OZONE CASE STUDY
Former Aerospace Degreasing Operation
Los Angeles, California
In-Situ Ozone Injection

Background

Historic activities at the site involved degreasing and industrial cleaning service using solvents, primarily tetrachloroethene (PCE) and trichloroethene (TCE) to support the growing aerospace industry in Southern California. Site investigations indicated the presence of volatile organic compounds (VOCs), including. PCE, TCE, cis-1,2-dicloroethene (1,2-DCE), 1,1-dichloroethane (1,1-DCA), 1,1-dichloroethene (1,1-DCE), 1,4-Dioxane and methylene chloride. Beginning in 2002, source removal occurred using soil excavation, as well as single and multi-phase extraction. Groundwater remediation began in 2004 using liquid oxidant injections and later achieved final closure levels using ozone gas injection.

Previous Remediation Efforts

Initially 822 tons of contaminated soil were removed by excavator and bucket auger. Starting in 2004, a multi-phase extraction (MPE) system was installed as an interim remedial measure. Between April and December 2004, approximately 16,000 pounds (lbs) of VOC's were removed from the vadose and shallow groundwater zones. In October 2004, a remedial action plan and WDR permit were approved to inject sodium and potassium permanganate. The liquid oxidant materials were injected at approximately twenty-six (26) Geoprobe locations between depths of 65 and 75 feet bgs. Dissolved-phase VOC concentrations were reduced by 1-to-2 order of magnitude, but still remained elevated (500 to 5,000 ug/L). Additional groundwater remediation was necessary on-site and immediately down gradient.

Solution

To build upon and exceed the successes of previous remediation technologies, Piper Environmental Group was contacted to supply an integrated rental ozone system large enough to achieve site closure. Piper's 28 pound per day (PPD) ozone system was selected for in-situ chemical oxidation based on several factors: first, ozone gas has a high oxidation potential and the ability to penetrate finer-grained aquifer materials where residual contamination is often locked; second, Piper's unit generated higher ozone delivery than other vendor equipment available for rent; lastly, based on ease of implementation and cost (as an expense item and not capitalized) and most importantly, the ability to reach site closure quickly. The system was pre-built at Piper's manufacturing facility and tested before it was shipped to the site. The system was then re-assembled on-site which allowed for immediate use.

Unique to this site was the need for angled injection wells that reached underneath occupied residences. Ozone was injected into the saturated and capillary fringe zones.

Soil Excavation Summary

- Former degreaser location: 522 tons of contaminated soil excavated at depths of 25-45 feet bgs
- Former staging area: 300 tons of contaminated soil excavated at depths of 0-6 feet bgs

Multi-Phase Extraction System

- Between April - December 2004, approximately 16,000 pounds of VOC's removed
- Shallow groundwater and vadose zones

Soil Vapor Extraction Equipment

- Began in December 2004 - Present
- 10 vapor extraction wells - alternating
- 250 CFM total flow

Ozone Monitoring System

- Health & Safety: Ambient Ozone monitor interlocked to shut down system in event of a leak

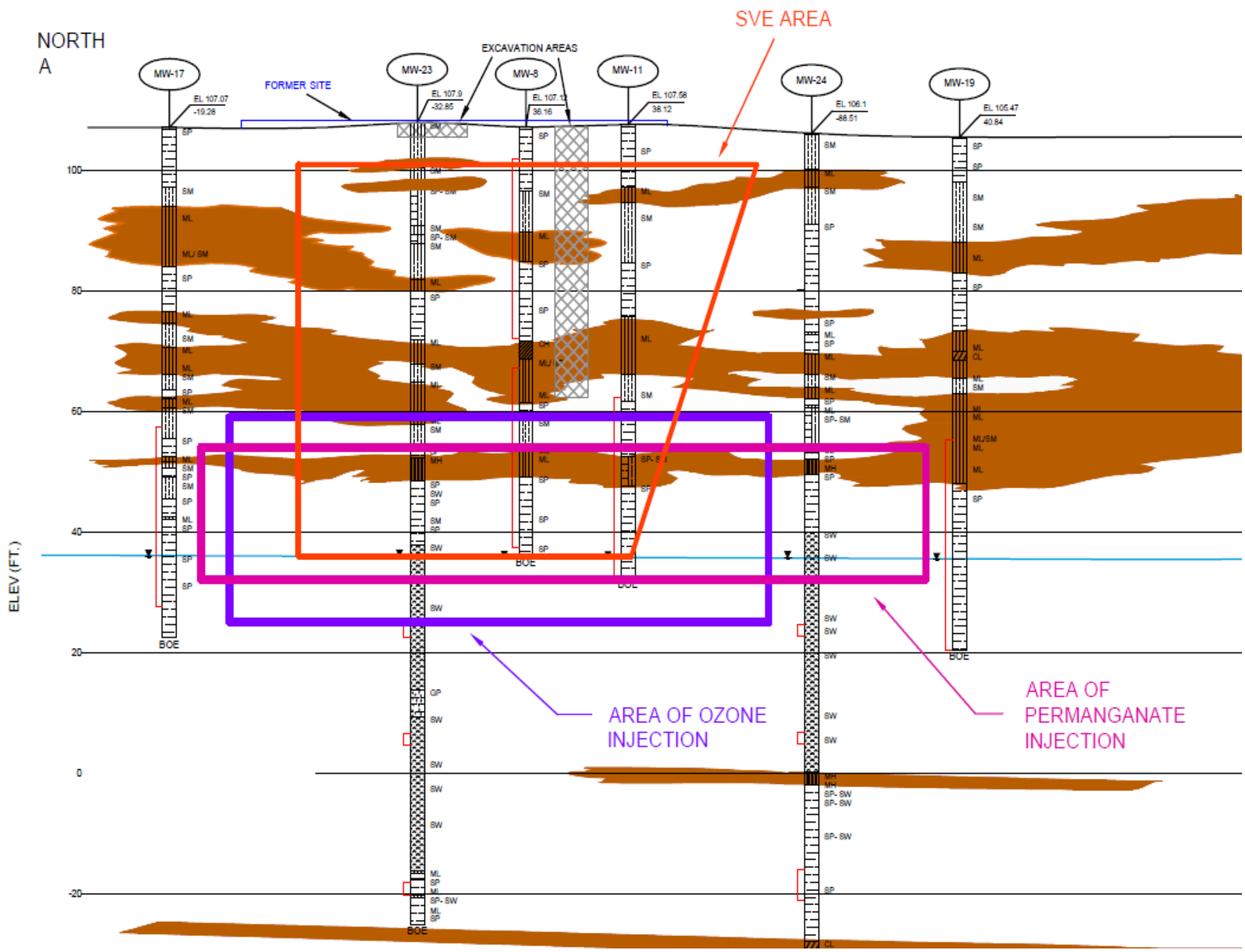
Ozone System Description

- Between September 2008 - June 2010
- Ozone generator producing 28 PPD
- Generator operated at 15 psig at 8 SCFM
- 16 ozone sparge wells
- 24 monitoring wells
- Depths of sparge points varied from 48 to 83 feet below ground surface
- 18,000 pounds ozone injected

Ozone Distribution

- Sixteen (16) sparge points
- Sixteen (16) programming stages to select 1 to 4 valves per stage for maximum gas control at a flow rate of 2 SCFM each
- Controlled from a HMI touch screen
- Final gas stream composition: ~2% ozone

The picture below illustrates the sub-surface contamination along with the remediation areas for the various cleanup methods.

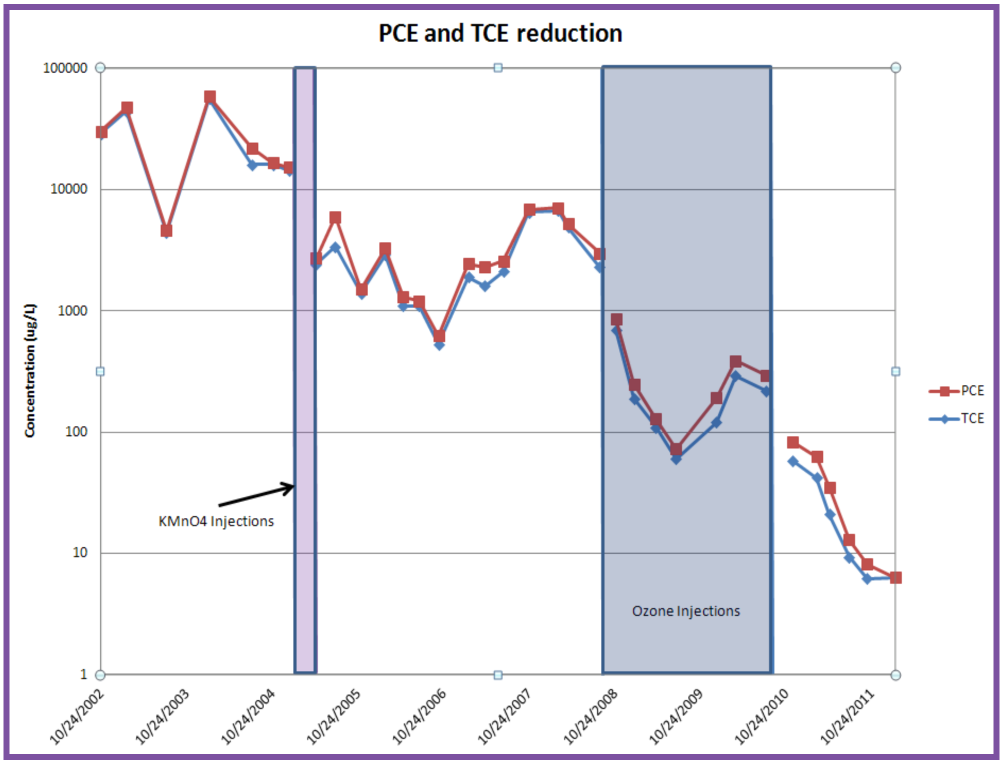


Results

PCE and TCE were primary Constituents of Concern (COC) and treatment success benchmark. The table and graph summarize concentrations of PCE and TCE in groundwater before and after permanganate and ozone in-situ remediation.

Permanganate was injected both off site along Buckles street to prevent the contaminants from migrating downstream as well as on-site. Permanganate injections significantly reduced contaminants; however, it did not accomplish site goals by the time its effects waned in 2006. Rebounding effects were exhibited between 2006 and 2008.

PCE and TCE Overall Reduction



Of particular interest is the continued downward trend of PCE & TCE after ozone shutdown. This effect is often the sign of a successful remediation design that addresses both dissolved-phase and sorbed-phase contamination. Other VOCs identified and tracked in the groundwater achieved similar success and include cis-1,2-dicloroethene (1,2-DCE), 1,4-Dioxane, and vinyl chloride (chloroethene).

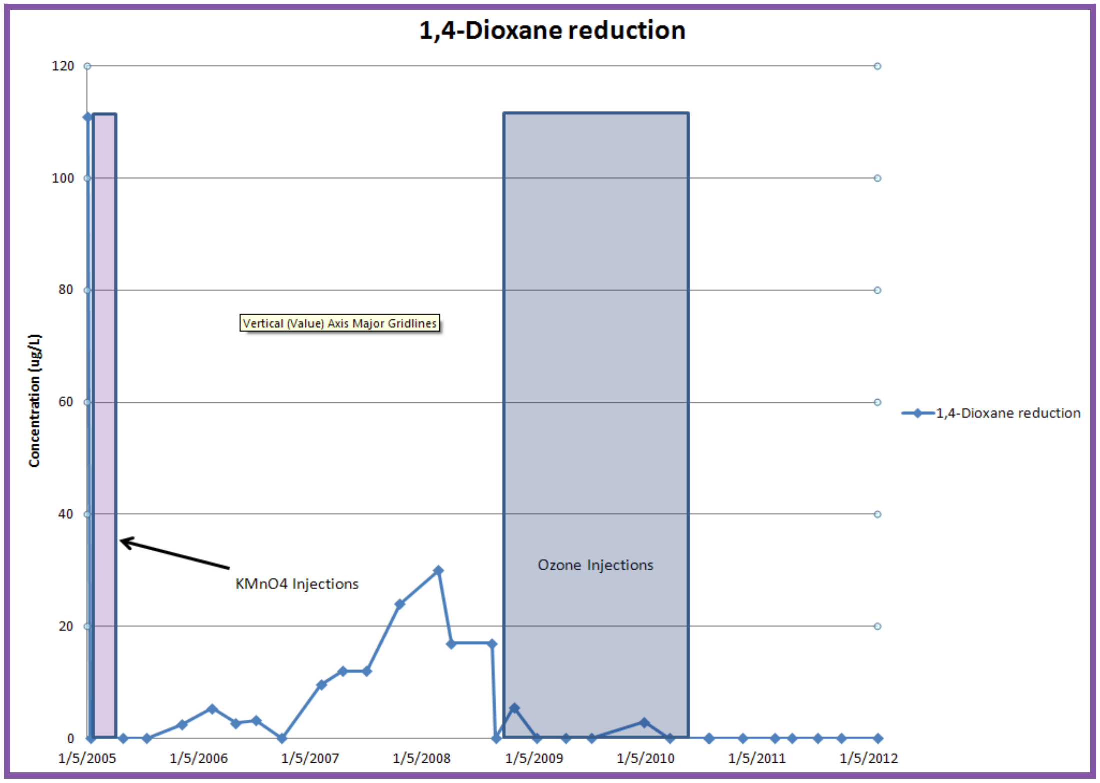
PCE Concentration (μg/L)

Mon. Well	Historic Max Conc.	**Permanganate Injection November 2004**	2006 Max Conc.	2008 Max Conc.	**Ozone Injection Begin September 2008**	1st Q 2009 Conc.	Reduction
MW-1	56,000		2,900	6,700		190	99.7%
MW-3	15,000		680	120		ns	99.2%
MW-10	15,000		230	180		130	99.1%

TCE Concentration (μg/L)

Mon. Well	Historic Max Conc.	**Permanganate Injection November 2004**	2006 Max Conc.	2008 Max Conc.	**Ozone Injection Begin September 2008**	1st Q 2009 Conc.	Reduction
MW-1	7,300		370	690		58	99.7%
MW-3	80,000		4,400	1,200		ns	99.2%
MW-10	18,000		6,100	1,500		70	99.1%

1,4-Dioxane Reduction by Ozone



The graph to the left summarizes the concentrations of 1,4-Dioxane in groundwater before and after in-situ remediation. Note immediate reduction with Permanganate and then rebound.

Ozone immediately reduced 1,4-Dioxane.

However, after ozone injection system had been off for 2 years, the 1,4-Dioxane concentrations are constantly non-detectable and no rebounding has been observed.

Chlorinated Solvents Information

Chlorinated solvents have properties that make them useful for degreasing oils. They are used widely and have been manufactured in large quantities. Some chlorinated solvents are dichloromethane, tetrachloroethene, trichloroethane, and tricholoroethene.

Chlorinated solvents in general are harmful to human health. They can cause or are suspected of causing cancer, and are toxic or harmful to aquatic organisms.

Spills and leaks of chlorinated solvents have caused widespread subsurface contamination in the environment. Commonly these contaminants are present in the subsurface in the form of non-aqueous phase liquids (NAPL, the bulk chemical product), as dissolved contaminants in ground water, associated with aquifer sediments, and as vapors in the unsaturated zone. Because the density of these NAPL's is greater than water, they tend to sink in ground water systems. which results in a complex dispersal and plume patterns, long-term sources in the subsurface, and difficult clean-up.

With special consideration and appreciation to our project partners:
Mr. Jeremy Squire of Murex Environmental (www.murexenv.com)
Ms. Yuechen Zhao of Murex Environmental (www.murexenv.com)

Additional products and services for in-situ and ex-situ applications are here: http://www.peg-inc.com

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.

11600 California Street Castroville, California 95012
Phone: 831- 632-2700 Fax: 831- 632- 2701