From Widely Used to Now Being Removed: Presence & Removal Methods for 1,4-Dioxane

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Engineering Sustainable Infrastructure for the Future



What is 1,4-Dioxane?

Sources [1,2]

- Initially produced ~1930's
- Solvent stabilizer for metal degreasers (e.g. 1,1,1-trichloroethane)
- Used in paint strippers, dyes, greases, varnishes, waxes
 Impurity in <u>household</u> detergents, antifreeze, cosmetics, deodorants, shampoos, and other products

[1] EPA (2017), Scope of the Risk Evaluation for 1,4-Dioxane (CASRN 123-91-1). [2] Mohr, Stickney, and DiGuiseppi. *CRC Press*. 2010

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- In 2016, 617,000 lbs released into environment
 - 2% Landfills
 - 9% Air
 - 10% Surface Wate
 - 79% Other

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In 1995, the Montreal Protocol **phased out the use of 1,4-dioxane** as a stabilizer. However, its persistence in the environment remains quite high.

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 [2] Mohr, Stickney, and DiGuiseppi. *CRC Press*. 2010

Physical & Chemical Properties





Chemical Property

Environmental Implications

Cyclic ether

Highly soluble in water (>100 mg/mL)

Low Henry's Law Constant

 $(K_{\rm H} = 4.88 \text{ x } 10^{-6} \text{ atm } \text{m}^3 \text{ mol}^{-1})$

Lower adsorption properties

 $(\log K_{ow} = -0.27)$

Chemically stable

Rapidly flows through water

Low volatility

Not likely to bioaccumulate or be slowed by porous materials

[3] United States. Environmental Protection Agency. Office of Solid Waste and Emergency Response. Technical Fact Sheet-1,4-Dioxane.

Toxicology

- Probable human carcinogen (IARC Class 2B)
- Hepatotoxin, neurotoxin, reproductive toxin
- Long-Term Exposure \rightarrow liver and kidney cancer
 - Rat study found **development of oral and liver cancer** after 12 weeks of oral ingestion! [4]





[4] Qiu, J. et al. 1,4-Dioxane Exposure Induces Kidney Damage in Mice by Perturbing Specific Renal Metabolic Pathways: An Integrated Omics Insight into the Underlying Mechanisms. *Chemosphere*, 2019, 228, 149-158.

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Release Routes

- Air
- Surface Water
- Landfills
 - Other
- **Consumer Products**
- Food Packaging
- Groundwater

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Release R

- Air
- **Surface**
- Landfills

Other

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Groundwater



[5] Environmental Working Group (2007). 1,4- dioxane. https://www.ewg.org/skindeep/ingredients/726331-1-4-dioxane/.

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[6]

[5] Environmental Working Group (2007). 1,4- dioxane. <u>https://www.ewg.org/skindeep/ingredients/726331-1-4-dioxane/</u>.
 [6] Suthersan, S., et al. Making Strides in the Management of "Emerging Contaminants". *Groundwater Monitoring & Remediation*, 2016, 36, 15-25.

Improper Disposal + Toxicity + Miscibility





Improper Disposal + Toxicity + Miscibility

1,4-Dioxane Groundwater Contamination &

Widespread Human Health Concern



No US Federal Regulation, But States Can Set Clean Up Standard



[6] Suthersan, S., et al. Making Strides in the Management of "Emerging [7] US Environmental Protection Agency (EPA). 2015. The third Contaminants". *Groundwater Monitoring & Remediation*, 2016, 36, 15-25. unregulated contaminant monitoring rule (UCMR3): data summary.

Luckily, Microbes Can Biodegrade 1,4-Dioxane



Bioremediation: Use of either naturally occurring or deliberately introduced microorganisms or other forms of life to consume and break down environmental pollutants.



Zhang, S., et al. Advances in Bioremediation of 1,4-Dioxane-Contaminated Waters. Journal of Environmental Management, 2017, 204, 765-774.

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-774

Table 1

Zhang, S.,

List of 1,4-dioxane degrading microorganisms and biodegradation rates. MO – Monooxygenase; THF – Tetrahydrofuran; TSS – Total suspended solids; N/A – Not available.

Strain	Induced enzyme	Biodegradation rate	Reference
Metabolism			
Pseudonocardia dioxanivorans CB1190	1,4-dioxane MO	$0.19 \pm 0.007 \text{ mg/h/mg-protein}$	Mahendra and Alvarez-Cohen (2005, 2006)
Actinomycete CB1190	N/A	0.33 mg/min/mg-protein	Parales et al. (1994)
Amycolata sp. CB1190	N/A	$0.92 \pm 0.29 \text{ mg/day/mg-protein}$	Kelley et al. (2001)
Pseudonocardia benzenivorans B5		$0.01 \pm 0.003 \text{ mg/h/mg-protein}$	Mahendra and Alvarez-Cohen (2006)
Mycobacterium sp. PH-06	MO	60 mg/L/day	Kim et al. (2009)
Acinetobacter baumannii DD1	MO	2.38 mg/h/L	Huang et al. (2014)
Pseudonocardia carboxydivorans. RM-31	N/A	31.6 mg/L/hr	Matsui et al. (2016)
Xanthobacter flavus DT8	N/A	Similar as CB1190	Chen et al. (2016)
Afipia sp. D1		0.052 to 0.263 mg/mg-protein/h	Sei et al. (2013)
Cordyceps sinensis (fungus)	MO	0.011 mol/day	Nakamiya et al. (2005)
Cometabolism			
Mycobacterium austroafricanum JOB5	Propane MO	0.40 ± 0.06 mg/h/mg-protein	House and Hyman (2010); Lan et al. (2013);
			Mahendra and Alvarez-Cohen (2006)
Rhodococcus ruber ENV425	Propane MO	10 mg/h/g TSS	Lippincott et al. (2015); Vainberg et al. (2006)
Pseudonocardia sp. strain ENV478	THF MO	21 mg/h/g TSS	Masuda et al. (2012); Vainberg et al. (2006)
Rhodococcus RR1	N/A	0.38 ± 0.03 mg/h/mg-protein	Mahendra and Alvarez-Cohen (2006)
Rhodococcus jostii RHA1	Propane MO	N/A	Hand et al. (2015); Li et al. (2013)
	1-butane MO		
Flavobacterium	N/A	N/A	Sun et al. (2011)
Pseudonocardia K1	THF MO	0.26 ± 0.013 mg/h/mg-protein	Mahendra and Alvarez-Cohen (2006)
Burkholderia cepacia G4	toluene-2- MO	0.1 ± 0.006 mg/h/mg-protein	Mahendra and Alvarez-Cohen (2006)
Ralstonia pickettii PKO1	toluene-p- MO	$0.31 \pm 0.007 \text{ mg/h/mg-protein}$	Mahendra and Alvarez-Cohen (2006)
Pseudomonas mendocina KR1	toluene-4- MO	0.37 ± 0.04 mg/h/mg-protein	Mahendra and Alvarez-Cohen (2006)
Aureobasidium pullmans NRRL 21064	N/A	6-8 mg/L within a day	Patt and Abebe (1995)
Graphium sp. (ATCC 58400) (fungus)	Propane MO	4 ± 1 nmol/min/mg dry weight	Skinner et al. (2009)
	THF MO	9 ± 5 nmol/min/mg dry weight	
Others			
Shewanella oneidensis	N/A	27.9 \pm 3.37 to 36.2 \pm 4.13 μ M/h	Sekar et al. (2016)
Enriched consortium-FS	МО	0.037 mg/h/mg-protein	Nam et al. (2016)
Enriched consortium-AS		0.078 mg/h/mg-protein	Nam et al. (2016)
SL-D(propanotroph strain)	N/A	20 mg/L within a day	Innovative Engineering Solutions Inc.IESI (2017)
CL-OUT [®]	N/A	Over 70% removal	Saul (2012)
(Pseudomonas putidastrain B,			
Pseudomonas putida stain E			
and Pseudomonas fluorescens strain G)			

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WHICH MICROBE DO WE CHOOSE?

Pseudonocardia dioxanivorans CB1190 (CB1190)



CB1190 grown on R2A Agar

SEM Image of CB1190

[9] Mahendra, S. and L. Alvarez-Cohen. *Pseudonocardia Dioxanivorans* Sp Nov., a Novel Actinomycete That Grows on 1,4-Dioxane. *Int. J. of Syst. and Evol. Micr.*, 2005, 55, 593-598.

CB1190 Aerobically Biodegrades 1,4-Dioxane



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Obstacles for CB1190: Low Oxygen



How Long Can CB1190 Survive Without Oxygen?

1,4-Dioxane Degraded After 1 Week Anaerobic



----- 0 Weeks Anaerobic (Positive Control)

-1 Week Anaerobic

Polasko, A. et al. A Mixed Microbial Community for the Biodegradation of Chlorinated Ethenes and 1,4-Dioxane. *Environmental Science & Technology Letters*, 2018, 6, 49-54.

1,4-Dioxane Degraded After 2 Weeks Anaerobic



---- 0 Weeks Anaerobic (Positive Control) ----- 1 Week Anaerobic ----- 2 Weeks Anaerobic

Polasko, A. et al. A Mixed Microbial Community for the Biodegradation of Chlorinated Ethenes and 1,4-Dioxane. *Environmental Science & Technology Letters*, 2018, 6, 49-54.

1,4-Dioxane Degraded After 3 Weeks Anaerobic



Polasko, A. et al. A Mixed Microbial Community for the Biodegradation of Chlorinated Ethenes and 1,4-Dioxane. *Environmental Science & Technology Letters*, 2018, 6, 49-54.

1,4-Dioxane Degraded After 4 Weeks Anaerobic

Polasko, A. et al. A Mixed Microbial Community for the Biodegradation of Chlorinated Ethenes and 1,4-Dioxane. *Environmental Science & Technology Letters*, 2018, 6, 49-54.

1,4-Dioxane Degraded After 5 Weeks Anaerobic

Technology Letters, 2018, 6, 49-54.

1,4-Dioxane Degraded After 100 Days Without O₂!

Polasko, A. et al. A Mixed Microbial Community for the Biodegradation of Chlorinated Ethenes and 1,4-Dioxane. *Environmental Science & Technology Letters*, 2018, 6, 49-54.

Summary & Significance

- **1,4-Dioxane is a threat to drinking water** in the U.S. that needs a variety of treatment options
- Benefits of microorganisms include: lower costs, less disruption to the land area, and complete mineralization of 1,4-dioxane
- Particularly, *Pseudonocardia dioxanivorans* CB1190 an ideal candidate for bioremediation
 - Uses 1,4-dioxane as carbon source
 - Survives under harsh environmental conditions (e.g. prolonged low O₂)

Alex & Dr. Shaily Mahendra at a contaminated groundwater site

Future Research & Applications

- Deploy CB1190 to field sites with varying dissolved oxygen
- Determine the threshold of O₂ CB1190 needs to break down 1,4-dioxane
- Investigate the mechanisms CB1190 uses to survive anaerobic incubation
- Test whether other 1,4-dioxane degrading microorganisms can survive without oxygen like CB1190

Alex in the lab during pandemic with social distancing

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THANK YOU FOR YOUR ATTENTION QUESTIONS?

СПАСИБО ЗА ВНИМАНИЕ! ЕСТЬ ВОПРОСЫ?