

Mass Reduction versus Mass Movement of Chlorinated Aliphatic Hydrocarbons During *In Situ* Chemical Oxidation Pilot Test

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Abstract. Pilot scale remediation using *in situ* chemical oxidation with traditional Fenton's chemistry resulted in significant reduction of chlorinated aliphatic hydrocarbons (CAHs) and other volatile organic compounds (VOCs) in an unconfined aquifer at a former liquid-waste disposal site. The three-injection-event pilot test first raised then answered questions regarding the movement of contaminant mass through phase transport processes in response to chemical injection. Groundwater sample results evaluated after the first and second injection events indicated a dramatic reduction in dissolved-phase contaminant concentrations. However, a gradual rebound in these concentrations near the injection well to levels above baseline concentrations, as well as the apparent increase in sorbed-phase contaminant concentrations in soil at the water table, emphasized a need to verify contaminant mass reduction as opposed to mass movement prior to full-scale application of the remedial technology. Contaminant mass estimates provided a basis upon which to evaluate the mass reduction versus movement phenomenon. Estimation of contaminant mass in the various aquifer media was undertaken prior to and after the third injection event. Estimates were based on VOC analysis of paired soil, groundwater and soil vapor samples collected from within a 15-foot radius of the injection well.

Installation Restoration (IR) Site 5, Unit 2, is located in the southern portion of the Naval Air Station North Island in Coronado, California. The site resides in a former embayment of the San Diego Bay, known as the Spanish Bight, which was filled with dredge materials from San Diego Bay in the early 1940s. The dredged fill materials now compose a shallow aquifer that is impacted with VOCs at concentrations of greater than 100 parts per million. Primary contaminants include *cis*-1,2 dichloroethene (DCE), vinyl chloride, and aromatic hydrocarbons in site soil and groundwater, as well as naphthalene and trichloropropane in site soil.

Spanish Bight silts and clay occur at approximately 10 feet below grade and provide a vertical barrier to contaminant migration. Groundwater occurs at approximately 5 feet below grade. Former liquid-waste pits in operation at the site from 1944 until the 1960s are the probable source of the contamination. Current site use is air operations in that the site lies within the final approach to an airfield runway. The site also lies between two putting greens within the air station's popular golf course. Several factors, including airfield-imposed height restrictions, the site's high visibility, and the shallow groundwater with limited vadose zone, led to pilot testing of an *in situ* remedial option.

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The *in situ* chemical oxidation pilot study encompassed three injection events and eleven sampling events over the course of 4 months. Chemicals used during the test were hydrochloric acid for pH adjustment, ferrous iron sulfate as a catalyst, and hydrogen peroxide as oxidant. Chemicals were applied through a single injection well that was screened throughout the shallow aquifer. Seven monitoring wells were installed within a 30-ft radius of the injection well at 5-ft radial intervals in the upgradient, cross-gradient and downgradient directions to monitor site groundwater. Three vapor probes were installed within 15 feet of the injection well to monitor soil vapor migration during injection activities.

Data gaps identified after the first two injection events indicated the need to verify that contaminant mass destruction rather than mass movement was occurring in response to the injection process. Although groundwater sample results after these events indicated significant contaminant reduction from baseline condition, soil and soil-vapor sample results were inconclusive and suggested phase transport of contaminant mass from sorbed to dissolved phases and through volatilization. The third injection event was designed to provide the data needed better evaluate contaminant movement.

Prior to the third injection event, soil, groundwater and soil vapor samples were collected on the same day from locations within a 15-ft radius of the injection well and analyzed to provide a pretest contaminant mass estimate. To determine soil boring locations, the test area was divided into quadrants. Two borings were placed in each quadrant and were located adjacent to groundwater wells and soil gas probes if these sample points were present within the quadrant. Soil sample intervals included vadose zone as well as water-saturated soil. The sample set included 4 groundwater samples, 32 soil samples, and 3 soil-vapor samples. A paired sample set collected under similar conditions after the test provided posttest data.

Mass calculations included those for all detected VOCs in soil, groundwater and soil vapor. Contaminant mass in the test area soil, groundwater and soil vapor was calculated from the following equations:

$$M_s = Vol_s \times C_{ave} \times \rho \quad \text{and} \quad M_f = Vol_f \times C_{ave} \times \eta$$

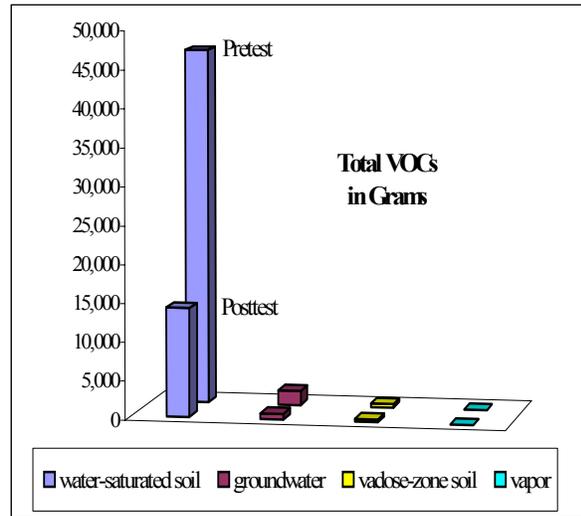
Where:

- M_s = Mass of a specific constituent in soil (g)
- Vol_s = Soil volume (yd³)
- C_{ave} = Average concentration of the specific constituent in soil, groundwater or vapor samples (g/kg)
- ρ = Soil density in kg/yd³
- M_f = Mass of a specific constituent in groundwater or soil vapor (g)
- Vol_f = Groundwater or soil vapor volume (L)
- η = Porosity (unitless)

Calculations of contaminant mass in vadose zone and saturated soils were made separately using the average of vadose-zone or water-saturated soil sample results, a 5-ft soil column and a density of 2,600 pounds per cubic yard (1,364 kg/yd³). Calculations of mass in groundwater and soil vapor were made using a 5-ft water or soil column and a porosity of 0.25.

The exercise revealed that roughly 95 percent of total VOC mass resided in soil at and below the groundwater table, constituting an ongoing source to groundwater. Mass estimates for target contaminants including *cis*-1,2 DCE and vinyl chloride, the primary contaminants in groundwater, indicated that 75 to 80 percent of their mass also resided in soil at and below the groundwater table.

Calculations made from third injection event results indicated a 68 percent reduction in total VOCs attributable to that event alone within a 15-ft radius of the injection well. As illustrated on the accompanying graph, the reduction occurred in water-saturated soil and in groundwater.



Note: Mass calculated for a 15-foot radius from injection well using pre- and post-third injection event sample results.

Calculations pointed to a 76 percent reduction in aromatic hydrocarbons and 45 and 60 percent reductions in *cis*-1,2 DCE and vinyl chloride, respectively. The calculations also show that contaminant mass movement into the vapor phase as a result of injection activities is insignificant given mass in soil and groundwater.

Dissolved-phase contaminant migration due to changes in the naturally occurring hydraulic gradient resulting from fluid injection also was evaluated during the pilot study. Although radial flow from the injection well within the study area occurred during the injection activities, groundwater gradients and flow directions estimated from gauging data collected prior to and after the third injection event showed a return to near-pretest conditions within 5 days after the test. Contaminant mass in groundwater calculated over the entire 30-ft radial pilot test area from pretest and posttest groundwater samples showed a decrease of 57 percent, about a 2.8 kg reduction, indicating mass destruction rather than migration. The calculated dilution effect of injected fluids within the 30-ft radius ranged from 6 to 11 percent over the course of the study.

In summary, test results indicate that although movement of contaminant mass from the sorbed to dissolved and vapor phases apparently occurs in response to chemical injection, contaminant mass reduction is by far the predominant phenomenon occurring as a result of the technology at the site.