Issues & Trends

June 15, 2021

1,4-Dioxane: A Contaminant of Emerging Concern

Angela Carey & Judy Fassbender

Zoom

- No video, please.
- Lines are muted.
- Questions?
    - Raise hand or use chat feature.
- Technical problems?
    - Zoom.us for help.

2021 Issues & Trends

Schedule at:

dnr.wisconsin.gov/topic/Brownfields/Training.html

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Today's recording and previous webinars at:

dnr.wisconsin.gov/topic/Brownfields/TrainingLibrary.html

Jodie Peotter

Chief - Brownfields, Outreach and Policy

Currently Out for Public Input
Updated Guidance

RR-0115 – *Guidance: Contaminated Sediment Fact Sheet*

Comment through July 1, 2021.

Public Comment at

https://dnr.wisconsin.gov/topic/brownfields/publicnotices.html

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1,4-Dioxane

A Contaminant of Emerging Concern

Issues & Trends - 2021

Angela Carey & Judy Fassbender

1,4-Dioxane

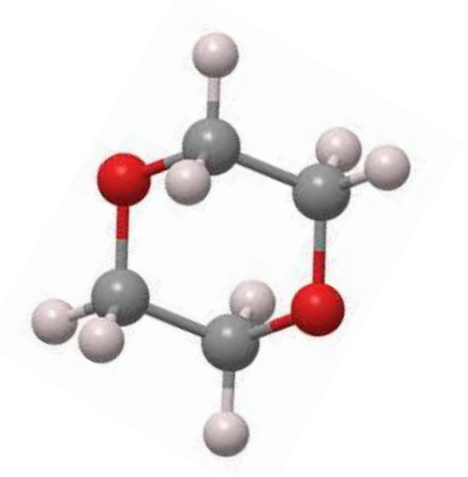
- Introduction
- History, use, and potential sources
- Regulations and standards
- Physical and chemical properties
- Fate and transport
- Sampling and analysis
- Scoping a site investigation
- Remedial options
- Summary

Focus of Presentation

- When to include 1,4-dioxane in a site investigation
- Upcoming changes to Wisconsin's standards
- Sampling considerations
- Analytical considerations
- Remedial challenges

1,4-Dioxane $C_4H_8O_2$

- Many other names including Dioxane, Para-Dioxane, p-Dioxane, Glycol ethylene ether, Diethylene ether, 1,4-Diethylene dioxide, 1,4- Dioxacyclohexane, Tetrahydro-1,4-dioxin, Tetrahydro-p-dioxin…
- Synthetic industrial chemical commonly used as a solvent stabilizer
- Classified by the EPA as likely to be carcinogenic to humans



1,4-Dioxane

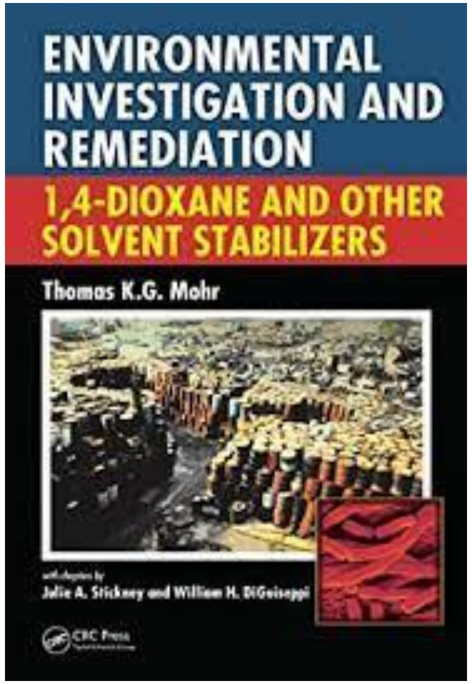
History, Use, and Potential Sources

History, Use, and Potential Sources

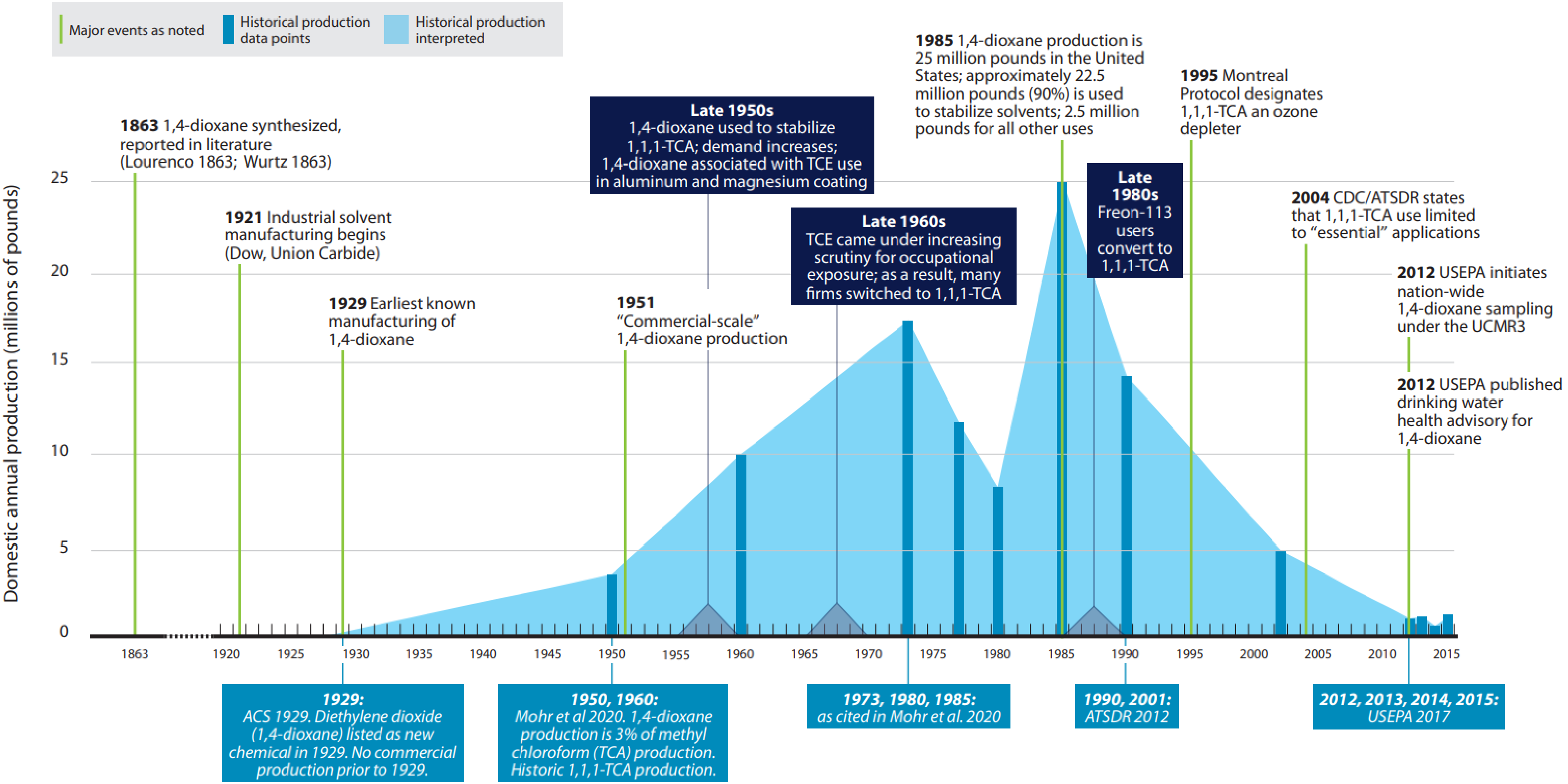
- Small scale manufacturing in the U.S. began in 1929
- Commercial-scale production began in 1951and peaked in 1985
- Domestic production trends follow solvent use in industrial and manufacturing settings, and regulatory changes as environmental hazards were identified.

History, Use, and Potential Sources

- Estimated 90% of 1,4-dioxane was used to stabilize the chlorinated solvent 1,1,1-trichloroethane (TCA).
- Production spiked in the mid-1980s as TCE was phased out in favor of TCA.
- Subsequent decline occurred as TCA was recognized as an "ozone depleting material."



History, Use, and Potential Sources



History, Use, and Potential Sources

- Solvent stabilizer
- Chemical process by-products
- Medical, pharmaceutical and biotechnical uses
- Plastics and polymers
- Inks, paints and coatings
- Adhesives
- Automotive fluids
- Consumer products

History, Use, and Potential Sources

- Wastewater discharges – production, processing and use
- Wastewater discharge - POTWs
- Septic systems
- Landfills
- Historical disposal practices/illegal dumping
- Unintended spills and leaks
- Intentional application of products

Regulations and Standards

Regulations

- Subject to multiple state and federal regulations
- Federal regulations include CERCLA, RCRA, CAA, CWA, TSCA, OSHA and FDA.
- Wisconsin's Spills Law, Wis. Stat. ch 292 and Wis. Admin. Code chs. NR 700-799 regulate discharges of 1,4-dioxane and the investigation and remediation of environmental media.

Regulations: The Spills Law and ch. NR 716

Under the Spills law, Wis. Stat. § 292.11(3) and Wis. Admin. Code § NR 716.07, Site Investigation Scoping, the state has the authority to require that contaminants of concern are included in a site investigation:

- When there has been a discharge of a hazardous substance or there is evidence of environmental pollution, and
- There is knowledge of current or historical activities at the site that would indicate that the contaminant may be present.

Wisconsin Standards

Environmental Media	Standard Groundwater: Wis. Admin. Code ch. NR 140 Soil: Wis Admin Code ch. NR 720	
Groundwater	Enforcement Standard (ES)	3.0 ug/L
	Preventive Action Limit (PAL)	0.30 ug/L
Soil	Industrial Direct Contact RCL	26.5 mg/kg
	Non-Industrial Direct Contact RCL	5.72 mg/kg
	Groundwater Protection RCL	0.0012 mg/kg

Wisconsin Standards

Proposed changes to Wis. Admin. Code ch. NR 140:

- lower groundwater ES and PAL
- lower groundwater protection RCL for soil
- More information on NR 140 groundwater quality standards updates can be found at: https://dnr.wisconsin.gov/topic/Groundwater/NR140.html

Summary of Cycle 10 Recommendations

Substance	New or existing	Enforcement Standard Recommended Value		Preventive Action Limit Recommended Value	
1,1-Dichloroethane	Existing	No change	850 µg/L	No change	85 µg/L
1,2,3-Trichloropropane	Existing	↓	0.3 ng/L	↓	0.03 ng/L
1,4-Dioxane	Existing	↓	0.35 µg/L	↓	0.035 µg/L

A Contaminant of Emerging Concern

- Persistent, mobile, and toxic
- Widespread distribution and use
- No federal drinking water standard
- Found in public and private drinking water sources
- Not typically considered in site investigations
- Physical and chemical properties make lab analysis challenging
- Ongoing research into sources of potential exposure and associated risks.

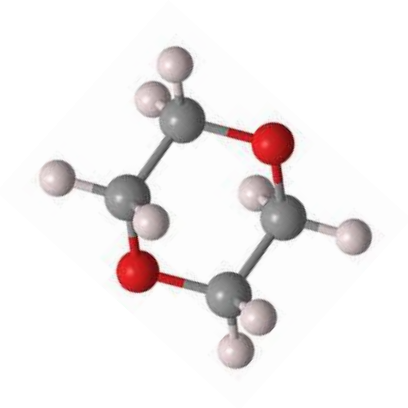
Questions ?

Physical and Chemical Properties

Physical and Chemical Properties

1,4-dioxane's physical and chemical properties affect:

- Fate and transport in environmental media
- Sampling and analysis procedures
- Remedial options



Properties that influence its behavior include:

- Low Henry's Law constant
- Low organic carbon partitioning coefficient
- Fully miscible with water

Physical and Chemical Properties

Low Henry's Law constant:

- Chemicals can be classified as volatile based on both their vapor pressure and Henry's Law constant at 25 °C.
  - Vapor pressure > 1 mm Hg (*38.1 mm Hg*)*
  - Henry's Law constant >1x10^{-5} atm-m^{3}/mole (*4.8 x 10^{-6} atm-m^{3}/mole*)*
- 1, 4-dioxane's volatilization is a moisture dependent process.
  - Volatilization from dry soil is likely
  - Volatilization from water is unlikely

* Values for 1,4-dioxane

Physical and Chemical Properties

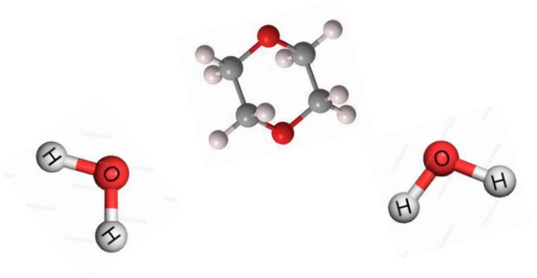
Low organic carbon partitioning coefficient (k_{oc}):

- Hydrophyllic compounds like 1,4-dioxane tend to remain in solution and sorb less to organic-rich carbon soil or sediment.
  - $K_{oc} = 0.54$
- 1, 4-dioxane's sorption potential is low and as a result:
  - Retention in the vadose zone is generally expected to be low
  - Migration into groundwater is generally expected to be high.

Physical and Chemical Properties

Density and miscibility:

- The density of 1,4-dioxane is similar to that of water:
  - 1,4-dioxane liquid density = 1.028 g/cm^3 at 25°C



- 1, 4-dioxane is more likely to:
  - Form a miscible solution in ground and surface waters

1,4-Dioxane

Fate and Transport

Fate and Transport

Once released, 1,4-dioxane can be destroyed through:

- Biodegradation, and
- Photodegradation

Biodegradation process are dependent upon elevated concentrations of 1,4-dioxane.

Aerobic biodegradation is the breakdown of organic contaminants by microorganisms when oxygen is present.

Photodegradation is the process by which the absorption of photons—particularly those with wavelengths in the UV–visible spectrum—causes a molecule to degrade.

Fate and Transport

Aerobic Biodegradation:

- Metabolic biodegradation where microbes use 1,4-dioxane as a carbon and energy source.
- Co-metabolic biodegradation where 1,4-dioxane is metabolized as a side-effect of degradation of other primary compounds.

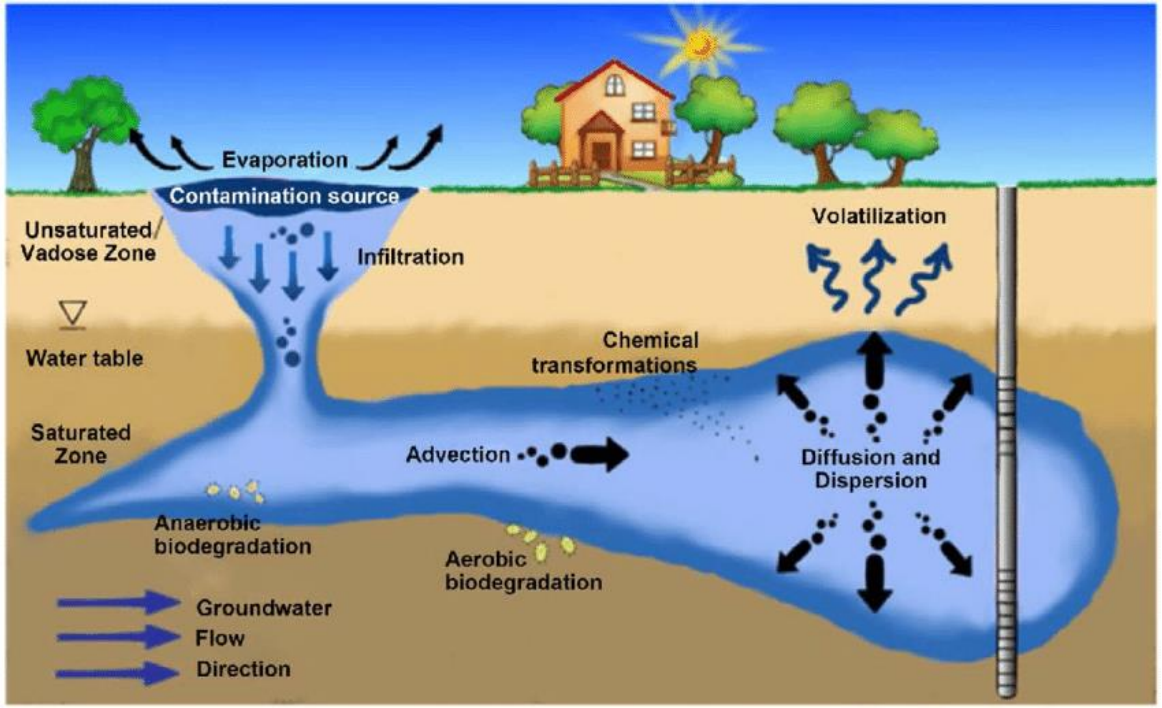
Photodegradation:

- In the atmosphere, 1,4-dioxane undergoes indirect photooxidation when energy is transferred from a radical species formed by UV light.

Fate and Transport

Primary transport processes include:

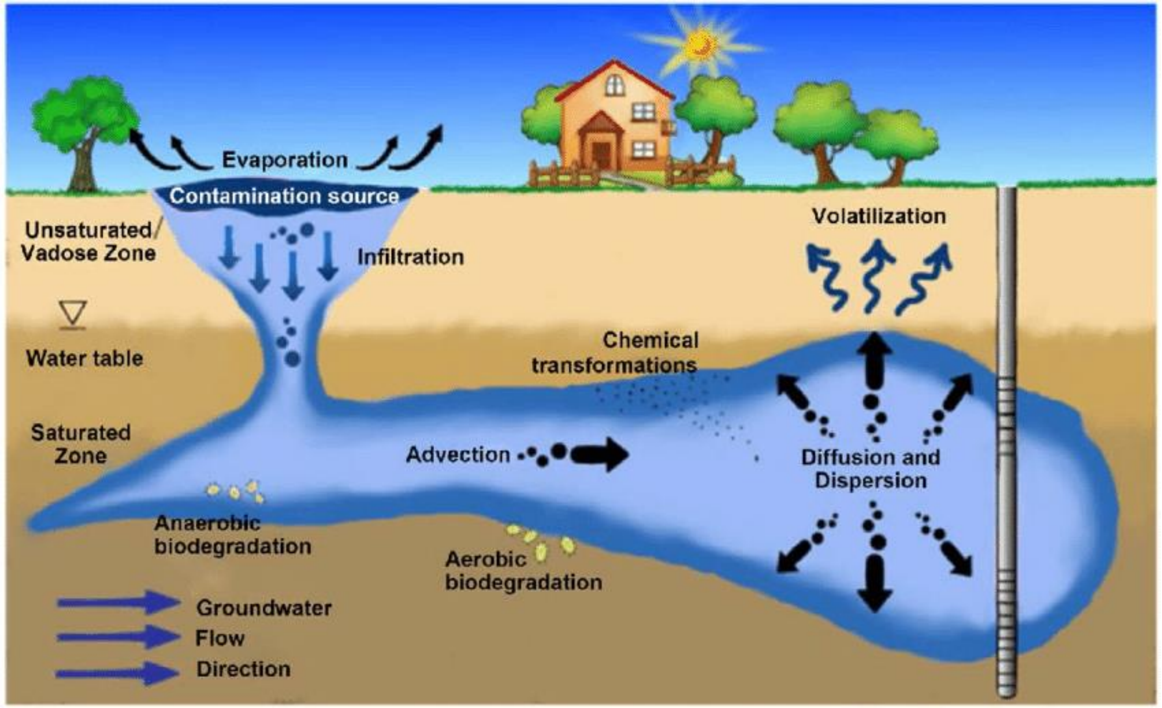
- Advective transport
- Matrix diffusion
- Groundwater-surface water interactions
- Evaporation/Volatilization



Fate and Transport

Advective Transport – mechanical transport of solutes along with the bulk flux of water.

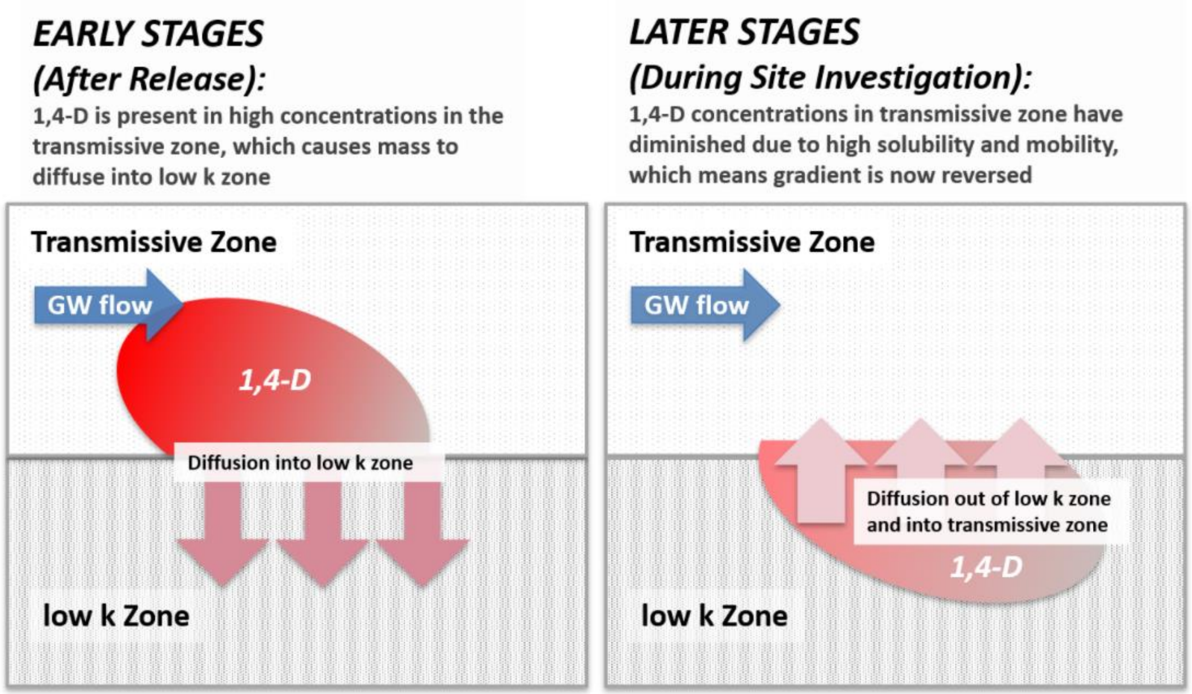
- Potential for rapid migration
- Dispersion and diffusion
- Low sorption



Fate and Transport

Matrix Diffusion – diffusion of solutes into and out of lower-permeability zones within a groundwater-bearing unit.

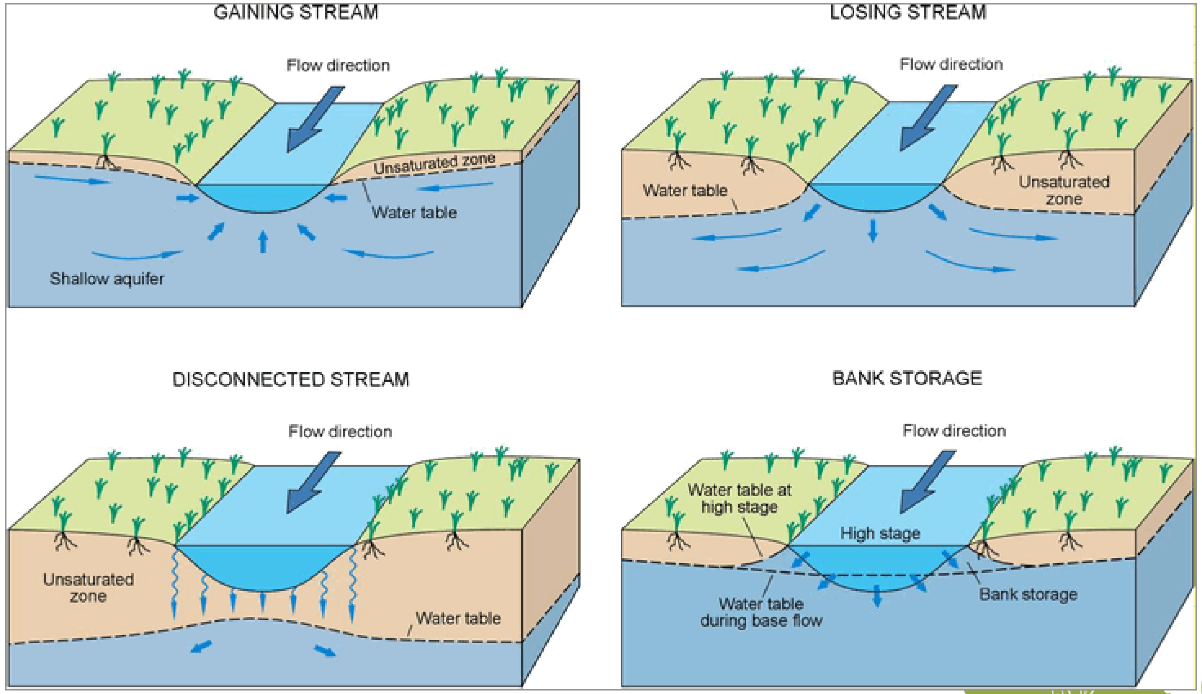
- High solubility and miscibility
- Long-term persistence and dilute plumes.
- More difficult to treat.



Fate and Transport

<u>Groundwater to Surface Water Discharges</u> – transport of solutes from groundwater to surface water.

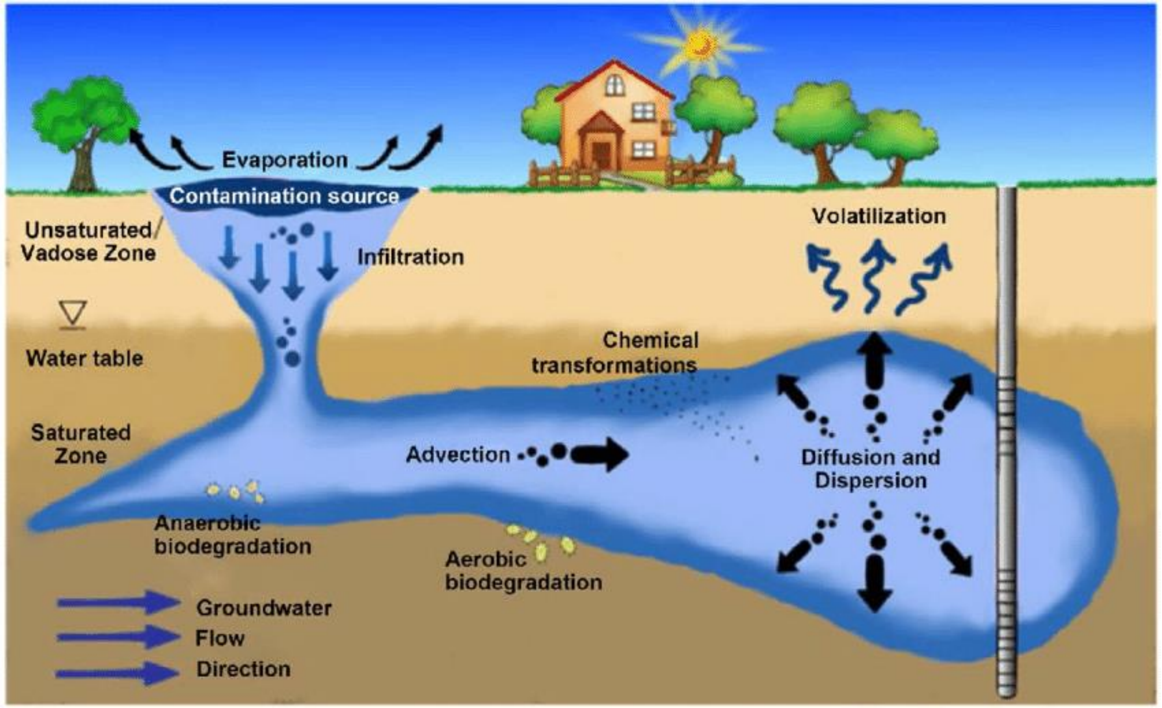
- Rapid migration
- Increase number of pathways and receptors
- Groundwater extraction systems



Fate and Transport

<u>Evaporation/Volatilization</u> – transport of solutes from liquid phase to vapor phase.

- Low Henry's Law constant
- Industrial grade products
- Vapor intrusion



Questions ?

Sampling and Analysis

Sampling and Analysis

- Conventional equipment can be used.
- Found in many detergents and can result in contamination of sampling equipment.
- Proper quality control (field and equipment blanks) can identify potential issues.

ITRC Guidance: Conventional Sampling Equipment and Techniques

MEDIUM	Solid Samples		Water Samples[1]		Air Samples
MATRIX	Soils	Sediments	Groundwater	Surface Water	Air
SAMPLING EQUIPMENT AND TECHNIQUES	Hand augers Direct push Split spoon En Core™ Terra Core™	Spade/shovel Eckman dredge Ponar grab Bucket or tube auger	Low-flow submersible pumps No purge passive or grab sampler[2] Bailers Volume purging Peepers	Dip samplers Direct fill Discrete-depth sampler Peristaltic pump	Canister Sorbent tubes

Sampling and Analysis

- Passive diffusion bags that are not water permeable
- Monitoring wells with low recharge rates may dictate sample volume/method selection
- Level of moisture in soil
- Consult ITRC's guidance on containers, preservation and holding times to select a method that meets remedial objectives.

Table 4-3. Containers, preservation, and holding times for 1,4-dioxane

Matrix	Analytical method	Typical collection volumes and containers & Containers	Preservative	Holding time (Schep et al. 2009 ▻)

Sampling and Analysis

Physical and chemical properties of 1,4-dioxane make analysis complicated and challenging:

- Difficult to purge or extract from water matrices
- Low level detection challenging
- Common co-contaminants interfere
- Method selection requires an understanding of the sample matrix, reporting requirements, and level of contamination.

Sampling and Analysis

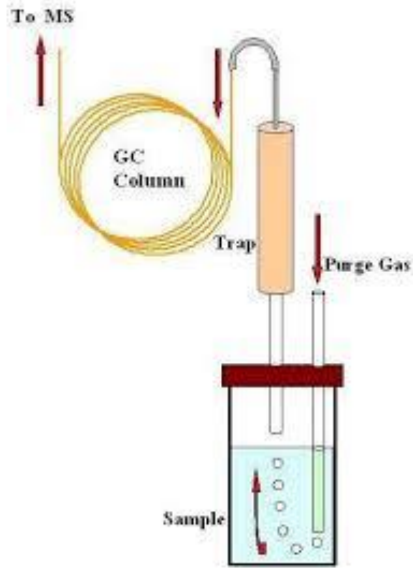
Before field work begins:

- Understand reporting limits required to meet remedial objectives
- Select a Wisconsin certified lab that can meet the necessary reporting limits
- Work with the lab prior to sample collection and analysis to ensure data quality

Sampling and Analysis

Analytical methods SW846 8260 and 8270 can generate accurate low-level data:

- Extraction preparation
- GC/MS with selective ion monitoring
- Isotope dilution
- QA/QC



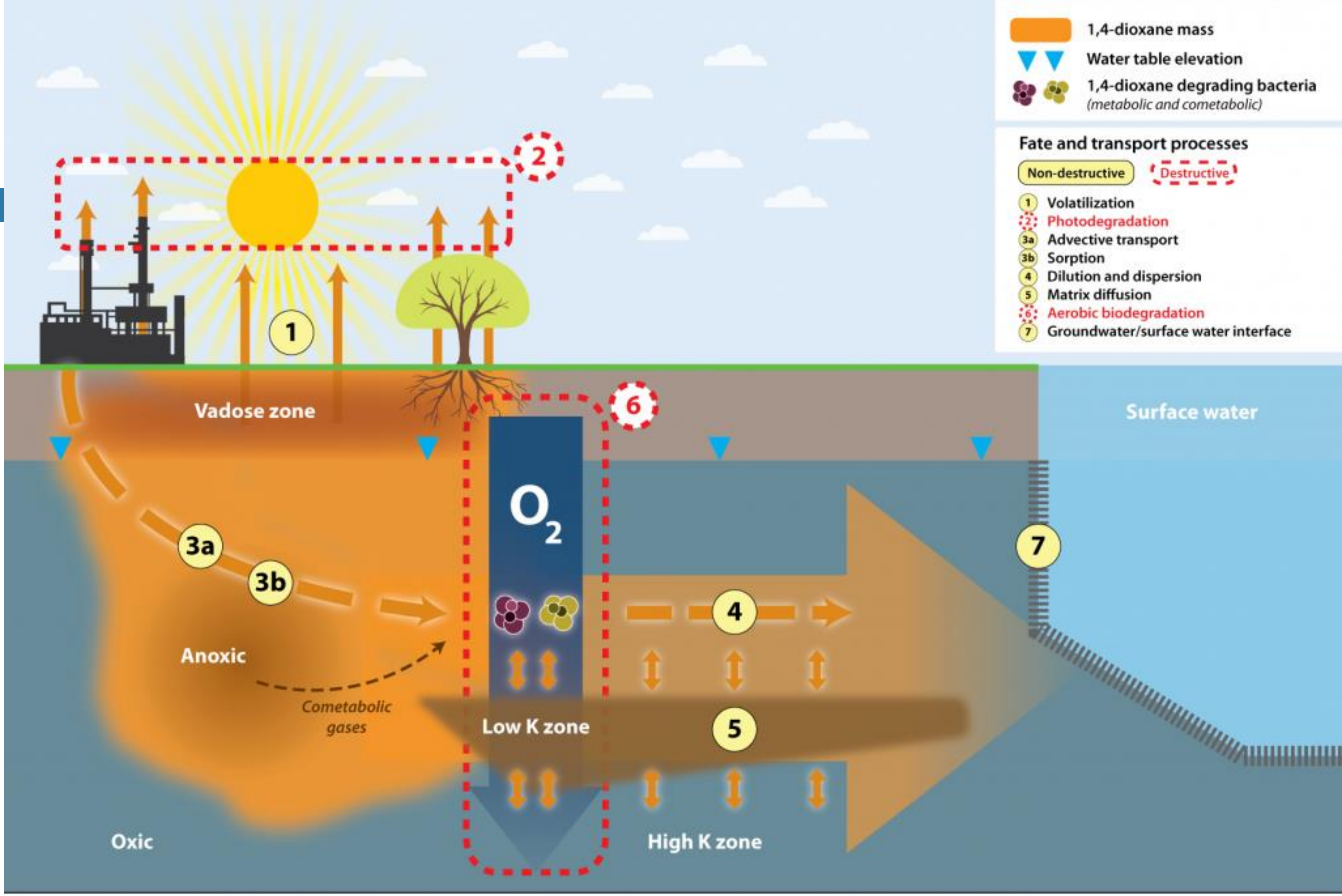
Scoping a Site Investigation and Conceptual Site Models

Scoping a Site Investigation, NR 716.07

- History of the site, activities, and land use
- Sample collections methods, decontamination procedures and QA/QC
- WI certified lab
- Remedial objectives including reporting limits
- Request a broad list of analytes initially and then focus investigation based on the results
- RR-101, SI Scoping: Identifying Contaminants of Concern

The CSM

1. Volatilization
2. Photodegradation
3a. Advective transport
3b. Sorption
4. Dilution and dispersion
5. Matrix diffusion
6. Aerobic biodegradation
7. Groundwater/surface water interface



Generalized figure for the fate and transport of 1,4-dioxane: In the absence of water or soil moisture 1,4-dioxane volatilizes (1) to the atmosphere where it is rapidly photodegraded (2). In the presence of water advective flow drives 1,4-dioxane into groundwater systems or plants via uptake through plant root systems (3a) with little retardation from sorption into organic matter (3b). In the saturated zone, attenuation of 1,4-dioxane occurs via dilution and dispersion (4), matrix diffusion (5), or aerobic biodegradation mediated by microbes (6). Transport of undegraded 1,4-dioxane to surface water may occur through groundwater–surface water interfaces (7).

Conceptual Site Model

- Groundwater is often the main media of concern.
- Advective transport and matrix diffusion can lead to large dilute plumes that may be distinctly different than their co-contaminants.
- History of various solvents used
- Biodegradation potential for chlorinated VOCs and 1,4-dioxane

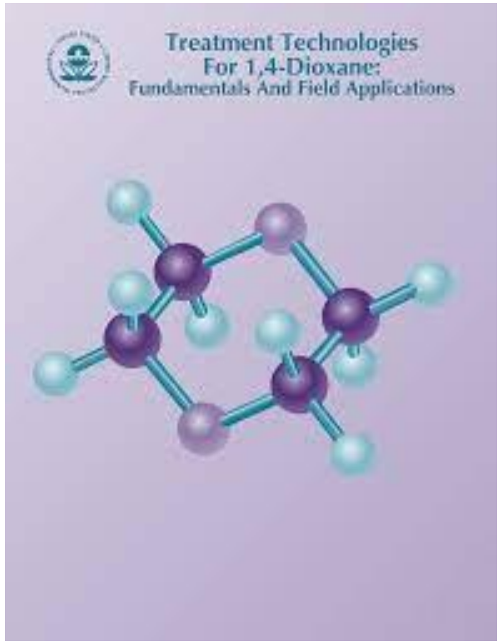
Conceptual Site Model

- Consider whether pure phase/technical grade 1,4-dioxane was discharged and whether soil continues to be impacted.
- Soil impacts may lead to vapor intrusion under certain conditions.
- Consider whether there is or has been a permitted discharge (WPDES or septic).

Remedial Options

Treatment Technologies

- Challenging to treat
- Conventional treatment ineffective
- In-situ and ex-situ treatment options
- Co-contaminants inhibit treatment
- Dependent on concentration.

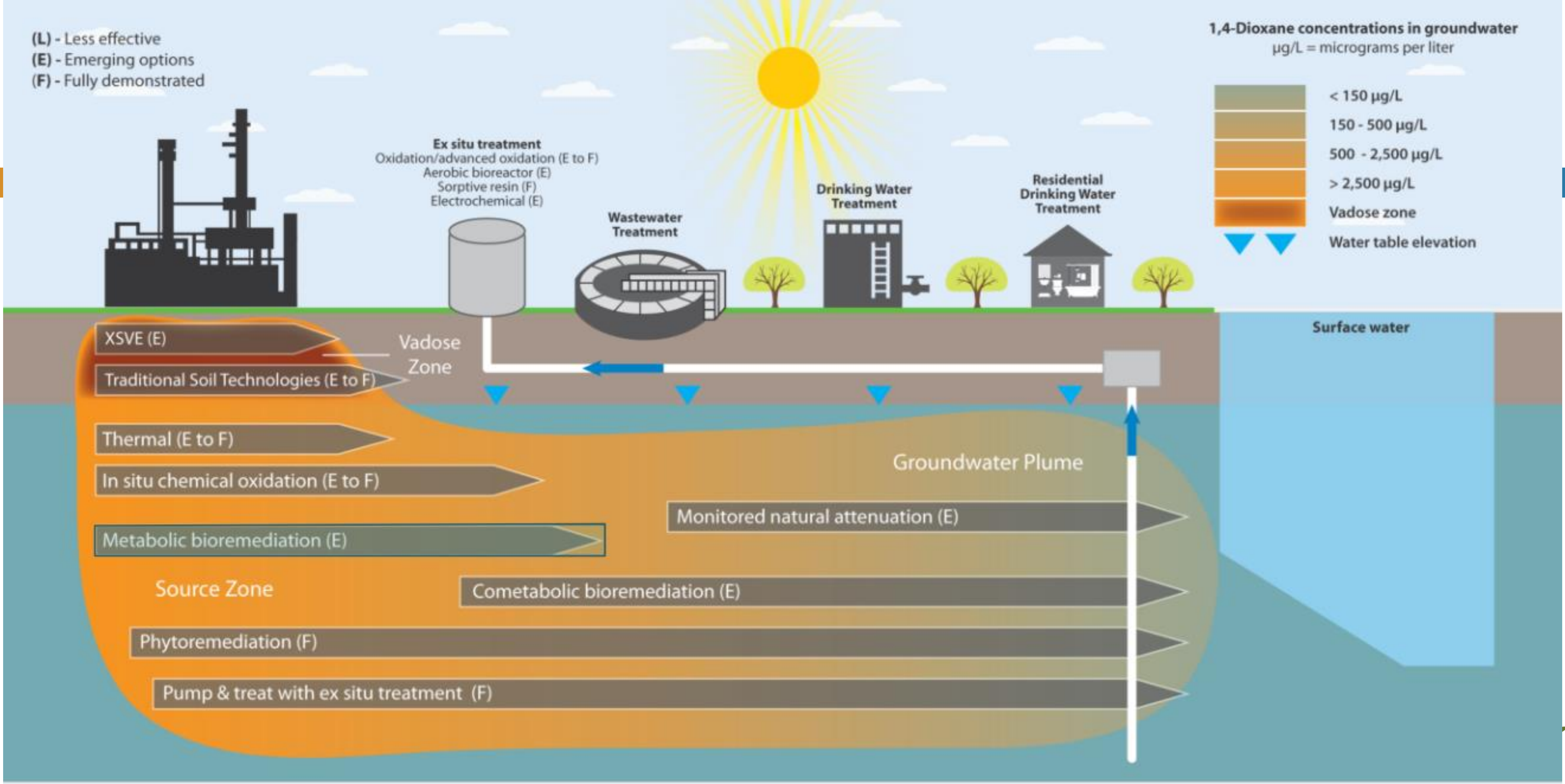


Treatment Technologies for Groundwater

Remedial Technology	In-Situ	Ex-situ
Fully Demonstrated	Chemical oxidation Phytoremediation	Advanced oxidation processes Sorptive resins
Emerging Options	Aerobic metabolic biodegradation Aerobic co-metabolic biodegradation Thermal remediation MNA	Electrochemical treatment Biological treatment Bioreactors using metabolic degradation Bioreactors using co-metabolic degradation with alkane gases
Less Effective Options	Anaerobic bioremediation, Air sparging/SVE, Zero-valent iron	GAC Air stripping, Ion exchange, Ozonation alone

Treatment Technologies for Soil

Remedial Technology	In-Situ	Ex-situ
Fully Demonstrated	Solidification/stabilization Phytoremediation	Excavation/disposal Ex-situ thermal desorption
Emerging Options	Extreme SVE In-situ chemical oxidation soil blending In-situ thermal remediation	
Less Effective Options	Traditional SVE Conventional biodegradation (Bioventing)	Conventional biodegradation (Bio-piles)



This figure illustrates where various technologies may be implemented across a 1,4-dioxane plume. It should be noted that the areas shown are schematic in nature, and certain technologies can be effective across a varying range of locations and concentrations. The actual deployment location of a technology will depend on site-specific conditions. Note that only fully demonstrated and emerging options are shown here. When more than one category is shown, it indicates that the technologies in that grouping have different categories. Less effective technologies are discussed in the text.

Summary

- Consider 1,4-dioxane in the SI scoping stage.
- Select appropriate sampling and analysis methods to meet remedial objectives.
- Review Wisconsin standards for all impacted environmental media.
- Consider remedial options that effectively address 1,4-dioxane.

Resources

- ITRC https://14d-1.itrcweb.org/
  - Web-based guidance "Technical Resources for Addressing Environmental Releases of 1,4-Dioxane"
  - Case Studies, Fact Sheets, References and Appendices
- DOD's Environmental Research Programs SERDP and ESTCP
  - Search for "1,4-dioxane" https://www.serdp-estcp.org/
  - SERDP Fact Sheet "New Developments in 1,4-Dioxane Site Management"
- EPA's Technical Fact Sheet – 1,4-Dioxane
  https://www.epa.gov/fedfac/technical-fact-sheet-14-dioxane

Questions ?

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