Evidence for natural attenuation of 1,4-dioxane in a glacial aquifer system

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Abstract

Although 1,4-dioxane is generally thought to be recalcitrant, recent studies suggest it may degrade in the subsurface under ideal conditions. A fuller understanding of natural attenuation processes affecting 1,4-dioxane is therefore needed to assess its potential for in situ bioremediation. This investigation employed multiple lines of evidence to evaluate attenuation of 1,4-dioxane at the Gelman Site beneath the city of Ann Arbor, Michigan, USA. Data from a network of groundwater monitoring wells were used to determine attenuation metrics at individual wells and at the scale of a prominent 1,4-dioxane plume. A series of plume maps and historical remediation data were used to calculate changes in aqueous phase mass storage, mass influx rates, and mass removal rates over a 12-year period (2005–2017). Individual point and plume-scale metrics indicate that attenuation may be occurring at rates too small to meaningfully contribute to remediation results at the site. Conversely, plume-scale mass balance calculations reveal a 1,4-dioxane storage surplus for the first 6 years, followed by a storage deficit during the remaining 6 years that cannot be explained by mass influx or removal estimates, respectively. Mass balance deficits observed in this aquifer system are attributable to biodegradation and/or unrecognized discharge to surface water and storm drain systems at rates similar to remedial pump-and-treat mass removal during 2011–2017.

Keywords Contamination · Solute transport · Natural attenuation · Groundwater monitoring · USA

Introduction

1,4-Dioxane is classified as a Group B2 probable human carcinogen (USEPA 2006). When released into groundwater, its high miscibility and low retardation factor (Mohr 2010; USEPA 2017) limit the ability of processes such as sorption to attenuate 1,4-dioxane concentrations as plumes migrate. Until recently, researchers thought that its molecular structure also made it resistant to biodegradation (DiGuiseppi et al. 2016); consequently, 1,4-dioxane is considered a persistent contaminant of concern.

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Ex-situ remediation technologies such as pump-and-treat with advanced oxidation processes, are the primary methods employed to treat 1,4-dioxane contaminated aquifers (Zenker et al. 2003). Extracted water containing 1,4-dioxane is mixed with hydrogen peroxide and ozone, or exposed to ultraviolet light, to break the carbon bonds (Stefan and Bolton 1998; Zenker et al. 2003). These processes are often expensive and less than 100% effective (USEPA 2006; Stepien et al. 2014).

Recent laboratory experiments have shown the potential for both aerobic (Li et al. 2010, 2015) and less commonly anaerobic (Shen et al. 2008) biodegradation of 1,4-dioxane. Li et al. (2010) investigated 1,4-dioxane degradation in biostimulated and bioaugmented microcosms under low to warm temperature conditions. Li et al. (2015) measured biodegradation of 1,4-dioxane in environmental samples from three sites in California. Shen et al. (2008) used enriched iron(III)-reducing bacteria cultivated from sludge at a wastewater treatment plant to degrade 1,4-dioxane.

Before in situ bioremediation can be effectively employed to address 1,4-dioxane, a fuller understanding of natural attenuation processes affecting 1,4-dioxane is needed. Provided that sufficient data are available, attenuation—including biodegradation under natural conditions—can be assessed

through field data analyses combined with conceptual and mathematical modeling (Alvarez and Illman 2006). Adamson et al. (2015), for example, used statistical analysis of 1,4-dioxane measurements to determine that natural attenuation of 1,4-dioxane may be occurring in the presence of trichloroethylene, 1,1,1-trichloroethane, or 1,1-dichloroethene at 191 sites selected from the California GeoTracker database and 131 monitoring wells at 14 United States Air Force installations in the Environmental Restoration Program Information Management System. In another study, Gedalanga et al. (2016) used a combination of traditional lines of evidence (i.e., temporal and spatial trends, source and plume mass estimates, and fate and transport modeling) along with biomarker and compound specific isotope analysis to evaluate intrinsic 1,4-dioxane biodegradation at a landfill site.

The purpose of this study is to evaluate potential natural attenuation of 1,4-dioxane, which is present without any known co-contaminants, in a glacial aquifer system beneath Ann Arbor, Michigan. To achieve this goal, multiple methods were employed including point attenuation analysis at individual monitoring wells, bulk attenuation analysis along a longitudinal plume axis, and mass balance and spatial moment analyses throughout the study area. The

results add to a growing body of evidence suggesting that 1,4-dioxane is subject to natural attenuation processes including biodegradation.

Background and conceptual site model

1,4-Dioxane was used at the former Gelman Sciences, Inc. site (hereafter referred to as the Gelman Site), in Washtenaw County, Michigan, over a period of approximately 25 years between 1960 and 1985. The release history is not well documented. The source area, where processed water containing 1,4-dioxane leached into the subsurface from unlined wastewater disposal ponds and a spray irrigation field (Mohr 2010), is shown in Fig. 1. The underlying glacial aquifer system sits within the Fort Wayne moraine (a remnant of the Pleistocene glaciation) and consists of interconnected shallow and deep aquifers with different hydraulic gradients (Cypher and Lemke 2009; Frahm 2011; Lemke et al. 2013; Pappas 2016; Pruehs 2016). The unconsolidated glacial sediments are 50–90 m (160–300 ft) thick and consist of approximately two-thirds aquifer and one-third aquitard material by volume as interpreted by Frahm (2011). Site investigations have documented 1,4-dioxane migration eastward and westward from

Fig. 1 Map of the study area in central Washtenaw County, Michigan, USA showing the location of the Gelman Sciences source area and cross section W–W'. The red line identifies the boundary of the groundwater use prohibition zone defining the Eastern Area

the Gelman property at different depths within the aquifer system (e.g., Pall Life Sciences 2006, 2007a, b, 2009).

Characterization of the Gelman Site began more than three decades ago. Water sampling in the mid-1980's detected 1,4-dioxane in groundwater adjacent to the source zone at concentrations as high as 210,000 ppb ($\mu\text{g/L}$) (Fotouhi et al. 2006). Shortly thereafter, remediation efforts began with the installation of monitoring and extraction wells that have grown to a network of more than 230 shallow, intermediate, and deep wells. After 1,4-dioxane was discovered in an Ann Arbor municipal water supply well (City of Ann Arbor 2004), an institutional control prohibiting groundwater removal for human use was established by court order in 2005. The Eastern Area of the Gelman Site, delineated by the groundwater removal prohibition zone shown outlined in Fig. 1, provides the setting for this investigation. Along with a series of wells located adjacent to Wagner Road on its western edge, the Eastern Area includes 12 extraction wells (Table 1) and approximately 100 monitoring wells with data on extraction rates, static water levels, and 1,4-dioxane concentrations. In 2017, Michigan regulators reduced drinking water standards for 1,4-dioxane in groundwater from 85 to 7.2 ppb. Recent monitoring well sampling within the prohibition zone indicates decreasing 1,4-dioxane concentrations in some wells; however, several of these wells continue to exceed the revised Michigan standard by more than 1,000 ppb.

1,4-Dioxane in the Eastern Area originated in the Gelman Sciences source zone and migrated eastward across Wagner Road along complex pathways through the glacial aquifer system. Hydraulic conductivities inferred from pump tests, coupled with eastward sloping hydraulic gradients, yield seepage velocities in the range of 0.2–0.3 m/day (0.5–1 ft/day).

Table 1 Summary of Eastern Area 1,4-dioxane extraction well data (2005–2017)

Well	Average annual pumping rate (GPM) ^a	Mass removed (kg)
AE3	19	27
LB1	70	752
LB2	53	194
LB3	58	463
LB4	79	385
DOLPH (TW-2)	33	82
TW-12	11	6
TW-16	17	114
TW-18	176	2,084
TW-19	67	666
TW-21	70	275
TW-23	43	31
Sum	—	5,079

^a Gallons per minute (3.785 L min^{-1})

Concentrations in the source area have decreased from historically high values of 10,000–200,000 ppb to current concentrations of 2,000 ppb or less in response to pump-and-treat activities over the past two decades. West of Wagner Road, the vast majority of remedial mass removal occurred between 2001 and 2010. Many of the extraction wells in the source area exhibit asymptotic concentration declines to levels approaching 100–900 ppb (see Fig. S1 of the electronic supplementary material (ESM)). This indicates that back diffusion of 1,4-dioxane from low permeability zones now serves as a secondary source west of Wagner Road. 1,4-Dioxane migration from the Gelman Sciences source zone into the Eastern Area decreased in response to the installation of two purge wells along Wagner Road: TW-18, which became operational in January 2006; and TW-21, which began pumping in June 2010. Complete hydraulic containment has not been established, however, so the flux of 1,4-dioxane migrating from the source area into the Eastern Area is inferred to have continued at a declining rate over time.

Approximately 5,100 kg of 1,4-dioxane have been removed from the Eastern Area since 2005 (Table 1) using a continuous pump-and-treat system. Average annual pumping rates and annual 1,4-dioxane mass removed by each extraction well are given in Tables S1 and S2 of the (ESM), respectively. 1,4-Dioxane concentrations observed in monitoring wells within the prohibition zone have been reduced from historical highs of approximately 10,000 ppb to levels between 1,000–2,000 ppb. These reductions, which are attributed to ongoing remediation efforts, may have been enhanced by natural attenuation.

Because the total mass of 1,4-dioxane released at the site is undocumented, it is difficult to estimate the amount of 1,4-dioxane that remains in the aquifer system. Nevertheless, changes in the distribution of 1,4-dioxane over time in the Eastern Area can be inferred from a series of concentration maps drawn using measurements from the monitoring well network. These maps are contained in reports posted on the Michigan Department of Environment, Great Lakes, and Energy (EGLE)—formerly Michigan Department of Environmental Quality (MDEQ)—Gelman website (MDEQ 2018a, b). Further, the maps, which provide a basis for the mass balance analysis described in the following, depict advancement of the then-applicable 85 ppb concentration contour to a position approximately 3 km east of the western boundary of the Eastern Area (Fig. 2), where it has remained more or less stationary since 2011.

Two potential hypotheses could explain the apparent stagnation of the inferred leading edge of the 85 ppb isoconcentration line. The current network of monitoring wells in the downgradient portion of the Eastern Area may be insufficient to track 1,4-dioxane as it migrates eastward toward the Huron River. Alternatively, natural attenuation could be degrading 1,4-dioxane at a rate approximately equal to that which advective and

Fig. 2 Approximate position of the leading edge of the plume defined by the 85 ppb isoconcentration line in 2017. The source zone is outlined in black. Wagner Road, the western boundary of the prohibition zone, is annotated. Monitoring and extraction wells used in the analyses are labeled

dispersive flux transport dioxane to the leading edge of the plume. Evaluation of the latter hypothesis provided the primary motivation for this investigation.

Methods

Multiple lines of evidence were used to evaluate natural attenuation within the Eastern Area of the Gelman Site. These included order-of-magnitude, point attenuation, and half-life analyses of concentration histories at individual wells, in addition to bulk attenuation, mass balance and spatial moment analyses to examine overall plume movement and evolution (Table S3 of the [ESM](#)). The investigation at individual wells focused on twenty Eastern Area monitoring wells experiencing concentration reductions over time with trends potentially resulting from natural attenuation processes. Bulk attenuation analysis examined 13 wells positioned along the inferred central axis of the plume to characterize how distance from the source zone relates to observed concentration changes. Mass balance and spatial moment analyses relied on the greater population of monitoring wells located in the Eastern Area and the adjacent source area.

Order-of-magnitude reduction

Order-of-magnitude values quantify the reduction of 1,4-dioxane concentration at individual monitoring wells. They were determined by taking the $\log_{10}$ of maximum concentration ratios:

$$OM_{red} = -\log_{10}(C_t/C_0) \quad (1)$$

where OM_{red} is the order of magnitude reduction, C_t is the most recent (2017) yearly maximum concentration, and C_0 is the historic maximum concentration detected in each well.

Point attenuation rates and half-lives

Point attenuation analysis was used to estimate first-order contaminant decay rates in individual monitoring wells, which were subsequently used to extrapolate the time required for 1,4-dioxane concentrations to decrease to the relevant Michigan standard at the respective well locations. Exponential regression of maximum yearly concentrations versus time yielded a first-order point decay rate coefficient (K_{point}) from the slope—an example is shown in Fig. S2 of the [ESM](#). The length of time needed to reduce concentrations by one half was then determined as:

$$t_{1/2} = \frac{\ln(2)}{K_{point}} \quad (2)$$

where $t_{1/2}$ is the half-life of the contaminant concentration at each well and K_{point} is the regression slope from the exponential regression performed at each well.

The time required to reduce 1,4-dioxane concentrations to acceptable regulatory standards was determined by:

$$t = \frac{-\ln \left[\frac{C_{goal}}{C_{start}} \right]}{K_{point}} \quad (3)$$

where C_{goal} is the applicable criterion and C_{start} is the y-intercept value from the exponential regression (USEPA 2002).

Bulk attenuation

1,4-Dioxane reduction in response to all attenuation processes (e.g., dispersion, sorption, biodegradation) was evaluated at the plume scale using maximum observed concentrations at wells located along the inferred axis of the plume. The natural log of the historical maximum concentration for each well was plotted against the distance from the source zone on the Gelman property to define a bulk attenuation decay coefficient (USEPA 2002):

$$K_{\text{bulk}} = \left(\frac{dC}{dx} \right) \left(\frac{V_s}{R} \right) \quad (4)$$

where $\frac{dC}{dx}$ is the change in concentration with respect to the distance from the source, V_s is the seepage velocity (assumed to be 110 m/year), and R is the retardation factor (assumed to be 1.0). If the effects of dispersion and sorption are small, K_{bulk} will approximate a first-order biodegradation rate (USEPA 2002).

The time required for any part of the plume to attenuate to Michigan groundwater standards as it migrates downgradient can be determined by:

$$t = \frac{-\ln \left[\frac{C_{\text{goal}}}{C_{\text{dgw}}} \right]}{K_{\text{bulk}}} \quad (5)$$

where C_{goal} is the applicable criterion, and C_{dgw} is the maximum measured concentration at a specified well downgradient from the source zone. Additionally, the distance contaminants will travel (L) before concentrations diminish to C_{goal} was calculated using:

$$L = \frac{V_s t}{R} \quad (6)$$

where t is the travel time determined from Eq. (5).

Mass balance

Changes in 1,4-dioxane mass storage within the Eastern Area aquifer system were analyzed using three components: (1) total influx of 1,4-dioxane crossing Wagner Road into the prohibition zone; (2) annual integrated estimate of total mass-in-place removed through pump-and-treat remediation efforts; and (3) total mass-in-place determined from Gelman concentration maps for 2005–2017.

The annual mass flux of 1,4-dioxane into the Eastern Area during 2008, 2012, and 2016 was estimated using hydraulic conductivity distributions (Fig. 3) and concentration contours along a profile parallel to Wagner Road (Fig. 4). Similar cross section concentration profiles for years 2012 and 2016 are included in Figs. S3 and S4 of the *ESM*. Hydraulic gradients near Wagner Road ranging from 6.8×10^{-4} to 2.1×10^{-3} were estimated from equipotential maps at shallow and deep plume levels (FTCH 2009a, b; Fleis and Vandenbrink, 2012a, b, 2016a, b). Horizontal hydraulic conductivity values assigned to aquifer (35 m/day) and aquitard (0.023 m/day) intervals were obtained from Pruehs (2016). Pruehs' (2016) analysis suggested that bedrock faults and fractures had relatively little effect on 1,4-dioxane transport, so potential dioxane transport through the Mississippian Coldwater Shale bedrock was neglected. Mass flux, calculated as the product of concentration and volumetric water flux determined using Darcy's Law, was integrated over the area of each cross section (Figs. 3 and 4; Figs. S3 and S4 of the *ESM*) at a resolution of $0.3 \text{ m} \times 0.3 \text{ m}$ ($1 \text{ ft} \times 1 \text{ ft}$) with an assumed effective porosity of 30%.

The annual mass of 1,4-dioxane removed through remediation was determined from monthly National Pollutant Discharge Elimination System (NPDES) reports posted on

Fig. 3 Cross-section W–W' modified from Frahm (2011) showing the distribution of aquifer (yellow) and aquitard (green) hydrofacies along the western boundary of the Eastern Area at Wagner Road. View looking downgradient. W–W' profile location shown on Fig. 1. Vertical exaggeration 6:1

Fig. 4 2008 1,4-dioxane concentration (ppb) used in integrated mass flux calculations. View looking downgradient. W–W' profile location shown on Fig. 1. Vertical exaggeration 6:1

the MDEQ Gelman selected documents website (MDEQ 2018a). Annual estimates of 1,4-dioxane storage within the Eastern Area were generated using published concentration maps for 2005–2017 (FTCH 2005a, b, 2006, 2008a, b, 2009c; d; Pall Life Sciences 2006; Fleis and Vandenbrink 2010, 2011, 2012c, 2013, 2014, 2015, 2016c, 2017). Concentration contours at the detection limit of 1 ppb were taken from maps generated by the Environmental Health Division of the Washtenaw County Health Department (Washtenaw County 2016). Shallow and deep plume concentration maps were digitized and integrated with net contaminated aquifer thickness maps over the Eastern Area at a 3 m × 3 m (10 ft × 10 ft) resolution. A uniform porosity of 30% was assumed. Potential sinks such as sorption, biodegradation, uncharted flow paths bypassing the existing monitoring well network, and undocumented discharges to surface streams and storm drains were not included in the analysis. Estimated changes in 1,4-dioxane storage within the Eastern Area were then compared with mass flux estimates to determine potential surpluses or deficits in the mass balance.

Spatial moments

Plume-scale changes in the spatial and temporal distribution of 1,4-dioxane within the Eastern Area were further investigated using spatial moment analysis (Freyberg 1986). The Monitoring and Remediation Optimization System (MAROS 3.0) decision support software (Ling et al. 2004; GSI Environmental 2012) was utilized to determine changes in the zeroth, first, and second spatial moments from available monitoring well data. The zeroth spatial moment represents an integrated measure of the total dissolved contaminant mass. The first moment provides the geographic position of the center of mass, and its change in location over time can be used as an indicator of mean solute velocity. The second moment can be used to infer an expanding, stable, or shrinking plume. MAROS output also

includes Mann-Kendall trend analysis to provide plume stability information (Ling et al. 2004).

Time series 1,4-dioxane concentration measurements from 52 monitoring wells were analyzed using MAROS over the period from 2006–2017. A uniform aquifer thickness of 40 m (130 ft) and a constant porosity of 30% were assumed. Yearly estimates of dissolved dioxane mass were plotted to evaluate trends in dioxane storage in the Eastern Area. Changes in the location of the center of mass were examined to evaluate plume stability.

Results and discussion

Order-of-magnitude reduction

Figure 5 compares the historic and most recent (2017) maximum concentrations for the 20 monitoring wells involved in the natural attenuation investigation. The well name designators ‘s’ and ‘d’ indicate shallow or deep screens at nested well locations but do not imply a particular absolute depth or elevation. Concentrations in most wells decreased between zero and one order-of-magnitude (Fig. 5; Table 2), similar to reductions reported by Adamson et al. (2015) for several 1,4-dioxane contaminated sites in California. The degree to which remediation and/or natural attenuation contributed to these concentration reductions is uncertain. Wells MW-72s and MW-15d experienced approximately two and four orders-of-magnitude reductions respectively, and their observed concentrations dropped below the Michigan 1,4-dioxane standard of 7.2 ppb. Reductions in wells MW-15s and MW-15d can be attributed to their proximity, 30 m (90 ft), to a nearby extraction well. Concentration reductions in MW-72s, which is located 1,100 m (3,600 ft) downgradient from the nearest extraction well, are harder to explain, particularly when compared to MW-72d, which is screened 20 m (67 ft) lower in elevation. Significant differences in both the maximum dioxane concentrations and the degree of reduction observed in

Fig. 5 Order of magnitude (OM) reductions of recent (2017) versus historical maximum well concentrations for 1,4-dioxane in the Eastern Area

MW-72s and MW-72d illustrate differential migration of 1,4-dioxane at various depths throughout the aquifer system that confound interpretation of order-of-magnitude analysis for individual wells.

Point attenuation rates and half-lives

Table 2 includes decay rate coefficients and half-lives calculated from first order regression analyses. Although concentrations are attenuated in every well, decay coefficients are small and predicted times for concentrations to fall below 7.2 ppb exceed 50 years in many cases. Relatively slow decay rates such as these could result from steady contaminant loading and/or the absence of significant biodegradation. Variability in attenuation behavior among the wells analyzed may result from differential effects of remediation or spatial variability of conditions favoring biodegradation within the complex glacial aquifer system. Additional analyses involving multiple wells were therefore examined to evaluate natural attenuation at a larger scale.

Bulk attenuation

Reductions in concentrations over time at wells located along the inferred longitudinal axis of the plume indicate that attenuation is occurring at those wells. If biodegradation is responsible for all or part of this attenuation, contaminant transport theory suggests that maximum concentrations at well observation points should decrease with increasing migration from the source (Domenico and Schwartz 1998). In the Eastern Area plume axis wells, the natural log of the maximum historical concentration regressed as a function of transport distance from the source zone generated a small negative slope (Fig. 6, dashed line), which could be consistent with biodegradation but is not statistically significant (p -value = 0.34). A similar regression using the easternmost 6 points on the chart

(Fig. 6, solid line), representing wells that are 500m or more downgradient from purge wells TW-18 and TW-21 along Wagner Road, yields a statistically significant regression (p -value = 0.037).

The observed decrease in maximum concentrations among the easternmost six wells along the plume axis was used in conjunction with the assumed seepage velocity to estimate a bulk attenuation decay coefficient of 0.017 year^{-1} (Eq. 4). The potential for 1,4-dioxane to reach the Huron River at the eastern boundary of the prohibition zone was then evaluated using estimated decay times (Eq. 5), and travel distances (Eq. 6), to decline to State of Michigan criteria. In MW-72d, dioxane concentrations began to decrease from maximum observed values of approximately 3,800 ppb beginning in 2012. Neglecting sorption and mass reductions from ongoing remediation, it would take an estimated 150 years along a potential transport distance of 17 km for dioxane concentrations to attenuate from 3,800 ppb to the groundwater/surface-water Interface (GSI) criterion of 280 ppb. Alternatively, it would require approximately 370 years and 41 km to reach the 7.2 ppb Michigan drinking water criterion. Further downgradient, near the mapped leading edge of the plume, well MW-83s recorded peak concentrations of approximately 650 ppb in 2010. Similar calculations yielded attenuation time and distance estimates of 50 years/5 km and 260 years/29 km to reach 280 or 7.2 ppb, respectively. Although the estimated travel times are sensitive to the assumed seepage velocity, the estimated travel distances are substantially larger than the 4.5 km length of the prohibition zone, suggesting high potential for 1,4-dioxane to reach the Huron River at relevant regulatory concentrations.

These estimates do not include the benefits of active site remediation, however. As 1,4-dioxane continues to migrate through the Eastern Area, a combination of remediation and attenuation are expected to reduce concentrations, even if the source of the plume has not been completely contained or removed. Therefore, a mass balance evaluation on the

Table 2 Observed concentrations and calculated natural attenuation metrics at individual wells

Well	Maximum historical concentration (ppb)	Recent (2017) maximum concentration (ppb)	Order-of-magnitude reduction	K_{point} decay coefficient	P -value for K_{point} decay coefficient	Half-life (years)	Decay time to 7.2 ppb (years from 1/1/1985)
MW-15 ^a	123	11	1.05	0.100	0.003	6.9	18
MW-15d ^a	5,400	1	3.73	0.385	<0.001	1.8	22
MW-30d ^a	1,626	240	0.83	0.308	<0.001	2.3	44
MW-72s ^a	168	2	1.88	0.308	<0.001	2.3	29
MW-72d ^a	3,788	1,300	0.46	0.076	<0.001	9.1	103
MW-79s	1,222	580	0.32	0.058	0.023	12.0	86
MW-81	550	320	0.24	0.085	<0.001	8.2	77
MW-83s ^a	644	420	0.19	0.079	0.106	8.8	79
MW-84s ^a	908	700	0.11	0.053	0.624	13.1	113
MW-85 ^a	2,476	1,100	0.35	0.069	0.006	10.0	105
MW-88	1,330	340	0.59	0.135	<0.001	5.1	57
MW-101	497	120	0.62	0.179	0.001	3.9	49
MW-105s ^a	3,803	620	0.79	0.182	<0.001	3.8	55
MW-105d ^a	1,104	250	0.65	0.146	<0.001	4.7	56
MW-106s ^a	1,676	280	0.78	0.179	<0.001	3.8	50
MW-108s ^a	2,946	360	0.91	0.220	<0.001	3.2	50
MW-108d ^a	4,054	1,200	0.53	0.102	<0.001	6.8	84
MW-115	1,304	430	0.48	0.117	<0.001	5.9	67
MW-116	1,215	420	0.46	0.141	0.006	4.9	60
MW-119	475	97	0.69	0.150	0.200	4.6	49
Minimum	123	1	0.11	0.053	–	1.8	18
Mean	1,765	440	0.78	0.154	–	6.1	63
Median	1,263	350	0.60	0.138	–	5.0	56
Maximum	5,400	1,300	3.73	0.385	–	13.1	113

^a Wells located along the central plume axis

Fig. 6 Bulk attenuation of 1,4-dioxane concentrations as a function of inferred transport distance along the central plume axis. Natural log of historical 1,4-dioxane concentrations are shown by black squares and recent (2017) maximum concentrations are shown as gray circles. Regression lines for historical maximum concentrations: dashed = all wells, solid = easternmost six wells

Eastern Area was completed using concentration data from 2005–2017 to evaluate the relative contributions of remedial and natural attenuation.

Mass balance

Figure 7 illustrates the areal distribution of 1,4-dioxane within the Eastern Area at the first (2005), middle, (2011) and final (2017) years of the analysis. A complete montage of maps illustrating changes in mapped 1,4-dioxane concentrations during the 12-year study period is provided in Fig. S5 of the [ESM](#). Annual estimates of aqueous phase dioxane mass are plotted in Fig. 8. Total dioxane mass in the Eastern Area ranged from 13,000 to 17,000 kg; however, the trend in mass storage shown in Fig. 8 indicates an increase followed by a reduction in mass during the period of investigation. From 2005 to 2011, 1,4-dioxane mass increased by approximately 3,600 kg. In contrast, from 2011 to 2017, the mass of 1,4-dioxane decreased by approximately 4,000 kg (Table 3). Mass balance calculations including estimated advective influx and measured remedial removal of dioxane, were therefore calculated separately for these two time periods.

1,4-Dioxane mass flux estimates across Wagner Road into the Eastern Area decreased from 150 kg/year in 2008 to 60 kg/year in 2012, and 40 kg/year in 2016. Decreasing dioxane transport into the Eastern Area over this time period is consistent with continuing pump-and-treat operations in extraction wells located on the former Gelman property and adjacent to Wagner Road. Assuming the mass influx rate was steady during the first 6 years, the 2008 influx estimate of 150 kg/year was extrapolated to generate an estimate of 900 kg influx from 2005 to 2011. Influx estimates for 2012 and 2016 were averaged and applied to generate an estimate of 300 kg during the period 2011–2017 (Table 3). During the same time periods, extraction wells within and adjacent to the Eastern Area removed 3,000 kg of dioxane from 2005–2011 and 2,100 kg of dioxane from 2011–2017 (Table 3).

Subsequent mass balance calculations yield a surplus of 5,700 kg during 2005–2011 and a deficit of 2,200 kg for 2011–2017 (Table 3). The net increase during the initial period represents an additional influx of approximately 950 kg/year that is not accounted for by our estimates. Assuming that 1,4-dioxane from this source continued to be added to the Eastern Area at the same rate during 2011–2017, the net mass deficit during 2011–2017 grows from 2,200 to 7,900 kg (1,300 kg/year). With or without this inferred additional influx, mass balance results suggest that natural attenuation, potentially from biodegradation, played an important role in reducing observed concentrations at the Gelman Site during the latter half of the study period.

Spatial moments

MAROS site summary and moment analysis reports for the Eastern Area are presented in Figs. S6–S10 of the [ESM](#). Results are generally consistent with the mass balance evaluation based on time series concentration maps (see section ‘[Mass balance evaluation](#)’). Zeroth spatial moment calculations show a clear trend of increasing dioxane mass over the first 6 years of the study period followed by decreasing dioxane mass during the remainder (Fig. S8 of the [ESM](#)). MAROS estimated changes in storage during the first half (+5,600 kg) and second half (–4,600 kg) of the study period (Fig. S8 of the [ESM](#)) compare well with those estimated from the concentration maps (Table 3). Overall, the dioxane mass storage estimates from zeroth moments reported here are less than those calculated with mapped concentrations and aquifer thickness maps (Fig. 8). These estimates scale directly with the average aquifer thickness input parameter, however, and thus could be adjusted. Mass estimates from zeroth spatial moments interpolated using Delaunay triangles (Ling et al. 2004) are arguably more objective than their map-based counterparts. For this study, however, they are considered less robust because they depend on the spatial distribution of monitoring wells

Fig. 7 1,4-Dioxane concentrations in the Eastern Area for years 2005, 2011, and 2017

and may be subject to overshoot or undershoot resulting from steep gradients generated by closely spaced data points proximal to areas with no data (McLean et al. 2019).

First-order moment analysis indicates that the calculated distance from the source area to the center of mass increased by approximately 300 m (1,000 ft) during the study period (Fig. S9 of the [ESM](#)). The location of the center of mass was relatively stable during the first 7 years, however,

followed by a period of moderate advance to the northeast from 2013 to 2017 (Figs. S9 and S10 of the [ESM](#)). This result may be driven by continuing migration of a dioxane slug beyond the reach of extraction wells in the vicinity of Wagner Road (i.e., near the western boundary of the Eastern Area) combined with the bifurcation of dioxane movement along two separate pathways to the east and northeast (Figs. 2 and Fig. 7 and Fig. S5 of the [ESM](#)). This result is interesting

Fig. 8 Integrated 1,4-dioxane mass estimates in the Eastern Area for the years 2005–2017

because it suggests that the center of mass may be advancing at the same time that the mapped leading edge appears to remain stable.

Potential 1,4-dioxane attenuation processes

Several potential mechanisms, including hydrodynamic dispersion, sorption, and biodegradation, may have contributed to the observed and inferred attenuation of dioxane in this study. In addition, mass flux through unidentified pathways offers another possible explanation for inferred 1,4-dioxane mass reductions in the Eastern Area. First order approximations using sorption coefficient (K_d) values inferred from the generally accepted range of retardation factors (ATSDR 2012) indicated that sorbed mass could equate to 5–30% of the total aqueous phase mass in the Eastern Area in 2011. However, declining aqueous phase 1,4-dioxane concentrations observed throughout the majority of the Eastern Area suggest that sorption processes did not represent a significant sink during the study period. Diffused mass estimates calculated using assumptions similar to those modeled by Adamson et al. (2016) also suggested that diffusion would not serve as a material source or sink of dioxane in the Eastern Area during the study period. Consequently, diffusion and sorption were assumed to be negligible in this investigation. Biodegradation and bypass are discussed in more detail in the following.

Aerobic biodegradation of 1,4-dioxane has been demonstrated in a growing number of laboratory investigations (e.g., Parales et al. 1994; Zenker et al. 2000; Kim et al. 2009; Sei et al. 2010; Mahendra et al. 2013; Li et al. 2014; Inoue et al. 2016; Zhou et al. 2016; Barajas-Rodriguez and Freedman 2018). Metabolic degradation of 1,4-dioxane has been demonstrated using a variety of bacterial strains including *Pseudonocardia dioxanivorans* CB1190 (Parales et al. 1994; Mahendra and Alvarez-Cohen 2005), *P. benzenivorans* B5 (Mahendra and Alvarez-Cohen 2006), and *Mycobacterium* sp. PH-06 (Kim et al. 2009). In the majority of these investigations, reduction of 1,4-dioxane concentrations was inversely related to increased bacterial cell growth, suggesting that these bacteria are capable of using 1,4-dioxane as a sole carbon and energy source. In cometabolic biodegradation studies, the addition of substrates such as tetrahydrofuran (THF) resulted in a lag time before 1,4-dioxane degradation was observed (Mahendra and Alvarez-Cohen 2006; Vainberg et al. 2006).

In recent field trials, Lippincott et al. (2015) stimulated in situ 1,4-dioxane biodegradation using propane bio-sparging and bioaugmentation at a United States Air Force base in California. Chu et al. (2018) demonstrated in situ aerobic cometabolic biodegradation of 1,4-dioxane to concentrations below 3 µg/L at the former McClellan Air Force Base near Sacramento, California.

Fewer investigations have examined 1,4-dioxane biodegradation under anaerobic conditions (Steffan 2007; Shen et al.

Table 3 Mass balance estimates

Parameter	Estimation method	2005–2011	2011–2017
Changes in mass storage (kg)	Interpolation from concentration contour maps	3,600	–4,000
Advective mass influx (kg)	Flux across cross section W–W' along Wagner Road	900	300
Remediation mass removal (kg)	Integrated extraction well volumes and concentrations	3,000	2,100
Net sources (kg)	Back calculated	5,700	–
Net sinks (kg)	Back calculated	–	–2,200

2008; Sekar and DiChristina 2014; Arve 2015). Steffan (2007) was unable to stimulate 1,4-dioxane biodegradation under nitrate, iron, sulfate, and methanogenic reducing conditions. Shen et al. (2008) used enriched Fe(III)-reducing bacteria cultivated from municipal wastewater treatment sludge, in conjunction with humic acid, to stimulate the degradation of 1,4-dioxane under anaerobic conditions. The study noted that 50% of the 1,4-dioxane was mineralized. Sekar and DiChristina (2014) demonstrated 1,4-dioxane biodegradation in experiments conducted under alternating aerobic and anaerobic conditions. Increased biodegradation was observed during the aerobic cycles, and little to no degradation occurred during the anaerobic cycles. Experiments by Arve (2015) suggested the potential for anaerobic biodegradation of 1,4-dioxane in Fe(III)-humic acid amended microcosms with the addition of acetate. However, none of these investigations has convincingly demonstrated anaerobic biodegradation of 1,4-dioxane.

Unrecognized discharge into surface-water bodies represents another potential sink for 1,4-dioxane in the Eastern Area. Subsurface flow along preferential flow paths bypassing widely spaced monitoring wells in the easternmost Eastern Area could permit dioxane to travel undetected to the Huron River, the expected discharge location for the aquifer system (Pappas 2016; Pruehs 2016). Alternatively, 1,4-dioxane contaminated water could discharge into the Allen Creek drain system (Fig. 1), which includes five principle tributaries that converge into an engineered outlet at the Huron River. Artesian conditions in the eastern portion of the Eastern Area contribute to this possibility. Recent sampling within the Allen Creek-West Park SW storm drain detected 1,4-dioxane at concentrations in the range of 4–19 ppb (MDEQ 2017, 2018c). Although these observations fall below the Michigan GSI standard, the presence of dioxane suggests that contaminated groundwater may be discharging into the Allen Creek drain. Expansion of the downgradient monitoring well network and continued storm drain sampling are necessary to determine the extent of 1,4-dioxane discharge to the Allen Creek drain and Huron River.

Limitations

This study is limited by the temporal and spatial resolution, and, in some instances, the availability of the site data upon which it is based. The monitoring well network provides a set of discrete concentration measurements at positions that were chosen to optimize remedial objectives. Consequently, the spatial density of monitoring wells is greater closer to the source zone and becomes sparser toward the leading edges of the plume. As a result, uncertainty in the definition of mapped concentrations and inferred mass distributions increases from west to east across the study area.

Results of plume scale analyses such as the mass balance and spatial moment calculations employed here are dependent on the distribution of control points—for example, the first moment analysis indicates a shift in the center of mass of approximately 300 m (1,000 ft) to the northeast between 2006 and 2017 (Fig. S10 of the ESM). Possible effects of this shift on mass balance estimates have not been quantified in this study; however, the distance is small relative to the overall dimensions of the plume in the Eastern Area and the effects are therefore expected to be negligible.

In addition, wells at the Gelman Site are not all sampled at the same time. Some are sampled on a monthly basis, while others are sampled less frequently (annually, bi-annually, or quarterly). Thus, measurements used to identify annual or historical maxima, as well as the changing distribution of 1,4-dioxane in the aquifer system, are subject to variable temporal resolution. Nevertheless, the 1,4-dioxane isoconcentration maps used to estimate changes in mass storage in this study were updated twice each year and are believed to provide a reasonable record of changes in 1,4-dioxane distributions over the 12-year study period.

Another limitation inherent in the 1,4-dioxane concentration map series is its utilization of the 85 ppb contour to define the limits of groundwater contamination. This is a result of the applicable regulatory standard when the maps were made. A sensitivity analysis was run to determine the fraction of 1,4-dioxane mass stored in low concentration zones around the perimeter of the plume that is not included in our dioxane mass calculations. Using the 1 ppb isoconcentration contour on the Washtenaw County Health Department Map (Washtenaw County, 2016), dioxane at concentrations between the 1 and 85 ppb contours was found to represent approximately 6% of the total mass, a relatively small fraction. Again, these calculations are based on maps that rely on the available monitoring well network and do not account for potential missing mass in areas where monitoring wells are absent.

First-order approximations suggested that sorption and diffusion cannot account for the inferred sources or sinks of dioxane in the Eastern Area during the study period; however, site-specific sorption (K_d) values have not been quantified. A separate investigation to determine sorption capability of the aquifer and the aquitard materials is planned using sediments from a site core. Evidence for back diffusion of dioxane from low permeability zones is present in the form of asymptotic concentrations observed in extraction wells west of the study area. Quantification of diffusion dynamics and the magnitude of diffusive mass storage in the Eastern Area, where historically lower concentrations have been observed, would require a separate modeling effort that is beyond the scope of this study.

Finally, although this study provides indirect evidence for biodegradation at the Gelman Site, quantification of degradation rates is not possible from the methods employed. Direct evidence, in the form of microcosm experiments using

environmental samples from the site, is required to confirm biodegradation activity. Relevant geochemical data characterizing subsurface REDOX conditions are not available in the public domain; however, geochemical measurements collected during low flow testing of six Eastern Area wells from December 2016 through March 2019 was recently released (D. Hamel, Michigan Department of Environment, Great Lakes, and Energy, unpublished data, 2019). The wells are screened at depths ranging from 29 to 53 m (94–174 ft) and are positioned along the central axis as well as the mapped perimeter of the plume (as defined by 85 ppb contour). These measurements demonstrate a wide variability in dissolved oxygen (DO) concentrations ranging from -0.05 to 3.28 mg/L, representing saturations of 0–22% oxygen based on equilibrium with the atmosphere at the respective sample temperatures. Oxidation-reduction potential (ORP) values ranged from -317 to $+138$ mV, suggesting anaerobic conditions in the range generally associated with nitrate and manganese reduction. These data displayed both temporal and spatial variability that is not readily explained by their position with respect to the plume. They may therefore reflect complexity that is governed by subsurface physical and biological heterogeneity. Determining the likelihood of aerobic and/or anaerobic biodegradation will require carefully designed microcosm experiments using 1,4-dioxane contaminated groundwater from the Gelman Site.

Conclusions

This investigation examined evidence for natural attenuation within a multi-layered aquifer system beneath the city of Ann Arbor, Michigan, USA. Results of the study are mixed. Observed decreases in 1,4-dioxane concentrations in monitoring wells within the Eastern Area of the Gelman Site demonstrate that attenuation is occurring. Most wells with decreasing concentrations have experienced less than one order of magnitude reduction, although several wells exhibited greater reductions that can be attributed to ongoing remediation. Small decay coefficients and large time estimates for concentration reductions to the Michigan drinking water criterion at individual wells indicate that natural attenuation may be occurring at rates that are too slow to meaningfully affect remediation results without enhancements (e.g., Lippincott et al. 2015). In contrast, mass balance and spatial moment analyses suggest that natural attenuation is occurring at a rate that could potentially contribute to remediation efforts. The estimated decrease in 1,4-dioxane mass storage during the second half of the study is approximately twice that of the mass extracted during the same period (Table 3). This implies that natural attenuation was responsible for removal of 1,4-dioxane from the Eastern Area at a rate similar to remedial pump-and-treat during 2011–2017.

1,4-Dioxane has been thought to resist attenuation due to its high miscibility, lack of sorption potential, and recalcitrant chemical structure. Nevertheless, the findings of this study and others (Mahendra and Alvarez-Cohen 2006; Mahendra et al. 2013; Li et al. 2010, 2015; Adamson et al. 2015; Gedalanga et al. 2016) provide evidence to suggest that 1,4-dioxane is subject to natural attenuation processes, including biodegradation. Evidence from the Eastern Area of the Gelman Site is insufficient to determine to what extent observed attenuation results from biodegradation, uncharted flows along preferential pathways, or surface discharges through storm drain systems, however. Thus, additional site-specific studies evaluating natural attenuation mechanisms including biodegradation along with hydrogeologic and numerical modeling studies to evaluate flow paths and surface discharge are necessary to support the findings in this study. The uncertainties illustrated here, coupled with the expensive and time-consuming nature of advanced oxidation treatments, underscore the need to better understand the ability of natural attenuation to enhance cleanup efficiency and potentially reduce costs at 1,4-dioxane contaminated sites.

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