THE PROBLEM WITH 1,4-DIOXANE

AUGUST 11, 2016

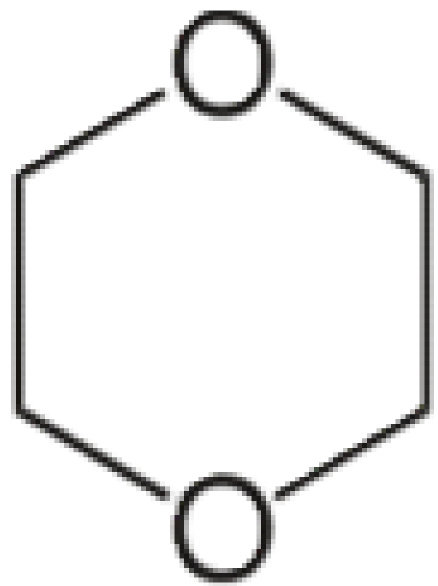
Agenda Sample

SOLUTIONS YOU CAN COUNT ON. PEOPLE YOU CAN TRUST.

- Introductions
- Characteristics of 1,4-Dioxane
- About 1,4-Dioxane
- Methodology
- Regulatory Standards
- DOW Chemical PT Study

About 1,4-Dioxane

- Found in personal care products, shampoos, cosmetics, paint strippers, grease, waxes, etc..
- Organic solvent - Was used as a stabilizer for 1,1,1-Trichloroethane
- Has been found in groundwater sites throughout the US
- Listed as an emerging contaminant in 2008 (EPA)



Trihydro

About 1,4-Dioxane

Exhibit 1: Physical and Chemical Properties of 1,4-Dioxane
(ATSDR 2012; Howard 1990; HSDB 2011)

Property	Value
Chemical Abstracts Service (CAS) Number	123-91-1
Physical Description (physical state at room temperature)	Clear, flammable liquid with a faint, pleasant odor
Molecular weight (g/mol)	88.11
Water solubility	Miscible
Melting point (°C)	11.8
Boiling point (°C) at 760 mm Hg	101.1 °C
Vapor pressure at 25°C (mm Hg)	38.1
Specific gravity	1.033
Octanol-water partition coefficient (log K_{ow})	-0.27
Organic carbon partition coefficient (log K_{oc})	1.23
Henry's law constant at 25 °C (atm-m^3/mol)	4.80×10^{-6}

Abbreviations: g/mol – grams per mole; °C – degrees Celsius; mm Hg – millimeters of mercury; atm-m^3/mol – atmosphere-cubic meters per mole.

https://www.epa.gov/sites/production/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf

Physical and Chemical Characteristics

Flammable Liquid
When exposed to Air or Light

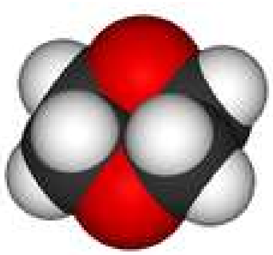
Unstable at Elevated Temperatures and Pressures

Weakly Retarded by Sorption to Soil Particles

Soluble / Miscible in Water

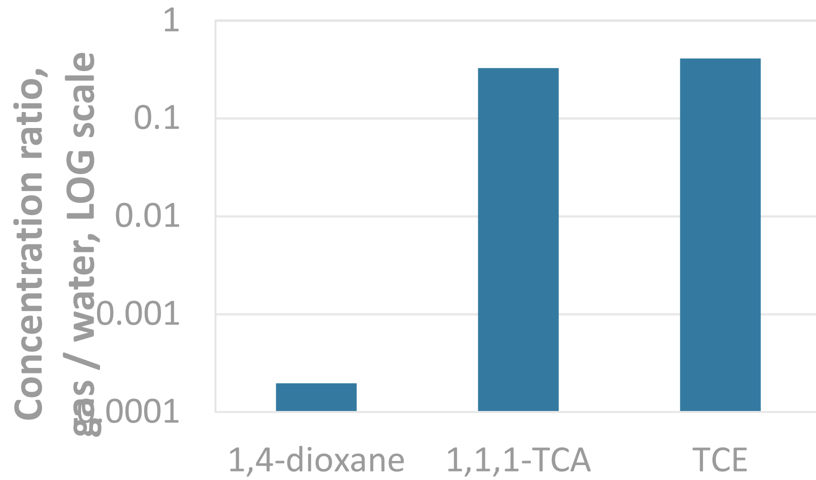
Boiling Point near Water

Low Vapor Pressure related to boiling point



1,4-Dioxane Chemical Properties: Henry's Law

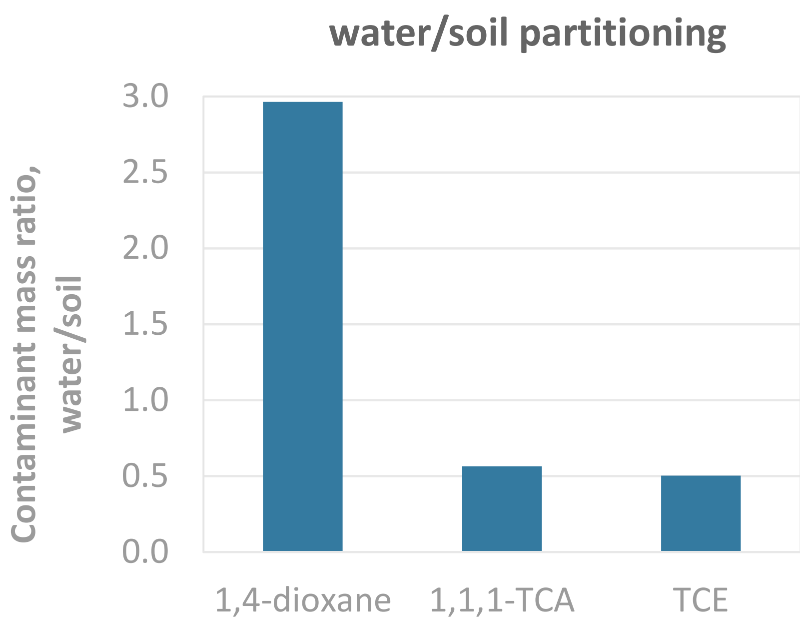
Very low Henry's Law constant, so 1,4-dioxane strongly prefers aqueous phase vs. gaseous phase



Howard, P. *Handbook of Env. Fate & Exposure Data for Org. Chem.* 1990; Martinez-Huitle and Andrade. *Quimica Nova.* 2011

1,4-Dioxane Chemical Properties: Sorption

- 1,1,1-Trichloroethane and Trichloroethylene can be indicators of 1,4-dioxane
- Does not sorb to soils but easily leaches from soil to groundwater
- Transported at rate similar to groundwater seepage velocity
- Typically found at leading edge of plumes
- Sorption to activated carbon is less effective

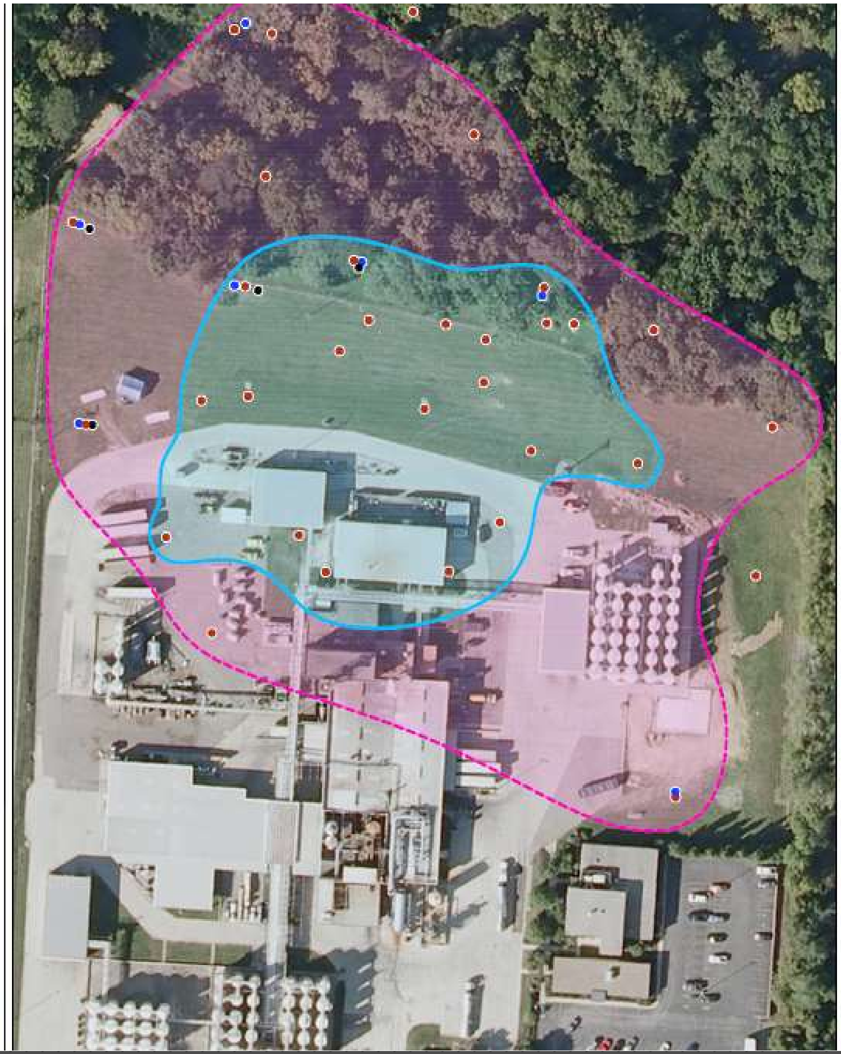


Howard, P. Handbook of Env. Fate & Exposure Data for Org. Chem. 1990; Martinez-Huitle and Andrade. Quimica Nova. 2011

Example Project Site

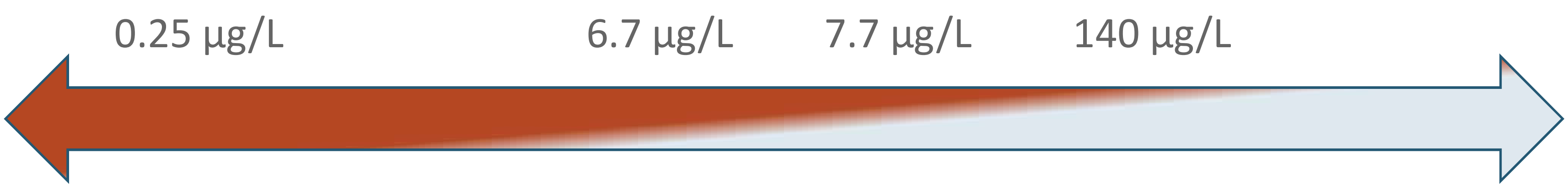
Industial Chemical Facility

- **Complex Setting**
  - Hydrogeology / geology
  - Surface water features to the west and north
  - Potential for other off-site sources
- **Impacts date back to the 1980s**
  - Chlorinated alkenes (PCE, TCE, DCE, VC)
  - Chlorinate alkanes (TCA)
- **1,4-dioxane**
  - Not part of original COC list; subsequently required
  - Plume extent expanded both vertically and horizontally
  - Conducted detailed analytical comparative analyses as part of site-specific risk assessment
  - Evaluating enhanced remedial alternatives (expansion of P&T; in situ bioremediation; ozone)



1,4-Dioxane Regulatory Standards for Groundwater

- No Federal Maximum Contaminant Level; USEPA MCL Goal - 0.35 µg/L
- USEPA Regional Screening Level – 0.46 µg/L
- State Standards – First proposed by Colorado in 2005 at 6.1 µg/L; since lowered to 0.35 µg/L (CDPHE 2012)



- No state standards in 20 states
- WHO suggest 50 µg/L as drinking water threshold

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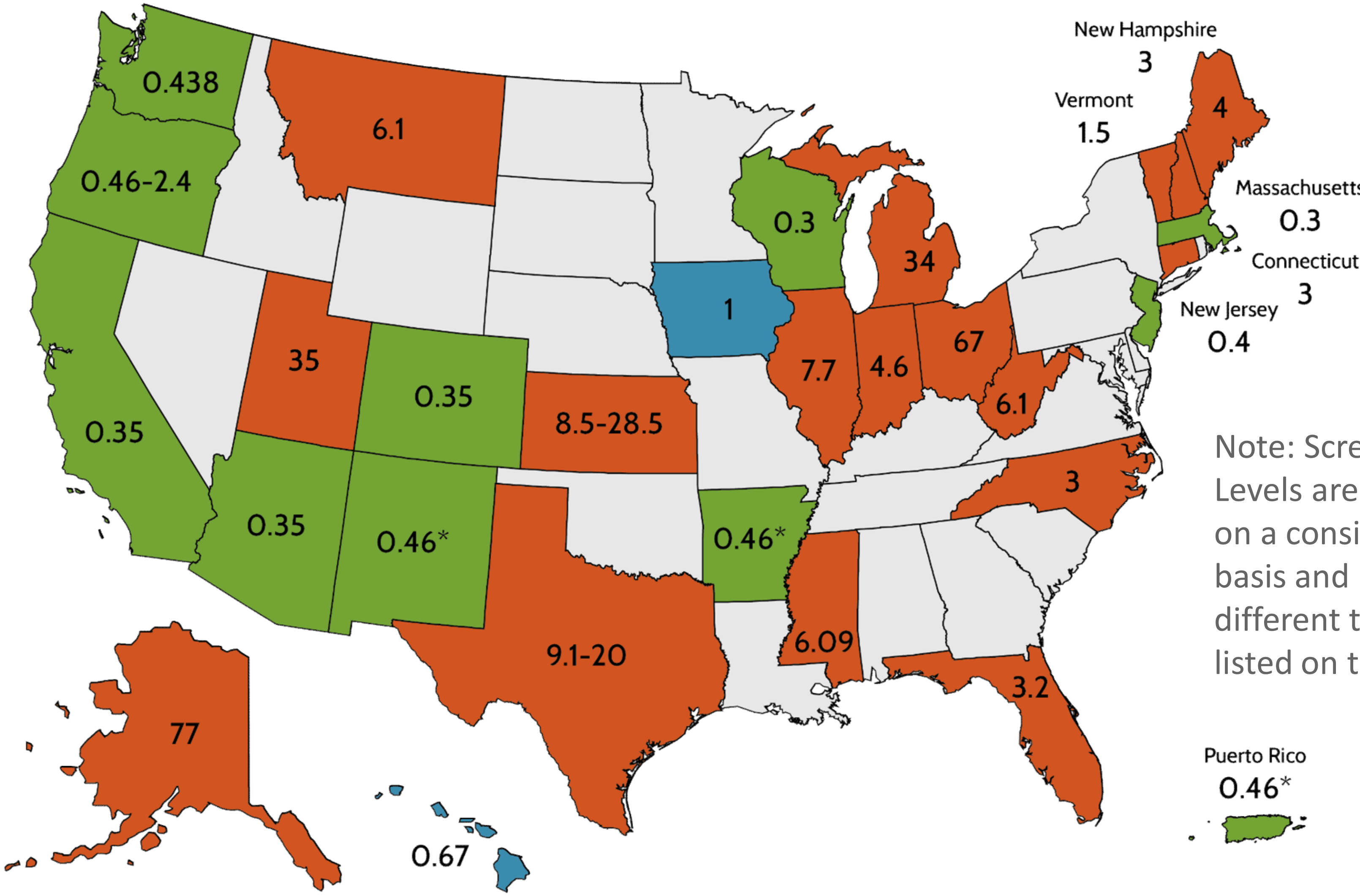
1,4-Dioxane Standard (µg/L)



Note: Screening Levels are revised on a consistent basis and may be different than those listed on this map.

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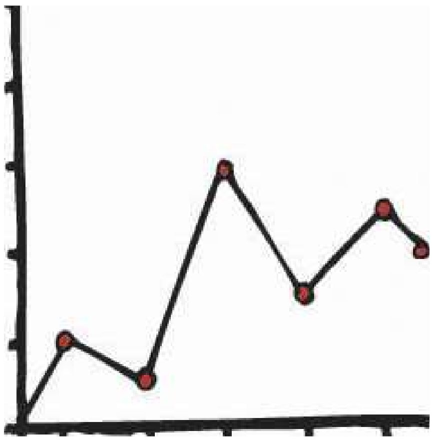
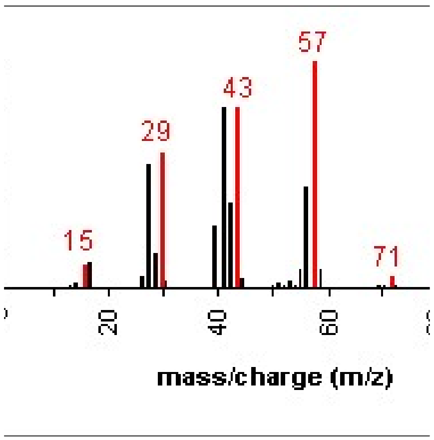
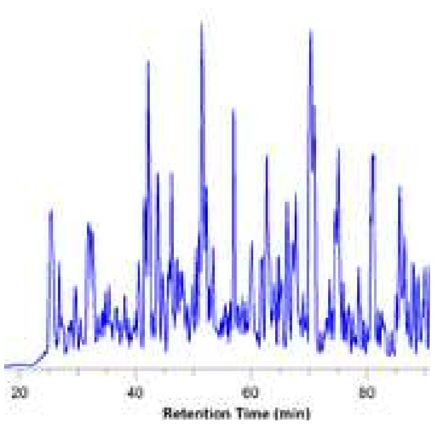
Analytical Issues







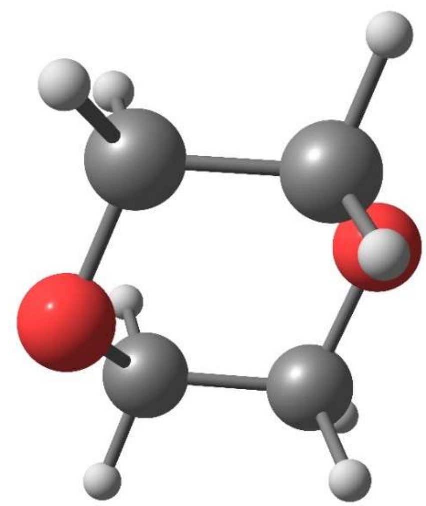
Inconsistent Results

Poor Recoveries

High Detection Limits

Need a Method that can…

- Provide low enough reporting limits
  - Several EPA methods for sample preparation and/or analysis are available that can reduce DLs to the low-ppb range
- Be more sensitive but also accurate
- Approved by regulatory bodies
- Provide repeatable results



Method	MDL (µg/L)	RL (µg/L)	Detection Limit Source	Sample Prep Method	Sample Volume	Matrices	EPA Approval
EPA 522	0.020 - 0.026	0.036 - 0.047	Method	Solid Phase Extraction	1000 mL	Drinking Water	Approved
EPA 1624	---	---	Method	Heated Purge and Trap	3 x 40 mL	Surface/waste water	Approved
SW-846 8260	36.8 - 150	150-200	Labs	Purge and Trap	3 x 40 mL/100 g	Water/Soil	Approved
SW-846 8260 (SIM)	0.5 - 10	---	EPA	Purge and Trap	3 x 40 mL/100 g	Water/Soil	Approved
SW-846 8260B (ID)	---	---	---	Purge and Trap	3 x 40 mL/100 g	Water/Soil	Approved
SW-846 8261A	1.0	1.1	Cincinnati Analytical Instruments	Vacuum Distillation	3 x 40 mL/100 g	Water/Soil	Approved
SW-846 5031/8260B	12	---	Method	Azeotropic Distillation	3 x 40 mL/100 g	Water/Soil	Approved
SW-846 8270C	0.23 - 1.0	0.2 - 0.5	Method	Liquid-Liquid Extraction	2 x 1 L/100 g	Water/Soil	Certification or Accreditation not available
SW-846 8270C (ID/SIM)	0.09	1.0	Labs	Liquid-Liquid Extraction	2 x 1 L/100 g	Water/Soil	Certification or Accreditation not available

8260 Preparation Methods	Addresses Solubility?	Addresses Boiling Point?	Meets Detection Limits?	Meets Performance Criteria?	EPA Approved?
SW-846 5030C	No	No	Sometimes	No	Yes
SW-846 5030C MOD	No (but Improved)	No (but Improved)	No (but Improved)	Yes	Yes
SW-846 5021A	No (but Improved)	No (but Improved)	No (but Improved)	Yes	Yes

8260/5030 is the only commonly used approved EPA method

State approved methods are State specific

Analytical Methods	Addresses Solubility?	Addresses Boiling Point?	Meets Detection Limits?	Meets Performance Criteria?	EPA Approved?
EPA 522	Yes	Yes	Yes	Yes	Drinking Water Only
EPA 1624 REV B	Yes	Yes	Yes	Yes	Surface and Waste Water Only
SW-846 8260B	See Preparation	See Preparation	No	No	Yes
SW-846 8261A	Yes	Yes	Yes	Yes	No
SW-846 8270C/D	Yes	Yes	Yes	Yes	No

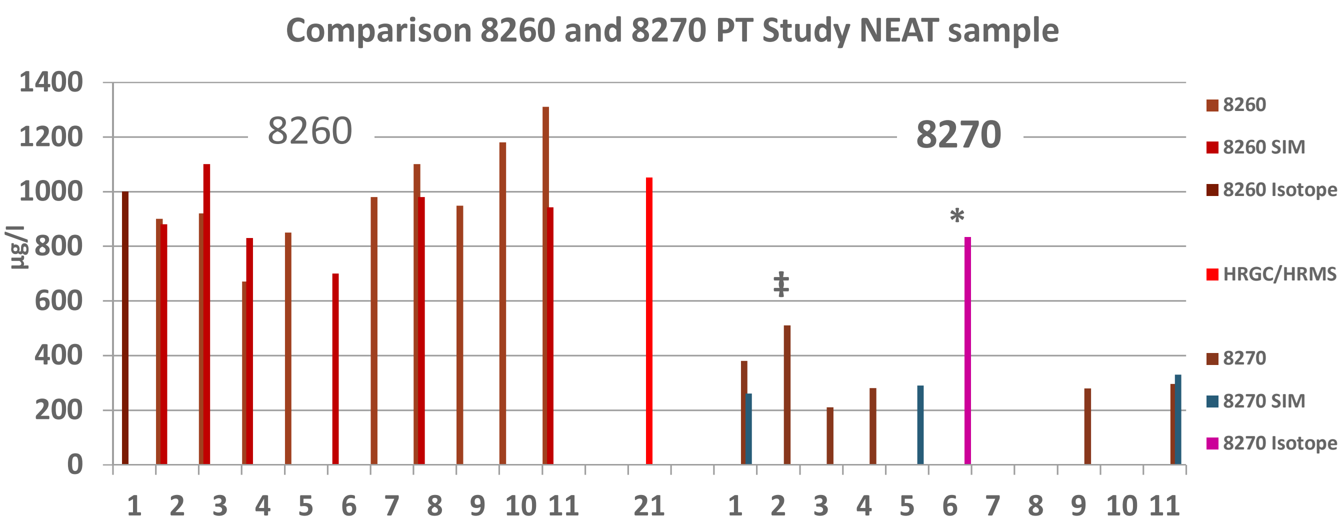
Analysis of 1,4-Dioxane

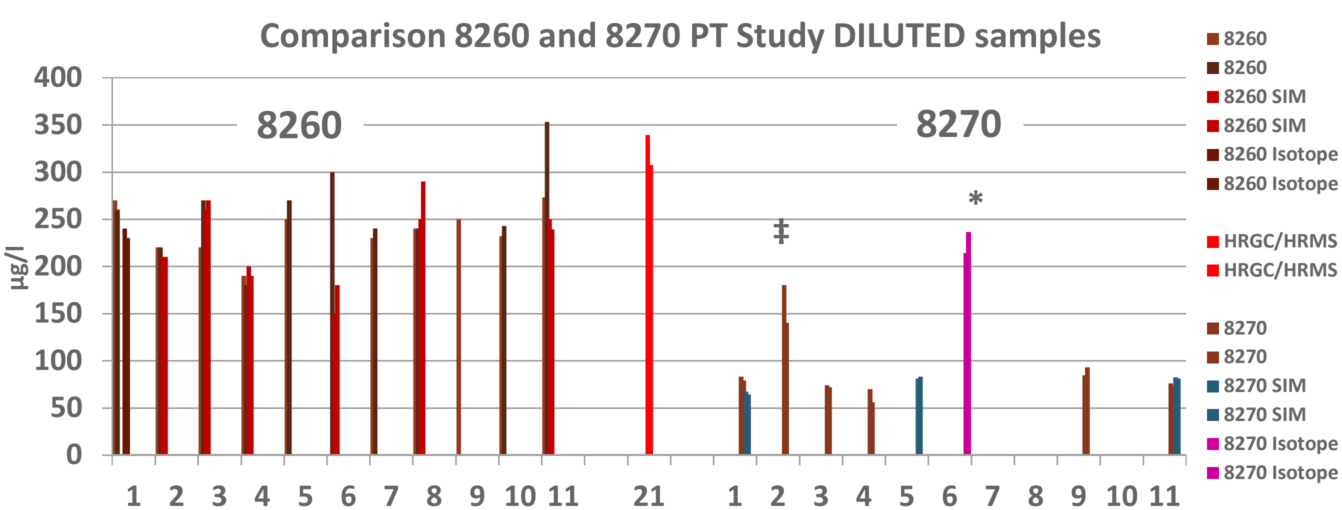
Results of comparability studies

Michael Wilken

Dow®

Annual DOW PT samples



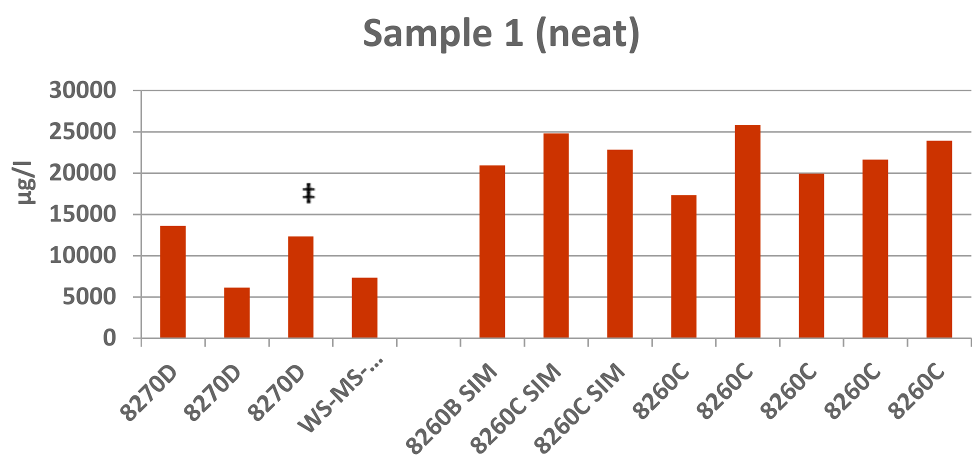


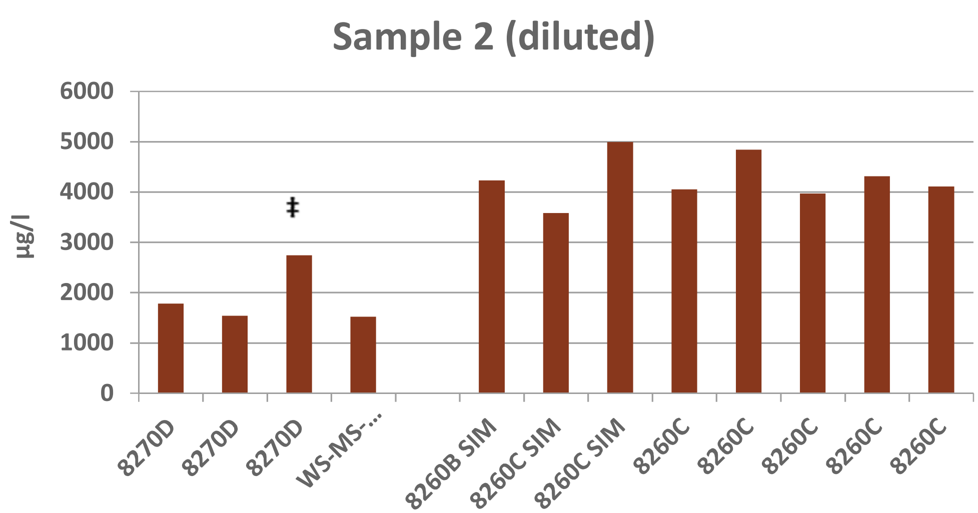
- Annual PT samples
- 11 preferred laboratories
- + 10 other laboratories
- Blended real samples
- for VOC, SVOC, metals, anions analysis
- 1,4-Dioxane with all available methods in the lab
- no 1,4-Dioxane spiked

* corrected for recovery rate

‡ continuous extraction

Direct comparison with different samples

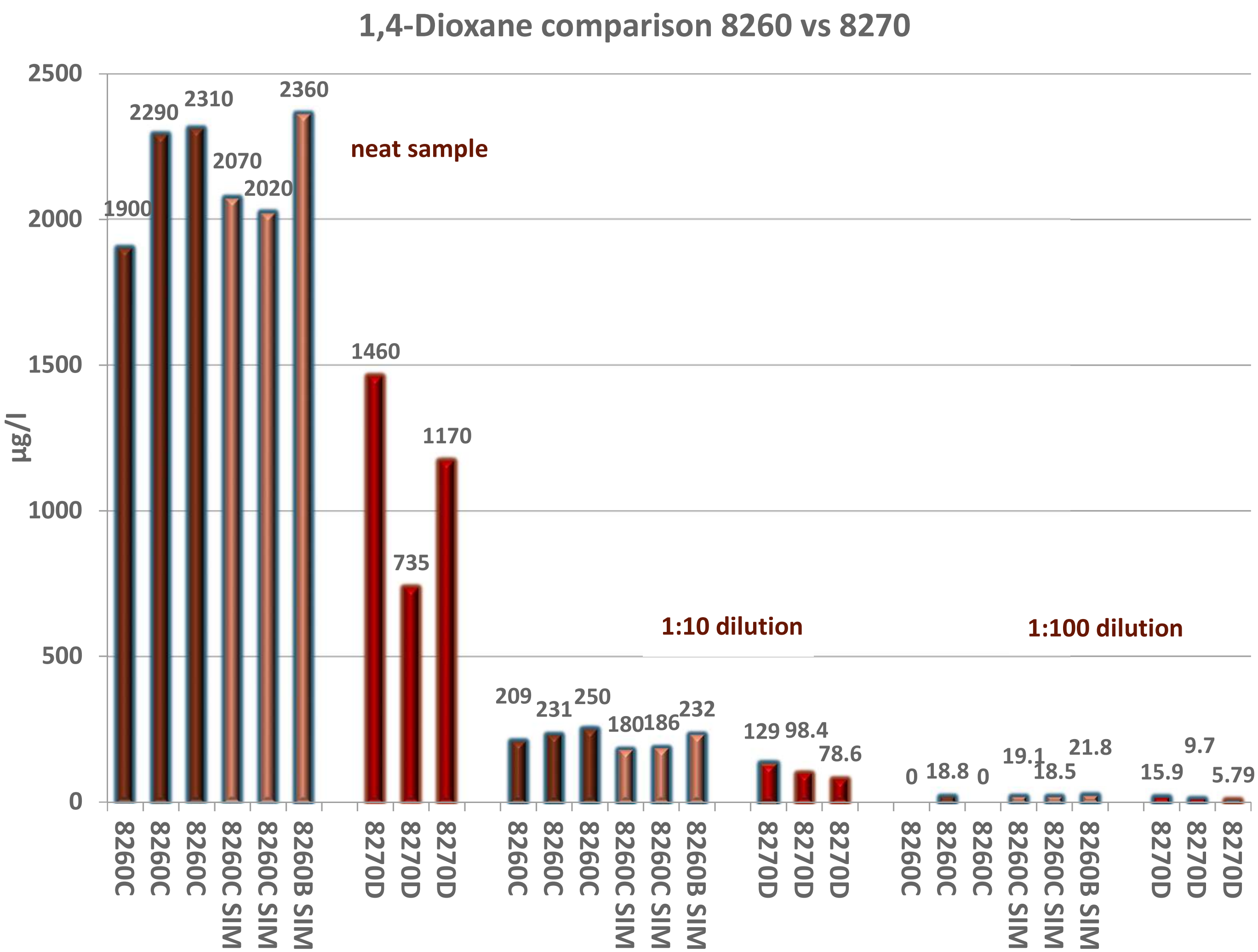




- 4 preferred laboratories
- Blended real samples
- 1,4-Dioxane with all available methods in the lab
- no 1,4-Dioxane spiked

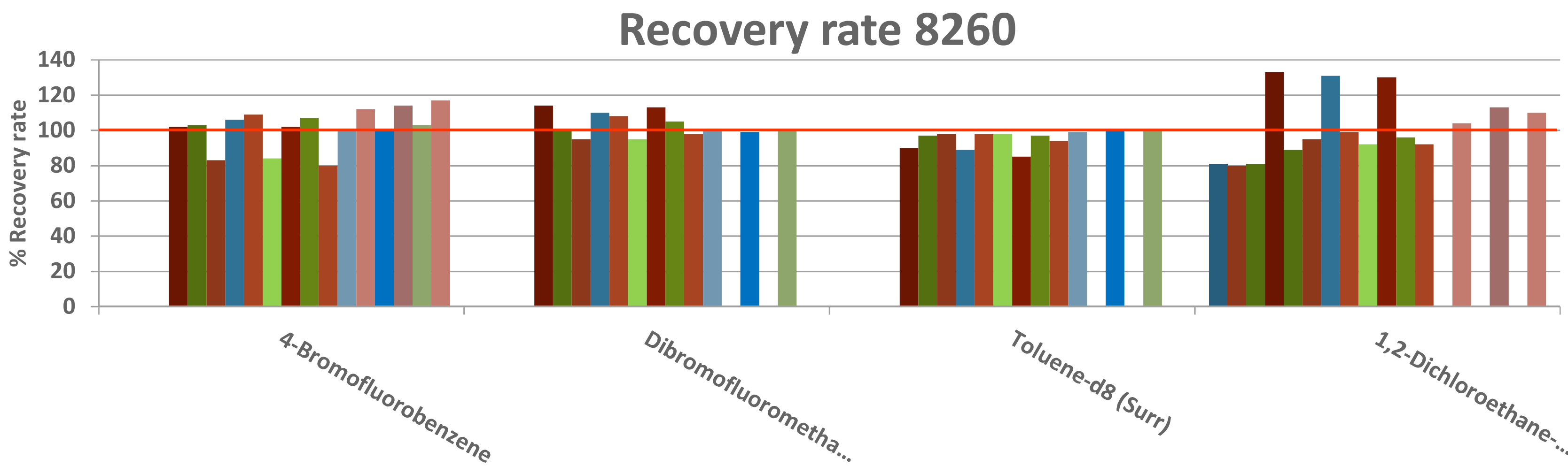
‡ continuous extraction

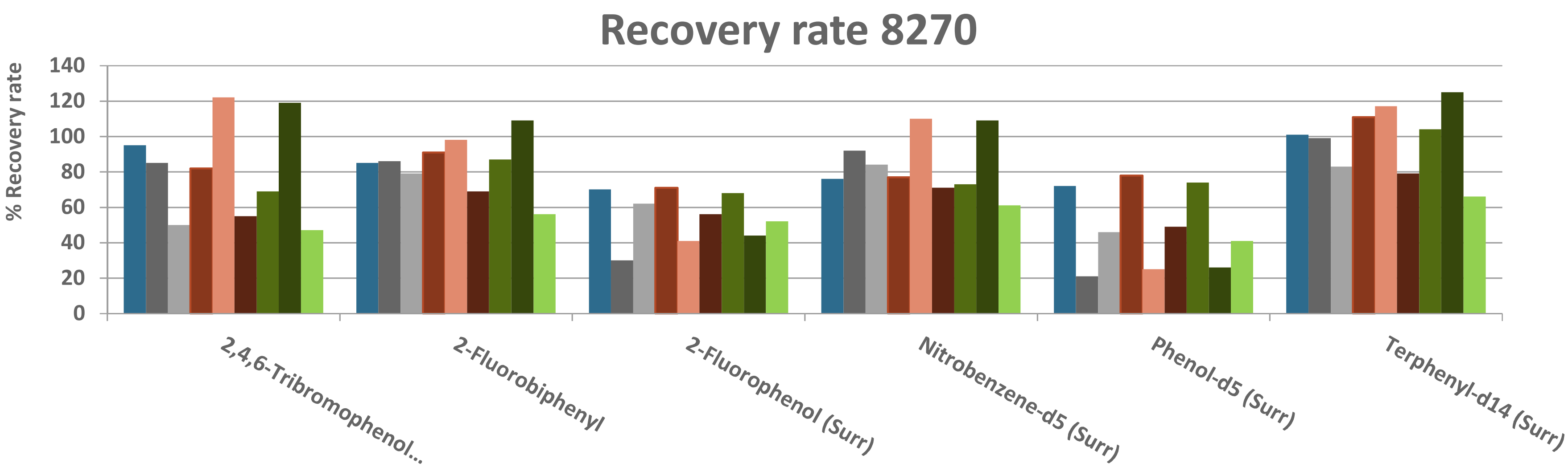
Direct comparison over wider concentration range



- 3 preferred laboratories
- Blended real samples
- Diluted 1:10 and 1:100
- no 1,4-Dioxane spiked

Recovery Rate Comparison





Summary

- Compared to all VOC methods (8260), the SVOC methods (8270) deliver substantially LOWER data in all studies with REAL WORLD samples
- The differences can be up to a factor of 3
- This may be due to
  - poor and insufficient extraction
  - no correction for surrogate recovery
- As VOC methods are not capable to analyze in sub ppb-range, and the drinking water method 522 does not ask for recovery correction as well, we are in the urgent need of a reliable method
- One step is the implementation of the Isotope dilution method

Questions?

WHAT WHY WHERE WHEN WHO HOW