FIELD APPLICATION OF IN SITU METHANOTROPHIC TREATMENT FOR TCE REMEDIATION

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ABSTRACT: In situ methanotrophic treatment technology (MTT) was evaluated at a site contaminated with chlorinated ethenes and hydrocarbons near a natural gas pipeline compressor station. The formation is characterized by approximately 50 ft (15 m) of saprolitic overburden above bedrock, and a depth to groundwater of 8 to 10 ft (2.4 to 3 m). The MTT system was automated and normally unattended. Air and methane were injected, along with nitrous oxide (N_2O) and triethylphosphate (TEP), as nutrient sources; TEP delivery was intermittent because of design issues. Trichloroethene (TCE) levels dropped from 2130 to 150 µg/L in the well initially exhibiting the highest concentration. The radius of influence of the air injection was approximately 30 ft (9 m). Methanotrophic bacteria increased over six orders of magnitude and eventually dominated the subsurface microbiota. The results indicate that, as long as nitrogen and phosphorus were reliably supplied, rapid (two to four weeks) growth of methanotrophs and associated oxidation of TCE followed. This pilot system was expanded to bioremediate the entire plume above bedrock; three additional injection wells were installed, along with observation wells, and a new TEP diffusion system was developed.

INTRODUCTION

Methanotrophic bacteria produce methane monooxygenase (MMO) to metabolize methane. This oxygenase is non-specific and oxidizes trichloroethene (TCE) to TCE epoxide, which breaks down rapidly into daughter products that are readily biodegradable (Wilson and Wilson, 1987). This is the principle behind methanotrophic treatment technology (MTT), as developed by the Gas Research Institute (GRI) in a multiyear, multidisciplinary research and development effort (Legrand, 1995). MTT was applied in situ at the U.S. Department of Energy's Savannah River site in 1993-94 to remediate a TCE plume. Air, methane, N_2O, and triethylphosphate (TEP) (nitrogen and phosphorus sources, respectively) were injected via a horizontal well to stimulate the growth of methanotrophs, achieving substantial growth of methanotrophs, production of MMO, and degradation of TCE (Hazen et al., 1997).

A gas transmission company and GRI contracted with Radian International LLC to evaluate in situ MTT at a natural gas pipeline compressor station, with subsurface contamination. The site is in rural Virginia. Depth to groundwater is 8 to 10 ft (2.4 to 3 m), and average groundwater velocity is 1.2 cm/day. The formation consists of approximately 50 ft (15 m) of saprolitic overburden

(hydraulic conductivity: 3×10^{-4} cm/s) above bedrock.. The maximum concentration of chlorinated volatile organic compounds (VOCs)—mainly tetrachloroethene (PCE) and TCE—is approximately 2000 µg/L; some hydrocarbon contamination is also present. The contamination is found throughout the saturated saprolite and the upper fractured bedrock. The areal extent of the plume is around 1 acre (0.4 hectare).

Objective. The objective of this project was to evaluate the feasibility and effectiveness of in situ MTT at this site by showing substantial (one order of magnitude) and rapid (a few months) degradation of TCE, the main contaminant of concern. The process had to be simple to install and operate.

MATERIALS AND METHODS

Plan and cross-sectional views of the well locations can be found in Figures 1 and 2, respectively. The injection well (IW-1) was installed within 5 ft (1.5 m) of existing Well MW-7 to target a TCE hot spot and allow monitoring from MW-7. Additional observation wells (OW-1 through OW-4) were installed as indicated, based on an expected radius of influence (ROI) of less than 20 ft (6 m). The injection well was constructed of 1-in. (2.5-cm) diameter galvanized steel casing with 1 ft (30 cm) of 2-in. (5-cm) diameter stainless steel, wire-wrapped well screen. Clean uniform sand was emplaced to 6 in. (15 cm) above the screened interval, and a 2.5 ft (75 cm) bentonite seal was placed above this filter pack. The remaining annulus was grouted to land surface. The observation wells were constructed of 2-in. (5-cm) diameter Schedule 40 PVC casing, and 18 to 30 ft (5.5 to 9 m) of screen. Two soil vapor sampling points were also installed.

The MTT equipment was installed inside a shed and included the following:

- A 3/4 hp (0.56 kW) air compressor with a 30-gal. (114-L) air tank;
- A supply of methane and N_2O in laboratory cylinders, and liquid TEP with a metering pump;
- Piping and valving to successively inject methane, N_2O, and TEP in the air line; mass flow controllers (MFCs) for CH_4 and N_2O; and
- A lower explosive limit (LEL) detector to prevent the methane concentration from exceeding 80% of the LEL.

The airflow was initially 0.85 scfm (24 L/min), resulting in 20 psig (138 kPa) of pressure at the wellhead. The pressure dropped gradually during the course of the test run, requiring the flow rate to be increased to 1.24 scfm (35 L/min) during the last four weeks of the test. Methane and N_2O flow rates were controlled by MFCs to 4% and 0.02% of the airflow, respectively. TEP was metered in at approximately 0.24 mL gas/min. The system was unattended, although several site visits were made during the test run.

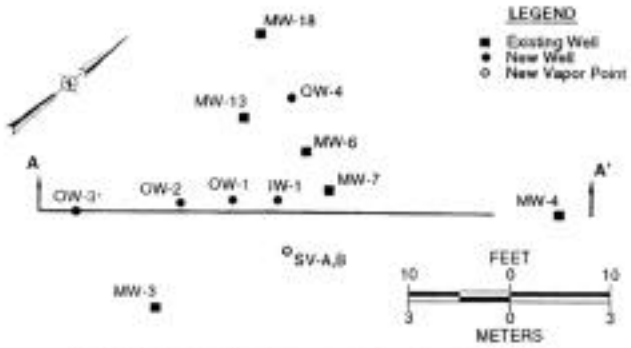

FIGURE 1. In situ MTT demonstration, plan view of wells

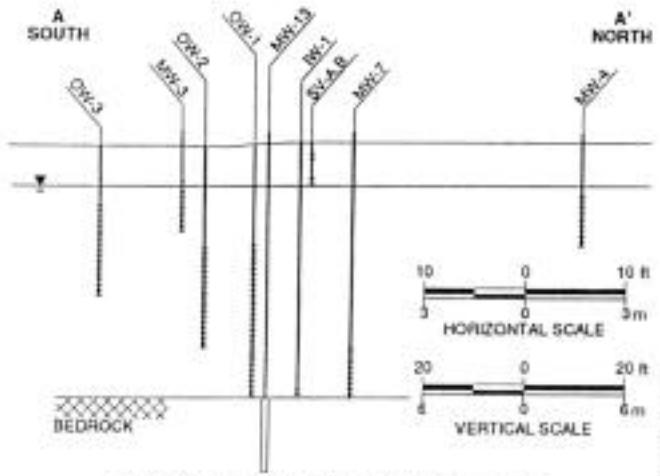

FIGURE 2. In situ MTT demonstration, cross section

RESULTS AND DISCUSSION

Operational history. The in situ MTT evaluation was operated for 139 days. At the beginning of the test, bubbling and pressure buildup were detected in Well OW-1, possibly due to short-circuiting from the nearby injection well. To prevent stripping of TCE, this well was tightly capped for the rest of the test run.

The methane feed was continuous for the first five weeks, then it was

pulsed on a schedule of 8 hours on/16 hours off. The feed was interrupted by an unknown malfunction from Day 66 to Day 72, and by an electronic problem from Day 78 to Day 97. The original design called for metering in liquid TEP at a rate of 7 µL liquid/min, on the assumption that it would evaporate in the line. However, the project budget did not allow for the necessary metering hardware, so we settled for a flow rate one order of magnitude higher. Unfortunately, liquid TEP backed up into the system and disrupted the operation of the N_2O MFC; as a result, the flow of N_2O was interrupted from Day 51 to Day 111.

Several alternative systems for TEP delivery were evaluated, including a cylindrical bubble contactor, which failed to evaporate TEP at a measurable rate. Ultimately, we delivered an aqueous phosphate solution to the wells during the last four weeks of the test. In summary, phosphorus was delivered to the subsurface during the first few weeks and the last few weeks of the test.

Subsurface Chemistry. The copper concentration was below the detection limit of 1.4 µg/L, well below inhibitory concentrations for methanotrophs. Chloride was found at concentrations of 20 to 70 mg/L, precluding its use as a proxy for the degradation of approximately 2 mg/L of chlorinated ethenes. Nitrogen (nitrate-nitrite and total Kjeldahl) and phosphorus (orthophosphate and total phosphorus) were well below 1 mg/L, indicating that macronutrients would have to be added. Total organic carbon ranged from 1 to 10 mg/L, dissolved oxygen concentrations ranged from 0.1 to 2.8 mg/L, and pH ranged from 5.4 to 6.6.

At the end of the evaluation, total Kjeldahl nitrogen was measured at 0.4 to 4 mg/L, whereas phosphorus (orthophosphate and total phosphorus) was mostly below the detection limit of 0.01 mg/L; the highest values were 0.11 mg/L, in Well MW-7. These low concentrations soon after the addition of the phosphate solution confirm that the subsurface environment is phosphorus-limited.

Soil gas was also sampled and analyzed for methane and TCE. Background levels of methane were 2 to 5 ppmV, and no background TCE was detected (detection limit: 0.005 ppmV). On Day 21, and again on Day 48, methane concentrations of up to 4% by volume were found. We assume that disruptions in nutrient delivery limited carbon uptake, which allowed methane to build up in the subsurface. On Day 139, after four weeks of optimal operation, the methane levels had dropped to between 2 and 20 ppmV; 0.95 ppmV of TCE was measured in one vapor sampling well.

System Performance. Figure 3 depicts VOC concentrations in MW-7—the well with the highest initial TCE readings; note that TCE concentration is read on the right-hand y-axis. Starting around 2000 µg/L, the concentration of TCE declined dramatically in the first three weeks of the test. Despite the nutrient disruptions, it continued to decline, albeit more gradually, to 150 µg/L. PCE went from 50 µg/L to nondetect in three weeks; PCE is not subject to any known aerobic metabolism or cometabolism, but its degradation can be enhanced by nearby methanotrophic activity (Enzien et al., 1995). In two and a half months, benzene went from 17 µg/L to nondetect, and trans-1,2-DCE went from 25 µg/L to nondetect. Surprisingly, cis-1,2-DCE fluctuated but no clear decline is evident. DCA declined

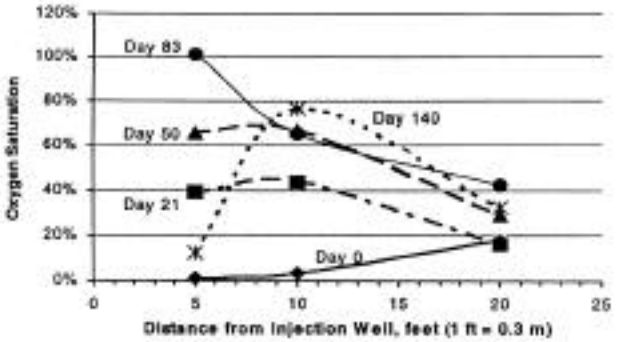

FIGURE 4. Oxygen saturation versus distance

become a dominant fraction of the microbiota.

Conclusions. In situ MTT using standard vertical wells is effective at rapidly cometabolizing TCE in the subsurface. An ROI of 30 ft (9 m) was achieved in this relatively tight formation. The pilot system described here was expanded to remediate the entire plume by the addition of two injection wells and two observation wells. The compressor, MFCs, and piping were upgraded to accommodate up to 5.3 scfm air (150 L/min) and correspondingly higher flow rates of other gases. A new TEP contactor was developed.

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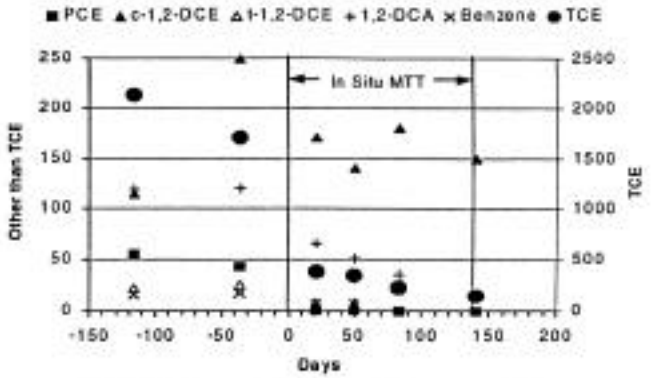

FIGURE 3. Impact of MTT on VOC concentrations (micrograms/L)

from 120 to 15 µg/L over the duration of the test.

There is some evidence of VOC displacement toward Wells OW-1 and OW-2. DCE and DCA increased slightly in OW-1, although the ultimate level was still below 100 µg/L; TCE increased from 200 to 660 µg/L in OW-1. We hypothesize that this displacement is due to mounding of the groundwater table caused by the air injection.

The pressure in the injection well was kept below 140% of the breakout pressure in order to minimize stripping and formation of preferential flow channels. The fact that some VOC levels remained constant or even increased in certain wells suggests that stripping was not a major factor in the VOC reductions achieved. That suggestion is reinforced by the fact that very little TCE was found in the soil gas at the end of the evaluation.

Radius of Influence. Oxygen saturation versus distance is shown in Figure 4. The bottom curve indicates that, initially, the groundwater was mostly anaerobic. The curves indicate that the ROI of the air injection eventually extended to approximately 30 ft (9 m). Note that the last set of data (Day 140) was obtained 24 hours after air injection was stopped, which explains the low saturation near the injection point. Helium tracing was conducted twice and supports the ROI estimate.

Growth of Methanotrophs. Methanotrophs were enumerated by using the most probable number procedure. On Day 94, very low counts were found (1 to 1500); note that there had been lengthy disruptions of the methane and N_2O delivery. On Day 140, however, methanotrophs in most wells exceeded the enumeration limit of 3.28×10^4, which demonstrates that, after methane, air, and nutrients are reliably supplied, massive methanotroph growth occurs in a matter of weeks. Total bacterial counts were between 2×10^6 and 3×10^7, indicating that methanotrophs had