1,4-Dioxane Remediation Technology Development
An Overview Based on 70+ Projects

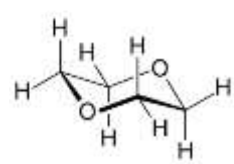
Paul M. Dombrowski, P.E.

NEWMOA 1,4-Dioxane Assessment & Remediation Workshop

Outline

- Overview of AECOM 1,4-Dioxane Sites
- Demonstrated Treatment Technologies
- Natural attenuation and bioremediation
- Developments to validate biodegradation

1,4-DIOXANE

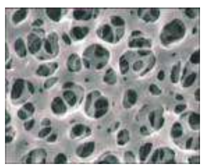


Page 2

What is 1,4-Dioxane?

- **Commonly known: Solvent stabilizer** and acid corrosion inhibitor used to prevent decomposition of **1,1,1-trichloroethane** (usually 3-4.5% by vol.)
- **Not commonly known**:
  - **Main or minor ingredient** of many products
  - Produced as **by-product** from polyester or nonionic detergent manufacturing process

Solvent Stabilizer of 1,1,1-TCA



Main ingredient: Cellulose Acetate Membrane Production

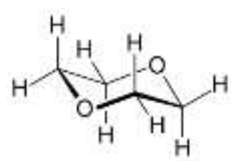
Byproduct from detergent production

Dioxane-free detergent on shelf of Costco

AECOM

1,4-Dioxane Properties

- Very low Henry's Law Constant
  - unlikely to volatilize into soil vapor



- Very low octanol-water coefficient (Kow)
  - unlikely to sorb to soil particles and is mobile in saturated soils
- High miscibility
  - migrates farther in groundwater than other groundwater VOCs

AECOM

Once Released…..

Air
- Readily evaporates, moderate vapor pressure of 40 mm Hg at 25˚C
- As a vapor, breaks down readily to form aldehydes and ketones

Soil
- Tends to migrate through soil rather than adsorb to particles (except for moist clay/silt)

Water
- Completely soluble in water
- Tends to stay dissolved, therefore low volatilization risk from groundwater
- Chemically stable, not expected to degrade naturally once in groundwater or surface water

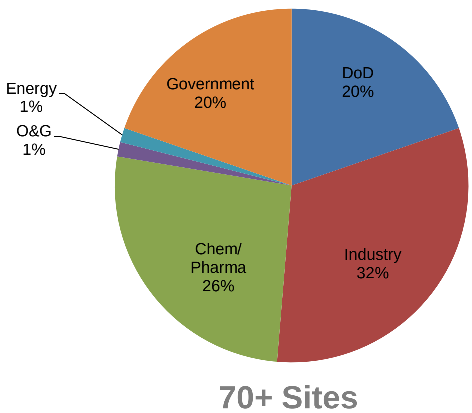
Regulatory Updates

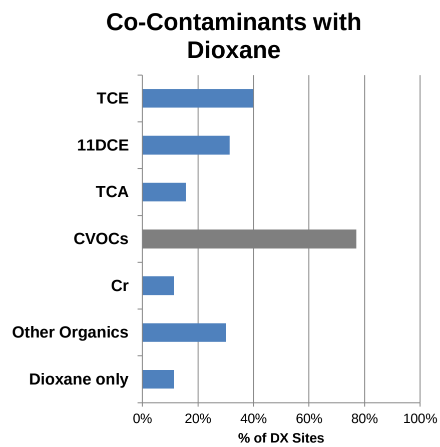
State	2009	Present
Alabama	--	0.67
Alaska	--	77
California	3	1
Colorado	6.1	0.35
Connecticut	--	3 or 50*
Florida	3.2	3.2
Georgia	70	70
Maine	--	4
Massachusetts	--	0.3
Michigan	85	0.67
Nevada	6.1	--
New Jersey	10	0.4 (draft)
New Hampshire	3	0.35
North Carolina	7	3
Pennsylvania	5.6	6.4
South Carolina	6.1	0.67
Texas	83	9.1
Wisconsin	--	3

-- values not found
*: bathing and showering
data are in micrograms per liter (ug/L)

- No Federal MCL
- More states now have criteria
- Criteria decreasing in many states
  - Numerous states have criteria < 1 ug/L

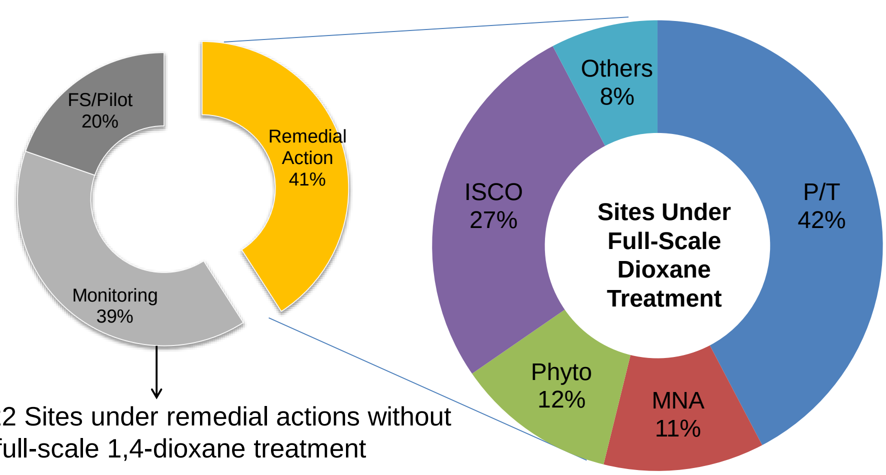
AECOM Survey of 1,4-Dioxane Sites





AECOM

AECOM Survey of 1,4-Dioxane Sites



22 Sites under remedial actions without full-scale 1,4-dioxane treatment

AECOM

AECOM Survey of 1,4-Dioxane Sites

Page 9

AECOM

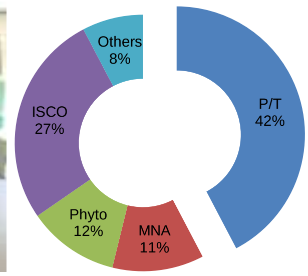
AECOM Site Observations

- Significant number of sites documented no detected 1,4-dioxane during site characterization
- 1,4-Dioxane plumes are commonly co-mingled with CVOCs, especially in source areas. CVOCs in source areas likely have remedy in place (ERD, air stripping) without considering dioxane
- Most 1,4-dioxane plumes have not been fully characterized
- Most sites have no long term monitoring data to support plume stability argument
- For several sites with cumulated data, natural attenuation was observed but biodegradation mechanisms could not be confirmed due to lack of diagnostic tools (additional lines of evidence)

Page 10

AECOM

Pump and Treat



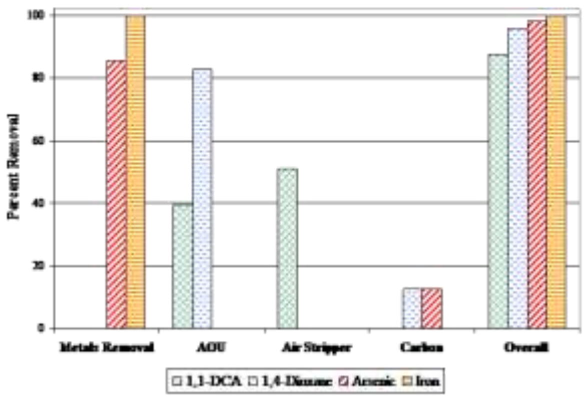
AECOM

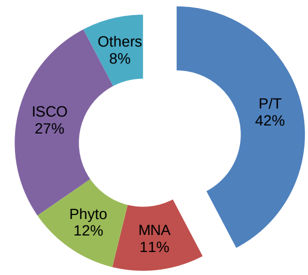
Example Pump & Treat Projects

COCs	Agency	Technologies
Dioxane, VOCs	RWQCB, Santa Ana region	LGAC for VOCs and **UV oxidation** for dioxane
Dioxane, perchlorate, VOCs, nitrate	Orange County Water District	LGAC for VOCs, ion exchange for perchlorate, **UV oxidation** for dioxane, regenerable ion exchange for nitrate.
Perchlorate, CVOCs, and dioxane	San Francisco RWQCB	**Advanced ozone/hydrogen peroxide oxidation** for dioxane, anion exchange for perchlorate, and the existing GAC vessels for polishing of residual VOCs and oxidation by-products
Dioxane, VOCs	EPA	SVE/DPE for soil and perched aquifer; ex situ advanced oxidation (**HiPOx)** for dioxane and VOCs
Dioxane, CVOCs	FDEP	P&T with **AOP technology**

AECOM

Pump and Treat



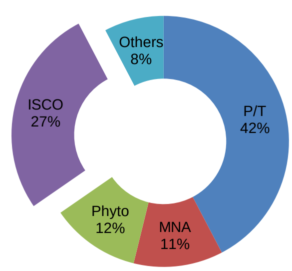


- Cost per mass of DX removal increased when plume is large and dilute
- Multiple treatment technologies may be required
  - Metals removal critical to performance of Advance Oxidation Units

AECOM

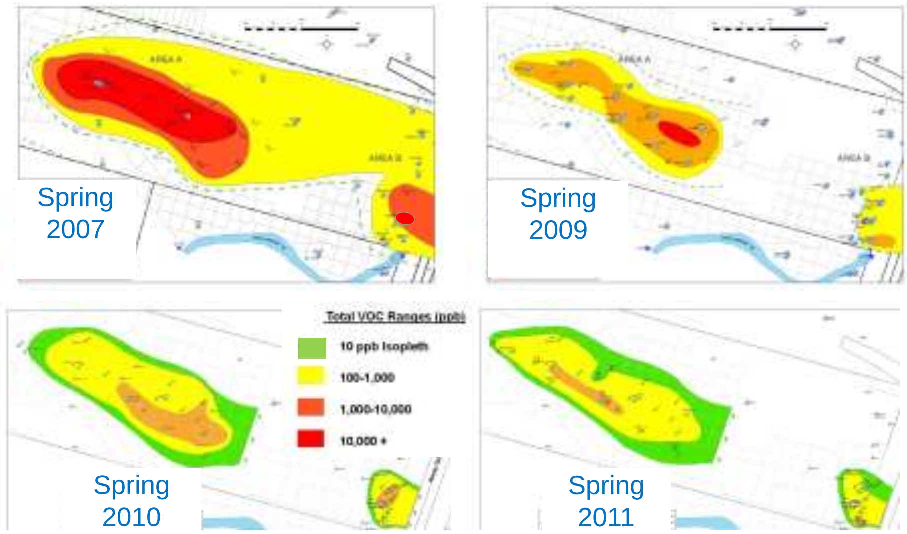
In-Situ Chemical Oxidation

- **Chemical Oxidants**
  - Alkaline activated persulfate
  - Peroxide activated persulfate
  - Catalyzed hydrogen peroxide
  - Ozone
- **Applicability**
  - Source treatment
  - Wide range of dioxane concentrations
  - Applicable for dioxane and co-contaminants
  - Repeated treatments are needed
  - The effectiveness is mixed and may be limited by oxidant distribution
  - Other polishing steps are needed to achieve end point (e.g., bio or MNA)
- **Regulatory Acceptance - High**



AECOM

ISCO Case Study (Total VOCs)



•Total VOCs defined as the sum of BTEX, PCE, TCE, cis-1,2-DCE, and 1,1,1-TCA.

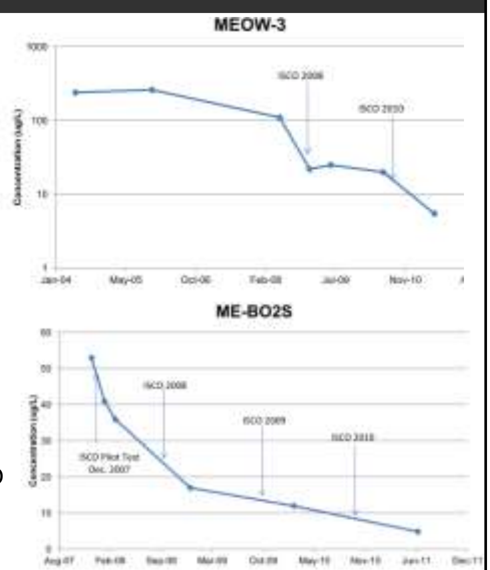
AECOM

ISCO Case Study

Area B (Dioxane Results)

MEOW-3				
Jun-08	Jun-09	Jun-10	Jun-11	Jun-12
110	25	20	5.5	0.87
ME-04a				
Jun-08	Jun-09	Jun-10	Jun-11	Jun-12
32	12	15	6.6	10
ME-BO2S				
Mar-08	Jan-09	Feb-10	May-11	Aug-12
36	17	12	4.9	10

- NH AGQS was 3 ug/L at time of ISCO
  - AGQS = 0.35 ug/L currently



AECOM

Phytoremediation

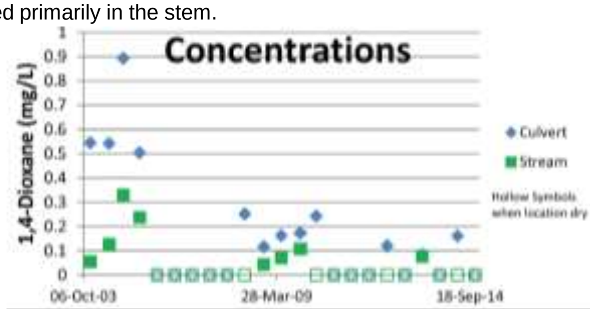
Definition: "direct use of green plants and their associated microorganisms to stabilize or reduce contamination in soils, sludges, sediments, surface water, or ground water ... Sites with low concentrations of contaminants over large cleanup areas and at shallow depths present especially favorable conditions for phytoremediation."
- U.S. EPA, 2011

- Plants can enhance the removal of contaminants by at least two mechanisms:
  - (1) direct uptake and, in some cases, in-plant transformations to less toxic metabolites; and
  - (2) stimulation of microbial activity and biochemical transformations in the root zone through the release of exudates and enzymes
- Half-life in the atmosphere is on order of hours

AECOM

Phytoremediation

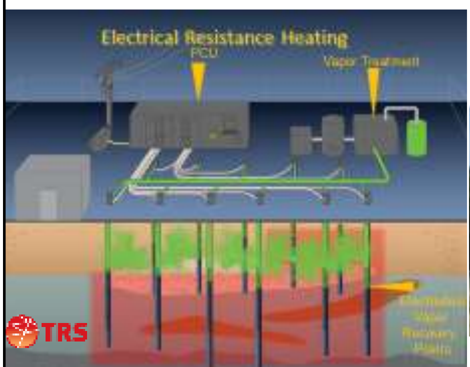
- Hybrid poplar trees have been used for phytoremediation of 1,4-dioxane
  - Extremely fast growing, hardy, and tolerant of high organics concentrations
  - Direct uptake of organics and, in some cases, transformation to less toxic metabolites.
  - Release of chemicals that may stimulate degrading populations of microbes
- 8 day Hydroponic Study (E.W. Aitchison, J.L. Schnoor, et. al., 1997)
  - 30-79% (average = 54%) of the dioxane mass removed from reactors
  - degradation by root-zone microorganisms minimal compared to plant uptake.
  - majority of 1,4-dioxane taken up into the plant was volatilized (average = 77%), with remaining mass concentrated primarily in the stem.
- AECOM Field Study
  - A pilot program was installed in March 2004, with subsequent full-scale system
  - designed for combined purposes of hydraulic control and 1,4-dioxane removal

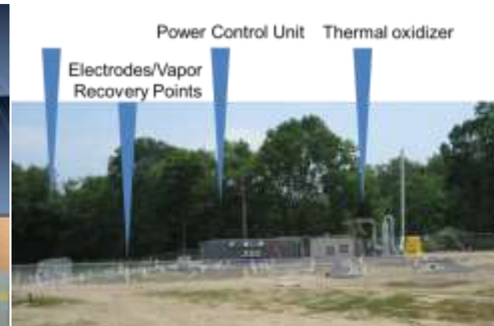


AECOM

In-Situ Thermal Remediation

Description: Subsurface soils heated (applied heat directly or generated in situ) to above the boiling point of the target VOCs contaminants (typically >100ºC) and evaporating VOCs from the soil. Vapors are collected from the subsurface through soil vapor extraction wells for subsequent above-ground treatment.

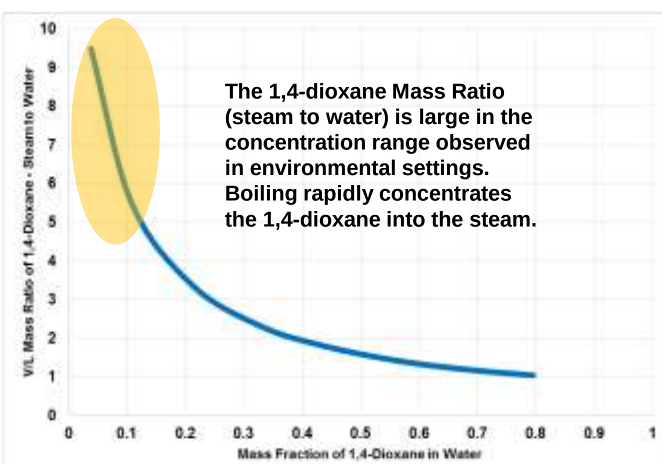




AECOM

In-Situ Thermal Remediation

Vapor-Liquid Mass Ratios during Steaming



- **Henry's Constant increases with temperature increases**

Source: Scheider and Lynch, J. Am. Chem. Soc., 65(6), 1943

AECOM

Thermal Remediation

1,4-Dioxane – Field Case Study

Condenser

Gases In

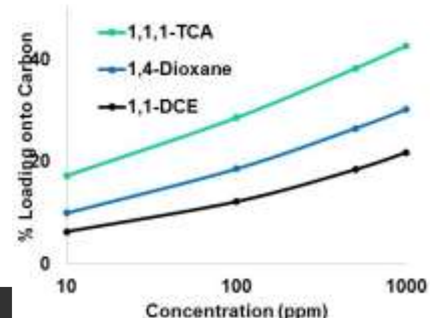
Gases Out

1,600 ppb
0.12 lb/day

Condensed Steam

94 µg/L
0.006 lb/day

- 95% remains in vapor phase
- Although GAC is poor for water-dissolved 1,4-dioxane, GAC works well for 1,4-dioxane vapor

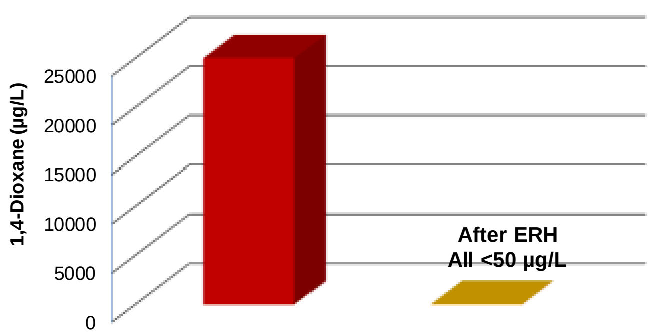


AECOM

Thermal Remediation

1,4-Dioxane – Field Case Study

Before ERH
1,000 to 90,000 µg/L



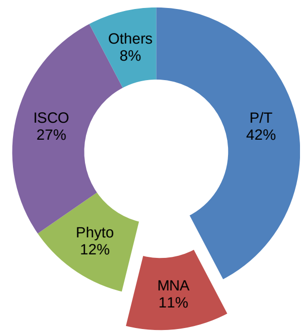
>99.8% Removal

TRS

AECOM

Monitored Natural Attenuation

- A common approach when CVOCs are under ERD treatment
- Not a primary risk driver compared to CVOCs
- Regulatory agencies are generally skeptical on MNA approach
  - *1,4-dioxane is relatively resistant to biodegradation in water and soil and does not bioconcentrate in the food chain (USEPA 2014 Fact Sheet)*
  - *Dioxane is considered to be not readily biodegradable (USEPA Problem Formulation and Initial Assessment for Dioxane, USEPA 2015)*

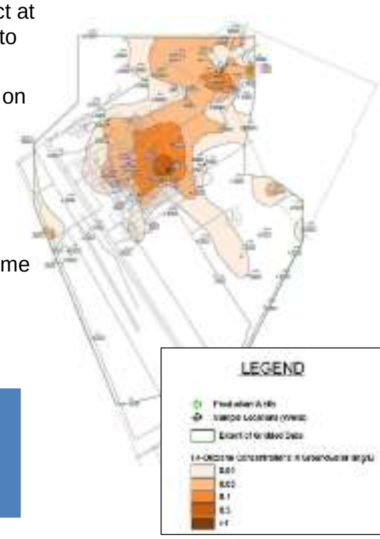


Page 23 AECOM

Polyester Manufacturing Plant /1,4-Dioxane Only

- Dioxane was generated as unwanted process byproduct at industrial facility that manufactured raw materials used to produce polyester
- Proposed MNA as sole remedy with leak control based on
  - No exposure risk
  - No off-site concern
  - >10 years of plume monitoring
  - Plume stability demonstrated
  - Site specific decay rates and predicted shrinking plume
- MNA approved in 2004 by state agency
- Plume has been shrinking as predicted, monitoring frequency reduced to 5 years

> - Investigation started in early 1990s
> - ~400- acre dioxane plume, largely contained on the 1,600-acre site
> - Iron reducing conditions
> - Degradation mechanisms were unknown

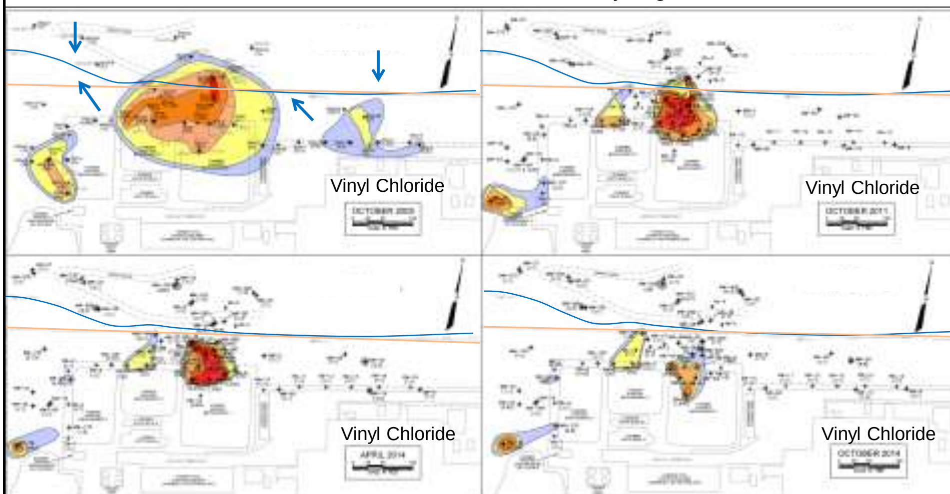


(Chiang et al, 2008)

Page 24 AECOM

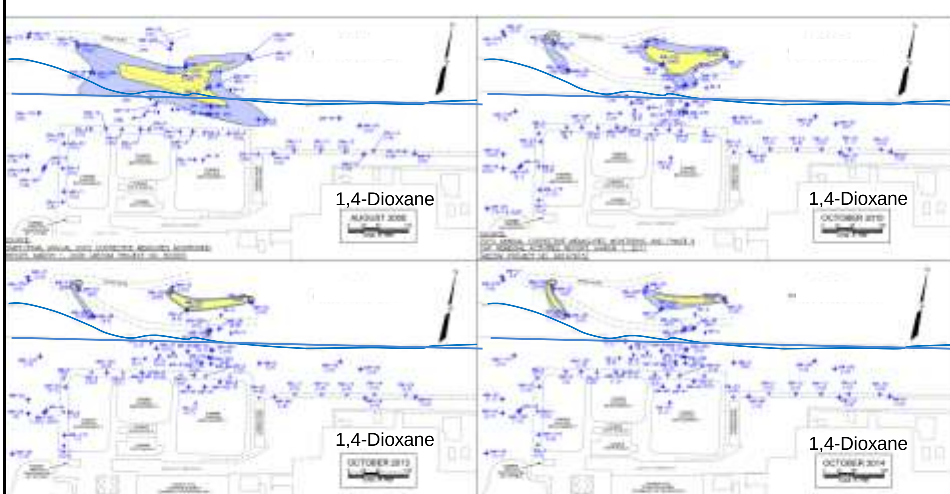
Industrial Site / ERD Remediated CVOCs

- Co-contaminants include TCE, DCEs, VC, total chromium
- 2006-Present: ERD
- Summer 2011: nZVI pilot study in the "Hot Spot" area
- May-July 2014: DPE and Recir. ERD
- No remedy targeted for dioxane



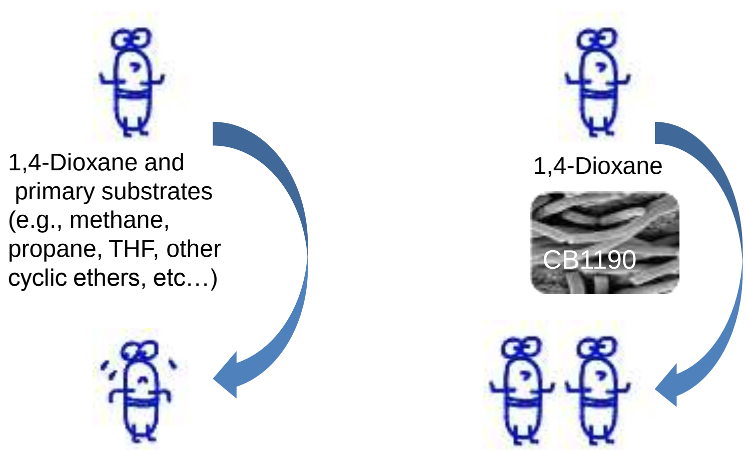
Industrial Site / 1,4-Dioxane

- High off-site dioxane concentrations
- CVOCs and dioxane may be from different sources
- Plume shrinkage after full-scale ERD (Why?)
- Dioxane plume remains off-site



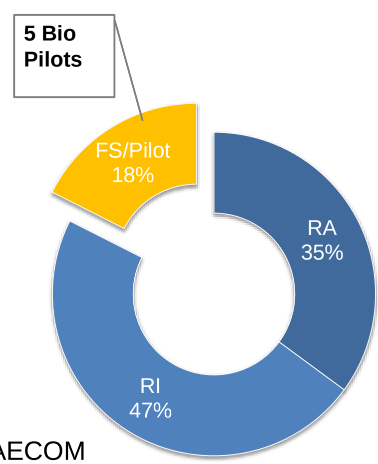
1,4-Dioxane is Aerobically Biodegradable

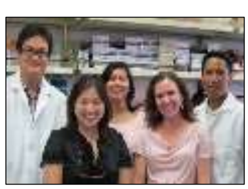
Co-Metabolic Biodegradation | Metabolic Biodegradation



Biodegradation Field Demonstrations

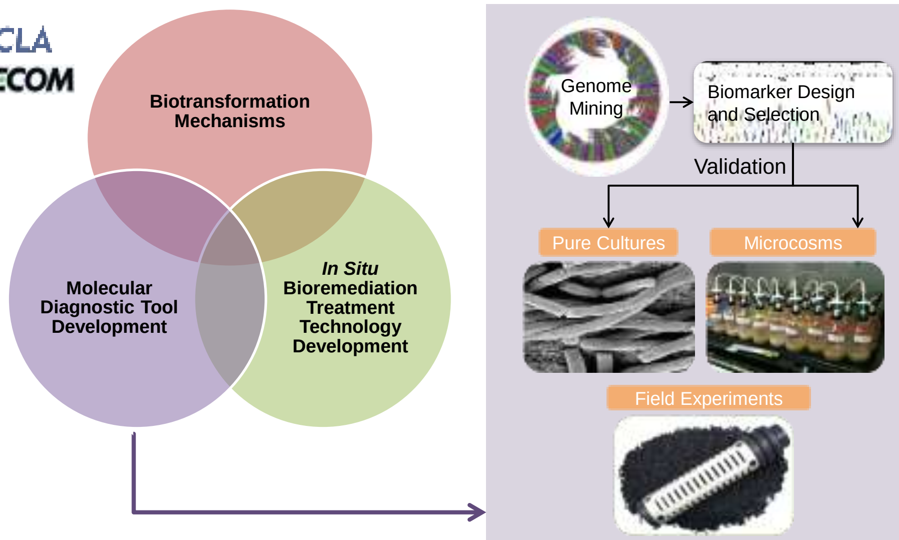
- Stable Isotope Probing to Verify MNA Potential (Chiang et al. 2012)
- Dioxane Biomarker Development (Gedalanga et al 2014)
- **Dioxane Biomarker Demonstrations**
- Cometabolic Biodegradation Pilot Studies
- CB1190 Bioaugmentation Pilot Study Updates (dioxane biodegrader)





UCLA and AECOM Team

Step Approach on Biomarker Applications

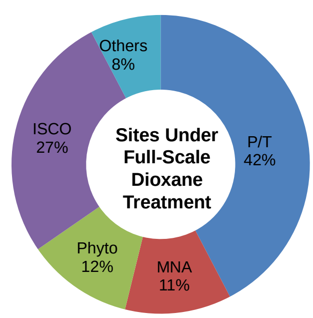


Contact Dora Chiang (dora.chiang@aecom.com) at AECOM for details

Page 29

Summary

- Current Technologies
  - Ex-situ advanced oxidation process
  - ISCO is proven and a feasible in-situ technology but polishing step is needed
  - Industry needs cost effective and sustainable options
- In-situ bioremediation is possible, but not widely applied, and no full-scale application yet
- MNA is possible but attenuation is not yet found ubiquitous, biotransformation needs to be differentiated from dilution
- Biomarkers and CSIA have been developed but more validation data are needed to confirm usefulness



Page 30