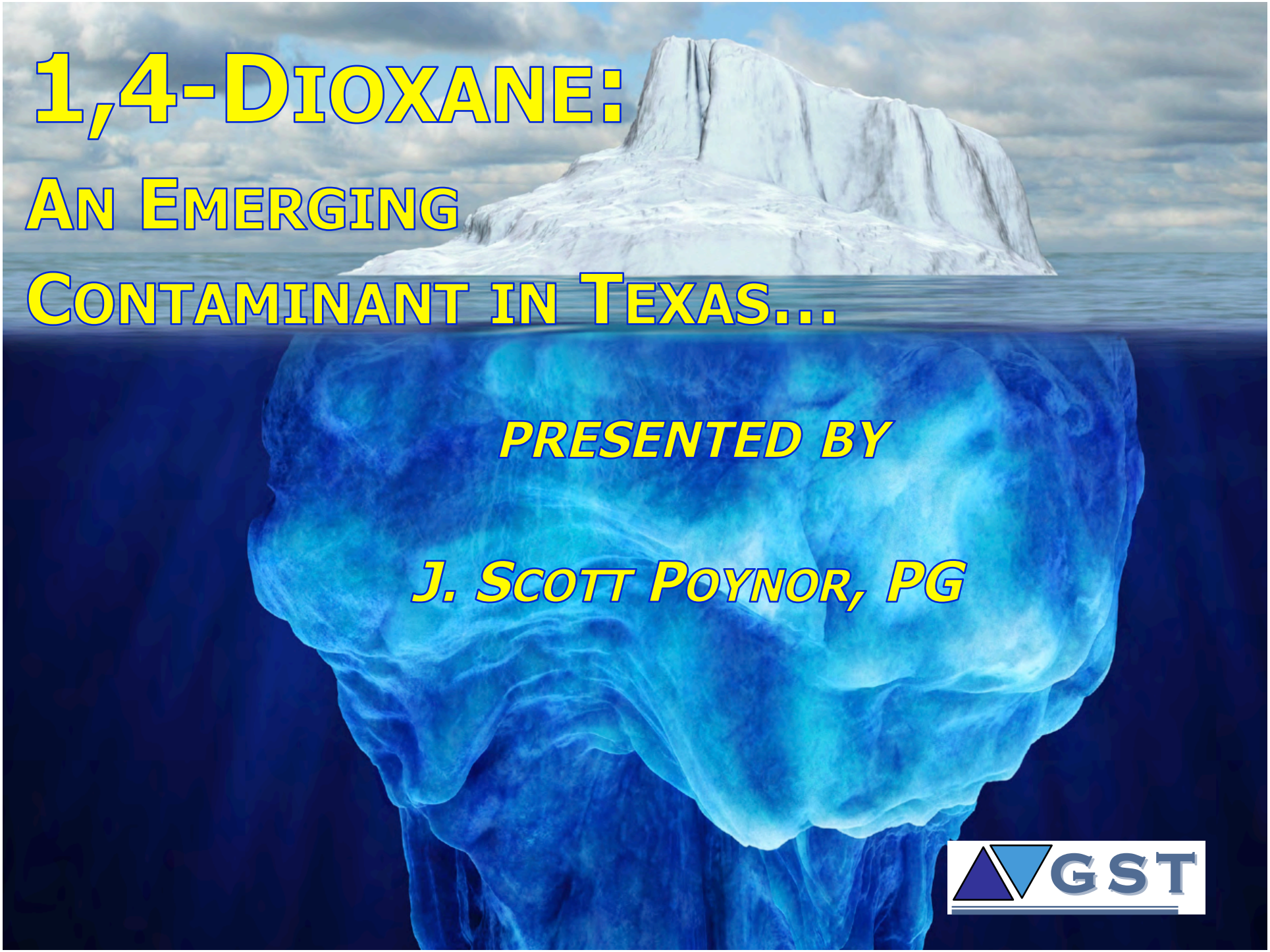
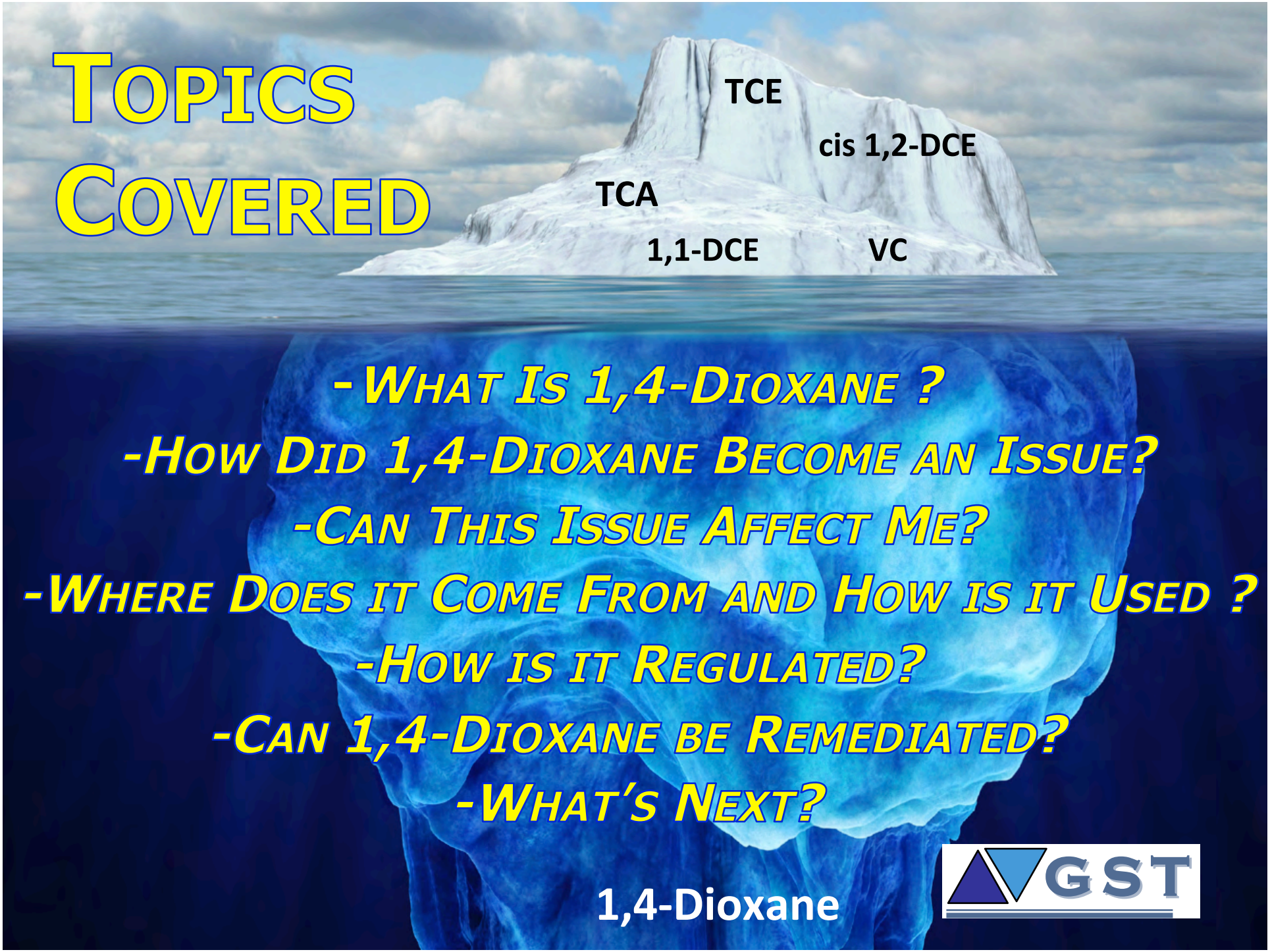
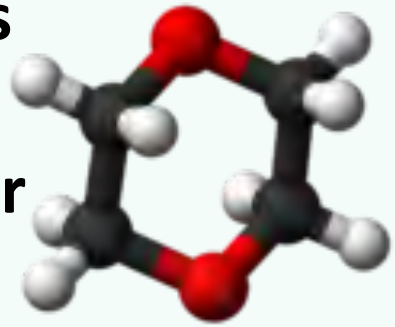

1,4-Dioxane:
An Emerging
Contaminant in Texas...
PRESENTED BY
J. Scott Poynor, PG
GST

Topics Covered



What is 1,4-Dioxane?

- 1,4-Dioxane is an EPA Emerging Contaminant
- Cyclic ether - a colorless, flammable liquid
- 1,4-Dioxane is highly soluble in water and is also soluble in oil
- 1,4-Dioxane is highly mobile in groundwater
- Diffusion transport of 1,4-Dioxane in groundwater is faster than other chlorinated solvents
- Can be a plume leading edge indicator in certain circumstances
- Migrates rapidly through soil with very poor adsorption



What Is An Emerging Contaminant?

EPA Defines An "Emerging Contaminant" As Follows

"Chemicals are being discovered that previously had not been detected or are being detected at levels that may be significantly different than expected. Additionally, risk to human health and the environment associated with their presence, frequency of occurrence, or source may not be known."

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How Did 1,4-Dioxane Become an Issue?

Air Force Plant 44 / Raytheon Superfund Tucson International Airport Area, Tucson, Arizona

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

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How Did 1,4-Dioxane Become an Issue?

Air Force Plant 44 / Raytheon Superfund
Tucson International Airport Area, Tucson, Arizona

- **GW Solvent Plumes found in 1981, delineated in 1982, NPL listing in 1983, pump and treat started in 1987, effluent was re-injected to slow plume migration toward the north**
- **1,4-Dioxane, a TCA stabilizer, is found in 2002 in the Tucson water supply wells**
- **Effluent sampling showed the AFP-44 treatment system was re-injecting water contaminated with 1,4-Dioxane**
- **The 1,4-Dioxane contamination affected ~9% of Tucson water supply**

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How Did 1,4-Dioxane Become an Issue?

Air Force Plant 44 / Raytheon Superfund
Tucson International Airport Area, Tucson, Arizona

- **Re-injection ceased in 2004**
- **May 2007 EPA ordered Air Force to fix the treatment system to remove 1,4-Dioxane**
- **The pump and treatment system was restarted in September 2009**
- **August 2011 EPA, AZ, Air Force Agreement to re-open the RI/FS for the AFP-44 site 24 years after the start of groundwater remediation**

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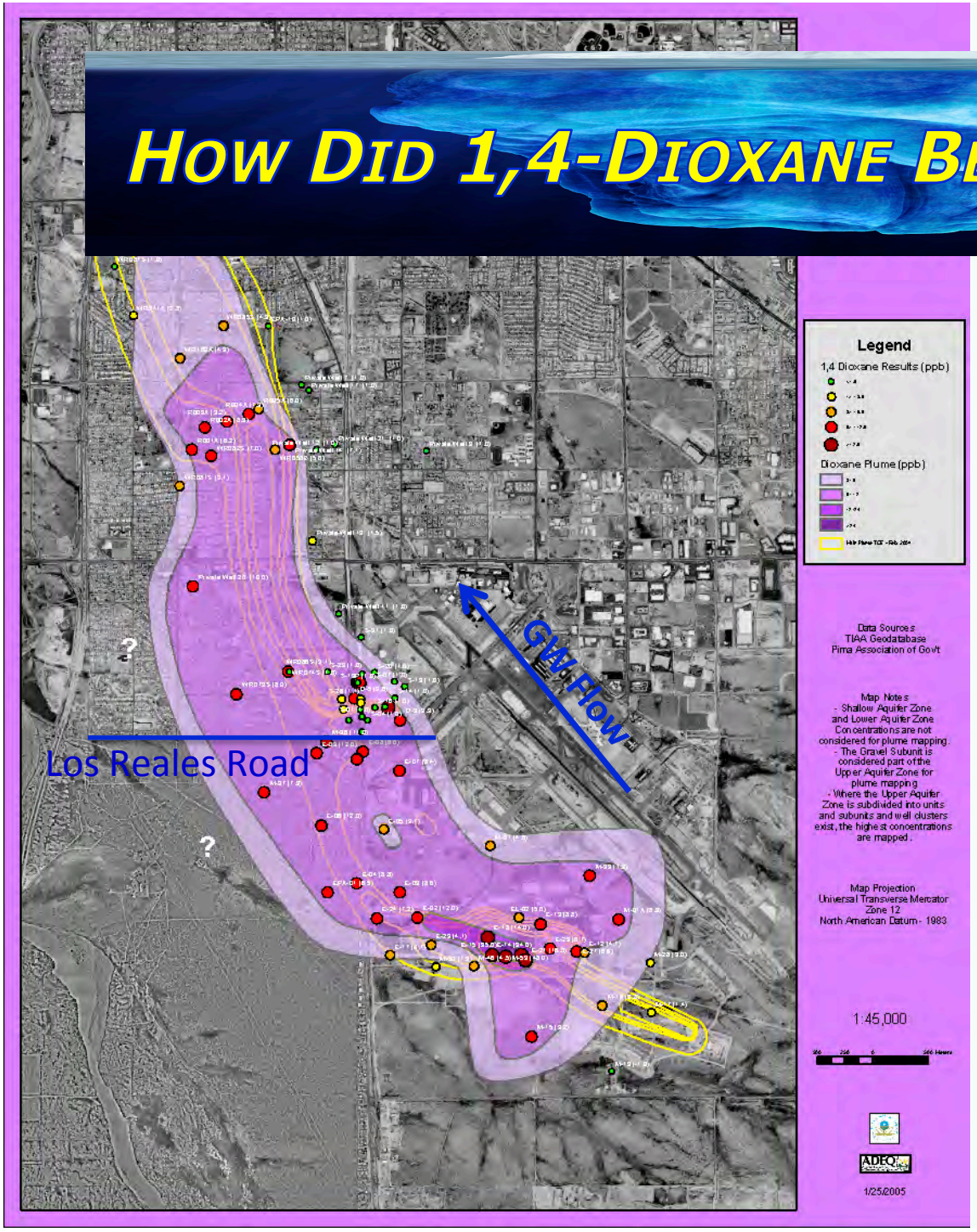
How Did 1,4-Dioxane Become an Issue?



Air Force Plant 44 / Raytheon Superfund

- ***Groundwater Plume measures approximately 5 miles long by ½ mile wide***
- ***1,4-Dioxane Impact north of blue line is from water re-injected from 1987-2004***

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How Was 1,4-Dioxane Missed?

- 1,4-Dioxane does not appear on the standard reporting list for VOCs by EPA method 8260 or SVOCs by EPA method 8270
- Both EPA methods 8260 and 8270 (GC/MS) are capable of reporting 1,4-Dioxane. However, reporting levels with these methods were historically elevated.
- In 2008 EPA released Method 522 with Selected Ion Monitoring (SIM) for the Drinking Water Program.
- In recent years, modifications to 8260 and 8270 have made 1,4-Dioxane detectable at much lower levels. Many laboratories can now run 522 or 8270 SIM that yield very low detection levels.

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Re-Assessing 1,4-Dioxane Health Risk

EPA Conducted New Risk Assessment

- In 2012, the EPA approved and funded a full Risk Assessment of 7 high priority chemicals which include six flame retardants and 1,4-Dioxane under the Toxic Substance Control Act (TSCA)
- The Risk Assessment was completed in 2013

Re-Assessing 1,4-Dioxane Health Risk

EPA Found Significant Risk

- The Risk Assessment findings published in EPA's Integrated Risk Information System (IRIS) indicate 1,4-Dioxane is "likely to be carcinogenic to humans by all routes of exposure" (oral, inhalation, and dermal)
- California Prop. 65 has had 1,4-Dioxane listed as a human carcinogen

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Re-Assessing 1,4-Dioxane Health Risk

Health Effects

- EPA Probable Human Carcinogen
- Non-Carcinogenic effects on Liver & Kidney

Regulatory

- No Federal MCL
- Tier I TOX Values – USEPA IRIS
- At least 12 States with Promulgated Water Stds.
- Many States with “Guidance” Values

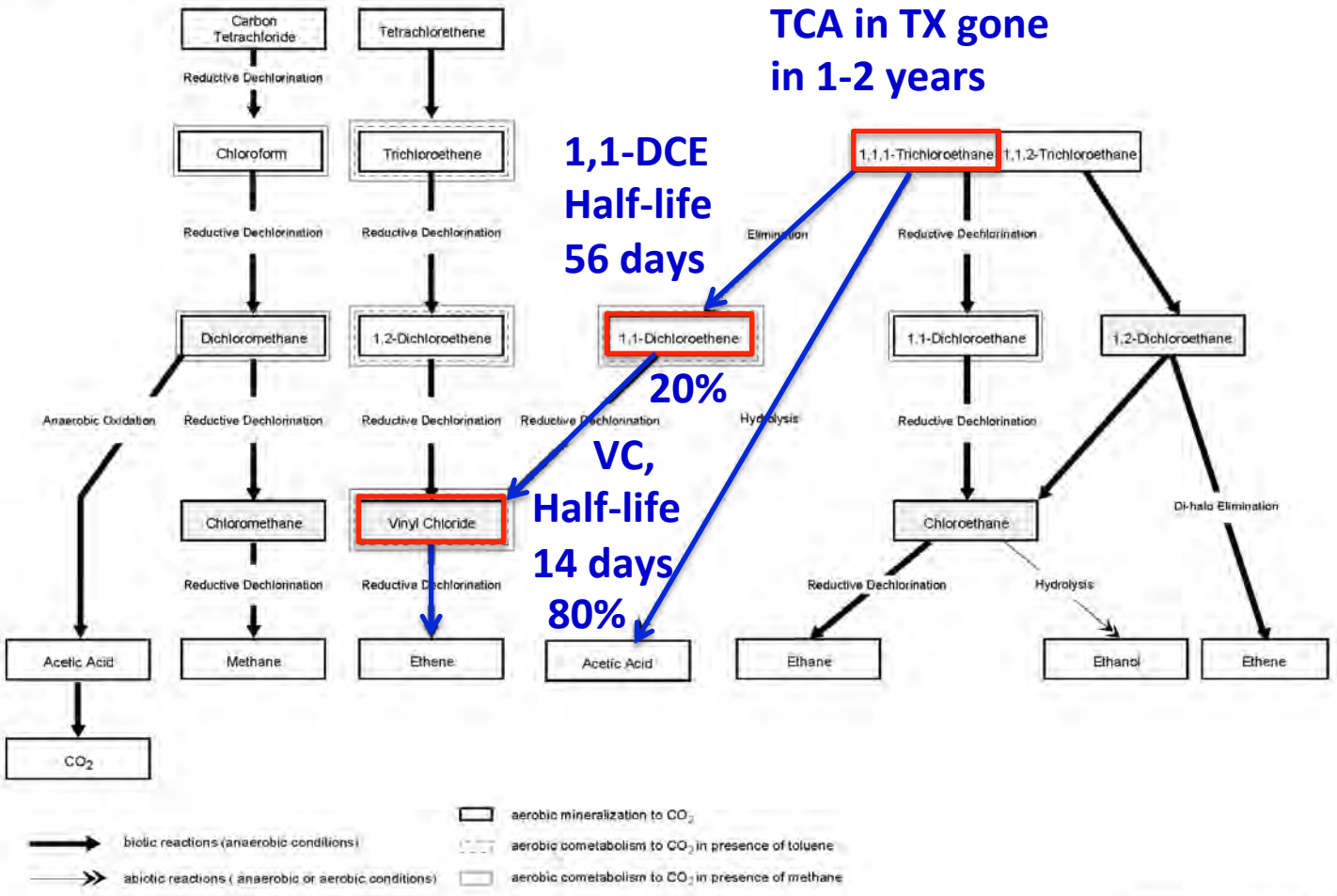
Re-Assessing 1,4-Dioxane in Soil and Groundwater?

- In January 2013, The Air Force Center for Engineering and the Environment (AFCEE) announced it is re-assessing 291 Superfund sites for 1,4-Dioxane testing
- This resulted from an internal AFCEE study that identified 1,4-Dioxane as a frequent co-contaminant with TCE, occurring at actionable levels in approximately 64% of impacted sites evaluated

1,4-Dioxane: Where Do We Need To Look?

TCA and its degradation products will probably be completely gone in 15-20 years

Figure 2: Common Degradation Pathways



ITRC - NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER:PRINCIPLES AND PRACTICES - FINAL MAY 1999, Appendix D

1,4-Dioxane: Where Do We Need To Look?

PCE, TCE and its degradation products probably persist at most sites for 1 to 2 orders of magnitude longer in than TCA

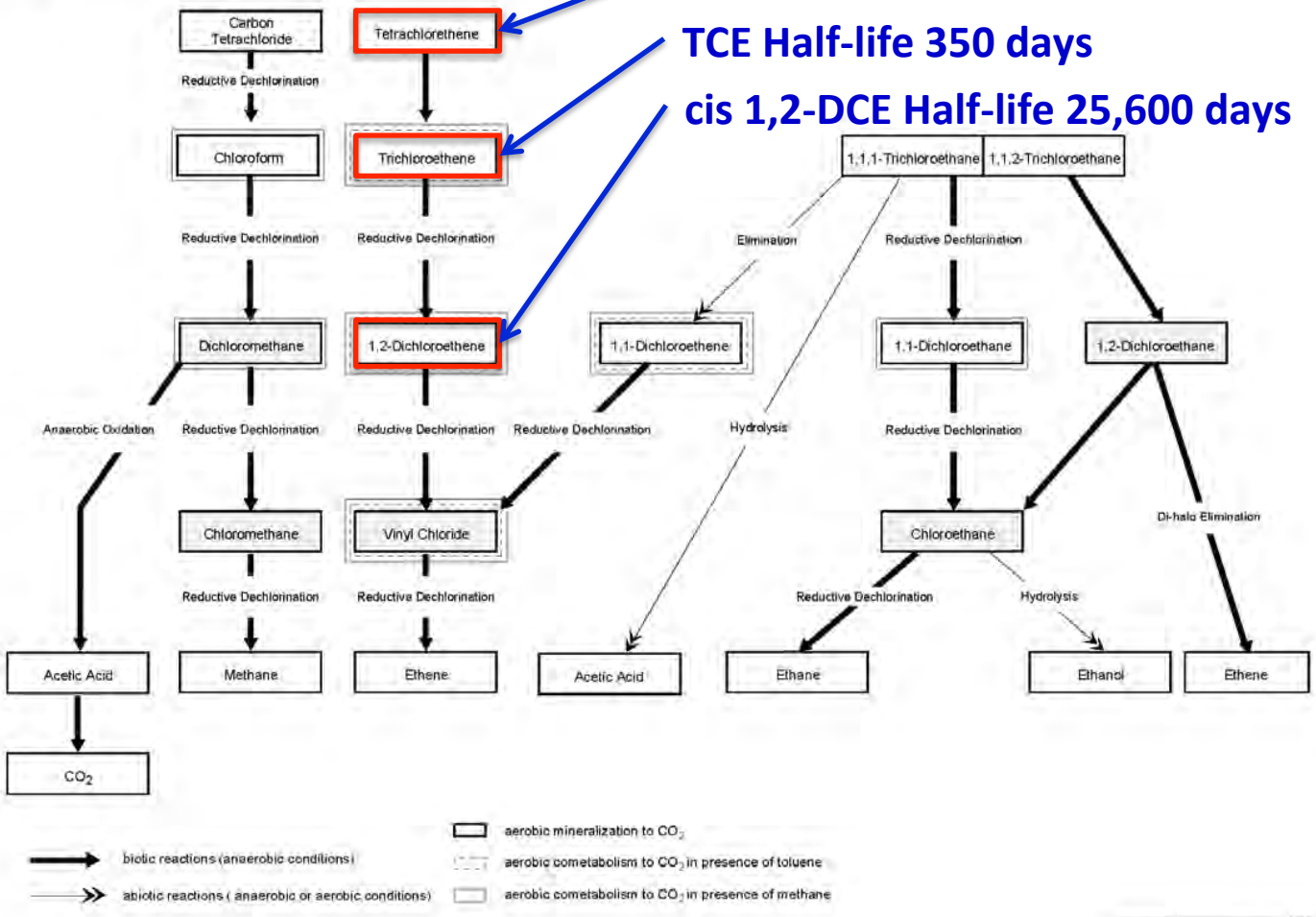
1,4-Dioxane is believed to be recalcitrant and to persist for similar time frames as the unsaturated chlorinated compounds

Figure 2: Common Degradation Pathways

PCE Half-life 1095 days

TCE Half-life 350 days

cis 1,2-DCE Half-life 25,600 days



ITRC - NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER:PRINCIPLES AND PRACTICES - FINAL MAY 1999, Appendix D

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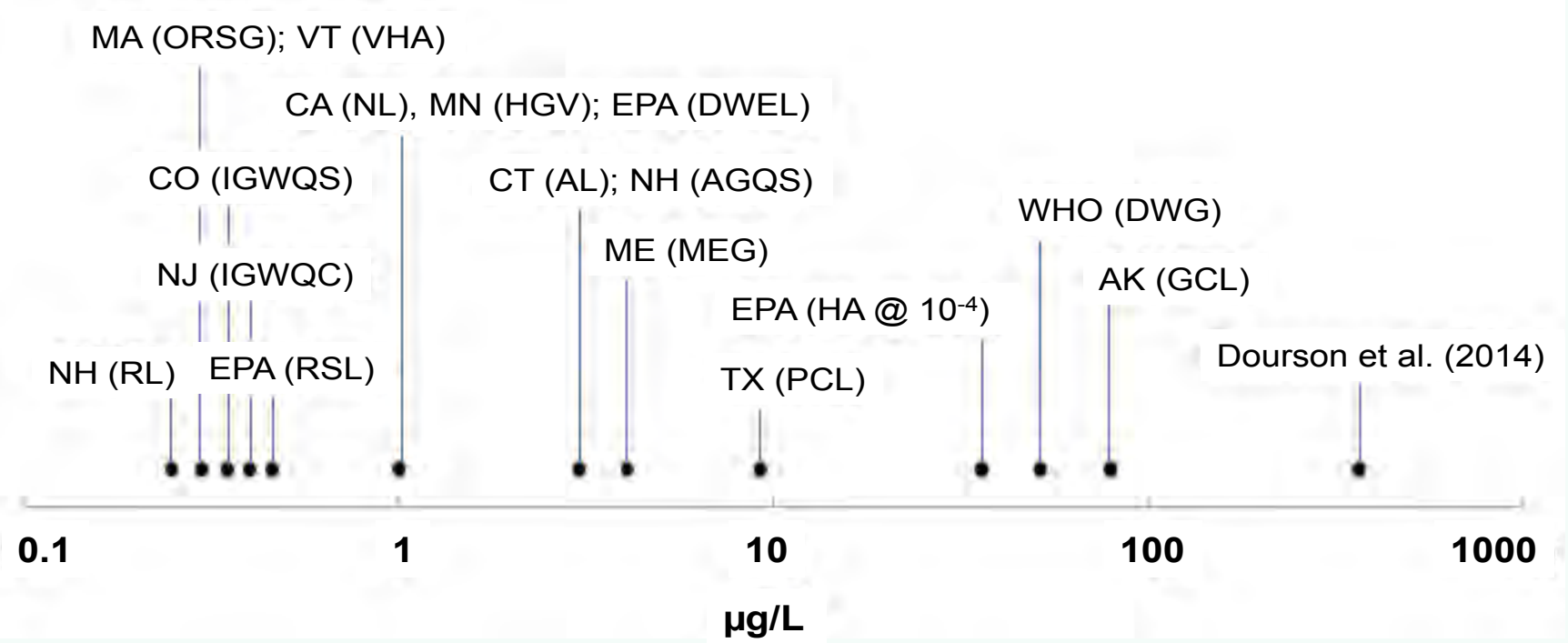
Re-Assessing 1,4-Dioxane Health Risk

Comparison of Regulatory & Guidance Risk-Based Values



2003 – 2017 TCEQ TRRP has had a 1,4-Dioxane PCL.
Current (2011-2017) Tier 1 Default PCL ($^{GW}GW_{Ing}$, 0.5 Ac, Residential) = 9.1 µ/L

Adopted from SERDP & ESTCP Webinar Series #52
https://serdp-estcp.org/Tools-and-Training/Webinar-Series/04-06-2017

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Re-Assessing 1,4-Dioxane in Soil and Groundwater?

Action Levels - Groundwater Action Levels Are Typically In The Single Digit PPB Range

- The TCEQ has a TRRP action level of 9.1 µg/L (Revised May 2011)
- EPA Regions III, VI and IX have a new screening level of 6.1 µg/L
- Florida DEQ Groundwater Clean-up Target Level of 3.2 µg/L
- California adopted a drinking water notification level of 1.0 µg/L
- EPA Region 3 Risk Based Concentration (ingestion) of 0.67 µg/L
- EPA IRIS E^{-6} Carcinogenic Oral Exposure Risk at 0.35 µg/L
- Massachusetts has revised drinking water guideline to 0.30 µg/L

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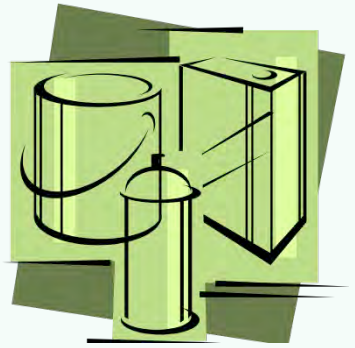
What are 1,4-Dioxane's Uses?

- Used as a Reagent Grade Solvent
- By-Product of Surfactant Production (*ethoxylation*)
- Used as a Chlorinated Solvent Stabilizer and Corrosion Inhibitor

What Are 1,4-Dioxane's Uses?

Used as a Reagent Grade Solvent



- Paint, varnish and lacquer solvent
- Solvent for extracting oils
- Ink solvent
- Coatings and adhesive solvent in celluloid film processing (Pall Gelman Site - Ann Arbor, MI)

What Are 1,4-Dioxane's Uses?

By-Product of Ethoxylation

- Ethoxylation is a chemical process used to create surfactants by combining ethylene oxide with an alcohol, amine or phenol under specific conditions
- Ethoxylation produces fabric softeners and foaming agents in laundry detergents and shampoos such as sodium laureth sulfate (SLS)
- The polymerization of ethoxylation forms 1,4-Dioxane as a byproduct. Consumer products containing SLS have been found to contain 1,4-Dioxane at concentrations up to 279 ppm

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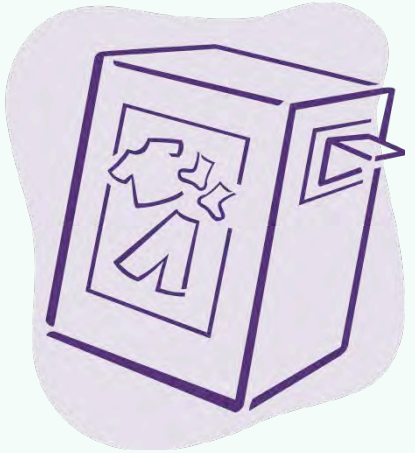
What Are 1,4-Dioxane's Uses?

By-Product of Ethoxylation

Laundry Detergents Tested (Organic Consumers Association)

- **Tide (P&G)* – 55 ppm**
- **Ivory Snow Gentle (P&G) – 31 ppm**
- **Tide Free (P&G)* – 29 ppm**
- **Purex– 25 ppm**
- **Gain 2X Ultra (P&G)* – 21 ppm**
- **Cheer BrightClean (P&G)*– 20 ppm**
- **Era 2X Ultra (P&G)* – 14 ppm**
- **Arm & Hammer – 5.0 ppm**
- **Wisk 2X Ultra – 3.9 ppm**
- **Woolite Complete Detergent – 1.3 ppm**
- **Unilever laundry detergent – 0.6 ppm**



* - P&G has committed to removing 1,4-Dioxane in laundry detergents by the end of 2013

http://www.naturalnews.com/028846_laundry_detergents_dioxane.html#ixzz2d6nfWM4w

What Are 1,4-Dioxane's Uses?

Used as a Solvent Stabilizer and Corrosion Inhibitor

- Chlorinated solvents, in particular 1,1,1 Trichloroethane (TCA), require a solvent stabilizer to preserve shelf life for marketability
- Chlorinated solvents tend to break down in the presence of light, heat and oxygen, or react with acids and metal salts
- Addition of stabilizers to chlorinated solvents provides necessary acid acceptors, metal inhibitors, and antioxidants
- Patent applications for stabilization by Dow chemist H.J. Bachtel in 1954 and 1955 led to much broader use of TCA starting in 1957

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What Are 1,4-Dioxane's Uses?

- Trichloroethylene (TCE) was the preferred solvent used in many industrial applications from the 1940s through the 1960s. In the late 1960s, TCE came under increasing occupational scrutiny because it was identified as an animal carcinogen
- As a result, many firms switched to 1,1,1 Trichloroethane (TCA) by the 1970s. TCA reached peak production in the mid 1980s.

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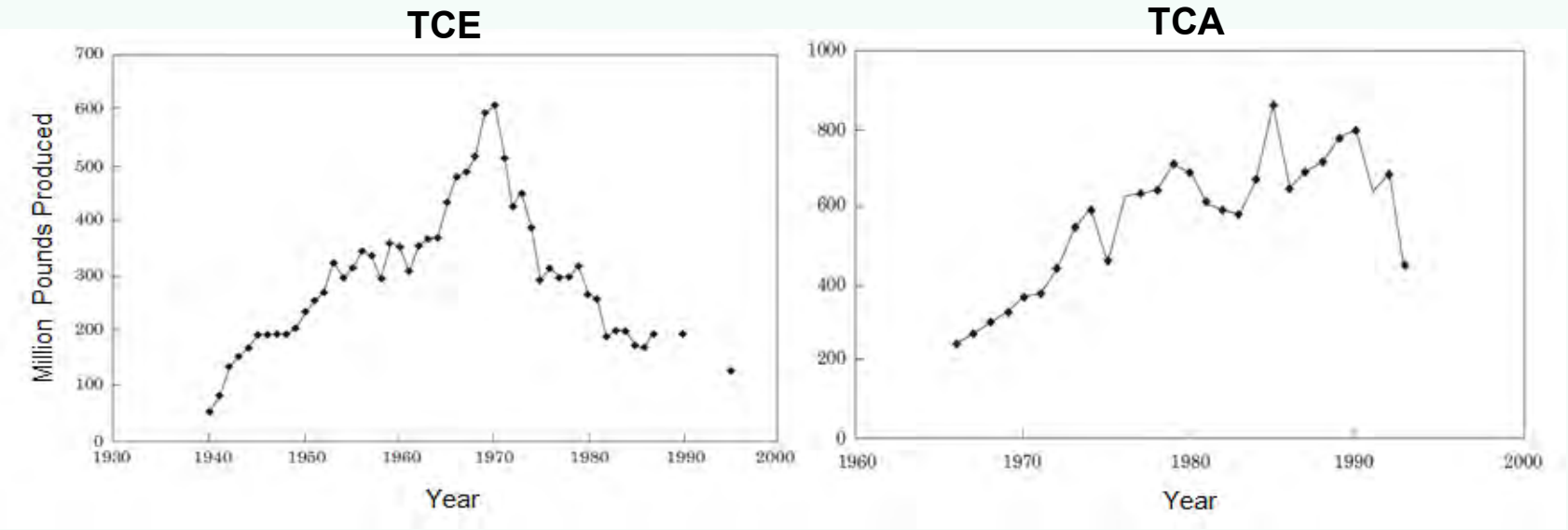
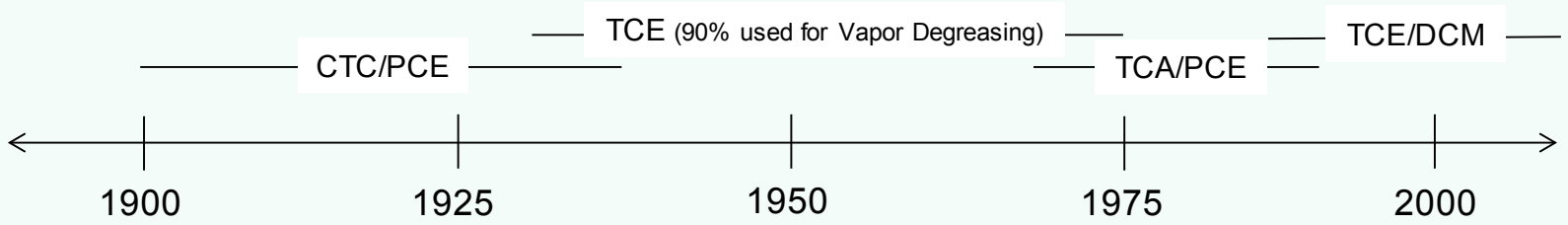
What Are 1,4-Dioxane's Uses?





Doherty, RE (2000), Journal of Environmental Forensics; Morrison et al. (2005), Ch. 12, Chlorinated Solvents, in *Environmental Forensics*

What Are 1,4-Dioxane's Uses?

- 1, 4 Dioxane was added as a stabilizer to TCA at 2% – 6% by volume
- Increased popularity of TCA dictated an increase in the use of 1,4-Dioxane

What Are 1,4-Dioxane's Uses?

- 1,4-Dioxane was manufactured from the late 1950s to present and widely used in commerce
- In 1985 alone, the Department of Commerce reported that 25 million pounds were produced for domestic commerce
- Approximately 90% of the 1985 production in the United States was used as a TCA stabilizer

What Are 1,4-Dioxane's Uses?

Chlorinated solvents were widely used as the preferred cleaner of metal parts and electronics, because they have high solvency for both cold cleaning and vapor degreasing

What Are 1,4-Dioxane's Uses?

- Cold Cleaning refers to direct liquid application in dipping, wiping or spraying
- Common examples of TCA cold cleaning
  - Dip solvent for metal parts cleaning
  - Spray solvent for circuit board cleaning
  - Electroplating electrode cleaning
- Vapor degreasing covers an object with a dense chlorinated solvent fog producing very clean, dry parts. TCA use in vapor degreasers peaked in the 1970s through the early 1980s

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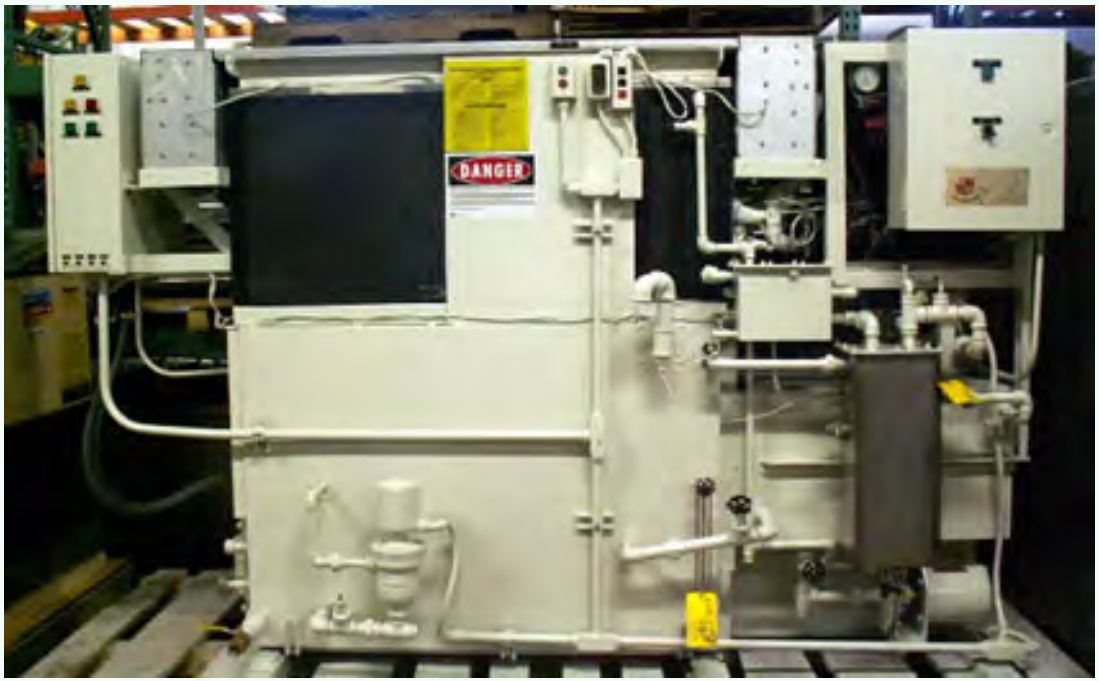
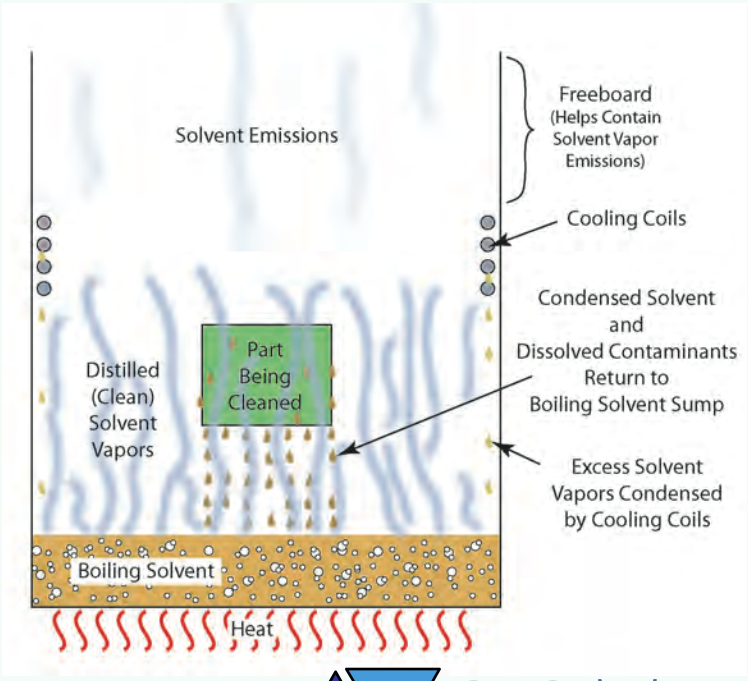
What Are 1,4-Dioxane's Uses?

Approximately 25,000 vapor degreasers were in operation domestically in 1979





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What Are 1,4-Dioxane's Uses?

- TCA boils at 78^{0}C, 1,4-Dioxane boils at 101^{0}C
- 1,4-Dioxane is concentrated in vapor degreasers with use
- A DOW Lab study found vapor degreaser still bottoms contained up to 15% 1,4-Dioxane (150,000 mg/L) after 30 days of use
- Still bottom waste containing up to 22% 1,4-Dioxane (220,000 mg/L) have been reported

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How does 1,4-Dioxane get into Soil and Groundwater?

Published Routine Disposal Practices Vapor Degreasing Sludge - 1964

[**American Society of Metals**, Metals Handbook: Heat Treating, 8th Edition, Volume 2. Metals Park, Ohio]

"Any procedure for disposal depends on local, state and federal regulations. In the absence of any clearly defined ordinances, the sludge is usually poured on dry ground well away from buildings, and the solvents are allowed to evaporate. If the sludge is free flowing, it is placed in shallow open containers and allowed to evaporate before the solids are dumped on the ground."

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How does 1,4-Dioxane get into Soil and Groundwater?

Published Chlorinated Solvent Waste Still Bottom Management Practices - 1972

[Chemical Hazards Bulletin, **American Insurance Association**, C-86, March 1972, New York, NY. Pg. 42]

"Waste mixtures should not be discharged into drains or sewers where there is a danger that the vapor may be ignited. In cases such as these, the waste should be removed to a safe location (away from inhabited areas, highways, buildings, or combustible structures) and poured onto dry sand, earth, or ashes, then cautiously ignited. Burning of chlorinated hydrocarbon wastes should be done only when permitted by controlling authorities and then under constant supervision."

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Re-Assessing 1,4-Dioxane in Soil and Groundwater?

Local Example – Old East Dallas

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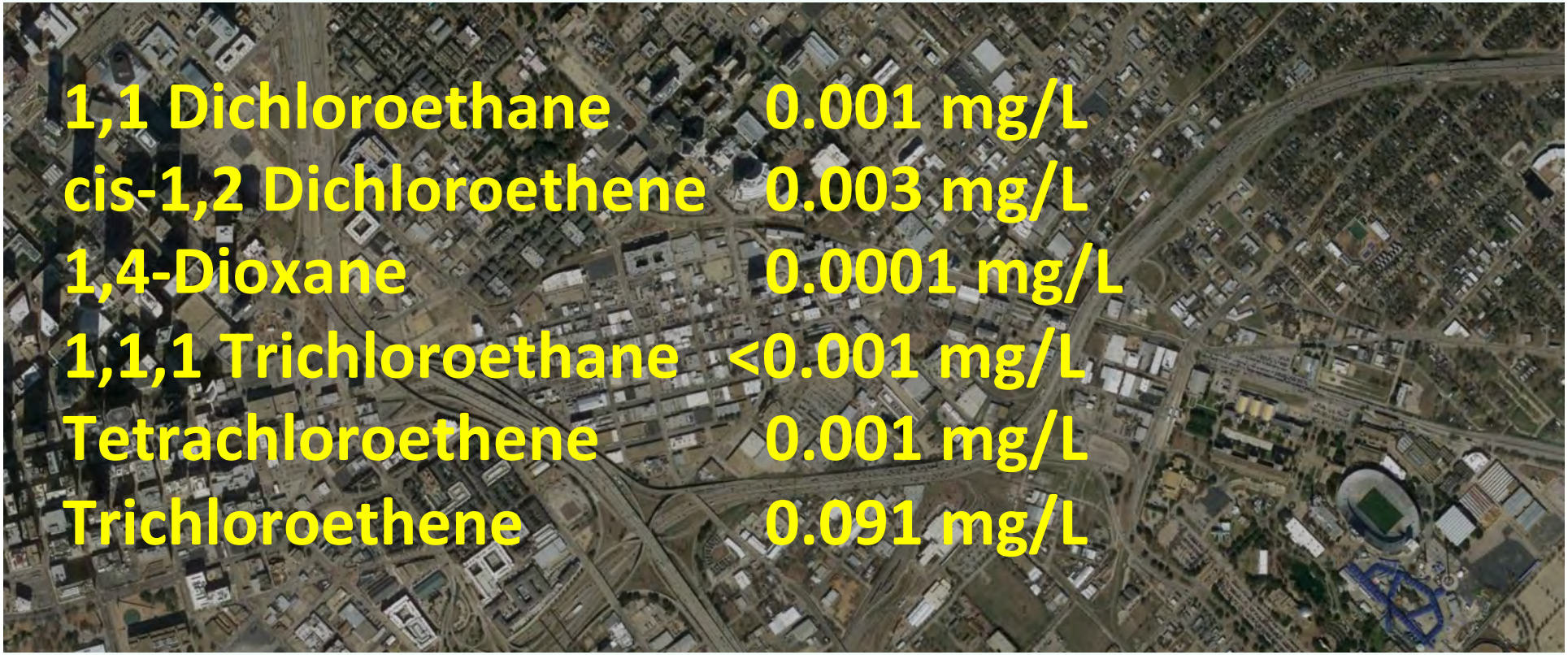
Re-Assessing 1,4-Dioxane in Soil and Groundwater?

Local Example – Old East Dallas



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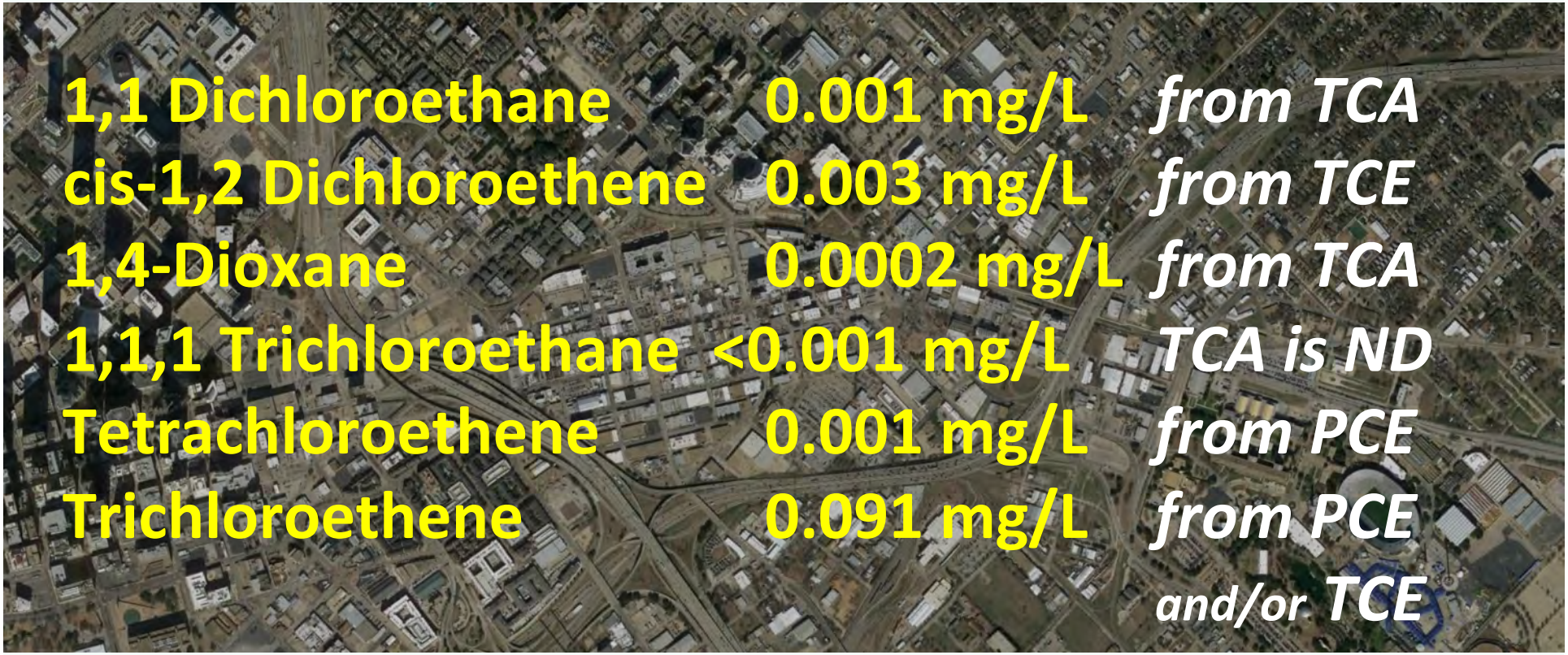
Re-Assessing 1,4-Dioxane in Soil and Groundwater?

Local Example – Old East Dallas



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1,4-Dioxane Remediation

Cleanup Challenges

- Very Stable; Difficult to Remediate
- Resistant to in- or ex-situ bioremediation
- Will not air strip
- Very poorly adsorbed by activated carbon

1,4-Dioxane Remediation

Groundwater Remediation Technologies

- EPA Superfund Innovative Technology Evaluation (SITE) Program recommends Advanced Oxidation as an active remedy
- Some phyto-remediation cases have demonstrated moderate success, with very limited applicability
- Closely managed ex situ bioreactors have demonstrated some success, however, throughput volume is limited
- Successful in situ bioremediation has yet to be demonstrated

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1,4-Dioxane Remediation

Groundwater Remediation Technologies

- Ex situ treatment systems have demonstrated 1,4-Dioxane destruction incorporating generation of ozone, hydroxyl free radical, sulfate free radical, superoxide anion and combinations thereof
- Successful in situ advanced oxidation is much more difficult than ex situ treatment. However, in situ treatment avoids inherent inefficiencies and long lifespan of pump and (ex situ) treatment

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1,4-Dioxane: Where Do We Need To Look?

- Locations where groundwater was impacted with chlorinated solvents which will be removed, treated then re-injected or sent to a surface water body (chlorinated solvent pump & treat)
- Sites where any 1,1,1-TCA, 1,1-DCE or 1,1-DCA is found in the shallow groundwater
- Sites with historic vapor degreasers use from the late 1950s to the early 1990s, regardless of what solvents or degradation products are currently observed in GW, because the 1,1,1-TCA and its degradation products will probably be gone

Re-Assessing 1,4-Dioxane in Soil and Groundwater?

- 1,4-Dioxane has not been historically tested for at the majority of TCA/TCE groundwater sites
- EPA and many State regulators are instituting policies for re-opening assessment at TCA/TCE groundwater sites where 1,4-Dioxane has never been tested
- As of 2013, EPA Region VI requires evaluation for 1,4-Dioxane testing at all TCA/TCE groundwater Superfund sites under 5 year review

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Re-Assessing 1,4-Dioxane in Soil and Groundwater?

- As of 2016, the TCEQ has started requesting 1,4-Dioxane analysis at TCA/TCE groundwater sites
- Currently, there is a reluctance to re-open an approved Affected Property Assessment Report, especially if a Response Action Plan has been submitted and approved prior to 1,4-Dioxane analysis
- The TCEQ may request 1,4-Dioxane analysis at sites in the beginning or middle of the APAR process that have TCA or TCE groundwater contamination. If the site has had historic vapor degreasing operations, the likely hood of required 1,4-Dioxane testing increases

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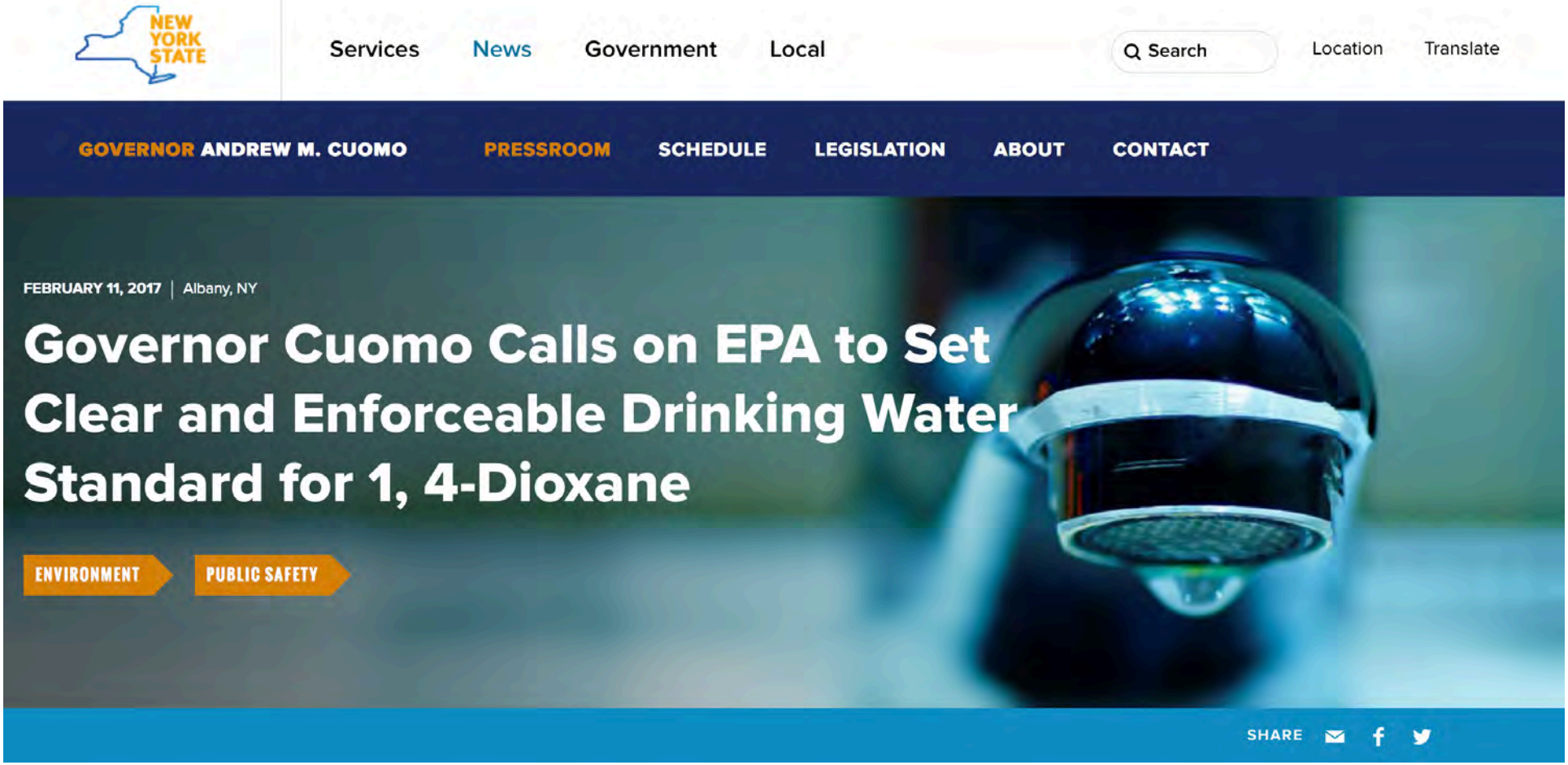
Will Public Opinion Affect Policy?



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Will Public Opinion Affect Policy?

State of New York
Executive Chamber
Albany 12224

Andrew M. Cuomo
GOVERNOR

"Given the absence of Federal leadership on these issues, New York has stepped in to fill the void"

"…Advanced Oxidation Process technology to remove 1,4-Dioxane from the water supply has been approved…" February 11, 2017

Acting Administrator
1200 Pennsylvania Avenue, N.W.

Ensuring clean drinking water is an issue that affects communities in every corner of the
federal leadership.

"As new contaminants continue to emerge on a regular basis in communities across the nation, states should no longer be left to fend for themselves. The federal government should provide actionable guidance…"

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Ramifications For Sites With 1,4-Dioxane Above Action Levels

- Increased liability for this emerging chemical of concern
- TRRP leaves the door open for sites to be re-opened or denied closure should 1,4-Dioxane be identified in the future as a chemical of concern
- Absent on almost all VCP Certificates of Completion at "closed" chlorinated solvent sites - Example - If 4 of 5 COCs are successfully remediated and listed on the VCP Cert. of Completion, but 1,4-Dioxane was unchanged (and not listed on Cert.), is the site really "CLOSED"?
- Potential liability for current discharge to the environment where 1,4-Dioxane is not being tested (and is present) in the effluent stream including to POTWs

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Ramifications For Sites With 1,4-Dioxane Above Action Levels

- Additional time and cost to determine its presence
- Potentially larger investigation areas due to high solubility and mobility
- Ineffective treatment for 1,4-Dioxane impacted water with traditional remediation methods
- Effective treatment for 1,4-Dioxane is available, but comparatively expensive and technically challenging
  - *Expensive and challenging compared to methods that do not work; potentially inexpensive compared to retained liability*

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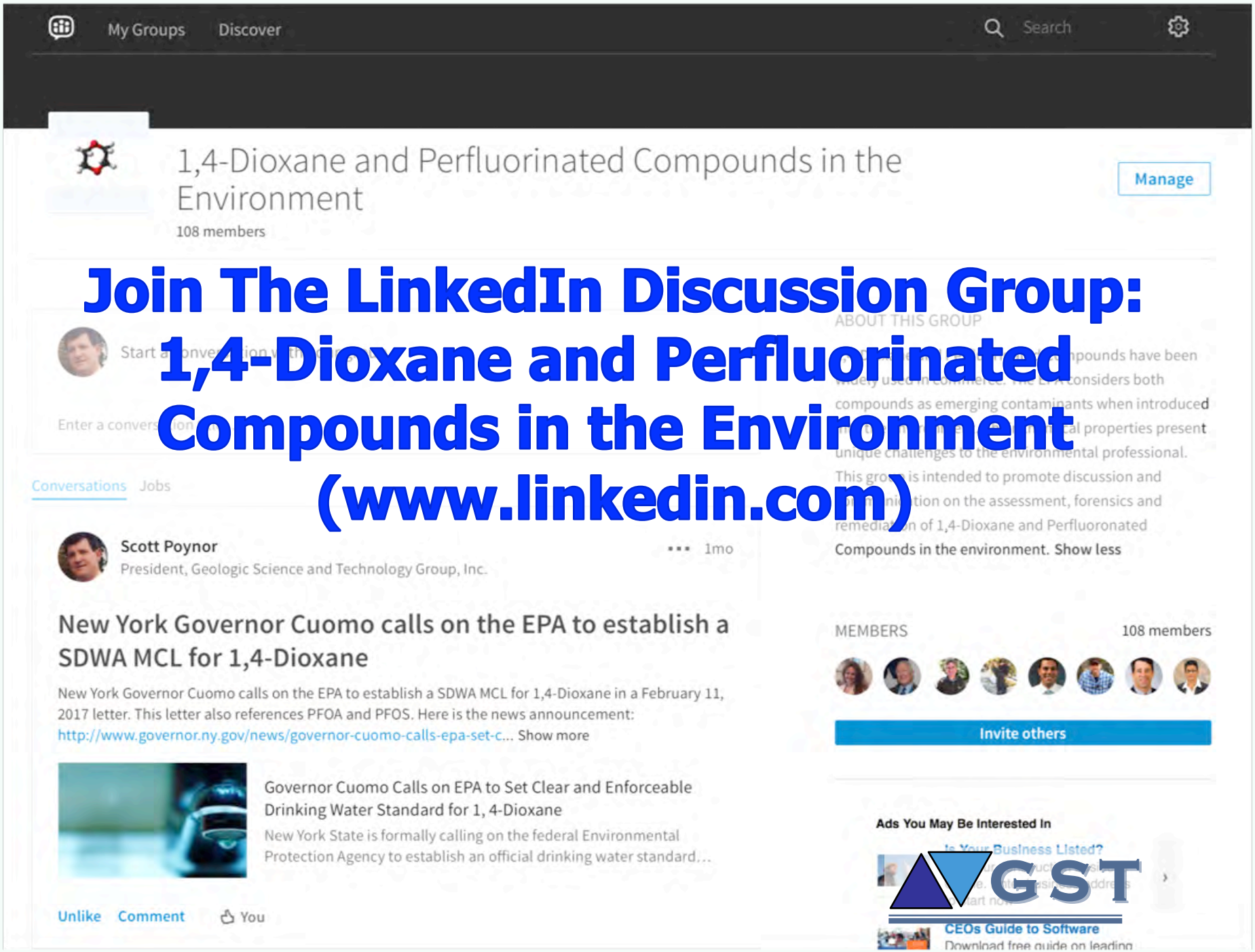
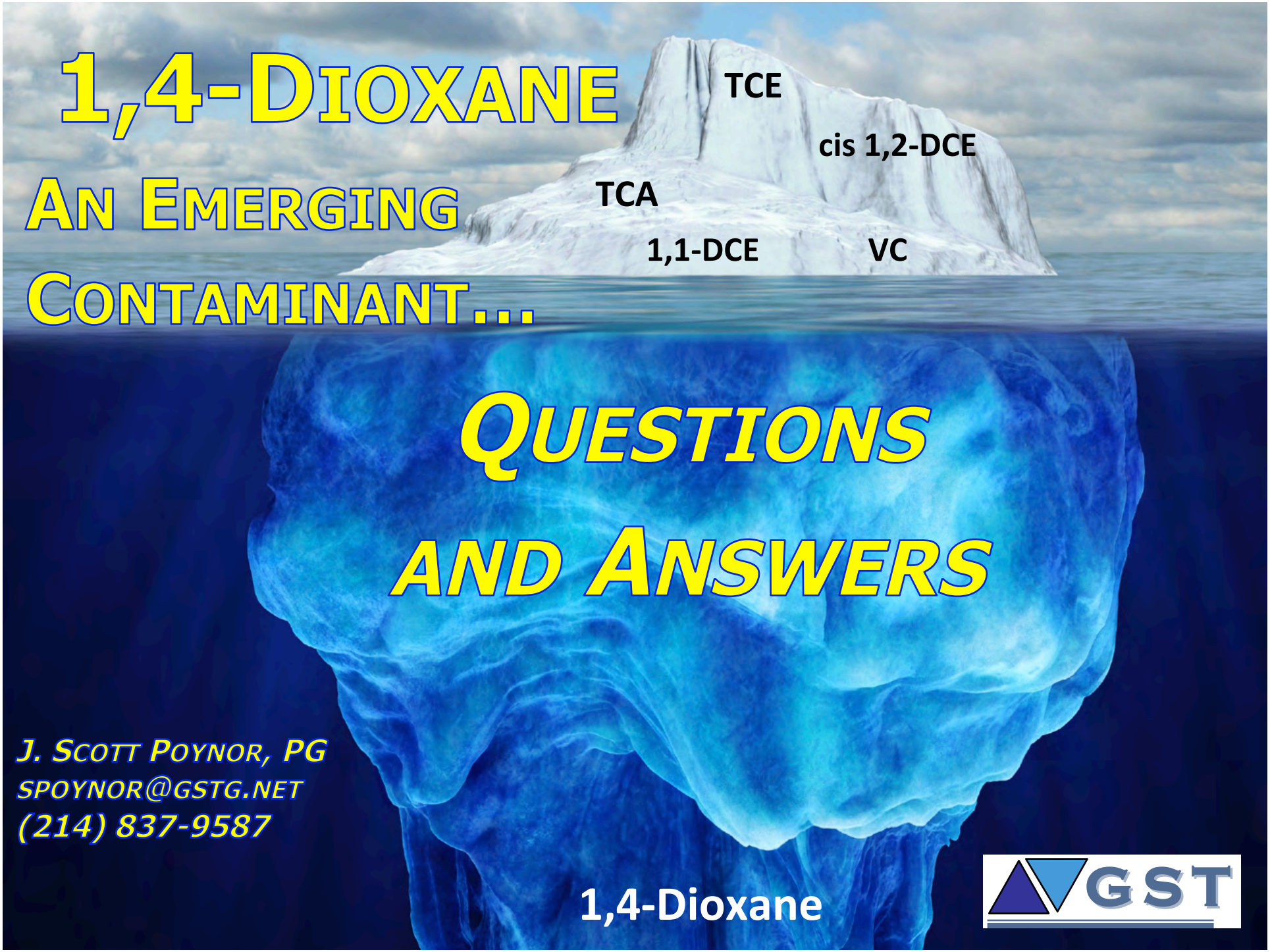

My Groups
Discover
Search
1,4-Dioxane and Perfluorinated Compounds in the Environment
108 members
Manage
Join The LinkedIn Discussion Group:
1,4-Dioxane and Perfluorinated Compounds in the Environment
(www.linkedin.com)
Start a conversation with
Enter a conversation
Conversations
Jobs
ABOUT THIS GROUP
compounds as emerging contaminants when introduced
unique challenges to the environmental professional.
This group is intended to promote discussion and
Compounds in the environment. Show less
Scott Poynor
President, Geologic Science and Technology Group, Inc.
1mo
New York Governor Cuomo calls on the EPA to establish a SDWA MCL for 1,4-Dioxane
New York Governor Cuomo calls on the EPA to establish a SDWA MCL for 1,4-Dioxane in a February 11, 2017 letter. This letter also references PFOA and PFOS. Here is the news announcement: http://www.governor.ny.gov/news/governor-cuomo-calls-epa-set-c... Show more
Governor Cuomo Calls on EPA to Set Clear and Enforceable Drinking Water Standard for 1, 4-Dioxane
New York State is formally calling on the federal Environmental Protection Agency to establish an official drinking water standard...
Unlike
Comment
You
MEMBERS
108 members
Invite others
Ads You May Be Interested In
Is Your Business Listed?
CEOs Guide to Software
Download free guide on leading

1,4-Dioxane

An Emerging Contaminant...



Questions and Answers

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