Introduction to 1,4-Dioxane

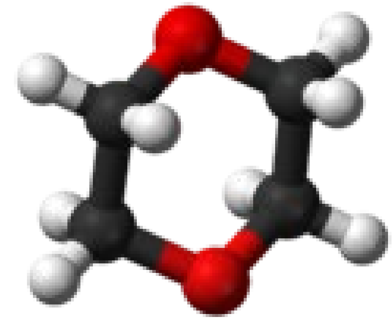
Hunter Anderson, Ph.D.

ACEC Meeting

Apr 19

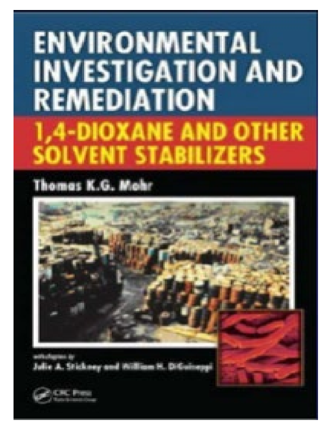
Background

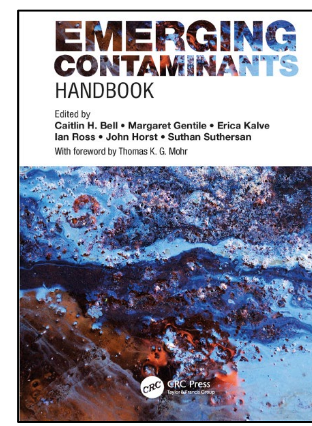
- **Miscible in water**
  - Challenging analytical method
  - Low risk from vapor intrusion
- **Increasing awareness as a contaminant since mid 2000's**
  - Lots of data exist to evaluate



	VP (mm Hg)	Solubility (mg/L)
1,4-Dioxane	38	**Infinite**
Water	24	Infinite
1,1,1-TCA	124	1,290
TCE	69	1,280

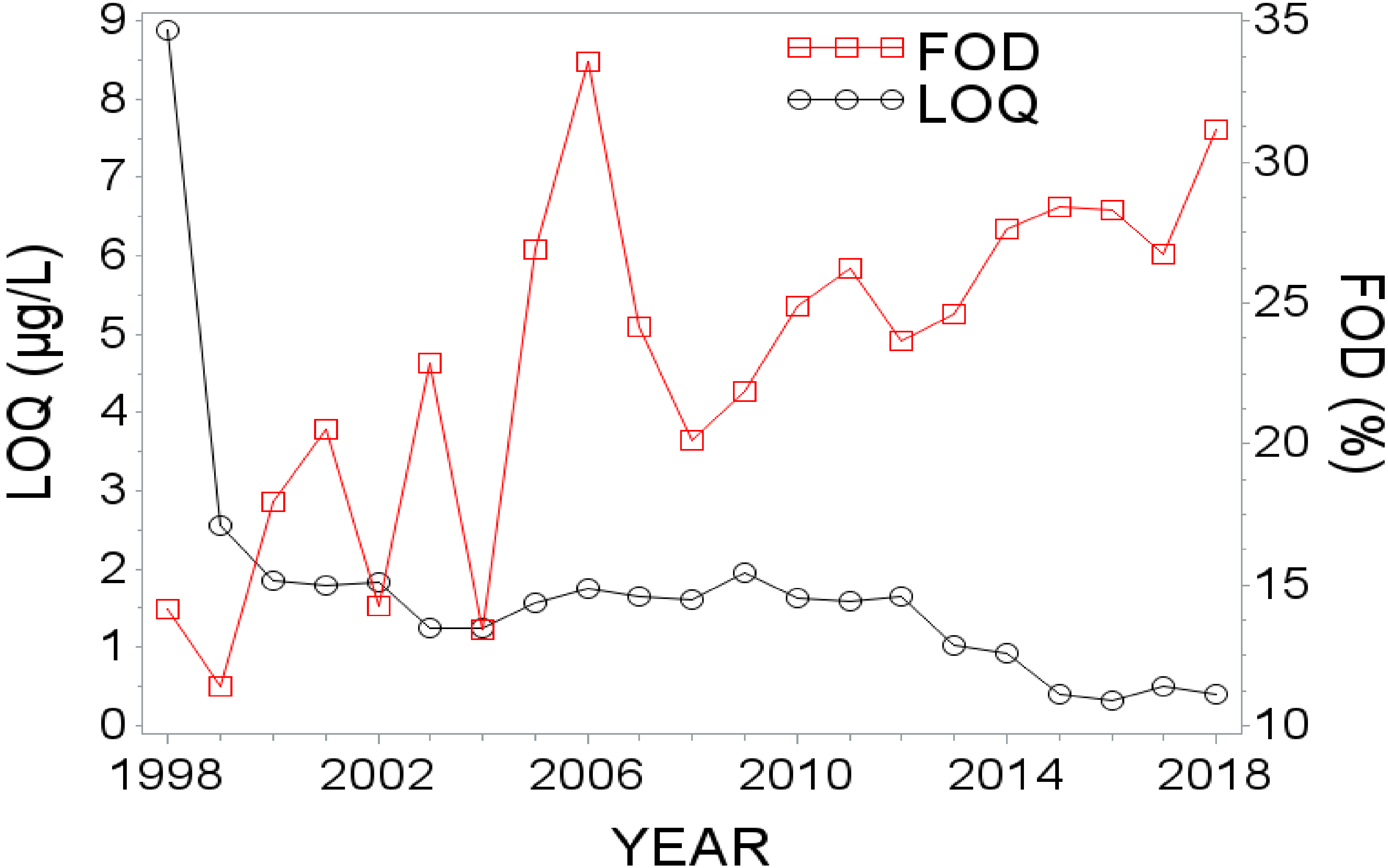
Critical References





AFCEC's Metadata

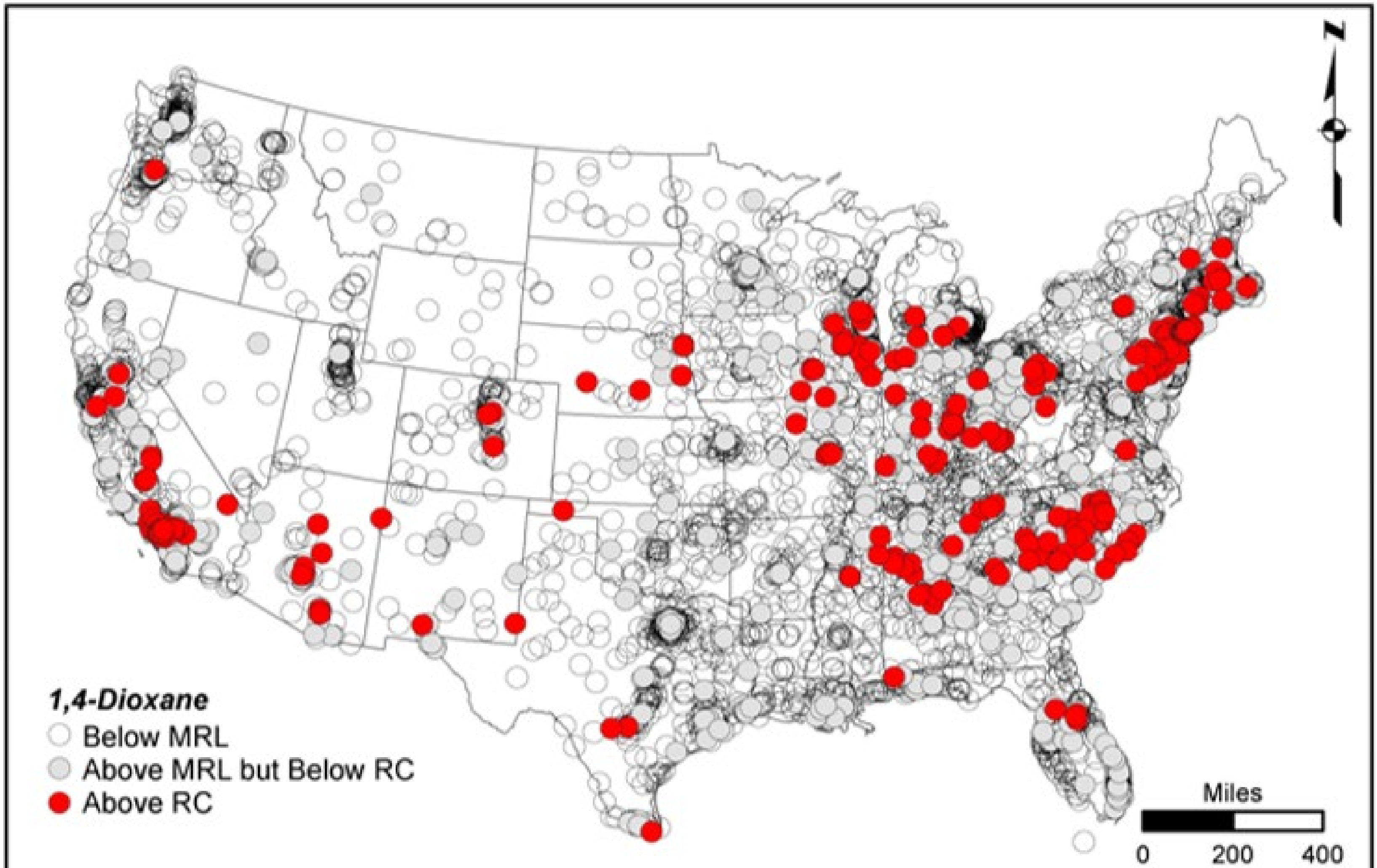
37,846 Total Groundwater Samples to Date



Contemporary Sources

- **Reagent grade solvent for specialized analytics**
  - Scintillation cocktails, etc.
- **Cellulose acetate membrane production**
- **Manufacturing byproduct (e.g., ethoxylation)**
  - Chemical food additives
    - Gluten-free bread (ethyl hydroxyethyl cellulose)
    - Ice cream (polysorbate 60)
  - Paints, detergents, coolants, de-icers, etc.
  - Personal Care Products (Black and Havery 2001)
    - e.g., Sodium laureth sulfate
    - Up to 279 mg/kg in cosmetic finished products
    - >85 mg/kg in children's shampoo

U.S. EPA's UCMR3 Results



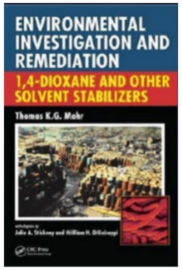
6.9% of PWSs > 0.35 µg/L; Adamson et al. STOTEN. 2017

Historic Sources

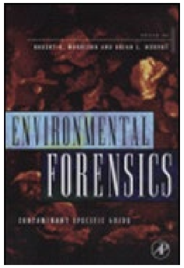
- **Chlorinated Solvent Stabilizers:**
  - **Acid Acceptors** – reacts with and chemically neutralizes trace amounts of HCL formed during degreasing operations
  - **Metal Inhibitors** – deactivates the metal surface and complexes metal salts that might form during degreasing operations
  - **Antioxidants** – prevents oxidation products

Quantity of Additives Needed Based on Physical Properties ↓

Chlorinated Solvent	Acid Acceptor	Metal Inhibitor	Antioxidant
TCA	x	x	
DCM (aka MC)	x	x	
TCE	x	x	x
CTC	----- Used as Metal Degreaser Before Stabilizers -----		
PCE	(VD grades only)	x	x



Mohr (2010)



Morrison et al. (2005)

Compiled from: Mohr (2010), Doherty (2000), Jackson and Dwarakanath (1999), and Morrison et al. (2005)

TCE Requires Stabilization

"Available in Standard Degreasing and General Solvent Grade, as well as special Dual-Purpose and High-Purity grades, ***PPG's trichlor grades incorporate a highly effective stabilizing system to help prevent solvent decomposition in each of their specific applications***"

Major US Manufacturers of TCE

Company	Approximate period of manufacture
Carbide & Carbon Chemicals	1922–1935
Diamond Shamrock	1969–1977
Dow Chemical	1921–present
Ethyl Corporation	1967–1983
Hooker-Detrex/Detrex Chemical	1947–1972
Hooker Chemical/Occidental Chemical	1956–1980
Niagara Alkali	1949–1955
Pittsburgh Plate Glass/PPG Industries	1956–present
R&H Chemical/E.I. Du Pont de Nemours	1925–1972
Westvaco Chlorine	1933–1949

Doherty, R.E. (2000): J Environ Forensics

Trichlorethylene

PPG

PPG's trichlorethylene or trichlor is a chlorinated solvent used for vapor degreasing, cold cleaning, cleaning of electronic components, flushing of liquid oxygen (LOX) and liquid hydrogen tanks, and various special applications including the production of polyvinyl chloride. Trichlor is an excellent solvent, and has no flash point or fire point. It is stable and non-corrosive.

Available in Standard Degreasing and General Solvent Grade, as well as special Dual-Purpose and High-Purity grades, PPG's trichlor grades incorporate a highly effective stabilizing system to help prevent solvent decomposition in each of their specific applications.

Properties & Characteristics

Among the properties which have contributed to trichlor's wide acceptance as a vapor degreasing agent are its high solvency, high stability and vapor density, low specific heat, relatively high boiling point, low latent heat of vaporization, and relative non-flammability in that it has no flash point or fire point.

In addition, PPG's trichlor incorporates an exceptionally effective stabilizing system to help prevent solvent breakdown caused by such contaminants as acids, alkalis, metal chips and fines, and exposure to oxygen, light and heat. The stabilizers also protect the parts being cleaned as well as the process equipment being used. Thus PPG's trichlor is effective for degreasing aluminum without staining or pitting, while protecting the solvent in properly operated degreasers from decomposition due to aluminum fines.

PPG's stabilizer system is a neutral type that uses catalytic regeneration to help prevent solvent decomposition. It includes ingredients to deactivate the effects of metallic contaminants, and also includes antioxidants. Additionally, it helps maintain a constant pH and provides resistance to sludge formation.

Since the major difference among available brands of trichlor is in the solvent stabilizers, the economic benefits of using PPG's trichlor in production degreasing are readily apparent.

General Application

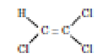
Trichlor is used primarily for vapor degreasing of zinc, aluminum, brass, bronze and steel parts during fabrication. Grades are also available for a variety of special applications.

Metal Fabrication—Aerospace, appliance and automotive industries use Trichlor in vapor degreasing operations to remove soils, metal chips and fines accumulated during fabrication. Trichlor is also used as a cold cleaning solvent and as a carrier solvent for certain painting processes.

Typical Properties

Trichlorethylene is a clear, water-white liquid at ordinary temperatures. It is volatile, sweet-smelling, and completely miscible with most organic liquids.

Chemical Names	Trichlorethylene; 1,1,2-trichlorethylene; ethylene trichloride
Chemical Formula	$CHClCCl_2$



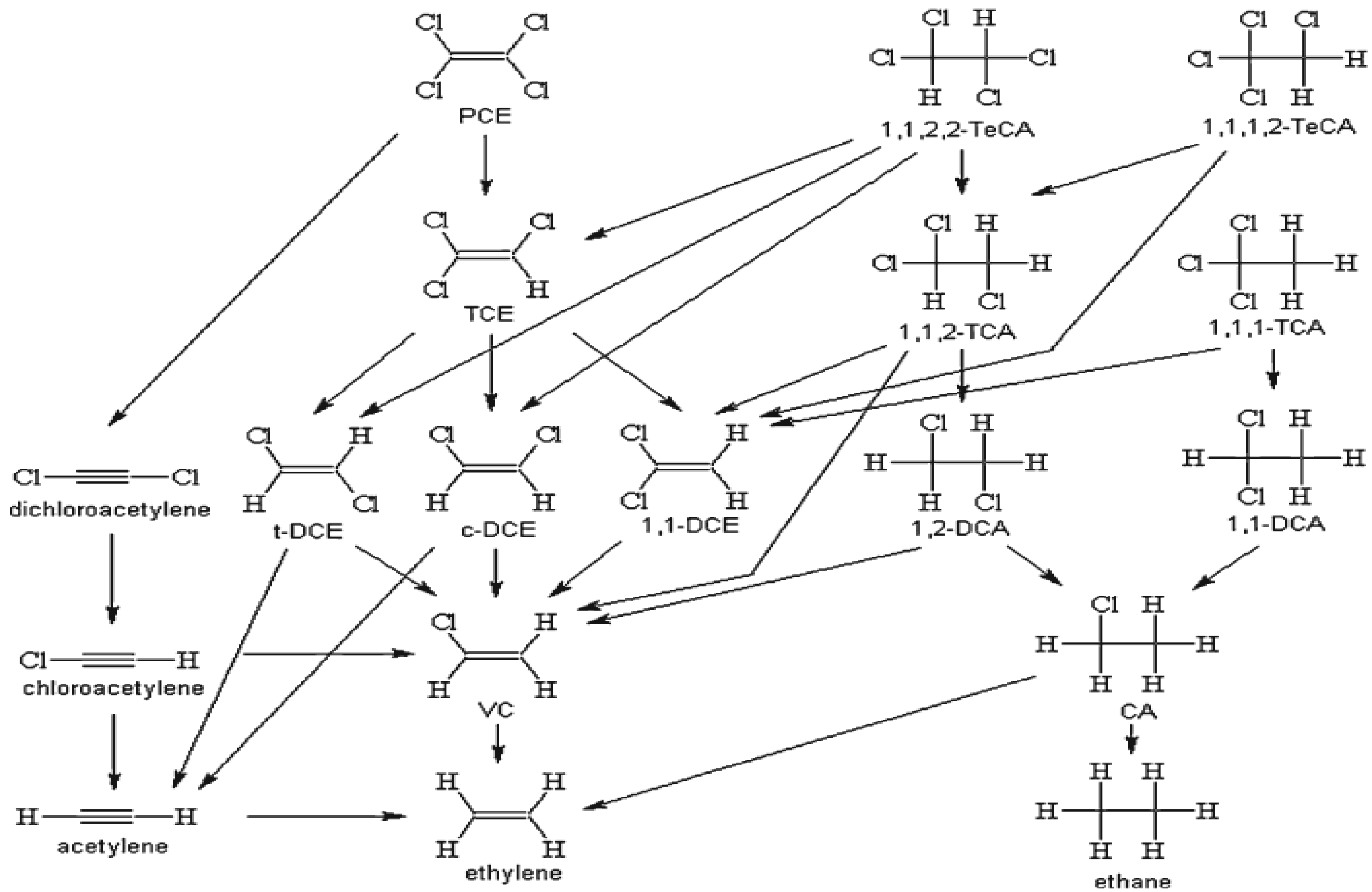
Molecular Weight	131.40
Boiling Point, °F	188.4
°C	86.9
Freezing Point, °F	-121.5
°C	-86.4
Pounds per Gallon at 68°F (20°C)	12.2
Kilograms per Liter at 20°C	1.46
Refractive Index, n g	1.4782
Dielectric Constant at 1000 cps and 16°C	3.42
Specific Heat at 20°C, cal/(g)(°C) or Btu/(lb)(°F)	0.225
Heat of Vaporization at 760 mm Hg, cal/g	57.2
Btu/lb	103.0
Vapor Density at 87°C and 760 mm Hg, g/l	4.45
lb/ft³	0.278
Specific Gravity of Vapor (air = 1)	4.54
Vapor Pressure at 20°C, mm Hg	57.8
Evaporation Rate at 77°F (25°C) (ether = 100)	28
gal/(ft²)(day)	0.5
Viscosity at 20°C, cps	0.58
Solubility at 25°C, g trichlor/100g water	0.11
g water/100 g trichlor	0.032
Azeotrope with Water, Boiling Point, °F	163.4
°C	73.0
Azeotropic Water Content, wt %	7.0
Flash Point (Tag open cup)	None
Fire Point (Tag open cup)	None

Specification and Typical Analysis, Degreasing and General Solvent Grade*

	Specification	Typical Analysis
Appearance	Clear, colorless	Clear, colorless
Color, APHA	15 maximum	6
Spot Test	No spot or stain	No spot or stain
Specific Gravity, 20°C/20°C	1.460 to 1.470	1.462
Nonvolatile Residue, wt %	0.0025	0.001
Free Chlorine	None	None
Moisture, ppm maximum	60	40
cloud point	No cloud at -10°C	No cloud at -10°C
Alkalinity, as NaOH at pH 7, %	0.001 maximum	0.0006
Acid Acceptance, as NaOH, %	0.165 minimum	0.185
Distillation Range (100%), °F	186.8 to 194	187.0 to 189.2
°C	86 to 90	86.1 to 87.7
pH	6.7 to 7.5	7.0

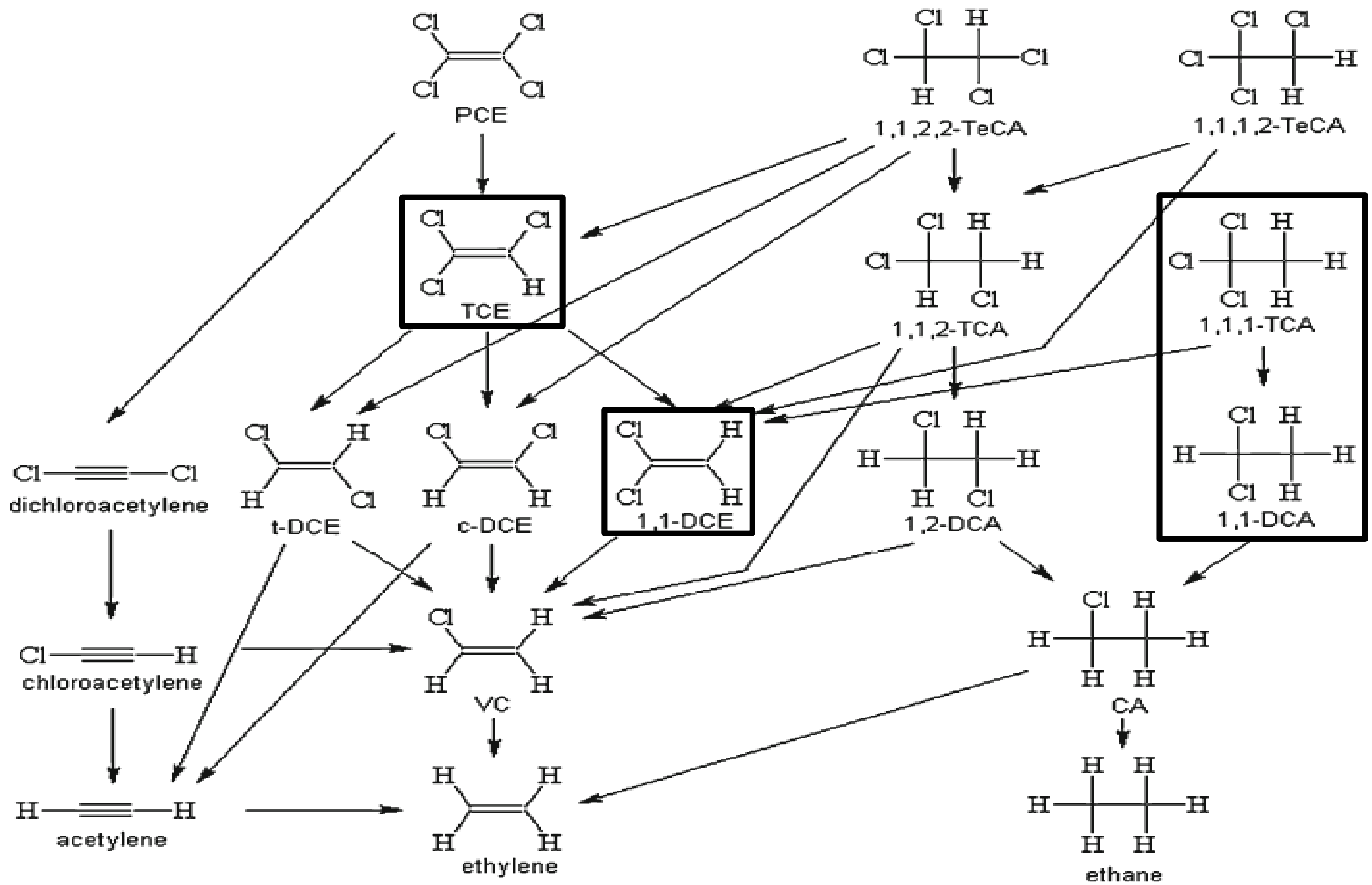
*The specifications and typical analyses for Dual-Purpose Grade and High-Purity Grade are available on request.

Co-Occurrence with CVOCs: Complicated by Degradation



Tobiszewski and Namiesnik (2012)

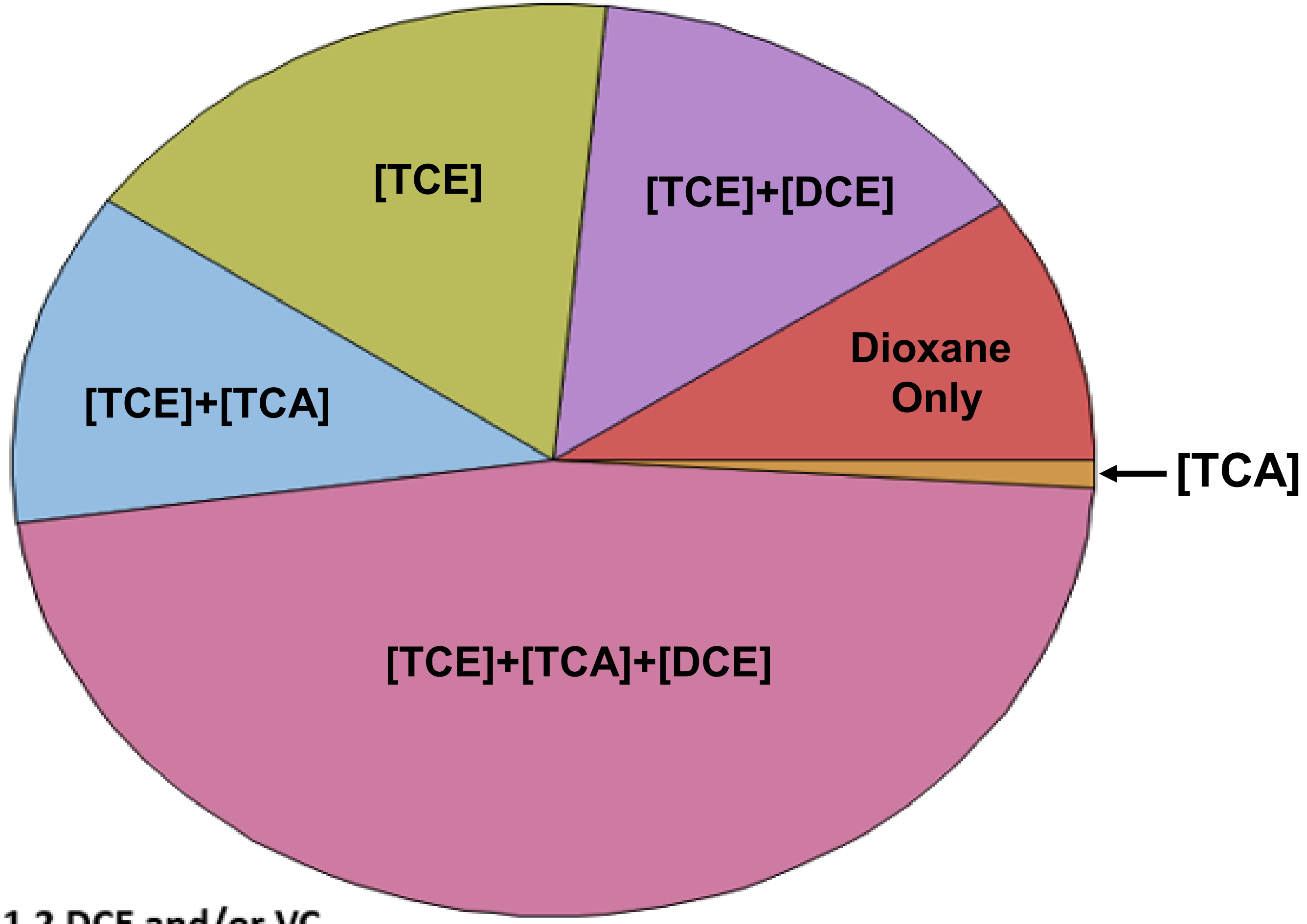
Co-Occurrence with CVOCs: Complicated by Degradation



Tobiszewski and Namiesnik (2012)

Co-Occurrence: AFCEC Data

2,383 Spatially-Discrete Monitoring Wells (includes "J" Flags)



[TCE] - TCE and/or 1,2 DCE and/or VC
[TCA] - 1,1,1 TCA and/or 1,1 DCA
[DCE] - 1,1 DCE

Co-Occurrence: Other Evidence

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

1,4-Dioxane pollution at contaminated groundwater sites in western Germany and its distribution within a TCE plume

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HIGHLIGHTS

- 1,4-Dioxane was evaluated in German groundwater and was detected at all sites tested.
- Max. concentrations of 1,4-dioxane exceed the 0.1 μg/L assessment value at each site.
- Highest concentration of 1,4-dioxane was detected in a VCH plume (152 μg/L).
- Depth distribution of 1,4-dioxane exhibited strong correlation with TCE.

GRAPHICAL ABSTRACT

Co-Occurrence: Other Evidence

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[†]

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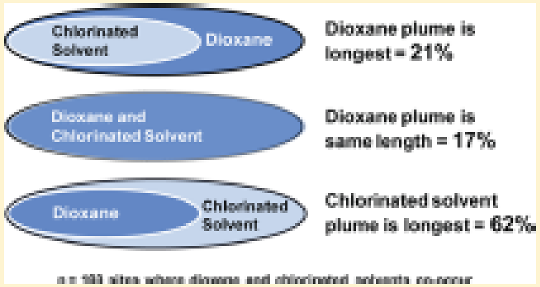
[‡]Department of Civil and Environmental Engineering, University of California, Los Angeles, California 90095, United States

[§]Department of Civil and Environmental Engineering, Rice University, Houston, Texas 77005, United States

Supporting Information

ABSTRACT: 1,4-Dioxane (dioxane) is an emerging groundwater contaminant that has significant regulatory implications and potential remediation costs, but our current understanding of its occurrence and behavior is limited. This study used intensive data mining to identify and evaluate >2000 sites in California where groundwater has been impacted by chlorinated solvents and/or dioxane. Dioxane was detected at 194 of these sites, with 95% containing one or more chlorinated solvents. Dioxane frequently co-occurs with 1,1,1-trichloroethene (1,1,1-TCA) (76% of the study sites), but despite this, no dioxane analyses were conducted at 332 (67%) of the sites where 1,1,1-TCA was detected. At sites where dioxane has been identified, plumes are dilute but not large (median maximal concentration of 365 μg/L; median plume length of 269 m) and have been delineated to a similar extent as typically co-occurring chlorinated solvents. Furthermore, at sites where dioxane and chlorinated solvents co-occur, dioxane plumes are frequently shorter than the chlorinated solvent plumes (62%). The results suggest that dioxane has not migrated beyond chlorinated solvent plumes and existing monitoring networks at the majority of sites, and that the primary risk is the large number of sites where dioxane is likely to be present but has yet to be identified.



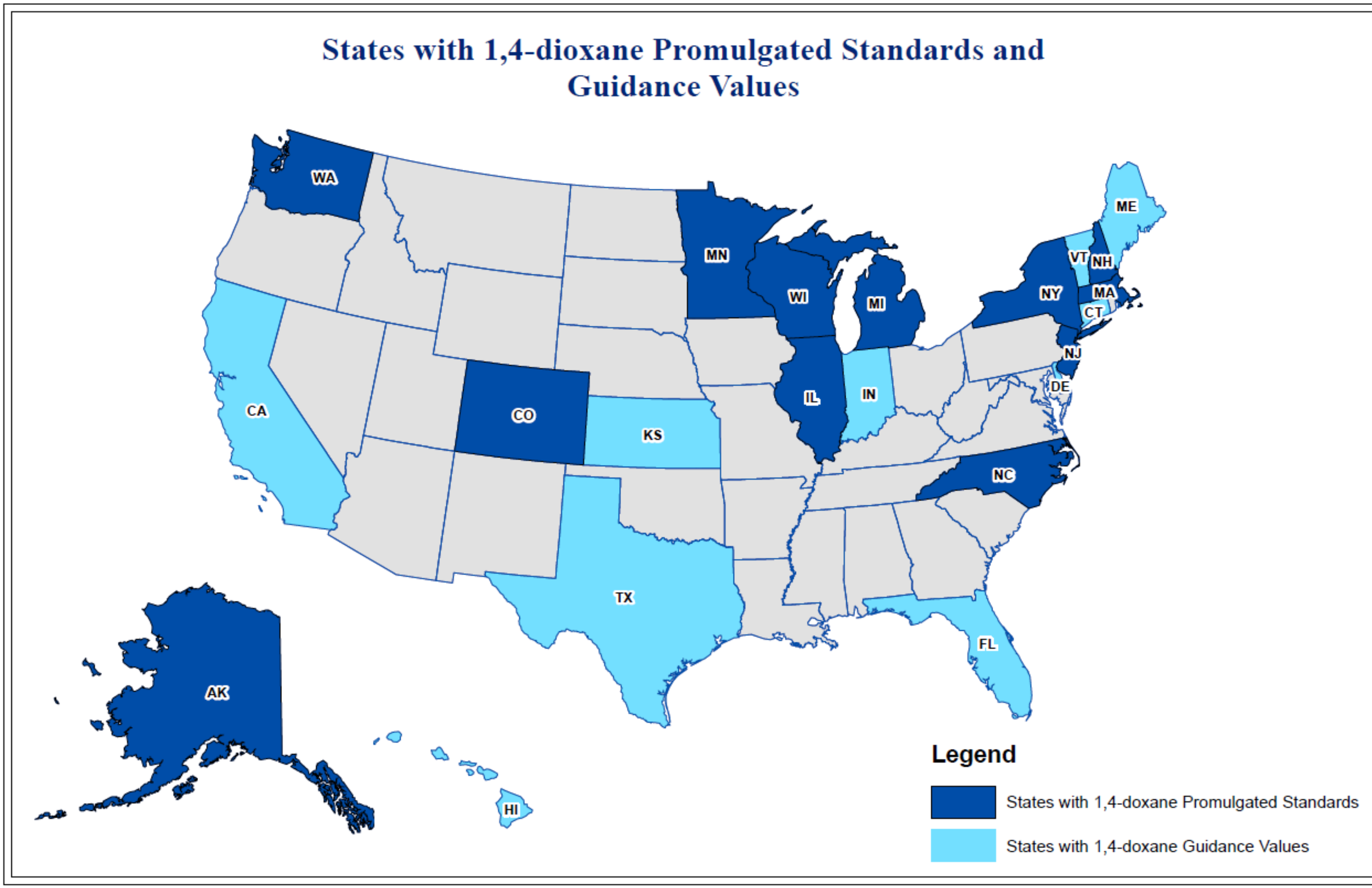
Health Effects

- **Human epidemiology studies**
  - Database is limited to two occupational studies
  - Insufficient to identify human health effects
- **Animal studies**
  - Kidney toxicity
  - Liver toxicity
  - Cancer
    - "Possibly carcinogenic to humans" – IARC (1999)
    - "Likely to be carcinogenic to humans" – EPA (2013)
    - "Reasonably anticipated to be a human carcinogen" – NTP (2016)
- **Cancer drives human health risk assessments**

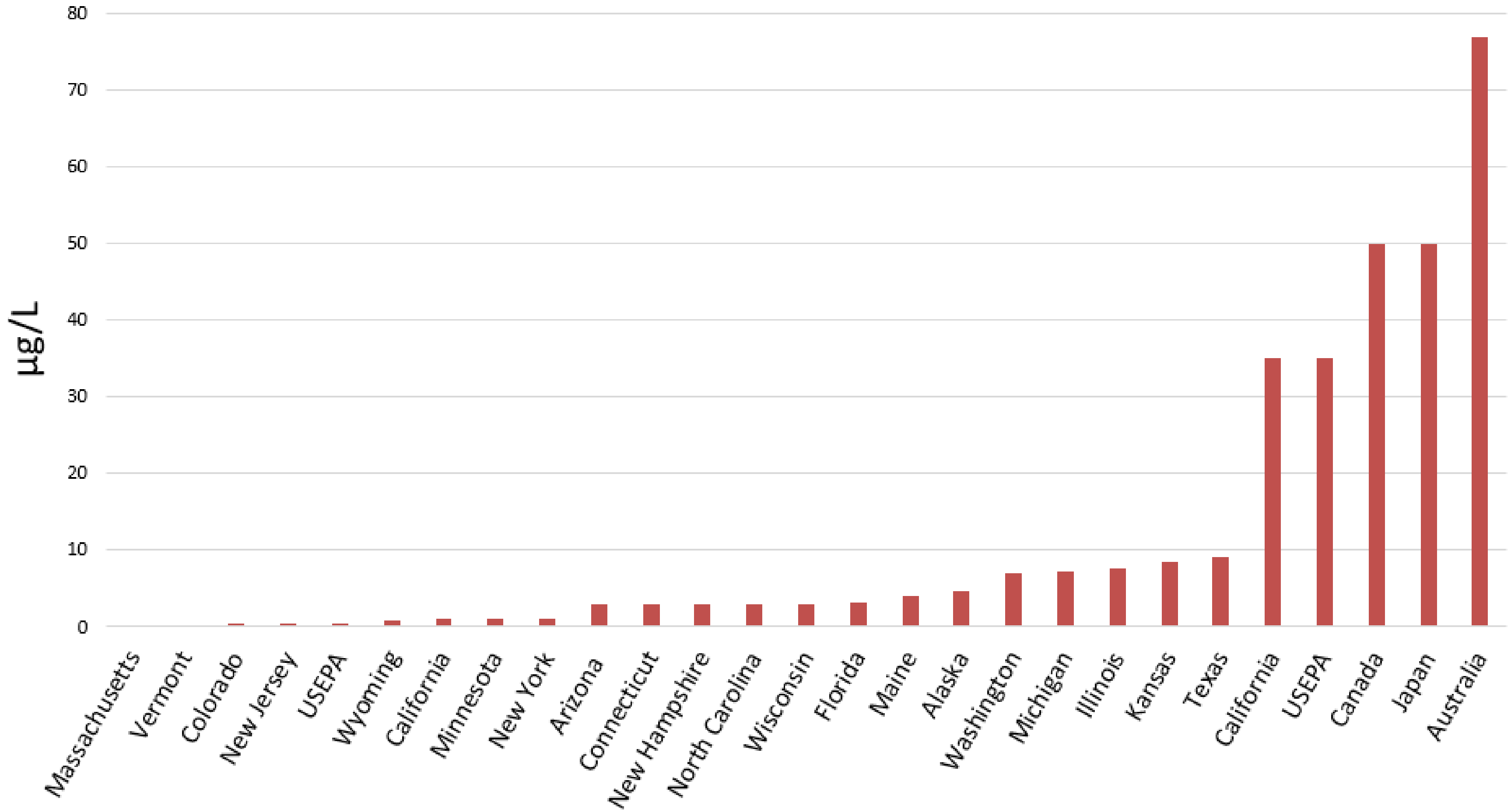
Regulatory Overview

- **U.S. EPA**
  - No MCL
  - CERCLA Hazardous Substance
  - Tier I tox values – USEPA/IRIS
    - RfD
    - RfC
    - Cancer slope factor
  - Office of Water DW Health Advisory
- **States**
  - Many states with published values
    - Difficult to distinguish “promulgated” from “guidance” values

1,4-Dioxane Regulatory Status



Risk-Based DW/GW Values

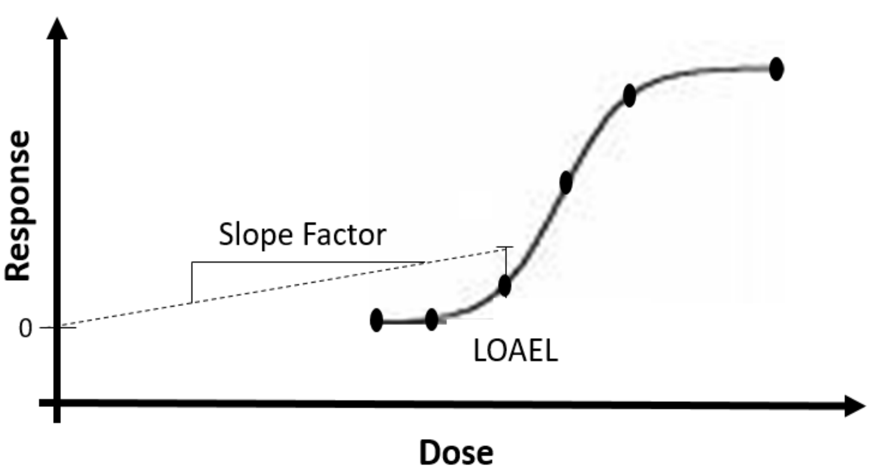


*Values shown may be for DW or GW and may be “guidance” or promulgated standard. Some agencies have several values.

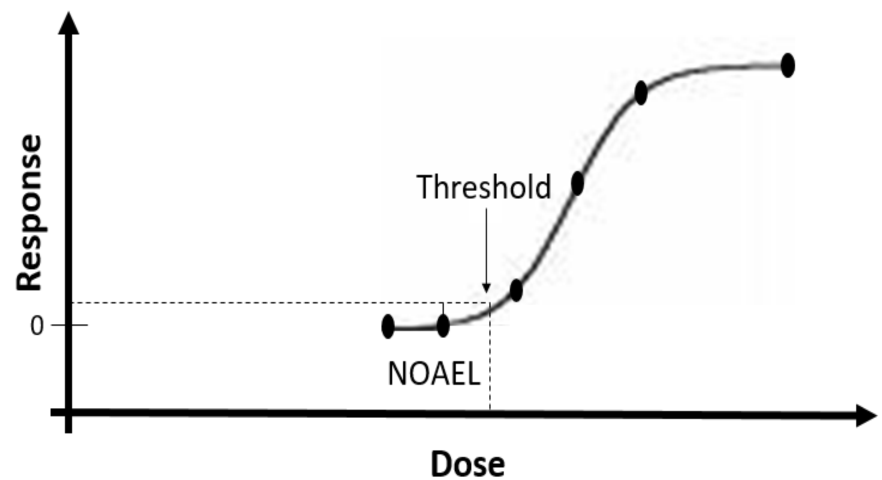
Why So Much Variability?

- **Policy decisions about acceptable cancer "risk range"**
  - 10^{-4} to 10^{-6}
- **Dose-response Modeling**
  - Low-dose extrapolation method

Linear Extrapolation (U.S. EPA)

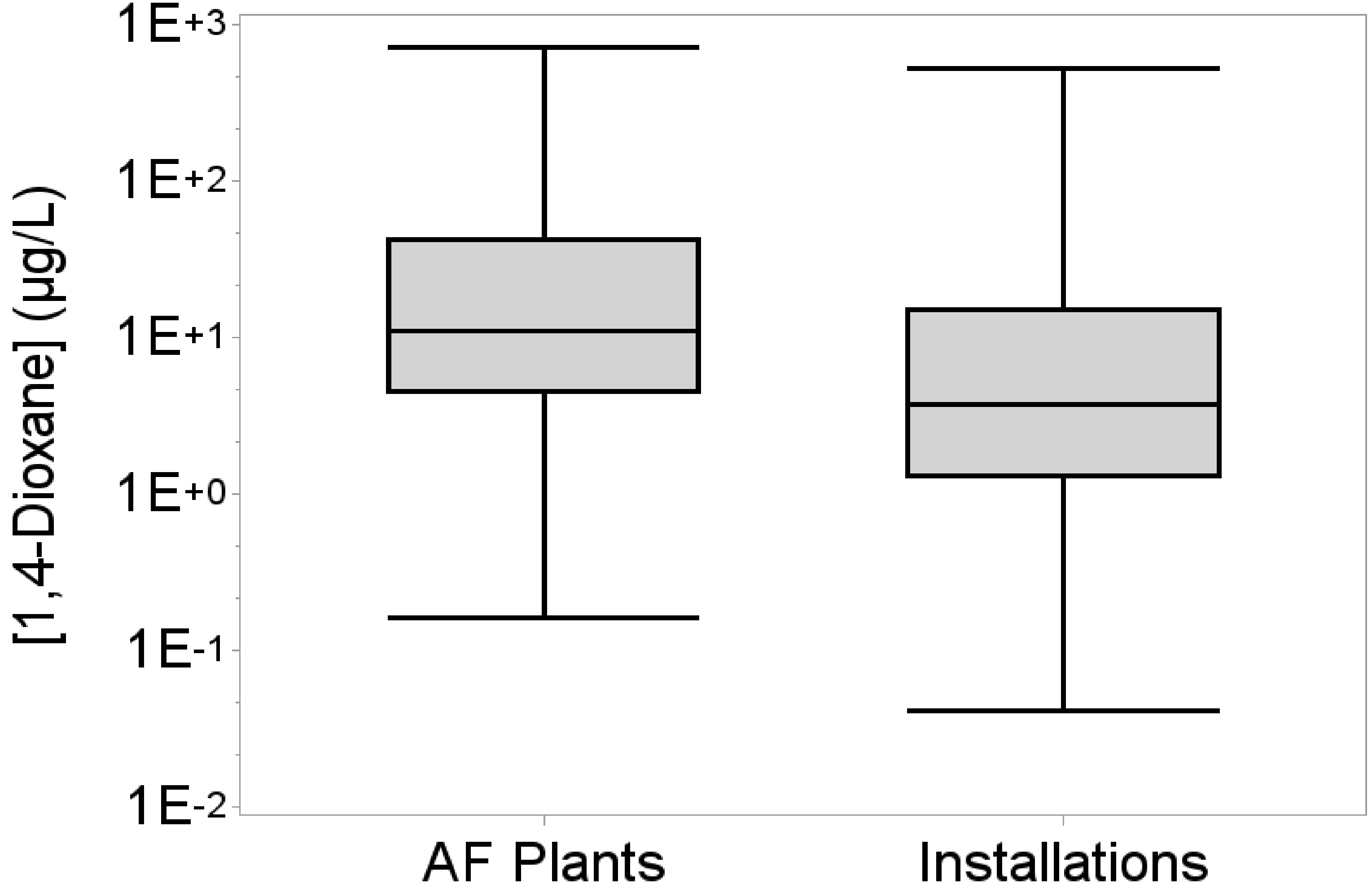


Threshold Extrapolation (Canada)



Numbers Matter: Most 1,4-Dioxane is Dilute

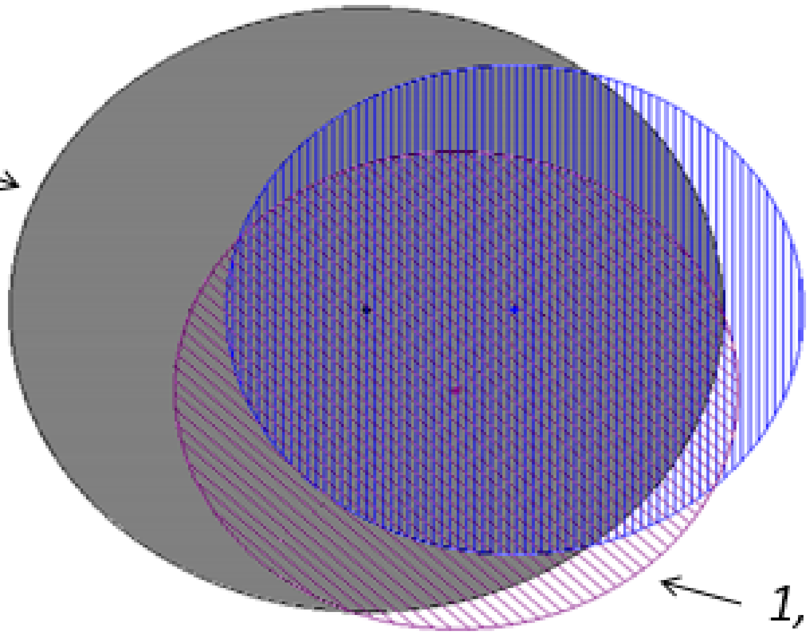
Historic Max [Groundwater] at AF Sites
(Excludes "J" Flags – 1,448 Monitoring Wells)



AFCEC's Programmatic Approach

Groundwater Sites (pre-RC) with TCA and/or TCE Past/Present Sources

(Emphasis on Waste Solvent Disposal Sites)



DEPARTMENT OF THE AIR FORCE
HEADQUARTERS UNITED STATES AIR FORCE
WASHINGTON, DC

MEMORANDUM FOR SEE DISTRIBUTION LIST

FROM: HQ USAF/A7C
1260 Air Force Pentagon
Washington, DC 20330-1260

SUBJECT: Guidance on 1,4 Dioxane, Environmental Restoration Program

[illegible]

MARK A. CORRELL, SES, P.E.
The Deputy Civil Engineer
DCS/Logistics, Installations & Mission Support

Phased Execution Approach:

1. Confirmation Sampling
2. Full-Scale Delineation
3. Remedy Evaluation

Conclusions

- **Multiple and diverse sources of 1,4-dioxane have contaminated watersheds across the country**
- **National exposures merit attention**
- **Highly variable and transient state regulations**
  - Lack of standardized regulatory risk assessment process
  - Chaos for agencies with multi-state portfolios
- **Scale of 1,4-dioxane observed at CVOC sites is larger than what can be explained by 1,1,1-TCA alone**
- **AFCEC is slowly executing programmatic policy to identify and respond to all 1,4-dioxane contamination at USAF CVOC sites**

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ARCADIS Design & Consultancy for natural and built assets

1,4-DIOXANE: CHEMICAL ANALYSIS, FATE, AND TRANSPORT

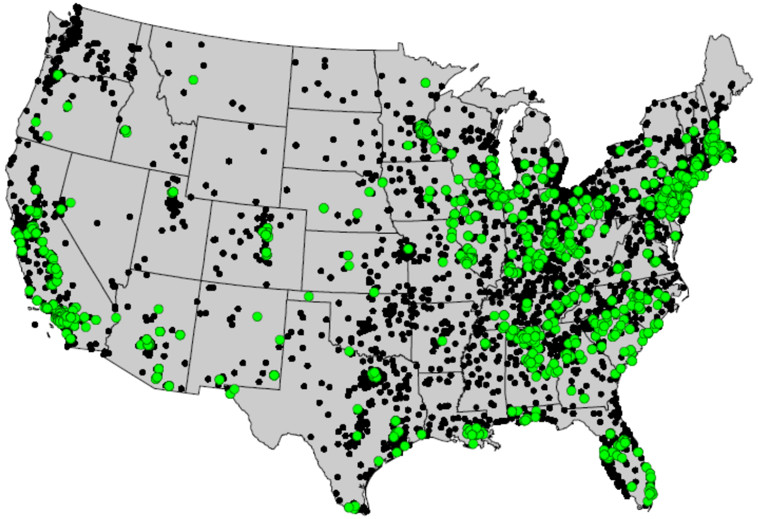
AKA 1,4-DIOXANE CHARACTERIZATION

April 2019

1,4-Dioxane Characterization

- Characterization approach
- Analytical methods
- Advanced analyses
- Fate and transport

But First, A Recap for Those Who Were Out



Occurrence

Sources

Consumer products

Detergents

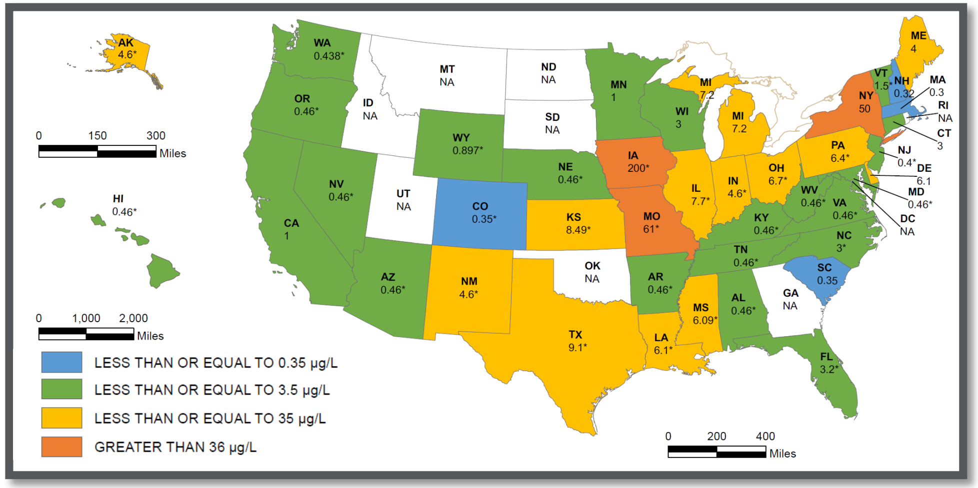
Paint / Dye / Grease

Manufacturing Byproduct

Direct use

Chlorinated solvents (1,1,1-TCA)

Regulation



The Physical and Chemical Properties

The Big Three: 1,4-dioxane is miscible in water, not very volatile, and does not readily sorb

	TCE	1,1,1-TCA	1,1-DCE	1,4-Dioxane
SOLUBILITY	**Moderate (1.1 g/L)**	**Moderate (0.91 g/L)**	**High (5.1 g/L)**	**Miscible**
VOLATILITY (approx. Henry's law constant)	**High (10^{-2})**	**High (10^{-2})**	**Moderate (10^{-3})**	**Low (10^{-6})**
SORPTION (log K_{oc})	**Low (1.81)**	**Moderate (2.18)**	**Low (1.48)**	**Very Low (0.54)**

Characterization Approach

Characterization Approach

Is 1,4-dioxane the MTBE of the chlorinated solvent world? Only kind of…

Existing monitoring infrastructure

- ✓Mostly present in groundwater vs. soil
- ✓1,4-Dioxane may no longer be in the CVOC source area
- ✓It is important to check the downgradient/sentinel monitoring wells
- ✓May need new downgradient wells

New investigation opportunities

- ✓Consider *Smart* Characterization™

What is *Smart* Characterization™?

High-resolution site characterization
- High-density soil and groundwater sampling
- Real-time results

Mass-flux-based perspective
- Hydrostratigraphic interpretations
- Permeability mapping
- Mass transport zones

Higher Return on Investigation™
- Shorten investigation timeframes
- Collect better data for decision making
- Focus remedial efforts

Effective remedial decision making
- Focus on high transport zones
- Mitigate risk strategically
- Minimize cost of infrastructure

Smart Case Study

- 30-acre former chemical manufacturing facility
- Purpose: identify CVOC source mass and co-occurrence of 1,4-dioxane
- Found: ~2-acre 1,4-dioxane plume, larger than the CVOCs

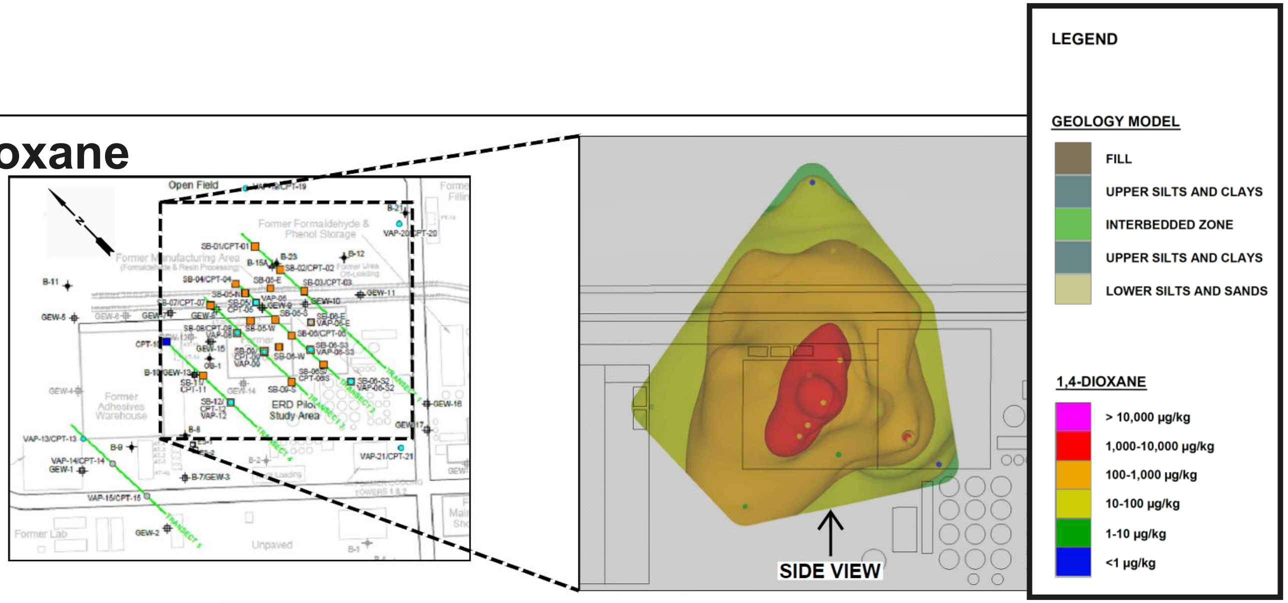
High-resolution site characterization
- 20+ CPT, whole core, and VAP locations
- Mobile lab with brick and mortar confirmation

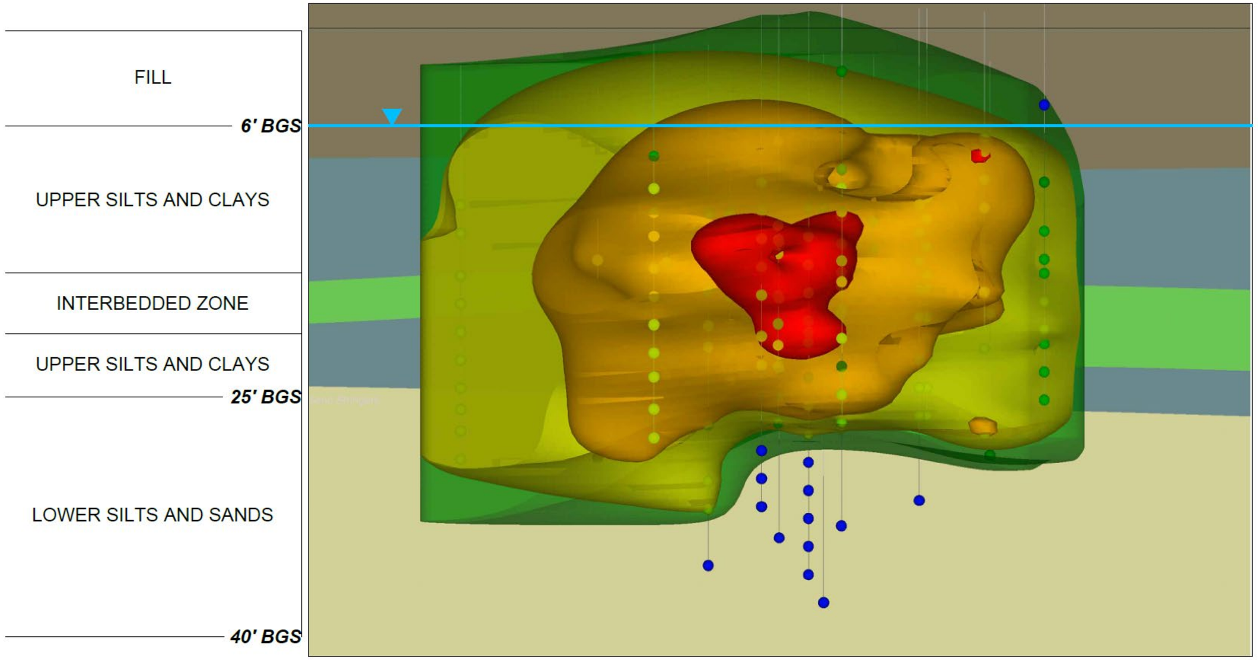
Mass-flux based perspective
- 3D visualization of hydro and COCs
- Located dominant groundwater flow zones

Higher Return on Investigation™
- Four field days
- 6 months from investigation to pilot testing

Effective remedial decision making
- Focused pilot/full-scale ISCO on high-flux zones
- Focused source mass removal to get MNA

1,4-Dioxane





Analytical Methods

Sampling Considerations

You may recall from a few slides ago, that 1,4-dioxane is present in detergents…this includes decontamination detergents used in field sampling

- Not typically listed as an “ingredient”, but might be present if one of the following is listed:
  alcohol ethyoxylate, alcohol ethoxysulfate, polyoxyethylene, anything with “laureth” in the name, sodium laureth sulfate, sodium lauryl ether sulfate (but not sodium lauryl sulfate), ammonium laureth sulfate, triethanolamine laureth sulfate, polyethylene glycol compounds, anything with “ceteareth” in the name, anything with “oleth” in the name, anything with “xynol” in the name, polysorbates, propylene glycol, and anything with the molecular structure $(C_2H_4O)_n$
- Trisodium phosphate may be an attractive alternative, but need to consider the presence of phosphate
- Potential for false positives is low, but occurs

1,4-Dioxane and Laundry Soap: Free and Gentle or a Marketing Free-for-All?

By Bill Chameides

Does Alconox or Liquinox contain 1,4-Dioxane?

Posted on 07 March 2014. Tags: 1-4 Dioxane, Alconox, dioxane, liquinox

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Q. Does Alconox or Liquinox contain 1,4-Dioxane?

Equipment blanks are a great addition to the sampling plan

Groundwater/Drinking Water Analysis

There are some lesser-loved methods, but these are the top contenders…

8260 VOC Method

- Purge and trap extraction (heated purge also available)
- CVOC interferences
- Poor recovery leads to low bias – surrogates/standards don't mimic 1,4-dioxane

8270 SVOC Method

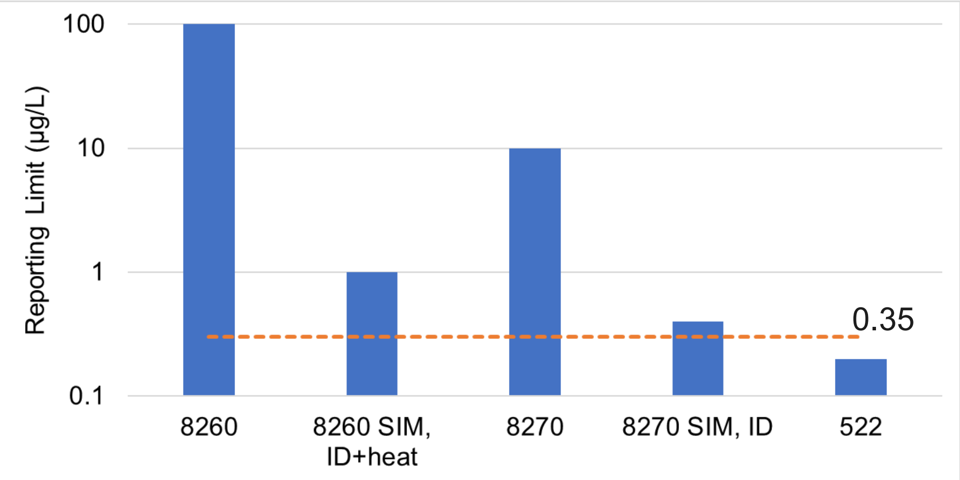
- Liquid-liquid extraction
- Avoids CVOC inferences
- Loss during concentration leads to low bias – surrogates/standards don't mimic 1,4-dioxane

SIM and ID Improve 8260 and 8270

- Selective ion monitoring – specifically looks for 1,4-dioxane, higher cost
- Isotope dilution – internal standard that allows lab to account for losses

522 Drinking Water Method

- Solid-phase extraction limits losses; includes selective ion monitoring and isotope dilution
- Limited availability, higher cost (standalone for 1,4-dioxane)
- May not be appropriate for groundwater (interferences and regulatory acceptance)



Objective	Approach
Low reporting limits	8270SIM with ID
Mid-range results	8260SIM with ID

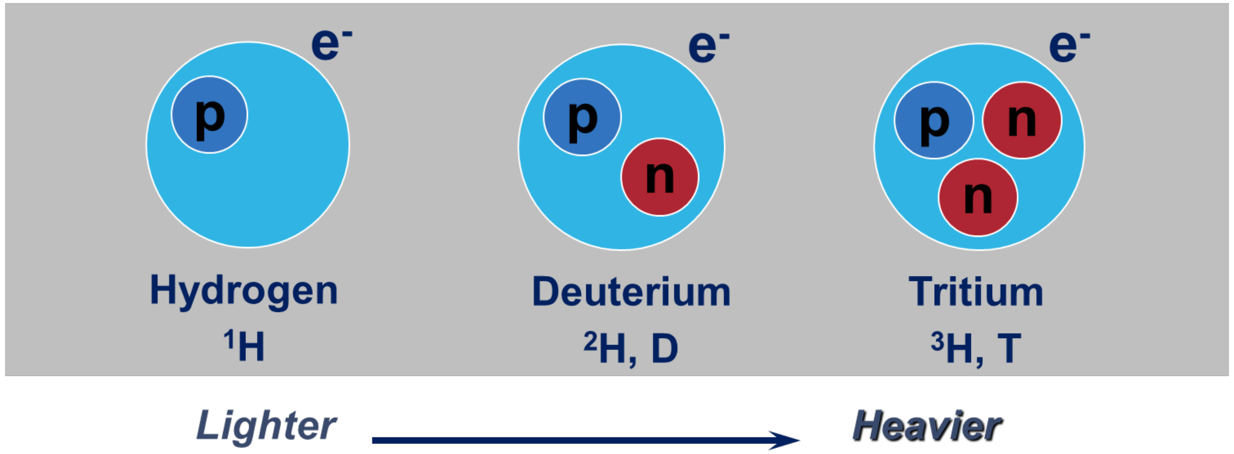
Soil/Soil Vapor/Indoor Air Analysis

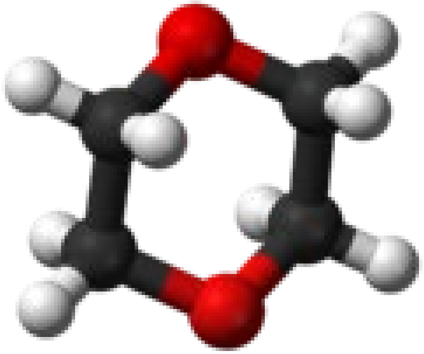
Soil	Soil Vapor/Indoor Air
• Similar recommendations as groundwater – 8260 or 8270 • SIM increases sensitivity • Preservation method can influence reporting limits for 8260	• TO-15 is the go-to method • NIOSH 1602 for worker monitoring • No notable biases/considerations • TO-14 should not be considered

Advanced Analyses

Compound-Specific Isotope Analysis

- Isotopes: same number of protons/electrons but different number of neutrons
- Microbes: like to use the light isotopes first
- CSIA: can distinguish between sources and/or destructive and non-destructive mechanisms
- For 1,4-dioxane: carbon and hydrogen are important isotopes





Compound-Specific Isotope Analysis

Recent Advances	Remaining Needs/Challenges
• Lower detection limits from commercial CSIA labs • Recognition that hydrogen may be more telling than carbon • Enrichment factors for both carbon/hydrogen	• Still lower detection limits, particularly for hydrogen • Comparing data across labs or methods • Confirmation of enrichment factors under different conditions • Field demonstrations to support bench-scale work

Molecular Biology Tools

Quantitative polymerase chain reaction (qPCR)

Fluorescence in-situ hybridization (FISH)

Phospholipid fatty acids (PLFA)

Enzyme activity probes (EAPs)

Microarrays

Stable isotope probing (SIP)

For MBTs to be useful:

- Meaningful genetic targets
- Translation to the field

ARCADIS Design & Consultancy for natural and built assets

Molecular Biology Tools

Recent Advances	Remaining Needs/Challenges
• Commercial availability of metabolic gene targets • Additional gene targets being identified/developed • Evaluation of mRNA vs. DNA • Demonstrated success with stable isotope probing (SIP)	• Available targets aren't comprehensive – false negatives • Some targets may be expressed for other processes • Challenge with investigating cometabolism • Best in a supported lines of evidence approach

Mobile Labs

Advantages

- Rapid analysis of many samples
- Facilitates adaptive investigation
- Focuses sampling for traditional analysis

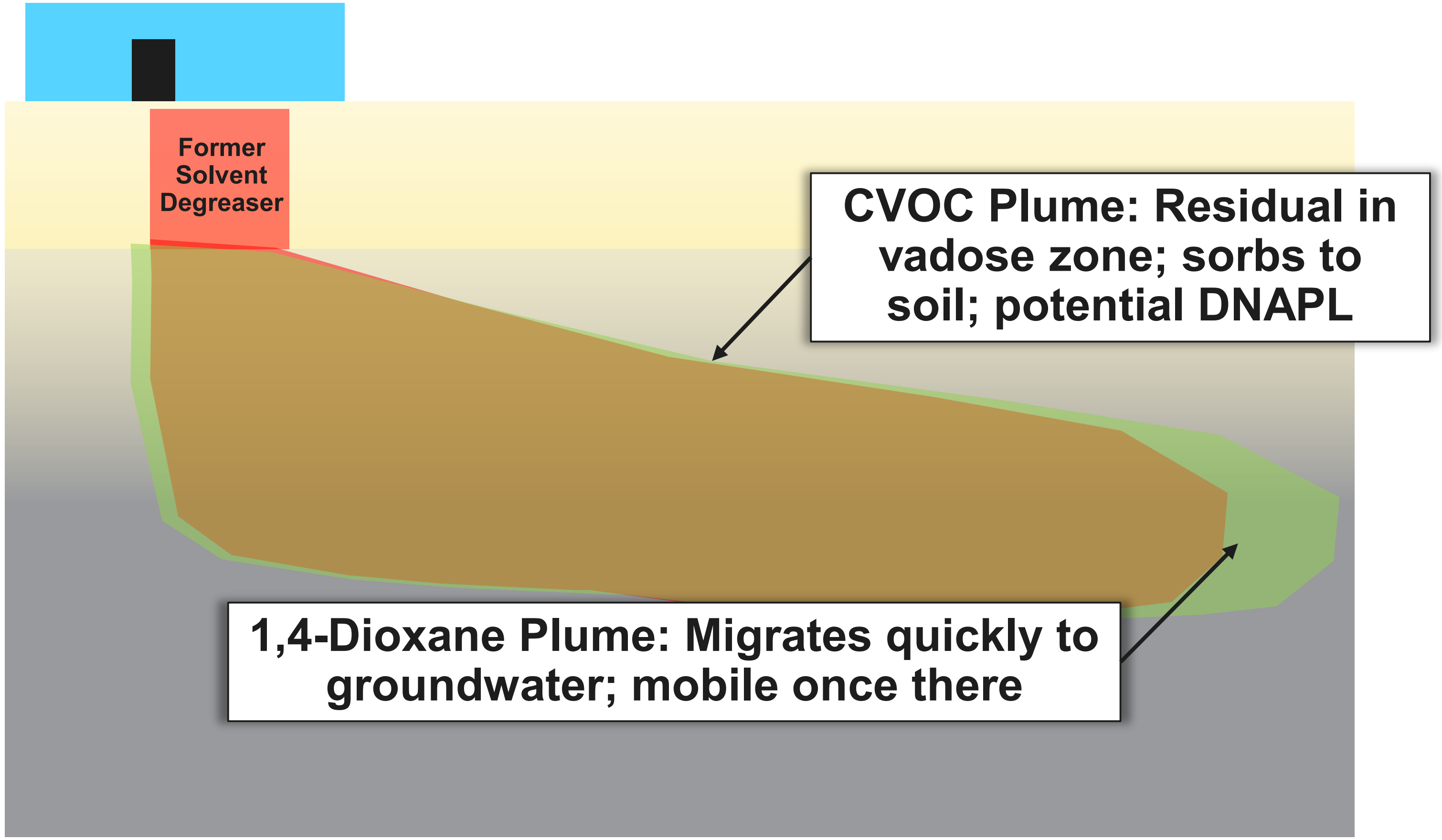
Cautions

- Analytical challenges may not be readily solved in field
- Complex constituent mixtures may cause interference
- Potential for low-bias may lead to false negatives
- Detection limits may preclude delineation to lowest standards

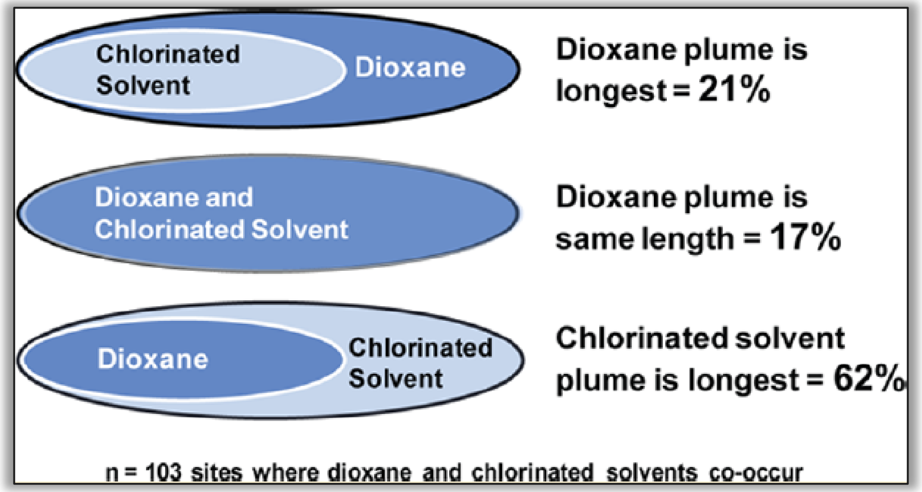
Mobile lab DQOs are different than "brick and mortar" DQOs

Fate and Transport

Expected Situation(s)

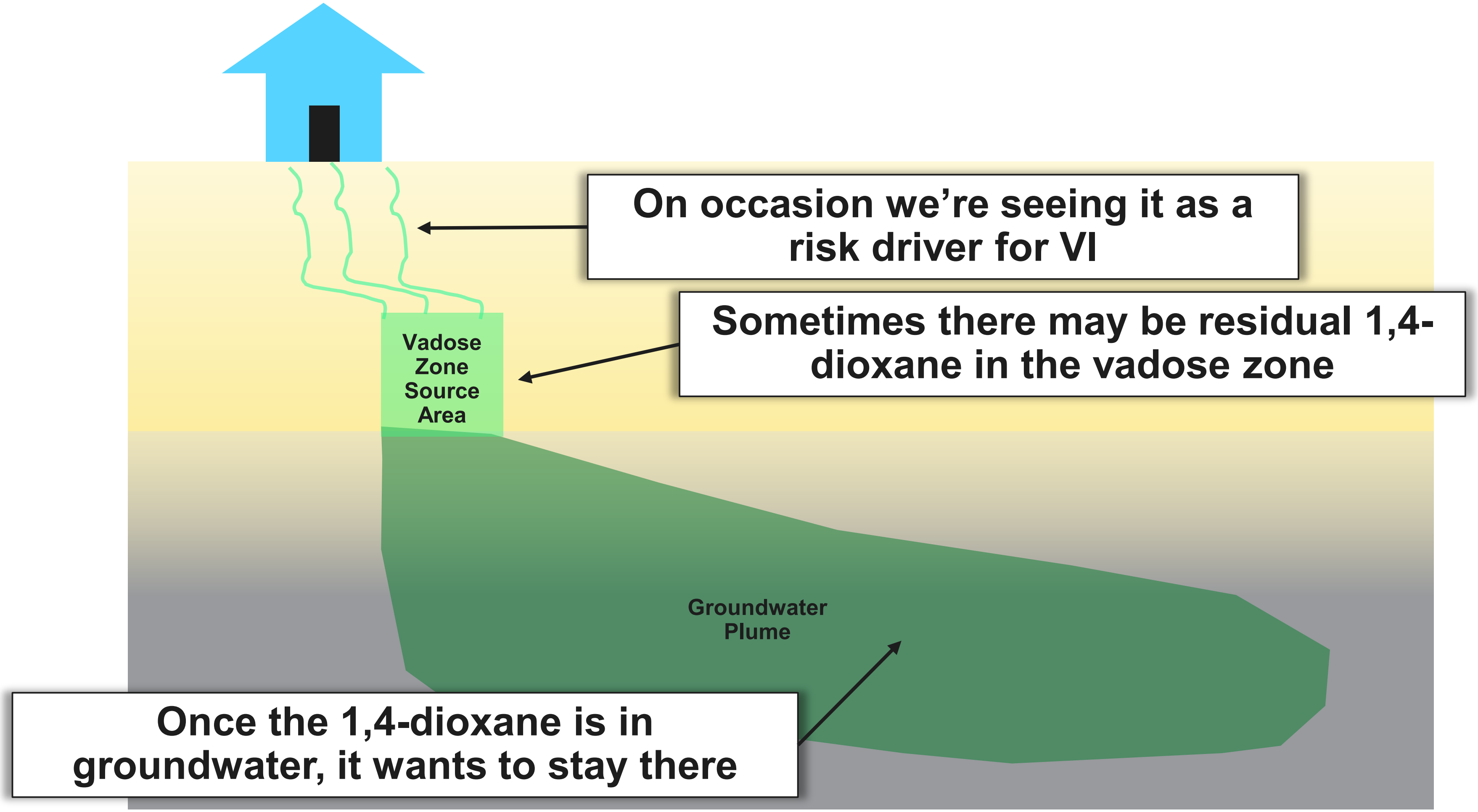


Some like to think of 1,4-dioxane as the MTBE of the chlorinated solvent world, but perhaps not quite…



Source: Adamson et al., 2014

Unexpected Situation: A VI Concern?



Unexpected Situation: High Concentrations

What you might expect…

Release Mechanism	Measured TCA Concentration	Expected 1,4-Dioxane Concentration
TCA storage tank (~4% 1,4-dioxane)	250 µg/L	10 µg/L
TCA solvent degreaser (~15% 1,4-dioxane)	70 µg/L	10 µg/L

How some sites are bucking the norm…

Note that TCA can quickly transform to 11DCE, but a similar 11DCE analysis yields the same results.

Site	Measured TCA Concentration	Expected 1,4-Dioxane Concentration	Measured 1,4-Dioxane Concentration
#1 (unknown)	<100 µg/L	Up to 2,000 µg/L	**41,000 µg/L**
#2 (degreaser)	110,000 µg/L	~4,000 µg/L	**360,000 µg/L**

What this All Means for Treatment

Know the tools in your toolbox

Consider *Smart* Characterization™

Look out for unexpected situations

Know your plume extents

Consider attenuation

Understand how 1,4-dioxane differs from co-contaminants

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Questions?

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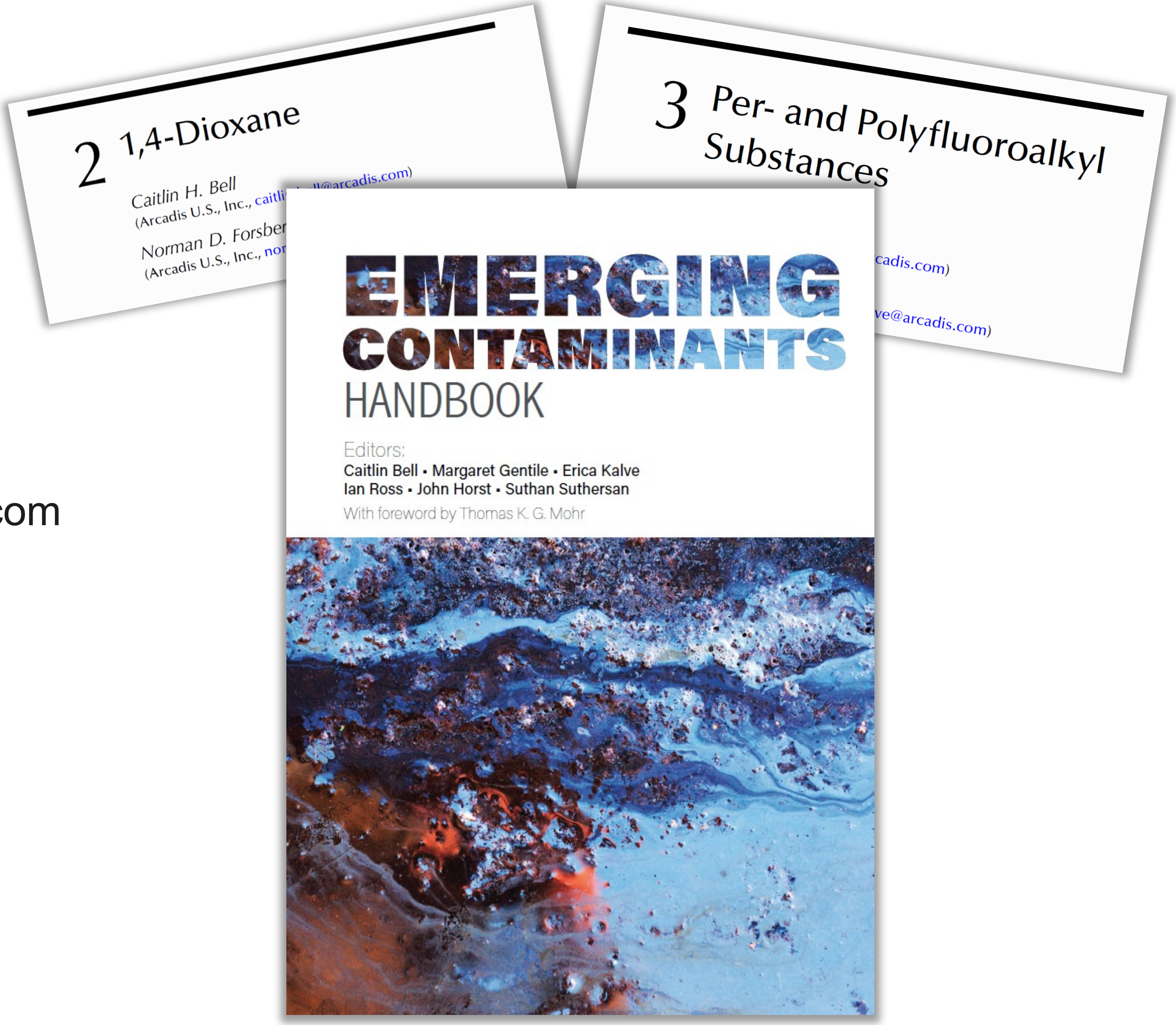

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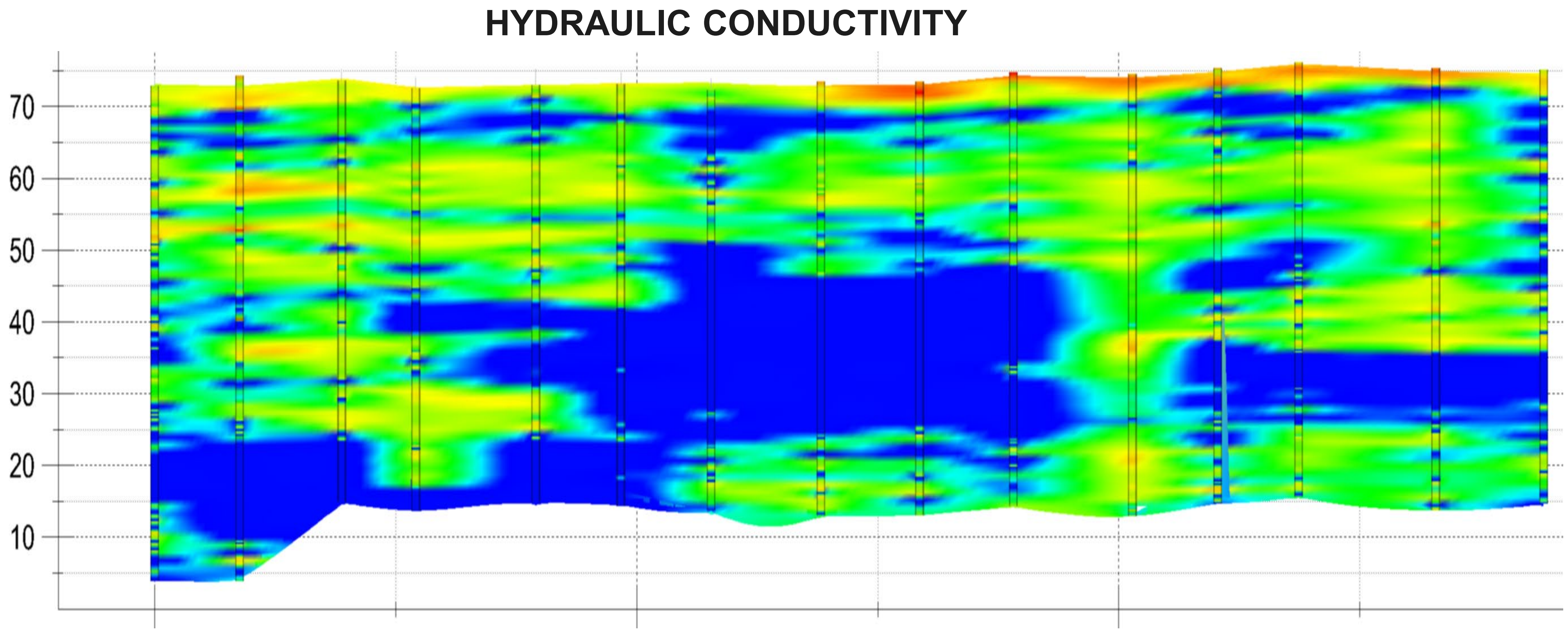
Extra Slides

Mass Flux-Based Perspective



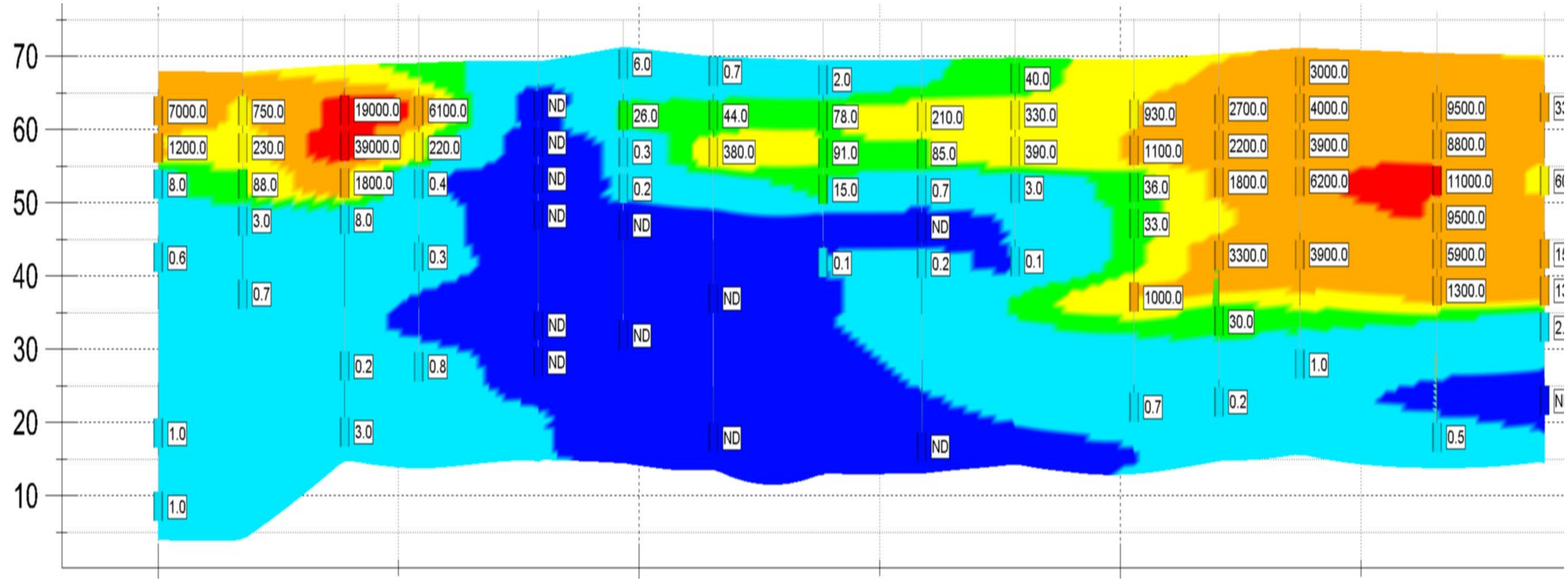
Start with aquifer properties

- HPT data
- CPT data

Mass Flux-Based Perspective

Mass Flux-Based Perspective

CONCENTRATION PROFILES

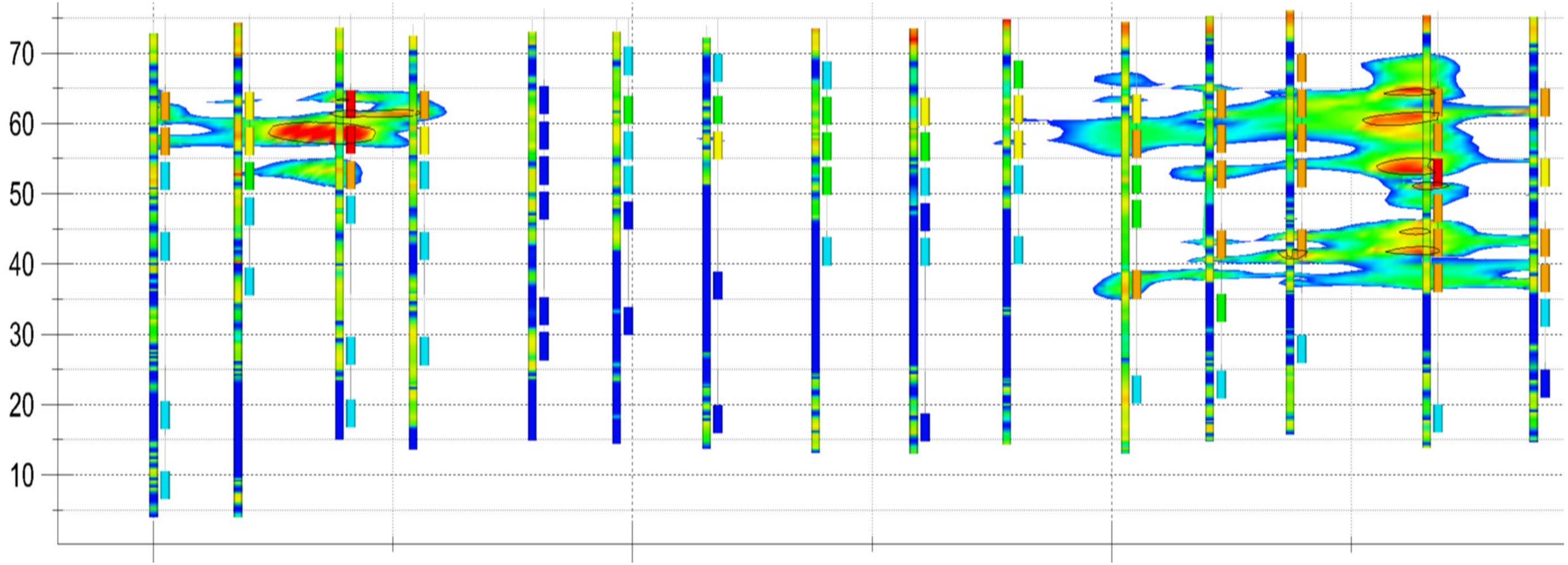


Layer on concentration information

- VAP samples
- Whole soil data

Mass Flux-Based Perspective

RELATIVE FLUX



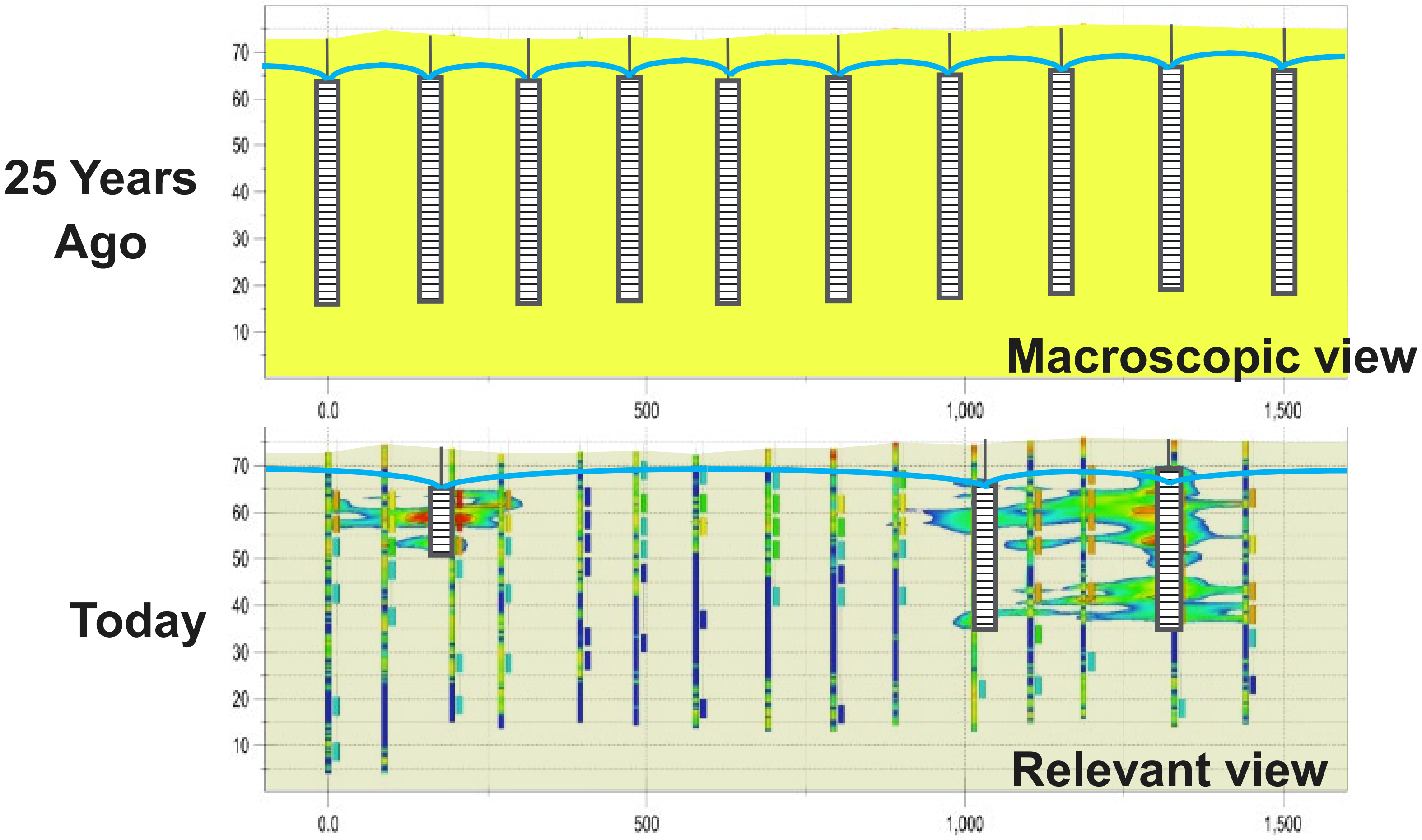
Visualize mass flux

- 2D
- 3D

Mass Flux-Based Perspective

>90% of contaminants often flow in **<10%** of aquifer volume

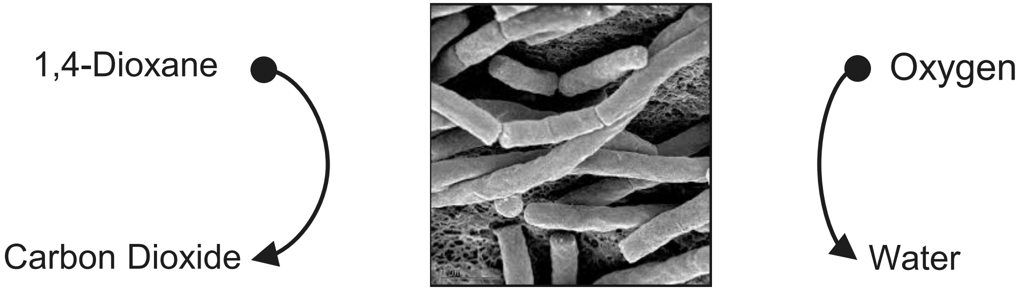
Targeted Flux-Based Remediation



Molecular Biology Tools

Metabolism vs. Co-Metabolism

Metabolism: *the goal is to produce energy*



(http://bacmap.wishartlab.com/organisms/1305)

- Currently known genes of interest encode monooxygenase enzymes

Co-Metabolism: *a fortuitous side reaction*

VI Modeling Results from Case Studies

1. Site specific data including groundwater, soil gas, depth to water, and soil type are used to evaluate potential exposures and risks due to 1,4-dioxane in the subsurface
2. In general, vapor intrusion of 1,4-dioxane is not expected to be an issue at most sites due to the limited potential for volatilization due to 1,4-dioxane solubility in water
3. Results indicate that based on vapor pressure and boiling point, vapor intrusion is not an exposure pathway that can be excluded without appropriate considerations for site specific characteristics

More Analytical Methods

Currently Available Methods

MATRIX	METHOD	INSTRUMENTATION	DETECTION LIMIT
Soil, Water	EPA SW 846 Method 8015	GC/FID	15 µg/L (MDL)
Soil, Water	EPA SW 846 Method 8240	GC/MS Purge and trap or direct injection	
Soil, Water	EPA SW 846 Method 8260	GC/MS	*
Soil, Water	EPA SW 846 Method 8260 SIM	GC/MS-SIM	0.5 - 10.0 µg/L (MDL)
Soil, Water, Tissue	EPA SW 846 Method 8261	VD/GC/MS	1.1 µg/L (MDL)
Soil, Water	EPA SW 846 Method 8270	GC/MS	0.23 - 1.0 µg/L (MDL)
Soil, Water	EPA SW 846 Method 8270 SIM	GC/MS-SIM	
Air	EPA Method TO-15	GC/MS	
Water	EPA Method 1624 (Note compound listed as a method analyte)	ID GC/MS	
Air	NIOSH 1602	GC/FID	
Water	EPA Method 522	SPE, GC/MS-SIM	0.020 -0.036 µg/L (DL)
Soil, Water	EPA Method 625 (Note: compound not listed as a method analyte)	GC/MS	

* When analyzed for with other chemicals of concern a purge and trap extraction method is generally the default (SW 846 5030 or 5035) when direct injection is not performed. This extraction method is inappropriate for 1,4-dioxane and will yield a high detection limit. What is required is an extraction method for volatile, nonpurgeable, water-soluble compounds such as Azeotropic Distillation.

https://clu-in.org/contaminantfocus/default.focus/sec/1,4-dioxane/cat/Detection_and_Site_Characterization/

In Situ and Ex Situ Treatment Technologies for 1,4-Dioxane

Brant Smith/Technical Applications Manager: ISCO
PeroxyChem

April 2019

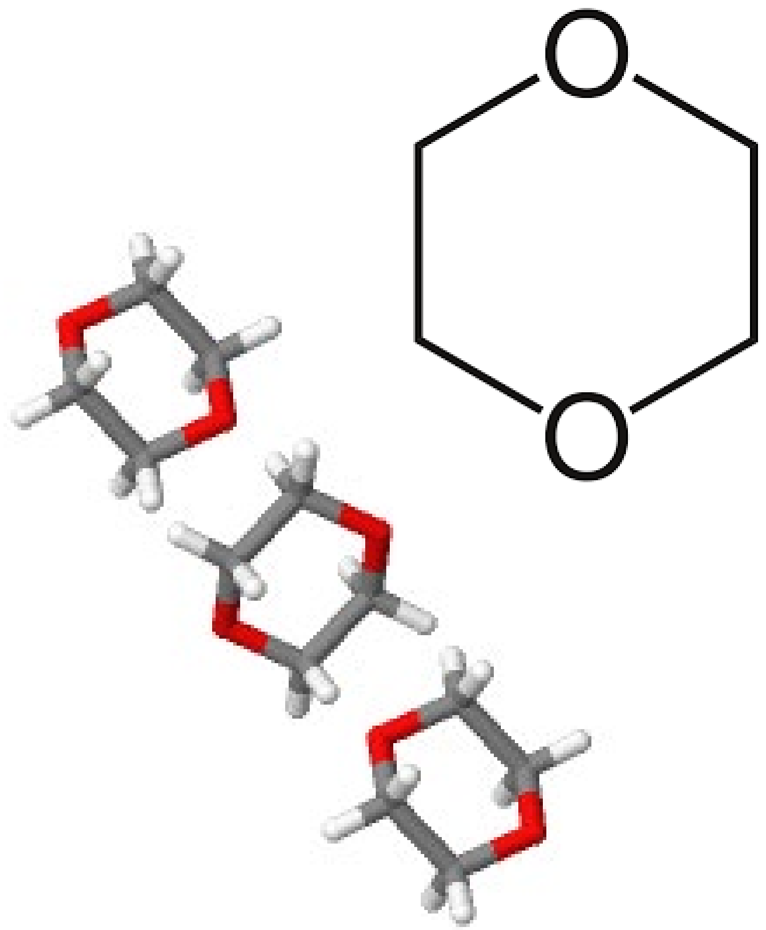
Overview

- 1,4-Dioxane is not PFAS
  - Conventional destructive treatment options
  - Sorptive treatment options
  - Emerging treatment options

- 1,4-Dioxane
  - Present in many waste streams including wastewater
  - This presentation will tend to focus on treatment at environmental sites

Why is 1,4-Dioxane Special?

- 1,4-Dioxane REALLY likes water
  - Miscible in water
  - Polar compound
  - Once in water, it wants to stay there (partitioning coefficients):
    - Negative Log K_{ow} (-0.27)
    - Low Henry's Coef (4.8×10^{-6} atm m^3/mole)



- 1,4-Dioxane is often co-mingled with other contaminants that have very different characteristics
  - Trichloroethene (TCE)
  - 1,1,1-Trichloroethane (1,1,1-TCA)

Soil-Groundwater Partitioning

PeroxyChem

- While primarily associated with groundwater, 1,4-dioxane has a low affinity for organic carbon
- Assuming F_{oc} of 0.005 (5,000 mg/Kg)
  - 1,4-Dioxane is primarily in the aqueous phase
  - Other contaminants are primarily sorbed to soil

$$K_d = K_{oc} * F_{oc}$$

Contaminant	Contaminant Distribution (%) GW	Contaminant Distribution (%) Soil
1,4-Dioxane	70%	30%
PCE	21%	79%
TCE	19%	81%
DCE	51%	49%
1,1,1-TCA	27%	73%
1,1-DCA	43%	57%
1,2-DCA	51%	49%
Carbon Tetrachloride	19%	81%
1,2-Dichlorobenzene	6%	94%
Benzene	40%	60%
Toluene	18%	82%

Treatment Technologies

Remedial technologies typically exploit some aspect of the contaminant:

- Partitioning Coefficients:
  - Vapor pressure:
    - Air Sparging/Soil Vapor Extraction (AS-SVE)
    - Thermally enhanced SVE
  - Organic Partitioning Coefficients
    - Activated Carbon
    - Etc
  - Henry's Law
    - Air stripping
    - SVE

- Chemical transformations
  - Bioremediation
  - Chemical oxidation
  - Chemical reduction
  - Chemical precipitation/Metals stabilization

A good engineer/scientist can get most technologies to "work." Questions are how well, how efficient and at what cost?

Partitioning Coefficients

PeroxyChem

Characteristics	Ratio/Comparison	Units	1,4-Dioxane	1,1,1-TCA
Vapor Pressure	Gas - Pure Phase	mm Hg @ 20 °C	29	96
Henry's Law	Gas/Water	atm-m3/mole	4.8×10^{-6}	1.8×10^{-2}
K_{ow}	Octanol/water	dimensionless	0.54	302
K_{oc}	Organic Carbon/Water	dimensionless	17	110

EPA Technical Fact Sheet: 1,4-Dioxane, Nov 2017

Watts "Hazardous Wastes: Sources, Pathways, Recpetors," Wiley, 1998

Air Stripping

Contaminant	Henry's Law Constant (atm-m3/mole @ 25 °C)
1,4-Dioxane	4.8×10^{-6}
TCE	9.1×10^{-3}
1,1,1-TCA	1.8×10^{-2}
1,1-DCE	2.1×10^{-2}
1,2-DCA	9.1×10^{-4}

- 1,4-Dioxane favors the aqueous phase
- Treatment would require large systems
- NOT FAVORABLE

Vapor Extraction

PeroxyChem

- Pure phase vapor extraction
  - 1,4-dioxane has lower vapor pressure than many other contaminants
  - Less efficient treatment possible

Contaminant	Vapor Pressure (mm Hg @ 20°C)
1,4-Dioxane	29
TCE	58
1,1,1-TCA	96
1,1-DCE	495
1,2-DCA	64

- Soil Vapor Extraction (SVE)
  - 1,4-Dioxane also partitions into moisture in soil
  - Effectively air stripping
    - NOT FAVORABLE
- Extreme SVE
  - Increase temperature
    - Beneficial non-linear response
  - Increase PVs flushed
- Not expected to be common remedy but a level of treatment likely

Sorption Technologies

Contaminant	K_{ow}	K_{oc}	F_{oc}	K_d	Contaminant Distribution (%)	
					GW	Soil
1,4-Dioxane	0.54	17	1	17.0	1%	99%
PCE	468	155	1	155	0%	100%
TCE	513	166	1	166	0%	100%
DCE	117	38	1	38	1%	99%
1,1,1-TCA	302	110	1	110	0%	100%
1,1-DCA	62	53	1	53.4	0%	100%
1,2-DCA	30	38	1	38	1%	99%
Carbon Tetrachloride	537	174	1	174	0%	100%
1,2-Dichlorobenzene	2,692	617	1	617	0%	100%
Benzene	135	59	1	59	0%	100%
Toluene	562	182	1	182	0%	100%

- 100% of "typical" carbon
  - 99% 1,4-dioxane on carbon at equilibrium
- Carbons are expected to act differently
  - Need to consider sorption capacity
  - 1,4-dioxane capacity low compared to most other contaminants
  - Low efficiency treatment possible
- Specific sorbents
  - DOW Ambersorb563™
  - >99% removal observed
  - Higher capacity

Bioremediation

- Aerobic co-metabolic treatment
  - i.e-Propane, ethane, isobutane, etc
- Aerobic-direct treatment
  - Bench scale evidence
  - Specific microbes
- Anaerobic
  - Still needs to be proven
- Kinetics:
  - Aggressive biosystem
    - Half life: “days”
  - Less aggressive system
    - Half life: “months”
- Common co-contaminants found to inhibit:
  - 1,1-DCE>TCE>TCA
- Common co-contaminants may not be treated
- Has promise as a remedy, but likely very complex, potential inhibition

Chemical Oxidation

PeroxyChem

- Activated Persulfate
  - Excellent
- Hydrogen peroxide
  - Excellent
- Ozone
  - Excellent
- Permanganate
  - Limited kinetics (half life of ~1 month at ~10 g/L)

Radical	Reaction Rate
Hydroxyl Radical	3.1×10^9
	2.5×10^9
Sulfate Radical	7.2×10^7
	1.6×10^7

Certain activation methods for persulfate and hydrogen peroxide are known to also treat 1,1,1-TCA, DCA(s), TCE and DCE

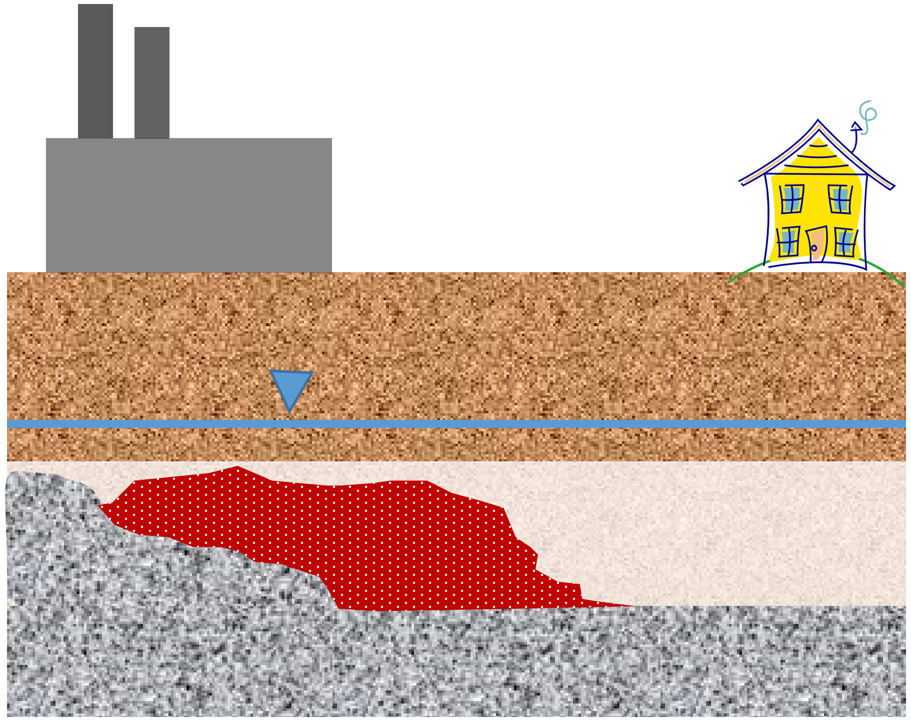
Applications

- Adsorption
  - Ex situ
    - Typically resins
- Vapor Extraction/Extreme Vapor Extraction
  - Vadose zone treatment
  - May need heat or extra pore volumes
- Bioremediation
  - Ex situ (bioreactors)
  - Saturated zone
    - Need to maintain co-metabolic conditions
- Chemical Oxidation
  - Ex situ
  - Saturated zone
  - Has been applied to vadose zones for other contaminants

Treating 1,4-Dioxane

Design Fundamentals

- Sufficient reagents
- Establish contact



Chemical oxidation, reduction, and bioremediation work by establishing contact between a sufficient mass of reagents with the contaminant mass in the subsurface

Sufficient Mass

- All transformative technologies (ISCO, ISCR, Bioremediation, etc) work by:
  - Adding a sufficient mass of reagents for the mass of contamination
  - Establishing contact of that mass with the contaminant
- Transformative technologies will react with:
  - Target demand
  - Non-target demand
- No system is completely efficient = Safety Factors
  - Remediation has inherent uncertainties (contaminant mass, contaminant distribution, reagent distribution, etc)
  - Application of reagents

Establishing Contact

PeroxyChem

- Contaminant partitioning between soil and groundwater largely dependent upon fraction of organic carbon on soil (F_{oc})
- 1,4-Dioxane tends to be in aqueous phase more than other contaminants

Contaminant	K_{oc}	F_{oc}	K_d	Contaminant Distribution (%)		F_{oc}	K_d	Contaminant Distribution (%)		F_{oc}	K_d	Contaminant Distribution (%)	
				GW	Soil			GW	Soil			GW	Soil
1,4-Dioxane	17	0.02	0.34	37%	63%	0.005	0.08	70%	30%	0.0001	0.00	99%	1%
TCE	166	0.02	3.32	6%	94%	0.005	0.83	19%	81%	0.0001	0.02	92%	8%
1,1,1-TCA	110	0.02	2.20	8%	92%	0.005	0.55	27%	73%	0.0001	0.01	95%	5%
DCE	38	0.02	0.76	21%	79%	0.005	0.19	51%	49%	0.0001	0.00	98%	2%
1,1-DCA	53	0.02	1.07	16%	84%	0.005	0.27	43%	57%	0.0001	0.01	97%	3%
1,2-DCA	38	0.02	0.76	21%	79%	0.005	0.19	51%	49%	0.0001	0.00	98%	2%

Establishing Contact

- Reagents and contaminants must contact each other
  - Contamination on soils
    - Injection or soil mixing of reagents
  - Contamination in groundwater
    - Permeable reactive barriers (PRBs)
      - Transects or source areas
      - Injected or trenched
    - Recirculation
    - Pull-push
    - Injection (can work, but may displace some GW)

Establishing Contact

PeroxyChem

KLOZUR® SP

Aqueous Reagents

"Solid" Contaminants

Injection Strategy

Aqueous Contaminants

"Solid" Reagents

KLOZUR® KP

PRB Strategy

Aqueous and Solid Reagents

Aqueous and "Solid" Contaminants

Soil Mixing

Case Study

Former Industrial Facility in the Northeast

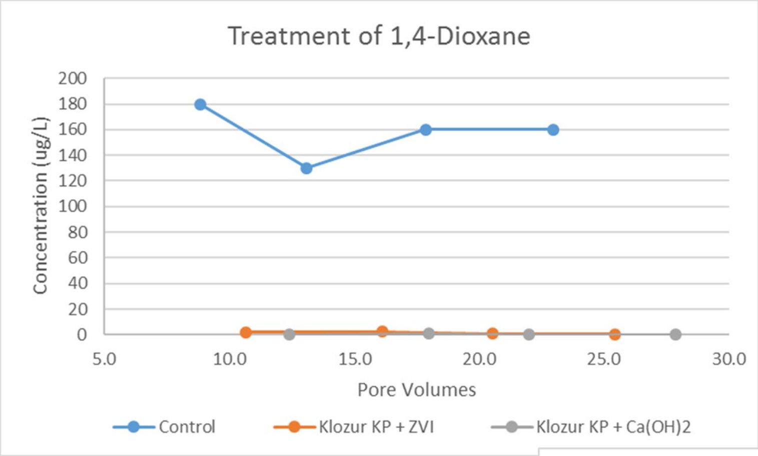
- Consultant: AECOM
- Residual 1,4-dioxane, TCA , and TCA daughter products
  - 1,1,1-Trichloroethane and 1,1,2-Trichloroethane (TCAs)
  - 1,1-DCA and 1,2-DCA
  - 1,1-DCE
- Silty soils with sand lenses
- Klozur KP PRB selected to establish contact with aqueous phase reagents

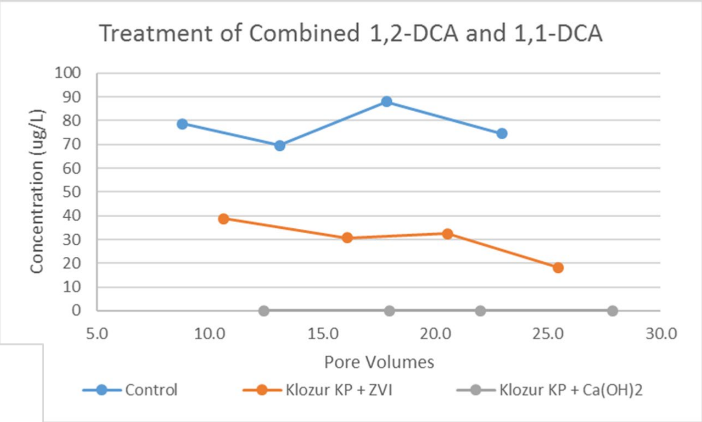
Klozur KP: Column Bench Test

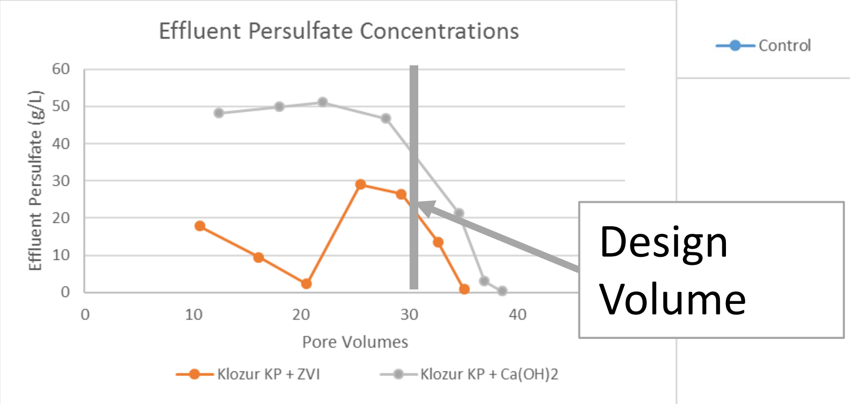
1) Oxidative pathway
   - 1,4-Dioxane

2) Reductive Pathway
   - DCA(s)

3) KP persisted intended 30 PVs

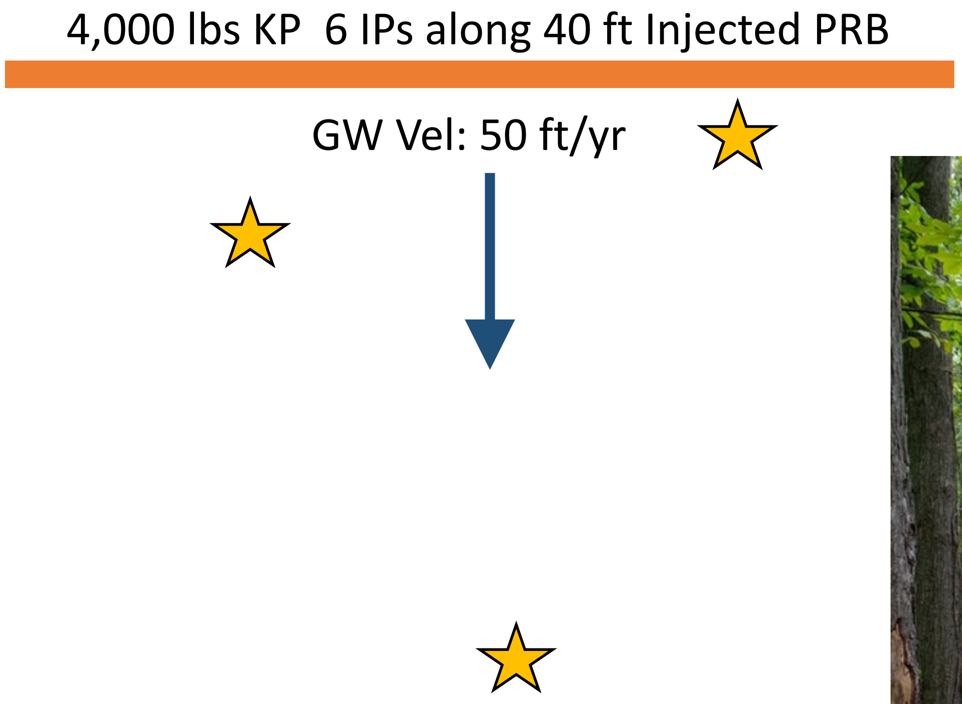






Pilot Study

- Pilot Conducted Early December 2017
- Injected PRB (40 ft)
  - Solid slurry
  - 6 DPT points
  - 20 to 30 ft bgs
  - Designed for 6 month persistence
- Reagents:
  - Klozur KP
  - Klozur SP
  - Hydrated Lime
  - 25% NaOH



Persistence and Distribution

PeroxyChem

4,000 lbs Klozur KP 6 IPs along 40 ft Injected PRB

GW Vel: 50 ft/yr

- Monitoring wells downgradient in targeted vertical interval:
  - Location 1 (~3 ft)
  - Location 2 (~10 ft)
  - Location 3 (~25 ft)

Event	Location 1	
	Persulfate (g/L)	pH
Baseline	NA	6.9
3 month	7.2	12
8 month	14.2	12

Event	Location 2	
	Persulfate (g/L)	pH
Baseline	NA	7.2
3 month	3	6
8 month	2.5	6.8

Event	Location 3	
	Persulfate (g/L)	pH
Baseline	NA	7.2
3 month	NA	NA
8 month	8	6.5

Treatment

PeroxyChem

4,000 lbs Klozur KP 6 IPs along 40 ft Injected PRB

GW Vel: 50 ft/yr

Event	Location 1: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	21	40	30	115	0%
3 month	0.2	nd	nd	0.2	99.8%
6 month	0.2	nd	nd	0.2	99.8%

* Detected VOCs not including acetone

Event	Location 2: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	44	72	55	184	0%
3 month	10	11	nd	26	86%
6 month	16	nd	16	34	82%

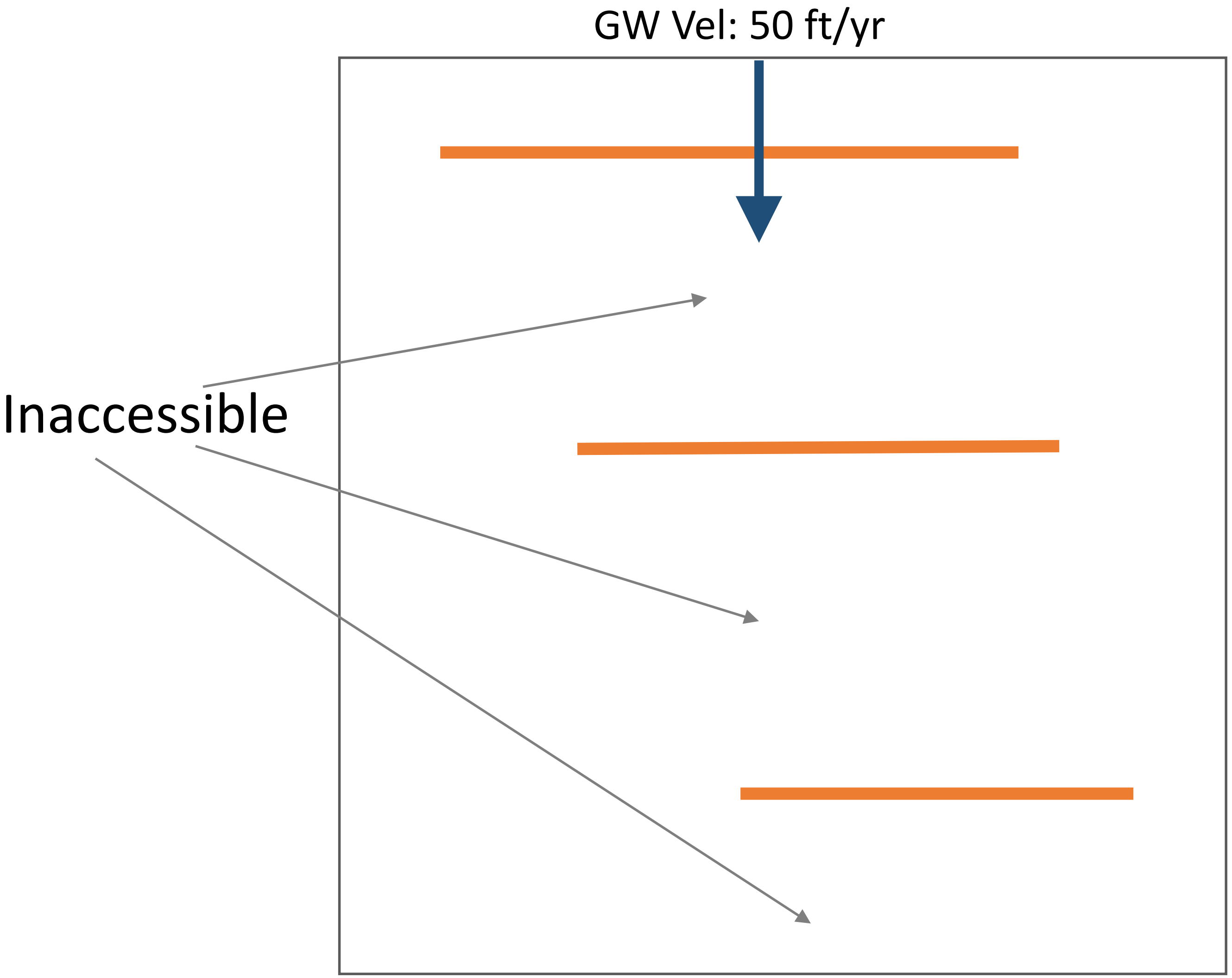
* Detected VOCs not including acetone

Event	Location 3: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	89	270	200	610	0%
3 month	46	82	69	216	65%
6 month	63	30	110	230	62%

* Detected VOCs not including acetone

Full Scale

- Implemented August 2018
- Three transects/PRBs
- Largely targeting 1,4-Dioxane
- Cut off source long enough and clean inaccessible zones



Summary

- Current technologies for 1,4-Dioxane
  - Primary
    - Sorption-resins
    - Chemical oxidant
  - Developing
    - Bioremediation
  - Have been tested:
    - Extreme SVE
- 1,4-Dioxane is different from most contaminants
  - Affinity for water
  - Typically co-mingled
- Treatment is more than technologies
  - Establish contact
  - Sufficient reagents at all times
- Treatment of 1,4-Dioxane and co-mingled contaminants is ongoing

Questions

Brant Smith
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Overview of the North Carolina Secretaries' Science Advisory Board

Department of Environmental Quality

Sandra L Mort, MS, PhD
Environmental Toxicologist, NC DEQ

DEQ

- *Providing science-based environmental stewardship for the health and prosperity of ALL North Carolinians*

DHHS

- *In collaboration with our partners, DHHS provides essential services to improve the health, safety and well-being of all North Carolinians.*

Secretaries Science Advisory Board's (SSAB) Overview and Purpose –

"To enhance the quality of life for all North Carolinians"

Broader scope for the "new" SSAB to -

- Assist DEQ and DHHS
- Achieve and maintain clean -
  - Air
  - Water
  - Land

With the objective to -

- Protect Public Health and Ecological Health
- Promote a vibrant economy

Agency Oversight and Direction

Agency Liaisons

DEQ – Assistant Secretary for Environment

DHHS – Deputy Secretary for Health Services

Science Support

DEQ Environmental Toxicologist

DEQ – DAQ, DWR, DWM staff

DHHS Div. of Public Health (DPH) staff

Make-up of the New SSAB

16 Member positions

PhD, MD and/or DVM level scientists with extensive environmental experience in the disciplines of:

- Toxicology
- Epidemiology
- Medicine, with Occupational or Environmental specialty
- Public Health Science
- Engineering
- Exposure and Risk Assessment

Also,

- County Health Director with environmental health or epidemiology
- DHHS State Health Director or the State Epidemiologist

The New SSAB -

Assist DEQ and DHHS in identifying and prioritizing

contaminants of emerging concern

Act as consultants to *DHHS* regarding establishing public health goals

The SSAB serves as an independent body of subject matter experts to provide consultation and review of human and ecological health-related activities of DEQ, DHHS and to provide risk recommendations to the EMC

The New SSAB -

Performs or recommends reviews of contaminant releases

- Derive, review, consult, or advise

Reviews effects of chemicals and recommend need and pace of regulation

Advises EMC on contaminant releases that come to the attention of the Board

NC SAB Risk Assessment Guidelines

- Establishes risk assessment as the basis for evaluations
- To advise the EMC of the scientific basis for these recommendations

SSAB → Risk Assessment

EMC → Risk Management

SSAB Review Process – Risk Assessment

SSAB's regulatory concentration recommendation considerations:

- Chemical-specific and media-specific factors of contaminant fate & transport
- Multi-media exposure impacts
- Multiple sources in a localized area
- Synergistic effects of mixtures

SSAB Review Process – Risk Assessment

SSAB's regulatory concentration recommendation considerations:

- Implications of uncertainty of: exposure concentrations, adverse effect levels, inter-species and intra-species response variability
  - Uncertainty Factors (UF)
  - Range of risk values
- Mode of Action (MOA)
- Pharmacokinetics, Pharmacodynamics
- Developmental and/or Reproductive effects

Activities of the New SSAB -

Department of Environmental Quality

PFAS GenX

GenX

- Chemours-Fayetteville Works
  - Manufactured, 2009
  - Byproduct vinyl ether production, 1980s
- Discharged to Cape Fear River
- USEPA ORD RTP and NCSU researchers identified in Cape Fear River
- Highly mobile, not removed by traditional drinking water treatment methods

NORTH CAROLINA
Department of Environmental Quality

GenX Review – Drinking Water Provisional Health Goal

SSAB asked to review DHHS' drinking water Provisional Health Goal decision matrix –

- DPH decision matrix
  - Toxicity studies
  - Sensitive population identification – age range
  - Exposure parameters - intake
  - Critical effect
  - Point of Departure (POD) – NOAEL, BMR
  - Uncertainty factors (UFs)
  - Chronic RfD

July 2017 drinking water PHG and use recommendations

NORTH CAROLINA
Department of Environmental Quality

GenX Review – Drinking Water Provisional Health Goal

SSAB asked to review DHHS' drinking water Provisional Health Goal (PHG) –

GenX DW PHG 140 ng/L and use recommendations -

- Do not use for: drinking, cooking, preparing baby formula
- May use for: bathing, washing dishes, laundry

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GenX Review – Drinking Water Provisional Health Goal

SSAB asked to review DHHS' drinking water Provisional Health Goal –

- December 2017
- Recommended Benchmark Dose Modeling approach
- Outside experts consulted
- Public input

SSAB confirmed DHHS GenX DW PHG process

- August 2018

Next steps:

- New toxicity and epidemiological studies
- USEPA GenX chronic oral RfD

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Trichloroethylene – Vapor Intrusion

Trichloroethylene (“TCE”)

- Common sub-surface contaminant
- Volatile, mobile, persistent
- Migration to indoor air environment → vapor intrusion

USEPA IRIS Program review update, 2011

- Non-cancer inhalation health values
- Developmental effects
  - Inhalation RfC critical effect
- Fetal cardiac malformation endpoint (FCME)
  - Potential long-term effects to child following short exposure
    - Hours
- Sensitive exposure population – Women in 1st trimester

Trichloroethylene – Vapor Intrusion

Indoor Air Action Levels

- DEQ, DHHS and USEPA Region 4 consensus
- Residential and occupational receptors
- Default USEPA human health risk estimation methods

DWM response guidance

- Specifies timeline for -
  - Notification of DWM
  - Identification of Sensitive Population
  - Initiation of mitigation activities
  - Risk communication
  - Confirmation of effective mitigation

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Trichloroethylene – Vapor Intrusion

Stakeholder concerns –

- Validity of the RfC science
- Public health (IRIS) vs. Occupational (OSHA) values
- Response guidance timeline

June 2018 – SSAB asked to review science supporting the IRIS RfC, fetal cardiac endpoint and DWM response guidance

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Trichloroethylene – Vapor Intrusion

SSAB review -

- Presentations by DEQ, DHHS, USEPA Region 4
- USEPA IRIS 2011 TCE review
- DWM literature review
  - Independent reviews of TCE toxicological science
  - Mode-of-action science
  - Epidemiological studies supporting cardiac effects and fetal cardiac malformation endpoint

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Department of Environmental Quality

Trichloroethylene – Vapor Intrusion

SSAB review -

- Summary report, October 2018
- Stakeholder comments
    - Rodent study submitted to USEPA
- Public comments
    - 30-day submittal period

SSAB final recommendation, February 2019

- Current science supports TCE IA ALs, FCME and Response Guidance
- Re-evaluate future new science, USEPA or ATSDR reviews

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Hexavalent Chromium Review

DHHS and DEQ request to the SSAB –

To review the current hexavalent chromium toxicological science related to related to a linear versus a non-linear exposure response and provide recommendations to the appropriate science to be used for development of regulatory standards protective of public health and the environment for groundwater and surface water.

Hexavalent Chromium Review

Threshold mechanism for cancer endpoint → **RfD**

or

Non-threshold mechanism for cancer endpoint → Cancer Slope Factor (**Cancer Potency Factor**)

Cancer Mode-of-Action (MOA) relates to the calculation DWR uses to derive groundwater (2L) and surface water (2B) regulatory values

NORTH CAROLINA Department of Environmental Quality

Hexavalent Chromium Review

Presentations by –

- USEPA – IRIS review status
- Threshold approach (RfD) –
  - TXCEQ, Health Canada
  - ToxStrategies, Inc.
- Non-threshold approach (Slope Factor) –
  - NJDEP, CAOEHHA

Literature review –

- IRIS literature review, ~1000 papers
- ~200 new articles
- SSAB decision expected mid-2019

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What's Next?

1. Complete the hexavalent chromium review and provide MOA conclusions to the DWR (2019)
2. Update review of the GenX DW PHG when the USEPA final chronic RfD is released (2020)
3. Update review of TCE indoor air Action Levels, as appropriate based on new science
4. Update SSAB SOPs

DEQ and DHHS are currently refining the list of the additional issues to be tackled by the SSAB, and

- Also, evaluating the new SSAB's structure and approach for future refinement to better serve the agencies and all North Carolinians

NORTH CAROLINA Department of Environmental Quality

Useful Links -

New SSAB web page –

- Meeting agendas, Minutes, Audio recordings
- Presentations, reports, public comments
- Members

- https://deq.nc.gov/news/key-issues/genx-investigation/secretaries-science-advisory-board

Prior SAB's archives –

- https://deq.nc.gov/about/divisions/air-quality/science-advisory-board-toxic-air-pollutants

To contact the SSAB or submit review comments –
Comments.sabreport@ncdenr.gov

NORTH CAROLINA
Department of Environmental Quality

DEQ SSAB Technical Coordinator -

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NORTH CAROLINA
Department of Environmental Quality

Questions?

Department of Environmental Quality

Vapor Intrusion: Assessment and Mitigation Options for Sites with Known or Suspected Chlorinated Solvent Contamination

Kelly G. Johnson, P.G.
NC Brownfields Project Manager

April 24, 2019

Department of Environmental Quality

Overview

- NC Brownfields Program
- Intro to Vapor Intrusion
- Intro to Chlorinated Solvents
- Vapor Intrusion Assessment, Common Issues, New Developments
- Vapor Intrusion Mitigation
- Case Study of NC Brownfields Site

NC Brownfields Property Reuse Act of 1997

- Create Special Class of Remediating Parties… "Prospective Developers" of Abandoned Sites
  - Did not Cause or Contribute to Contamination (Only Non-Polluters Receive Benefits)
  - Must Agree to Make Site Safe for Reuse
- Brownfields Agreements between DEQ and Prospective Developers
  - Provide Liability Protection in Return for Measures That Make Property Safe for Reuse
  - Ensure Enforceability of Land Use Restrictions
  - Provide Them With a Tax Incentive to Assist in Costs

NC Brownfields Redevelopment

- Recycling Program for Abandoned/Underutilized Properties
  - 530 Completed Brownfields Agreements in NC
  - Facilitated $17 Billion in Capital Investment in Property Recycling
  - Put 10,000+ Acres Back in Play
  - Safe for Reuse Typically Means Focus on Assessing/Mitigating Vapor Intrusion

The Dillon Mixed Use Development in Raleigh, NC

Image Sources: The Dillon
https://thedillonraleigh.com/downtown-raleigh-dillon-supply-warehouse-walls-still-standing/
https://thedillonraleigh.com/public-art-coming-to-the-dillon/

Intro to Vapor Intrusion

- Within the subsurface, contaminants may exist in the following phases:
  - Solid phase by adsorbing onto the organic fraction of soil;
  - Aqueous phase by dissolving in groundwater and pore water;
  - Non-aqueous phase liquid (NAPL); and/or
  - Gaseous phase, by accumulating in the interstitial space of soil particulates as soil gas.

Thus, soil matrix and groundwater sampling and analysis should be considered for site characterization **in addition** to soil gas sampling to ensure that all potential phases of Volatile Organic Compounds (VOCs) are evaluated and their associated exposure pathways.

- Easy to miss potential on-site sources if only look at Soil/GW

Reference:
California EPA Dept. of Toxic Substances Control, Advisory Active Soil Gas Investigations, July 2015

Intro to Vapor Intrusion

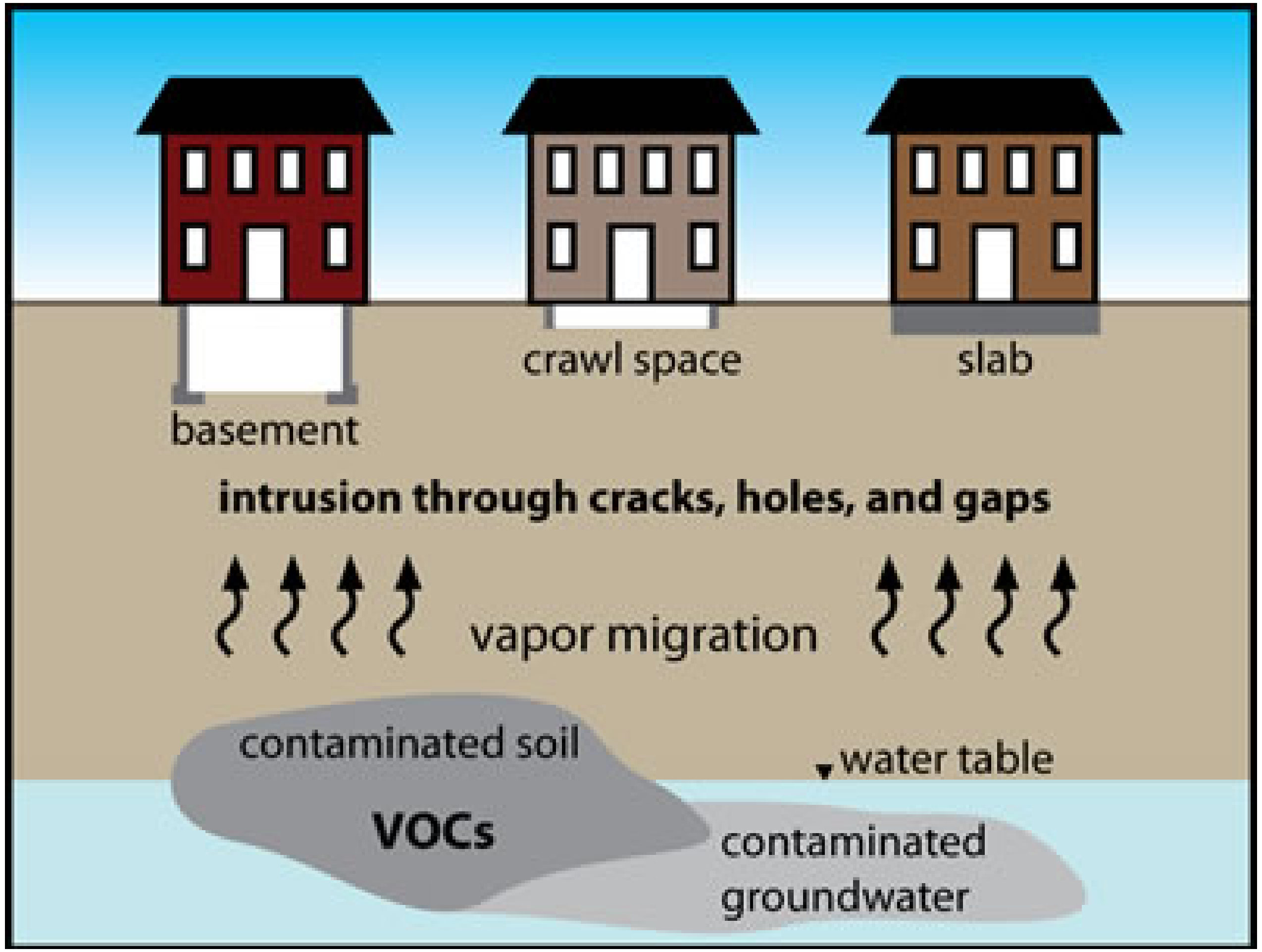


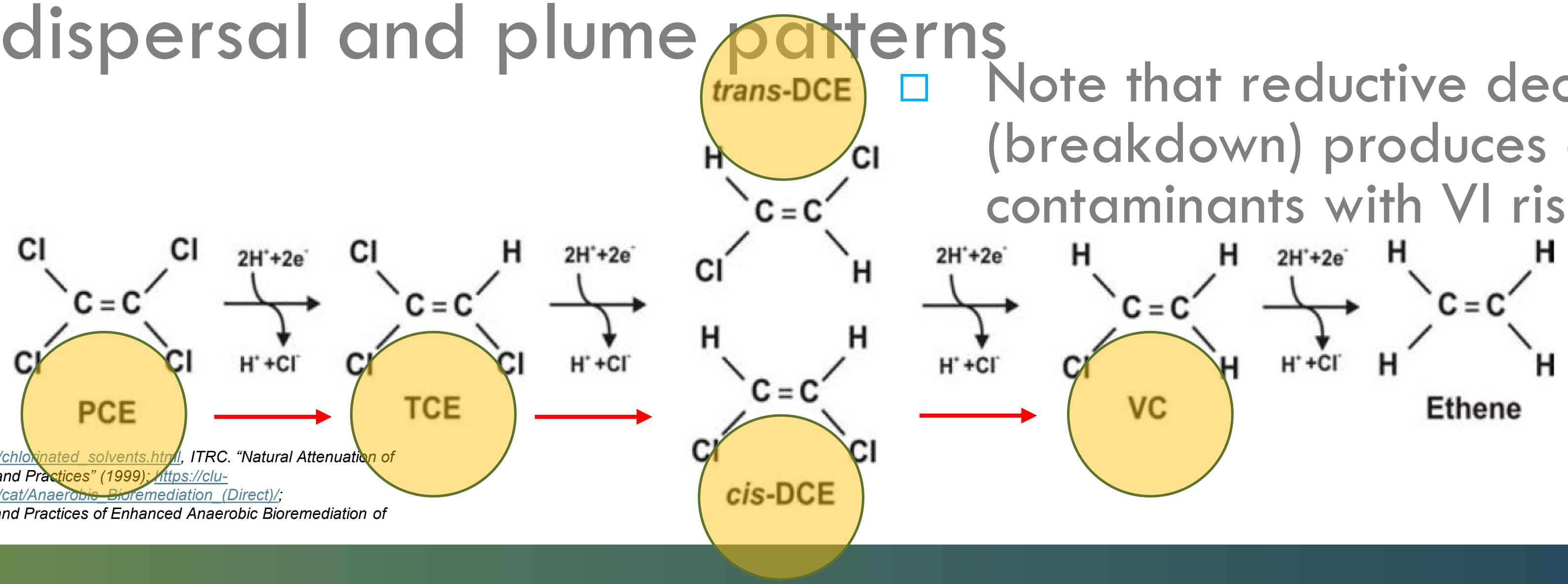
Image Source: EPA Brownfields and Land Revitalization Technology Support Center – Vapor Intrusion
https://brownfieldstsc.org/roadmap/spotlight_vi.cfm

- **Vapor Intrusion (VI)** = Migration of Vapor-Phase Contaminants from the Subsurface into an Overlying Building or Structure
- A Complete **Vapor Intrusion Pathway** May Result in Unacceptable Risk to Occupants
- Soil / Groundwater Land Use Restrictions Can Be Ineffective vs. Addressing Vapor Intrusion
- Removal of Source Material and/or Remediation Activities May Not Be Sufficient to 'Screen Out' Site for Vapor Intrusion Risks

Intro to Chlorinated Solvents

- Have properties that make them useful for degreasing fats, oils, waxes, and resins
- Persistent in environment depending on sub-surface conditions
- Most chlorinated solvents are denser than water and hydrophobic
- Due to density, can sink in groundwater systems resulting in complex dispersal and plume patterns

- Note that reductive dechlorination (breakdown) produces additional volatile contaminants with VI risks

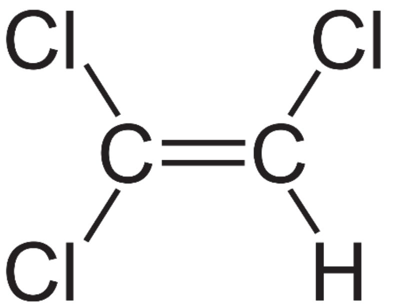


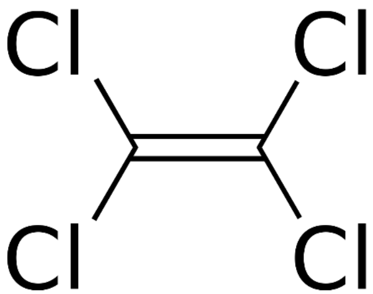
References: https://toxics.usgs.gov/investigations/chlorinated_solvents.html, ITRC. "Natural Attenuation of Chlorinated Solvents in Groundwater: Principals and Practices" (1999); https://clu-in.org/techfocus/default.focus/sec/Bioremediation/cat/Anaerobic_Bioremediation_(Direct)/;
Image Source: Parsons Corporation. "Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents" (2004)

Two Common Chlorinated Solvents:

- **Trichloroethylene** (TCE)
  - Primarily used as degreaser or as extraction solvent
  - Still found in consumer products such as paint remover, adhesives, and spot removers

- **Tetrachloroethylene** (PCE or PERC)
  - Primarily used in dry cleaning of fabrics,
  - Still found in consumer products such as paint removers, brake and wood cleaners, and glues

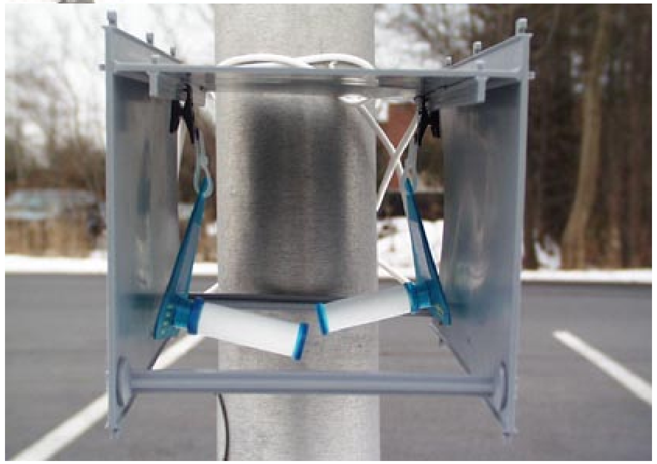




Reference: https://toxics.usgs.gov/investigations/chlorinated_solvents.html
TCE Structural Formula Image Source: Wikipedia by Kermikungen
TCE Drum Image Source: http://www.shangindustry.com/sale-9078147-trichloroethylene.html

PCE Structural Formula Image Source: Wikipedia by Calvero
Neon Dry Cleaning Image Source: https://bucco.us/difference-organic-perk-dry-cleaning/

Vapor Intrusion Assessment



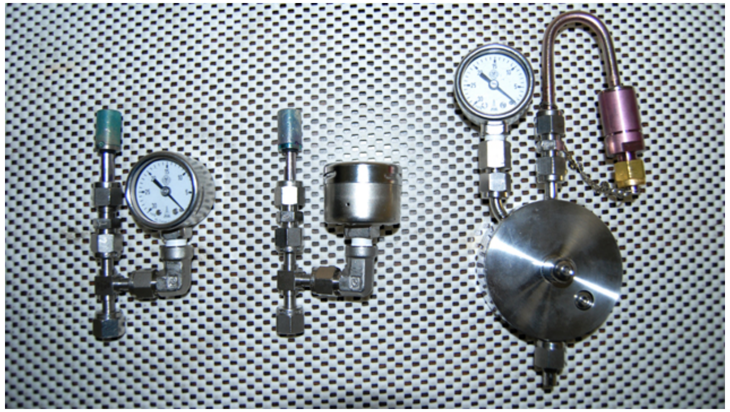
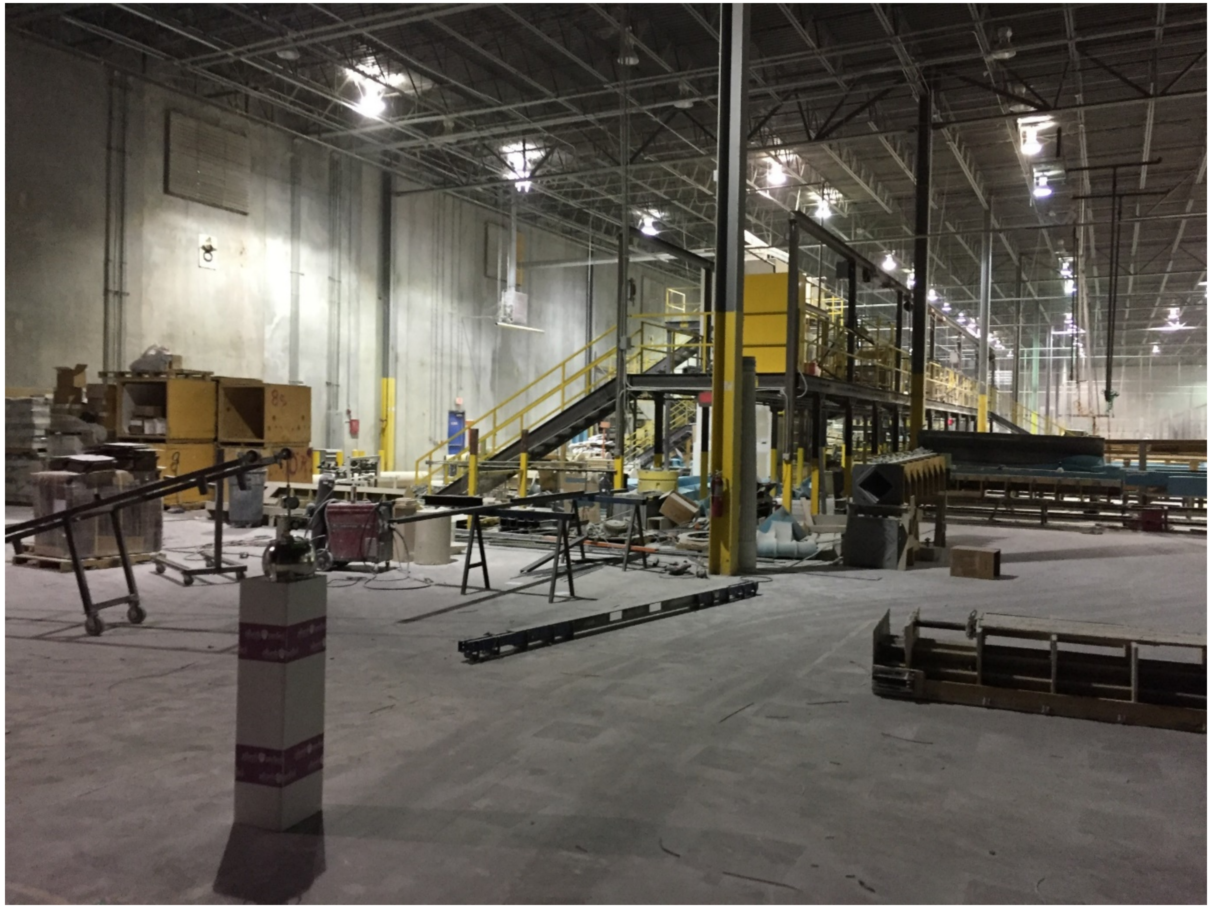


Image Sources:
https://www.osha.gov/dts/sltc/methods/partial/pv2120/pv2120.html; http://www.smartcityweb.net/blog/2013/06/13/campionatori-diffusivi-radiello/; https://sites.google.com/a/eto.vurv.cz/monitoring-imisi/monitoring-imisi/vyzkumna-zprava/3-analyza-legislativy-statu-evropske-unie-v-oblasti-sledovani-imisi-a-hodnoceni-jejich-vlivu-na-zemedelstvi/3-08-pasivni-system-vzorkovani-imisnich-polutantu-radiello/3-08-1-princip-fungovani; http://www.aaclab.com/analytical-services/sampling-equipment-media.html; http://www.unitedchemists.com/airsampling.aspx; http://www.itrcweb.org/PetroleumVI-Guidance/Content/Appendix%20G.%20Investigation%20Methods%20and%20Analysis%20Toolbox.htm; https://www.esclabsciences.com/products/quality

Assessing Large Buildings for VI Can Be Challenging



- Try to understand the historical uses of the building
- Old facility layouts (fire/evacuation maps, insurance maps, etc.) and personnel interviews can help target assessment areas
- Unfortunately, may be best to assume the worst VI possibility to protect public health

Indoor Air

- Typically Last Step Investigative Step
- However, Most Applicable Data to Determine Human Exposure Conditions
  - Also More Susceptible to Interferences (Background Sources) Than Soil Gas
- Indoor Air is Highly Variable Due to Building Characteristics and Weather
- Understand Difference Between Non-Detect and Detections Below Screening Levels

Residential Sample Duration	24 Hours
Non-Residential Sample Duration	8 Hours

Lotions and Sunscreen

Compound	Sunscreen	Body Lotion	Cancer ($\mu g/m^3$)	Noncancer ($\mu g/m^3$)
Ethanol	110,000	150	n/a	n/a
Ethyl acetate	11,000	-	n/a	73.00
MTBE	48	-	9.400	3,100.00
TPH (C5-C11)	93,000	2,800	n/a	n/a
(C5-C8) Aliphatics	-	1,200	13.000	630.00
(C9-C10) Aromatics	640	-	n/a	3.10
(C9-C12) Aliphatics	39,000	4,400	0.540	100.00

Lotions
- Sunscreen
- Mildly scented body lotion

Sunscreen FAQ: *An aerosol sunscreen was recalled for fire hazards. People were applying it then going to a heat source (grill) and combusting.*

Slide Source: H&P Presentation "Unexpected Sources of Petroleum Hydrocarbons and Chlorinated Solvents in Indoor Air" January 13, 2014

Importance of Indoor Air Surveys

Shampoo & Conditioner

- Middle shelf brand
- According to European and Canadian reports, carcinogens are in almost every brand

Compound	Shampoo	Conditioner	Cancer ($\mu g/m^3$)	Noncancer ($\mu g/m^3$)
1,4-Dioxane	87	-	0.490	31.00
Chloromethane	170	88	n/a	94.00
Ethyl acetate	6,500	120	n/a	73.00
Isopropylbenzene	-	280,000	n/a	420.00
(C9-C12) Aliphatics	11,000	32,000	0.540	100.00

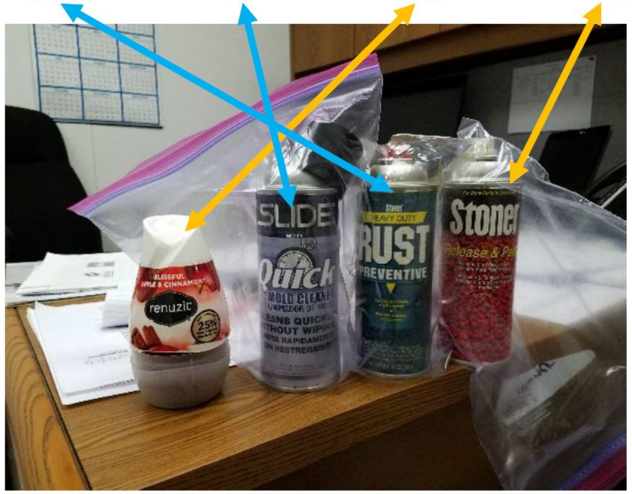
Again, a Daily Use Product!

H&P

Slide Source: H&P Presentation "Unexpected Sources of Petroleum Hydrocarbons and Chlorinated Solvents in Indoor Air" January 13, 2014

MATCHING GAME – DRAW ARROWS TO MOBILE LAB HEADSPACE TCE CONCENTRATIONS

ND $\mu g/m^3$ ND $\mu g/m^3$ 8.0 $\mu g/m^3$ 5.2 $\mu g/m^3$



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GOLDER

Slide Source: Golder "Case Study – Complete Vapour Intrusion Mitigation Services for an Industrial Plant. December 5-6, 2018

Sub-Slab Soil Gas

- Placement of Points is Important
  - Away from Exterior Walls, Cracks, Etc.
- Should Attempt to Generally Describe Material Below Slab
  - Gravel, Sand, Clay
- Elevated Concentrations of VOCs **Requires** Additional Assessment of VI Pathway (Indoor Air)
- However, Lower Concentrations of VOCs Does Not Necessarily Mean No VI Risk (Preferential Pathways)

Exterior Soil Gas

- Should Only be Used for Undeveloped Lots or Due to Access Restrictions
- If VI Concern is From **Off-Site** Contamination: Multiple Depth Samples Can Be Valuable
- Minimum Depth for Exterior Soil Gas Sampling in NC is 5 Feet
- Possible to Miss On-Site Sources
- Note that Development May Result in Higher/Lower VI Risks

More Invasive Soil Gas Installation Methods = Longer Equilibration Time Before Sampling

Soil Gas Installation Method	Recommended Equilibration Time
Direct Push	2 hours
Hollow Stem / Hand Auger	48 hours
Sub-Slab (Core/Drill, Build with Bentonite)	2 hours
Sub-Slab with Minimally Invasive Points (i.e., Vapor Pins or Similar)	20 mins

Note: This is a sawed contraction joint in a new slab (does not fully penetrate slab). However, still should have placed at least 5 feet away

- Leak Check Required For All Soil Gas Points Prior to Sampling
- Leak Check Must Include Include Probe Point **AND** Entire Sampling Train
  - Sample Canister, Tubing, Valves/Fittings, Etc.

- Shroud
- Helium Source
- Entire Sampling Train
- Helium Detector

Leak Check Shroud Image Source: http://www.advancedgeoservices.com/environmental

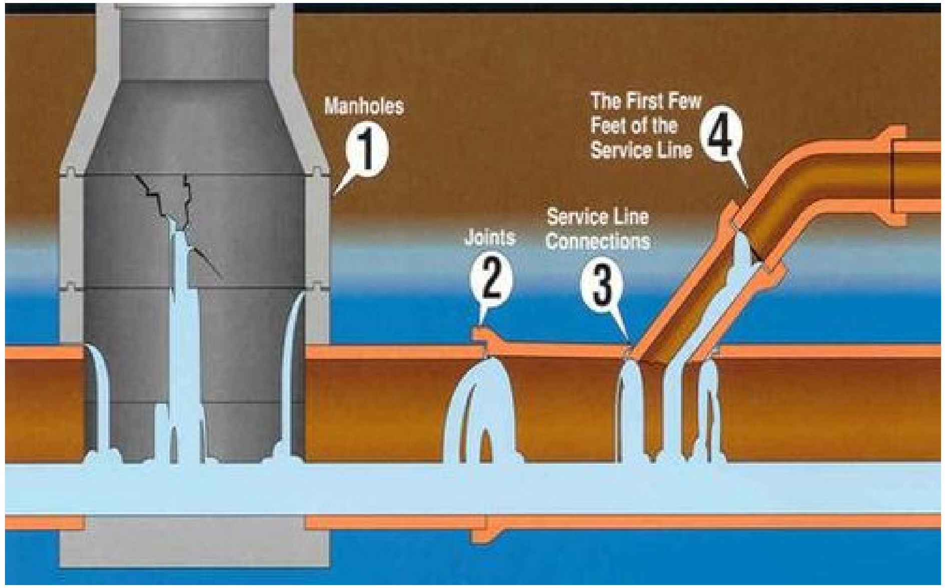
Vapor Intrusion Assessment

Common Issues

- 1 ppbv ≠ 1 µg/m^3
- 0" Hg Final Vacuum
- Sufficient Reporting Limits
- Recommend Collecting Indoor Air and Sub-Slab Soil Gas Concurrently to Evaluate Background Air Sources
  - Collect Indoor Air First

New Developments

- Preferential Pathways
  - Can Result in Higher Indoor Air Concentrations Than Expected
  - Vapors Can Travel Long Distances From Source Areas Along Sewers and Utilities
  - Video Inspections
  - Tracer Tests



Infiltration Image Source: Environmental Data Services
http://www.e-d-s.com.au/inflow-infiltration-studies

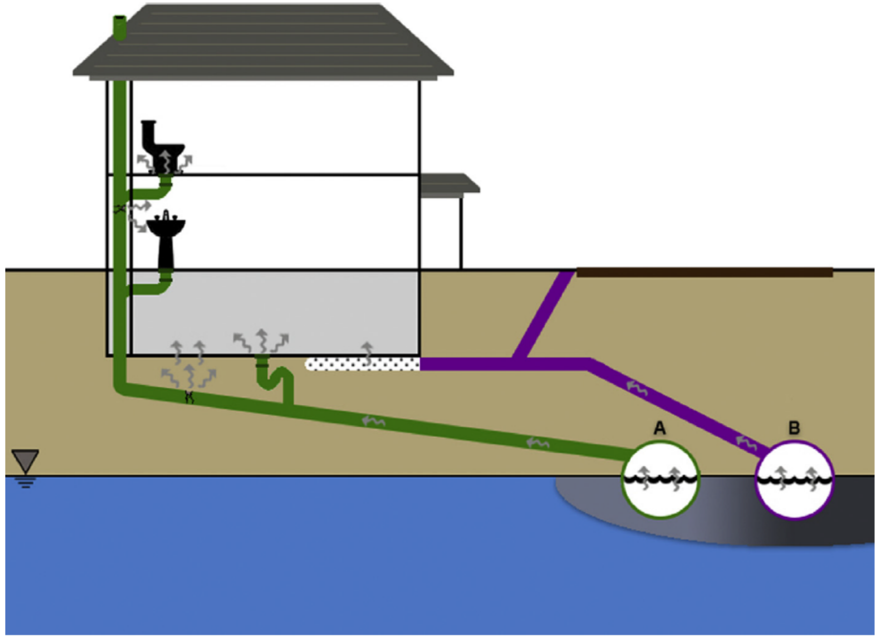
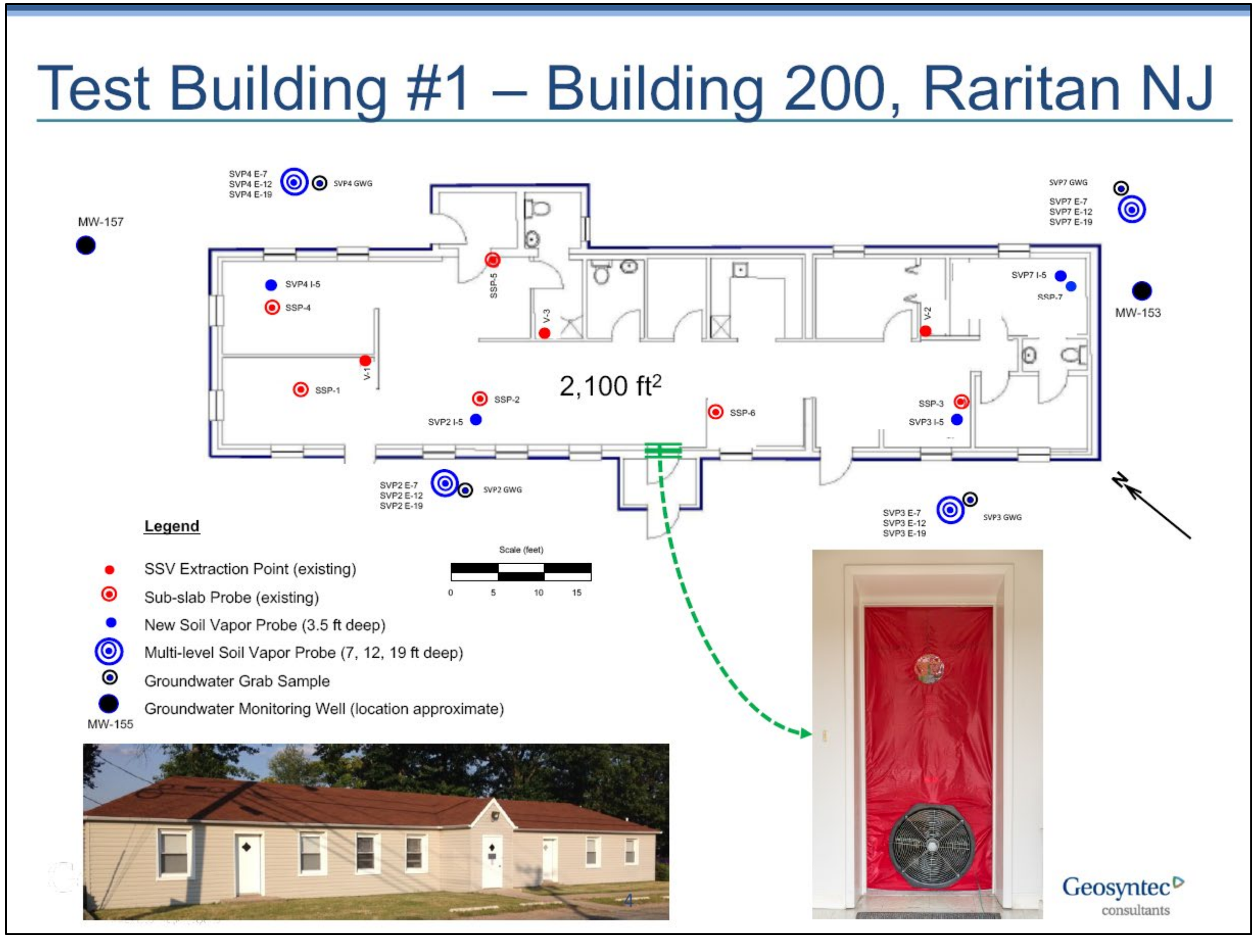


Fig. 2. Simplified Conceptual Model for Sewer Preferential Pathway Vapor Intrusion: A) Sanitary sewer line, B) Storm sewer or land drain system connected to building foundation drain (not applicable for some buildings). In some older sewer systems, sanitary and storm water flow through a combined sewer system.

Please cite this article in press as: McHugh, T., et al., Recent advances in vapor intrusion site investigations, Journal of Environmental Management (2017), http://dx.doi.org/10.1016/j.jenvman.2017.02.015

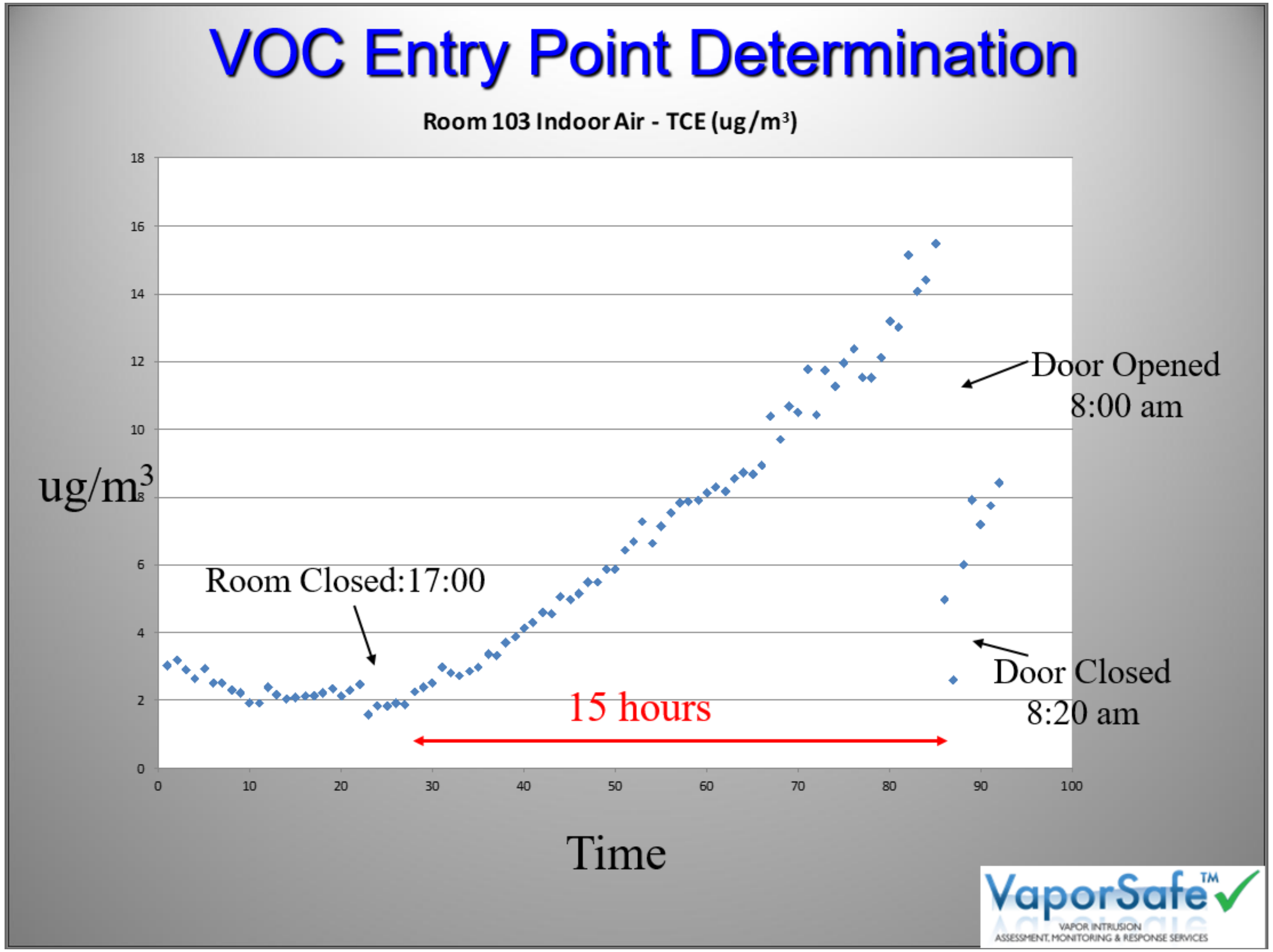
- Controlled Building Pressure Testing
  - Address Spatial & Temporal Variability (Induce 'Worst-Case')
  - May Allow Differentiation of Background Contributions vs. VI-Related Contributions



Building Pressure Control Slide Source: Geosyntec Consultants "Building Pressure Cycling for Vapor Intrusion Assessment". March 21, 2017

New Developments

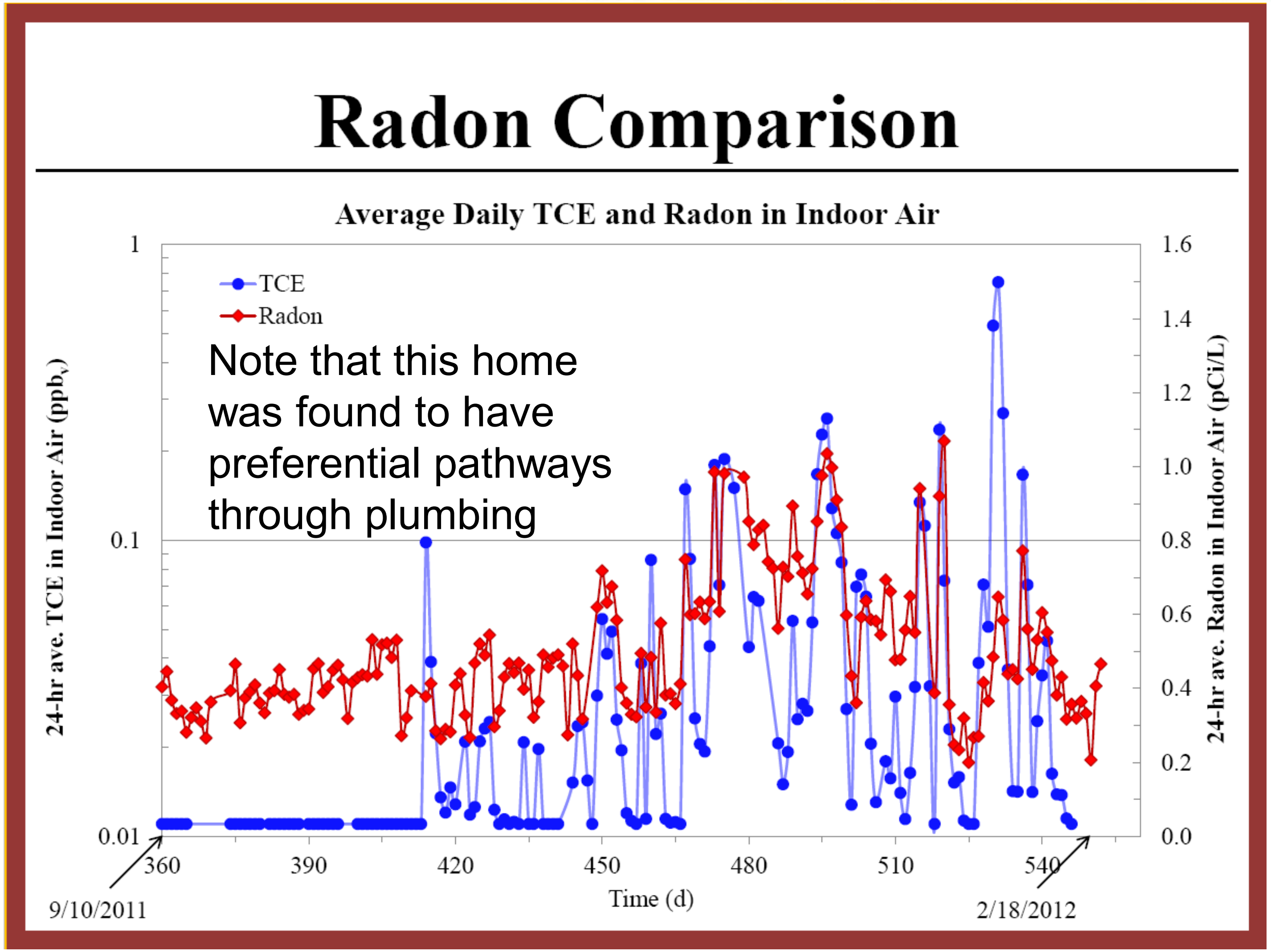
- Real-Time Monitoring of Volatile Organic Compounds (VOCs) in Indoor Air
  - Several Companies Developing Capability
  - Can Help Understand Building Characteristics
  - May Still Need to Combine with Sampling via EPA Methods and Certified Labs



VOC Slide Source: Hartman and Kram "Rapid Resolution of Vapor Intrusion Challenges via Automated Continuous Real-Time Monitoring". Dec 2018

New Developments

- Radon as Tracer for VI/Complete Pathway
  - Continuous Logging of Indoor/Ambient Radon
  - Could Help Target 'Peak' Indoor Air Sampling Times
  - Additional Research Needed

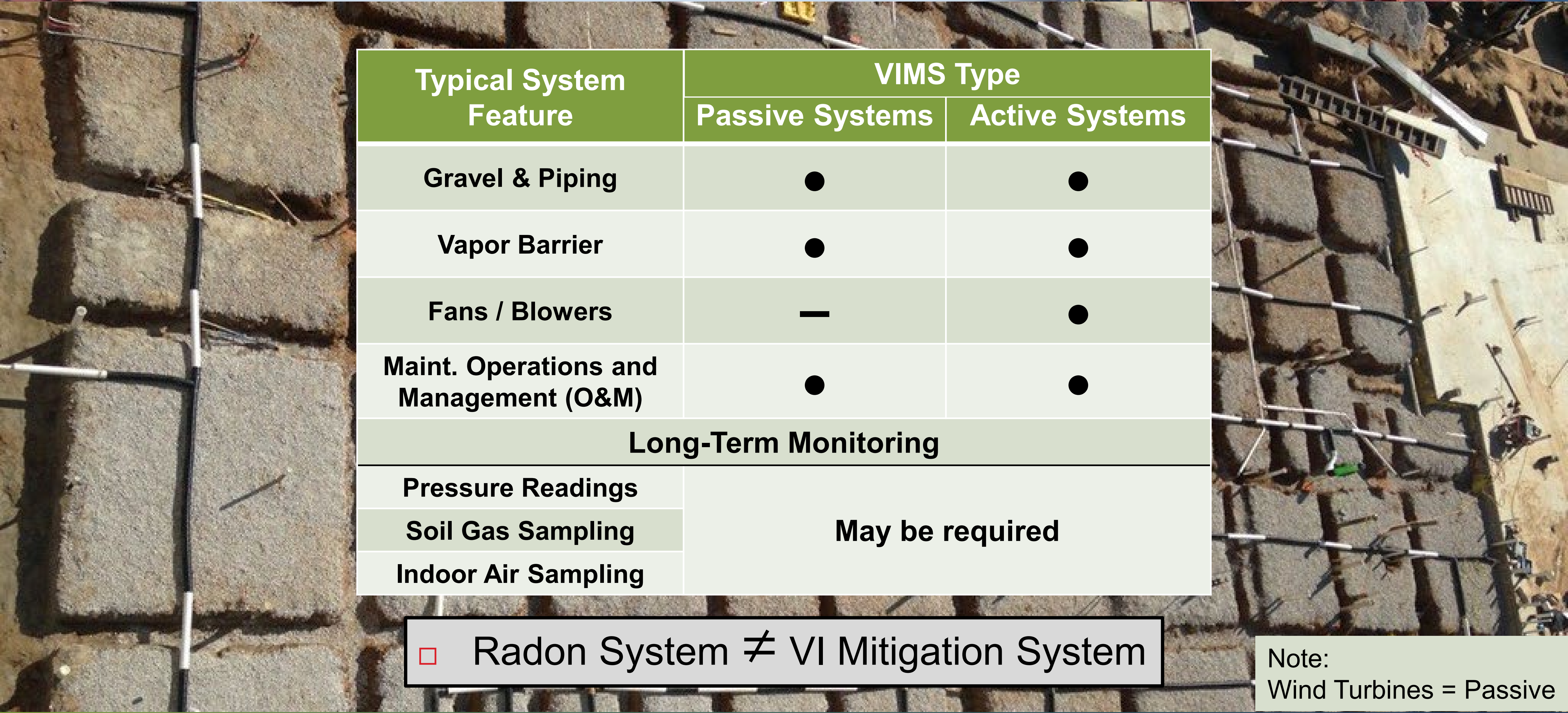


Radon Comparison Slide Source: ASU/SERDP, Holton "Long-term and Short-term Variation of Indoor Air Concentration at a Vapor intrusion Study Site". March 22, 2012

Vapor Intrusion Mitigation Systems

- Institutional Controls
  - Admin / Legal
    - Land Use Restrictions
  - Educate Employees or Tenants of Risk
  - Vacate Certain Areas
- Engineering Controls
  - Adjust HVAC for More Positive Pressure or Makeup Air
  - Air Filtration (interim)
  - Seal Openings (IMPORTANT)
  - Mitigation Systems
    - Vapor Barriers
    - Active Depressurization
    - Passive Venting

Vapor Intrusion Mitigation Systems



Typical System Feature	VIMS Type	
	Passive Systems	Active Systems
Gravel & Piping	●	●
Vapor Barrier	●	●
Fans / Blowers	—	●
Maint. Operations and Management (O&M)	●	●
Long-Term Monitoring		
Pressure Readings	May be required	
Soil Gas Sampling		
Indoor Air Sampling		

- Radon System ≠ VI Mitigation System

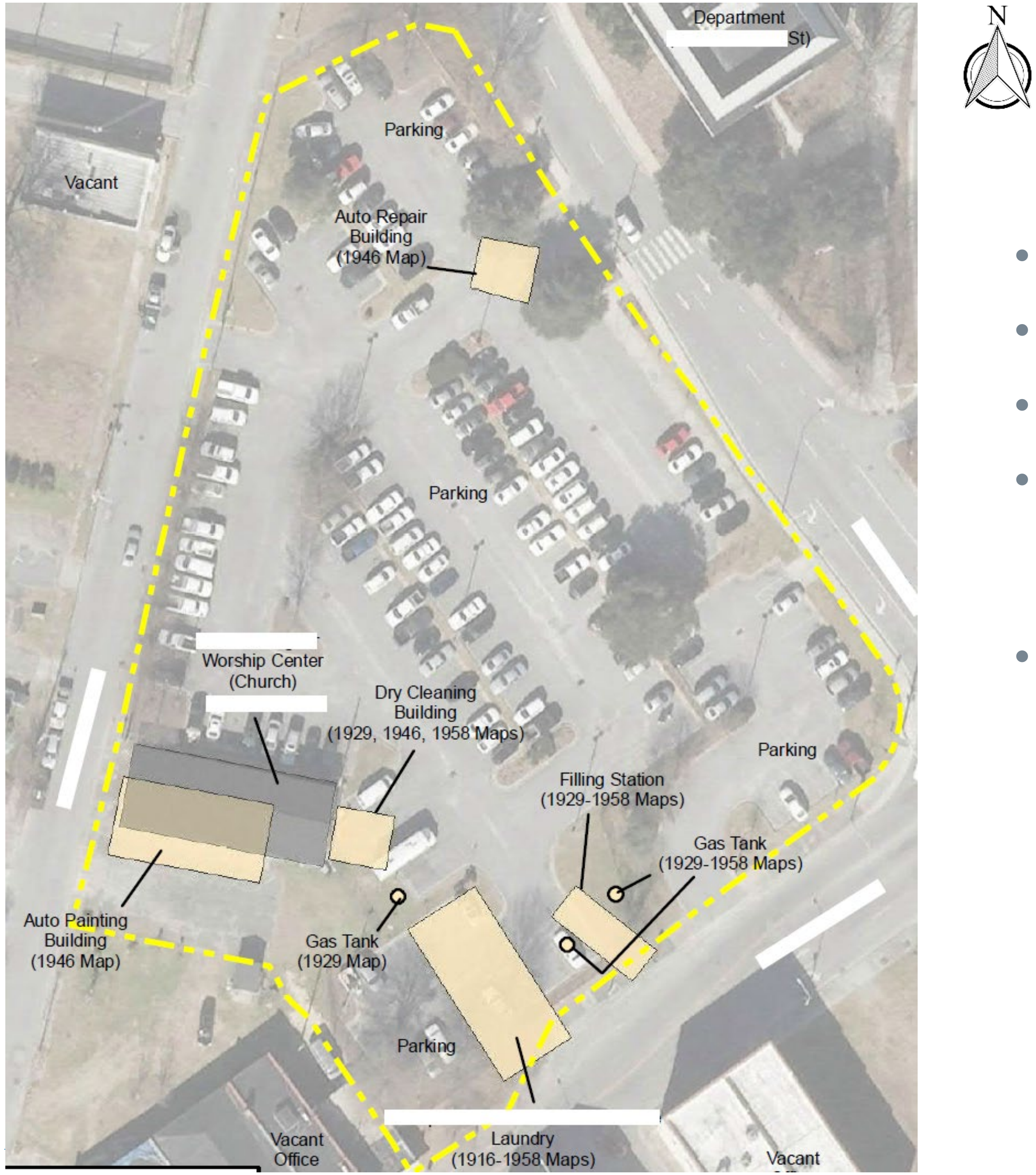
Note:
Wind Turbines = Passive

VI Mitigation of an Existing Building (Retrofitting)

- Requires a thorough environmental assessment and understanding of the building
  - Preferential pathways, block wall cavities, slab cracks, etc.
- Cost can vary greatly depending on scale of contamination and the building/sub-slab characteristics

VI Mitigation in New Construction

- Typically cheaper than retrofitting an existing building
- Consult with your engineer **early** in design process to reduce costs
  - For example, sometimes possible to replace moisture barriers with vapor barriers or using a planned gravel layer as a venting layer
- Consider designing around contaminated areas with parking lots or recreation space (with no enclosed spaces)



Case Study

- Eastern North Carolina
- Sanborn Fire Insurance Map coverage for 1900-1958
- By 1916: developed with a steam laundry
- By 1929: a gasoline station was built; a large tobacco warehouse was also built; and the laundry had expanded to include **dry-cleaning**
- Between 1970 – 1988: Most buildings were demolished by local municipality for parking

Reference available upon request. Reports are publically available. Map by Terracon.

Case Study

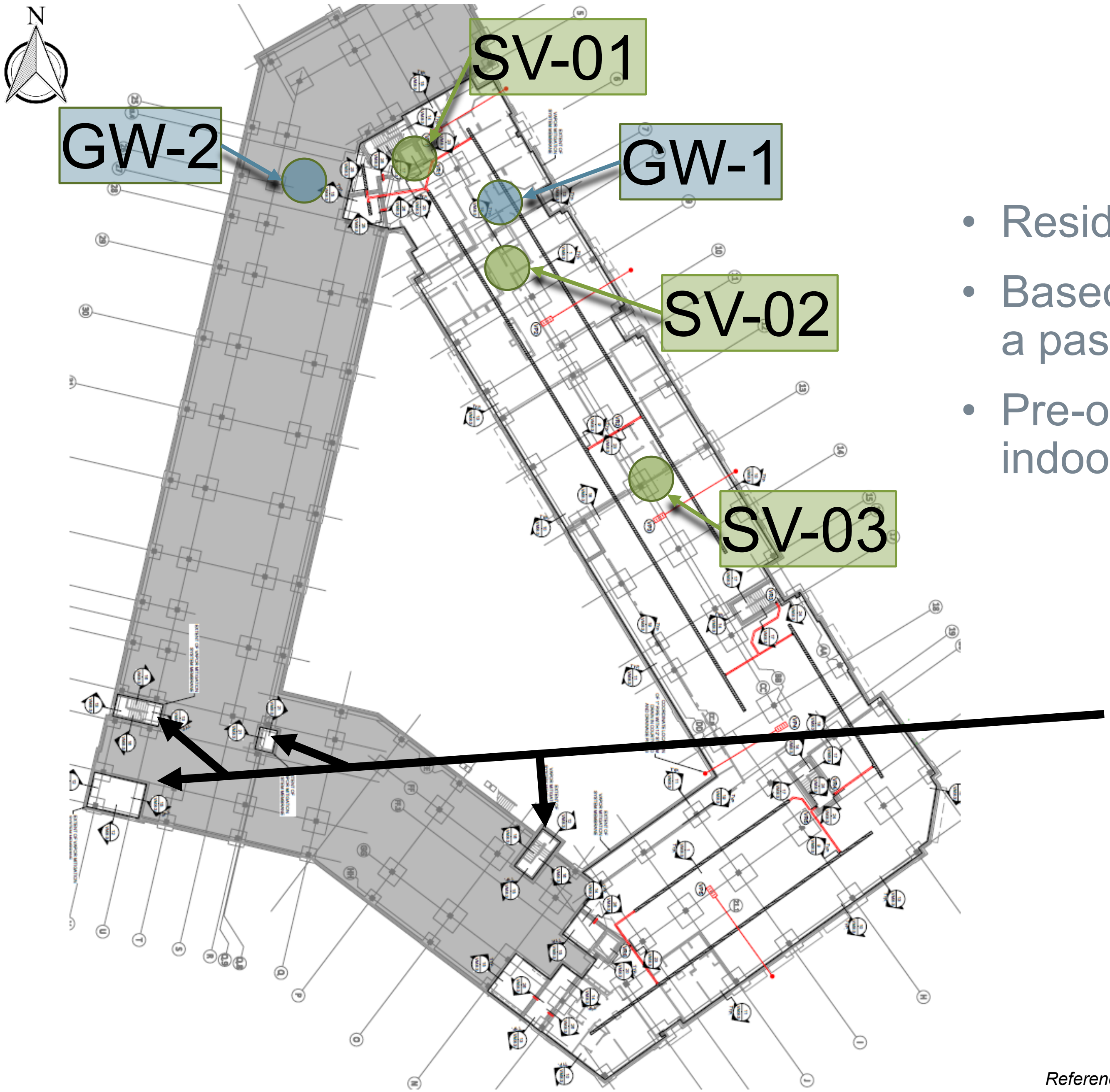
- Conducted Soil, Groundwater, and Exterior Soil Gas Assessment
- No Soil Impacts of VOCs
- Chlorinated Solvents = Primary Risk
  - Possibly Associated with Old Auto Repair

GROUND WATER	GW-1 (2016)	GW-2 (2016)	Residential VI Screening Level for Groundwater
PCE (μg/L)	9.6	15.8	12
TCE (μg/L)	18.9	23.8	1.0

EXTERIOR SOIL GAS	SV-01 (2017)	SV-02 (2017)	SV-03 (2017)	Residential VI Screening Level for Soil Gas
PCE ($\mu g/m^3$)	949	1,750	723	280
TCE ($\mu g/m^3$)	165	64.3	86.3	14

Reference available upon request. Reports are publically available. Map by Terracon.
DEQ DWM VI Screening Levels (February 2018 Version). Sample locations are approximate.

Case Study



- Residential structure with some 1st floor retail
- Based on exterior soil gas results, consultant designed a passive mitigation system
- Pre-occupancy testing included sub-slab soil gas and indoor air

Note that the western portion of site is a parking garage (grey shading), but elevators/stairwells and other enclosed spaces still have a vapor barrier

Reference available upon request. Reports are publically available. Map by Terracon. Sample Locations are Approximate.

Conclusion

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To find more about NC Brownfields:

www.ncbrownfields.org

Contact me if interested in participating in the new ITRC VI Mitigation Team

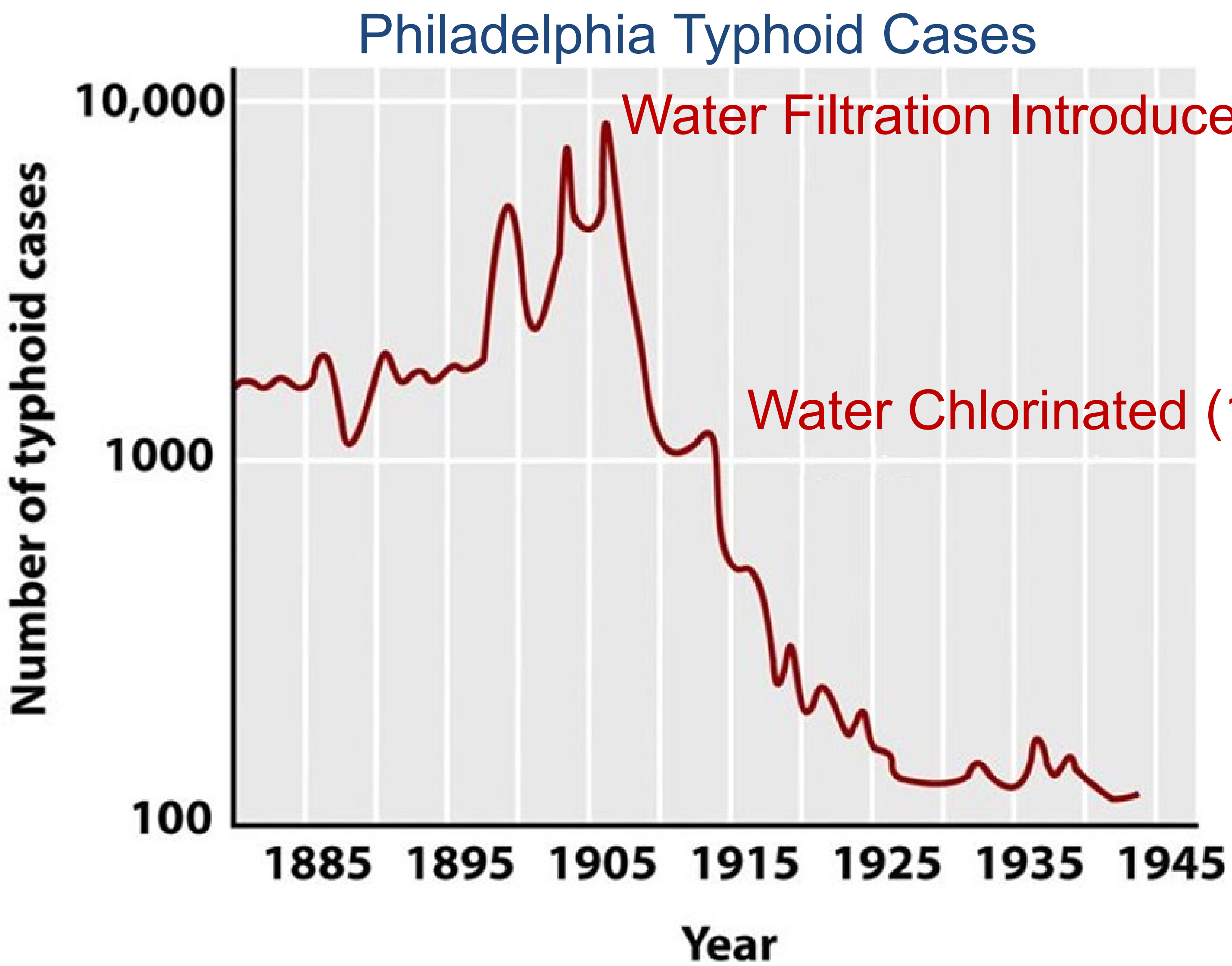
Bromide and Safe Drinking Water

PRESENTED BY
Amber Greune

4/24/2019

Geosyntec consultants

Disinfection for Safe Drinking Water



Source: https://slideplayer.com/slide/6893209/ The Encyclopedia of Greater Philadelphia

Disinfection Byproducts in Drinking Water

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$$

$$HOCl + DOM \longrightarrow DBPs$$

DOM = Dissolved Organic Matter

DBPs = Disinfection Byproducts (potentially harmful to human health)

THMs and HAAs = Trihalomethanes and Haloacetic Acids, subsets of DBPs

$$HOCl + DOM \longrightarrow THMs + HAAs + \ldots$$

Role of Bromide in THM and HAA Formation

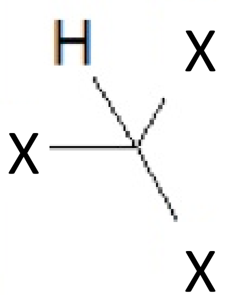
Hypochlorous and **hypobromous** acids formed during chlorination

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$$

$$HOCl + Br^- \longrightarrow HOBr + Cl^-$$

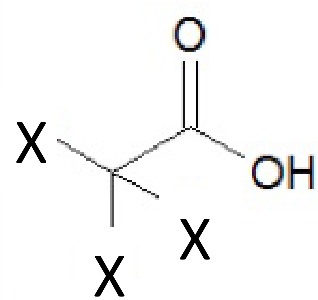
$$DOM + HOCl/HOBr \longrightarrow THMs + HAAs$$

Trihalomethanes (THM)



Chloroform
Bromodichloromethane
Dibromochloromethane
Bromoform

Haloacetic acids (HAA)



Chloroacetic acid
Bromoacetic acid
Dichloroacetic acid
Bromochloroacetic acid
Dibromoacetic acid
Trichloroacetic acid
Bromodichloroacetic acid
Chlorodibromoacetic acid
Tribromoacetic acid

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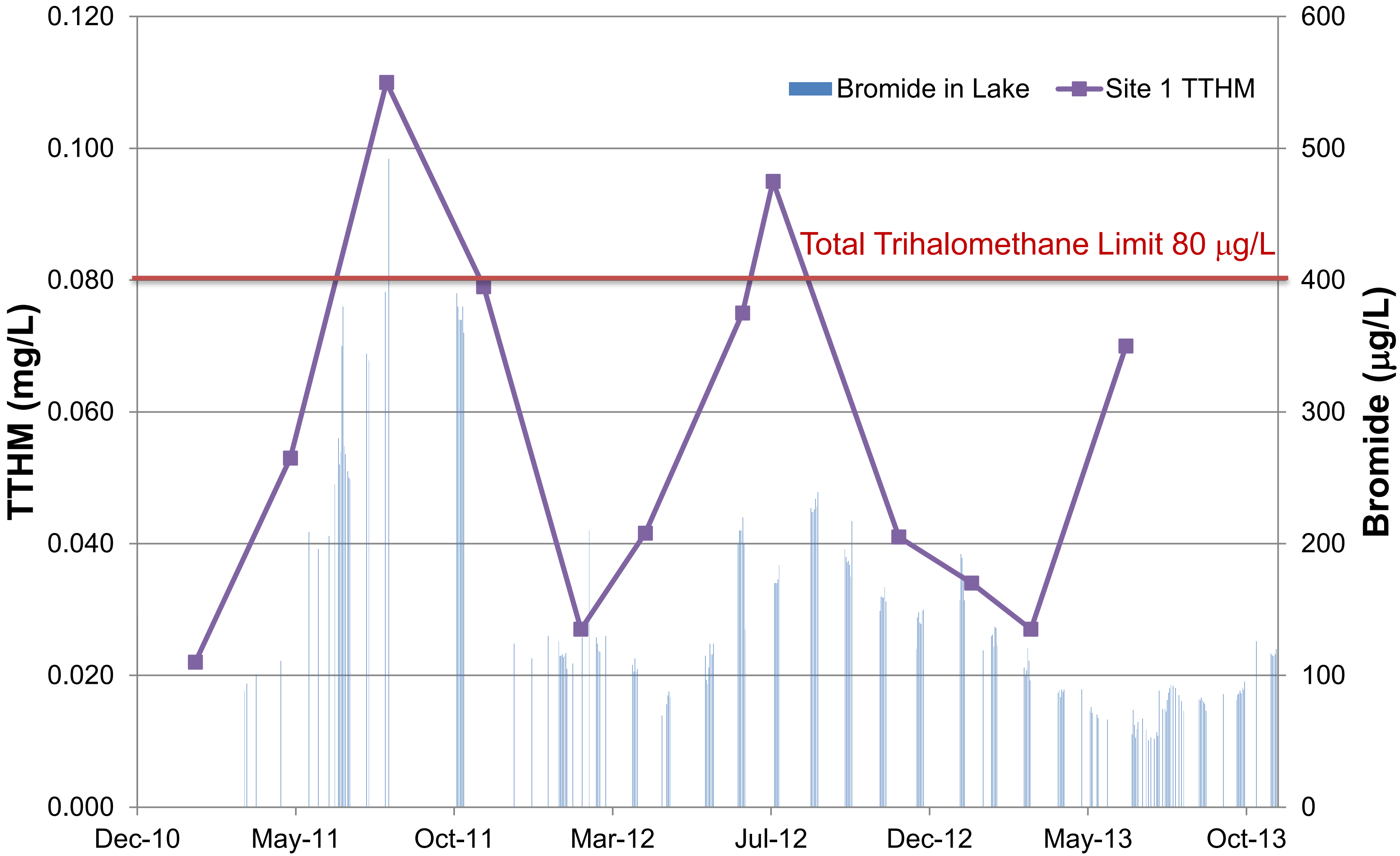
Role of Bromide in THM Formation



Bromide Sources

Oceans
Largest Natural Source
~65 mg/L bromide

Inland Freshwater
~0.05 mg/L bromide

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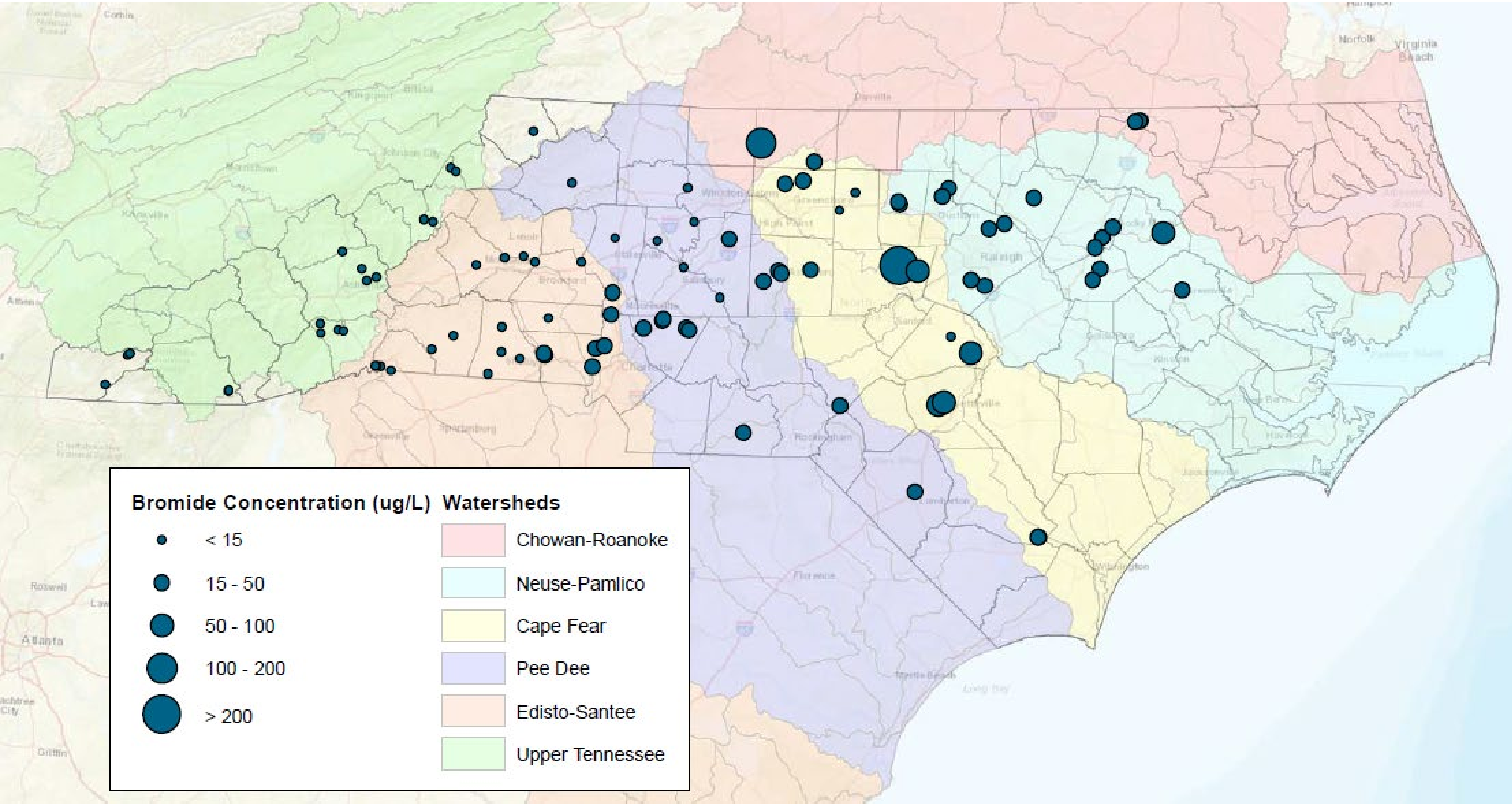
Bromide Sources



Bromine Uses

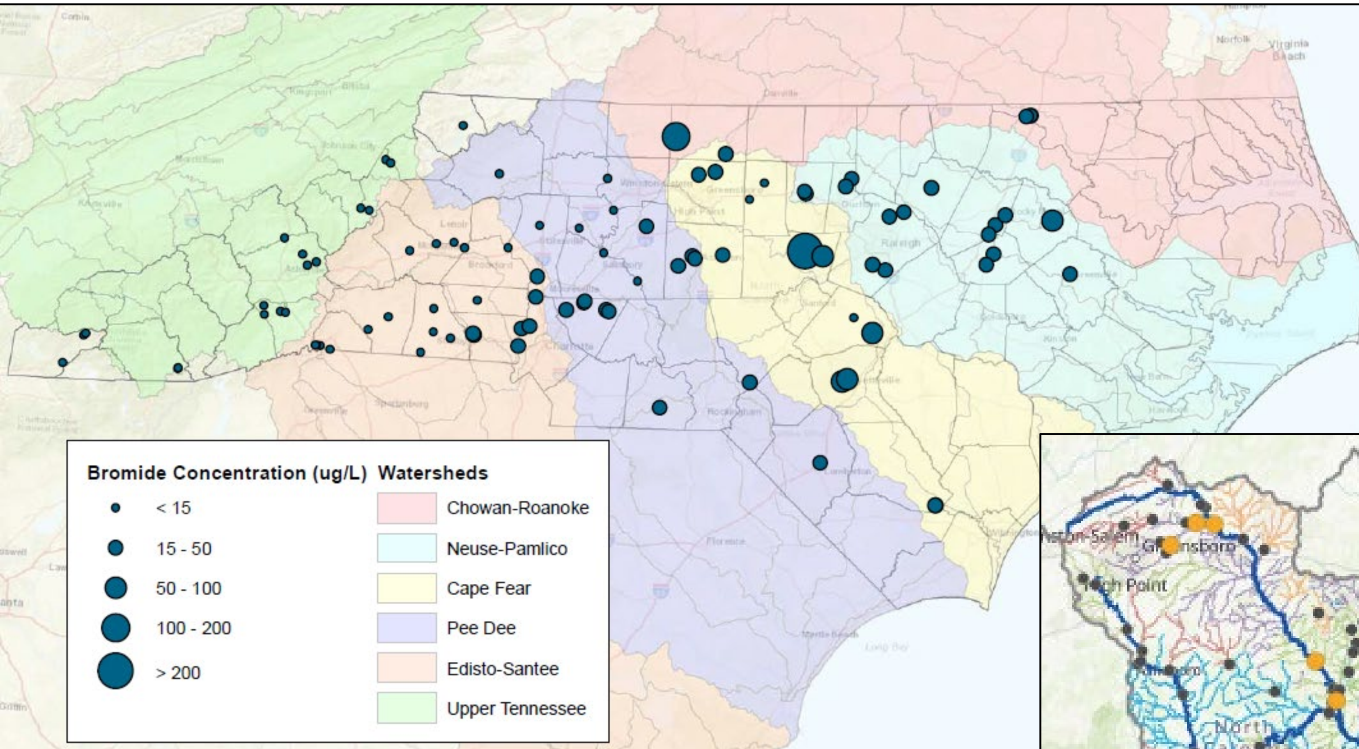
Historical

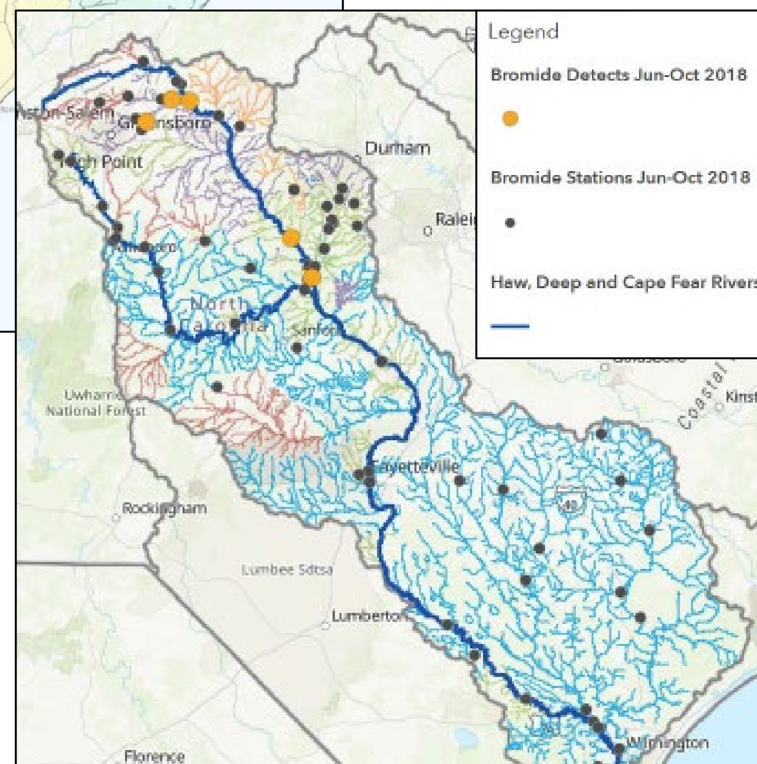
- Ethylene dibromide

Current

- Coal-fired power plants
- Shale gas extraction
- Oil drilling
- Flame retardants
- Water disinfection
- Food industry
- Tire rubber
- Batteries
- Photography
- Medicine
- Cosmetics

NC Bromide Sources





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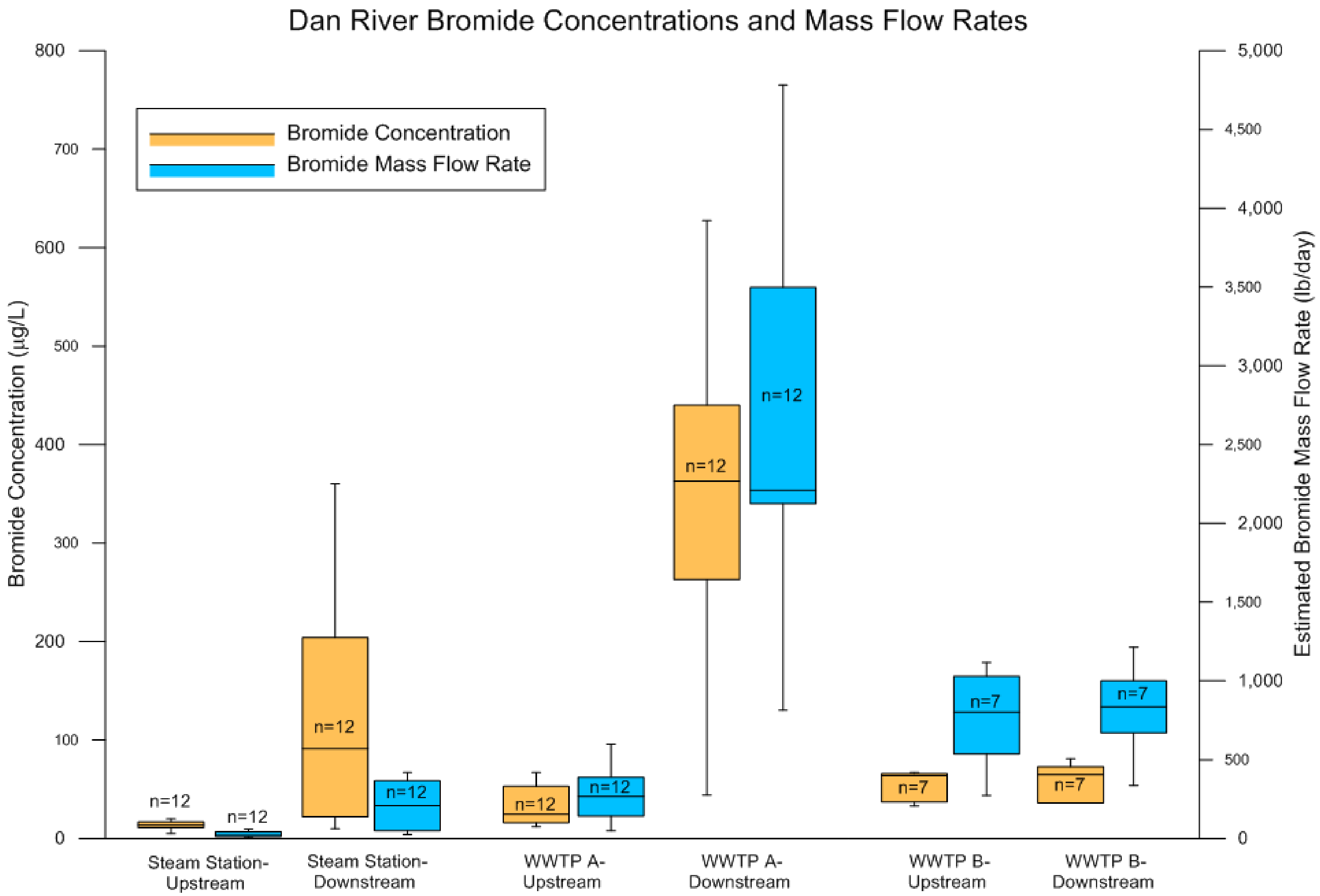
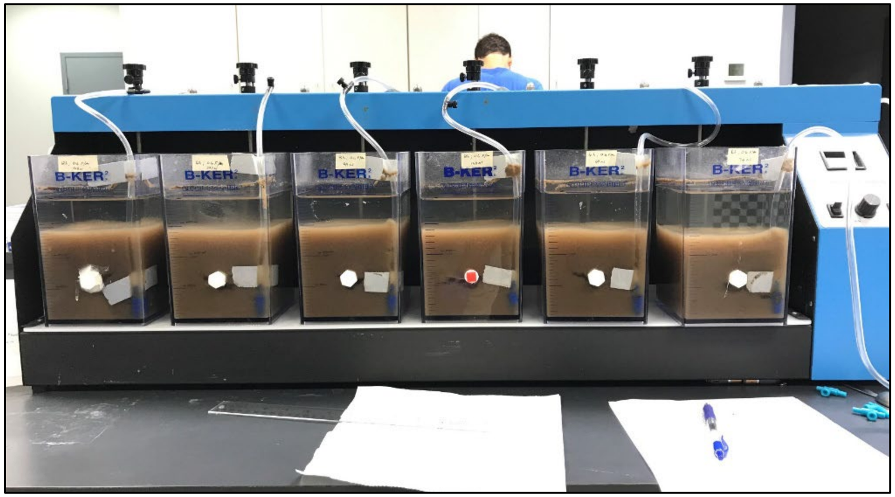
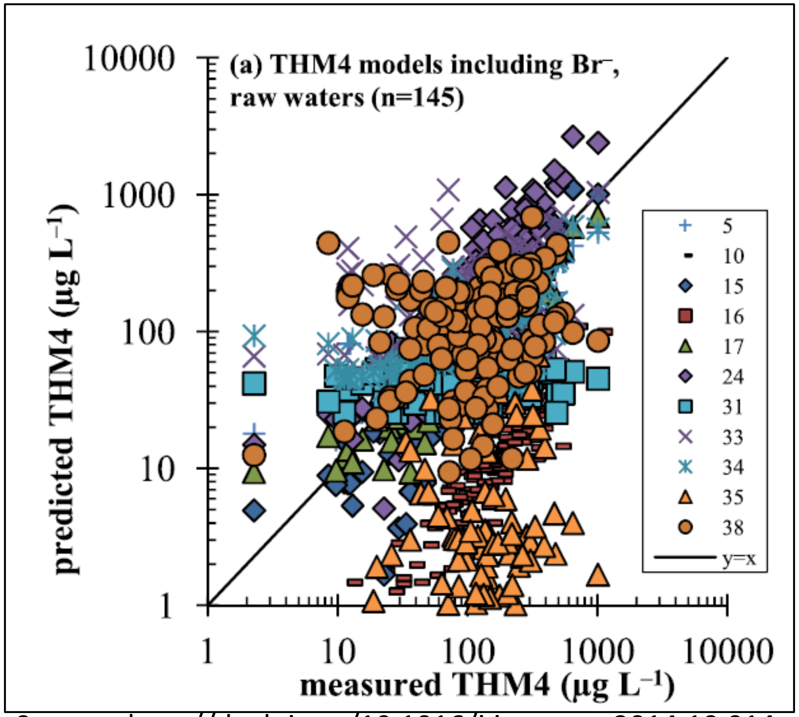
NC Bromide Sources



Challenges

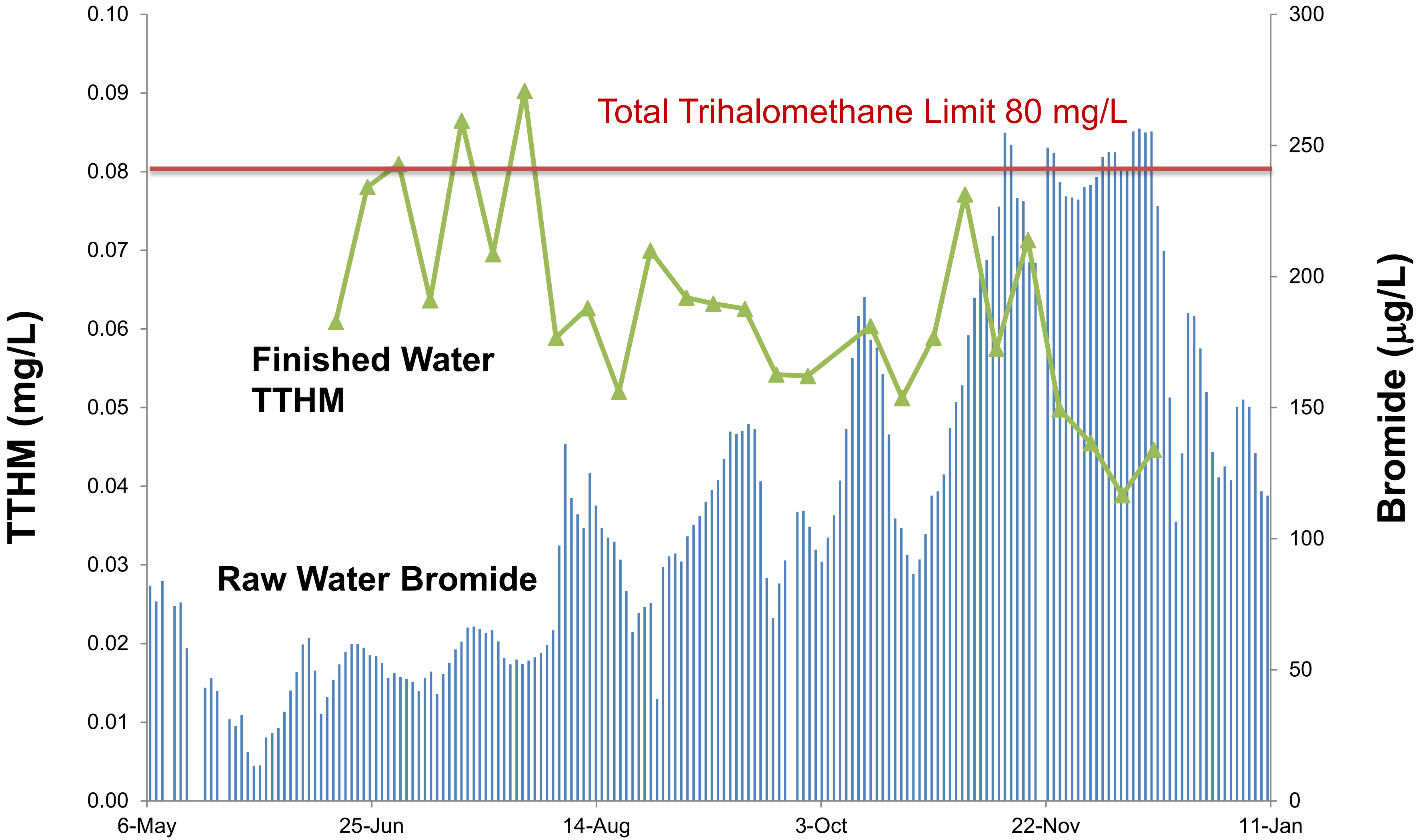
- It's hard to remove bromide from water
- There is not always clear relationships between raw water bromide concentration and disinfectant byproduct formation
- Bromide discharges to surface waters are not regulated



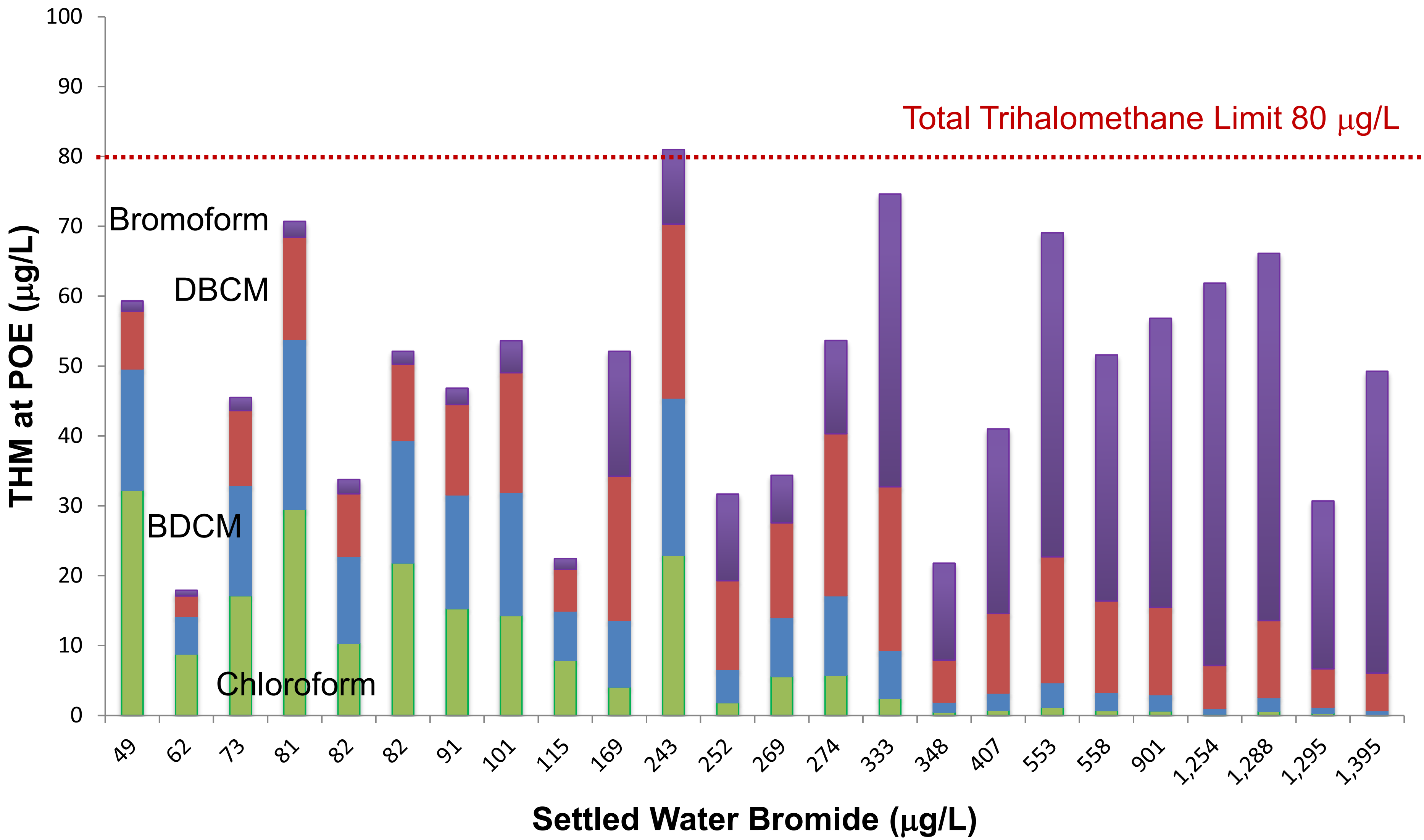


Source: http://dx.doi.org/10.1016/j.jenvman.2014.10.014

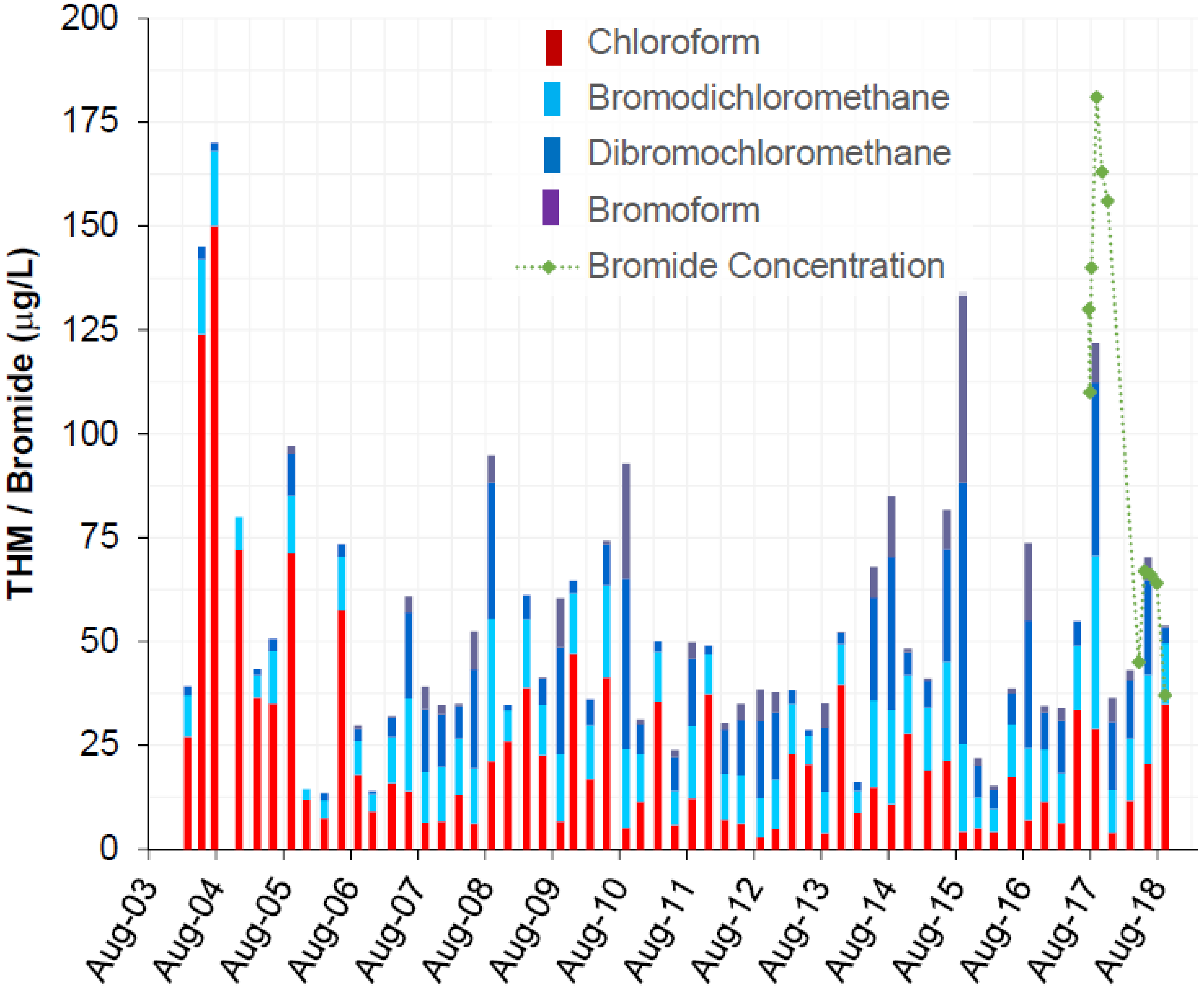
Many Factors Influence DBP Formation



THM Speciation



Lack of Data


Chloroform
Bromodichloromethane
Dibromochloromethane
Bromoform
Bromide Concentration
THM / Bromide (µg/L)
200
175
150
125
100
75
50
25
0
Aug-03
Aug-04
Aug-05
Aug-06
Aug-07
Aug-08
Aug-09
Aug-10
Aug-11
Aug-12
Aug-13
Aug-14
Aug-15
Aug-16
Aug-17
Aug-18

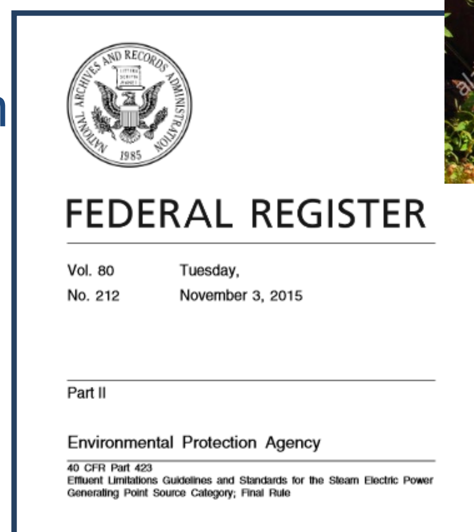
What Can We Do?

Drinking Water Treatment

- Optimize removal of dissolved organic material
- Shorten water residence time
- Alternative disinfectant options: chloramines, ozone, UV
- Coordinate with upstream industries

Industries

- Limit / eliminate bromide concentrations in discharges
- Coordinate with downstream drinking water plants



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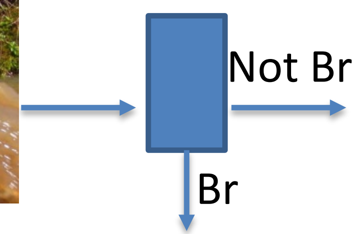
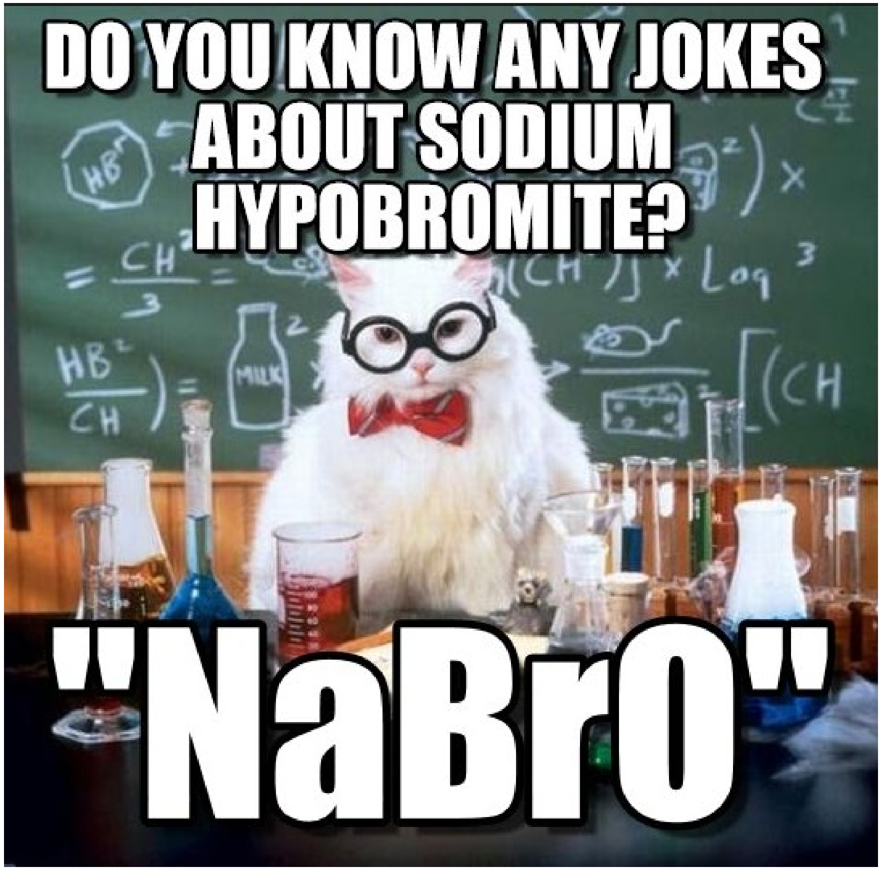
40 CFR Part 423
Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category; Final Rule



Amber Greune

agreune@geosyntec.com

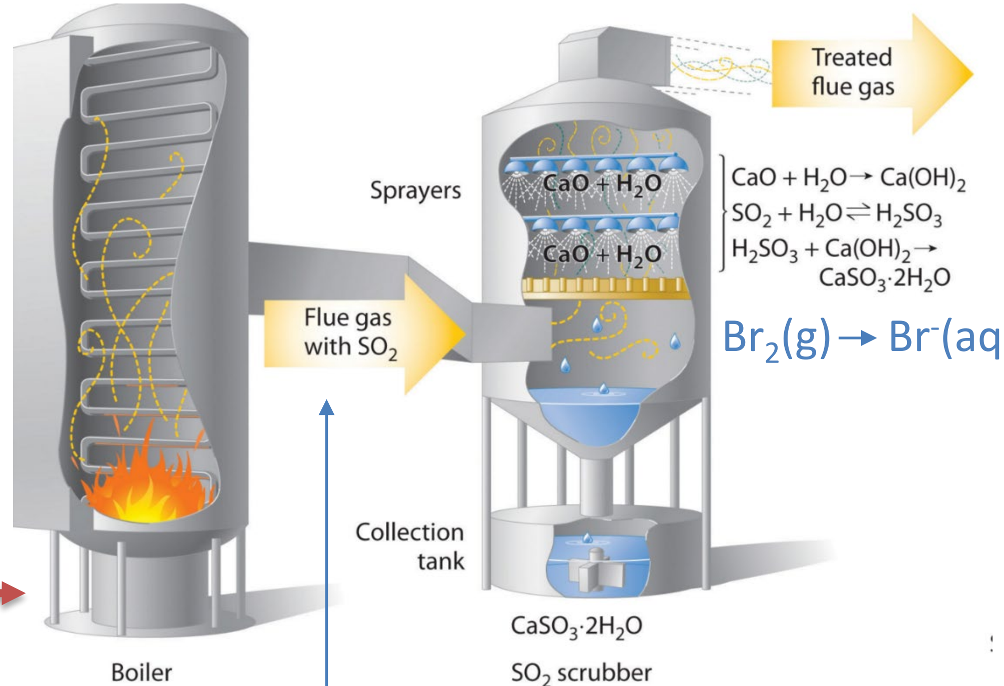
(919) 424.1832



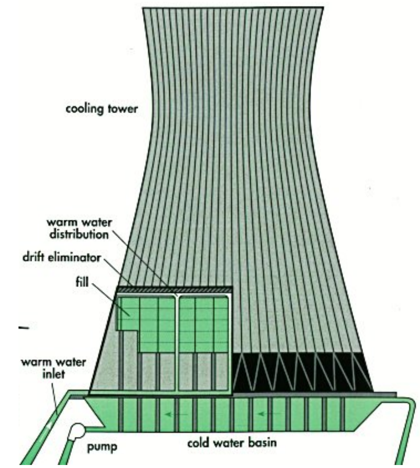
Reference Slides

Bromide Sources in Power Plants

Coal naturally contains 0.5 – 90 mg/kg Br (Vainikka et al 2012); equivalent to ~ 0.002% Br



$Br_2(g) \rightarrow Br^-(aq)$



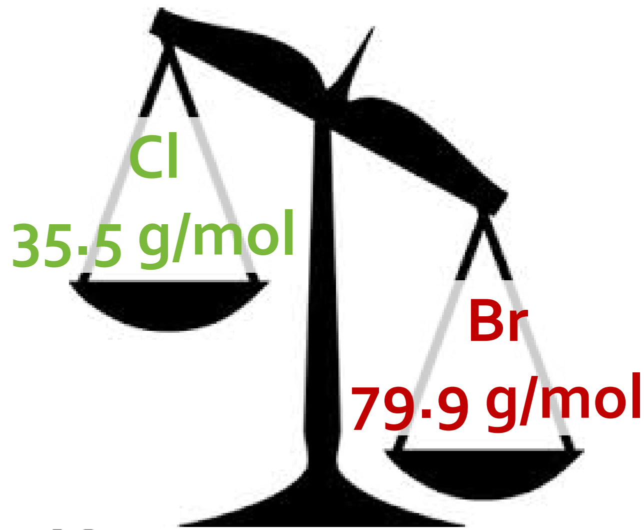
Bromide added as a biocide

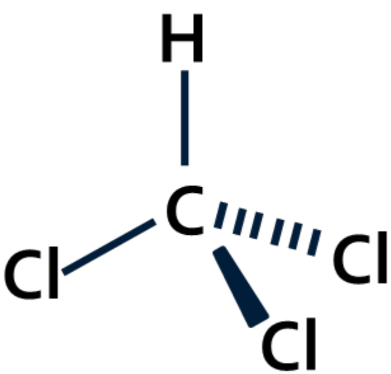
Bromide is added for enhanced Hg^0 capture ($CaBr_2$, Br-PACs, NaBr)

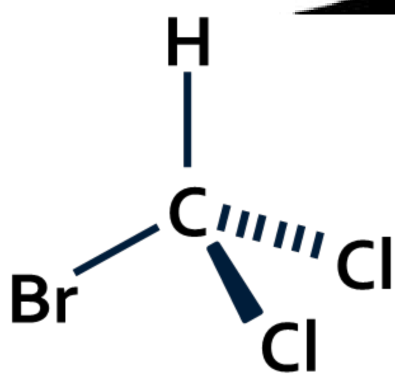
Roughly 100% of the bromide that was in the coal and added for Hg^0 capture ends up in the FGD wastewater

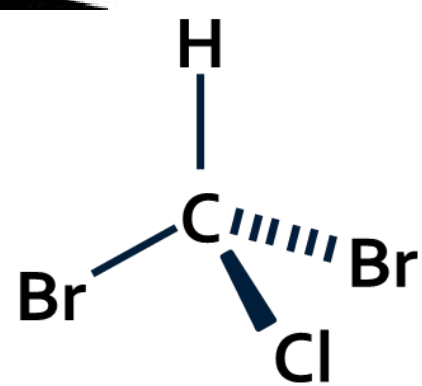
- [Br^-] ranged from 43-96 mg/L in FGD wastewater (EPA 2009)
- [Br^-] increased from 114 mg/L (baseline FDG supernatant effluent) to 575 mg/L ($CaBr_2$ addition trial) (Frank 2011)

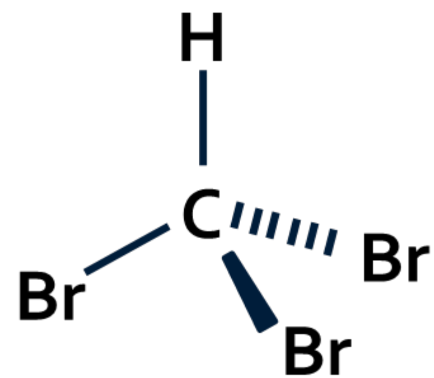
Why Pick on Bromide?




Chloroform


Bromodichloromethane


Dibromochloromethane


Bromoform

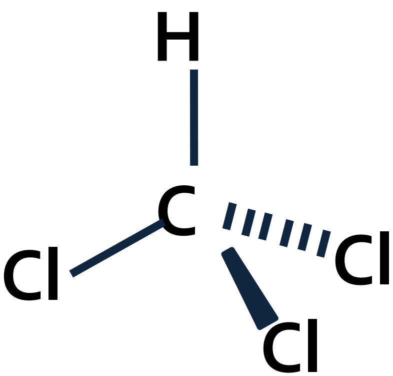
Regulatory Compliance

Total Trihalomethanes (TTHM) ≤ 80 µg/L

	Quarter 3, 2003 Raw Bromide = 50 µg/L			Quarter 3, 2012 Raw Bromide = 106 µg/L		
	µmol/L	µg/L	Weight Percent	µmol/L	µg/L	Weight Percent
Chloroform	0.44	53	68%	0.21	25	27%
Bromodichloromethane	0.11	18	23%	0.20	32	34%
Dibromochloromethane	0.03	7	9%	0.14	29	31%
Bromoform	0	0	0%	0.03	7	8%
TTHM	0.58	78	100%	0.57	93	100%

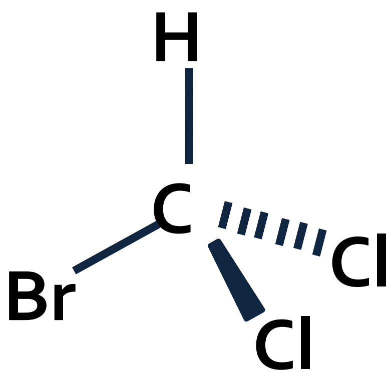
Human Health Risk

The one in a million excess cancer risk is associated with different concentrations of each of the THM species



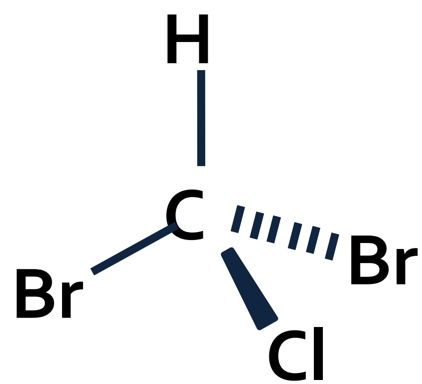
Chloroform

N/A



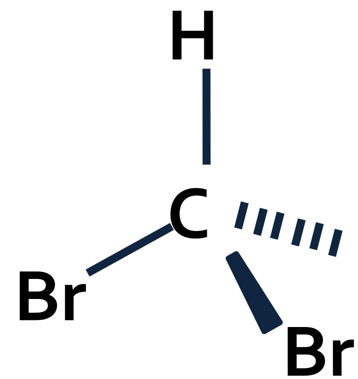
Bromodichloromethane

0.6 μg/L



Dibromochloromethane

0.4 μg/L

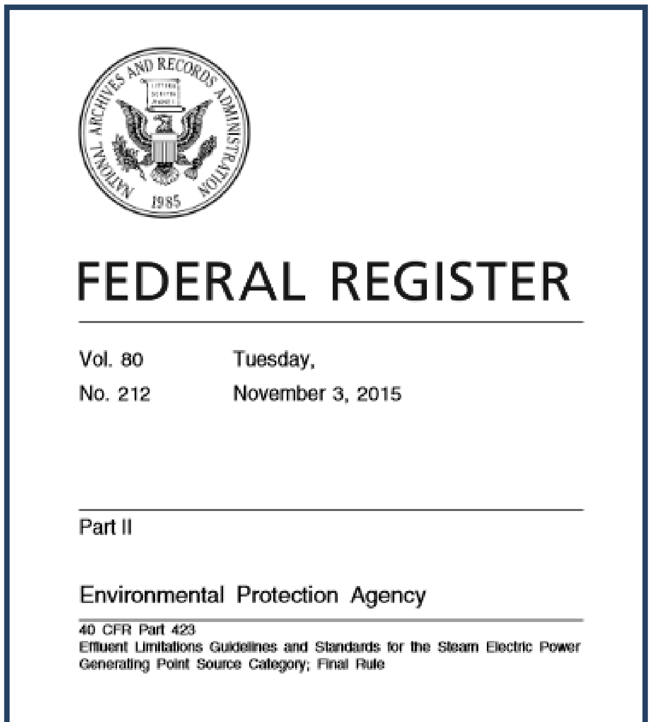


Bromoform

4.0 μg/L

Potential Regulations

Effluent Limitation Guidelines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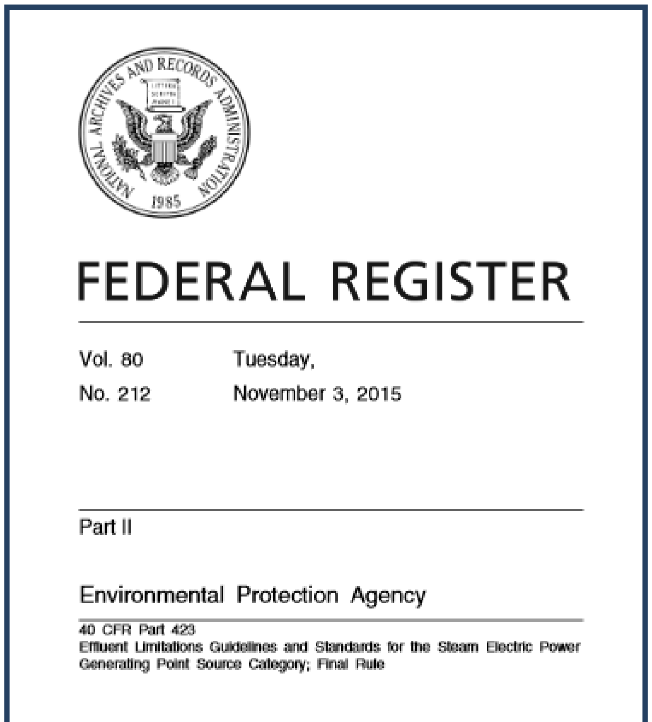
Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category; Final Rule

*"A … recent study found increased levels of **bromide** in rivers used as drinking water after **FGD systems** were installed at upstream steam electric power plants.*

*With **bromides present** in their drinking water source waters at increased levels, **carcinogenic disinfection by-products** (brominated DBPs, in particular trihalomethanes (**THMs**)) began forming, and at one drinking water utility, violations of the THM MCL began occurring."*

Potential Regulations

Effluent Limitation Guidelines



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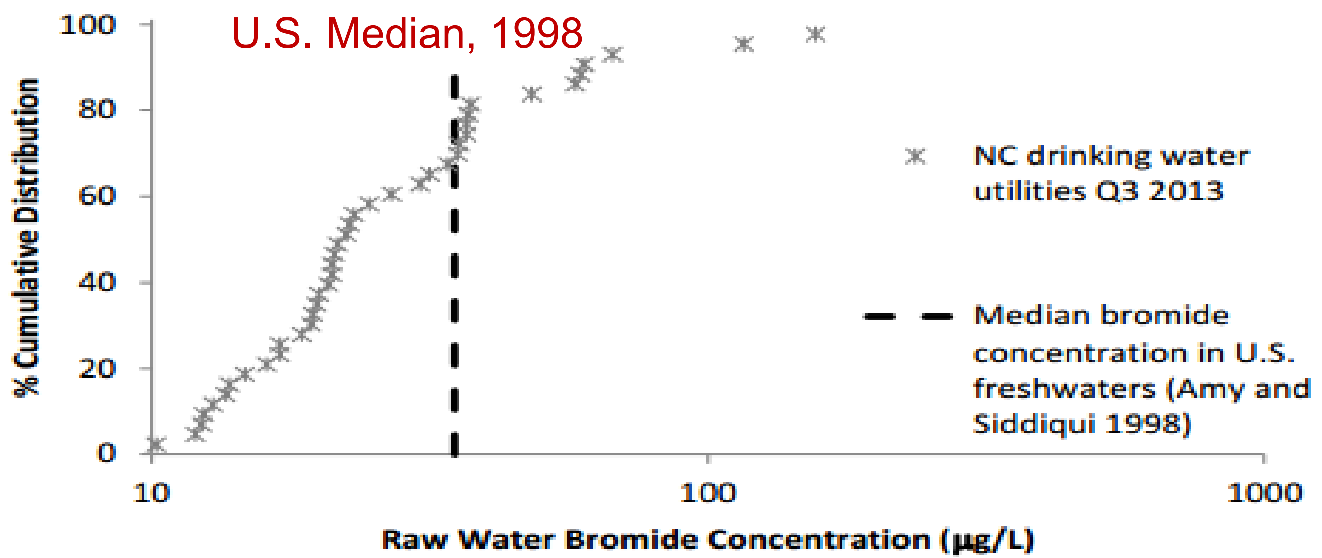
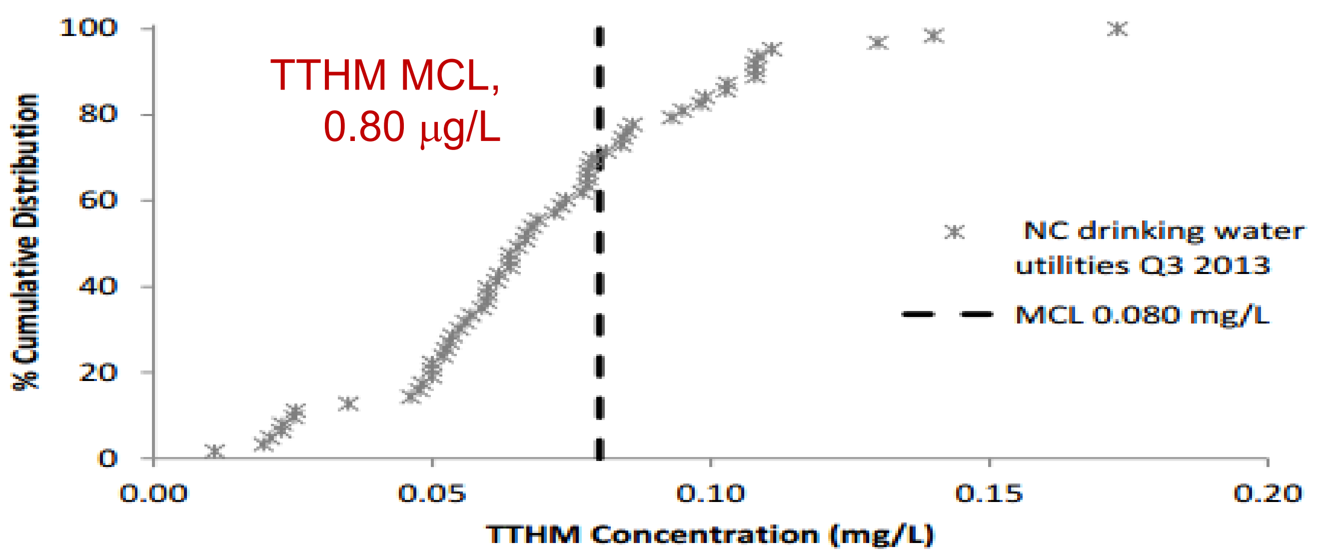
*"Depending on site-specific conditions and applicable state water quality standards, it may be appropriate for permitting authorities to establish **water quality-based effluent limitations on bromide**, especially where steam electric power plants are located upstream from drinking water intakes.*

Bromide and Safe Drinking Water



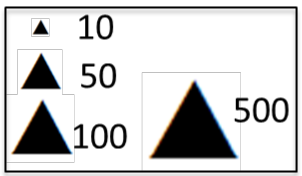
NC raw water intakes, Q3 2013

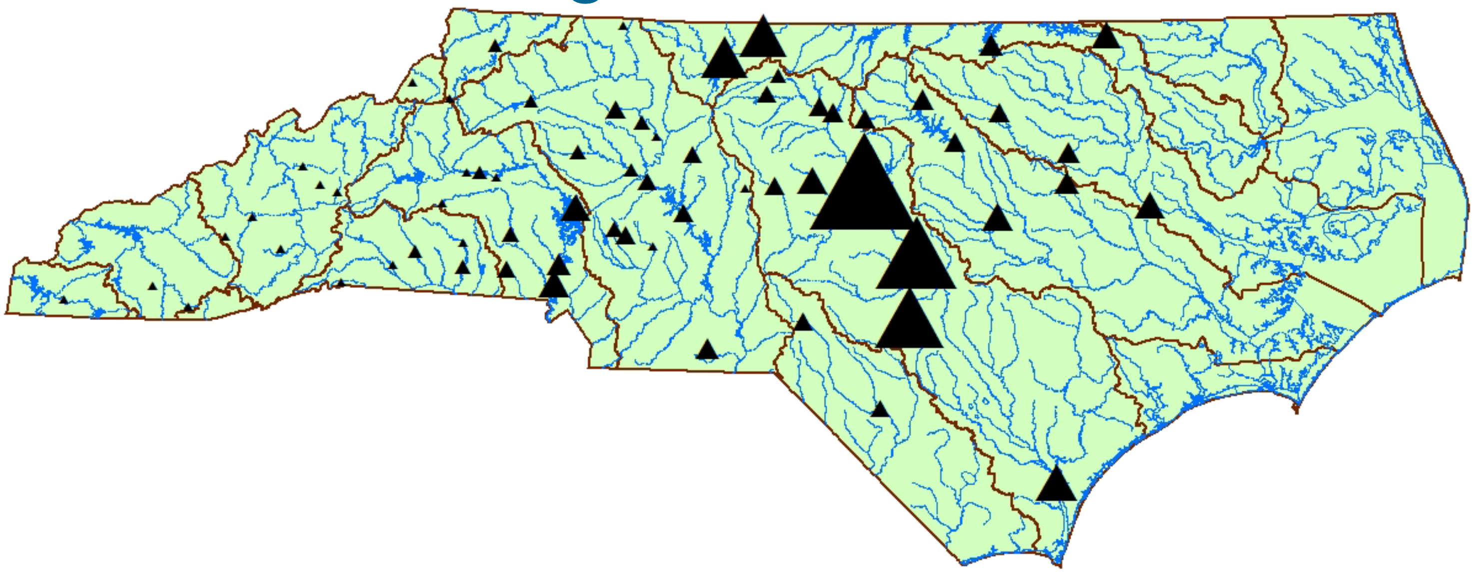


NC drinking water distribution system, Q3 2013

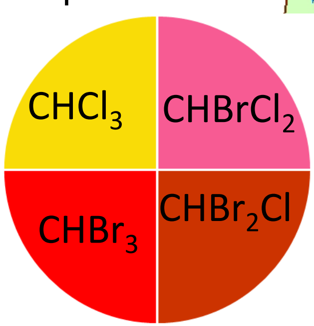
Bromide and Safe Drinking Water

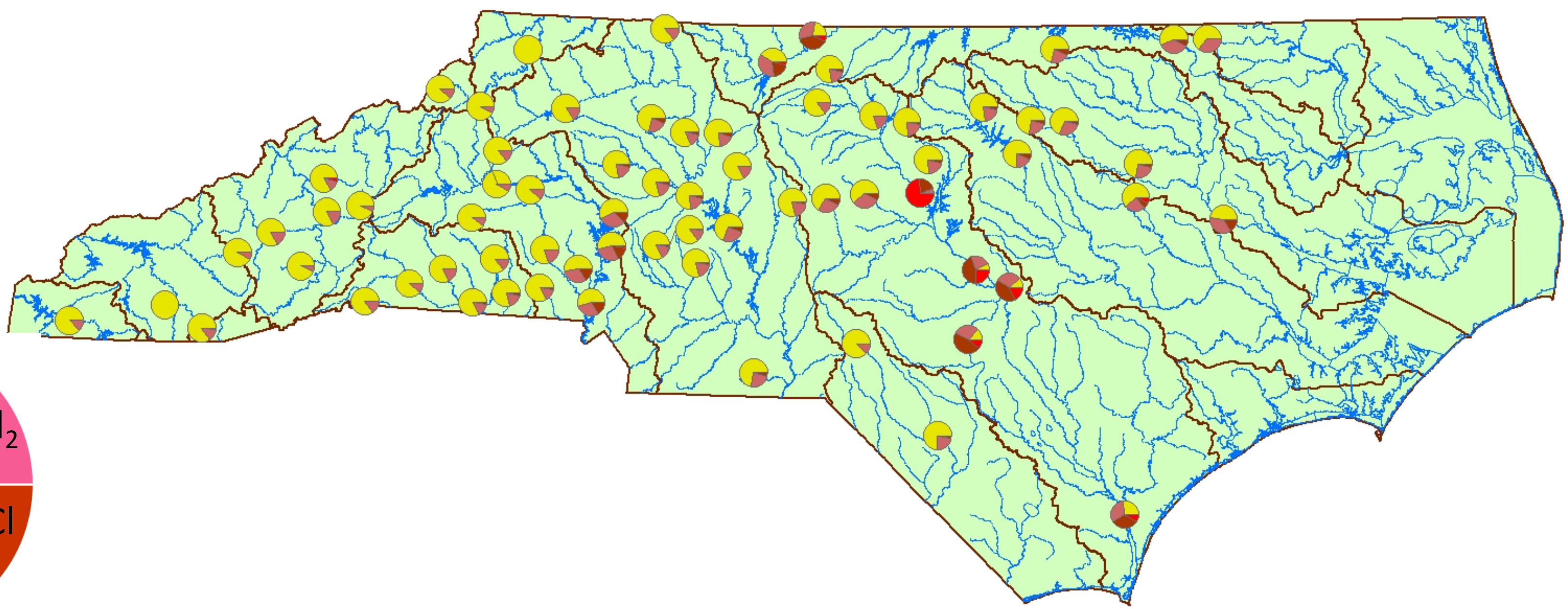
Raw Water Bromide Concentration (μg/L)





THM Speciation





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Geosyntec's Perspectives on the Optimal Management of Emerging Contaminants

PFAS and Other Emerging Contaminants Conference

Peter J. de Haven, P.E. (GA, NC)
Raleigh, NC
04/24/2019

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Emerging Contaminants: Definition

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General Definition

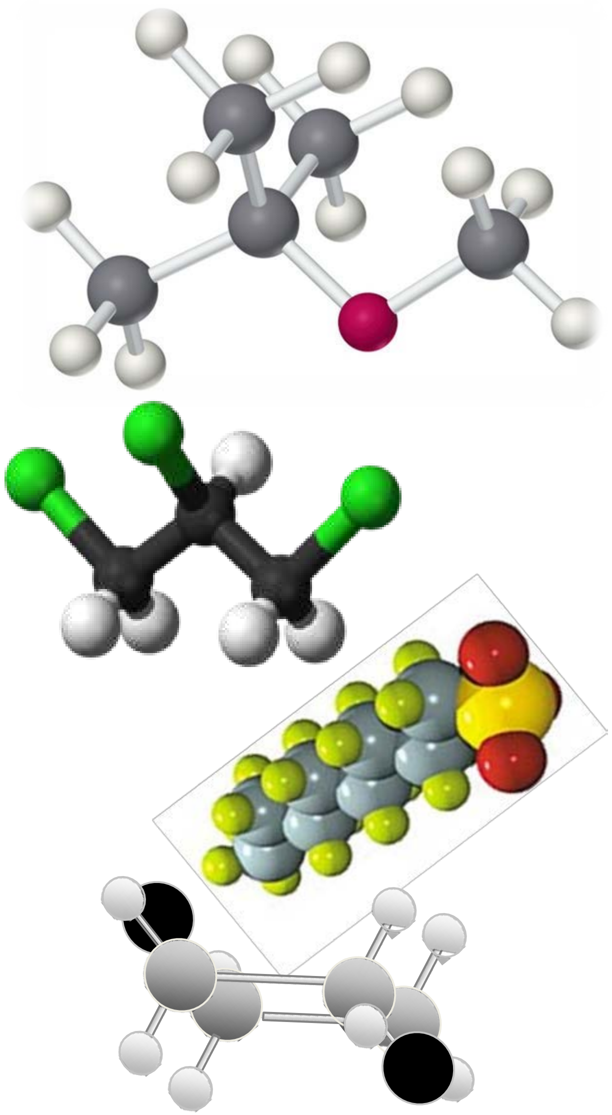
- Characterized by a real or perceived threat to human or ecological health
- Lack of published health standards
- Not regulated at the U.S. federal level

"… previously unknown, unrecognized, unanticipated, unsuspected, or unregulated chemical pollutants"

Christian Daughton, USEPA

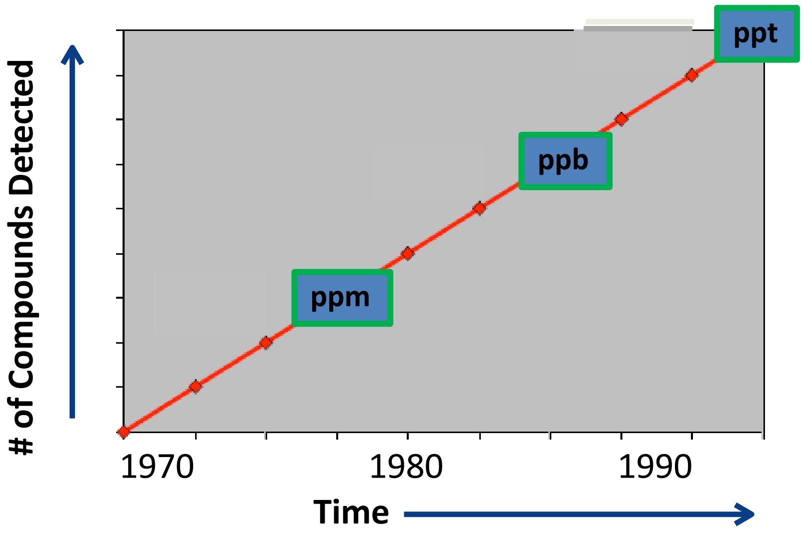
Emerging Contaminants: Examples

Compound Class	Example Compounds
Industrial additives	1,4-dioxane, 1,2,3-TCP
Gasoline additives	MTBE, TBA
Other industrial chemicals	PFASs, PBDEs
Pharmaceuticals	Antibiotics and other drugs
Personal care products	Polycyclic musks
Volatile organics	1,1-DCA
Disinfection byproducts	NDMA
Inorganics/explosives	Perchlorate, RDX
Pesticides/herbicides	Diazinon
Surfactants/residues	Triclosan, alkylphenol polyethoxylates



ECs: How They "Emerge"

- Many contaminants are emerging just now despite 20 to 50 years of manufacturing and use
- Newly detectable using improved analytical methods
- Availability of new data (e.g., effects on endocrine system or other endpoints not previously evaluated)
- Receiving public attention, media coverage



You won't find what you don't look for!

Overview of Challenges
Technical

- Scientific data gaps leading to technical uncertainties
- Analytical/risk challenges
  - High risk → Low target levels (ppb or ppt)
  - Quality assurance issues (false positives)
  - Need for new/improved analytical methods
- Management challenges
  - May be highly soluble, migrate easily in groundwater
  - Low volatility, difficult to air-strip
  - Low affinity for granular activated carbon
  - Difficult to chemically oxidize
  - Resistant to biodegradation

Overview of Challenges
Legal

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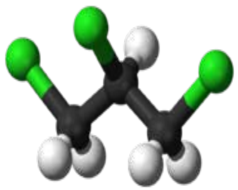
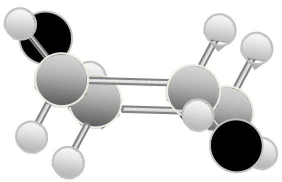
- Uncertain liability when water quality meets current standards but trace levels of emerging contaminants are present
  - Is the water “safe”?
- Defining standard of care for controlling contaminants
- Impact on engineering community
  - Who should have known what, when?
  - Environmental Due Diligence implications
- Proliferation of product liability, damage claims and toxic tort cases

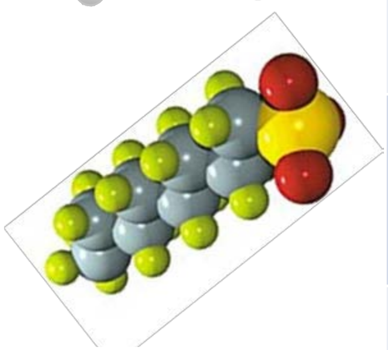
Overview of Challenges
Regulatory

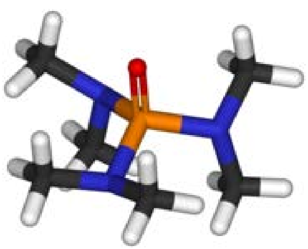
- No uniform U.S. product stewardship program for new chemicals
  - E.g. Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH in EU)
  - ~60,000 unregulated compounds worldwide
  - 558 in USEPA's IRIS database
- Slow pace of regulatory determinations
  - May require scientific study to fill data gaps
- Often non-scientific drivers for regulation (media coverage, litigation)

Emerging Contaminants Overview









Parameter	Challenges	Lessons Learned/ Successes
1,2,3-TCP	Solvent, Fumigant Non-Pt. Sources, Trace Toxin Recalc. to Bio/Reduction	Zero-Valent Zinc (Successfully Piloted 2014)
1,4-Dioxane	Toxic, Mobile, Persistent Leading Plumes Costly Treatment	TreeWell Technology Development of In Situ Aerobic Culture
PFAS	Toxic, Mobile, Persistent (Variably) 1000's of Molecules, Costly Treatment	Field Real-Time Inst. Thermal Persulfate Smoldering Techn.'s
Hexamethyl-phosphor-amide	Toxic, Mobile, Persistent Leading Plumes Limited Treatment Options	Conceptual Site Model Refinements (Source Depletion, Eco/HH Risk Priorities)

Overall Lessons Learned (1)

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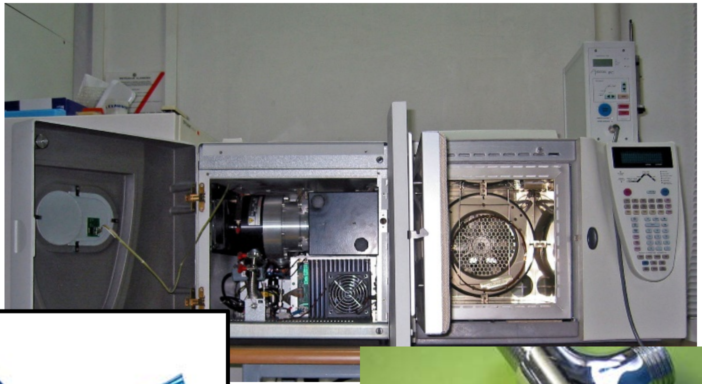
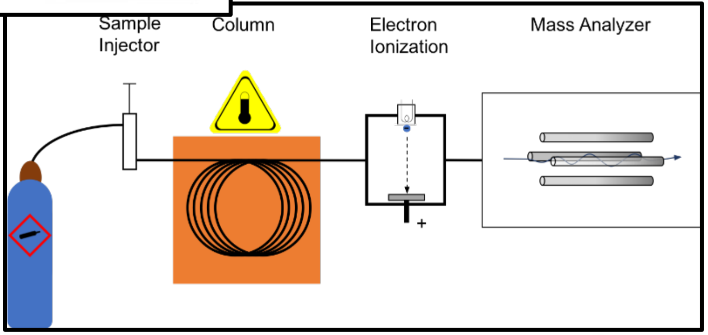
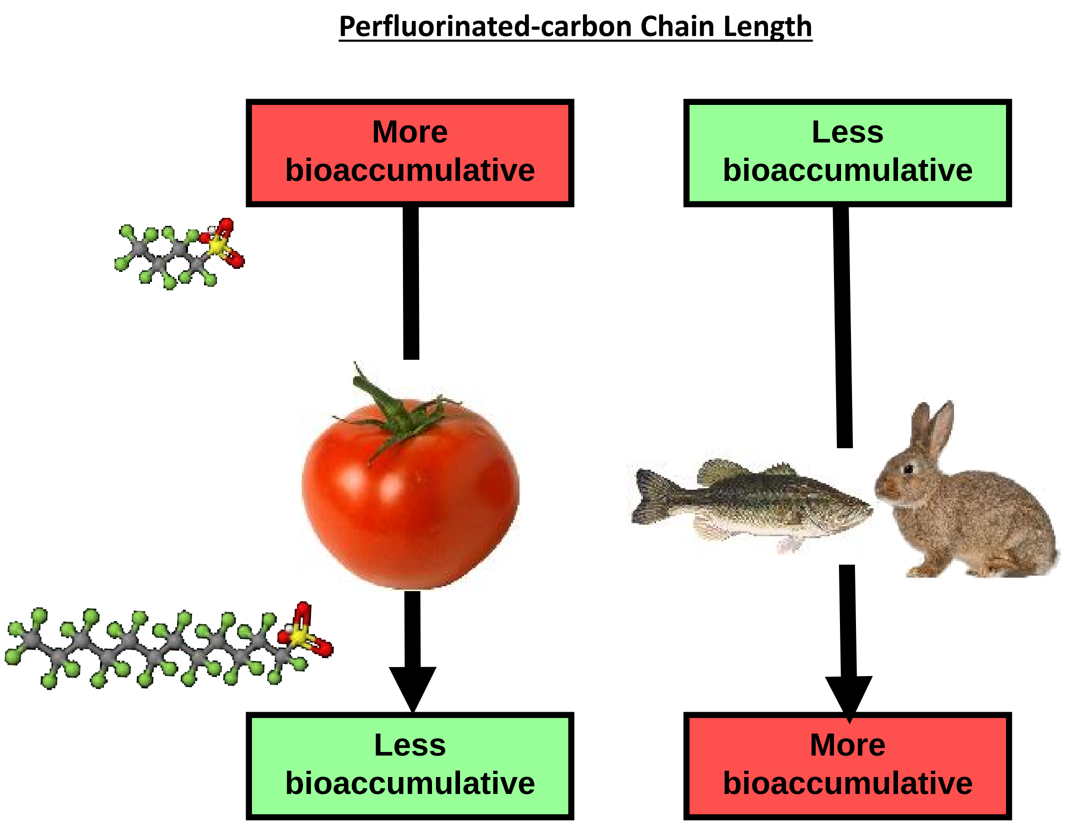
- Characterize properly
  - Appropriate analytical methods
  - Data validation, laboratory audits
  - Appropriate field methods (false positives/negatives)
- Don’t cut corners!





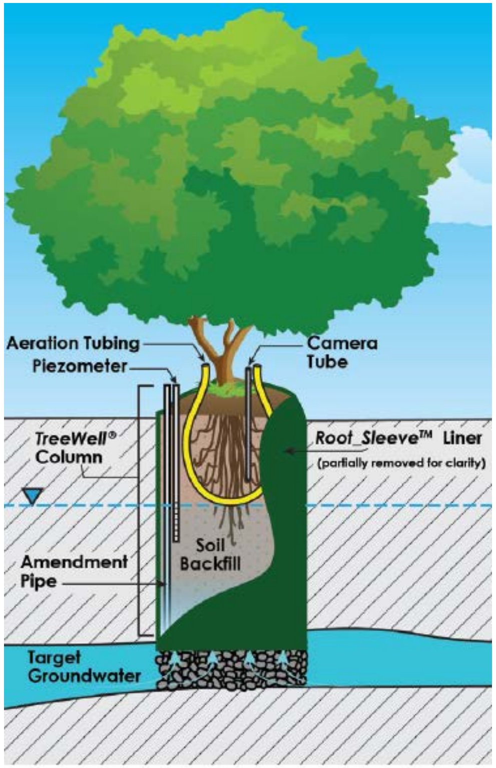
Overall Lessons Learned (2)

- Know your Conceptual Site Model:
  - Physical/chemical properties
  - Key biouptake mechanisms
  - ➔Key risk endpoint



Overall Lessons Learned (3)

- Consider new management strategies
  - Existing remedial technologies may not handle a new EC
  - Entirely different approach may bear fruit:
    - Pump+treat to TreeWells
    - Ex situ to in situ and back again



The *TreeWell*® System

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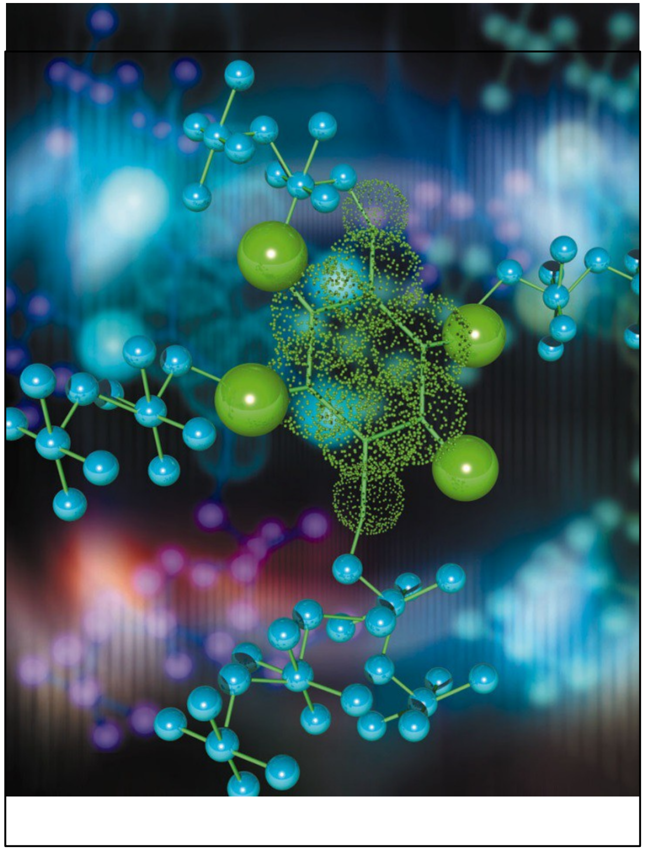

Questions?

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Greensboro's Response to PFAS

Wednesday April 24, 2019

Michael Borchers, PE
Water Resources Department

GREENSBORO

Agenda

- Per- and Polyfluoroalkyl Substances (PFAS)
- Detection of PFAS
  - Investigation
  - Sampling / Results
- Risk Communications
  - Notifications / Communications
- Proactive Measures
  - PAC Feed System and GAC
  - GCHD Well Testing
- Next Steps

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PFAS Development and Use

- Per- and Polyfluoroalkyl Substances (PFAS)
  - Large group of man-made chemicals used in industry and consumer products worldwide since 1950’s
  - “Aqueous Film Forming Foam” (AFFF) was developed in 1960’s by 3M for U.S. Navy
  - Carpets, clothing, furniture fabrics, paper packaging for food, dental floss, cleaning products and cookware resistant to water, grease or stains

PFAS In the News

EPA releases PFAS action plan

The U.S. Environmental Protection Agency (EPA) issued its much-anticipated action plan for per- and polyfluoroalkyl substances (PFAS) on Feb. 14, pledging to make a regulatory determination on whether to issue a maximum contaminant level (MCL) by the end of the year, but stopping short on promising to issue an MCL.

New Hanover County collaborates with DEQ to sample landfill leachate

POSTED JANUARY 30, 2019 AT 10:14 AM CATEGORY: ENVIRONMENTAL MANAGEMENT • HEALTH • NEWS RELEASE

NEW HANOVER COUNTY, NC - New Hanover County has proactively volunteered to be the first landfill to participate in North Carolina Department of Environmental Quality's (NCDEQ) new landfill leachate sampling protocol.

Landfill leachate is formed when rainwater infiltrates and percolates through waste. At New Hanover County's landfill, this leachate is treated through a reverse osmosis (RO) system and the treated wastewater is then discharged into the Northeast Cape Fear River, downstream of Cape Fear Public Utility Authority's water intake facility.

Vermont PFAS testing, treatment bill advances

VTDigger

The Vermont Senate unanimously passed a bill last week that would set drinking water standards for five PFAS contaminants and require testing of public water supplies by the end of this year. The legislation would require managers of public water supplies to test to ensure levels of five PFAS contaminants — PFOA, PFOS, PFHxS, PFHpA and PFNA — are below a combined 20 parts per trillion, which is the state's health advisory.

PFAS prime time

New Jersey DEP leads nation, orders firms to clean up

North Jersey Record

NJ Spotlight

New Jersey stepped up its nation-leading efforts to curb toxic PFAS chemicals Monday by ordering five industrial companies to pay for the investigation and cleanup of contaminated sites, and hand over details on their manufacture, use and discharge of the chemicals.

UPDATED: FEBRUARY 15, 2019 | 4:43 PM

Pa. to begin its own process of setting health limit for two PFAS chemicals

As EPA launches national PFAS plan, Pennsylvania says its people 'can't wait' for federal government

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PFAS Detection and Response

PFOS / PFOA

- Detected in 2014 as part of UCMR 3 study
  - Three out of four quarterly samples above the reporting detection limit of 40 ng/l or ppt
  - Testing revealed 10 distribution samples with PFOS concentration > 40 ng/L
- Council approved investigation – December 2015
  - Field investigation started mid 2016
  - Subsequent testing in watershed revealed PFOS concentration's > 10,000 ng/L
  - Primary Source - Area surrounding and including PTIA

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Watershed Investigation Team

HDR Engineers, Inc.

- Background Data Analysis and Source Assessment
- Field investigation and Sampling Plan
- Treatability Analysis - Bench and Pilot Testing
- Stakeholder Coordination / Engagement

NC State University

- Laboratory Analysis

Water Supply and Stormwater Divisions

- Field investigation and Sampling
- Stakeholder Engagement
- Interim Treatment

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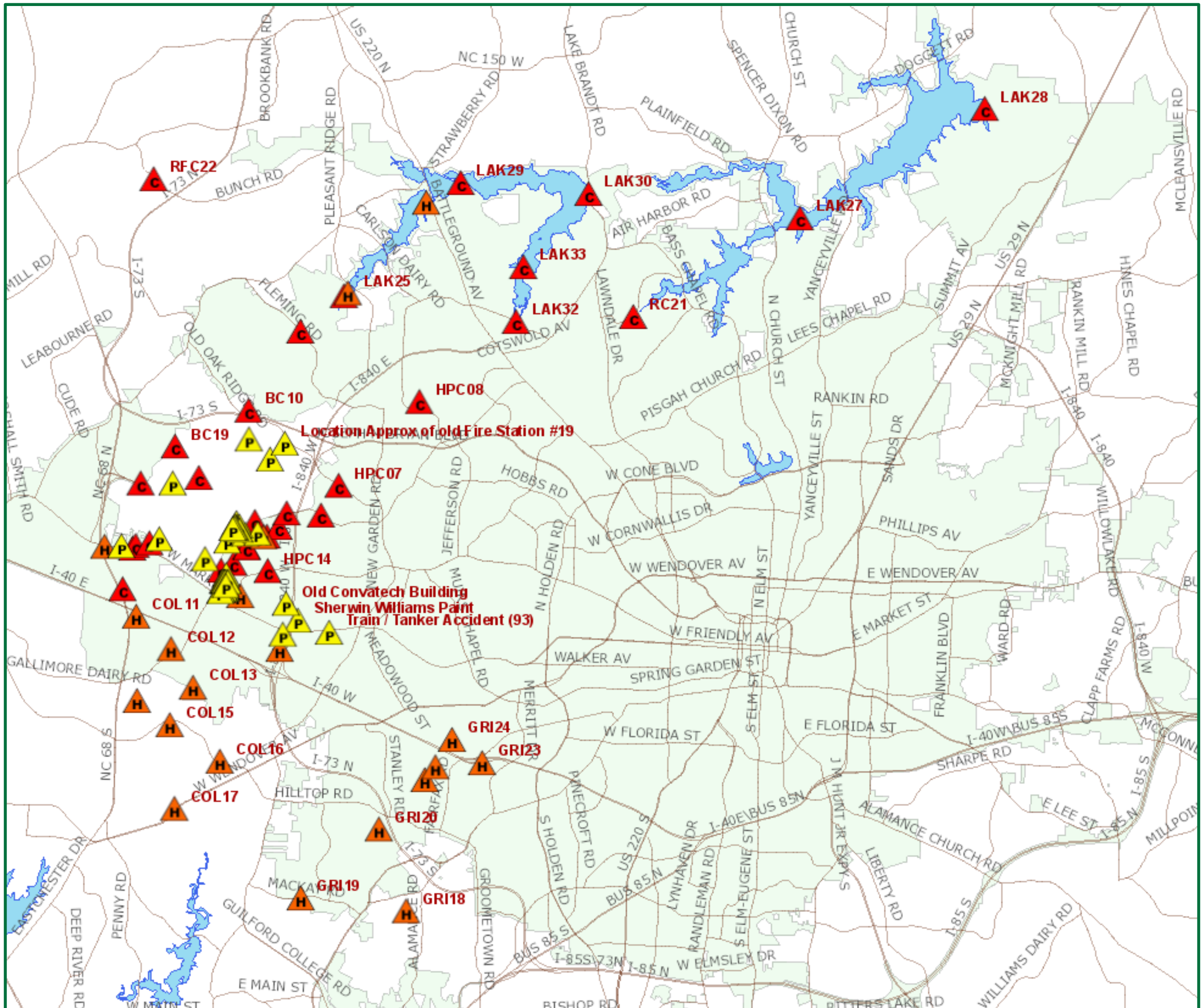
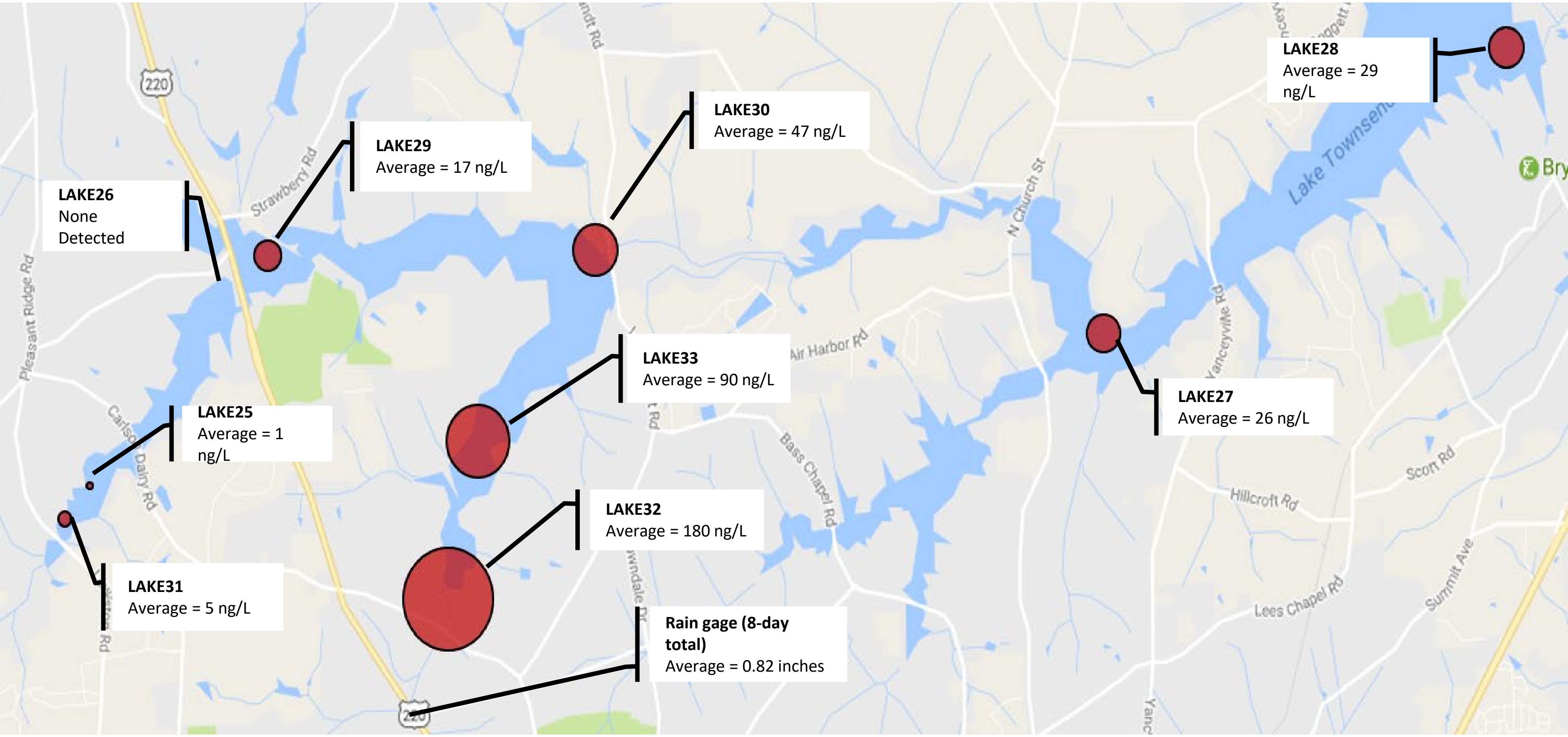
Sampling Sites



GREENSBORO

Lake Results – Total PFOS Results



- Bubbles drawn to scale using the average from all PFAS data
  - Highest concentrations in LAKE32 and LAKE33 (Lake Brandt)
  - Lowest concentrations in LAKE25 and LAKE26 (Lake Higgins)

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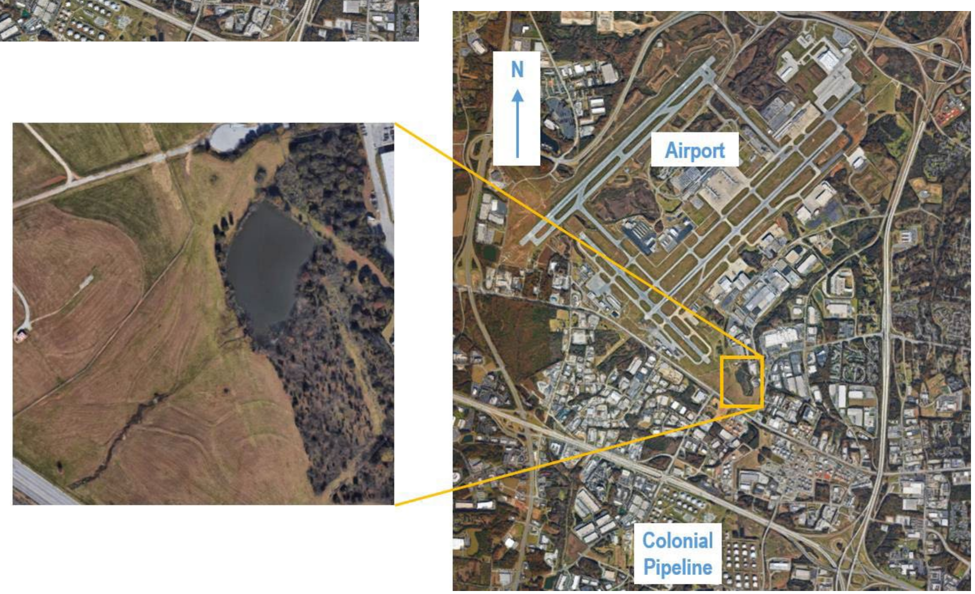
Groundwater Sampling Sites

US Airways (HAECO) Groundwater Wells

- 11 wells sampled with highest PFOS 994 ng/l



FINA Groundwater Wells

- 13 wells sampled with highest PFAS 1,588 ng/l

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Notifications and Communications

Public Notification – HAL Exceedance

- July combined PFOS and PFOA sample results for Mitchell WTP POE - 80 ppt
  - First exceedance of an HAL since monitoring began in 2014
- State PWS contacted
  - Encouraged public notification and transparency
- Press Release and Memo to CMO / City Council
  - Background / History
  - Investigation
  - Stakeholder Engagement
  - Immediate and Long Term Proactive Measures

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Proactive Measures

Proactive Response Measures

- Operational Response Protocol Developed
  - Utilization of Townsend WTP and interconnects to minimize / curtail flow from Mitchell WTP
  - Resampling and maintain external communications
  - Purchased temporary PAC feed system

- Increased Drinking Water Sampling
  - 2016 - Quarterly sampling (including interconnects)
  - May 2018 – Monthly sampling and posting results online - monthly water quality report
  - July 2018 – Weekly sampling and posting
    - https://www.greensboro-nc.gov/departments/water-resources/water-system/pfos-pfoa-updates/pfos-pfoa-sample-results

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Powdered Activated Carbon and Feeder

Powdered Activated Carbon

- Treatment very effective in removing PFOS and PFOA

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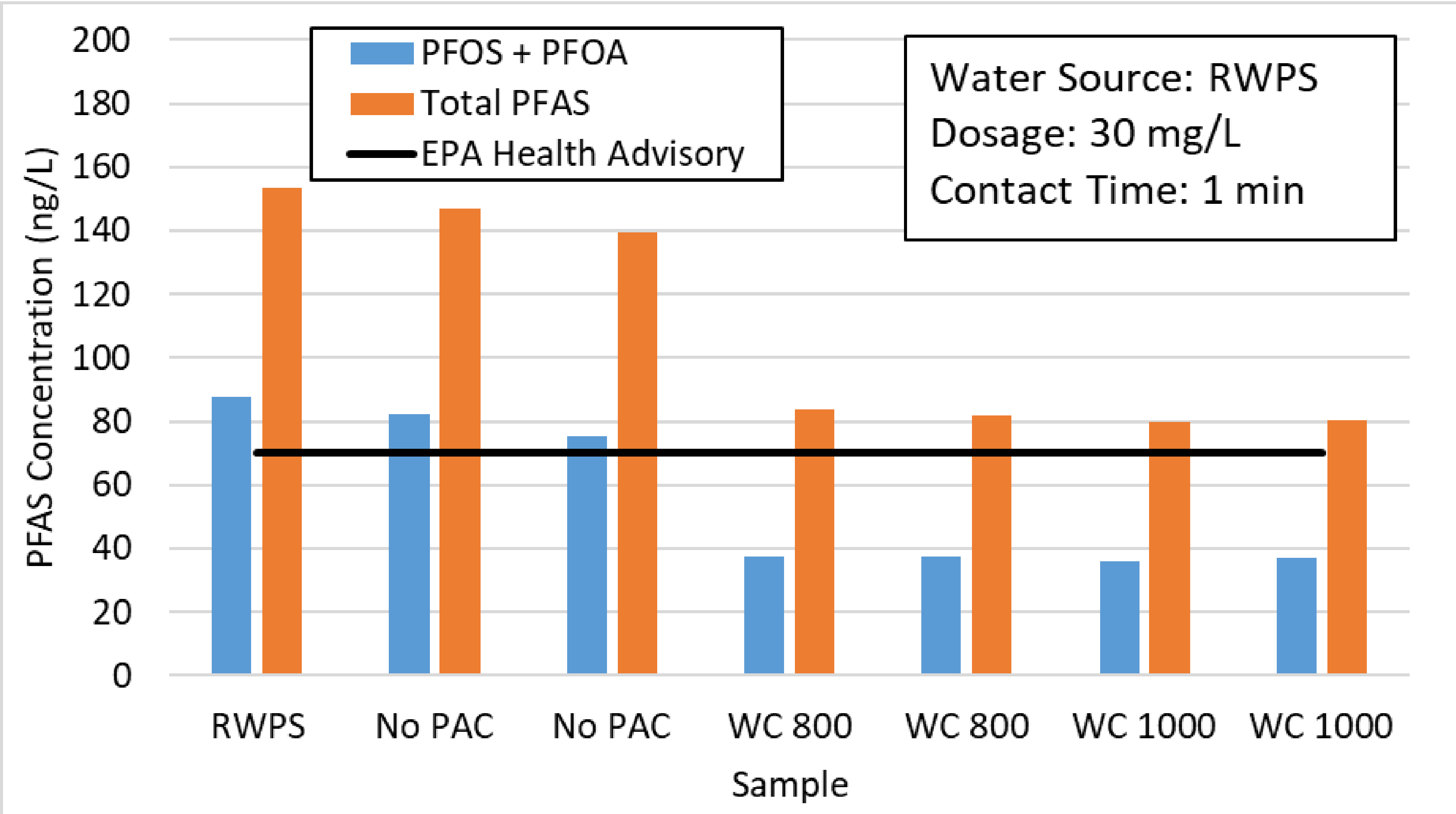
Bench Testing Results



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Proactive Measures Cont.

Additional Measures

- Granular Activated Carbon (GAC) Pilot Testing
  - Treatment effective for removing PFOS and PFOA
- Source Investigation Stakeholder Meetings
  - Voluntary chemical inventory
  - Identify alternative product for training purposes
  - Contact city and contain / treat releases due to emergency response
- Predictive Fate and Transport Model Development
  - Consultant evaluation of correlation between upper watershed samples and treatment plant intake

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County Well Sampling

State / County Well Testing

- Collaborative Effort Between Guilford County Health Department (GCHD) and NCDEQ Division of Waste Management
  - Community Meeting on 12/4/18
  - 42 Private Wells Sampled on 12/18 - 12/19
  - Results showed no samples exceeded HAL
  - 3 samples had PFOS / PFOA above LOQ

Second Round of County Well Testing

- Late Spring / Summer 2019

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Next Steps on the Journey

Uphold Consumer Confidence & Trust

- Carry Out Final Report Recommendations
- Transparency and Proactive Follow Through
  - Ongoing stakeholder engagement
  - Staff availability – questions and concerns

PFAS Treatment

- Short-Term PAC System
- Long Term CIP Plan - GAC Feed System Design

GCHD Support

- Long Term Water Supply Partnering
  - Feasibility Studies for alternate water service for wells > HAL

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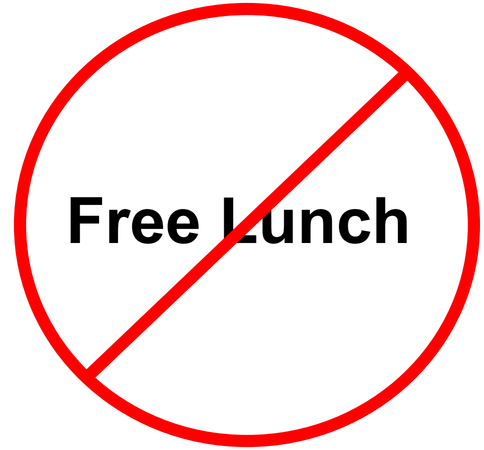

Questions?

Turning Science into Law: The Process for Setting Health-Based Exposure Limits

ACEC of North Carolina

Sean M. Sullivan

April 24, 2019

Topics

Safe Drinking Water Act

EPA's PFAS Action Plan

North Carolina's Default Rules for Surface Water and Groundwater Quality Limits

NC Science Advisory Board

Applicability of the 2L Rules to Emerging Compounds

Safe Drinking Water Act

Evaluation of Unregulated Contaminants

- Unregulated Contaminant Monitoring Rules (UCMR) – to develop data about unregulated substances in public water systems
  - Once every five years (next one due by 2021)
  - No more than 30 substances
- Candidate Contaminant List (CCL) – EPA uses toxicology information and information about prevalence of a substance in drinking water from the UCMR to develop the list of candidates to enter the Regulatory Determination Process
- Regulatory Determination (RD) – EPA must decide whether to regulate five substances on the CCL every five years (next one due 2021)
  - Potential health effects of the substance
  - Likelihood of substance being present at concentrations that can cause adverse health effects
  - In a significant number of public water systems
  - Good opportunity to reduce public health risk by regulating the substance

Safe Drinking Water Act

Two Key Concepts for Setting Standards

- Maximum Contaminant Level Goal (MCLG) – maximum concentration at which no known or anticipated health effects will occur, including an adequate margin of safety
  - Starting point for an MCL
- Maximum Contaminant Level (MCL) – enforceable concentration limit for a contaminant

Setting the MCLG

- Carcinogens – set at zero unless there is a dose that is known to be safe
- Non-carcinogens – set using the reference dose (concentration at which no adverse health effects are expected to occur based on a lifetime of daily exposure)

Setting the MCL

- MCL must be set as close to the MCLG as "feasible"
- If there is no reliable method to measure contaminant concentrations that is technically and economically feasible, EPA establishes a "treatment technique" instead

Safe Drinking Water Act

Feasible – the lowest concentration that can be achieved using:

- Best available technology or treatment approaches
- Other methods that EPA concludes are available (based on actual use in the field, not only in a lab)
- And, EPA can consider the costs of these methods in determining if a treatment method is feasible

Once EPA establishes the "feasible" concentration, EPA then performs a Health Risk Reduction and Cost Analysis (HRRCA)

- Analyze quantifiable and unquantifiable benefits of the feasible concentration versus increased costs from the feasible concentration
- Incremental costs and benefits of feasible concentration versus other levels
- Health effects on general population and sensitive subgroups
- Other factors (data quality, nature of the health risk from the contaminant)

If the benefits of the feasible concentration do not justify the costs, EPA can adjust the MCL to a level where the costs are justified by the benefits.

Safe Drinking Water Act

Implications of MCLs and MCLGs for Cleanups

- EPA policy is to adopt the MCLG as a groundwater cleanup target, as long as the MCLG is something other than zero.
- EPA uses the MCL in cases where the MCLG is zero.
- Strange federal dichotomy – If you're cleaning up a known/suspected carcinogen, your cleanup standard takes the cost of drinking water treatment into account. Otherwise, it doesn't.

Topics

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EPA's PFAS Action Plan

Short-Term Actions (completion within the next two years)

- Propose MCLs for PFOA and PFOS
- Improved analytical methods for drinking water
- New analytical methods for PFAS and precursors in other media
- Guidance on groundwater cleanups
- Final Toxicity Assessments
  - PFBS and GenX in 2019
  - Five additional PFAS in 2020

EPA's PFAS Action Plan

Long-Term Actions

- Consider requiring reporting for PFAS releases in TRI reports
- Consider establishing numerical surface water quality criteria
- Examine existing information and begin to send information requests to support development of ELGs for NPDES permits
- Include PFAS in next UCMR and use data to develop national prevalence information
- Continue studying ecological risk and atmospheric transport

Topics

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NC Science Advisory Board

Applicability of the 2L Rules to Emerging Compounds

Default Rules for Surface Water and Groundwater Quality Limits

Surface Water Quality Standards

- 15A NCAC 02B.0208 – numerical approach for establishing surface water quality standards for toxic pollutants
  - Aquatic life – cannot cause chronic toxicity; in absence of direct measurements thereof, limit is:
    - Fraction of the the lowest LC50 that predicts no effect chronic level (using acceptable acute/chronic ratio); or
    - 0.05 or 0.01 X lowest LC50
  - Human Health – Cancer and non-cancer health effects
    - Non-cancer focuses on effects from consumption of fish tissue and water consumption
      - Fish tissue focuses on effects to 70kg adult based on average lifetime consumption
      - Water consumption focuses on effects to 10kg child consuming 1 liter of water per day
    - Cancer – focuses on not causing increase in lifetime risk greater than 1X10-6
      - Based solely on consumption of fish. Cancer risk from water consumption is addressed in the WS classifications.

Default Rules for Surface Water and Groundwater Quality Limits

Water Supply Watersheds

- WS-I through WS-V classifications all require that surface waters meet applicable MCLs
  - 15A NCAC 02B.0212, 0214, 0215, 0216, 0218
- There are also specific standards for carcinogens and non-carcinogens for each class of water supply watersheds.
  - Standards are based on both water consumption and fish tissue consumption.

Default Rules for Surface Water and Groundwater Quality Limits

2L Rules – Groundwater – 15A NCAC 02L.0202(d&f)

- Standards must be set as “the least of”:
  - Systemic threshold concentration (non-carcinogenic effects) based on effects to 70kg human
  - Concentration corresponding to increase in lifetime cancer risk of 1 X10-6
  - Taste threshold limit
  - Odor threshold limit
  - Maximum Contaminant Level (MCL) established by EPA for drinking water from public water systems
  - National secondary drinking water standard – 15 contaminants directed towards odor, taste, color, etc.
- EMC can establish a standard that is less stringent than the MCL or the secondary standard if:
  - More recent data from certain sources supports a less stringent standard
  - It will not endanger human health or the environment
  - Compliance with the MCL or the secondary standard will “produce serious hardship without equal or greater public benefit”

Topics

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NC Science Advisory Board

Applicability of the 2L Rules to Emerging Compounds

Science Advisory Board

Re-Chartered in July 2017 to Assist DEQ and DHHS in Establishing Health-Based Exposure Limits for Environmental Contaminants

- Meets at least six times per year
- Makes recommendations on:
  - Need for reviews or evaluations of releases to the environment
  - How to regulate releases to the environment
  - Urgency of establishing such regulations
  - Consult with DEQ on regulation of releases, including establishment of acceptable exposure levels
  - Recommend acceptable concentrations of contaminants based on a “range of risks”
  - Evaluating multi-media effects of releases
  - Availability of new information about a contaminant and the implications for existing standards
  - DHHS’s efforts to establish health goals
  - Identifying emerging contaminants and need for evaluation of their health effects

Science Advisory Board

Factors in making recommendations on "range of risk" concentrations:

- Have toxicological principles been appropriately applied in development of media-specific exposure concentration?
- Should substances with adverse reproductive / developmental effects "be treated with risk assessment factors"?
- Should synergistic effects of contaminant mixtures be considered?
- Should acceptable concentrations of contaminants be adjusted because of presence of multiple sources in a localized area?
- How should uncertainties be incoporated into the development and revision of acceptable concentration limits?

What isn't here? – **COST CONSIDERATIONS AND ACTUALLY SETTING THE STANDARDS**

Science Advisory Board

Recent Actions

- February 2019 – concurrence with DEQ's proposed AAL for methyl bromide
- February 2019 – concurrence with DEQ's recommended action levels for TCE in indoor air
- October 2018 – concurrence with DHHS's proposed drinking water health goal for GenX

Ongoing Evaluations

- Hexavalent chromium

Science Advisory Board

Decision re GenX

- 140ppt standard is appropriate based on non-carcinogenic effects
- Insufficient information available to determine status as carcinogen

Consistency with Federal Approach

- Because the recommended health limit is based on non-carcinogenic effects, 140ppt is the equivalent of a NC-only MCLG for GenX
- Consistent with CERCLA and the NCP to use a non-zero MCLG as a cleanup target for GenX

Topics

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Applicability of the 2L Rules to Emerging Compounds

Applicability of the 2L Rules to Emerging Compounds

2L Rules – What if there's no established standard?

- 15A NCAC 02L.0202(c) – "Substances which are not naturally occurring and for which no standard is specified shall not be permitted in concentrations at or above the practical quantitation limit in Class GA or Class GSA groundwaters."
- Practical Quantitation Limit – "lowest concentration of a given material that can be reliably achieved among laboratories within specified limits of precision and accuracy by a given analytical method during routine laboratory analysis." 15 NCAC 02L.0102(15).
- According to DEQ – any detection of any non-natural substance above its PQL is a violation that can trigger corrective action under 02L.0106 unless there is an established standard for that substance
- Interim Maximum Allowable Concentration (IMAC) – 02L.0202(c) – allows any person to petition DEQ to establish an IMAC for a substance that does not have an established standard.
    - If DEQ establishes an IMAC, it must "initiate action" to consider adoption of a standard for that substance.

Applicability of the 2L Rules to Emerging Compounds

2L Rules – What if there's no established standard? (cont'd)

- Establishing an IMAC appears to be the only way to avoid the conclusion that the detection of an unnatural substance without a standard constitutes a violation that establishes corrective action authority under 02L.0106.
  - How do you establish an IMAC for an emerging contaminant? The whole idea is that we don't have enough information about these contaminants to set a standard.
    - What would that IMAC petition look like?
    - DEQ is supposed to "initiate action" to consider a binding standard within three months of adopting an IMAC. Given the lack of information about an emerging contaminant, would DEQ really want to lock itself into having to initiate a rulemaking proceeding?
  - If I were DEQ's lawyer – I wouldn't be in a hurry to establish a standard.
    - Promulgating a rule takes time and money, and it opens the door to someone seeking judicial review of it.
    - The current structure gives DEQ corrective action authority under the 2L rules for any detection above the PQL, so why limit yourself?
    - As more data comes in about a substance, you might learn that you need to reduce the standard again – more time and money, plus the political blowback of setting a standard that wasn't stringent enough.

Applicability of the 2L Rules to Emerging Compounds

What is the PQL for an Emerging Compound?

- We are talking about parts per trillion in many cases, and sometimes less than 1ppt. Are lab results really that reliable?
  - Consider the potential for sample contamination – DEQ has established strict requirements for employees sampling for GenX (including limits on types of clothing and not eating fast food before taking samples).
  - Do we really know enough about these substances to know these precautions will be effective and produce a reliable, accurate result?

Chemours Consent Decree and Modified Title V Permit

Changing Understanding of Emissions of GenX from Fayetteville Works

- Original 2016 estimate – 66.6 lbs/year
- October 2017 revision to 2016 estimate – 594 lbs/year
- April 2018 calculation by DEQ – 2,758 lbs/year

Discovery of Atmospheric Deposition

- Early to mid-2017, GenX is primarily a surface water issue
- Mid to late 2017, DEQ discovers the extent of groundwater contamination and identifies air emissions as likely source
- January to April 2018, rainwater sampling identifies deposition as far as 20 miles from the facility

April 6, 2018 – DEQ sends a 60 day notice to Chemours of DEQ's intent to modify the Facility's Title V permit

Chemours Consent Decree and Modified Title V Permit

Basis for the 60-Day Notice

- 15A NCAC 02Q.0519(a)(2) – conditions under which the permit was issued have changed
- 15A NCAC 02Q.0519(a)(7) – modification necessary to carry out "the purpose of NCGS 143, Article 21B."

Changed Conditions

- Stack testing determined significantly higher emissions of GenX than previously thought
- Emissions are resulting in atmospheric deposition of GenX
- GenX deposition is causing violations of NC *groundwater quality standards*

Purpose of NCGS 143, Article 21B

- NCGS 143-211 establishes "clear mandate" for environmental protection
- Statute endorses a "total environment of superior quality"
- Coordinated protection of air and water resources, including groundwater

Purposes of Article 21B?

"Total environment of superior quality"

- Chemours' new Title V permit cites 02Q.0519(a)(7) (purposes of Article 21B) as the basis for requiring installation of a thermal oxidizer and reduction of GenX emissions by 99.99%
- Also provides the basis for requiring a shutdown/malfunction plan
- And provides the basis for establishing enhanced LDAR requirements

New annual emissions limit of 23.027 lbs/year

- My question – if any detection of GenX in groundwater is a violation, is this new limit sufficient to prevent any atmospheric deposition capable of causing a detection above the PQL?
- Seems more likely that it's sufficient to prevent any detection above the health-exposure limit established by the SAB (140 ppt).
- If it's the latter – seems like DEQ is exercising its enforcement discretion on the basis of an SAB opinion, which means the SAB recommendation is a de facto 2L standard for GenX that hasn't gone through rulemaking at the EMC.

Bottom Line

The real action on emerging compounds in North Carolina is at the Science Advisory Board

- Unlikely DEQ is going to initiate rulemaking to establish a 2L standard quickly and petitioning to establish an IMAC isn't really feasible.
- Therefore – SAB recommendations are likely to guide DEQ's exercise of its enforcement discretion.

The regulated community needs to participate in the SAB's process!

Contact Information

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Emerging Compounds: Liability in the Real World

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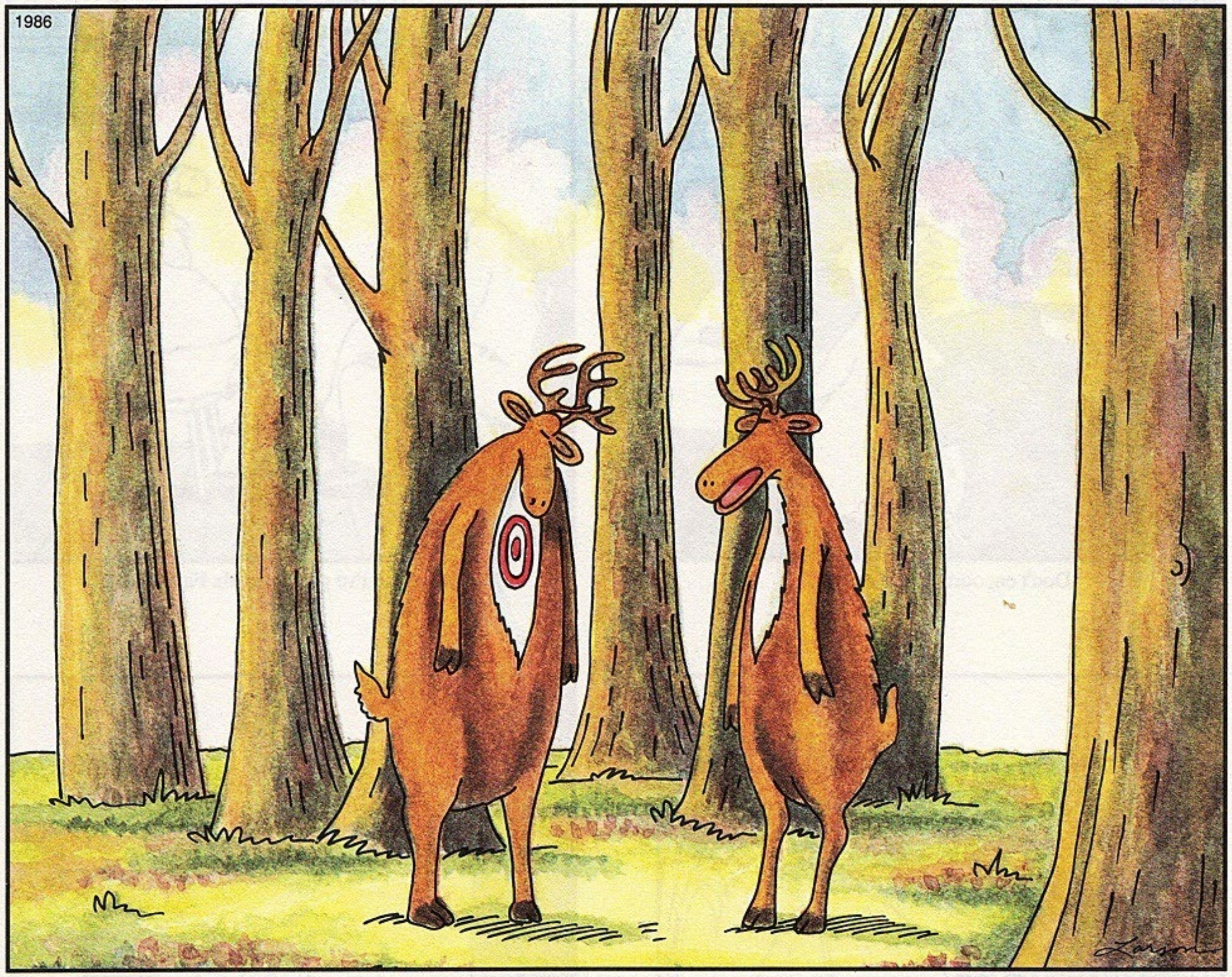
WILLIAMS MULLEN



"Bummer of a birthmark, Hal."

WILLIAMS MULLEN finding yes®

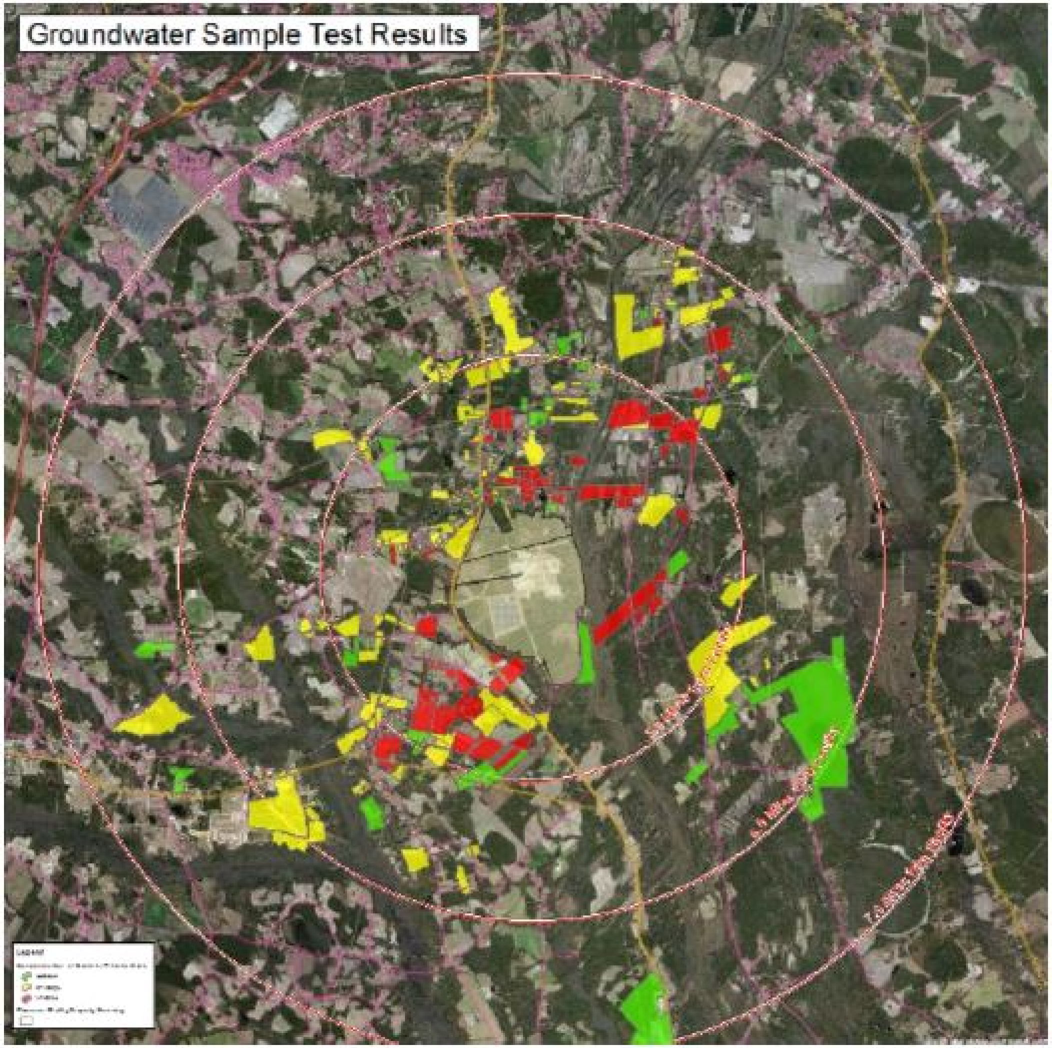
QUESTION: Are sources of ECs liable beyond DEQ?

ANSWER: Yes

- Understand the Risks
- Causes of Action
- Next Steps

Understand the Risks

Consider this from DEQ…



Well Sampling Results in the Chemours area, Approximate distances from facility boundary:

Northeast – 5.5 miles
West – 1.8 miles
Southwest – 3.9 miles
East – 2.6 miles

GenX: NC health goal = 140 ng/l

Red = > 140 ng/l
Yellow= 0-140 ng/l
Green = Non detect

Division of Waste Management

Combined Phase I, II, III , IV (partial) Private Well PFAS Data, also Includes Robeson Co. and DEQ-collected Data

Private Well Water GenX Summary	Combined Well Data
Distance from Chemours' border	Up to 5.5 miles
Well Collection Dates	9/6/2017 – 3/26/2018
Number of Wells tested	837
Number of Exceedances of the GenX Provisional Health Goal	207
Number of Not-Detected ("ND") GenX Analyses	178
Number of GenX Detections Less than the Health Goal [a]	450
Maximum Detected GenX Concentration	4000 ng/L

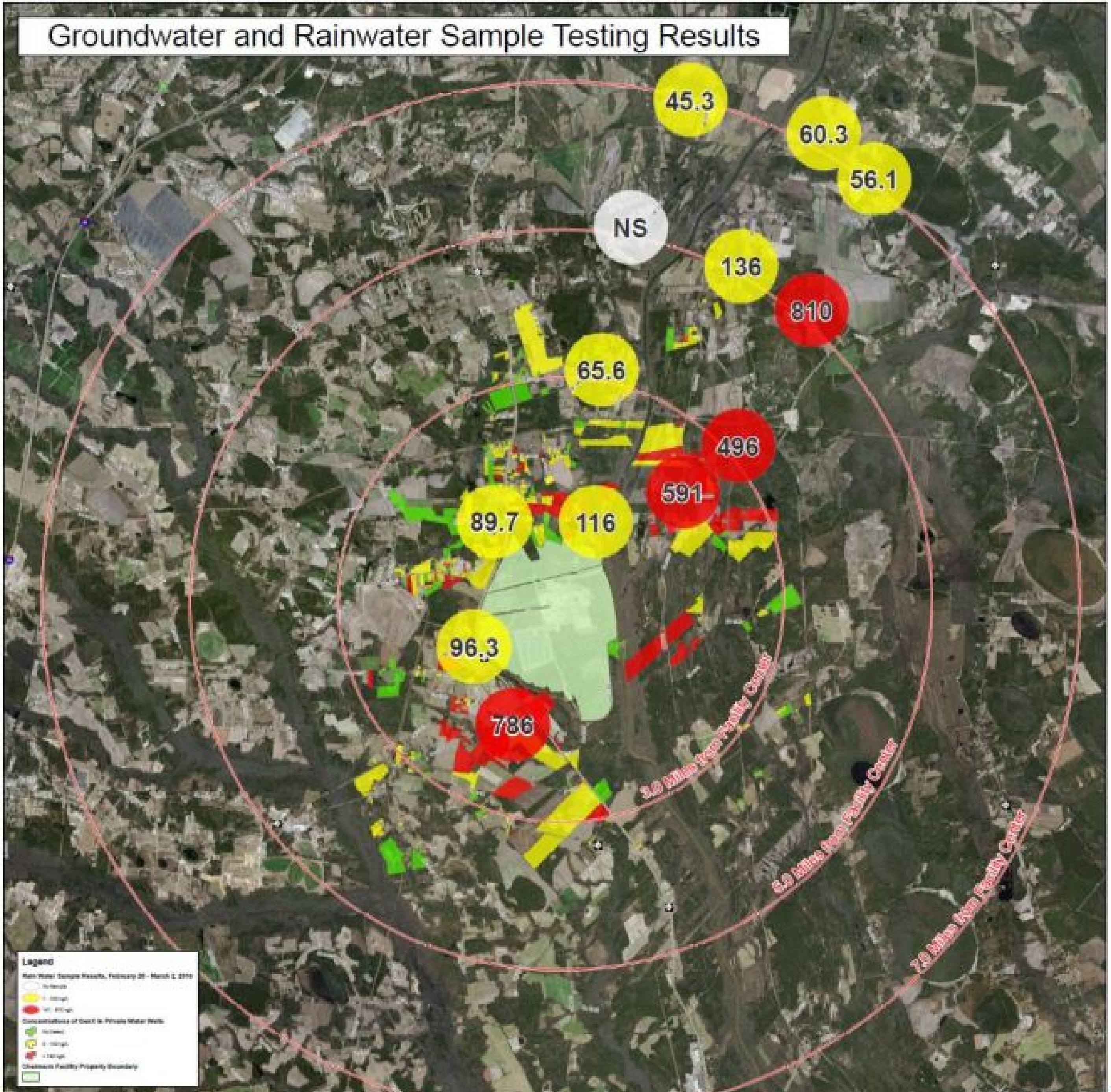
a. The NC DHHS Provisional Drinking Water Health Goal for GenX is 140 ng/L (July 2017)

Emerging Compounds

DAQ's investigation involving GenX and other PFAS from Chemours

- GenX emissions data
  - Started with only estimates
  - Required stack tests
  - Method development
  - First of its kind measurements

Chemours 2016 emissions estimates as originally reported to DAQ	Chemours revised 2016 emissions estimates as of October 2017	Latest emissions estimates, including information from January 2018 stack test measurements
66.6 lb/yr	594 lb/yr	2758 lb/yr


Groundwater and Rainwater Sample Testing Results
45.3
60.3
56.1
NS
136
810
65.6
496
591
89.7
116
96.3
786

Understand the Risks

Contaminants in…

- Groundwater
- Surface water
- Air deposition

Understand the Risks

First, Your Client Must Understand the Risks…

Rule 1: Court rules govern…even if it places you at odds with your client.

Understand the Risks

FRCP 34: Requests to Produce

- Documents
- Reports
- Photographs
- Electronic mail…

If it may lead to discovery of evidence...

Understand the Risks

FRCP 30: Depositions may be taken

- Under oath
- Written
- Admissible to impeach/evidence

NOTE: Perjury to not tell the truth

Understand the Risks

Rule 2: Pictures in your ESA or report show things…

Understand the Risks

Groundwater Sources…

Understand the Risks

Understand the Risks

Air Emissions Sources…

Understand the Risks

Understand the Risks

Surface Water Sources…

Understand the Risks

Understand the Risks

Understand the Risks

Understand the Risks

How would you explain those photographs?

Understand the Risks

Rule 3: …And words mean things…

Understand the Risks

"Concentrations of [contaminants] observed during the second semiannual 2012 sampling event <u>exceed secondary maximum contaminant levels</u>."

Understand the Risks

9/26/90

Randy:

I'm concerned about DHEC's possible reaction to our "violating" outfalls

Understand the Risks

(3) In spite of (2), it would be possible to dredge without impact and dispose of/treat the spoils properly. Net impact to river would be positive.

(4) Costs for (2) may be unacceptable — ballpark perhaps:
$6M – dredge & landfill
$12M – dredge & containment
$25M on up for incineration options

(5) How dredging should proceed, or fit into the overall site remediation, so the lawsuit would appear to have merit.

(lower) (6)

(7) On the stand, I will deny all of the above.

Understand the Risks

The Best Rule Is Common Sense

- Writing
- Records

Partnering with legal counsel can help…

Understand the Risks

This…

Understand the Risks

"PCE was detected at the highest concentration in the …sampling point GW-3…(10,000 ppb)."

Understand the Risks

Not that…

Understand the Risks

PCE appeared to have been released to the ground in the vicinity of boring SB-3 due to the detection of PCE in the shallow soil at concentrations exceeding the RSL at this location. Additionally, PCE in groundwater, at concentrations potentially exceeding the MCL, appeared to extend over a distance of at least 400 feet southeast of the main building. PCE was detected at the highest concentration in the apparent downgradient sampling point (GW-3) where the <u>PCE concentration detected in groundwater (10,000 ug/1) exceeds one percent of the solubility of PCE</u>. This elevated concentration <u>suggests that the sampled groundwater may have come into contact with dense non-aqueous phase liquid (i.e., free phase PCE).</u>

Understand the Risks

This…

Understand the Risks

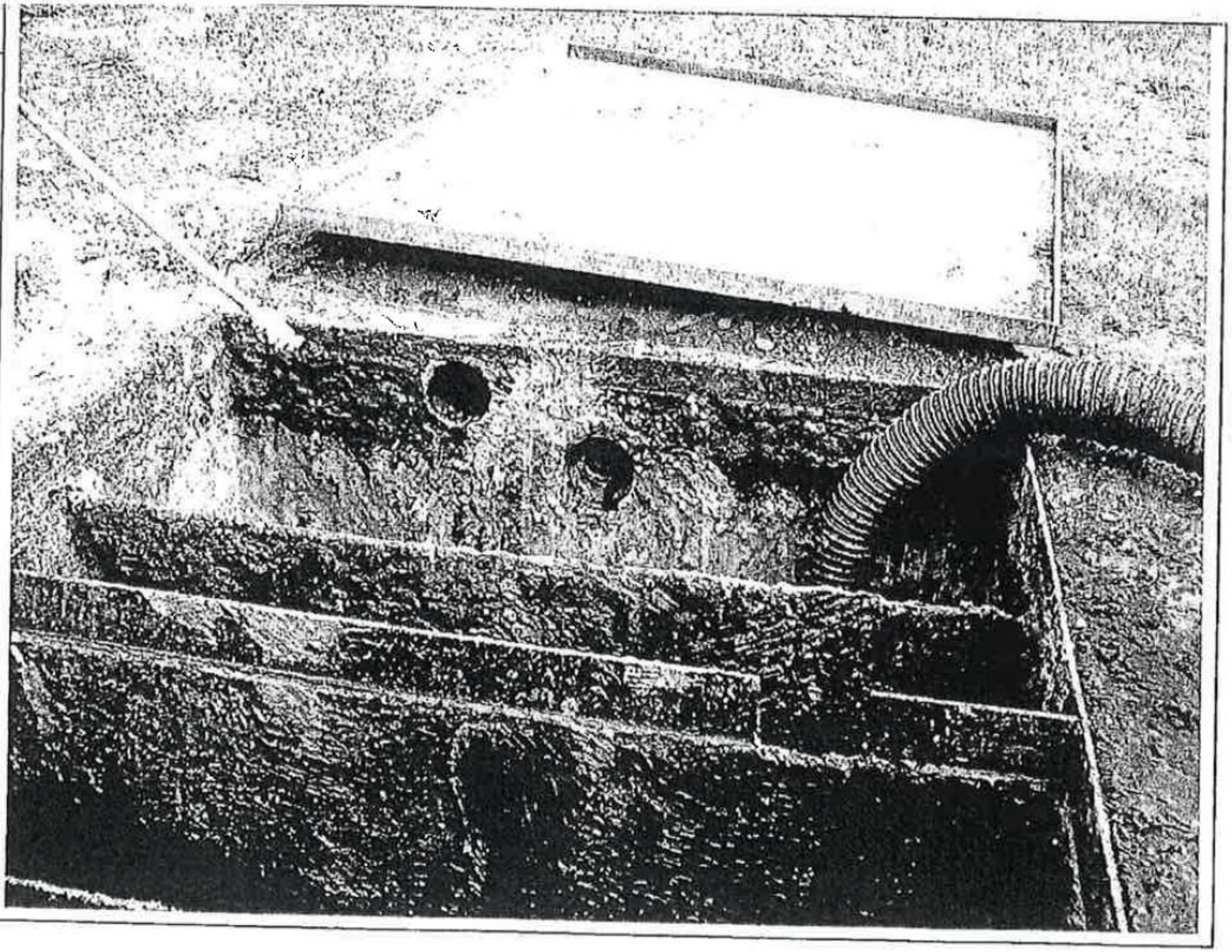
"…but apparently is connected to a 4 PVC that may lead east-northeast toward the property fence line."

Understand the Risks

Not that…

Understand the Risks

Photo No. 6	
View Direction of Photo: East-Northeast Date of Photo: 03/22/2012	
Description: View of metal sump pit at rear of building. Inlet drain (upper hole) connected to floor sump inside building. Outlet (middle hole) is currently plugged, but apparently is connected to a 4" PVC that leads east-northeast toward the property fence line and potentially to the property line southeast of the facility.	



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So How Do the Rules Work in Court?

Causes of Action

General Common Law: Three Causes of Action

1. Negligence
2. Trespass
3. Nuisance

Causes of Action

Negligence Elements

1) Duty of Due Care/Breach of Duty
2) Legally Protected Injury
3) Causal Relationship, i.e. "Proximate Cause"

Causes of Action

1) **Duty Owed/Breach**

    a. "Foreseeable" risks

    b. "Unreasonable" response

NOTE: Take into account "level of skill…".

Causes of Action

2) Legally Protected Injury – Off Premises

- Activities
- Artificial Conditions

QUESTION: Are EC artificial conditions?

Causes of Action

3) Proximate Cause

- Cause-in-fact
- Legal Cause

QUESTION: Can EC be a cause-in-fact of diminution in property value?

Causes of Action

2. Trespass to Land

- Interference
- "Quiet Possession"
- Intentional

Causes of Action

POP QUIZ

- Client is source of EC in Air Emissions
- Enters Plaintiffs Property
- Detectable at < Levels of Concern
- Not forced to evacuate

QUESTION: Trespass established?

Causes of Action

3. **Nuisance to Land**

- Interference
- Loss of Use and Enjoyment
- Intentional

NOTE: Actual entrance to property not required.

Causes of Action

POP QUIZ

- EC in Neuse River
- 1.5 miles away
- Client is the Source
- Not detectable onsite

QUESTION: Nuisance established?

Causes of Action

General Defenses:

- Statute of Limitations (3 years)
- No Intent
- No Duty
- No Damages

NOTE: "Continuing" Trespass and Nuisance.

Causes of Action

POP QUIZ

- 1960 to 1970 - - Plant discharged EC to surface water
- Client purchased plant in 1988
- ECs discovered in stream, yards, and houses in 2018

QUESTION: Does Client have liability?

One More Thing…

Once you know, you have a duty to prevent.

Next Steps

Next Steps:

So…How do I do my job and protect my client?

Next Steps

Remember: Whatever is in a Photograph, Report, or Letter can and will be used against your Client, unless…

IT IS PRVILIEGED.

Next Steps

Privilege means - -

- Conclusions and findings conditionally protected from disclosure

BUT…Underlying data may not be protected

Next Steps

Three Privileges

- Attorney-Client Communication
- Work product of Attorneys
- Critical Self-Evaluation

Next Steps

Attorney-Client Communication

- Purpose is legal advice
- Communication to Attorney
- Made Confidence
- Not disclosed

Next Steps

Use of Consultants: Acceptable Under Attorney's directions

1. Precaution against disclosure
2. Agent to Attorney
   - "Translating data for the attorney"
   - Facilitate Legal advice
3. Purpose – to provide legal advice

Trade Comm'n v. TRW, Inc.

Next Steps

In-house Counsel Qualify but…

- Not as "business advisor" role
- May become a witness

U.S. v. Chevron

Next Steps

Ethical Considerations of Attorney:

May disclose to - -

- Defend against allegations of crime
- Stop intent to commit crime

Model Rules of Professional Conduct

Next Steps

Work Product Privilege

Qualified Privilege - - may be waived:

- Substantial showing
- Necessity or justification
- Information not available

Hickman v. Taylor

Next Steps

Work Product Privilege

Privilege: Work of the Attorney - -

- Documentation
- Anticipation of litigation - - "some litigation"
- Prepared by or for a party

Id.

Next Steps

Work Product Privilege

Scope: Includes - -

- Consultant’s work
- Prepared on Attorney’s behalf
- Mental impressions, conclusions, and opinions

QUESTION: Is an aerial with Concentric Circles included?

Next Steps

Work Product Privilege

Argue: Soil and Groundwater data - -

- Accessible to all parties
- Necessary for legal conclusion

QUESTION: Is it re-producible?

Next Steps

Critical Self-Evaluation

- Confidential
- Critical, self-evaluative, deliberative
- “Public interest” in confidentiality outweighs disclosure

Bredice v. Doctors Hospital, Inc.

Next Steps

Critical Self-Evaluation

Goal: Encourage voluntary evaluation and disclosure programs - -

- SEC compliance
- Health care (doctor reviews)

Next Steps

Critical Self-Evaluation

May be waived- -

- Public Need
- Not available through other sources
- Degree of harm
- Prejudice to an investigation

Next Steps

Steps to protect you and your client

Step No. 1: Evaluate liability of the client.

Step No. 2: Do not put it in photographs, charts, or writing until the client is advised.

Step No. 3: Use Attorney Privileges.

And relax, you have earned it…


HAZARDOUS
WASTE