated using steam, however, then the 1,4-dioxane needs to be treated in that waste stream. So, as with other sorbent technologies, you only remove 1,4-dioxane from water, you don't destroy it.

## Less Effective Ex Situ Technologies

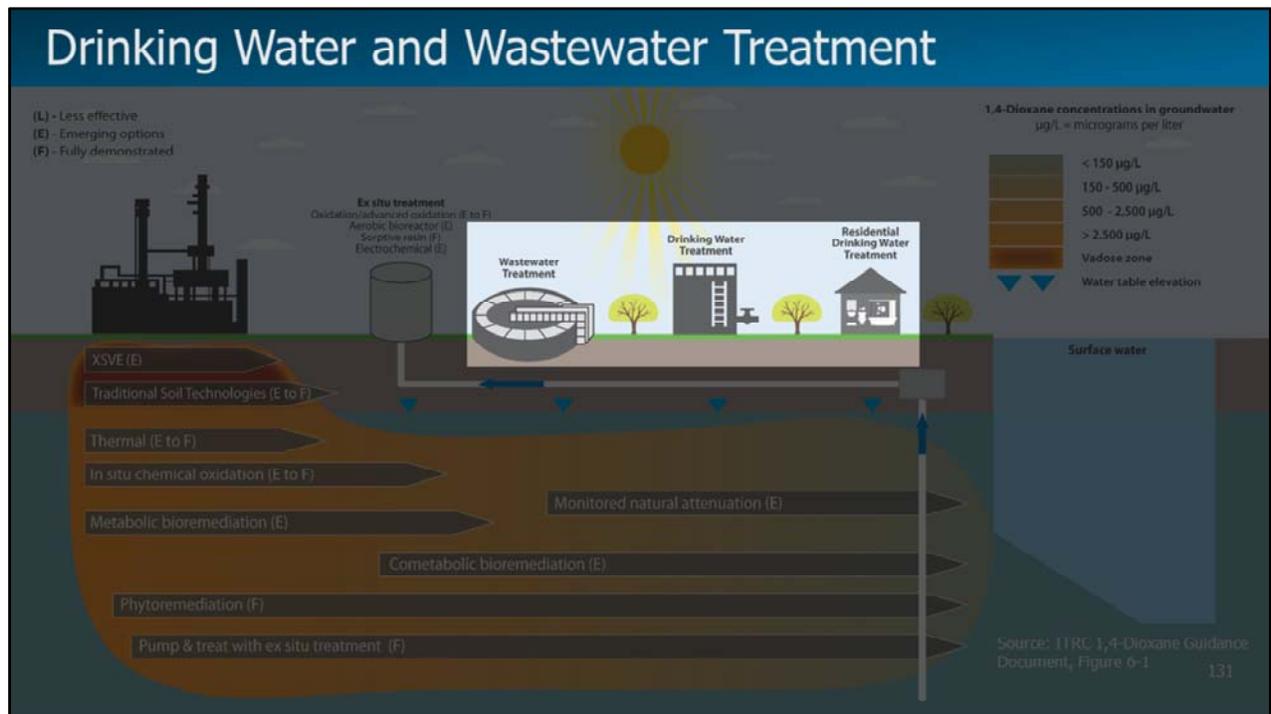


Note that less effective technologies may still impart *some* benefit, but may not reach targets



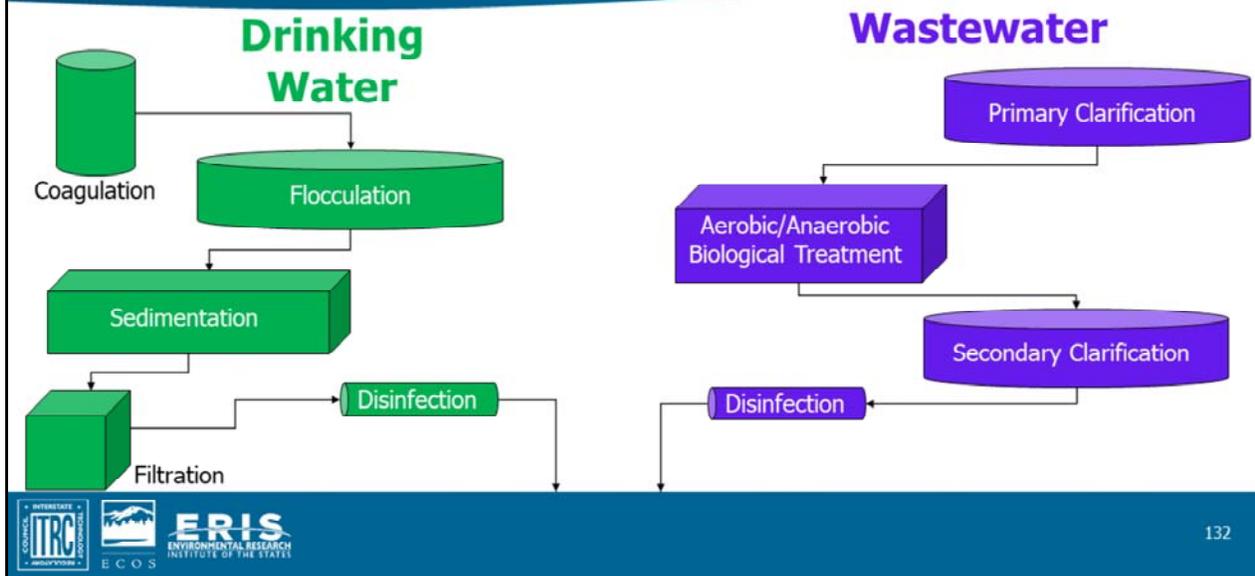
130

1min: With that in mind, we did want to touch on some of the less effective ex-situ treatment technologies. Mostly because these technologies are commonly employed for treatment of other compounds, including the chlorinated solvents that 1,4-dioxane may be co-located with. Note that while these technologies might be less effective at removing 1,4-dioxane from water, there may still be upwards of 50% removal when these technologies are applied. Air stripping is one that is commonly used for removing chlorinated solvents from water but won't remove much 1,4-dioxane at the same time. Ion exchange and reverse osmosis are technologies that haven't shown high 1,4-dioxane removal due to the size and charge of the molecule. Liquid-phase granular activated carbon is another technology commonly used to remove chlorinated solvents from water, but due to 1,4-dioxane's low sorption coefficient, use of LGAC needs to be specifically designed to monitor for 1,4-dioxane breakthrough. It may not be a feasible option at high flow rates, but may have application for residential treatment. – 1min

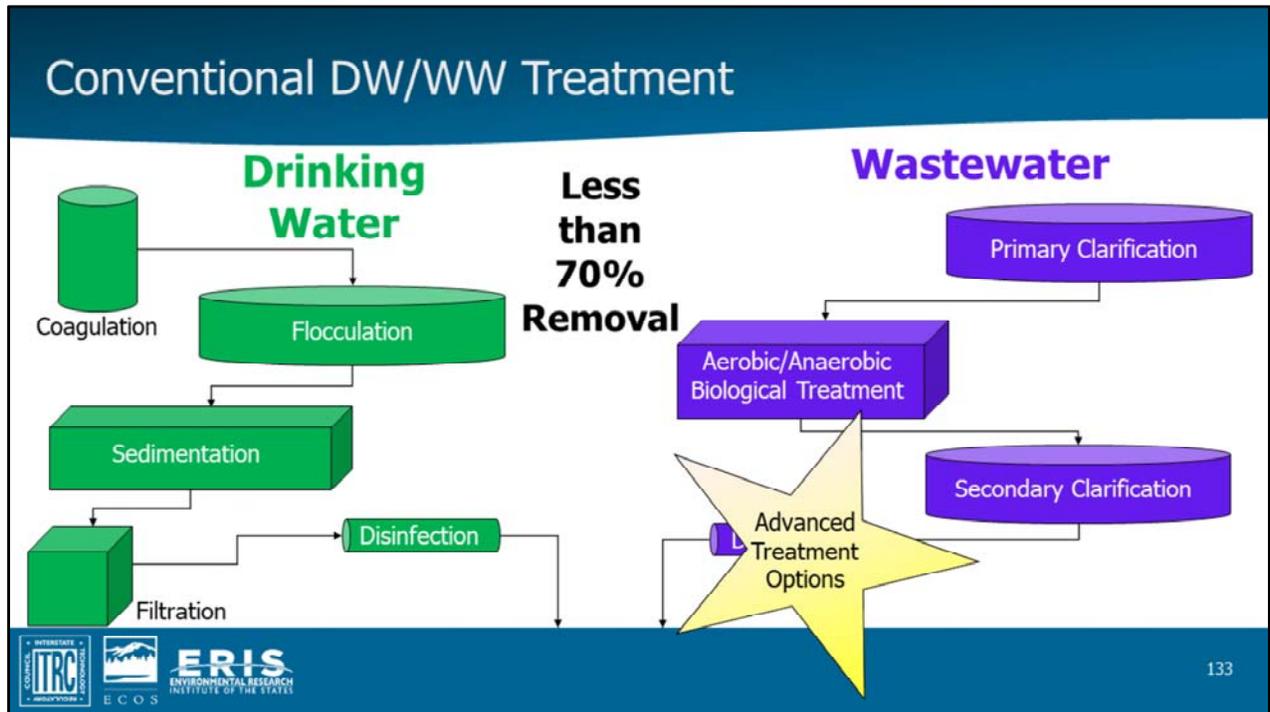


10 sec: Now we shift gears one last time to our last topic, drinking water and wastewater treatment.

## Conventional DW/WW Treatment



45 sec: Since, 1,4-dioxane has made its way into many drinking water sources, and since it's present in many personal care products, it's important to consider how well it's treated using conventional drinking water and wastewater treatment processes. As shown in these very simplified flow diagrams, drinking water and wastewater treatment plants conventionally rely on physical removal of constituents with some focused biological treatment. As we've talked about today, the physical/chemical properties of 1,4-dioxane mean it doesn't readily volatilize or sorb to particles that might be removed via these processes. While the disinfection processes employs oxidative processes, these aren't typically strong enough to destroy 1,4-dioxane.



15 sec: Therefore, it's common to see something like only 50 to 70% max removal of 1,4-dioxane through a drinking water or wastewater treatment plant. In some cases, as is now happening on Long Island, this may not be enough. In these cases, there are advanced treatment options that can be employed to remove 1,4-dioxane from the water stream. Many of these are similar to the ex-situ treatment technologies we discussed earlier, such as AOPs. –

## 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

1min: The last topic to cover related to drinking water treatment is to discuss residential drinking water treatment. Like we mentioned when discussing activated carbon treatment, if designed properly LGAC can be effective for residential drinking water treatment. Several LGAC vessels can be staged in a basement or a shed to treat all of the water entering the house, and breakthrough monitoring and changeouts should be scheduled to maintain a high level of security that clean water is being provided. Note that things like small carbon filters for pitchers in refrigerator or on faucets do not provide the same level of protection. Likewise, commonly used particulate filter, water softening devices, and UV disinfection systems will not adequately remove 1,4-dioxane from water before use.

## Remediation and Treatment Technologies

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

1,4-Dioxane concentrations in groundwater  
µg/l = micrograms per liter

150 µg/l

- 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

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

1 min: So, in summary, there are many options for 1,4-dioxane treatment of soil, soil vapor, groundwater, drinking water, and wastewater. Different options should be applied under different situations and selection should be based on site-specific information. Don't forget that there are several technologies that are used for treatment of other common compounds, like chlorinated solvents, that aren't as effective at treatment 1,4-dioxane. We hope this presentation was helpful in providing an overview of 1,4-dioxane treatment technologies. Please remember that you can visit the web-based 1,4-dioxane guidance document for more details on all of these technologies.

## Thank you for attending! Questions & Answers?

- ▶ 1,4-Dioxane Modules will be hosted for separate viewing On Demand
- ▶ Questions? [itrc@itrcweb.org](mailto: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/feedback.cfm>



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Thank you, **[Speaker Name]**. At this time we will open the questions and answers portion of our training. At any time you can type in your question in the Q&A pod in the bottom right corner of your screen. We will try to get through as many of those questions as we can.

So let's go to our phone lines - if you would like to ask a question out loud this is your opportunity to do so. It's Pound 6 to unmute.

**[PAUSE.... IF NO ONE ASKS A QUESTION, READ OUT TYPED QUESTIONS]**

Thank you **[Speaker Name]**. The Clu-In training page will remain active in case you'd like to access it at a later time.

We would like to hear back from you today so please be sure to fill out the online feedback form that's linked on this last slide. You can also access the feedback form by clicking Feedback in the related links section and then clicking browse to. Filling out the feedback form and certifying that you participated will allow you to receive a certificate of completion.

If you need further clarification on the answers or would like to ask more questions, feel free to email us at [training@itrcweb.org](mailto:training@itrcweb.org) and we will follow up with our trainers to get your questions answered. Or you are welcome to follow up with our trainers directly.

Special thanks to our participants today. We appreciate you taking the time out of your busy schedules to join us today. Thank you to our expert trainers for being here today and for their contribution to the ITRC document.

As a reminder, ITRC archives all its training classes, so if you find that you have additional time or looking for additional training opportunities, please visit Clu-In and the archived trainings to see if there are other courses that might interest you.