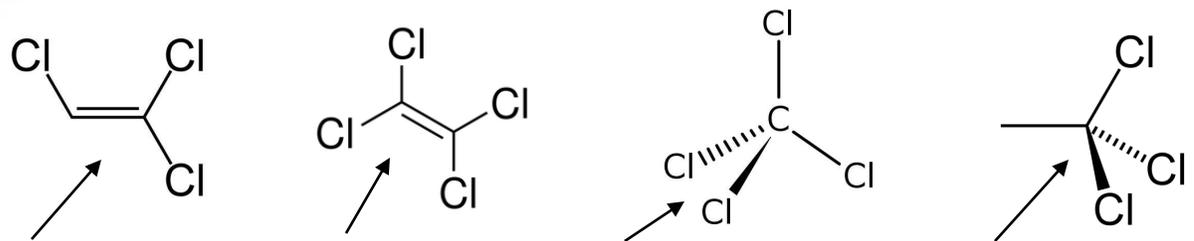




Technical Brief: DNAPL Destruction with Ozone

Piper Environmental Group Inc. has successfully treated dense non-aqueous phase liquids (DNAPL) with ozone at various sites. DNAPLs are as their name suggests, liquids that are both immiscible with water and denser than water. Thus DNAPLs generally have downward mobility at contaminated sites and typically consists of compounds such as chlorinated solvents [trichloroethylene (TCE)^{1,2}, tetrachloroethene (PCE), 1,1,1-trichloroethane (TCA)³, carbon tetrachloride (CTC)], polycyclic aromatic hydrocarbons (PAHs)^{4,5}, coal tar, creosote, polychlorinated biphenyl (PCB), mercury, and extra heavy crude oil.⁶ These chemicals have been introduced to numerous groundwater and soil sites through contaminated sites such as degreasing facilities, dry cleaners, wood treaters, and former manufactured gas plants.⁶ DNAPLs such as TCE and PCE are some of the most common chemicals found at highly contaminated sites throughout the United States.



Trichloroethylene, Tetrachloroethene, Carbon Tetrachloride, and 1,1,1-trichloroethane
Figure 1: Examples of DNAPLs

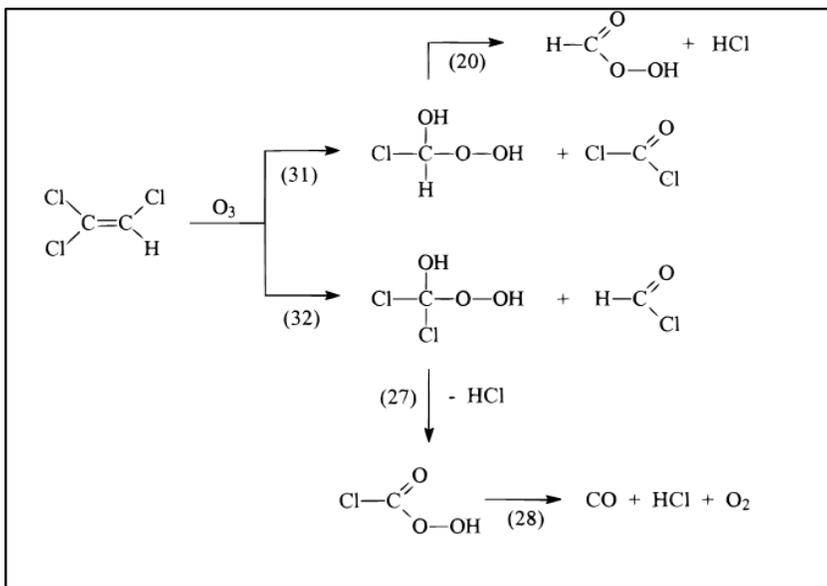
DNAPLs have become notorious throughout the environmental remediation community because their unique physical and chemical properties, including: low solubility, high specific gravity and density, as well as immiscibility in water leads to a tendency to remain sorbed to organic material in soil and makes them difficult solvents to remove from soil and groundwater.⁶ Due to these characteristics, traditional processes such as pump and treat have proven generally ineffective for removal of vapor, sorbed-phase contamination and DNAPL sources. The high specific gravity of these solvents gives them rapid downward mobility and as a result, DNAPLs released to the subsurface have capacity to sink below the water table where they provide a long-term source of contamination.⁷ This downward movement often produces three major zones in which DNAPL can be found within the ground. The first, known as the source zone, is the location that has the highest concentration of potentially mobile DNAPL. The source zone is most likely to be found beneath the water table, due to the high specific gravity of the DNAPL solvents.³ Areas through which DNAPL has already moved are known as residual zones. Lastly, the third zone is considered to be the plumes of dissolved contaminant radiating from either the source or residual zones.⁸



Figure 2: Typical Manufactured Gas Plant

A variety of technologies including in-situ thermal treatment, in-situ chemical oxidation, surfactant/co-solvent flushing, and in-situ bioremediation have been applied to treat DNAPL sources. However, this review will primarily focus on the effectiveness of ozone based chemical oxidation on several common contaminants found at DNAPL rich sites.

The reaction products and processes of ozonation of chlorinated solvents often found at DNAPL sites such as trichloroethene and tetrachloroethene have been extensively investigated. In a lab study conducted by Dowideit and von Sonntag, reactions of ozone with these chlorine substituted ethane derivatives in aqueous solutions were studied. Exposure of trichloroethene (TCE) to ozone gas (O₃) produces numerous pathways to a variety of formic and chloroformic peracids.⁹ These compounds proceed to react with reaction intermediates present in solution, resulting in formic peracid, hydrochloric acid, water, carbon dioxide and oxygen.⁹ Hydrochloric acid is a strong acid, and thus dissociates into chloride ions (Cl⁻) and hydrogen (H⁺).⁹ Figure 1 below taken from the Dowideit and von Sonntag study displays the proposed mechanism and formation of products from the ozonation of trichloroethene. The reaction pathway resulting in the production of formic peracid (reactions 31 and 20) illustrated below, predominates over the formation of chloroformic peracid (reactions 32, 27 and 28) by a ratio of 22:1.⁹



Ozone reactivity has been proven to be inversely proportional to the degree of chlorination of the target compound. As a result, the direct pathway ozone oxidation rate of tetrachloroethene, or PCE, (rate constant of $k \leq 0.1 \text{ M}^{-1} \text{ s}^{-1}$) is a slower reaction.¹⁰ Observation of the gas phase ozonation of tetrachloroethene at 25 °C revealed major byproducts such as oxygen, phosgene (Cl₂CO) and trichloroacetyl chloride.¹¹ Minor byproducts such as tetrachloroepoxide, carbon monoxide, carbon dioxide, and chlorine were also detected.¹¹ Compounds such as tetrachlorosuccinic acid, dichloroacetic acid, trichloroacetic acid, carbon dioxide and ions were detected during a similar study of tetrachloroethylene oxidation in aqueous solution using hydroxyl radicals.¹²

Figure 3: TCE ozone oxidation reaction pathway⁹



Figure 4: Ozone barrier at Former MGP

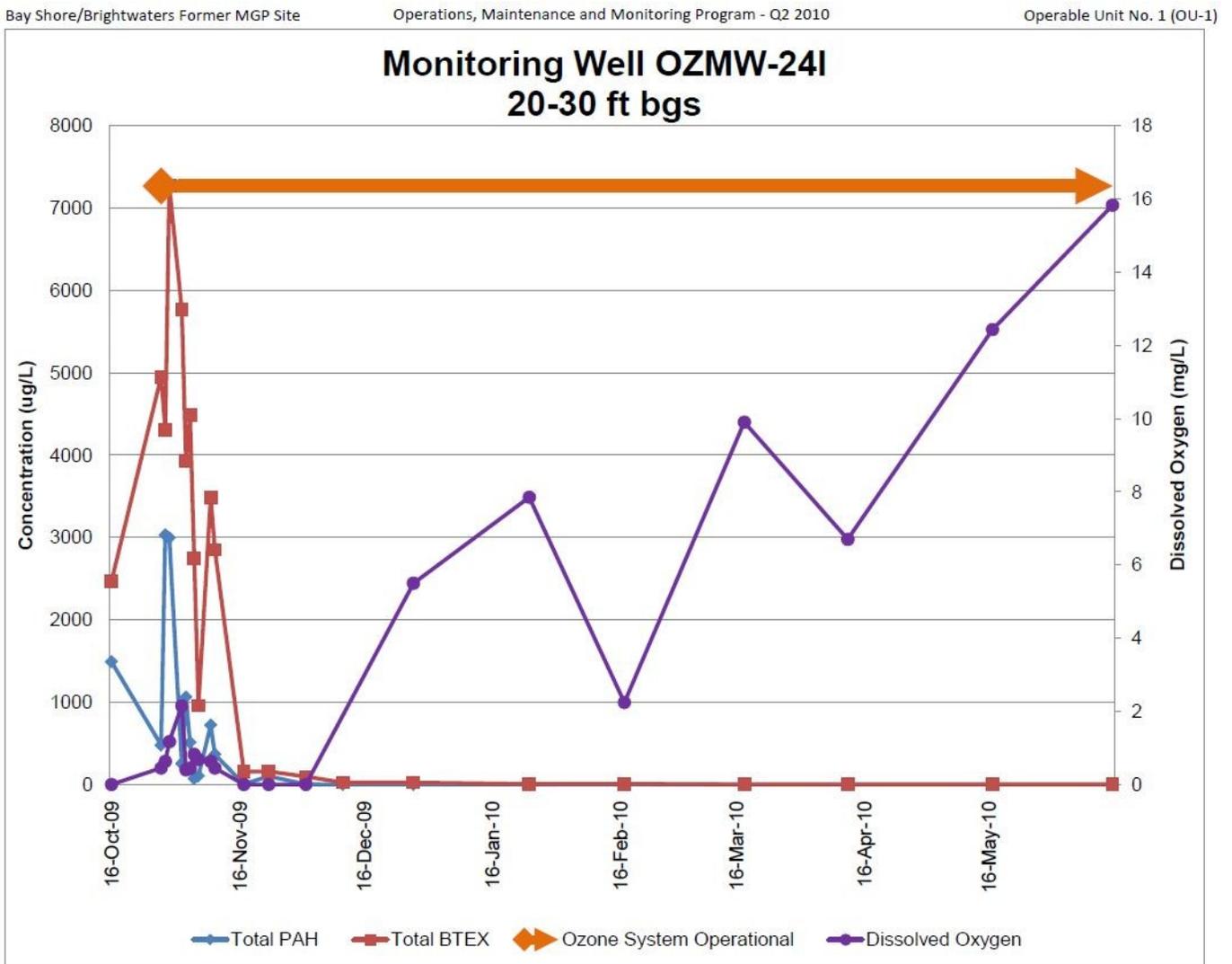


Figure 5: Ozone well field installation

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Studies indicate the direct pathway interaction between ozone and these chlorinated ethenes is slow, and generally advise hydrogen peroxide be used in conjunction with ozone Advanced Oxidation Process (AOP) to facilitate the oxidation breakdown process. However, ozone is effective as a stand-alone treatment as results indicate.

DNAPLs also encompass a category of contaminants called creosotes, which are mainly derived through tar distillation. Creosotes are mainly comprised of a type of compound called a polycyclic aromatic hydrocarbon (PAH). Upon exposure to ozone, PAHs degrade into a variety of compounds including polycyclic aromatic compounds (PAC), dead end products such as carbonyl compounds, ketones, quinones, dicarboxylic acid anhydrides, and coumarins.¹⁴ Creosote PAHs also degrade into carboxylic acids and phenols, which eventually deteriorate into harmless compounds such as carbon dioxide, water, and other inorganic species.¹⁵



GEI Consultants, Inc.

Figure 6: Former MGP COC reduction

Ozone has proven effective in oxidizing trichloroethenes and tetrachloroethenes, PAHs, creosotes, and additional DNAPL contaminants. Ozone can be introduced into contaminated zones as a gas or by dissolving ozone in water. When injected into the ground as a gas, ozone reacts with contaminants through the direct oxidation pathway while providing an oxygen-rich environment to aid compound degradation under aerobic conditions.⁸ When dissolved in water, ozone undergoes spontaneous decomposition to the highly reactive hydroxyl radical, which accelerates decomposition of the desired DNAPL compounds. However, oxidants that are introduced into an aqueous solution have limited contact between the oxidant solution and the DNAPL surfaces, so injection methodology must be carefully designed. This restricted interaction between ozone and the contaminants of concern (COC) is one of the challenges often encountered in DNAPL remediation.⁸ Care must also be taken in order to prevent plume and source zone migration while remediation is underway. Advanced Oxidation with H₂O₂, as well as other in-situ oxidation processes are also effective in DNAPL degradation due to the rapid production of hydroxyl radicals. At Piper Environmental Group, Inc. we are able to custom design optimal ozone remediation systems and methods as needed in order to successfully remove DNAPL from contaminated groundwater and soil sources. To complete this task all contaminants and historical analysis and trends are required.

¹ Piper Environmental Group Inc. (2012, March). *Ozone Case Study: Mixed Industrial & Dry Cleaners Site, Southern California*

² Piper Environmental Group Inc. (2012, April). *Ozone Case Study: Former Aerospace Degreasing Operation, Los Angeles, California*

³ Piper Environmental Group Inc. (2012, May). *Ozone Case Study: Active Truck Stop Spill Central Point, Oregon*

⁴ Piper Environmental Group Inc. (2012, March). *Ozone Case Study: Former Manufactured Gas Plant Site, Bay Shore/Brightwaters, New York.*

⁵ Piper Environmental Group Inc. (2010, November). *Ozone Case Study: Former Manufactured Gas Plant Site, Santa Barbara, California.*

⁶ *DNAPL Remediation: Selected Projects Approaching Regulatory Closure* (United States EPA, Comp.). (2004, December).

⁷ GeoSyntec Consultants. (2004, April). *Assessing the Feasibility of DNAPL Source Zone Remediation: Review of Case Studies* (Contract Report No. CR-04-002-ENV).

⁸ CLU-IN US EPA. (2013, May 17). Dense Nonaqueous Phase Liquids (DNAPLs): Treatment Technologies. Retrieved July 2, 2013, from [http://clu-in.org/contaminantfocus/default.focus/sec/Dense+Nonaqueous+Phase+Liquids+\(DNAPLs\)/cat/Treatment+Technologies/](http://clu-in.org/contaminantfocus/default.focus/sec/Dense+Nonaqueous+Phase+Liquids+(DNAPLs)/cat/Treatment+Technologies/)

⁹ Dowideit, P., & von Sonntag, C. (1998). Reaction of Ozone with Ethene and Its Methyl- and Chlorine-Substituted Derivatives in Aqueous Solution. *Environ. Sci. Technol.*, 32(8), 1112-1119.

¹⁰ Karimi, A. A., Redman, J. A., Glaze, W. H., & Stolarik, G. F. (1997). Evaluating an AOP for TCE and PCE removal. *Journal of American Water Works Association*, 89(8), 41-53.

¹¹ Bailey, P. S. (1978). *Ozonation in Organic Chemistry* (Vol. 1). New York, NY: Academic Press, Inc.

¹² Mertens, R., & von Sonntag, C. (1994). Reaction of the OH radical with Tetrachloroethene and Trichloroacetaldehyde (Hydrate) in Oxygen-free Aqueous Solution. *J. Chem. Soc. Perkin Trans.*, 2181-2185.

¹³ Clancy, P. B., Armstrong, J., Couture, M., Lussky, R., & Wheeler, K. (1996). Treatment of Chlorinated Ethenes in Groundwater with Ozone and Hydrogen Peroxide. *Environmental Progress*, 15(3), 187-193.

¹⁴ Glaze, W.H.; and J. W. Kang (1988, May). "Advanced Oxidation Process for Treating Groundwater Contaminated with TCE and PCE: Pilot-Scale Evaluations," *J. American Water Works Assoc.* pp. 64-72.

¹⁵ Lundstedt, S. (2003). *Analysis of PAHs and their transformation products in contaminated soil and remedial processes*. Solfjadern Offset AB.

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.



Figure 7-8: Trailer Mounted System