



# Implications of matrix diffusion on 1,4-dioxane persistence at contaminated groundwater sites



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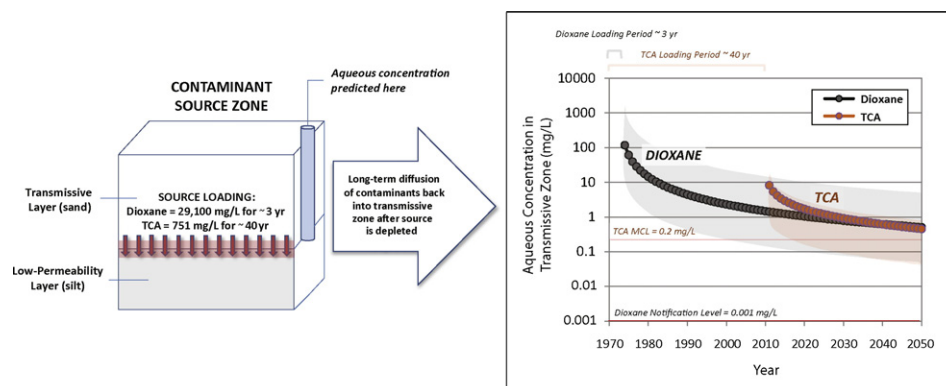
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## HIGHLIGHTS

- Persistence of dioxane due to matrix diffusion was examined using modeling.
- Dioxane exhibited higher degree of diffusion-based mass storage than TCA.
- Diffusion resulted in aqueous dioxane concentrations in excess of criteria.
- Matrix diffusion may be even more relevant for dioxane than chlorinated solvents.
- Source zone treatment may have limited benefit for dioxane because of distinct mass distribution.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Management of groundwater sites impacted by 1,4-dioxane can be challenging due to its migration potential and perceived recalcitrance. This study examined the extent to which 1,4-dioxane's persistence was subject to diffusion of mass into and out of lower-permeability zones relative to co-released chlorinated solvents. Two different release scenarios were evaluated within a two-layer aquifer system using an analytical modeling approach. The first scenario simulated a 1,4-dioxane and 1,1,1-TCA source zone where spent solvent was released. The period when 1,4-dioxane was actively loading the low-permeability layer within the source zone was estimated to be <3 years due to its high effective solubility. While this was approximately an order-of-magnitude shorter than the loading period for 1,1,1-TCA, the mass of 1,4-dioxane stored within the low-permeability zone at the end of the simulation period (26 kg) was larger than that predicted for 1,1,1-TCA (17 kg). Even 80 years after release, the aqueous 1,4-dioxane concentration was still several orders-of-magnitude higher than potentially-applicable criteria. Within the downgradient plume, diffusion contributed to higher concentrations and enhanced penetration of 1,4-dioxane into the low-permeability zones relative to 1,1,1-TCA. In the second scenario, elevated 1,4-dioxane concentrations were predicted at a site impacted by migration of a weak source from an upgradient site. Plume cutoff was beneficial because it could be implemented in time to prevent further loading of the low-permeability zone at the downgradient site. Overall, this study documented that 1,4-dioxane within transmissive portions of the source zone is quickly depleted due to characteristics that favor both diffusion-based storage and groundwater transport, leaving little mass to treat using conventional means.

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Furthermore, the results highlight the differences between 1,4-dioxane and chlorinated solvent source zones, suggesting that back diffusion of 1,4-dioxane mass may be serving as the dominant long-term “secondary source” at many contaminated sites that must be managed using alternative approaches.

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## 1. Introduction

1,4-Dioxane (dioxane) is an emerging groundwater contaminant that poses significant challenges for safe and effective site management (Zenker et al., 2003; Mohr et al., 2010; Stuart et al., 2012; United States Environmental Protection Agency, USEPA, 2013; Postigo and Barcelo, 2015). It is a likely human carcinogen that is widely prevalent in soil and water environments impacted by chlorinated solvents (Anderson et al., 2012; Adamson et al., 2014; Adamson et al., 2015) due to its extensive use as a stabilizer for 1,1,1-trichloroethane (TCA) formulations (Abe, 1999; Mohr et al., 2010). There are still significant gaps in characterizing the extent of the problem, and our understanding of the behavior of dioxane in the subsurface is relatively limited and primarily based on its chemical characteristics. Due to its high solubility and limited ability to sorb to aquifer solids, it is expected to migrate rapidly in groundwater, particularly relative to co-occurring chlorinated solvents that are more subject to retardation. While there is recent evidence that dioxane plume footprints at many sites may not be larger than those of co-occurring contaminants (Adamson et al., 2014), there remains a potential for future plume expansion. These concerns are further exacerbated by the perceived recalcitrance of dioxane in the environment.

These characteristics also shape our interpretation of how a dioxane source zone differs from a chlorinated solvent source zone, and importantly, the appropriateness of various remedial options. Dioxane may be released as part of a chlorinated solvent dense non-aqueous phase liquid (DNAPL) and thus initially occupy the same source zone. In this case, it would be expected to be a relatively minor component, based on reports of 3% to 15% dioxane in TCA mixtures on a mass basis (Mohr et al., 2010). However, given that dioxane is essentially miscible in water, these NAPL compositions would still result in high effective solubilities based on an application of Raoult's Law (Mohr et al., 2010). As a result, it is anticipated that dioxane concentrations would be very high in the period following release and then diminish rapidly as dioxane mass was depleted from the source zone. If significant attenuation capacity was absent at a site, this would result in a high concentration plume that could travel downgradient for long distances. Depending on flow conditions, dioxane plume concentrations will eventually decline, but there is a risk that these lower strength plumes will cross into adjacent properties and/or pose risk to downgradient receptors. Conversely, TCA and other co-occurring chlorinated solvents are less subject to migration but may be present in the source zone at elevated concentrations for a more extended period. Because of this, the source zone would be expected to be dominated by chlorinated solvents and there may be no easily-discernible long-term source for dioxane.

A critical limitation of this type of conceptual model for dioxane source zones is that it ignores the potential contribution of matrix diffusion processes in sustaining elevated dioxane concentrations within the source zone and the downgradient plume. Matrix diffusion is used to describe the processes by which contaminants diffuse into and out of lower-permeability zones (e.g., clays, silts, bedrock) within a heterogeneous or fractured groundwater-bearing unit (Sale et al., 2013). This can result in significant long-term storage of contaminant mass due to the lack of advective flushing and the potential for sorption within these low-permeability zones. The release of these contaminants via back diffusion into adjacent transmissive zones has the potential to serve as significant and persistence secondary source, even after the primary source (e.g., NAPL) has been depleted or removed (Parker et al., 2008).

The importance of matrix diffusion on source and/or plume longevity is increasingly being recognized (Sudicky et al., 1985; Ball et al.,

1997; Liu and Ball, 2002; Parker et al., 2004; Chapman and Parker, 2005; Parker et al., 2008; Payne et al., 2008; West and Kueper, 2010; Rasa et al., 2011; Seyedabbasi et al., 2012; Chapman et al., 2012; Stroo et al., 2012; Leeson et al., 2013; Brown et al., 2012; McDade et al., 2013; Suthersan et al., 2013; Sale et al., 2013; Hadley and Newell, 2014; Matthieu et al., 2014; Yang et al., 2015). A recent report by the National Research Council (2013) emphasizes the need to better understand how matrix diffusion processes impact conceptual site models and projected remediation timeframes at “complex and difficult” sites (NRC, 2013). To-date, most of the research on matrix diffusion has focused on chlorinated solvents, which have relatively limited aqueous solubilities (generally ranging from low hundreds to low thousands of mg per L). As a result, the period during which a chlorinated solvent source can diffuse into adjacent low-permeability zones (i.e., the loading period) may be quite long. Studies involving higher solubility compounds with less sorptive capacity are less common (Rasa et al., 2011; Yang et al., 2015). Using modeling and field data from a gasoline spill site, Rasa et al. (2011) demonstrated that diffusion of methyl *tert*-butyl ether and *tert*-butyl alcohol mass into and out of lower-permeability silt layers contributed to persistence of these compounds in transmissive zones at a site even after the source was depleted.

Given the high solubility of dioxane, it is clear that a significant concentration gradient will exist to drive diffusion processes within heterogeneous formations (Mohr et al., 2010). However, it is less clear if the loading period for dioxane is sufficiently long such that diffusion should be considered an important process when evaluating management of dioxane-contaminated sites. This study tests the hypothesis that storage of dioxane mass within low permeability zones is significant and can contribute to concentrations in that are likely to be above acceptable limits for decades or longer. This is accomplished by modeling several different release scenarios to compare the impact of matrix diffusion on dioxane concentration and mass trends relative to those expected for co-occurring chlorinated solvents.

## 2. Methods

Concentrations and mass in the lower-permeability and transmissive zones for different scenarios were evaluated using a set of analytical solutions to matrix diffusion models described below. Simulations were performed with the help of the Matrix Diffusion Toolkit, a publicly-available free software tool developed for the Department of Defense to evaluate the potential impact of these processes on site trends (Farhat et al., 2013). Input values for representative concentrations and loading periods were selected using simple dissolution models that are also described below.

### 2.1. Matrix diffusion models

The impact of matrix diffusion on contaminant mass, concentration, and mass discharge was estimated using two different analytical models that have been coded into the Matrix Diffusion Toolkit. This first of these models was originally developed by Parker et al. (1994) and expanded in a guidance document for the Air Force (AFCEE, 2007). It is based on a simplified conceptual model of a two-layer aquifer system (a transmissive layer and a low-*k* layer) and considers two different time periods: (1) a *loading period* where there is a constant concentration of contaminants (e.g., NAPL) in the transmissive zone that drives contaminants into the low-*k* zone; and (2) a *release period*, where the transmissive zone is assumed to have no concentration, and an upper-range estimate of release from the low-*k* zone is generated. The source

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