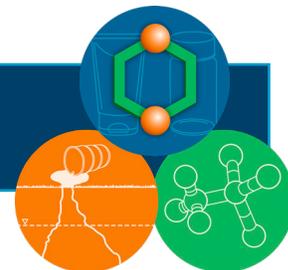




# Environmental Fate, Transport, and Investigation Strategies: 1,4-Dioxane



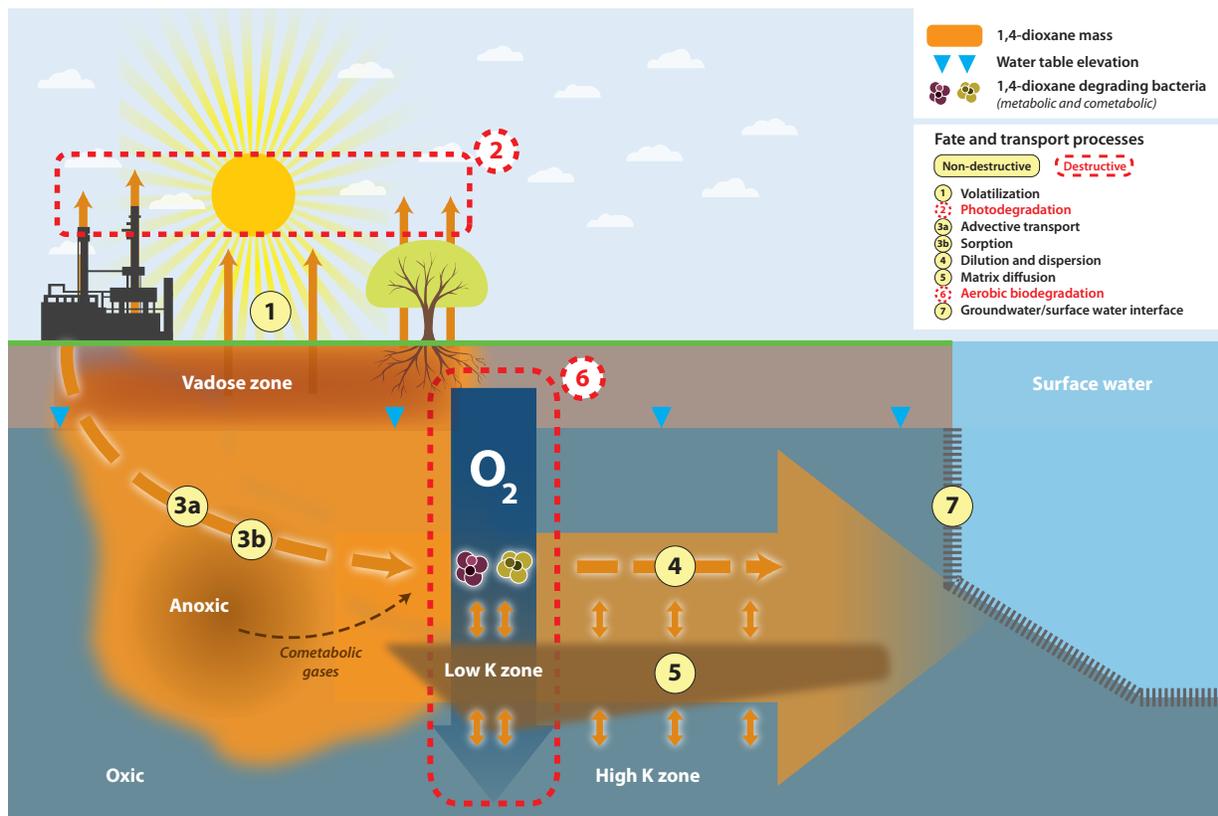
The Interstate Technology and Regulatory Council (ITRC) has developed a series of six fact sheets to summarize the latest science and emerging technologies regarding 1,4-dioxane. The purpose of this fact sheet is to:

- describe how the physical and chemical properties of 1,4-dioxane affect the primary processes relevant for behavior and movement of 1,4-dioxane in the environment
- provide a helpful framework for developing a site conceptual model for 1,4-dioxane
- highlight how an effective investigation into the distribution of 1,4-dioxane in the environment might differ from an investigation for its common co-contaminants.

Note: ITRC is developing a 1,4-dioxane guidance document for publication in late 2020. The guidance document will provide additional details on 1,4-dioxane fate and transport.

## 1 Introduction

The fate and transport of 1,4-dioxane (Chemical Abstracts Service [CAS] Registry Number #123-91-1) in the environment is controlled by the compound's physical and chemical properties, media transport characteristics, and the favorability of conditions for biodegradation. Figure 1 shows 1,4-dioxane's fate and transport processes in a generalized conceptual site model, and Table 1 presents details.



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.

**Figure 1. Generalized fate and transport of 1,4-dioxane.**

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**Table 1. Summary of selected fate and transport processes for 1,4-dioxane**

Process (See Numbers Shown in Figure 1)	Description	Key issues and implications for 1,4-dioxane	Relevance for site characterization
<b>Non-destructive and cross-media processes</b>			
Volatilization (1)	Transfer of liquid-phase contaminant to vapor phase	<ul style="list-style-type: none"> <li>• <b>Low volatilization potential</b> for 1,4-dioxane once it is dissolved in water limits potential for vapor intrusion (Henry's law constant: <math>4.8 \times 10^{-6}</math> atm-m<sup>3</sup>/mol), but lack of volatilization may promote transfer of mass from the vadose zone to groundwater.</li> <li>• Partitioning to air from dry surfaces may be relevant in some cases based on vapor pressure for 1,4-dioxane (40 mm Hg) (USEPA 2018).</li> </ul>	Low
Partitioning to solid phase/adsorption (3b)	Sorption of contaminant to organic carbon fraction or pore water within soil and sediments	<ul style="list-style-type: none"> <li>• <b>Low sorption potential</b> for 1,4-dioxane in soils (log <math>K_{oc} = 1.23</math>) (ATSDR 2012).</li> <li>• Low sorption enhances the potential for migration following release.</li> <li>• The presence in soil may be due to partitioning of 1,4-dioxane to vadose-zone pore water (Hinchee et al. 2018).</li> </ul>	Low
Advective transport/dispersion/dilution (3a, 4)	Transport of contaminant within flowing fluid (e.g., groundwater) coupled with the influences of smaller-scale mechanical and molecular forces	<ul style="list-style-type: none"> <li>• Potential for <b>rapid migration can occur when 1,4-dioxane is released</b> to groundwater and surface water.</li> <li>• Rapid migration is compounded by a relative lack of sorption compared to common co-occurring contaminants.</li> <li>• Dispersion and diffusion can contribute to further spreading and dilution of plumes.</li> </ul>	High
Matrix diffusion within porous media (5)	Diffusion of dissolved mass in and out of lower-permeability zones (e.g., clays, silts, and rock) within groundwater-bearing unit	<ul style="list-style-type: none"> <li>• Contributes to long-term persistence of groundwater plumes (Adamson et al. 2016): the <b>high solubility and miscibility of 1,4-dioxane</b> may exacerbate (&gt;1,000 g/L) (USEPA and SRC 2019).</li> <li>• It is more difficult to remediate contaminants in low-permeability zones.</li> </ul>	Moderate
Groundwater-to-surface-water discharge (7)	Transport of dissolved mass by discharge of groundwater-to-surface-water body	<ul style="list-style-type: none"> <li>• The advective flow of streams and rivers can contribute to <b>rapid migration once 1,4-dioxane has reached the receiving stream</b>.</li> <li>• This increases the potential for exposures in aquatic ecosystems.</li> <li>• Discharge of effluent from a groundwater extraction system to surface water may also contribute to cross-media transfer unless the system is designed to treat 1,4-dioxane.</li> </ul>	Moderate
<b>Destructive processes</b>			
Photodegradation (2)	Interaction between ultraviolet (UV) light and hydroxyl radicals resulting in chemical transformation within air and surface water	<ul style="list-style-type: none"> <li>• 1,4-Dioxane is a <b>weak absorber of UV light</b>.</li> <li>• Indirect photolysis in the presence of hydroxyl radicals can readily occur in the atmosphere or near a water surface (USEPA 2018).</li> <li>• Direct photolysis in surface water is not expected (governed by the light intensity, angle of light entry, turbidity, and dissolved organics in water).</li> </ul>	Moderate
Biodegradation (6)	Microbial degradation via metabolism and/or cometabolism	<ul style="list-style-type: none"> <li>• The presence of <b>dissolved oxygen is required</b> (Barajas-Rodriguez and Freedman 2018).</li> <li>• 1,4-Dioxane biodegradation rates may be inhibited by several common co-occurring chlorinated solvents (Zhang, Gedalanga, and Mahendra 2016), low oxygen concentration, low concentrations of 1,4-dioxane (for metabolic degradation), and the lack of a suitable co-substrate (for cometabolic degradation).</li> </ul>	Moderate

**Notes: "Relevance for site characterization" is a qualitative measure of relevance based on two criteria: (1) the extent to which the process contributes to a change in concentration, reduces migration, and/or transfers 1,4-dioxane from one matrix to another; and (2) the potential for 1,4-dioxane to be present in the matrix (or matrices) where the process generally occurs.**

As discussed in the *History of Use and Potential Sources* fact sheet, 1,4-dioxane is and has been used in a wide range of products and industrial processes. Two types of 1,4-dioxane usage are of particular importance: as a chemical additive to chlorinated solvents, and as industrial-grade products (that is, technical grade >95% 1,4-dioxane or American Chemical Society (ACS) reagent grade >99% 1,4-dioxane). Each of these uses has different implications for 1,4-dioxane fate and transport:

- Chlorinated solvents are present at many sites with environmental concerns; however, many investigations did not historically include 1,4-dioxane as a constituent of concern. Furthermore, as discussed below, conditions that are conducive to biodegradation of 1,4-dioxane are distinct from those that are conducive to biodegradation of chlorinated solvents.
- There are key differences in the fate and transport of 1,4-dioxane when it is released as an industrial-grade product as opposed to when released as an aqueous mixture, most importantly in the case of a release of industrial-grade 1,4-dioxane to a dry surface (that is, a surface with insufficient moisture to dissolve the quantity of 1,4-dioxane released). Specifically, industrial-grade 1,4-dioxane has the potential to evaporate from dry surfaces into vapor because of its relatively high vapor pressure. If a drum of liquid, industrial-grade 1,4-dioxane is spilled on a dry surface, the rate of evaporation depends on vapor pressure, temperature, wind speed, atmospheric

## Environmental Fate, Transport, and Investigation Strategies: 1,4-Dioxane *continued*

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conditions, solar radiation, ground conditions, the dimensions of the 1,4-dioxane spill, and volatility and diffusion characteristics (Thibodeaux 1979). In contrast, if 1,4-dioxane is released in an aqueous mixture, it has little propensity to transfer from water into the vapor phase based on its low Henry's law constant (that is,  $4.8 \times 10^{-6}$  air to moles per cubic meter for water [atm m<sup>3</sup> /mol]; see Table 1). This Henry's law constant demonstrates the tendency for 1,4-dioxane to remain in water once dissolved.

Infiltration of 1,4-dioxane through soil and into groundwater occurs with minimal retardation because of its miscibility in water and low potential for adsorption to organic carbon (low partitioning coefficient, *K<sub>oc</sub>*; see Table 1 for additional information) (USEPA 2018). Figure 1 shows a generalized depiction of 1,4-dioxane's fate and transport. Although there is minimal potential for retardation via sorption in the aquifer matrix, a 1,4-dioxane plume may appear to move more slowly than the average groundwater velocity as a result of diffusion into and back out of low-permeability zones (matrix diffusion). Although chemical characteristics of 1,4-dioxane suggest greater mobility than chlorinated solvent co-contaminants released at the same locations, the empirical data suggest that the plumes are likely to be co-located (Adams et al. 2014). In some cases (Mohr et al. 2020), 1,4-dioxane plumes can extend well beyond the organic co-contaminant plumes. These circumstances may be due to oxygen-poor aquifer conditions that are conducive to biodegradation of the co-contaminants but not of 1,4-dioxane. Conversely, under oxygen-rich conditions, 1,4-dioxane biodegradation is more favorable than chlorinated solvent co-contaminant biodegradation.

The primary destructive process for 1,4-dioxane in the subsurface is biodegradation by aerobic metabolic and cometabolic processes. 1,4-Dioxane metabolism is most likely to occur where concentrations are sufficiently high to support population growth, whereas cometabolism is more likely where 1,4-dioxane concentrations are lower but where cometabolic substrates are available. The first step in currently known 1,4-dioxane biodegradation pathways is mediated by a variety of monooxygenase enzymes. The functionality of these enzymes depends on oxygen availability, although enzymes may remain active even at low oxygen concentrations (Bell et al. 2016). Intermediate products have been identified in multiple degradation pathways (Mahendra et al. 2007, Huang et al. 2014, Chen et al. 2016, Deng, Li, and Li 2018). In general, 1,4-dioxane biodegradation intermediates are innocuous products that are readily biodegraded. These intermediates are not expected to accumulate in the environment, are not common laboratory analytes, and generally do not have regulatory criteria. Microbial 1,4-dioxane biodegradation may be enhanced in the root zone of plants (that is, rhizodegradation) (Kelley et al. 2001). 1,4-Dioxane may also be removed from the subsurface via water uptake by plants (Ouyang 2002, Aitchison et al. 2000). In this case, plants may transport 1,4-dioxane from groundwater to the atmosphere, where indirect photolysis is the ultimate fate. No abiotic degradation mechanisms are known under natural subsurface conditions.

Undegraded 1,4-dioxane in groundwater could eventually be discharged to surface water or extracted at water supply wells. When 1,4-dioxane is not identified as a contaminant and targeted for treatment, use of this contaminated groundwater and surface water may redistribute the 1,4-dioxane back into the environment (for example, via irrigation or effluent water reuse programs). 1,4-Dioxane treatment is discussed in more detail in the Remediation and Treatment Technologies fact sheet.

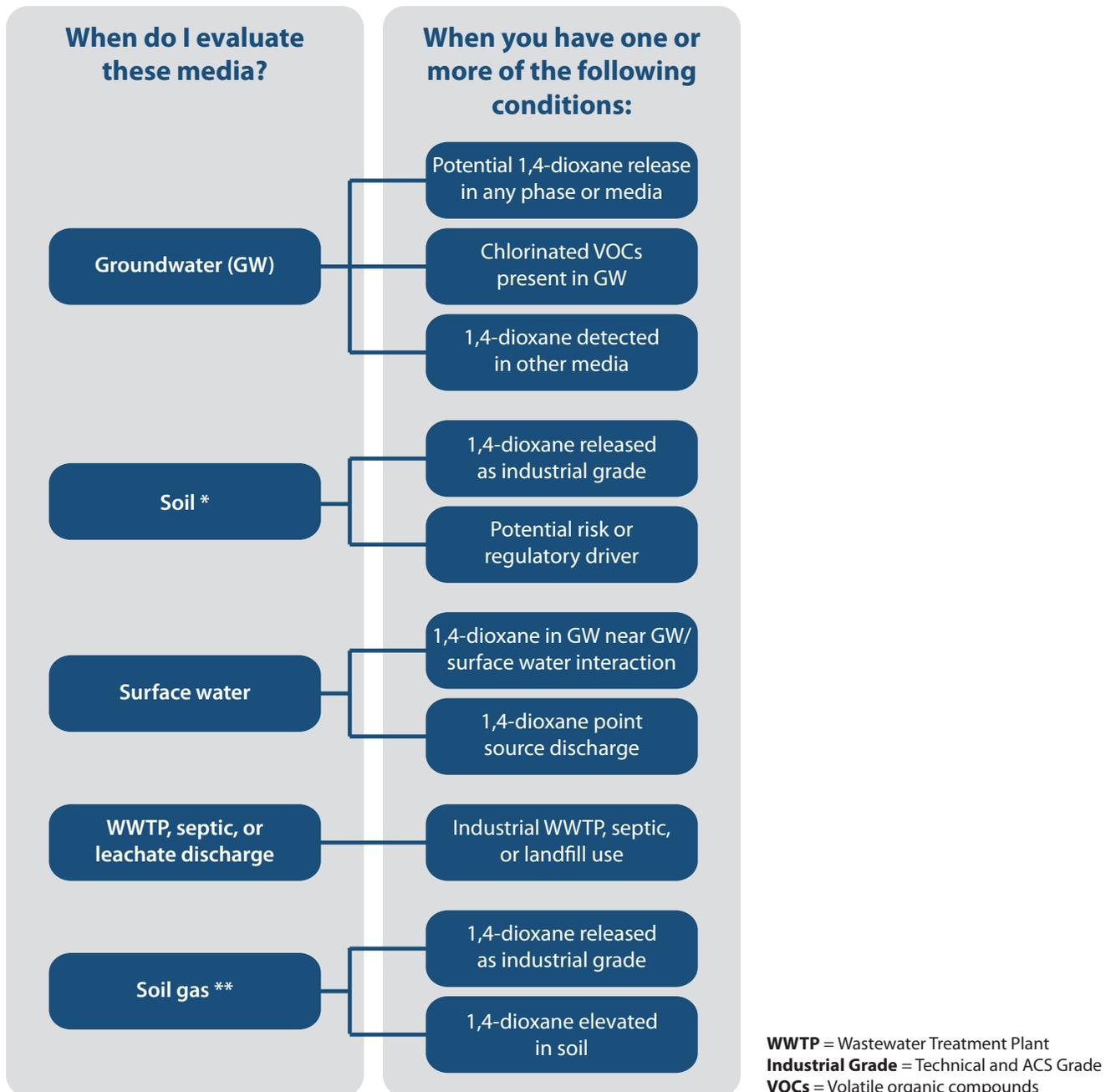
While 1,4-dioxane could reach aquatic and terrestrial biota, the limited data available suggest that bioaccumulation potential is negligible at concentrations typically associated with impacted groundwater (USEPA 2018).

## 2 Investigative Strategies

In approaching a site with suspected 1,4-dioxane impacts, there are several questions related to site operations, site history, and chlorinated solvent use that can help the investigator evaluate the likelihood of 1,4-dioxane being present and determine the media to be sampled. Figure 2 is a generalized flow chart to focus the rationale for sampling and media to be sampled. Although unique circumstances can alter this flow, it can be useful in guiding sampling activities for the vast majority of sites.

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Guidance for targeting media for 1,4-dioxane assessment at sites with potential 1,4-dioxane use and/or release



\* Information on 1,4-dioxane in soil is still evolving. The decision to sample soil will depend on site-specific factors.

\*\* The need to sample soil gas should be determined in consideration of a comprehensive vapor intrusion evaluation as per regulatory guidance.

**Figure 2. Guidance for targeting media for 1,4-dioxane assessment at sites with potential 1,4-dioxane use and/or release.**

**Note:** Figure 2 presents a graphic that can be used to guide assessment activities for potential 1,4-dioxane sites but should not be considered comprehensive and/or definitive. Site-specific factors will affect the conceptual site model. Therefore, this figure should be used in conjunction with a thorough assessment of the source, pathways, and receptors performed by knowledgeable professionals.

## Environmental Fate, Transport, and Investigation Strategies: 1,4-Dioxane *continued*

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Once the investigator has identified potential release mechanisms and potentially impacted media, the fate and transport processes described in Figure 1 and Table 1 provide a framework for developing and refining the conceptual site model through investigation, specifically:

- As noted earlier, 1,4-dioxane has significant potential to enter and remain in groundwater, migrate rapidly, and be subject to matrix diffusion effects. Empirical evidence shows that the footprint of 1,4-dioxane in groundwater may not necessarily be distinct from that of co-occurring chlorinated solvents like trichloroethene (TCE) and 1,1-dichloroethene (1,1-DCE) (Adamson et al. 2014), possibly due to uses of these compounds that predated the release of 1,4-dioxane. However, these data should not preclude a thorough site-specific investigation of the extent of 1,4-dioxane migration.
- Known 1,4-dioxane biodegradation processes are aerobic (Zhang, Gedalanga, and Mahendra 2017). These processes are distinct from anaerobic biodegradation processes that act on chlorinated organics, which often co-occur with 1,4-dioxane (Adamson et al. 2014) reported that 95% of sites with 1,4-dioxane detections also had detections of one or more chlorinated volatile organic compounds [VOCs]).
- In redox transition zones, end products of anaerobic biodegradation of other organics (such as ethane) may facilitate 1,4-dioxane biodegradation (Hatzinger et al. 2017).

The above observations, as well as details regarding the history of use (see the History of Use and Potential Sources fact sheet), highlight how a 1,4-dioxane investigation strategy may be influenced by site-specific characterization efforts for co-occurring contaminants that may already have been performed. As noted above, we should not assume that a 1,4-dioxane plume has necessarily extended beyond the boundaries of a chlorinated solvent plume; however, the potential for rapid migration remains a key consideration and may lead to additional delineation requirements specifically for 1,4-dioxane. Advanced characterization methods may support site investigation for 1,4-dioxane. Such methods may include high-resolution sampling (for example, vertical aquifer profiling) for 1,4-dioxane concentrations along with detailed observations of hydrostratigraphic characteristics and/or applications of advanced analytical methods such as the Environmental Molecular Diagnostic Tools at <https://www.itrcweb.org/emd-2>. Media-specific flow properties, geochemistry, and locations and characteristics of potential sensitive receptors should guide an investigation of the distribution of 1,4-dioxane in the environment (see the Toxicity and Risk Assessment fact sheet).

### 3 References

The references cited in this fact sheet, and the other ITRC 1,4-Dioxane fact sheets, are included in one combined list that is available on the ITRC web site.

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