



# STATES/EPA ANNUAL WASTE SITE CLEANUP MEETING

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Connecticut Department of Energy and Environmental Protection

## 1,4-DIOXANE: EMERGING CONTAMINANT ISSUE

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## WHAT IS IT?

- Solvent stabilizer and corrosion inhibitor often found with TCA
- By-product of manufacturing
- Also used alone as a solvent
- Wide variety of applications



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## USES OF 1,4-DIOXANE

- As the Main Ingredient
  - Cellulose Acetate Membrane Production
  - Scintillation Counting Cocktails/Bray's Solution
- Synthesis of other products
  - Brominated flame retardants
  - Pharmaceutical industry
  - Paper industry (coated paper)



Source: T. Mohr, Midwest GeoSciences Webinar, March 19 & 21, 2013.



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## USES OF 1,4-DIOXANE (cont.)

- As a Minor Ingredient
  - Magnetic Tape Production
  - Tissue Preservative in Histology
  - Inks and printing operations
  - Painting, coating and stripping
  - Polyurethane medical devices
  - Brake cleaning sprays and fluids
  - Wood glue and contact cement
  - Loosening agent for hardware




Source: T. Mohr, Midwest GeoSciences Webinar, March 19 & 21, 2013.



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## USES OF 1,4-DIOXANE (cont.)

- Produced as By-Product
  - Photographic film recycling (dimethyl terephthalate, DMT)
  - Aircraft deicing fluid
  - Ethoxylated surfactant production
  - Resin production
  - PET plastic production 
  - Antifreeze Production



Source: T. Mohr, Midwest GeoSciences Webinar, March 19 & 21, 2013.



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## FACILITIES / OPERATIONS

### Where 1,4-Dioxane Could Be Found

Degreasing operations	Electroplating/polishing
Paints, varnishes, lacquers, strippers	Inks, dyes, coatings, and adhesives
Pharmaceutical plants	Polymers, plastics, rubber manufacture
Semiconductors, electronic components	Commercial printing and photographic equipment
Pulp, paper, fiber manufacture	Explosives
Personal care products (cosmetics, detergents, shampoos)	University landfills



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## CHEMICAL PROPERTIES OF 1,4-DIOXANE

- Colorless, flammable liquid with faint pleasant odor
- Cyclic ether ( $C_4H_8O_2$ )
- Specific gravity 1.033
- Evaporates readily
- Boiling Point  $101^\circ C$
- Mobile in soils (low  $K_{oc}$  1.23,  $\log K_{ow}$  -0.27)
- Completely soluble in water
- Relatively non-volatile in water (very low Henry's Law Constant of  $4.88 \times 10^{-6} \text{ atm}\cdot\text{m}^3/\text{mol}$ )



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## WHAT HAPPENS TO 1,4-DIOXANE when it's released to...

### Air

- Readily evaporates, moderate vapor pressure of 38.0 mm Hg at 25°C
- As a vapor, breaks down readily to form aldehydes and ketones



### Soil

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



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## WHAT HAPPENS TO 1,4-DIOXANE when it's released to...

### Water

- Completely soluble in water = travels ahead of other solvents in plume (similar to MTBE)
- Tends to stay dissolved, therefore low volatilization risk from groundwater
- Chemically stable, not expected to degrade once in groundwater or surface water



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## WHY DO WE CARE?

- EPA - Probable Human Carcinogen
  - Kidney and liver effects
  - Updated IRIS tox. data
- Widespread use
- Persistence - not expected to biodegrade
- Found in drinking water supply wells



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## EMERGING CONTAMINANT HISTORY

- 2001 - White Paper by Thomas Mohr
- 2003 - EPA Region 1 brings it to state's attention, begin looking at NPL and RCRA CA sites
- 2004 - CT DPH establishes private drinking water well Comparison Value of 20  $\mu\text{g}/\text{L}$
- Oct. 2011 – CT DPH establishes new action levels for ingestion & dermal contact based on IRIS updates
- Feb. 2012 – CT DPH Private Well Fact Sheet
- May 2012 – CT DEEP presentation to LEPs, regulated community at Remediation Roundtable meeting



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## ANALYTICAL METHODS

- Initially, lab methods had high reporting limits
- Newer methods have lower detection limits
  - Modified EPA Method 8260 SIM
  - Modified EPA Method 8270 SIM (good if high conc. of other chlorinated VOCs, no need to dilute sample) (1 µg/L)
  - EPA Method 8261A (vacuum distillation with cryogenic trapping – rec. by T. Mohr)
  - EPA Method 522



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## REGULATORY STANDARDS

State	Groundwater Standards
Connecticut	3 µg/L – Private wells - drinking water 50 µg/L – bathing/showering
Rhode Island	Not established; tested at Superfund sites
Massachusetts	0.3 µg/L - Drinking water supplies 3 µg/L - GW-1 areas (water supply zones) 6,000 µg/L - GW-2 areas (vol. risk near bldgs) 50,000 µg/L - GW-3 areas
Vermont	20 µg/L
New Hampshire	3 µg/L → 0.35 µg/L
Maine	4 µg/L – drinking water 72,000 µg/L – worker exposure



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## TREATMENT OPTIONS



### FOR 1,4-DIOXANE



#### Not Effective

- Air stripping (unless soil is dry)
- Ion exchange

#### Limited Effectiveness

- GAC filters - Depends on influent water quality
- Reverse osmosis
- Biorem.

#### EFFECTIVE

- Advanced Oxidation
- In-situ Thermal Treatment
- \$\$\$



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## TREATMENT OPTIONS

### FOR POTABLE WELLS

- GAC filters with frequent monitoring & filter change-outs
- Bottled water
- Bisco Environmental residential ozone/peroxidation treatment system (to be tested)
- WATER MAIN EXTENSION



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## CT CASE STUDIES

- Sites with Polluted Potable Wells
  - Durham Meadows NPL site – 16 wells with max. 14DX 58  $\mu\text{g/L}$ , TCE 110  $\mu\text{g/L}$ ; GAC filters; bottled water provided to 7 houses; water main extension planned.
  - Tylerville State Superfund Site, Haddam – 15 wells with max. 14DX 65  $\mu\text{g/L}$ , TCE 330  $\mu\text{g/L}$ ; other wells without 14DX; GAC filters; bottled water provided to 5 houses; multiple potential source areas; water supply study in progress.



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## CT CASE STUDIES

- Sites with Polluted Groundwater
  - Solvents Recovery Service New England NPL site, Southington, (max. 4.3 mg/L) – in-situ thermal treatment
  - Upjohn/Pharmacia/Pfizer, North Haven – in-situ thermal
  - Susan Bates RCRA CA site, Chester – some detections following massive historic release from TCA tank
- Site with Polluted Soil
  - Henlopen, Danbury – 65 mg/kg under building, discovered in SVE effluent; max 220  $\mu\text{g/L}$  in overburden GW, 31  $\mu\text{g/L}$  in bedrock GW; permanganate injections into GW, soil removal



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## OTHER CONSIDERATIONS

- Collocation with TCE
- 1,4-Dioxane can penetrate mineral structure of clay liners (T. Mohr)
- Retained in unsaturated silts/clays at 10-100x concentration as in adjacent sands, diffuses into immobile pore spaces (T. Mohr)
- Other solvent stabilizers of concern?



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## 1,4-DIOXANE RESOURCES

Mohr, Thomas K.G., 2010. Environmental Investigation and Remediation: 1,4-Dioxane and other Solvent Stabilizers.

EPA Technical Fact Sheet

[http://www.epa.gov/fedfac/pdf/technical\\_fact\\_sheet\\_14-dioxane\\_2013.pdf](http://www.epa.gov/fedfac/pdf/technical_fact_sheet_14-dioxane_2013.pdf)

CLU-IN <http://clu.in.org/contaminantfocus/default.focus/sec/1,4-Dioxane/cat/Overview/>

ATSDR <http://www.atsdr.cdc.gov/toxprofiles/tp187.pdf>

CT DPH Fact Sheet:

[http://www.ct.gov/dph/lib/dph/environmental\\_health/eoha/pdf/1\\_4\\_dioxane.pdf](http://www.ct.gov/dph/lib/dph/environmental_health/eoha/pdf/1_4_dioxane.pdf)



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