Technical Brief: 1,4-Dioxane Emerging Contaminant Destruction using Ozone

1,4-Dioxane ($C_4H_8O_2$) is a colorless liquid with a faint sweet odor similar to that of diethyl ether. It is classified as an ether. Due to its stabilizing qualities, this compound is commonly found in the presence of chlorinated solvents such as 1,1,1-trichloroethane (TCA), and 1,1-dichloroethylene. "Stabilizers" such as 1,4-dioxane have proven useful because they scavenge hydrochloric acid produced through the hydrolysis of solvents and oils in order to prevent solvent degradation.[1] Recent testing has exposed the presence of dioxane in numerous groundwater investigations across the country. However, due to its polar, electron-rich oxygen atoms, 1,4-dioxane is hydrophilic and easily miscible with water.[2] This ability to mix easily with water has made 1,4-dioxane one of the more mobile solvents released into soil. As a result, dioxane plumes have been found to be significantly larger than plumes of other common solvents found nearby. High water solubility combined with low volatility has created challenges for effective remediation and treatment technologies to remove the contaminant from groundwater.

Due to its strong oxidation potential (2.1V), Piper Environmental Group, Inc. (Piper) has repeatedly used ozone (O_3) as an effective means for removal of 1,4-dioxane from groundwater. Analysis of specific data gathered from remediation projects conducted in Oregon, Ohio and California have proven the effectiveness of ozone only oxidation in the destruction of 1,4-dioxane from groundwater at the proper dose , concentration. gas flowrate, injection pressure, and liquid flowrate.

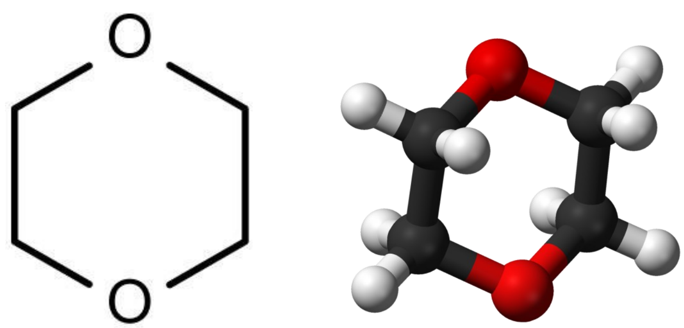

Figure 1: 1,4-Dioxane Molecule in 2-D and 3-D

In depth studies by others recommend the rate of 1,4-dioxane oxidation from groundwater is greatly increased with the application of Advanced Oxidation Processes (AOP), which increase the rate of ozone decomposition into the hydroxyl free radical. Piper postulates excellent contact and mixing design, controlling high concentration ozone flow and pressure is the key to success with 1,4-dioxane destruction.

The rate of hydrocarbon oxidation in groundwater using ozone has been studied extensively. Research conducted by Hoigne and Bader has proven that during water treatment, ozone spontaneously decomposes via a complex mechanism that produces highly reactive intermediate hydroxyl free radicals, oxidation potential of 2.8V,[3, 4] Hydroxyl free radicals perform direct oxidation with the O_3 molecule. Due to ozone's high solubility in water, the concentration of the gas present in the reaction is high, but this direct oxidation process is documented from lab studies and shown to be considerably slower than the reaction involving creation of the hydroxyl free radical,. While acknowledging the studies, Piper has repeatedly demonstrated destruction with ozone as a stand alone treatment.[5, 6]

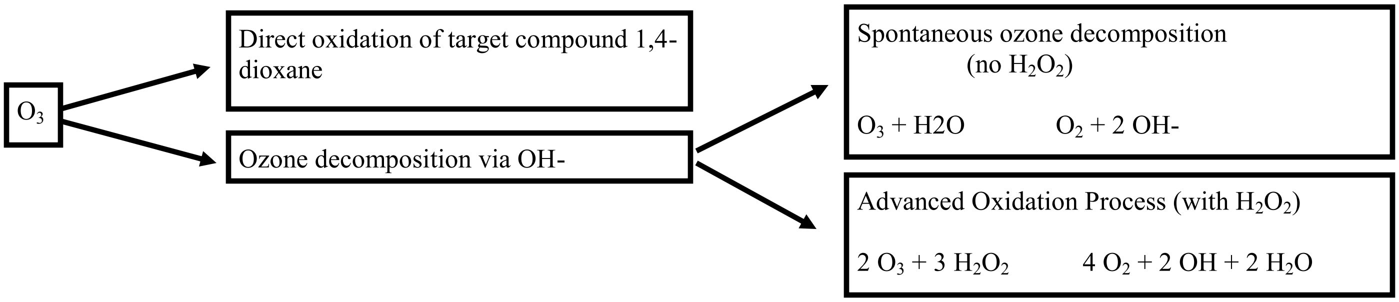

Figure 2: Oxidation pathways for 1,4-dioxane

A study conducted by Stefan and Bolton of The University of Western Ontario was directed at understanding the mechanism and products of 1,4-dioxane degradation through the UV/H_2O_2 AOP. Since this process also results in the rapid production of hydroxyl free radical molecules, it is safe to assume that their results are an accurate profile of the likely products generated from the oxidation of 1,4-dioxane. As the experiment proceeded, it was noted that within the first 5 minutes of exposure, 90% of the initial concentration of 1,4-dioxane was depleted, resulting in four primary reaction intermediates: 1,2-ethanediol mono- and di-formate esters, formic acid, and methoxyacetic acid.[7] These four intermediates react again with hydroxyl radicals, O_2, and H_2O molecules in solution to produce glycolic, acetic, and oxalic acids. The ozone secondary intermediates are then further oxidized to produce carbon dioxide and water as the final products.[7]

1,4-Dioxane Reduction

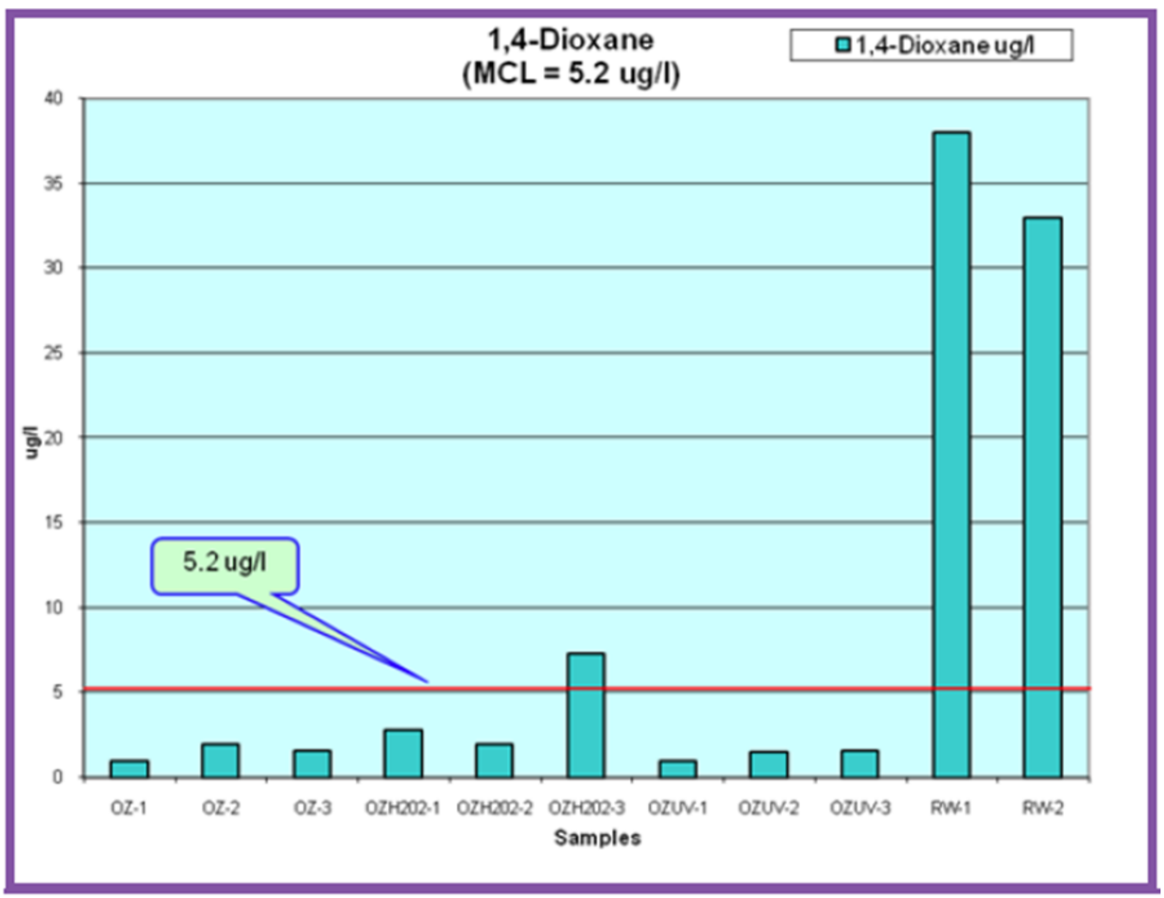

Figure 3: Ex-Situ Ozone, Ozone + H_2O_2, Ozone + UV, (site source)[9]

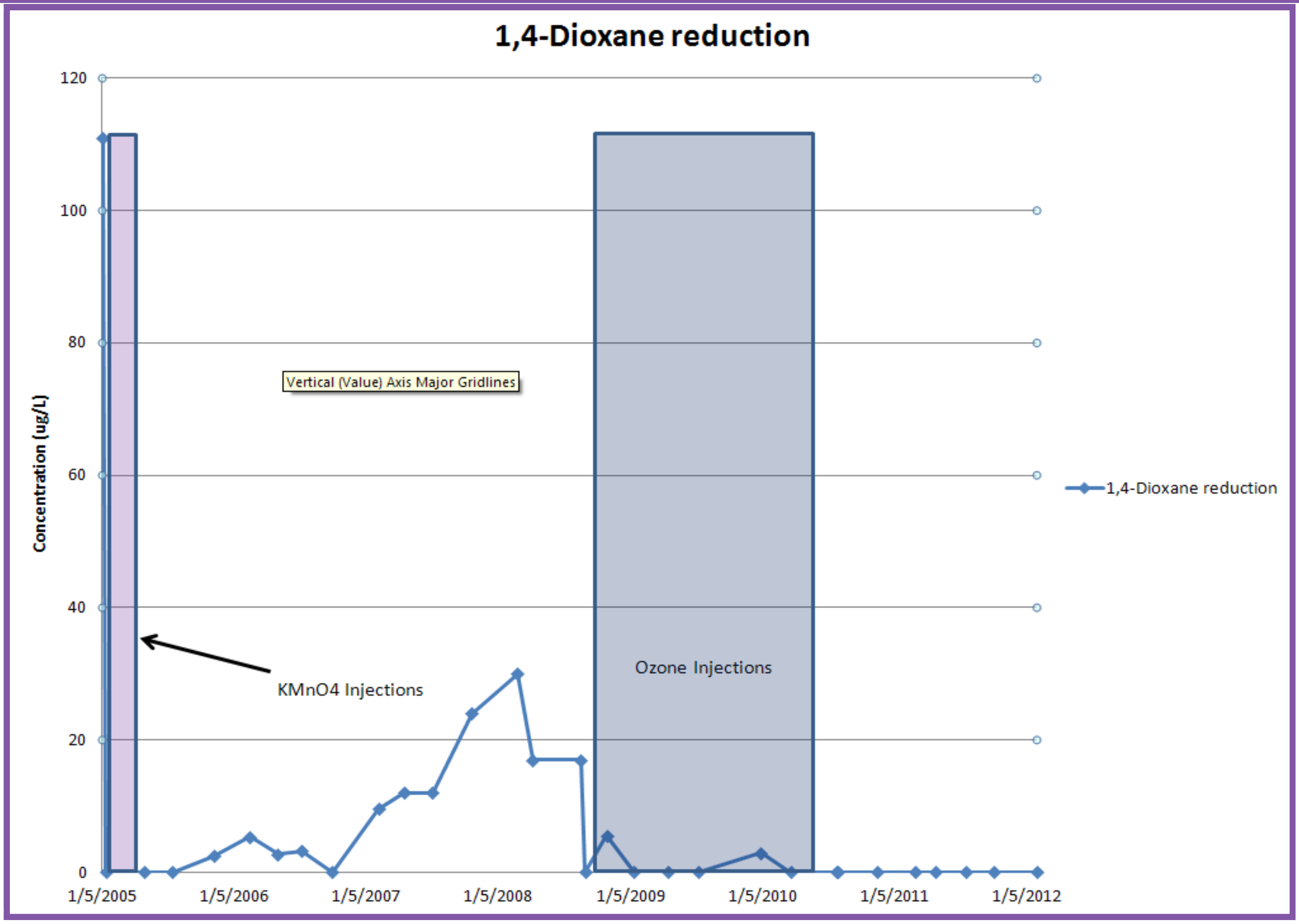

Figure 4. In-Situ Ozone only in Los Angeles[8]

Toxic and hazardous organic compounds found in groundwater are easily removed through in-situ or ex-situ chemical oxidation with ozone gas. Piper has proven this process effective in our analyses of several remediation projects. An ex-situ pilot program was conducted in Oregon on groundwater containing high concentrations of 1,4-dioxane, 1,1-dichloroethane, and toluene. In figure 4 above, ozone only treatments (OZ 1-3) were just as effective as the Advanced Oxidation trials (OZ/H_2O_2 1-3 and OZ/UV 1-3). RW-1 and RW-2 serve as raw, untreated groundwater control samples. Ozone only treatments also proved effective during in-situ groundwater remediation treatments at a Los Angeles, CA site. Figure 4 demonstrates the effectiveness of ozone only treatment in comparison to previous in-situ potassium permanganate ($KMnO_4$) injections. Rebound of 1,4-dioxane concentrations occurred following $KMnO_4$ treatments, but was not detected in the years following in-situ ozone only injections at the same site.

Piper's field studies and systems have demonstrated effectiveness of ozone only remediation demonstrated in our investigations. Laboratory studies have shown that the addition of hydrogen peroxide increases the rate of hydroxyl free radical production and in turn, the rate of degradation of 1,4-dioxane. Two of our studies indicate ozone or ozone with UV (as an AOP process) are optimal treatment methodologies. At Piper, we are capable of designing successful ozone or advanced oxidation processes for your remediation needs upon request, but our proven case studies show that addition of hydrogen peroxide or any additional chemicals is not necessary.

Figure 5. Advanced Oxidation process in Ohio[10]

Figure 5 is an Advanced Oxidation Process for 1,4-Dioxane and approximately 150 other measureable contaminants placing a demand on the ozone system. AOP was deemed the appropriate technology due to the heavy and varied loading at the site.

AOP's involve the rapid generation of highly reactive hydroxyl free radical intermediates, which in turn cause a significant increase in the rate at which oxidation of the target compound occurs.

To understand the optimal treatment methodology, extensive analysis for all possible contaminants, metals, bacteria, iron, manganese, COD, BOD, etc. must be conducted. From that an onsite pilot system is highly recommended.

[1]Moyer, Ellen. *1,4-Dioxane: Regulatory Developments, Uses, Properties, Assessment, and Remediation*. N.p.: n.p., 2008. Print.

[2]USEPA, Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications, December 2006.

[3]Sumner, Ann Louise, and Michelle Simon. "Laboratory Investigations of Mechanisms for 1,4-Dioxane Destruction by Ozone in Water." Chlorinated and Recalcitrant Compound Conference Monterey,

[4]Hoigne, J., and H. Bader. "Ozonation of Water: Role of Hydroxyl Radicals as Oxidizing Intermediates." *Science, New Series* 190.4216 (1975): 782-84. Print.

[5]Huling, Scott G., and Bruce E. Pivetz. *In-situ Chemical Oxidation*. Comp. United States Environmental Protection Agency. N.p.: n.p., n.d. Print.

[6]United States Environmental Protection Agency, comp. *Alternative Disinfectants and Oxidants Guidance Manual*. N.p.: n.p., 1999. Print.

[7]Stefan, Mihaela I., and James R. Bolton. "Mechanism of the Degradation of 1,4-Dioxane in Dilute Aqueous Solution Using the UV/Hydrogen Peroxide Process." *Environmental Science & Technology* 32.11 (1998): 1588-95. Print

[8] Piper Environmental Group Inc. (2012, April). *Ozone Case Study: Former Aerospace Degreasing Operation, Los Angeles, California*

[9] Piper Environmental Group Inc. (2012, May). *Ozone Case Study: Active Truck Stop Spill Central Point, Oregon*

[10] Piper Environmental Group Inc. (2012, March). *Ozone Case Study: Industrial Chemical and Solvent Plant Advanced Oxidation with Iron Control, Ohio.*

Company Profile

Piper Environmental Group, Inc. offers ozone technology, equipment, and services for a wide-range of environmental applications. The company designs, manufactures, and integrates ozone systems and related equipment for short and long-term projects, offering equipment for rent or purchase. Services include project design assistance, oxidation pilot studies, contract service, equipment repair, consulting. Our area of expertise is large remediation projects.

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