Emerging Contaminant Spotlight: 1,4-Dioxane

This edition of Peroxygen Talk focuses on the emerging contaminant 1,4-dioxane (referred to here as dioxane) and its impact on the environment. In addition, regulatory drivers for dioxane will be reviewed and the effective use of Klozur® activated persulfate to remediate dioxane contaminated groundwater will be discussed.

Environmental and Health Impacts

Dioxane [CAS No 123-91-1] is a clear, heterocyclic ether with the molecular formula $C_4H_8O_2$. Its primary use is as a stabilizer for chlorinated solvents, particularly 1,1,1-TCA (trichloroethane), representing 90% of the volume of dioxane produced[1]. It also may be found in consumer products (soaps, cosmetics, pharmaceuticals) and is used as a solvent in paints, dyes, resins, plastics and other products. It is fully miscible in water and has a low volatility. Dioxane is highly hydrophilic, and will not readily bind to soils. As a result, it is very mobile in ground water, and may be found at the leading edge of a solvent plume. It has been documented that dioxane plumes may measure twice the length and affect an area up to six times greater than the associated solvent plumes[2].

Frequently 1,4-dioxane is found at chlorinated solvent sites, in particular where 1,1,1-TCA was used as a degreasing agent. However, until recently, analytical methods for dioxane were not sensitive enough to measure low ppb levels, and dioxane is not often part of a standard monitoring program for chlorinated sites. As a result, dioxane often is not detected until after a remedial action plan is in place. This may necessitate expanding monitoring networks and incorporation of new remediation technologies that can adequately treat dioxane. Because of its low volatility and high solubility, dioxane has a high potential of entering the soil and ground water. The EPA's Toxic Chemical Release Inventory (TRI) estimated a total of 1.15 million lbs of dioxane and 273,693 lb of 1,1,1-TCA containing dioxane were released through 2002[3].

The most common route for human exposure to dioxane is inhalation[4] (ie: workers handling dioxane). Human health effects via inhalation include impacts on the liver and kidneys, being the main effected organs. It is an irritant to the eye, nose, lung and skin. Currently, there are no data regarding health effects of human exposure via an oral route. While there is inadequate evidence of carcinogenicity in humans, dioxane has been shown to cause cancers in laboratory animals. As a result, in 1997 the US EPA listed dioxane as a group B2 probable human carcinogen. IARC also lists dioxane as a group 2B carcinogen.

Regulatory Drivers for 1,4-Dioxane

At present, there is no federally enforceable maximum containment level (MCL) for dioxane. However, the US EPA has listed a health advisory for dioxane at a drinking water concentration of 3 ppb (µg / L). In addition, several EPA regions and states have developed their own guidelines for dioxane. In 2004, Colorado became the first state to establish an enforceable standard for dioxane in groundwater. Table 1, reprinted in part from reference 3, lists the current Region and State guidance for dioxane in water (this table does not include soil clean up guidance).

State or Region	Type of Guidance	Matrix	Concentration
EPA Region 3	Risk based concentrations	Tap water	6.1 ppb
EPA Region 6	Human health medium specific screening levels	Tap water	6.1 ppb
EPA Region 9	Preliminary remediation goals	Tap water	6.1 ppb
California	Health based advisory levels	Drinking water	3 ppb
Colorado	Water quality standard	Groundwater and surface water	6.1 ppb (3.2 ppb by March 2010)
Delaware	Uniform risk based remediation standards	Groundwater	6 ppb
Florida	Soil cleanup target levels	Groundwater	3.2 ppb
Maine	Maximum exposure guideline	Drinking water	3.2 ppb
Massachusetts[5]		Drinking water	3 ppb
Michigan	Generic cleanup criteria and screening levels	Drinking water	350 ppb (industrial) 85 ppm (residential)
Missouri	Target concentration	Groundwater	3 ppb
New Hampshire[5]		Drinking water	3 ppb
North Carolina[6]		Groundwater	7 ppb
Pennsylvania	Medium specific concentrations for organic regulated substances in groundwater	Groundwater	5.6 ppb (used aquifer – residential) 24 ppb (used aquifer – non residential) 56 ppb (nonuse aquifer – residential 240 ppb (nonuse aquifer – non residential)
South Carolina	Drinking water regulation and health advisory	Drinking water	70 ppb
Texas	Protected concentration levels	Groundwater	18.6 ppb (industrial) 8.3 ppb (residential)
West Virginia	Risk based concentrations	Groundwater	6.1 ppb

Table 1: Summary of Region and State Guidance for 1,4-Dioxane in Water

Using Klozur Activated Persulfate to Remediate 1,4-Dioxane Impacted Soil and Groundwater

Dioxane is not efficiently removed by most conventional water treatment process. In a recent publications[3,7], the EPA lists several methods for the treatment of dioxane. These treatment methods are mainly *ex situ* applications, and include oxidation via UV activated hydrogen peroxide, combinations of ozone and hydrogen peroxide, absorption onto activated carbon, and bioremediation which requires long resonance times to be effective. For *in situ* applications, Klozur persulfate has been shown to be highly effective in destroying dioxane. In addition, as dioxane is typically found at chlorinated solvents sites, Klozur persulfate also is capable of destroying compounds such as TCE, PCE, 1,1,1-TCA, DCA and methylene chloride, allowing for a single remediation approach for treating the entire contaminated site. This is an advantage for activated persulfate over other technologies, such as permanganate zero valent iron, which can not treat dioxane and the chlorinated solvents in one approach.

Laboratory and field data demonstrate that the four major Klozur persulfate activation chemistries[8], chelated iron, heat, peroxide and high pH, are effective in activating the persulfate for the elimination of dioxane. However, if a recalcitrant contaminant such as 1,1,1-TCA is also present, it is then recommended that either heat, peroxide or high pH activation be used. The following are results for several field applications of Klozur persulfate for the treatment of dioxane.

Site 1: North Carlonia
Data Courtesy of Redox Tech[9]

Monitoring Well	1,4-Dioxane concentration (µg / L)		
	Pre-treatment	Post-Treatment	% Reduction
MW-1	50,000	< 5	99.9
MW-7	3,220	< 5	99.8
MW-14	3,020	< 5	99.8
MW-17	3,400	Non detect	100

Table 2: Dioxane Reduction Data for Site 1.

Site 2: California
Data Courtesy of JAG Consulting[10]

Monitoring Well	1,4-Dioxane concentration (µg / L)		
	Pre-treatment	Post-Treatment	% Reduction
MW-1	42,000	39,000	7.1
MW-9	18,000	120	99.3
MW-4	260,000	21,000	91.9

Table 3: Dioxane Reduction Data for Site 2.

Site 3: North Carolina
Data Courtesy of Redox Tech[9]

This site is located in the Piedmont of North Carolina, and contains a divided warehouse and active manufacturing building. Solvents containing 1,1,1-TCA, 1,1-DCE and 1,4-dioxane were released. There was a potential receptor through vapor intrusion into the building, and the remediation goal was to reach realistic clean-up targets in order for the property to be sold. Approximately 100,000 lbs of Klozur SP was injected, and different activation schemes were utilized, including 5 million BTU's of steam, and 200 lb of sodium hydroxide. Oxidant injection over 90 direct push was performed (30 points being inside the building). The following table shows data from a selection of these wells, where the dioxane concentrations were the highest prior to treatment.

Well ID	Initial Compound Concentration (ppb)				Post Injection Results (ppb)			
	DCE	TCA	Combined DCE + TCA	Dioxane	DCE	TCA	Combined DCE + TCA	Dioxane
MW1	27800	96000	123800	29000	< 1	3740	< 3741	< 5
MW1v	89000	99800	188800	24	< 16	360	< 376	< 5
MW1d	4950	4390	9340	< 5	< 7	4220	< 4227	< 5
MW7	5670	57700	63370	199	< 8	7240	< 7248	< 5

Table 4: Dioxane Reduction Data for Site 3.

These case studies demonstrate that Klozur activated persulfate is a very effective *in situ* remediation approach for 1,4-dioxane.

End Notes

1,4-dioxane is by definition an “emerging” contaminant in that the human health effects are unknown but with indication of being a potential carcinogen, there is a lack of federal guidance on allowable groundwater concentrations, and that many states have become pro-active in setting their own groundwater concentration standards. In addition, many chlorinated solvent sites with probable dioxane contaminantion are not yet monitoring for this contaminant, or are beginning to monitor only after the site remedial action plans, which do not address dioxane, are already in place.

Klozur activated persulfate provides an effective means of treating dioxane contaminated groundwater. But the true benefit of using Klozur persulfate is that not only can it treat the dioxane contamination, it also has the oxidative power to destroy the chlorinated solvents, including TCA and DCA, that often accompany dioxane contamination.

[1] Report on Carcinogens, 11th ed. National Toxicology Program, 2005

[2] Walsom, G and B. Tunnicliffe. “1,4-Dioxane – A little Known Comound”. **Enironmental Sci and Eng.** May, 2002.

[3] “Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications”, EPA Office of Soild Waste and Emergency Response, EPA 542-R-06-009, 2006.

[4] California Office of Environmental Health Hazard Assessment, “Memorandum: 1,4 Dioxane Action Level”, 1998.

[5] “Health Consultation: 1,4-Dioxane in Private Drinking Water Near Naval Air Station Whidbey Island, Ault Field, Oak Harbor, WA”, US Dept of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR), 2005.

[6] North Carolina DENR, Div of Water Quality, Groundwater Section, “Ground water section guidelines for the investigation of soil and groundwater contamination: chlorinated solvents and other dense non-aqueous phase liquids” July 2003

[7] Zenker, M., R. Borden and M. Barlaz. “Occurence and Treatment of 1,4-Dioxane in Aqueous Environments“. **Environmental Sci and Eng.** 2003.

[8] *Peroxygen Talk*, January 2006

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