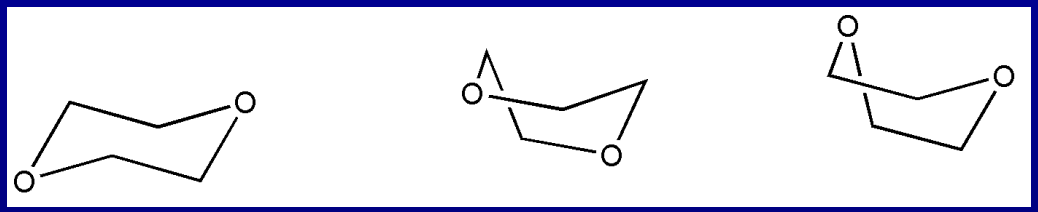
1,4-Dioxane in California's Drinking Water – Source Assessment and Exposure Estimation



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Groundwater Resources Association of California

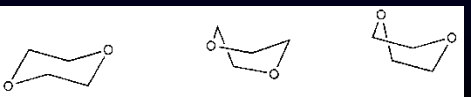
October 3, 2017

Hilton Arden West Hotel, Sacramento, CA

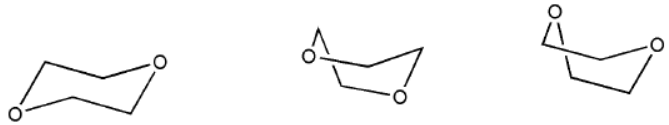
Disclaimer –
This presentation has not been reviewed, or endorsed or funded by the author's employer, the* Santa Clara Valley Water District. *All of the information and viewpoints presented are the author's alone.

Today's Presentation:

1. Introduction – 1,4-Dioxane in California - History
2. Results from 3 Years of UCMR3 testing for 1,4-dioxane
3. Sources of 1,4-dioxane
4. Probable explanation of UCMR3 results based on mass balance and "Contaminant Archeology"
5. Prospects for source identification by marker chemicals
6. Drinking water sources not yet tested
7. Implications for water utilities and remedial project managers



Santa Clara Valley Water District



1,4-Dioxane

and other

SOLVENT STABILIZERS

WHITE PAPER

June 14, 2001

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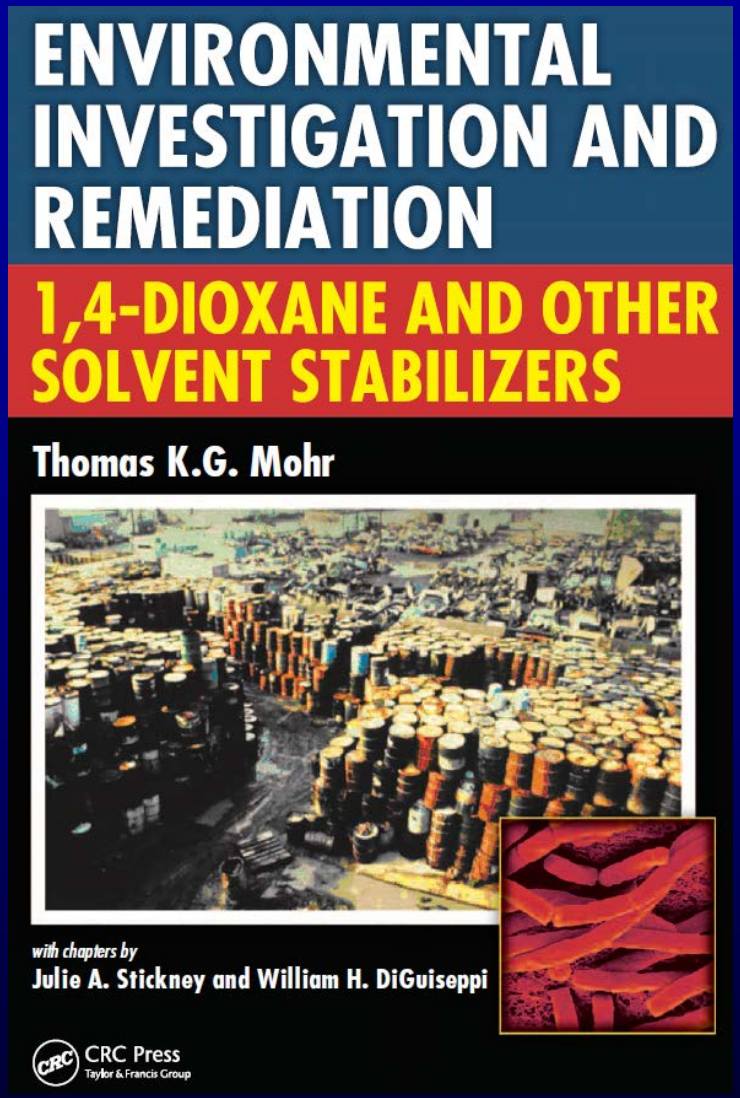
2001



2010

CATALYSIS:

The White Paper motivated regulators to take a 2nd look at solvent release sites:

- **2002 SFBRWQCB Survey of 15 Silicon Valley Sites with highest 1,1,1-TCA concentrations**
- **2003 DTSC Sampling Survey of 32 Sites with high TCA**
- **2004 EPA Superfund Groundwater Forum review of Superfund case files identified 50 with 1,4-Dioxane as TICs**
- **Other states followed, e.g. New Hampshire Landfill Survey, and discovery of high 1,4-dioxane in many PWS Wells**

- **2008 Testimony to *Science Advisory Board* re: CCL3/UCMR3**
- **2009 – EPA Method 522 Solid Phase Extraction – MS/MS**
- **2010 – EPA 1,4-Dioxane Toxicity Review**
- **2013-2015: UCMR 3 Testing for 1,4-Dioxane > 0.07 µg/L**

1. Unregulated Contaminant Monitoring Requirements Round 3:

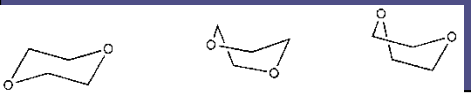
- UCMR3 List selected from Contaminant Candidate List 3 based on:
  - likelihood of widespread detection,
  - health risk,
  - detectability

My 2008 testimony to the *Science Advisory Board* :

- expect widespread occurrence of 1,4-Dioxane based on frequent occurrence of 1,1,1-TCA and it's breakdown prodcuts, 1,1-DCE and 1,1-DCA, in supply wells.

- 1,4-DX is persistent (recalcitrant) and highly mobile

- New analytical capabilities (EPA 522) can reliably fill the data gap caused by inadequate VOC analytical methods



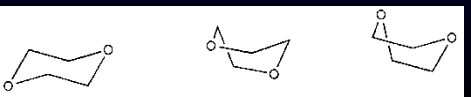
2. UCMR3 Requirements and Testing

- 4,864 Public Water Systems with >10,000 connections assigned testing for 1,4-DX between 2013 and 2015.

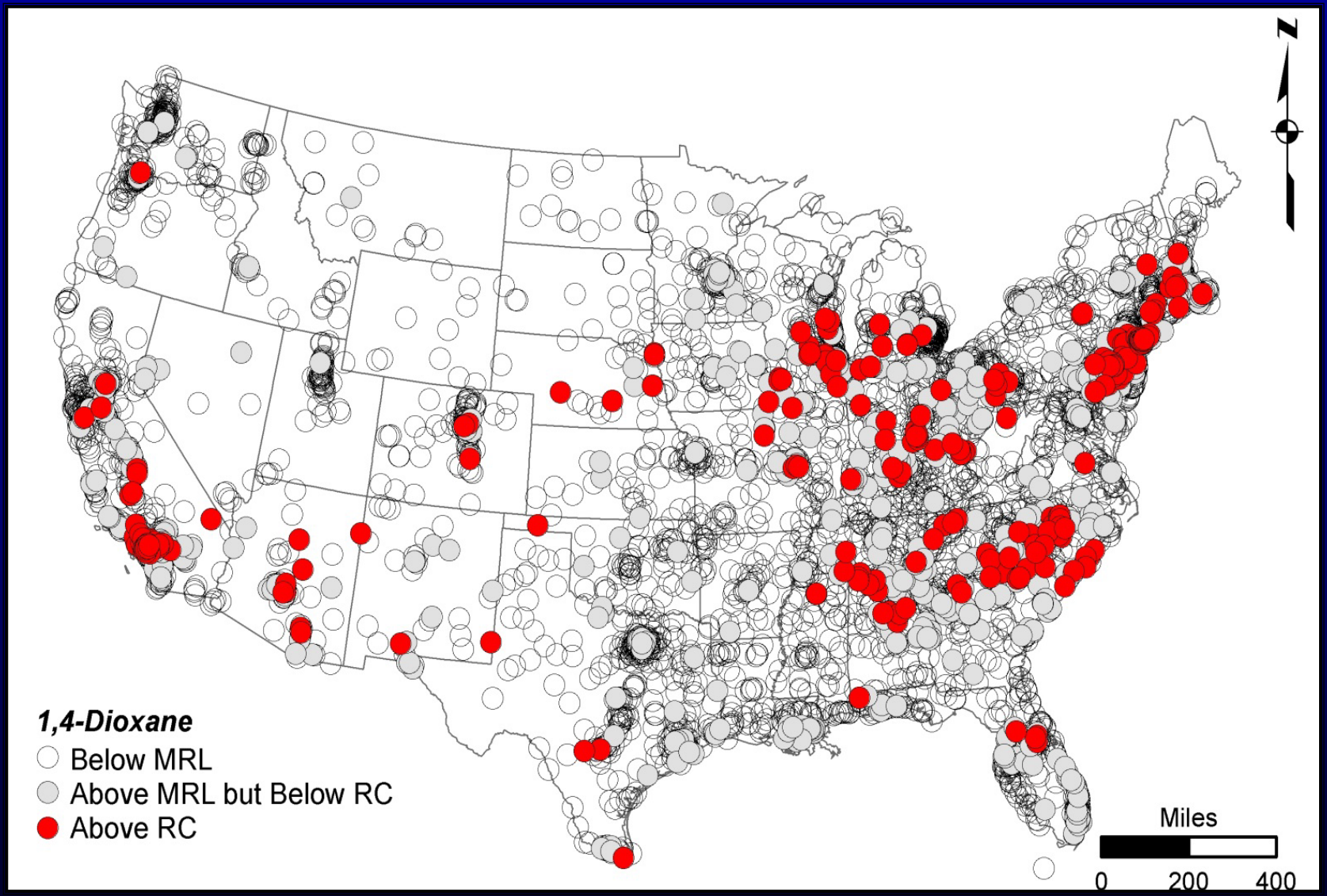
- Samples collected
  - groundwater (n = 41,111)
  - surface water (n = 27,800)

- 1,4-Dioxane by EPA Method 522 with a MRL of 0.07 μg/L.

- EPA 522 is a single-analyte test using solid phase extraction and tandem mass spectrometry, at a cost of ~$120 per sample.

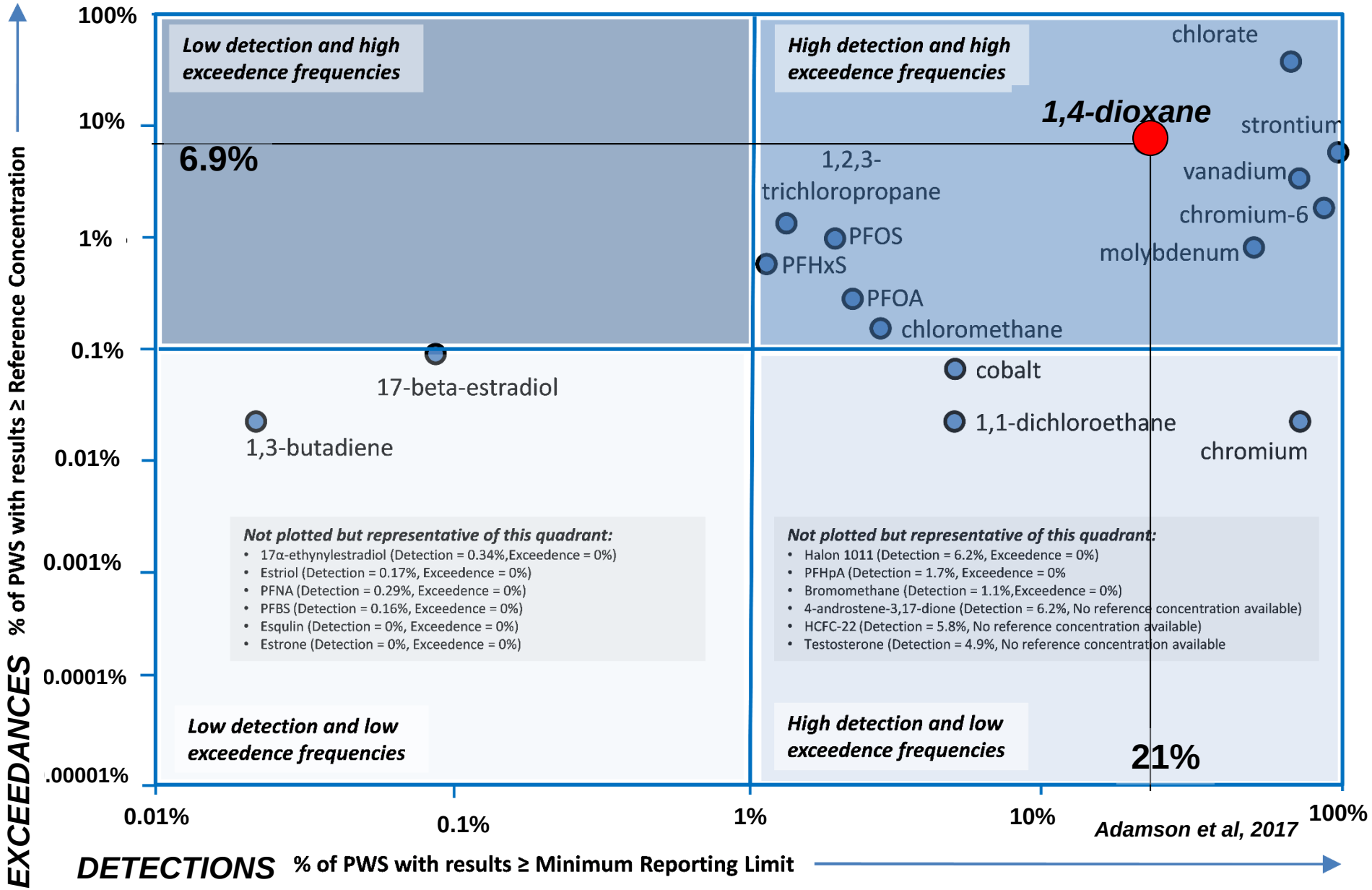


2. UCMR3 1,4-Dioxane by EPA 522: Results

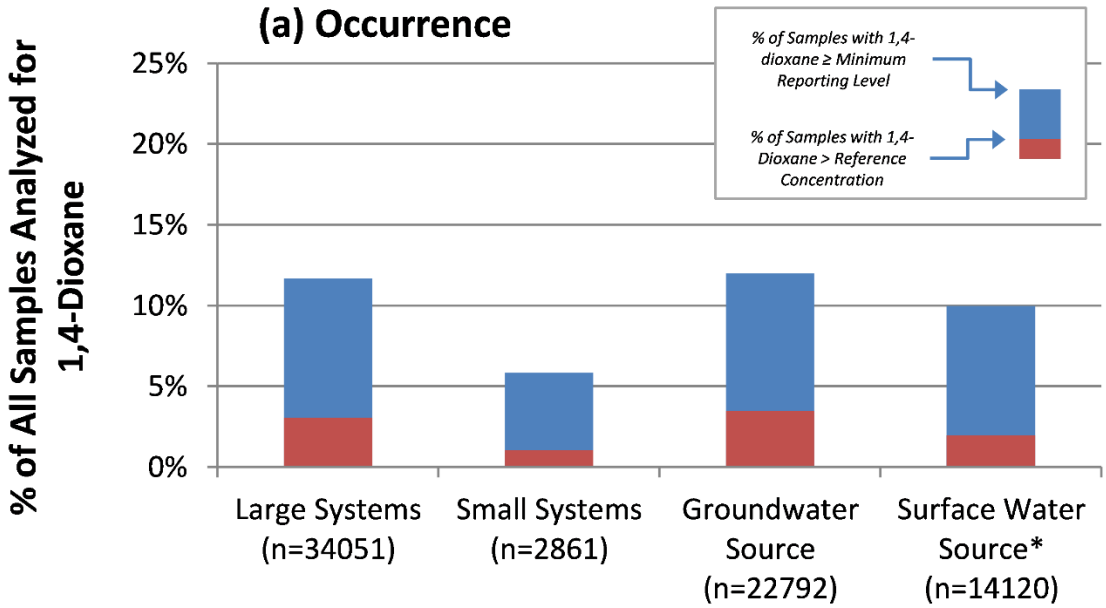


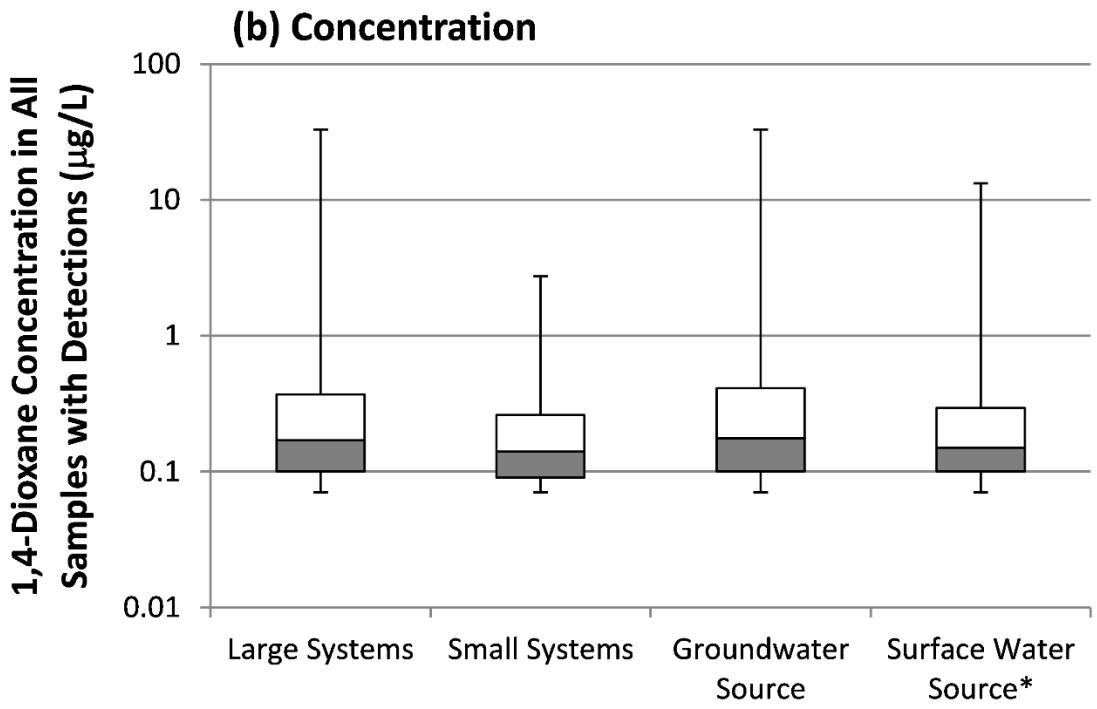
Data summarized from: http://water.epa.gov/scitech/datait/databases/drink/ncod/databases-index.cfm
In: Adamson et al, 2017, Science of the Total Enviironment

2. UCMR3 1,4-Dioxane by EPA 522: Compared to other UCMR3 analytes (for all of USA)



2. UCMR3 Results - USA



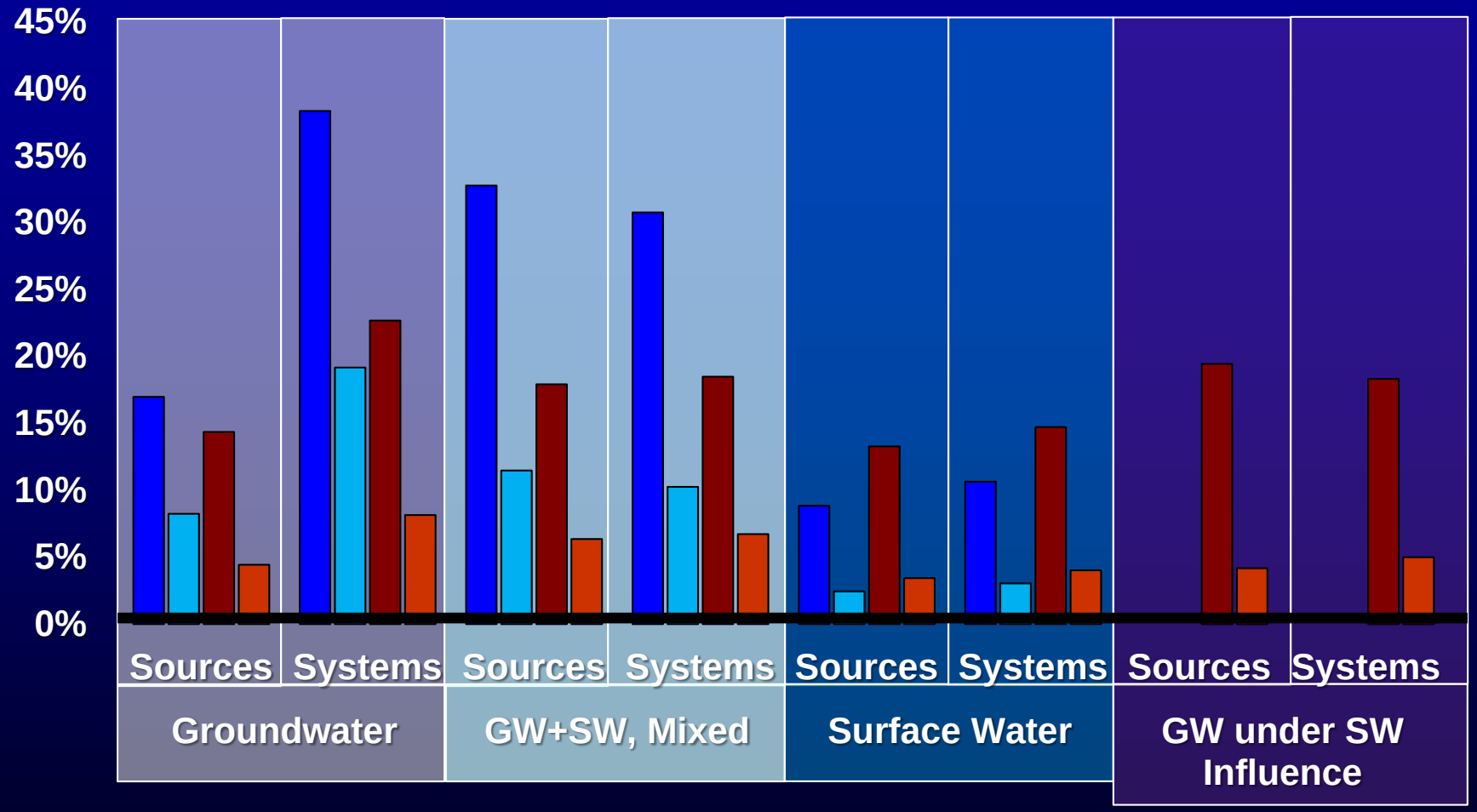


- **1,4-Dioxane detected in samples from 21% of 4864 Public Water Systems,**
- **1,4-DX > health-based reference concentration (0.35 µg/L) at 6.9% of these systems**

1,4-Dioxane Drinking Water Occurrence Data from the Third Unregulated Contaminant Monitoring Rule. **Adamson, Piña, Cartwright, Rauch, Anderson, Mohr, and Connor, 2017 Science of the Total Environment**

2. UCMR3 1,4-Dioxane by EPA 522: How does California compare?

UCMR3 Dioxane Results: California vs USA



- CA > 0.07 ug/L MRL
- CA > 0.35 ug/L HAL
- USA > 0.07 ug/L MRL
- USA > 0.35 ug/L HAL

3. Sources of 1,4-Dioxane

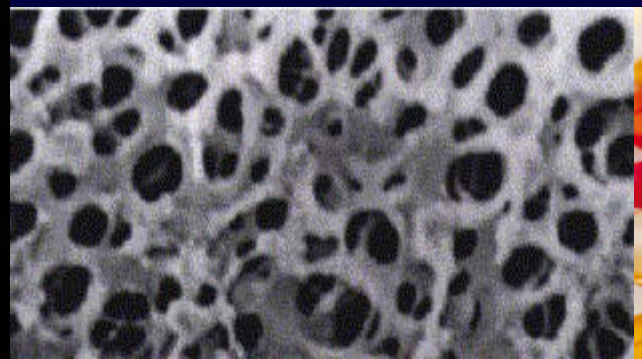
Direct uses of 1,4-Dioxane:

- **Cellulose Acetate Membrane Production**
- **Scintillation Counting Cocktails (University Landfills)**
- **Brominated Flame Retardant Production**
- **Pharmaceutical industry**

- **All TCA uses, especially vapor degreasing**

In 1985, 90% of all US 1,4-DX produced stabilized TCA

1,4-Dioxane is a by-product of: aircraft de-icing fluid; anti-freeze; ethoxylated surfactants; resins; PET plastic, polyethylene glycol products, others.

3. Sources of 1,4-Dioxane

1,4-Dioxane was a stabilizer of TCA

(methyl chloroform)

- **TCA formulation include 2.5 – 4% 1,4-dioxane**
- **1,4-DX boils hotter than TCA; concentrates to ~15% w/w**
- **Use of TCA was phased out in 1996 Montreal Protocol (banned ozone-depleting compounds)**

TCA had many uses:

• vapor degreasing	22%
• Cold cleaning	41%
• Aerosol spray propellant	10%
• Adhesives	12%
• Coatings and Inks	8%
• Electronics	6%

In 1985, ~165 million pounds TCA was used for vapor degreasing, 1,4-dioxane gets concentrated in liquid due to higher boiling point

- **~25,000 vapor degreasers operated in USA in the 1980s**
- **> 2/3 of TCA produced in USA was stabilized with 1,4-dioxane**

1,4-Dioxane was <u>not</u> a stabilizer of TCE *(trichloroethylene)*

3. Sources of 1,4-Dioxane - surfactants

Detergents	mg/kg
Tide Laundry Detergent	85**
Ivory Snow Laundry Detergent	31
Tide Free Laundry Detergent	29**
Purex Laundry Detergent	25
Gain 2X Ultra Laundry Detergent	21
Cheer BrightCLEAN Detergent	20
Era 2X Ultra Laundry Detergent	14
Planet Ultra Liquid Detergent	6.1
Arm & Hammer Laundry Detergent	5
Wisk 2X Ultra Laundry Detergent	3.9
Clorox Green Works Natural	<0.2
Ecos Laundry Detergent	<0.2
Sun Burst Laundry Detergent	<0.2

Shampoos	mg/kg
Clairol Herbal Essence Body Envy	24
Aura Cacia Natural Aromatherapy Bubble Bath	14.9
Clairol Herbal Long Term Relationship Shampoo for Long Hair"	14
Clairol Herbal Essence Drama	10
Gerber Grins & Giggles Gentle & Mild Aloe Vera Baby Shampoo	8.4
Healthy Times "Baby's Herbal Garden Pansy Flower" Shampoo	8.2
Sea-Chi Organics Shampoo	7.5
Pantene Pro-V Shampoo	6.5
Others	
Dial Antibacterial Hand Soap	18
Disney "*Clean as Can Bee*" Body Wash	8.8

More info at www.1-4dioxane.com

Source: David Steinman, March 9th, 2010

1,4-Dioxane in consumer products as an impurity of ethoxylated surfactants (*ppm*)

*** TIDE is now produced dioxane-free*

3. Sources of 1,4-Dioxane - surfactants

What about other surfactant uses?

PHOEN

Environmental Labor
587 East Middle Turnpike, P.O.Box 37
Tel. (860) 645-1102 Fa

Draft Progress Report

January 16, 2013

FOR:

Sample Information

Matrix: OIL

Location Code: *Car Wash Soap Co*

Rush Request: 24 Hour

P.O.#:

Custody Inforr

Collected by:

Received by:

Analyzed by:

Laboratory Data

Project ID: DIOXANE TEST

Client ID:

Parameter	Result	RL/ PQL	Units	Dat
1,4-dioxane				
1,4-dioxane	760000	100000	ug/kg	01/1

760 mg/kg 1,4-dioxane in car wash soap

New Hampshire DES January 2013

4. Explanation of UCMR3 Results

Do we see TCA in wells/sources with 1,4-DX?

TCA is relatively unstable in groundwater. It breaks down via hydrolysis to 1,1-dichlroethylene with a half-life of ~ 2.9 years (Vogel and McCarty, 1987; Wing, 1997)

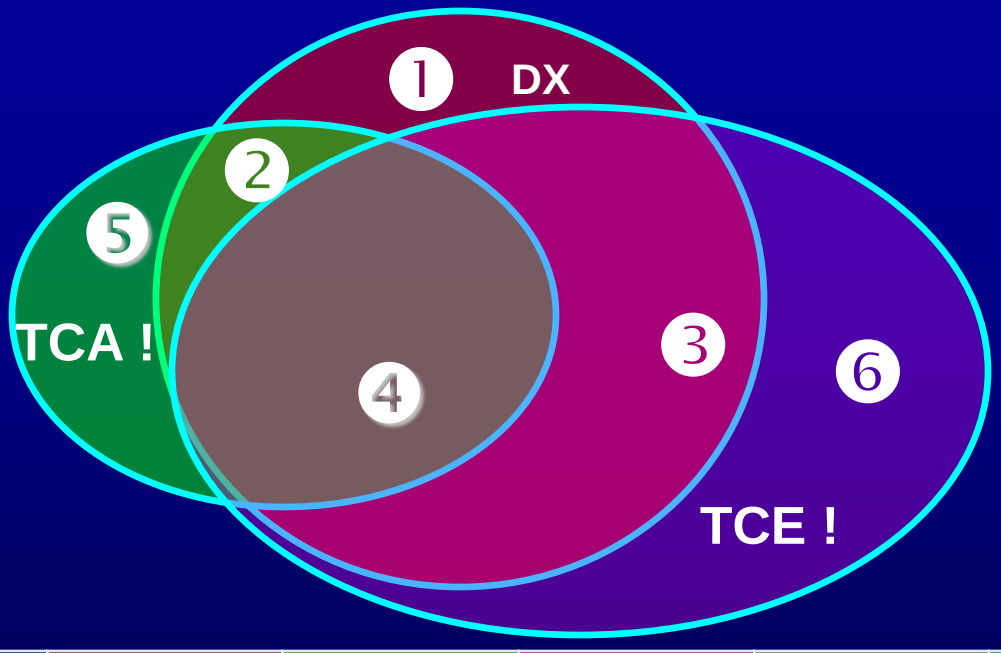
TCA hydrolysis yields ~ 25% 1,1-DCE and ~75% acetic acid. 1,1-DCE is persistent; vinegar biodegrades.

TCA biodegrades to 1,1-dichloroethane via reductive dechlorination.

After 23 years, ~99.6% of TCA will be converted to 1,1-DCE and/or 1,1-DCA

1,4-DX should therefore be associated with 1,1-DCE and 1,1-DCA. Where TCE was used before TCA, 1,4-DX is frequently co-located with TCE + cis-1,2-DCE (e.g. see Anderson 2012; Adamson 2014)

4. Explanation of UCMR3 Results



Co-location of 1,4-DX with chlorinated solvents in drinking water : California drinking water data, 2010-2013

	1 DX only, no TCA! or TCE!	2 DX +TCA!, no TCE!	3 DX + TCE!, no TCA!	4 DX + TCE! + TCA!	5 TCA!, no DX	6 TCE!, no DX
Count	121	4	47	60	34	728
%	34%	1.1%	13%	17%	0.4%	7.8%

TCA ! = count if any of 1,1,1-trichloroethane, 1,1-dichloroethylene, 1,1-dichloroethane are detected
TCE ! = count if any of trichloroethylene, cis or trans-1,2-dichloroethylene are detected

4. Explanation of UCMR3 Results

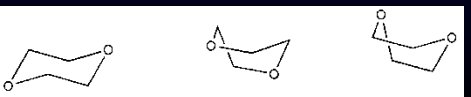
Order of magnitude comparison of 1,4-dioxane mass from different sources that may contribute to drinking water detections:

TOTAL MASS – ***not the amount released to groundwater***

- ~170,000 tons from use as a stabilizer for TCA (1980 – 1995) [1]
- ~ 780 tons in wastewater from detergents, soaps, shampoos @ 1 μg/L; 1980-2013 [2]
- ~ 560 tons from plastics & resins, 1980 – 2013 [3]
- ~ 190 tons from printing, 1980 – 2013 [3]

∴ 1,4-dioxane mass associated with solvent uses is ~220-fold greater than 1,4-dioxane mass associated with non-solvent uses

1) Based on 1985 1,4-Dioxane production and use data; TCA was banned in USA in 1996
2) Based on Ann Arbor & Orange County CA WWTP influent/effluent data and 2005 USA Public Supply Water Use (USGS Circular 1344); 45% outdoor use
3) Extrapolated from 1988-1997 US EPA Toxic Release Inventory "data"



4. Explanation of UCMR3 Results

What is the risk of 1,4-dioxane in drinking water from wastewater effluent upstream of drinking water intakes? **(*Simonich, et al, 2013*)*:**

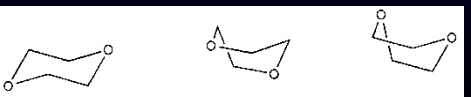
Measured dioxane concentrations in domestic wastewater effluents from 40 different WWTPs ranged from <0.30 to 3.30 *µ*g/L, with a mean concentration of 1.11 ± 0.60 *µ*g/L.

Dilution factors for 1,323 drinking water intakes across USA ranged from 2.6 to 48,113, with a mean of 875 .

Probability that 1,4-dioxane in drinking water would exceed EPA 0.35 *µ*g/L Health Advisory Level (HAL) due to upstream WWTP effluent is ~0.3%.

* *Integr Environ Assess Manag. 2013 Oct;9(4):554-9.*

BUT, USA 1,4-dioxane detection rate in drinking water from surface water sources is 9.7%, with 1.9% of sources > 0.35 µg/L HAL. ***What are the other dischargers of 1,4-dioxane to rivers?***



4. Explanation of UCMR3 Results

Does this rule out surfactants in wastewater as a source of 1,4-dioxane detections in drinking water?

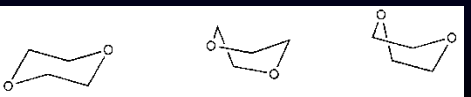
Pathways for wastewater contribution of 1,4-dioxane to drinking water:

- **Septic leach field effluent migrating to domestic wells**
- **POTW effluent discharges to surface water sources**
- **Sewer line exfiltration to groundwater sources: 1%? 5%? 10%??**

Is the mass loading sufficient to produce detections?

Where septic, recycled water, or sewer line exfiltration play a significant role in groundwater recharge, 1,4-dioxane may be present from wastewater/surfactant sources. Surface water sources are more likely to include 1,4-dioxane from upstream wastewater effluent.

Example: ½ acre lots, all septic: detergents + shampoos for a 3-person household ~ 1 mg DX/day ≅ 0.4 µg/ L DX/day after dilution



5. Identifying 1,4-DX sources by chemical markers?

UCMR2: Nitroso-amine compounds by EPA 521 in groundwater – detection rate was 0.43%

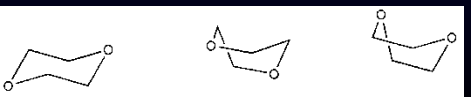
UCMR3: Preliminary results for EPA 539 hormones (e.g. 17-beta-estradiol) in groundwater – detection rate is ~ 2.4%.

Number of groundwater sources with 1,4-dioxane <u>and</u> a nitroso-amine compound <u>or</u> an EPA 539 hormone compound: 2

Both samples are in one Long Island water system.

17-alpha-ethynylestradiol (an ovulation inhibitor) and testosterone were detected together with 1,4-dioxane at <0.5 µg/L.

Wastewater is unlikely to be a major source of 1,4-dioxane in municipal supply wells. Domestic wells and small water systems may be more vulnerable to 1,4-dioxane contamination from wastewater sources.



6. Recommendations for water utilities:

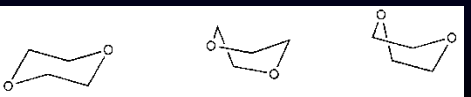
- While no MCL has been set for 1,4-dioxane (or will be anytime soon), high rate of detection seen in UCMR3, low EPA HAL (0.35 µg/L) and low state standards make routine monitoring for 1,4-DX advisable.

- PSWs with <10,000 connections not in UCMR3 should test for 1,4-DX as due diligence.

- There remain hundreds of locations where 1,1,1-TCA was used but there has been no subsurface investigation of potential 1,4-dioxane releases. PSWs w/CVOC detection history = test DX.

- Recycled water projects should be managed with multi-generational impacts in mind (1,4-dioxane is very persistent).

- Wastewater is a valuable commodity that must be protected against contamination. Recycled water producers: lobby detergent companies to take out 1,4-dioxane.



6. Implications for water utilities

Municipal Well operators who cannot replace supply lost to 1,4-dioxane contamination face expensive treatment costs.

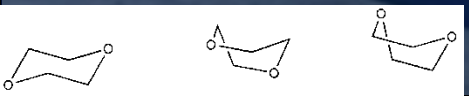
Example from Delaware (2014 Costs/$):

Combined Flow Rate in 2 wells: ~ 1,500 gpm	Trojan Low Pressure UV-Peroxide	Calgon Medium Pressure UV-Peroxide	APT-Water Ozone-Peroxide
Equipment & Construction Cost	~ $3.1 M	~ $2.9 M	~ $3.8 M
Annual O & M Cost	~ $120 K	~ $225 K	~ $77 K
10-year total cost	~ $4.3 M	~ $5.1 M	~ $4.5 M

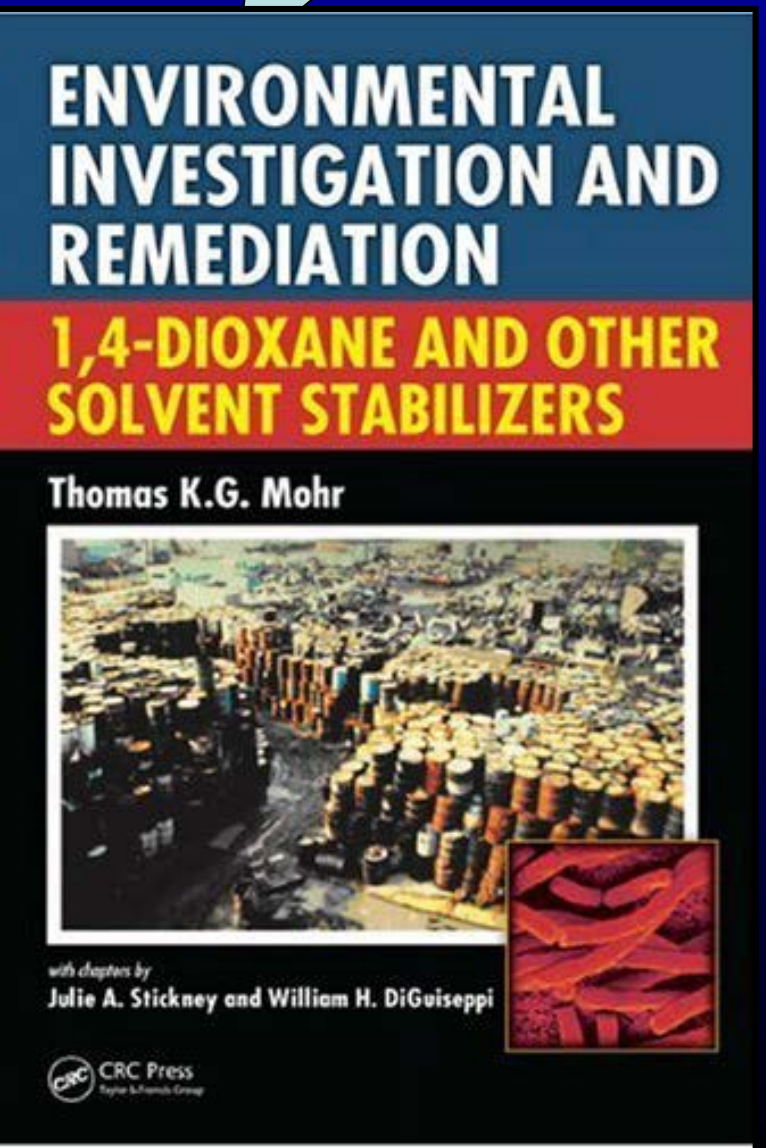
Civardi, et al., 2014

7. Marketplace for 1,4-dioxane remediation services

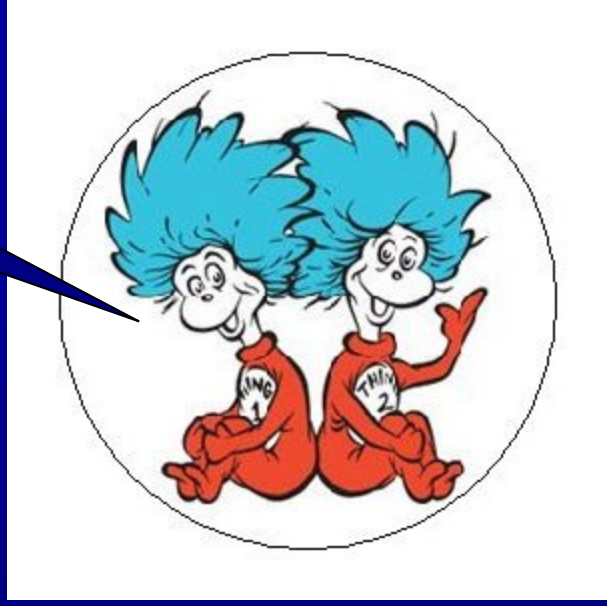
- In California alone, there are hundreds of sites where TCA has been detected but 1,4-dioxane has not been tested
- Detections of 1,4-dioxane in municipal wells have not been matched to sources – it's likely many of California's ~340 water systems with 1,4-dioxane detections represent undiscovered sources
- TCA was banned in 1996 – 22 years later the number of sites dealing with 1,4-dioxane is still growing.
- Recent work by Adamson, Anderson, Mahendra, Newell (ES&T, 2015) finds strong evidence for attenuation at majority of 1,4-dioxane sites – by 1 or more order of magnitude (as expected)
- Advances in CSIA and molecular tools enhance ability to leverage attenuation in the 1,4-dioxane remediation toolbox



Available in 100+ university libraries in 20+ countries



Thanks for listening!



Questions?

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3. Sources of 1,4-Dioxane

Scintillation Counting Cocktails – 90%+ 1,4-Dioxane

Dioxane-base cocktail = 8 g butyl-PBD, 100 g naphthalene, diluted to 1 L with dioxane Thompson & Olehy, 1975. ES&T

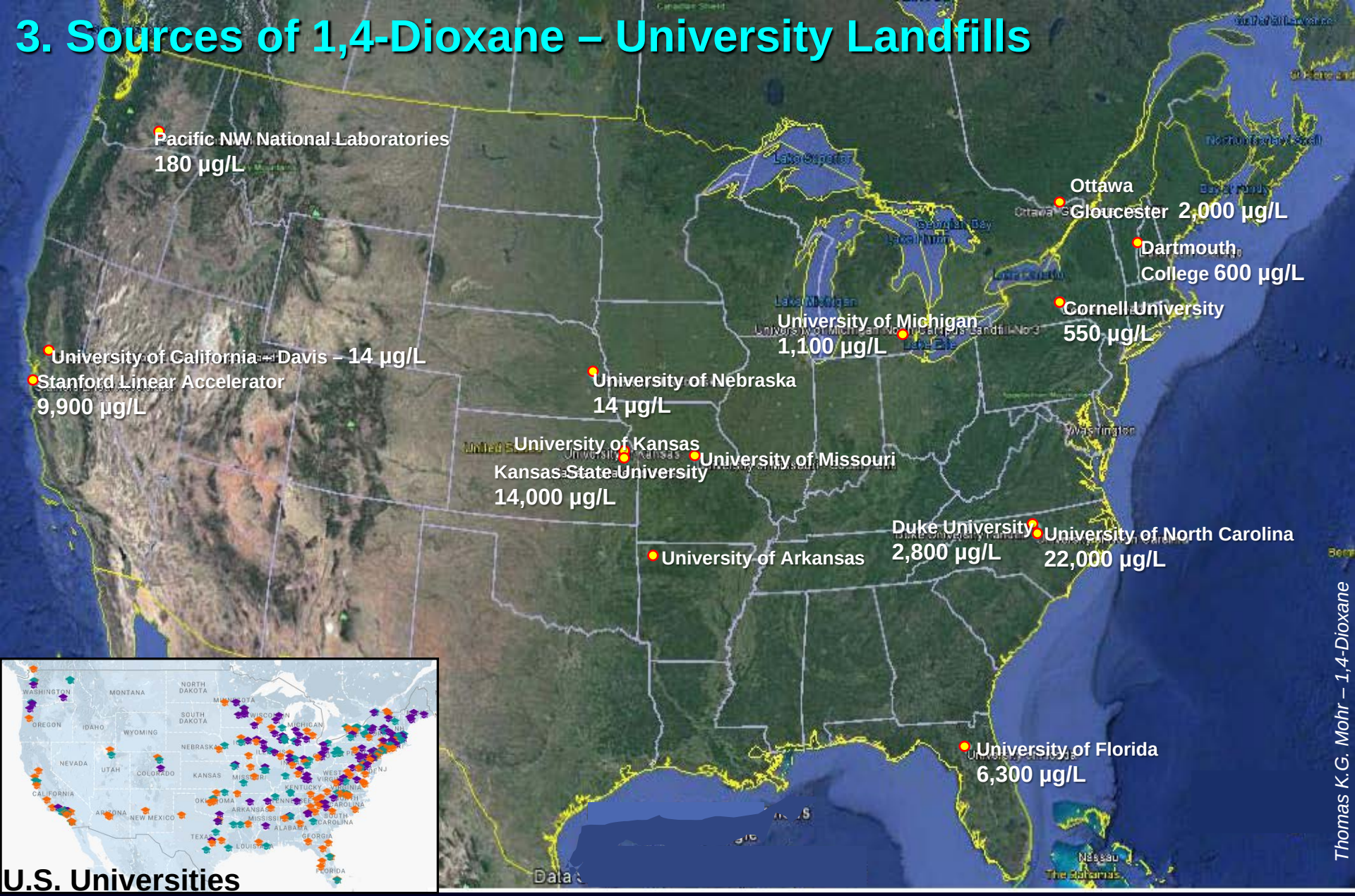
A few universities had their own landfills; irradiated lab animal carcasses buried with lab waste including *Bray's solution* 1,4-DX scintillation counting fluid in the 1960's and early 1970's.

***Most* universities and govt/private research labs sent LSC wastes off-site for disposal or incineration, or as fuel in cement kilns. Many solutions were considered "drain disposable".**

1989-1993: Nat'l Insts Health shipped 696,361 liters of Liquid Scintillation Counting vials for disposal.

US EPA, 1996 EPA 402-R-96-015

3. Sources of 1,4-Dioxane – University Landfills



Few universities have landfills; hundreds of labs used 1,4-dioxane for liquid scintillation counting. Pre-RCRA disposal likely to local municipal landfill; post RCRA to cement kilns, incinerators, TSDF including injection wells. 1,4-DX replaced by toluene in LSC cocktails in early 1970s re: toxicity.

Wait - 1,4-Dioxane in Surface Water ??

Not expected (dilution and rapid mixing) but not unprecedented.

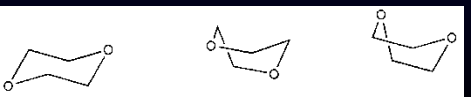
Documented 1,4-Dioxane Detections in Surface Waters

Location	Date	Detection (ppb)	References
Quinnipiac River, Connecticut	1987	1700	ATSDR (2007)
Tuscarawas River, Ohio	1993	>300	OEPA (1994)
Nakdong River, Korea	2003	119	Park et al. (2005)
Shinano River, Japan	2002	0.39	Kawata et al. (2003)
Agano River, Japan	2005	0.26	Tanabe et al. (2006)
Shinano River, Japan	2005	0.10	Tanabe et al. (2006)

Mohr, DiGuiseppi, Stickney, 2010

1,4-Dioxane has *low aquatic toxicity*, therefore many discharge permits allow high concentrations of 1,4-dioxane.

USA surface water discharge limits range from 3 *µ*g/L upstream of a drinking water reservoir in San Jose to 3,000 *µ*g/L to an Ohio river.



UCMR3 Surface Water Detections of 1,4-Dioxane

Maximum SW detection = 13.3 µg/L in Sanford, North Carolina, downstream from a major pharmaceutical plant.

A massive PET resin plant located on the Cape Fear River has 20,000 µg/L 1,4-Dioxane in groundwater . . .
NC Stormwater discharge permit Benchmark Value for DX = 730 µg/L

7. Marketplace for 1,4-dioxane remediation services

. . . ***is growing*****. Read the headlines:**

Seaboard Chemical Plant behind Randleman Lake 1,4-Dioxane woes

Casella Looking at Options for Water Line to Charlton Homes

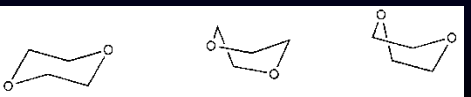
North Jersey Water Commission to test Reservoir for 1,4-Dioxane from Ringwood Superfund Site

Dingell to DEQ: 'Finalize Stricter cleanup standards for 1,4-Dioxane'

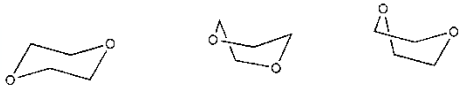
Downstream Communities Worry about Triad's 1,4-Dioxane

Cleanup Standards have been lowered in several states

Will attenuation make cleanup unnecessary?



1,4-Dioxane Occurrence with TCE

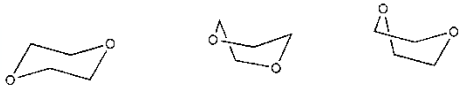


1,4-Dioxane Co-Location with TCE Plumes

Co-occurrence of 1,4-Dioxane with TCE in Chlorinated Solvent Plumes at US Air Force Installations: Fact or Fiction
Anderson, R.H, Anderson, J.K., Bower, P.A., 2012
Integrated Environmental Assessment and Management

- **Queried Air Force ERPIMS database for 1,4-dioxane, TCA, and TCE**
- **ERPIMS has 5,788 MWs from 49 installations with records for 1,4-dioxane, TCE, and TCA**
- **781 MWs contained levels of 1,4-dioxane ≥ RL; detection frequency for 1,4-Dioxane is 13.5%; for TCE 71.8% and TCA 11.8%**
- **64.4% of all 1,4-dioxane detections *independently associated with TCE***
- **<1% of MWs with 1,4-dioxane had TCA detections without also having TCE detections**
- **"site investigations should consider 1,4-dioxane as a potential co-contaminant of TCE"** ***"Site investigators should consider that 1,4-dioxane is often co-located with TCE"***

1,4-Dioxane Occurrence with TCE



Co-occurrence of 1,4-Dioxane with Trichloroethylene

How can the association of 1,4-dioxane with TCE be so strong if 1,4-dioxane was not a stabilizer of TCE as Mohr claims in his book?

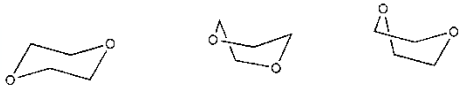
3 reasons:

1) **Timing, sequence, and duration of solvent usage and release**
2) **Relative mobility and persistence of the solvents TCE and TCA with 1,4-dioxane as a stabilizer**
3) **Investigation histories, analytical capabilities, and monitoring well placement and timing**

Typical sequence of solvent usage:

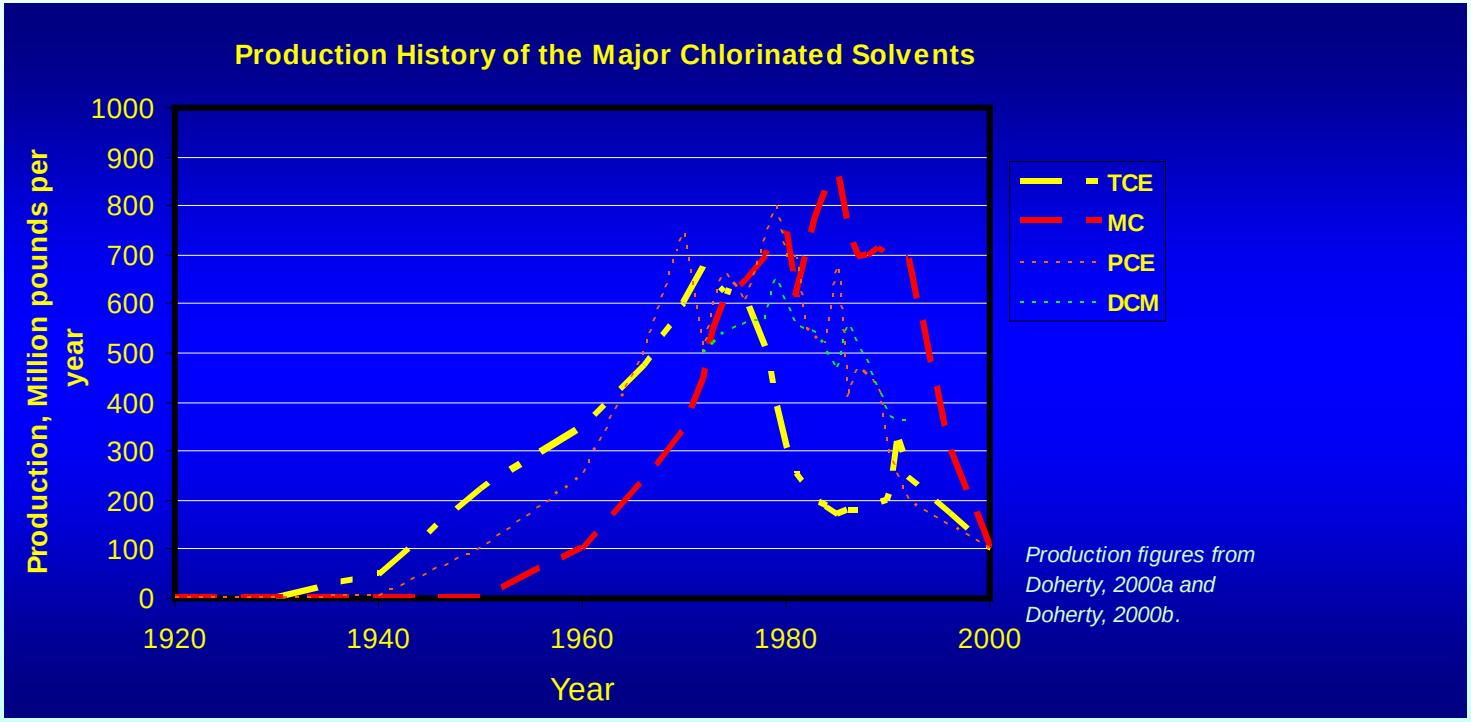
6.3 At Air Force Plant 44, the Air Force's operating contractors used and disposed of metals, chlorinated solvents and other substances at Air Force Plant 44 since 1951. At Air Force Plant 44, trichloroethylene (TCE) was used in several degreasers and as a general-purpose solvent from the 1950s through the mid-1970s. By the mid-1970s, TCE was replaced with 1,1,1 trichloroethane (TCA) as the dominant solvent in use at Air Force Plant 44. In the late 1980s, TCA was discontinued in favor of limited freon use and aqueous degreasers.

1,4-Dioxane Occurrence with TCE

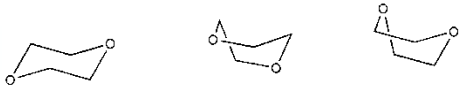


TCE usage in 1960s and 1970s was generally followed by TCA usage In 1970s, 1980s until 1996 when TCA was banned (Montreal Protocol)

- **TCE released earlier, could therefore migrate further**
- **TCE less prone to abiotic degradation than TCA**
- **TCE relatively immune to biodegradation in well oxygenated aquifers**
- **TCE is retarded more than 1,4-dioxane**
- **As a result, 1,4-dioxane may "catch up" to TCE**

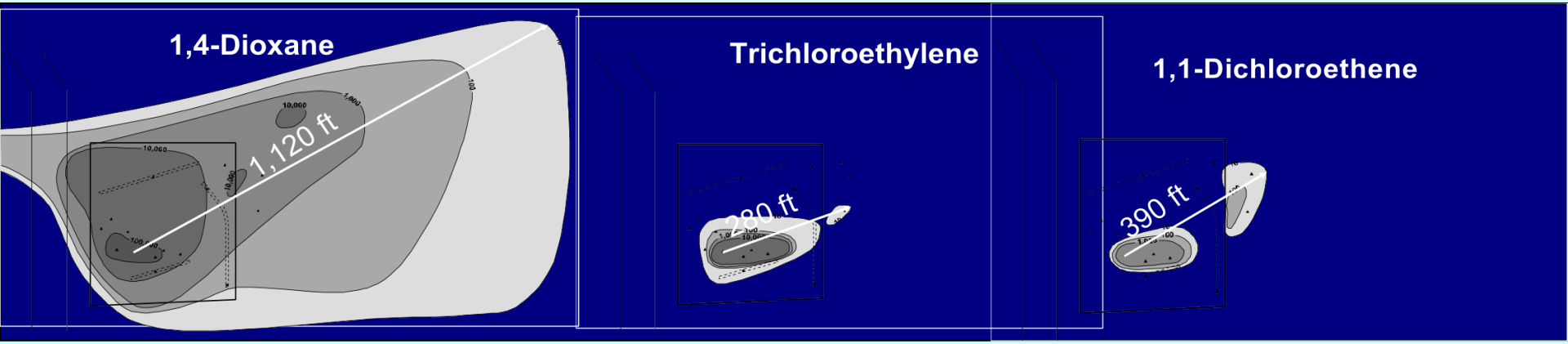


1,4-Dioxane Occurrence with TCE



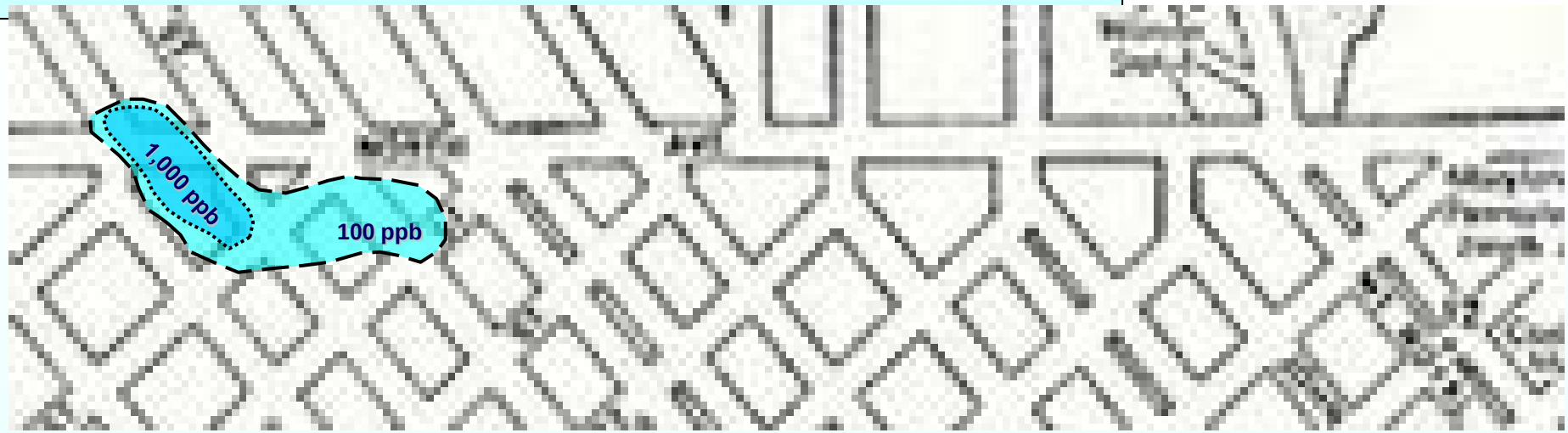
Fate and Transport Properties Governing Distribution of TCE, TCA, DCE, and 1,4-Dioxane

Contam-inant	Solubility, mg/L	KO_C	Retardation Factor	Hydrolysis Half-Life
TCE	1,100	160	~2.0 - 2.4	-
TCA	4,400	81 – 89	~1.9	2.9 yrs
1,1-DCE	2,500	1.04 – 1.65	~1.5	-
1,4-Dioxane	1,000,000	0.27	~1.1	-



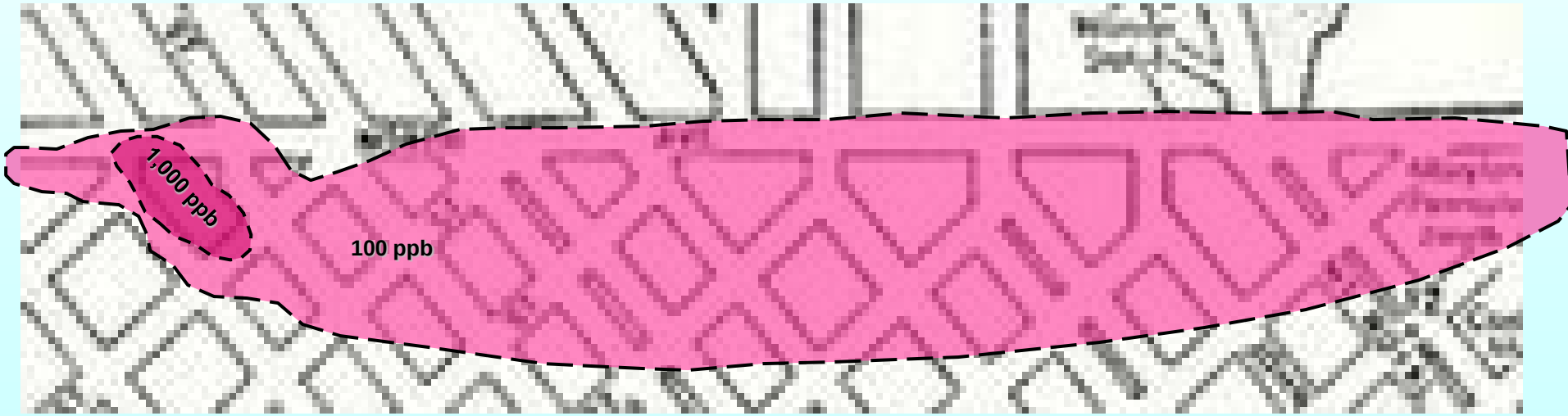
1,4-Dioxane Co-location with TCE

The plumes are real; the location is fictitious



Distribution of 1,1,1-trichloroethane: ~700 ft

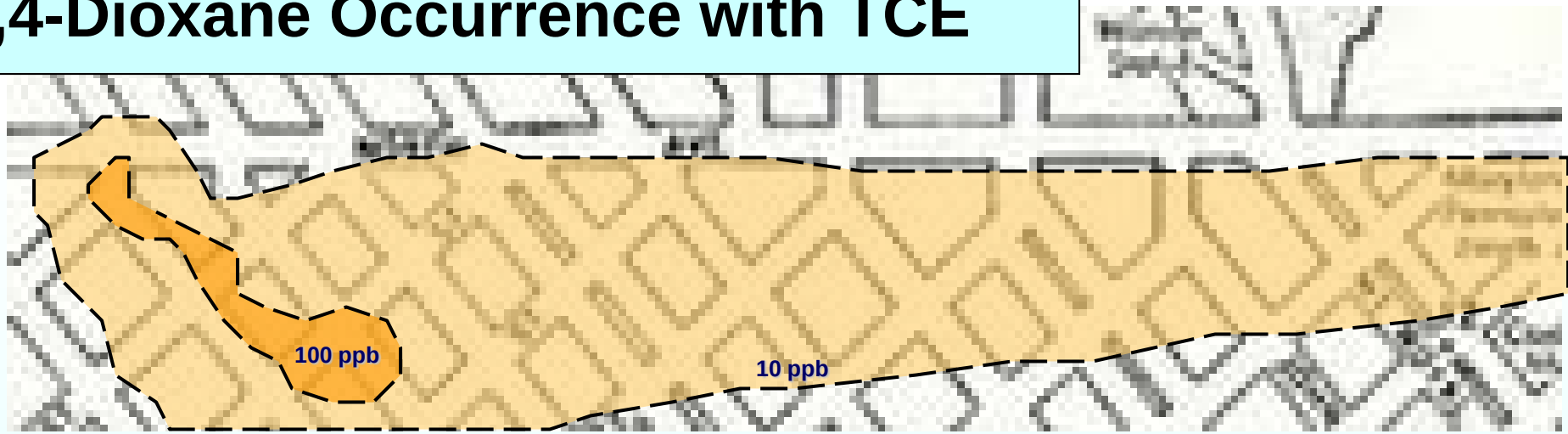
mapped to 100 ppb contour



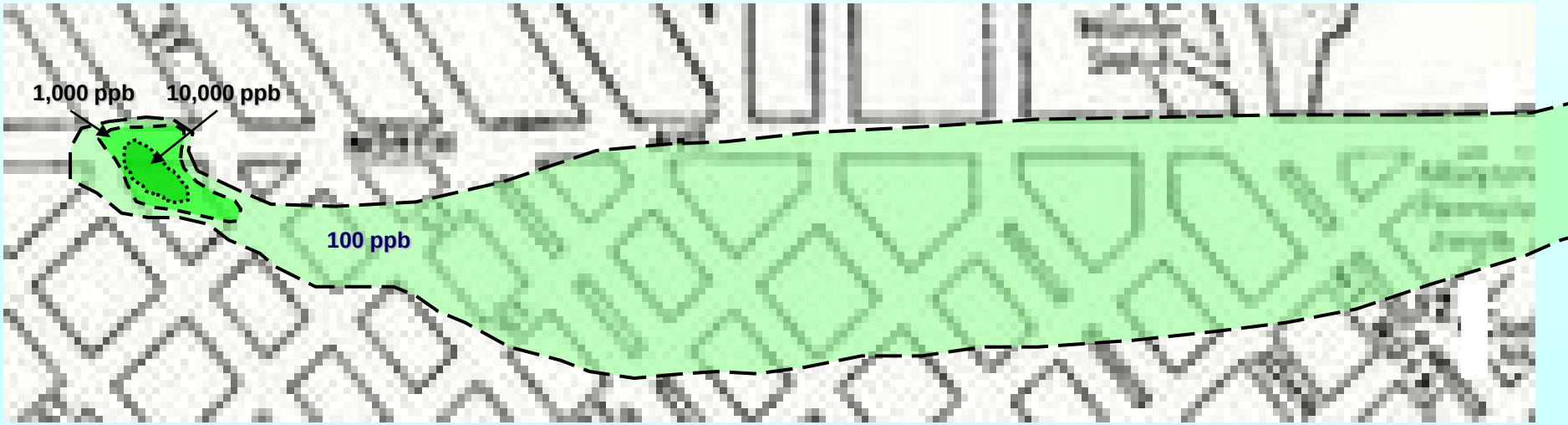
Distribution of 1,1-dichloroethylene: ~2,700 ft

mapped to 100 ppb contour

1,4-Dioxane Occurrence with TCE



Distribution of trichloroethylene: >3,000 ft mapped to 100 ppb contour (dark orange; and 10 ppb contour (light orange).



Distribution of 1,4-dioxane: >3,000 ft mapped to 100 ppb contour

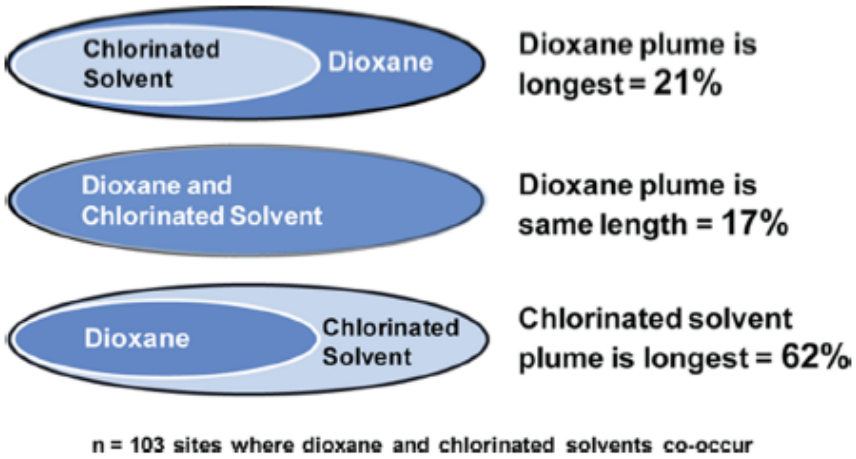


Figure 2. Frequency of dioxane plume lengths exceeding chlorinated solvent plume lengths at sites with co-occurring compounds.

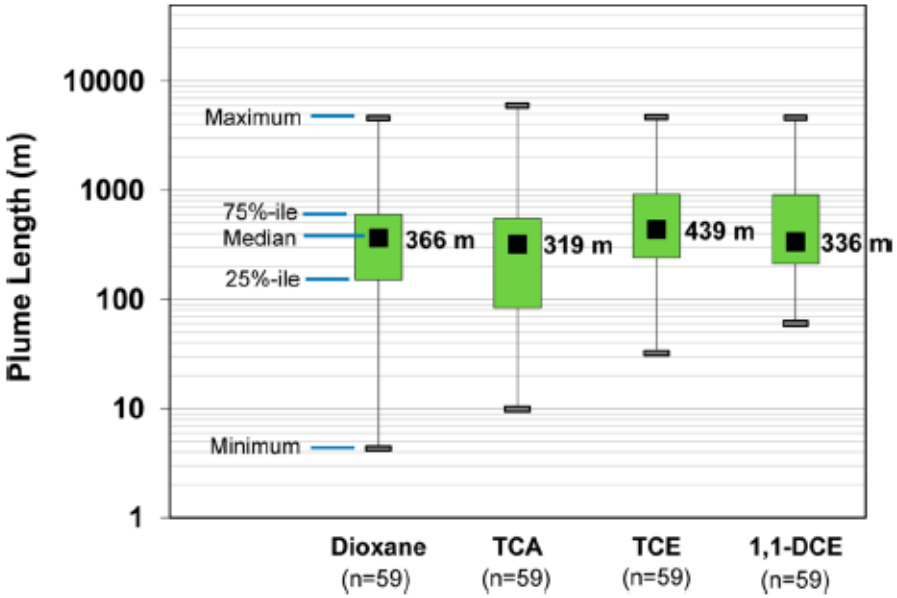


Figure 3. Distribution of plume length estimates for dioxane, 1,1,1-TCA, TCE, and 1,1-DCE at sites where all four compounds are detected.

Environmental Science & Technology Letters
Letter
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A Multisite Survey To Identify the Scale of the 1,4-Dioxane Problem at Contaminated Groundwater Sites

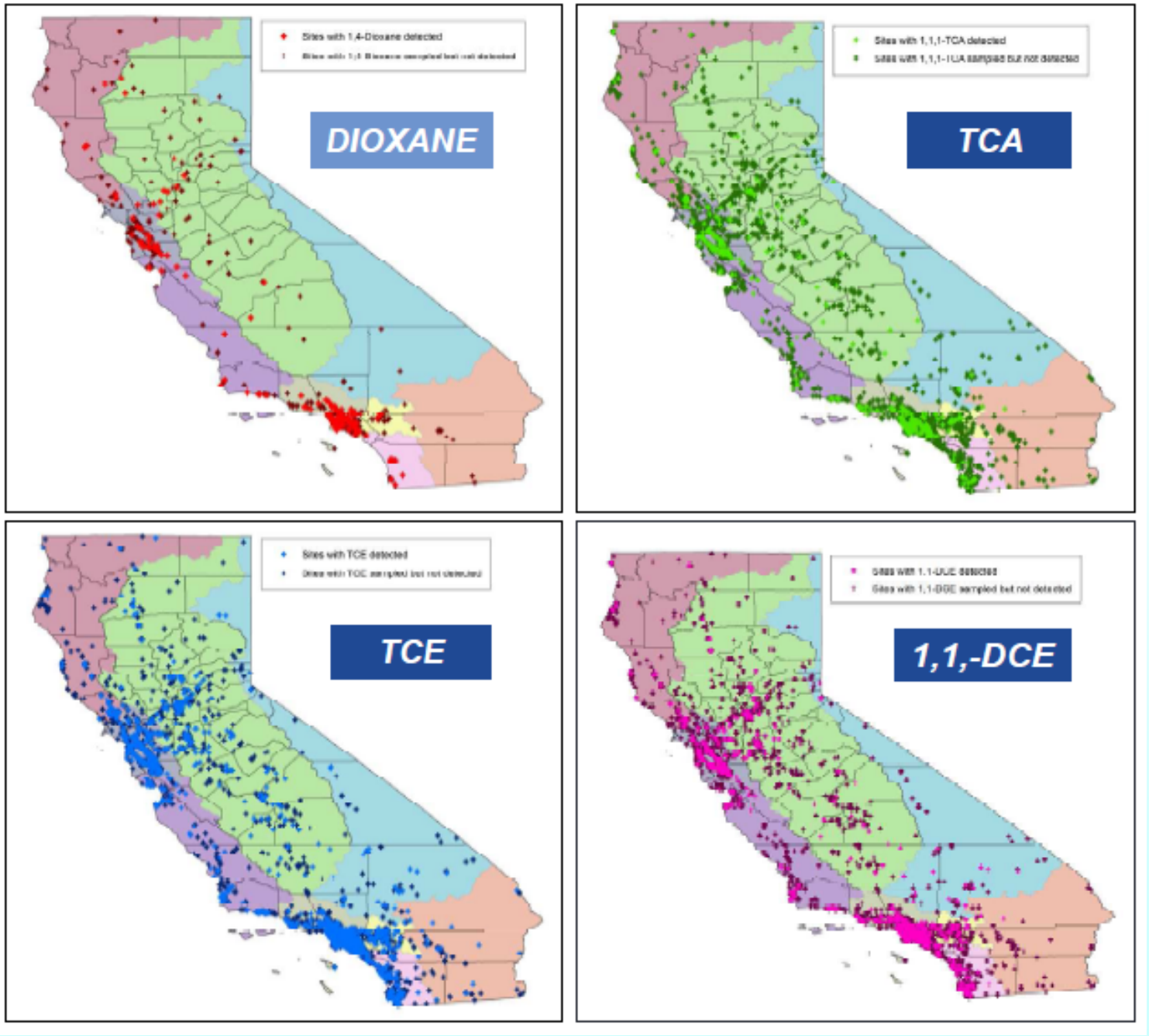
David T. Adamson,*,† Shaily Mahendra,‡ Kenneth L. Walker, Jr.,† Sharon R. Rauch,† Shayak Sengupta,§ and Charles J. Newell†

2014 article by Adamson/Mahendra/Newell offers insights into 1,4-dioxane plume behavior.

If 1,4-dioxane's properties make it more recalcitrant and retarded less by sorption or biodegradation than 1,1,1-TCA or 1,1-DCE, why doesn't it migrate much further as I have asserted in the Dioxane Book?

Possible explanations/ideas to explore:

- **Variability of 1,4-dioxane mass strength**
- **Possible contribution of TCE to 1,1-DCE**
- **1,4-dioxane polarity allows it to diffuse into smaller pores than more hydrophobic CVOCs, so more mass is retained in silts and clays**
- **relative duration of TCE vs TCA use**



Adamson, et al, 2014 Environmental Science and Technology Letters