

Atmosphere of wet basements as a novel route for potential residential exposure to 1,4-dioxane vapor

Robert E. Bailey^{1,2} and Rita Loch-Caruso^{2,3}

Abstract

Detection of 1,4-dioxane has been reported in shallow groundwater in neighborhoods of the city of Ann Arbor, Michigan. Michigan has a voluntary 1,4-dioxane shallow groundwater screening level based on its potential for vapor intrusion. Calculations show that if 1,4-dioxane-contaminated water were to enter a basement and evaporate, potentially unhealthy concentrations of 1,4-dioxane could arise in homes with damp basements under certain conditions. Potential residential risk is suggested if: 1) shallow groundwater is within 3 m of the surface, 2) groundwater 1,4-dioxane concentration exceeds 150 µg/L, and 3) a basement has higher humidity than the upper floors. Different from vapor intrusion, this suggests that liquid water intrusion with subsequent volatilization within a structure may be a novel exposure pathway for 1,4-dioxane.

Addresses

¹ Bailey Associates, 424 Little Lake Drive, Suite 13, Ann Arbor, MI, 48103, USA

² Coalition for Remediation of Dioxane, Washtenaw County, MI, USA

³ Department of Environmental Health Sciences, University of Michigan, 1415 Washington Heights, Ann Arbor, MI, 48109, USA

Corresponding author: Bailey, Robert E. (bob.bailey734@gmail.com)

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1,4-Dioxane pollution, Shallow groundwater, Protective air concentration, Vapor intrusion, Volatilization, Indoor air pollution.

Introduction

A plume of groundwater contaminated with 1,4-dioxane is approaching the land surface in central Ann Arbor, Michigan. This near-surface contamination is the result of eastward migration of 1,4-dioxane-contaminated groundwater from the Gelman Sciences, Inc. site along a path with decreasing land elevation [1,2]. The chemical and physical properties of 1,4-dioxane lead it to persist and move with the water underground. It is miscible

with water and does not readily volatilize from water [3]. Nonetheless, if liquid water contaminated with 1,4-dioxane were to enter a residence, then there is the potential for a hazardous vapor concentration from volatilization inside the residence even if groundwater concentrations present low vapor intrusion risk.

In this article, we describe calculations that illustrate the difference in risk potential from contaminated groundwater for evaporation of liquid water containing 1,4-dioxane in a basement compared with vapor intrusion. This project was initiated to explore a basis for evaluating the potential risk from 1,4-dioxane in shallow groundwater in residential areas using the city of Ann Arbor, Michigan, as an example.

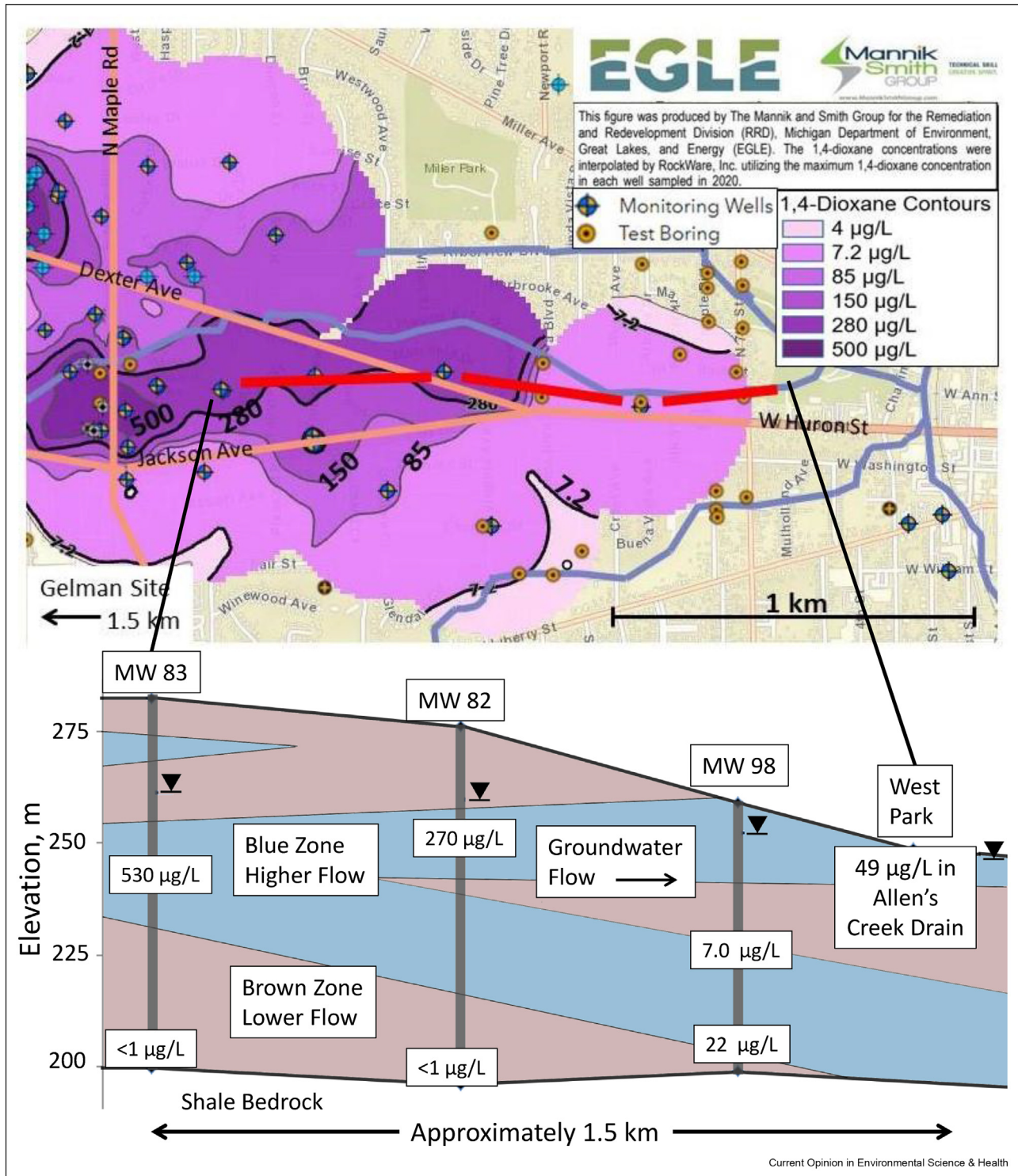
Site description

Wastewater management practices from 1966 to 1986 at Gelman Sciences, Inc. allowed 1,4-dioxane to contaminate groundwater [4*]. The resulting contamination plume, defined by concentrations above 1 µg/L, has spread laterally to an estimated area approximately 1.5 km wide by 7 km long (10 km²). The eastern portion of this groundwater plume is shown on the map in [Figure 1](#) (top panel).

The underlying geology of this area is approximately 50–90 m of unconsolidated glacial deposits above relatively impermeable Mississippian Coldwater Shale [5,6,7**]. Hydrogeological analysis delineating the extent of 1,4-dioxane contamination has revealed a complex series of interconnected aquifers as illustrated in the cross-sectional representation in [Figure 1](#) (bottom panel) [2]. The cross section shows that land elevation slopes down from the west to the east, toward the Huron River (not shown), with decreasing distance between the land surface and the water table.

Recent publically available 1,4-dioxane concentrations detected in permanent monitoring wells [8] are shown along the cross section in [Figure 1](#) and indicate that high concentrations of 1,4-dioxane exist upgradient at elevations that are at or near the ground surface elevations downgradient. Without mitigation, this is expected to allow the 1,4-dioxane to flow downgradient where it can come in contact with home basements as it approaches the surface. Groundwater containing approximately

Figure 1



The eastern section of the 1,4-dioxane plume in the city of Ann Arbor, Michigan. (Top panel) Estimated location of the 1,4-dioxane contamination. The purple shaded areas denote 1,4-dioxane concentrations between 4 and 500 µg/L with labelled concentration contour lines. The 1,4-dioxane concentration contours for 7.2 µg/L and 85 µg/L are included because they are the current and prior (pre-2017) Michigan cleanup criterion for 1,4-dioxane in groundwater used as a drinking water source, respectively. The heavy red line indicates the cross-sectional area illustrated in the bottom panel. The map was created using the interactive web map of the Gelman Site of 1,4-dioxane contamination [11]. (Bottom panel) Representation of the layered hydrogeology along a west-to-east cross section of the city. Recent concentrations of 1,4-dioxane detected in monitoring wells and the Allen's Creek Drain have been added to show their locations. The static water levels are indicated by. Adapted from Pall Life Sciences [2] using publicly available data [8,11]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

300 µg/L 1,4-dioxane arrived at an upstream monitoring well in 2017 having traveled about 650 m in 7 years. Thus groundwater containing significant concentrations of 1,4-dioxane can be expected to approach the surface in the mid-2020s under current conditions. Approximately 200 residences are located in the area down-gradient where the groundwater is close to the surface.

However, after the report of 1,4-dioxane detection in shallow water in 2016, sampling began of seeps, stormwater drains and surface water in the city. Although 1,4-dioxane has not been detected in seeps and creeks, it was detected for the first time at a low concentration (1.1 µg/L) in the pond in the area in 2021 and it has been detected in the area's stormwater drains [8]. One branch of the Allen's Creek storm drain roughly parallels the cross section shown in Figure 1, starting near the western boundary of Ann Arbor with outflow of untreated water into the Huron River to the east. Concentrations of 1,4-dioxane have increased in this branch of Allen's Creek drain in the area shown in Figure 1 from 4.4 µg/L in 2017 to a recent maximum of 49 µg/L in 2020 [8,10]. Because 1,4-dioxane has not been detected in Allen's Creek stormwater drain samples from upstream, the 1,4-dioxane detections in the Allen's Creek drain may be due to infiltration of contaminated shallow groundwater into the storm sewer [7**].

Protective air concentrations of 1,4-dioxane

For this project, we focused on increased cancer risk from inhalation exposure to 1,4-dioxane. The United States (U.S.) Environmental Protection Agency (USEPA) classifies 1,4-dioxane as "likely to be carcinogenic to humans" [12*]. We used target risk levels of 1 in 1,000,000 and 1 in 100,000 excess cancers with an average life expectancy of 78 years and exposure for 26 years (90th percentile), consistent with USEPA human exposure assessment assumptions [13,14]. For our calculations, we assumed a chronic wet/damp basement 350 days per year, which is consistent with the high water table and wet basements common near the area in Ann Arbor where 1,4-dioxane was detected in near-surface water. There has been no regular monitoring of shallow groundwater. The static water levels in 4 monitoring wells close to the shallow groundwater have been relatively stable over the past 15 years with the maximum variation approximately 0.6 m [11]. We applied the USEPA inhalation unit risk value of $5\text{E-}06$ ($\mu\text{g}/\text{m}^3$)⁻¹ for increased cancer due to continuous 1,4-dioxane exposure [15], and we estimated the protective residential air concentrations of 1,4-dioxane using the USEPA Vapor Intrusion Screening Level Calculator [16] to be 0.63 µg/m³ and 6.3 µg/m³ for target risk levels of 1 in 1,000,000 and 1 in 100,000, respectively.

Exposure via vapor intrusion

A potential route of exposure to 1,4-dioxane in groundwater is through vapor intrusion from chemical volatilization into the soil gas followed by diffusion through the soil and concrete into living space [17*,18,19*]. Volatilization of a chemical from water solution is characterized by its Henry's Law Constant. The Henry's Law Constant (HLC) for 1,4-dioxane is 4.80E-06 atm·m³/mol at 25 °C [12]. The HLC is a function of temperature and can be calculated at other temperatures using the chemical's enthalpy of vaporization and then converted to a dimensionless partition coefficient (concentration in air divided by concentration in water) using the USEPA Vapor Intrusion Screening Level Calculator [16]. The calculated dimensionless air/water partition coefficients for 1,4-dioxane at various temperatures are: 1.96E-04 at 25 °C; 1.61E-04 at 21 °C; 9.02E-05 at 10 °C; 5.34E-05 at 1 °C.

Using the USEPA median attenuation factor, 0.003, for soil gas chlorinated solvent vapor migration through the concrete slab into a residence [20], an indoor residential protective air concentration of 0.63 µg/m³ 1,4-dioxane would be reached with a 1,4-dioxane concentration of 210 µg/m³ in the soil gas near a home. At 10 °C, the 1,4-dioxane water concentration that would be in equilibrium with an air concentration of 210 µg/m³ is calculated by dividing the air concentration by the air/water partition coefficient, 9.02E-05, and adjusting the units to give 2330 µg/L of 1,4-dioxane in the shallow groundwater. This is the concentration of 1,4-dioxane in shallow groundwater that could lead to an indoor air concentration of 0.63 µg/m³, the target risk level of 1 in 1,000,000 excess cancers, assuming there is only vapor intrusion and no contaminated liquid water entering the basement. At a target risk level of 1 in 100,000, the corresponding concentrations of 1,4-dioxane would be ten-fold greater: 23,300 µg/L in the shallow groundwater and 6.3 µg/m³ in the residential air. The latter estimate is a little over an order of magnitude higher than the calculated value for increased risk of 1 in 100,000 by the Michigan Toxics Steering Group Volatilization to Indoor Air Workgroup, which was 1900 µg/L in the shallow groundwater [21]. However, the Michigan 1,4-dioxane concentration was calculated using the USEPA 95th percentile attenuation factor, 0.03 [20], whereas we used the median attenuation factor, 0.003. If the shallow groundwater were warmer, for example 21 °C after a long hot summer, the vapor pressure of 1,4-dioxane over the groundwater would be greater. In this case lower, groundwater concentrations of 1,4-dioxane could lead to 0.63 µg/m³ of 1,4-dioxane in a basement, 1304 µg/L versus 2330 µg/L, applying our assumptions and calculated as above.

Examination of 20 other organic solvents in industrial use found that the combination of 1,4-dioxane's low volatility from water solution and relatively high volatility was only shared with a few. Fortunately, the other compounds with this combination of properties are reported to be more biodegradable than 1,4-dioxane. Most common solvents volatilize from water solution.

Liquid infiltration

Because the 1,4-dioxane-contaminated groundwater is nearing the surface in Ann Arbor neighborhoods that have many damp residential basements due to a high water table, the USEPA and Michigan shallow groundwater vapor intrusion calculations are not applicable to the wet basement conceptual site model associated with the Ann Arbor 1,4-dioxane plume. Basements typically extend 1.5–2 m below the ground surface. Thus, groundwater less than 3 m below the surface could contact the basement floor through capillary action. There is a need to consider an alternative method to assess the risk posed by shallow groundwater infiltrating a residential basement.

If liquid water containing 1,4-dioxane were to enter a basement and evaporate, the 1,4-dioxane would also evaporate. Dry concrete is porous because some of the water used in mixing evaporates leaving pores that can allow water to move through by capillary action and in the presence of hydrostatic pressure. Capillary action pulls water through the concrete as long as the relative humidity and air circulation allow the water to evaporate at the surface of the concrete. This is why basement floors are often damp unless steps are taken to prevent moisture access to the bottom of the slab. The rate of 1,4-dioxane entering a home by this route depends on the concentration of 1,4-dioxane and the rate of its water solution moving through the basement floor. The concentration of 1,4-dioxane in the air is directly proportional to its concentration in the liquid water and the humidity due to evaporation of this liquid water which has entered the basement. There is not expected to be a large change in rate of water movement until the concrete surface approaches saturation.

The rate of water moving through a concrete floor is estimated by the "Calcium Chloride Test" [22]. This test can be used by flooring contractors to determine what types of flooring are likely to be successful in a basement. It is simple in that a small dish of anhydrous calcium chloride is weighed and placed on the concrete floor under a metal or plastic cover. A water emission rate of 3 lbs per day per 1000 ft² (approximately 1.5 L per day per 100 m²) is a conservative value for installation of many types of flooring [23,24].

The indoor concentration of 1,4-dioxane vapor is directly related to water vapor concentration (humidity). As such,

indoor air concentration of 1,4-dioxane arising from groundwater infiltration will depend on 1) the rate that groundwater enters the space, 2) the volume of the space, and 3) the rate that water and 1,4-dioxane vapor leave the indoor space expressed as the ventilation rate [19*]. The ventilation rate is measured by air changes per hour (ACH) and can vary in U.S. residences by more than a factor of ten. The USEPA Exposure Factors Handbook, in combining many different studies of residential air exchange rates, reports a median ACH of 0.45 and 10th percentile ACH of 0.18 [25]. Substantial air exchange between the basement and upper floors of older houses, average age 78 years (average construction date ca. 1934, range 1880s–2005), in Detroit has been reported by Du et al. [26]. The median ACH for these houses was 0.35 in the living area and 1.1 in the basements.

For simplicity in these calculations, a basement with a ceiling height of 2.5 m (approximately 8 ft) at a temperature of 21 °C was used with ventilation rates of 0.18 ACH, 0.45 ACH and 1.1 ACH. At an input rate of 1.5 L contaminated water per 100 m² – day, the calculated steady state increase in humidity, 0.556 g/m³, is an increase of the relative humidity at 21 °C of only 3.03% with a ventilation rate of 0.45 ACH, a dry and comfortable basement. If the water entering the basement contains 1130 µg/L of 1,4-dioxane, the steady state air concentration of 1,4-dioxane would reach the 1 in 1,000,000 target risk concentration of 0.63 µg/m³.

If a larger quantity of polluted water enters the basement, Table 1 shows the calculated potential atmospheric concentrations of 1,4-dioxane at different ventilation rates. Polluted water intrusion into a residence could lead to an excessive exposure to 1,4-dioxane in a residential basement even when there is minimal hazard from vapor intrusion. At a constant water intrusion rate, mixing between air in the basement and upper floors, and increasing the basement air exchange rate, would reduce basement humidity and air concentration of 1,4-dioxane. The critical factor is humidity due to groundwater infiltration. The difference between the humidity in the basement and the upper floors could serve as a proxy for the infiltration of groundwater. The most extreme case would be a flooded basement, with 100% relative humidity, where the only factor is the air/water partition coefficient of 1,4-dioxane [17*].

It would be valuable to have measurements of groundwater 1,4-dioxane concentrations, groundwater infiltration rates, and indoor 1,4-dioxane measurements to further evaluate this potential exposure route. The City of Ann Arbor initiated a study to test selected damp basements for 1,4-dioxane vapor as well as the shallow groundwater. However, no measurements were found of 1,4-dioxane vapor in damp basements in contact with contaminated groundwater to confirm or refute this proposed model.

Table 1

Estimated protective 1,4-dioxane concentrations in shallow groundwater in contact with residential buildings with damp or wet basements at 21 °C and different ventilation rates.

Basement Increased Relative Humidity from Groundwater Intrusion	Ventilation Rate	Protective 1,4-Dioxane Concentration in Shallow Groundwater	
		↑ Cancer Risk of 1 in 1,000,000	↑ Cancer Risk of 1 in 100,000
7.6% (dry, 1.5 L/100 m ² /day)	0.18 ACH	454 µg/L	4540 µg/L
30% (damp, 5.9 L/100 m ² /day)	0.18 ACH	115 µg/L	1150 µg/L
3.03% (dry, 1.5 L/100 m ² /day)	0.45 ACH	1130 µg/L	11,300 µg/L
30% (damp, 14.8 L/100 m ² /day)	0.45 ACH	115 µg/L	1150 µg/L
1.24% (dry, 1.5 L/100 m ² /day)	1.1 ACH	2772 µg/L	27,720 µg/L
30% (damp, 36.3 L/100 m ² /day)	1.1 ACH	115 µg/L	1150 µg/L
100% (flooded)	Low	3.9 µg/L	39 µg/L

Mitigation

Among mitigation options, the ideal mitigation would be for the polluter to clean up the groundwater. There is no assistance, financial or otherwise, for mitigation by individual homeowners under current cleanup response activities. The best option for an individual homeowner would be to prevent contaminated water from entering the basement, perhaps with a combination of waterproofing and improved footing drainage. This would not be simple and might require pumping of the recovered water if the water table is so high that gravity drainage is not feasible, which is a realistic possibility in the affected area. Another homeowner option would involve increased ventilation to prevent elevated indoor air concentrations of 1,4-dioxane, whether passive or active, requiring increased energy use and expense.

Dehumidification with ordinary homeowner dehumidifiers would not be adequate to control the atmospheric concentration of 1,4-dioxane. To control the air concentration of 1,4-dioxane, the amounts of both water and 1,4-dioxane in the dehumidifier condensate would need to equal the amounts entering the basement. Using the damp basement with median ventilation example in Table 1 in which the incoming water contains 115 µg/L 1,4-dioxane, the dehumidifier condensate would need to also contain 115 µg/L 1,4-dioxane. A dehumidifier blows air over a cooling coil to remove moisture in the air by condensation and then warms the air up again. A typical homeowner dehumidifier water condensing coil operates at an effective temperature of close to 1 °C yielding cold water. At that temperature, the air/water partition coefficient for 1,4-dioxane would be 5.43E-05 (above). If the concentration of 1,4-dioxane in the room air is 0.63 µg/m³, then the concentration of 1,4-dioxane in the condensate would be only 11.8 µg/L rather than 115 µg/L. Thus, under these basement conditions, the humidifier would fail to reduce the indoor air 1,4-dioxane concentration significantly.

Conclusions

This report describes a novel, previously unrecognized exposure pathway for 1,4-dioxane. Simple calculations show the potential for exposure to hazardous concentrations of 1,4-dioxane vapor in some residences in Ann Arbor, Michigan, and possibly other locations where 1,4-dioxane contaminated shallow groundwater could enter a basement. It is suggested that it would be prudent to consider testing for the presence of indoor 1,4-dioxane vapor if: 1) shallow groundwater contains more than 150 µg/L 1,4-dioxane, and 2) contaminated groundwater is within 3 m of the surface, and 3) the basement is more humid than the upper levels of a house. Although these specific screening values are theoretical, without confirmatory measurements, they nonetheless illustrate the need for further study of this exposure pathway for 1,4-dioxane and possibly other contaminants with similar chemical properties.

Credit Authorship contribution statement

Robert E. Bailey: Conceptualization, Methodology, Investigation, Visualization, Writing – original draft, Writing – review & editing, Rita Loch-Carusio: Conceptualization, Funding acquisition, Methodology, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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* of special interest

** of outstanding interest

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