High Resolution Site Characterization of 1,4 Dioxane Sites using a New On-site, Real-time Analysis

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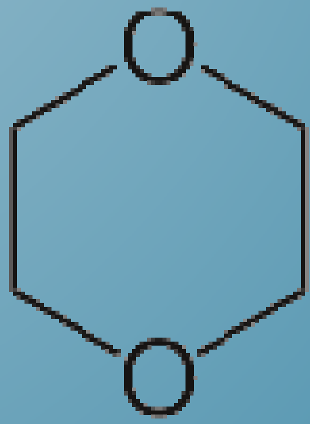
High Resolution Site Characterization of 1,4 Dioxane Sites using a New On-site, Real-time Analysis

- Brief history of 1,4 Dioxane use
- Why be concerned about 1,4 Dioxane
- Current regulatory environment
- Available methods for Soil and GW analysis
- Field analysis of 1,4 Dioxane using US EPA Method 8265
  Method Development and Validation
- Brief case study using on-site 1,4 Dioxane analysis
- Conclusions



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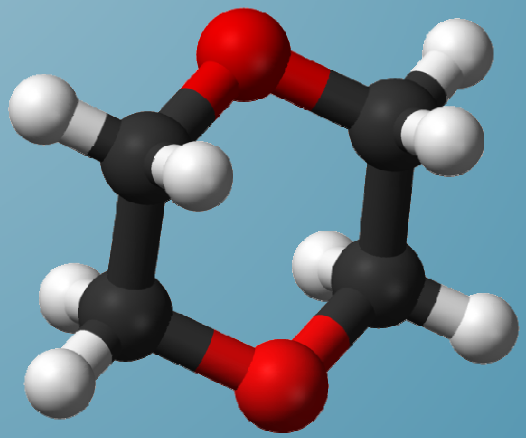
Brief History of 1,4 Dioxane and Its Use

- Cyclic ether, stable, totally miscible with water
- Identified in 1863, used primarily as a solvent from the 1920s to 1950s.
- 1960 – Used as a stabilizer for methyl chloroform (1,1,1 trichloro ethane, TCA) which would otherwise breakdown when exposed to metals (Al, Fe, Zn) particularly $AlCl_3$
- As much as 5 wt% in TCA
- Also used in some paint strippers, varnishes waxes and in cosmetics, deodorants and food additives



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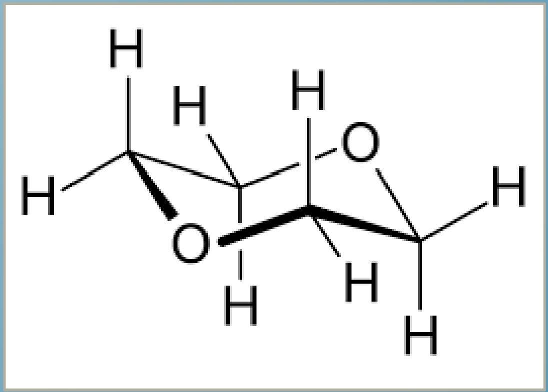
Why be concerned about 1,4 Dioxane

- Over 600,000 tons 1,1,1 TCA used at over 6000 Facilities
- California Public Water Supply survey 2004-2014 found **171 out of 1244** sampled active or standby drinking water supply wells containing 1,4 Dioxane, 168 of these > 1 ug/L (CA Notification Level)
- USEPA (2009) added 1,4 Dioxane to the Unregulated Contaminant List an indication that it may need to establish a MCL
- Drinking water suppliers are testing for 1,4 Dioxane under USEPA Unregulated Contaminants Monitoring Program
- US EPA Health Advisory Level of 0.35 ug/L
- Some states have already set Target Cleanup Levels for GW



Bottom Line:
Many closed TCA site are being re-investigated for 1,4 Dioxane

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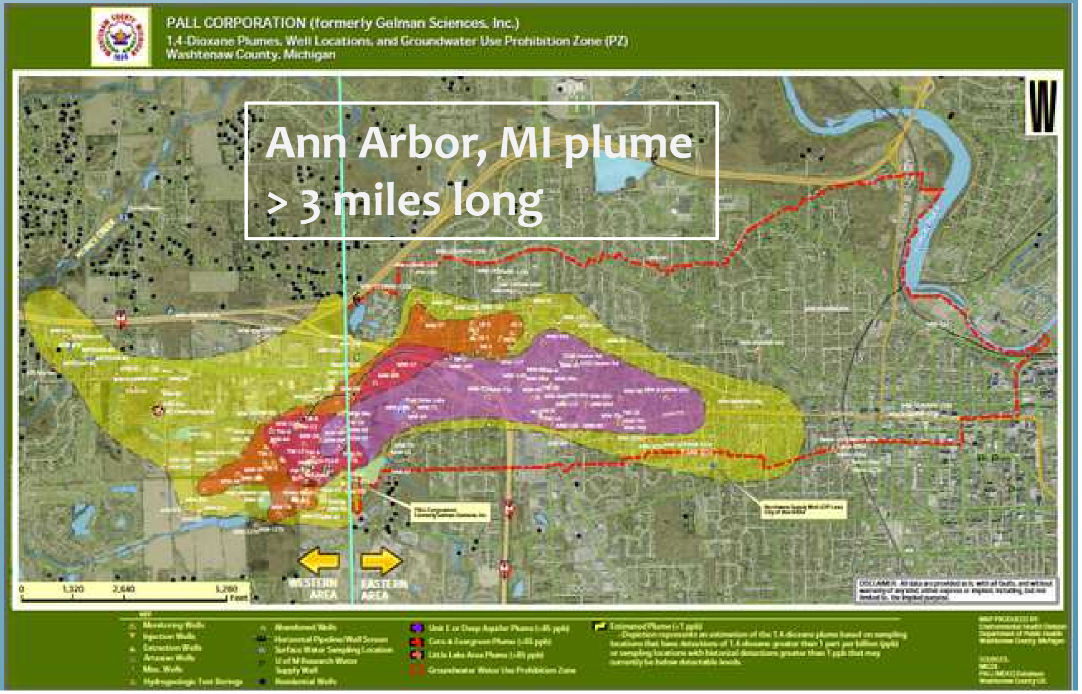
Current Regulatory Environment

- US Air Force 2008 AFCEE report listed 18 states and 3 US EPA Regions with Advisory, Guidance or Target levels for drinking water and GW
- Many states in the AFCEE report also had soil cleanup and soil threat to GW levels
- State levels for drinking water and GW from 0.35 to 16 ug/L
- US EPA IRIS 0.35 ug/L 10^{-6} cancer risk (2013)
- US EPA Drinking Water Screening Level at 0.67 ug/L (2013)



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Available Methods for Soil and GW Analysis of 1,4 Dioxane

MATRIX	METHOD	INSTRUMENTATION	LOD
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 w/ Heated headspace	2.5 µg/L (MDL)
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	
Water	EPA Method 1624	ID GC/MS	
Water	EPA Method 522	SPE, GC/MS-SIM	0.020 -0.036 µg/L (DL)
Soil, Water	EPA Method 625	GC/MS	

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Field analysis of 1,4 Dioxane using US EPA Method 8265

DSITMS is the basis of US EPA Method 8265

- No GC, 2-3 minute run times, purge/mass spectrometry for VOCs
- VOC analysis of GW, soil and vapor up to 80 client samples/day
- 1,4 Dioxane analysis up to 60 client samples per day with QC
- Rapid, accurate and precise
- Real-time **QUANTITATIVE** data to support real-time decisions in the field

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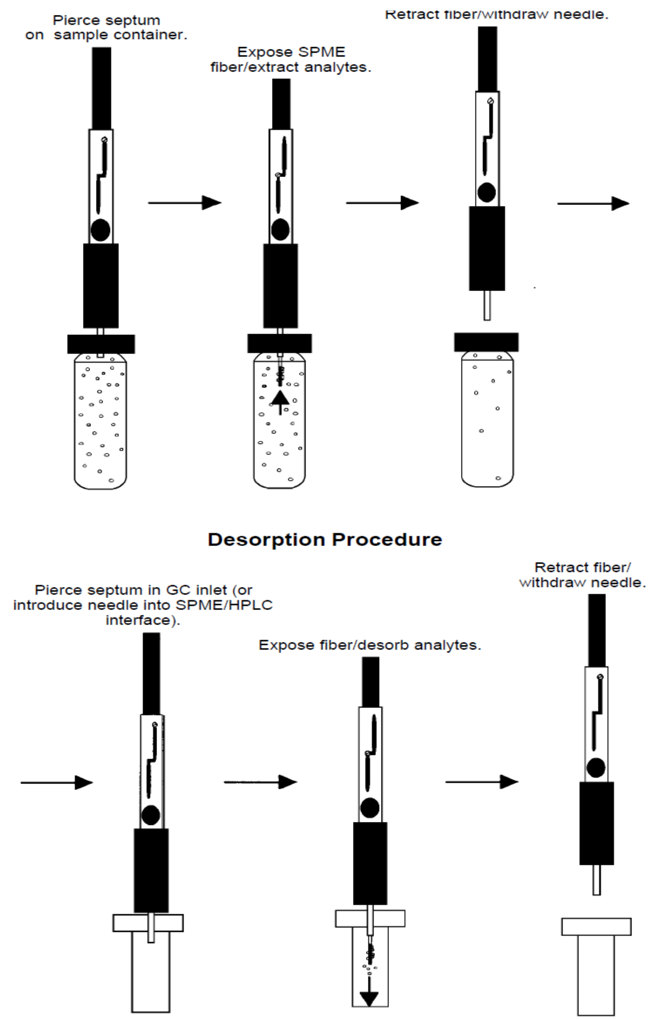
Field analysis of 1,4 Dioxane using US EPA Method 8265

Solid phase micro extraction (SPME)

- Contaminant extracted passively onto absorbent coated fiber
- Absorbed contaminant thermally desorbed into direct sampling ion trap mass spectrometer (DSITMS)
- 1,4 Dioxane identified by mass and quantified by DSITMS response

Solid Phase Micro Extraction



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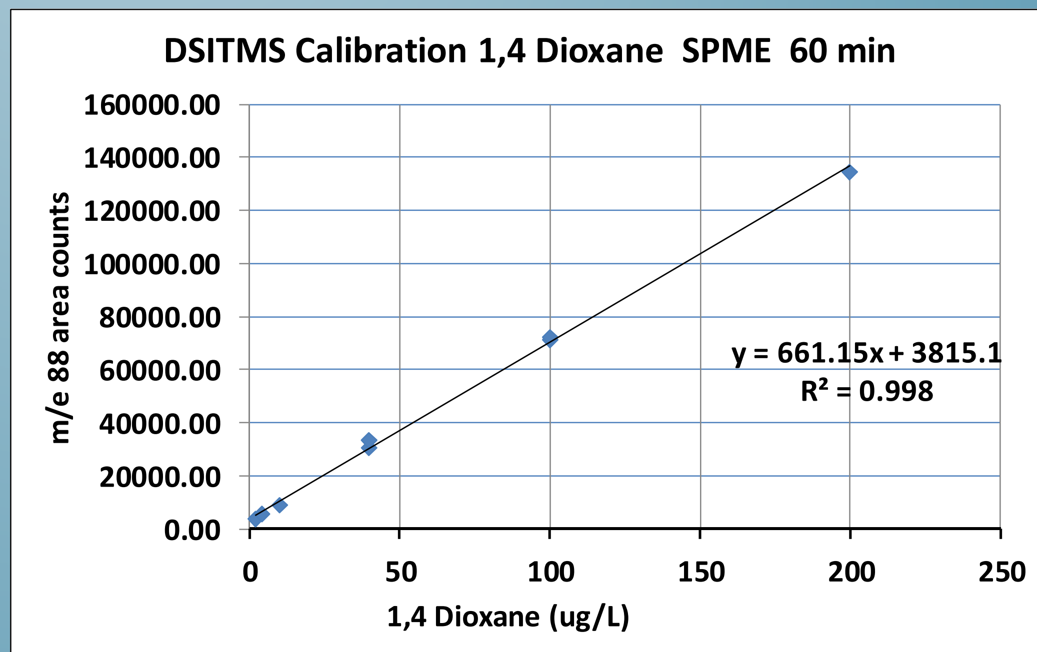
Field analysis of 1,4 Dioxane using US EPA Method 8265

- SPME extraction applicable to GW and soil extracted with water
- LODs of 2-5 µg/L for GW and 10-15 µg/L for soil
- SPME extraction can be performed after VOC analysis on same sample



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Method based on Shirey and Linton (J. Chrom. Sci., Vol 44, 444-450, 2006)

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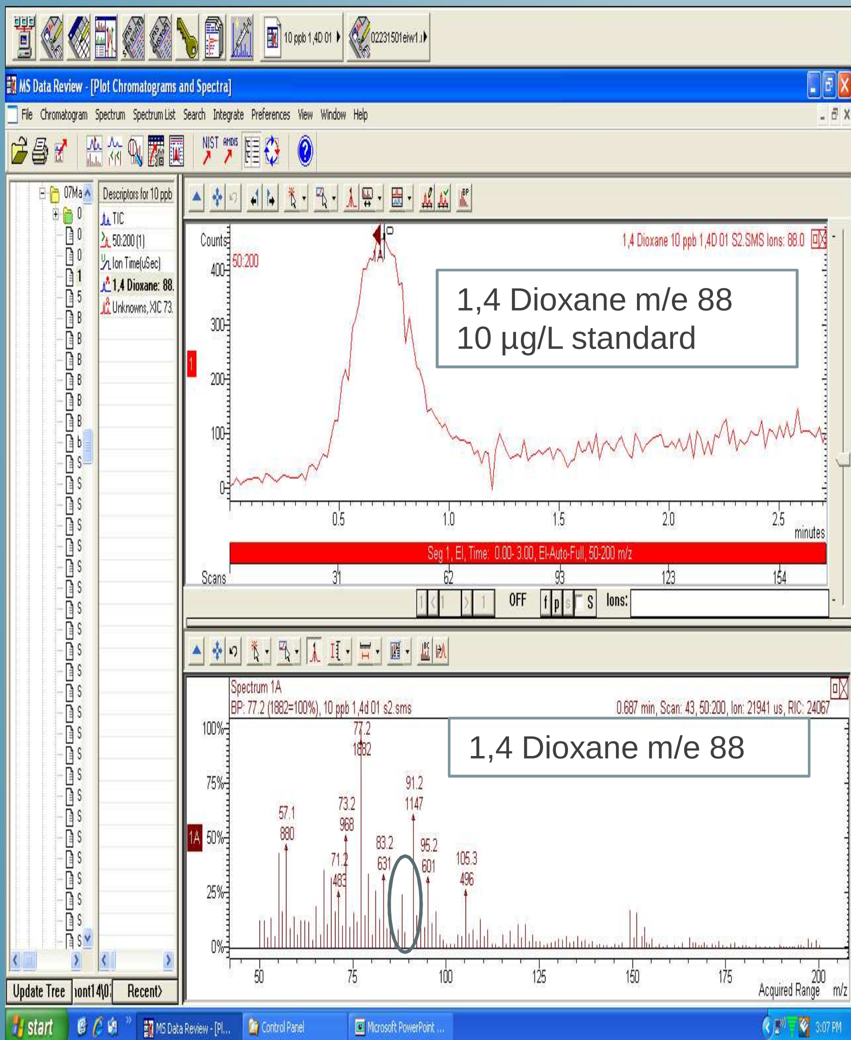
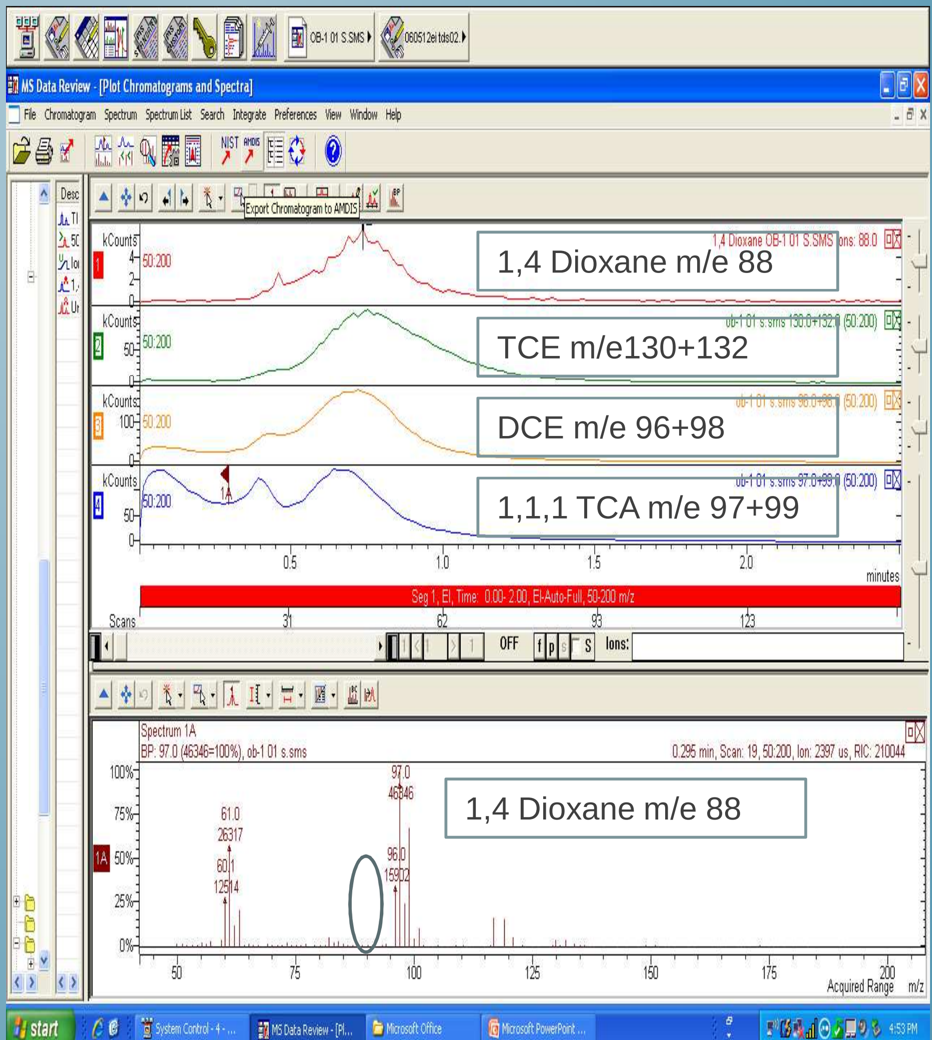
Field analysis of 1,4 Dioxane using US EPA Method 8265

Example DSITMS Response for Standards and Field Samples





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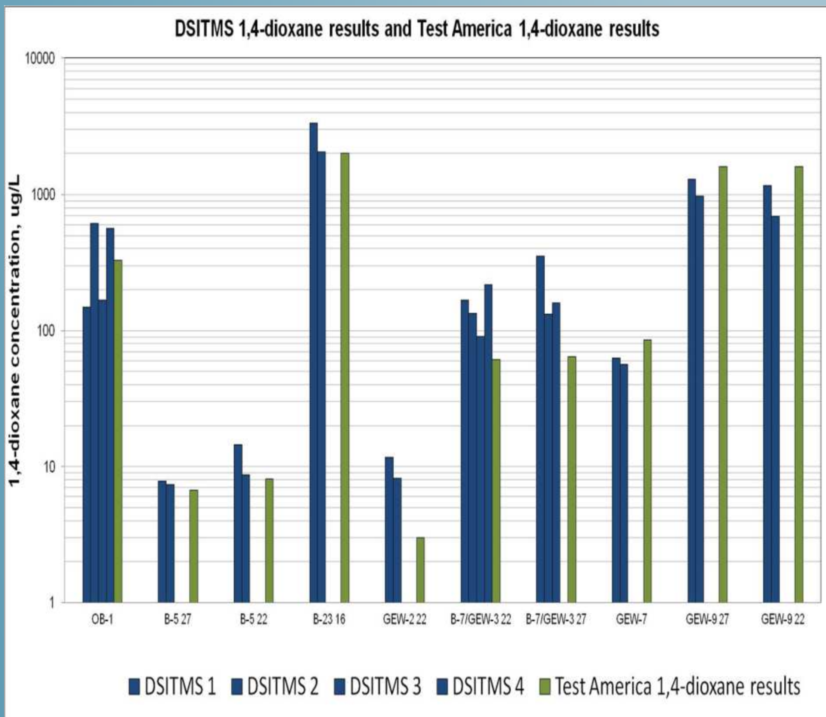
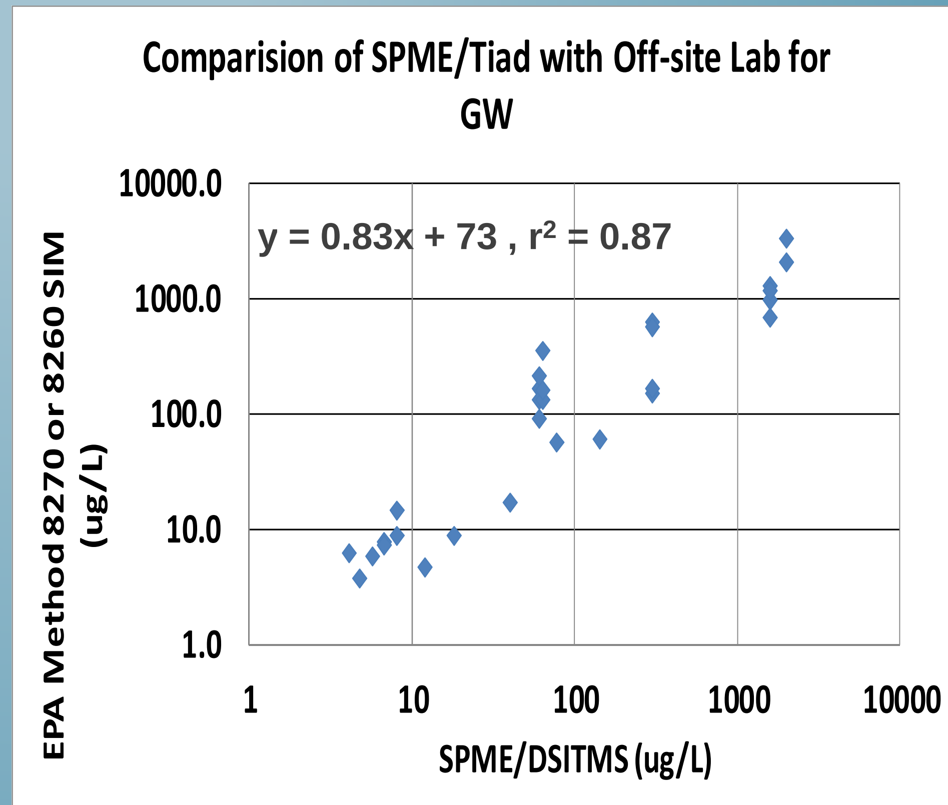
1,4 Dioxane SPME/DSITMS Method Validation Studies

Initial GW Validation Study



All GW Split samples to date



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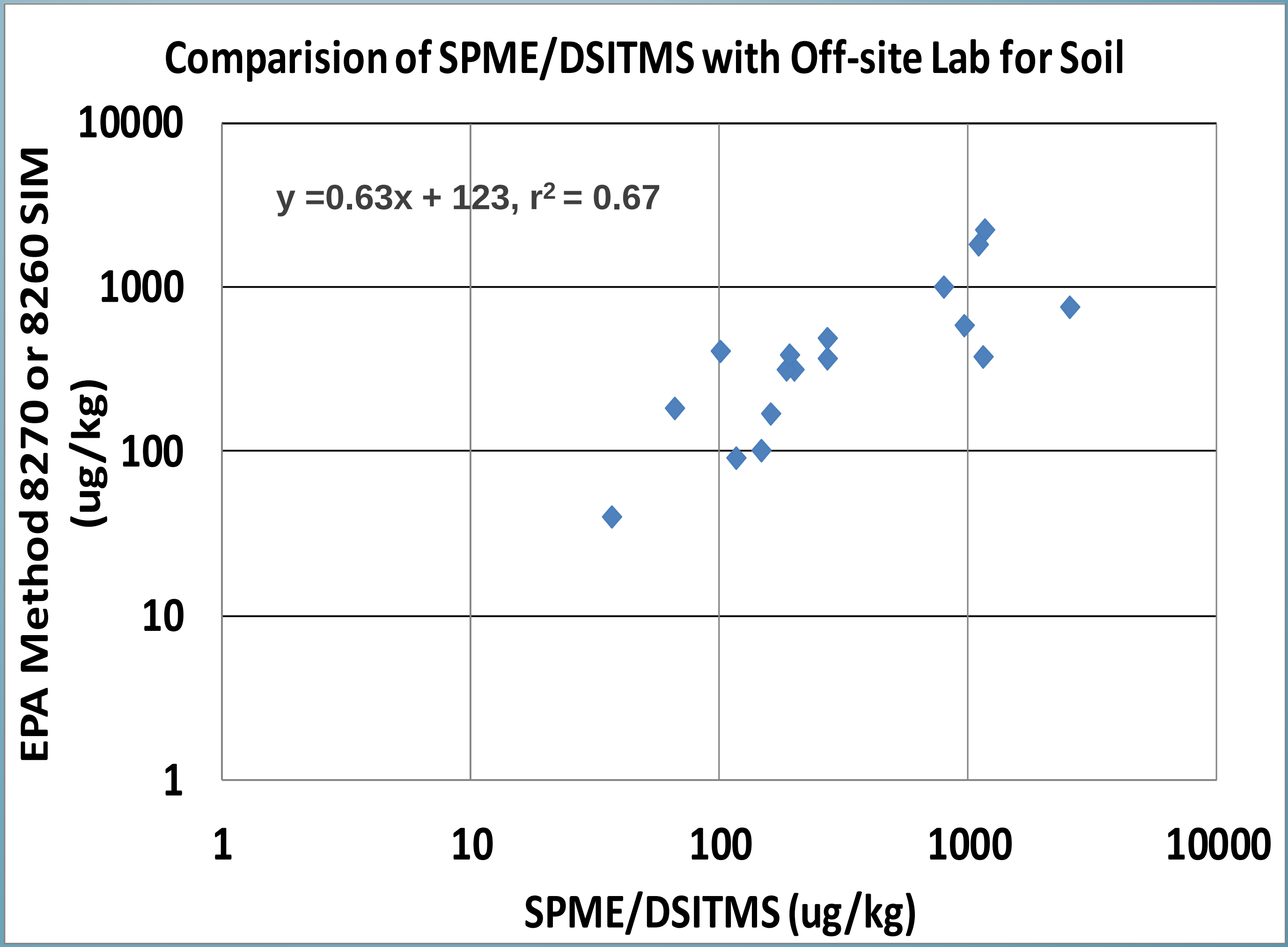
High Resolution Site Characterization of 1,4 Dioxane Sites using a New On-site, Real-time Analysis

1,4 Dioxane SPME/DSITMS Method Validation Studies

Soil samples collected co-located

Remember:

THERE IS NO SUCH THING AS A SOIL SPLIT SAMPLE w/o HOMGINIZING



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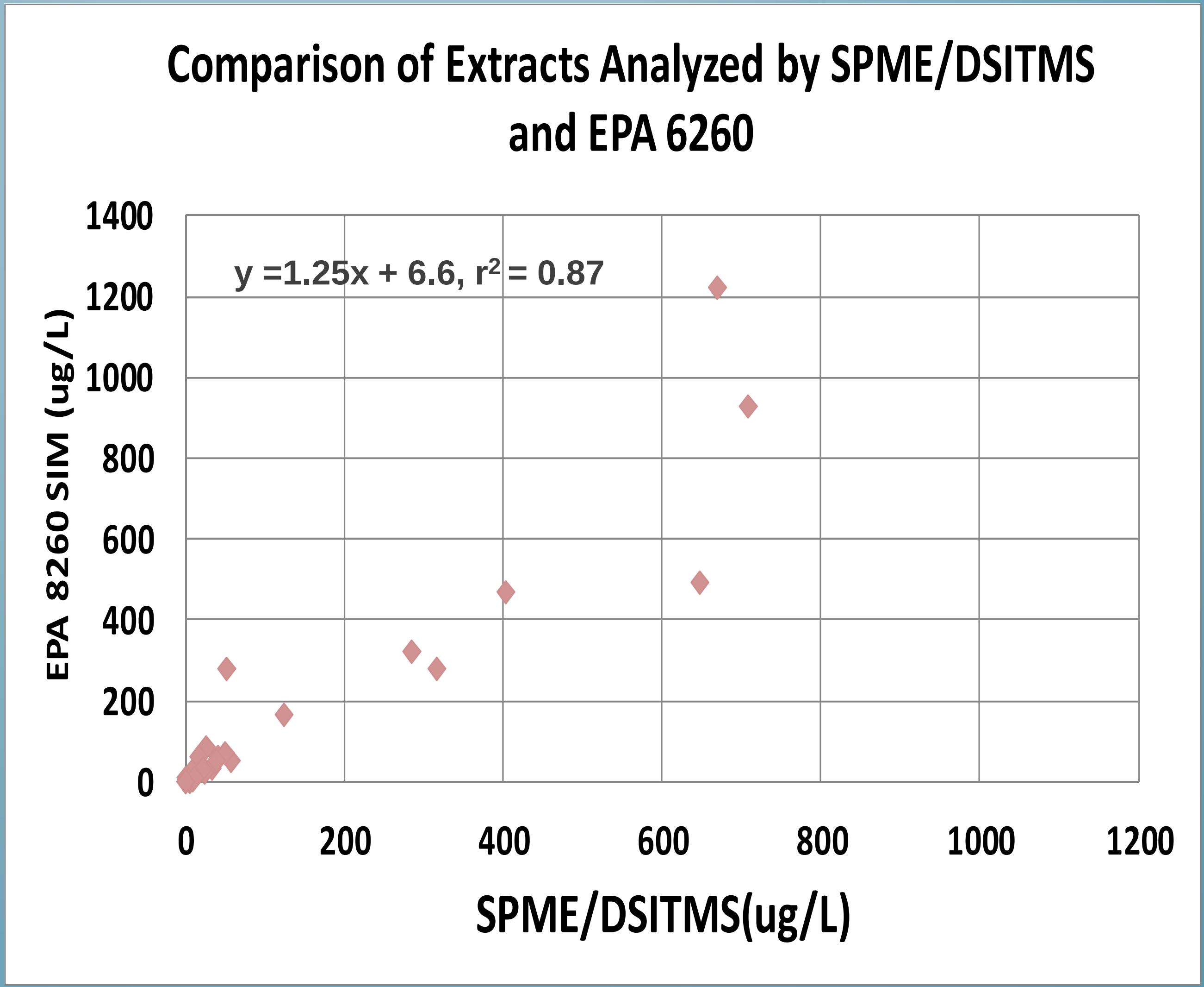
1,4 Dioxane SPME/DSITMS Method Validation Studies

Removed heterogeneity for soil samples collected co-located

Split extracts of soils between field analysis by SPME/ DISTMS and fixed lab heated head-space/EPA 8260



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Field analysis of 1,4 Dioxane using US EPA Method 8265

Methods development and validation indicate the SPME/DSITMS approach is capable of providing data to support real-time, on-site decision making

This analysis has supported rapid, cost effective development of high resolution data sets

Accurate, high resolution data sets allow project managers to develop accurate conceptual site models

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High Resolution Site Characterization of 1,4 Dioxane Sites using a high resolution New On-site, Real-time Analysis

Why you need 1,4 Dioxane data

Why measure permeability instead of gradient?

Hydraulic gradient

Top of mountain to bottom

Permeability

Actual path

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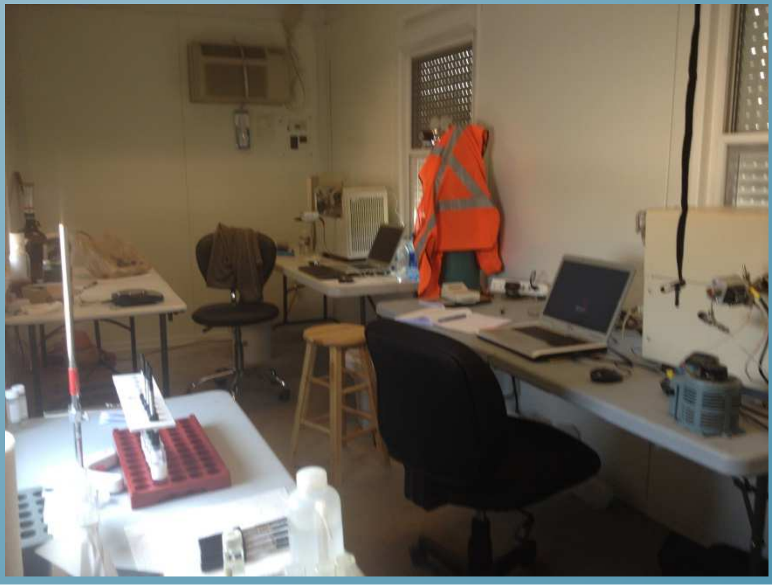
High Resolution Site Characterization of 1,4 Dioxane Sites using a New On-site, Real-time Analysis

Brief case study using on-site 1,4 Dioxane analysis

Summary of Field Work To Date using SPME/DSITMS Analysis

Site	Location	1,4 Dioxane	1,4 Dioxane	VOC	VOC	Field Days	Field Days
		Soil	GW	Soil	GW	1,4 Dioxane	VOC
1	CA	146	21	400		5	3.5
2	MI	831	9	549	9	15.5	9
3	CA	107				2	



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Brief case study using on-site 1,4 Dioxane analysis

Site History:

- Former manufacturing facility
- Previous investigations identified 1,4 Dioxane plume (> 1 mile)
- Source area identified but not yet characterized

Objectives:

- Delineate 1,4 dioxane source area
- Further characterize chlorinated VOC source

Approach:

- High resolution saturated soil sampling using two sonic drill rigs to approximately 100 ft BGS
- On-site 1,4 Dioxane and VOC analysis using EPA Method 8265

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High Resolution Site Characterization of 1,4 Dioxane Sites using a New On-site, Real-time Analysis

Brief case study using on-site 1,4 Dioxane analysis

On-site 1,4 Dioxane and VOC analysis using EPA Method 8265

- Two DSITMS instruments with operators; one for 1,4 Dioxane and one for VOCs
- Predominantly saturated soil sampling with modified US EPA Method 5035 aqueous extraction
- VOCs and 1,4 Dioxane analyzed on single sample extract
- 831 soil (25 locations) and 9 GW 1,4 dioxane in 15.5 field days
- 549 soil (15 locations) and 9 GW VOC in 9 field days

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High Resolution Site Characterization of 1,4 Dioxane Sites using a New On-site, Real-time Analysis

Brief case study using on-site 1,4 Dioxane analysis

Significant costs savings realized using on-site 1,4 Dioxane analysis

- Real-time data allowed dynamic work strategy to locate sampling points
- On-site 1,4 Dioxane analysis saved enough compared to two week off-site analytical costs to pay for the sonic drilling program (> $125K)

Investigation Findings

- Limited 1,4 Dioxane source mass remaining in perched zone – unlikely to leach
- No hotspots in deep overburden
- Footprint of source area plume smaller than original estimate

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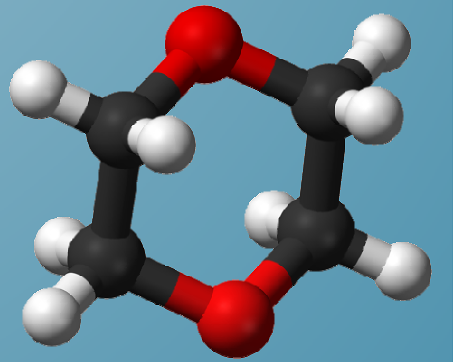
Conclusions

Regulatory enforcement at sites with 1,4 Dioxane contamination underway at many sites and is immanent at many others

Experience with other contaminants (VOCS, MTBE and others) supports the collection of high resolution data

High resolution CSMs greatly increase the success of and reduce the costs of site remediation

A cost effective on-site analysis is now available to provide high resolution CSMs for 1,4 Dioxane contamination in soil and GW



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Questions

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