Long Term Stability of 1,4-Dioxane and Analysis by GC/MS-SIM SPME

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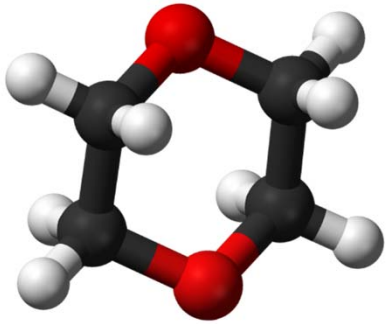
1,4-Dioxane

Properties

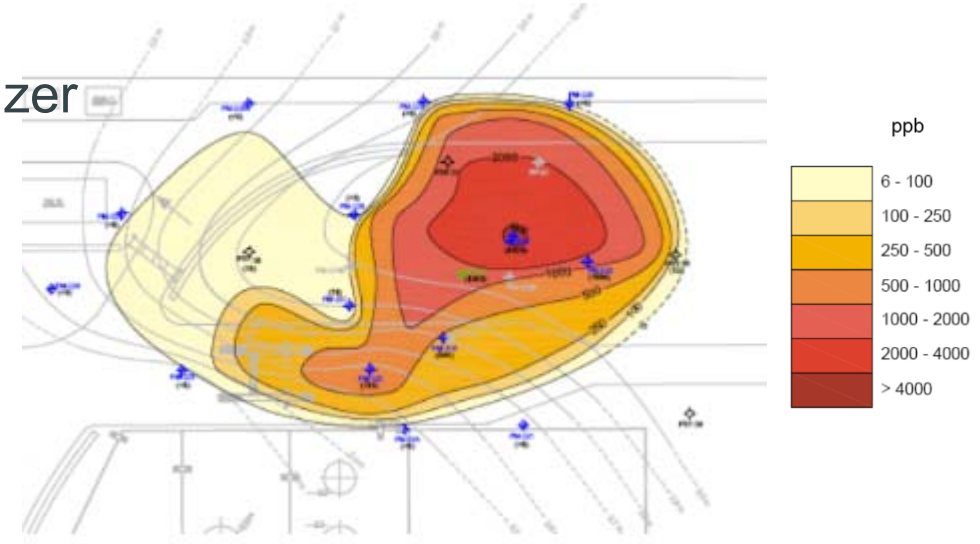
- Cyclic ether
- Miscible in water
- Highly mobile
- Volatile organic compound
- Recalcitrant to degradation



1,4-Dioxane

Pathways to release

- Storage tank release
  - Up to % level groundwater
- Chlorinated compound stabilizer
  - Potential co-elution issues
  - Lower relative concentration
- Personal care products
  - Groundwater at trace levels



Regulatory Approaches to Analysis

EPA 624/8260 with Purge and Trap

- RL ~250 ug/L scan
- RL ~1 ug/L SIM
- Poor purging efficiency
- 7 to 14 day hold time
- No headspace
- Kept at 0-6C
- High solids pose an issue
- Isotope dilution needed for accurate results
  - Recovery varies ~75%

Atomx P&T – 5mL volume

Regulatory Approaches to Analysis

EPA 625/8270 with Liquid/Liquid extraction

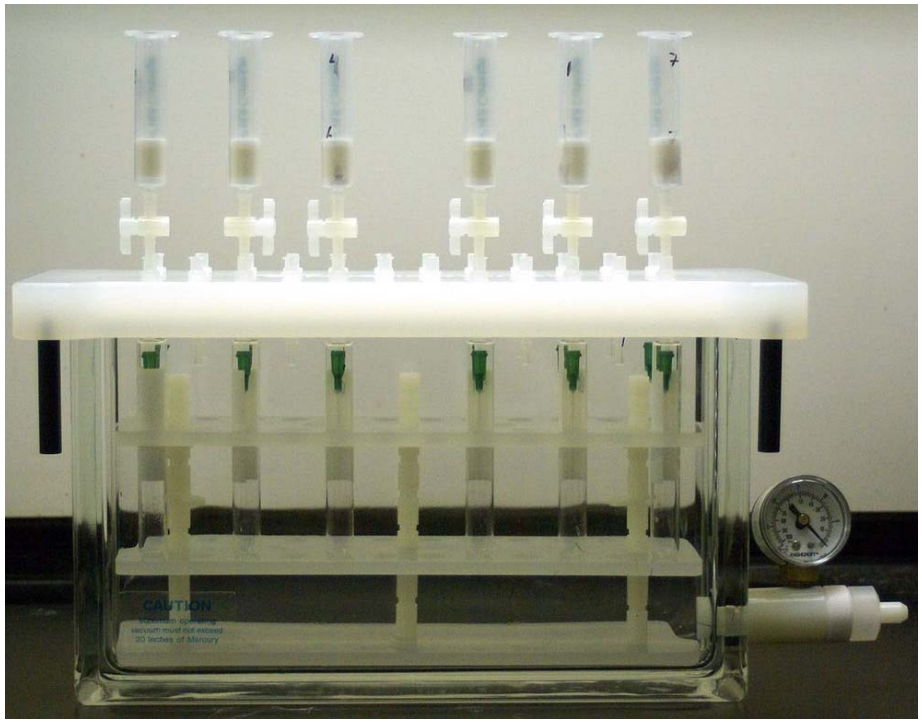
- RL ~5 ug/L Scan
- RL ~0.2 ug/L SIM
- Consumes 150+ mL solvent
- Limited throughput
- 7 day hold time
- Kept at 0-6C
- Requires significant sample volume
- Isotope dilution needed for accurate results
  - Recovery varies ~50%

Thom, the co-op

Regulatory Approaches to Analysis

EPA 522 for drinking water

- SPE with GC/MS-SIM
- RL ~0.15 ug/L
- d8-THF as ISTD
- d8-1,4-D as Surrogate
  - Recovery is good, but ID is better
- Limited throughput
- 28 day hold time
- Kept at 0-6C



By Jeff Dahl - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=3055299

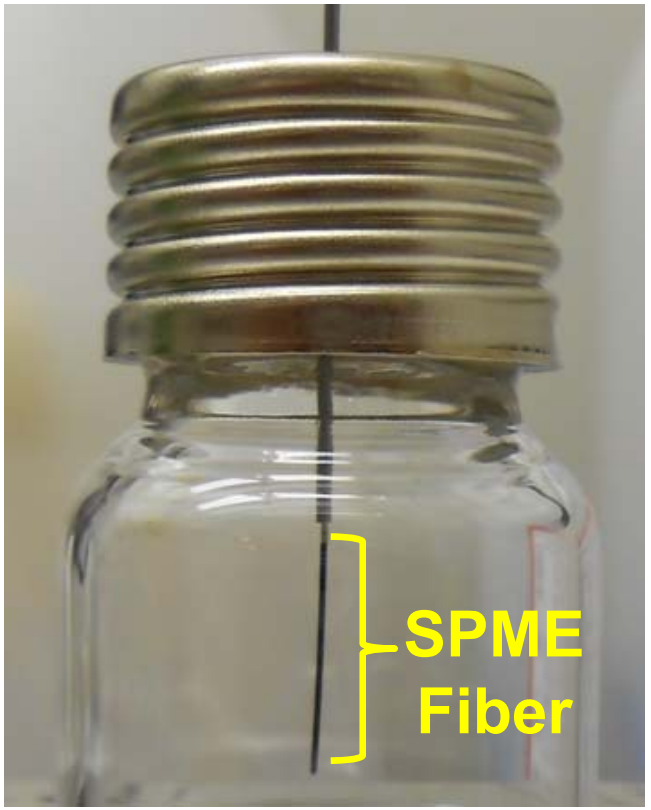
Logistical Challenges

- Sample shipment internationally takes time, luck, courage
- Plume mapping benefits from many samples
- Real time results maximize efficiency of sampling event
- Isotope dilution for accuracy and precision
- If 1,4-dioxane acted the way that hold times indicate, we'd all be happier

GC/MS-SIM SPME

Gerstel MPS2 autosampler for automation

- Supelco “Light Blue” CAR/PDMS 85 um/23 ga
- 10 mL sample
- 4 ug d8-1,4-dioxane
- 0.1 ug $^{13}C_4$-1,4-Dioxane
- 2.5 g NaCl
- 55C headspace extraction for 10 min
- Desorption for 1 min
- Condition for 5 min at 260C
- Batch process with MassHunter for speed



GC/MS-SIM SPME

GC Column:

RTX-Volatiles 30 m x 0.25 mm x 1 µm with 1.3 mL/min He

Inlet:

1.6 mm Topaz SPME liner, 260C, 2:1 split

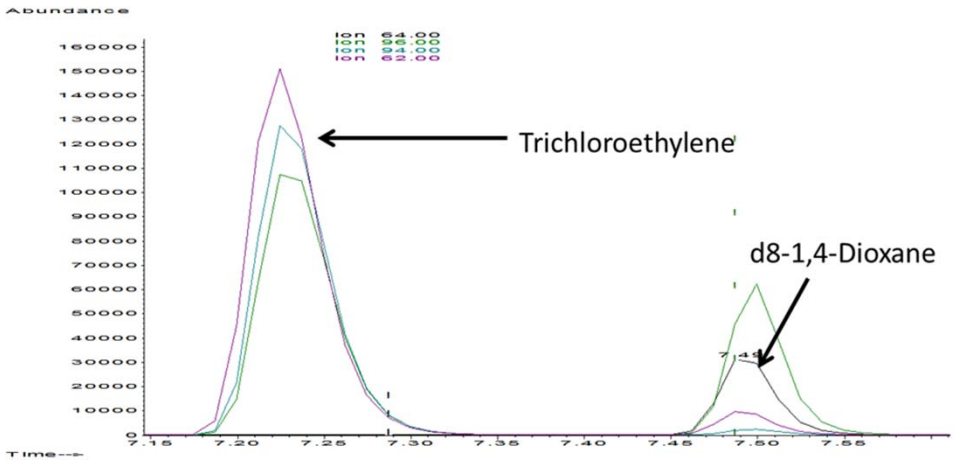
Oven:

40C for 4 min, then 8C/min to 120C, then 30C/min to 270C, hold 1 min

MS:

SIM – 58, 61, 64, 88, 92, 96 at 60 ms dwell

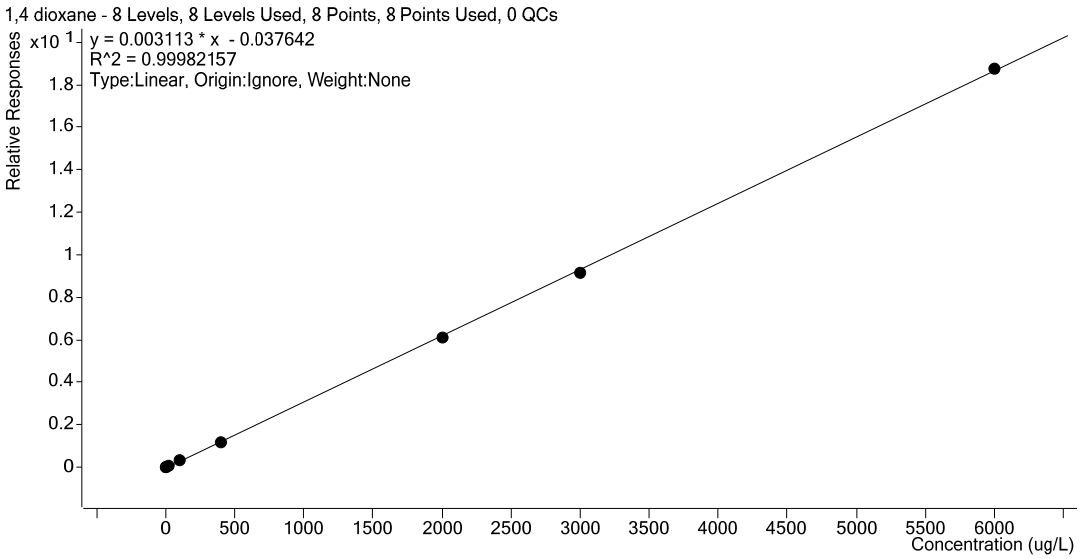
Method used on Agilent 5973, 5975, and 5977 MSD

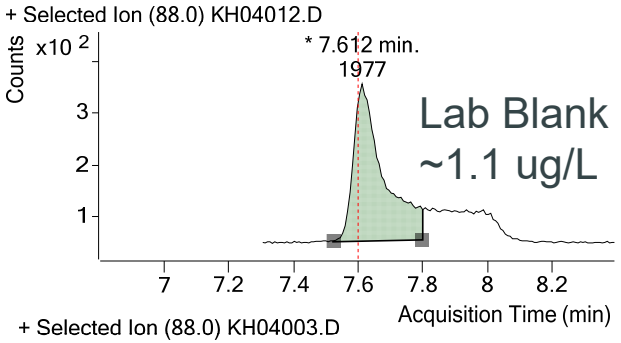


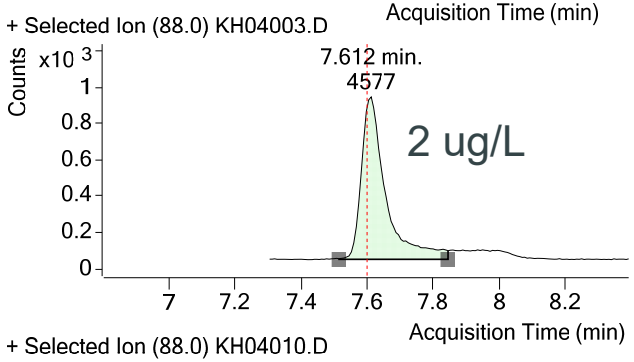
DL and Linearity

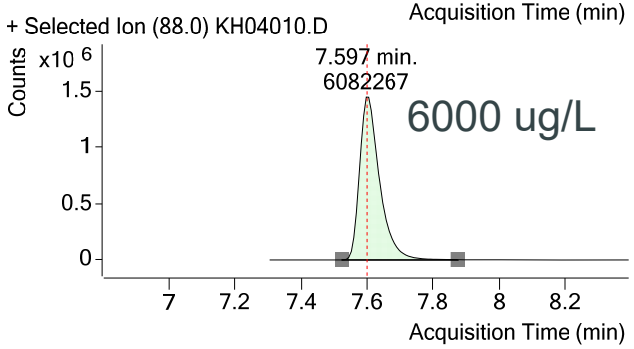
Routine PQL at 2 ug/L for 10 mL sample

Linear range 2 to 6000+ ug/L

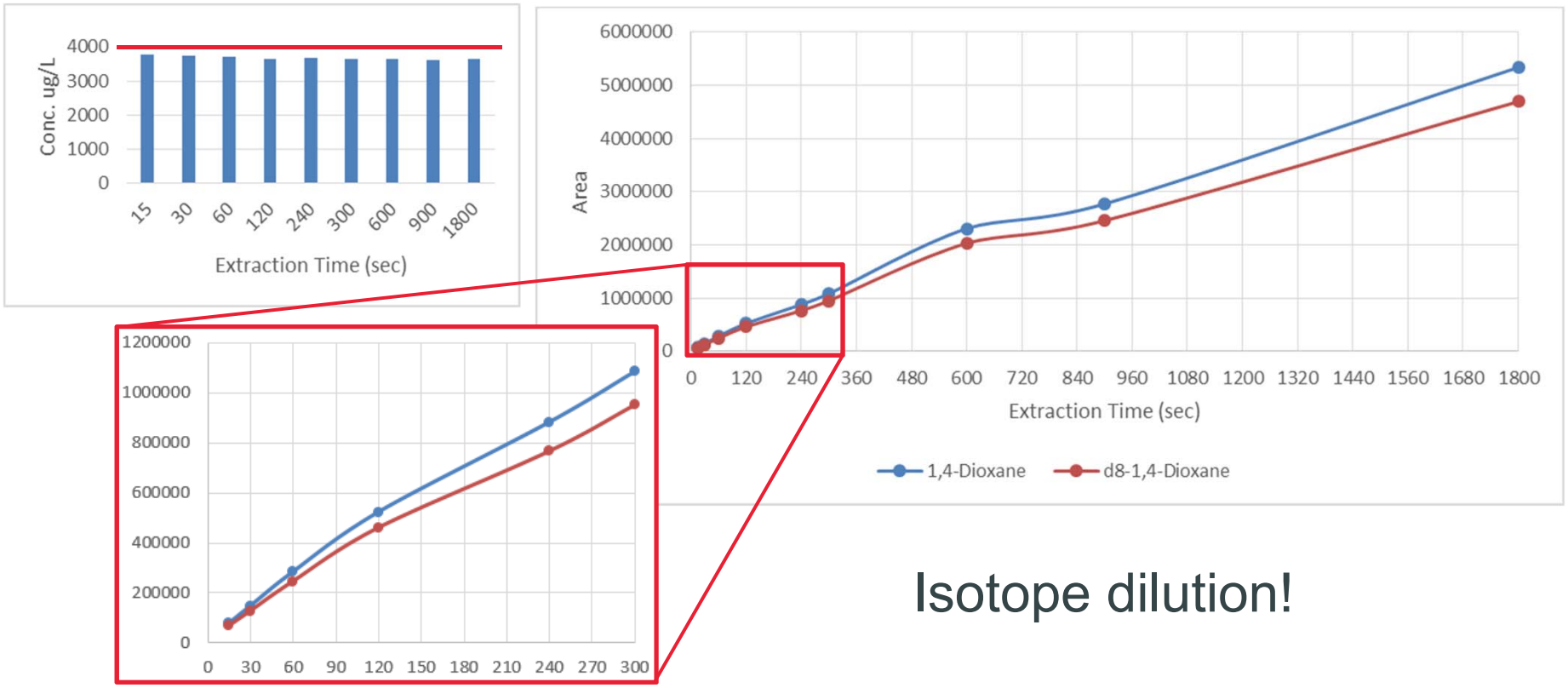








SPME Extraction Efficiency



Isotope dilution!

Cost per Analysis

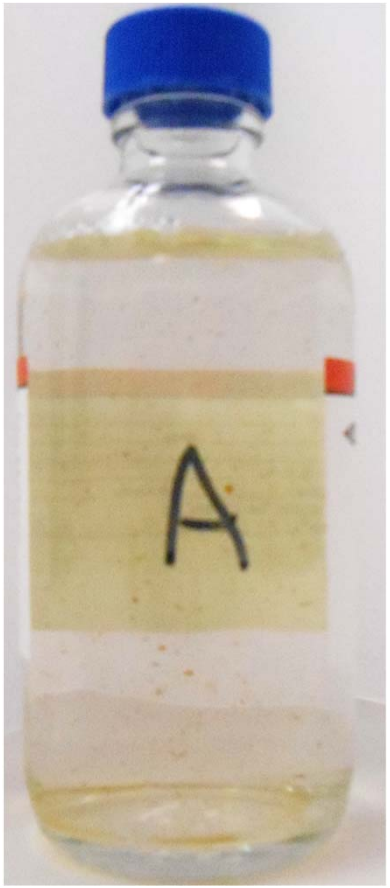
ISTD d8-1,4-Dioxane	$0.04/sample	Analyst time	5 min
SURR $^{13}C_4$-1,4-Dioxane	$0.01/sample	Instrument time	30 min
Salt	$0.05/sample		
SPME fiber (300 injections)	$0.53/sample	~48 samples/day on GC	
Vials/caps	$1.50/sample		
Solvent	~$0/sample		

Under $3/sample materials/supply

PT Samples

"A" sample ~30 ppb

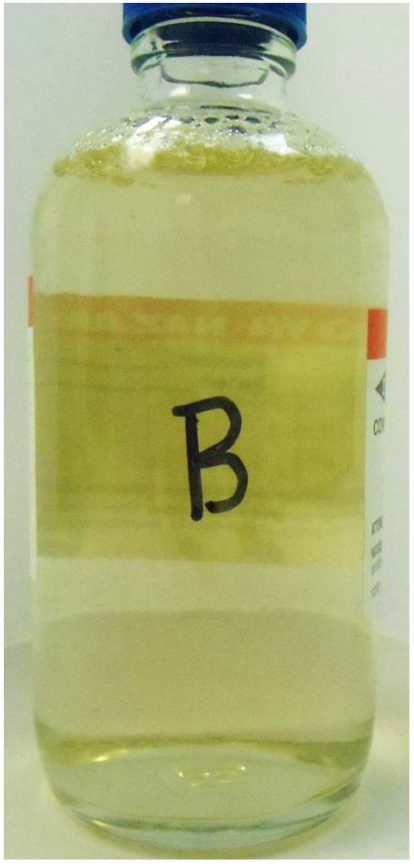
- 25 groundwater samples from SA wells with Trichloroethene contamination
- Stored with headspace
- Filtered at 1.2 um
- pH ~7



PT Samples

"B" sample ~ND at 2 ppb

- Moderate salinity industrial effluent composite from NA
- Stored with headspace
- Filtered at 1.2 um
- pH ~8



PT Samples

"C" sample ~14,000 ppb

- Blend of 1 SA and 1 EU well each with HPLC water dilution
- Stored without headspace (mostly)
- Filtered at 1.2 um
- pH ~6

Year 6 Analysis (2017)

- Samples prepared in triplicate
- Analysis by GC/MS-SIM SPME
- Samples stored with headspace
- Ambient samples stored in cabinet

Sample	Concentration (ug/L)
A27-1 Warm	29
A27-2 Warm	26.8
A27-3 Warm	26.5
AVG	27.4
STDEV	1.41
RSD	5.10%

Sample	Concentration (ug/L)
A29-1 Cold	25.4
A29-2 Cold	24.1
A29-3 Cold	25.3
AVG	24.9
STDEV	0.76
RSD	3.10%

2011 Avg ~27 ppb (n=11)

No significant difference between initial samples, 6 year old sample, or 6 year ambient storage samples

Year 6 Analysis (2017)

- Samples prepared in triplicate
- Analysis by GC/MS-SIM SPME
- Samples stored with minimal headspace
- Ambient samples stored in cabinet

Sample	Concentration (ug/L)
C17-1 Warm	12600
C17-2 Warm	12700
C17-3 Warm	12700
AVG	12700
STDEV	97.9
RSD	0.80%

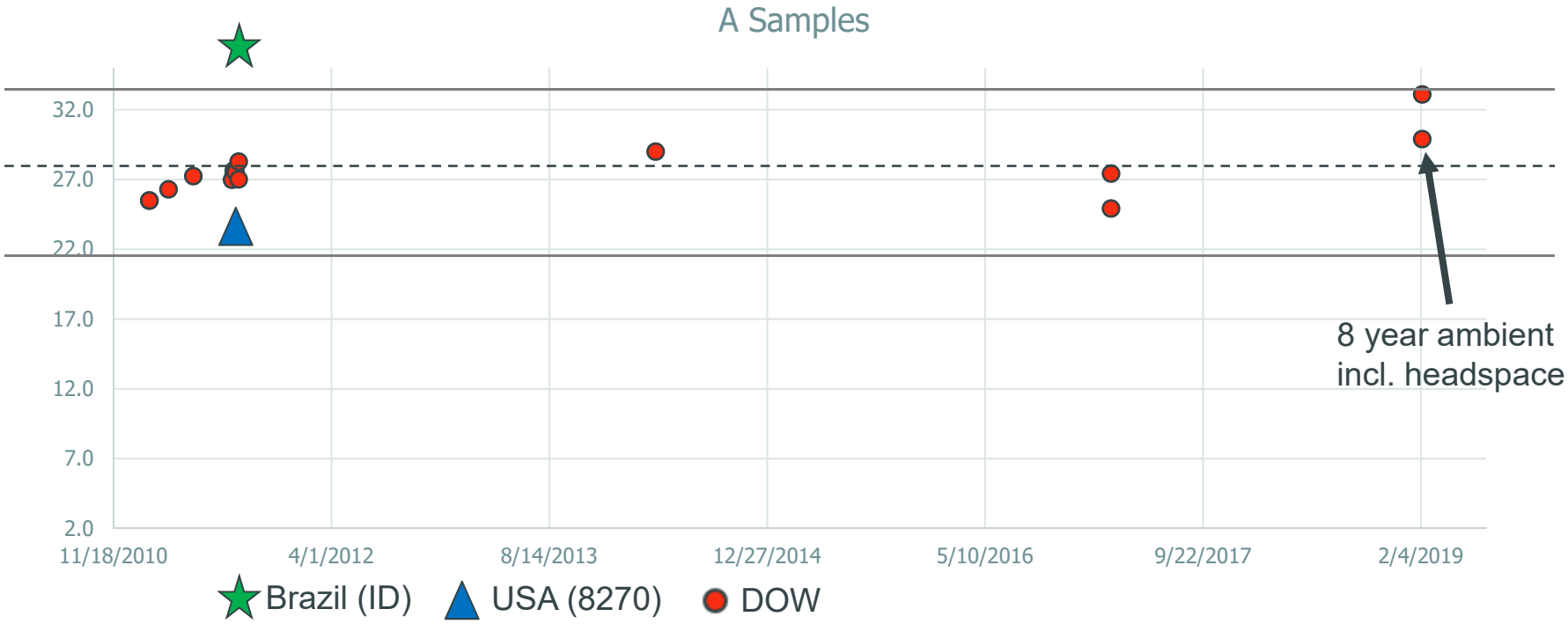
Sample	Concentration (ug/L)
C22-1 Cold	12600
C22-2 Cold	12500
C22-3 Cold	12400
AVG	12500
STDEV	93
RSD	0.70%

2011 Avg ~12900 ppb (n=11)

No significant difference between initial samples, 6 year old sample, or 6 year ambient storage samples

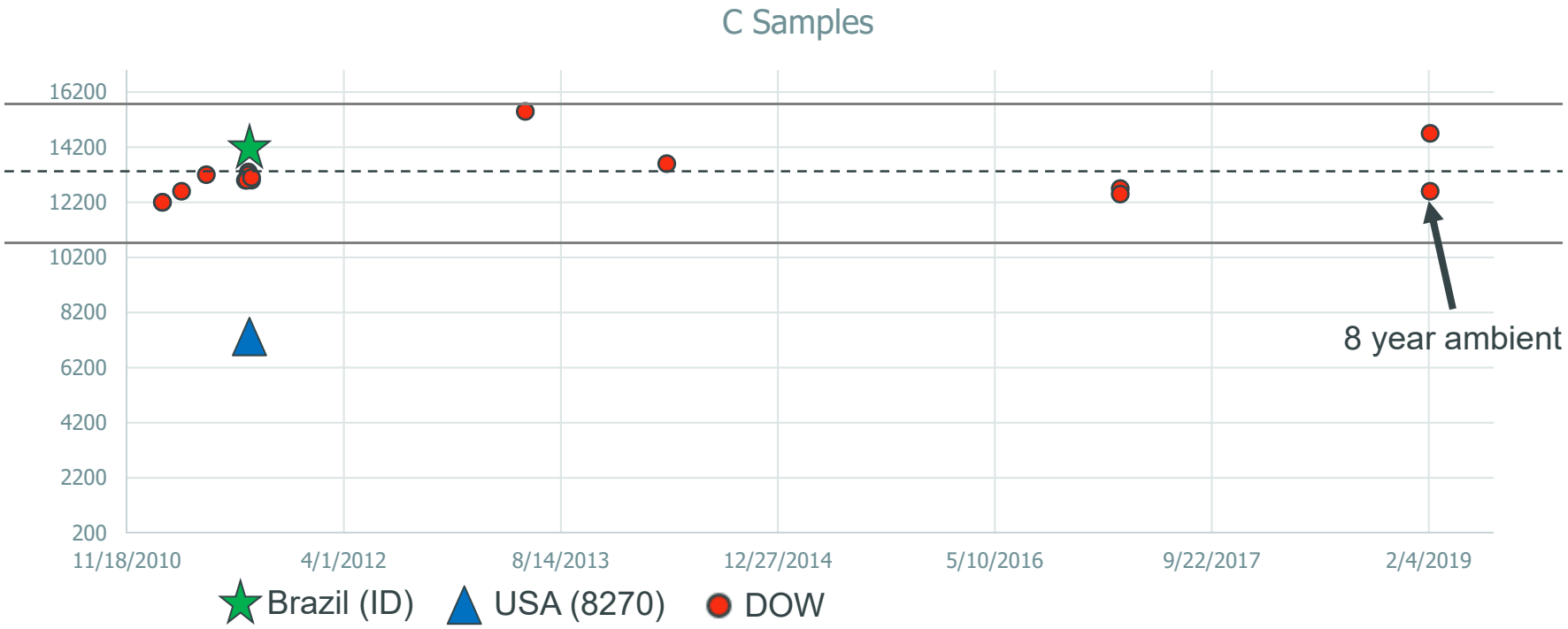
8 Year Trend

Average	27.8 ug/L
+3xSTDEV	33.4 ug/L
-3xSTDEV	21.7 ug/L



8 Year Trend

Average 13100 ug/L
+3xSTDEV 15700 ug/L
-3xSTDEV 10600 ug/L



Conclusion

GC/MS-SIM HS-SPME offers a robust, sensitive, and inexpensive way to analyze water samples for 1,4-dioxane.

1,4-dioxane, without microbial degraders, remains stable for several years in aqueous samples. Acid preservation could be beneficial.

Investigatory samples could remain viable for several years.

PT samples could remain useful for a decade.

Thank You

Questions?