

***IN SITU* OZONATION TO REMEDIATE RECALCITRANT ORGANIC CONTAMINATION**

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In situ ozonation has been successfully applied to remediate soil and groundwater contamination at numerous industrial facilities contaminated by chlorinated solvents, wood treating chemicals and polycyclic aromatic hydrocarbons (PAHs). *In situ* ozonation has been used in pilot and full scale applications to initially oxidize target contaminants and to subsequently enhance the activity of the indigenous bacterial colonies. This paper will discuss the successful, full-scale application of *in situ* ozonation at two former manufactured gas plant (MGP) sites in Dubuque, Iowa and Long Beach, California.

The site in Dubuque, Iowa, is administered under CERCLA by Region VII EPA. Remedial efforts on site have included an extensive excavation of impacted soils with treatment by co-burning in a utility boiler. A fast track implementation of an ozone sparging system was constructed within a confined aquifer to employ the combined effects of chemical oxidation and bioremediation on the MGP contaminants.

In situ ozone sparging was initially field tested, then selected for full-scale implementation for treatment of the silty sand aquifer on-site. Ozone sparging was selected based on its ability to oxidize high molecular weight PAHs such as benzo (a) pyrene while enhancing *in situ* aerobic bioremediation.

The target treatment area is the silty sand unit, a confined aquifer encountered at a depth of 25 to 36 feet below grade. Residues generated from the original gas manufacturing operations consist of tar, oils, and emulsions containing PAHs. Initial concentrations within the silty sand unit were as high as 5400 ppm total PAHs and 120 ppm carcinogenic PAHs in soil. Baseline dissolved contaminants ranged as high as 6,400 ppb naphthalene and 58 ppb benzo (a) pyrene.

Ozone sparging significantly reduced DNAPL, PAH, and BTEX concentrations associated with MGP wastes at the PNG site. Initial testing on site over the first 12 week injection period reported a dissolved contaminant concentration reduction of greater than 70% in the area of treatment for both BTEX and PAH contaminants. A comparison of groundwater analytical data from the December 2000 and March 2001 sampling events indicates the following trends with respect to groundwater quality within the target aquifer:

- Sharp decrease in BTEX concentrations at one well located within the main area of residual contamination was observed. Benzene and ethylbenzene concentrations both decreased by an order of magnitude. Concentration trends for PAHs were mixed, however acenaphthene and naphthalene were not detected in the groundwater sample from this well for the first time since monitoring began (1994). The non-detection of naphthalene at this location represents a decrease of two orders of magnitude.

- BTEX concentrations within the central area of the sparge zone decreased by a minimum of 50 percent, while a corresponding sharp increase in PAH concentrations (particularly naphthalene) occurred.
- BTEX concentrations at relief wells located downgradient of the treatment area also decreased by a minimum of 50 percent. Corresponding decreases in PAH concentrations, particularly naphthalene, were noted in these groundwater samples.
- DNAPL measurements in four newly installed monitoring wells within the target aquifer and located side-gradient (east) to flow direction indicated no DNAPL. This finding indicates that the main area of residual contamination is laterally bounded.

A full-scale, *in situ* ozonation system to remediate polycyclic aromatic hydrocarbons (PAH) in soil and groundwater began operating in early 1999 at a former manufactured gas plant (MGP) site in Long Beach, California. The site is under an elevated roadway interchange adjacent to the Los Angeles River flood control channel, requiring *in situ* remediation.

Residues generated from the original gas manufacturing operations consist of tar, oils, and lampblack containing (PAHs). Initial concentrations of the primary constituents were as high as 2,484 mg/kg for total PAHs, 100 mg/kg for benzo (a) pyrene (BaP), and 27,800 mg/kg for total petroleum hydrocarbons (TPH) in soil. Baseline dissolved contaminant concentrations ranged as high as 912,000 ug/l for TPH, 4,820 ug/l for benzene, 20,000 ug/l for naphthalene, and 340 ug/l for BaP.

An *in situ* ozonation system was constructed at the site utilizing a combination of vertical and horizontal wells to effectively distribute ozone in the subsurface. A total of 33 vertical sparge wells, constructed of Teflon, Viton, and 316 stainless steel and screened at a depth of 25 feet, were installed throughout the contamination plume. In addition, a single 360-foot horizontal well with a 135-foot screened section in the middle was installed through the center of the plume at about 6 feet below the water table.

Ozone, generated on site from a pure oxygen feedstock, was pulsed into the wells in both the saturated and vadose zones to promote chemical oxidation and enhanced biodegradation. A soil vapor extraction system with an ozone destruct catalyst was used to prevent unreacted ozone from reaching the surface.

After the first quarter of ozone treatment, groundwater sampling revealed that initial dissolved contaminant concentrations were reduced to below detectable levels. In particular, BaP was reduced to below the MCL level of .2 µg/l. Separate phase mixtures of heavy oils and PAHs accumulated in wells after three months of ozonation, indicating significant desorption from soil of MGP residues. In addition, the character of the oils changed during the remediation indicating enrichment of the light fractions along with depletion of the heavy fractions. After two quarters of soil sampling showed no consistent trends, soil concentrations began to sharply decrease during the third and fourth quarters. The site has been closed using an industrial risk scenario.