Post Injection Evaluation of In-Situ Chemical Reduction as Treatment Remedy for Nitro-Aromatic Compounds

Group #2

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BACKGROUND

An In-Situ Chemical Reduction (ISCR) work plan has been developed to address impacted soil and groundwater in the vicinity of a Resource Conservation and Recovery Act (RCRA) facility's former nitro-aromatic compounds manufacturing and railcar loading operations area. Environmental assessment activities conducted in the area of concern have included two RCRA Facility Investigations (RFIs) dated 1992 and 1998, evaluated under both the former Texas Risk Reduction rules, and under the current Texas Risk Reduction Program (TRRP), as well as the ongoing groundwater corrective action program monitoring and reporting activities under the facility's RCRA Compliance Plan. Persistent groundwater protection standards (GWPS) exceedances have been observed in groundwater samples from monitoring wells in the railcar loading area, since the 1980s. Nitro-aromatic compound concentrations in groundwater remain close to those observed in 1992 groundwater event samples in one monitoring well, while concentrations have generally increased in a second monitoring well.

ISCR has been selected as a potential response action to reduce source area chemicals of concern (COCs) that are impacting groundwater at the subject facility. The ISCR work plan uses a patented reagent solution (Cool-Ox®-R) to reduce nitro-aromatic compound concentrations, as well as other associated COCs. Cool-Ox®-R has successfully and effectively promoted the reduction (i.e., destruction) of a broad group of organic chemical constituents including hydrocarbons, organo-halides, and nitrogenous organic compounds at other similarly impacted sites. The ultimate byproducts of the selected chemical degradation process are nitrate, nitrite, and carbon dioxide.

The effect of Cool-Ox®-R on the chemical destruction of dinitrotoluene was explained by Cassidy (et. al.), WMU. The Cool-Ox®-R mechanism developed by Lundy, is a method of in-situ control of the chemical oxidation reaction discovered by HJH Fenton in the 19th century. The method is based on hydrogen peroxide chemistry where hydrogen peroxide is produced in-situ by the hydrolysis of calcium peroxide. The reactions leading to the abiotic destruction of DNT are explained below.

$CaO_2(S) + 2H_2O \rightarrow Ca(OH)_2(S) + H_2O_2$ (1)

$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{+3}$ (2)

$Fe^{+3} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+$ (3)

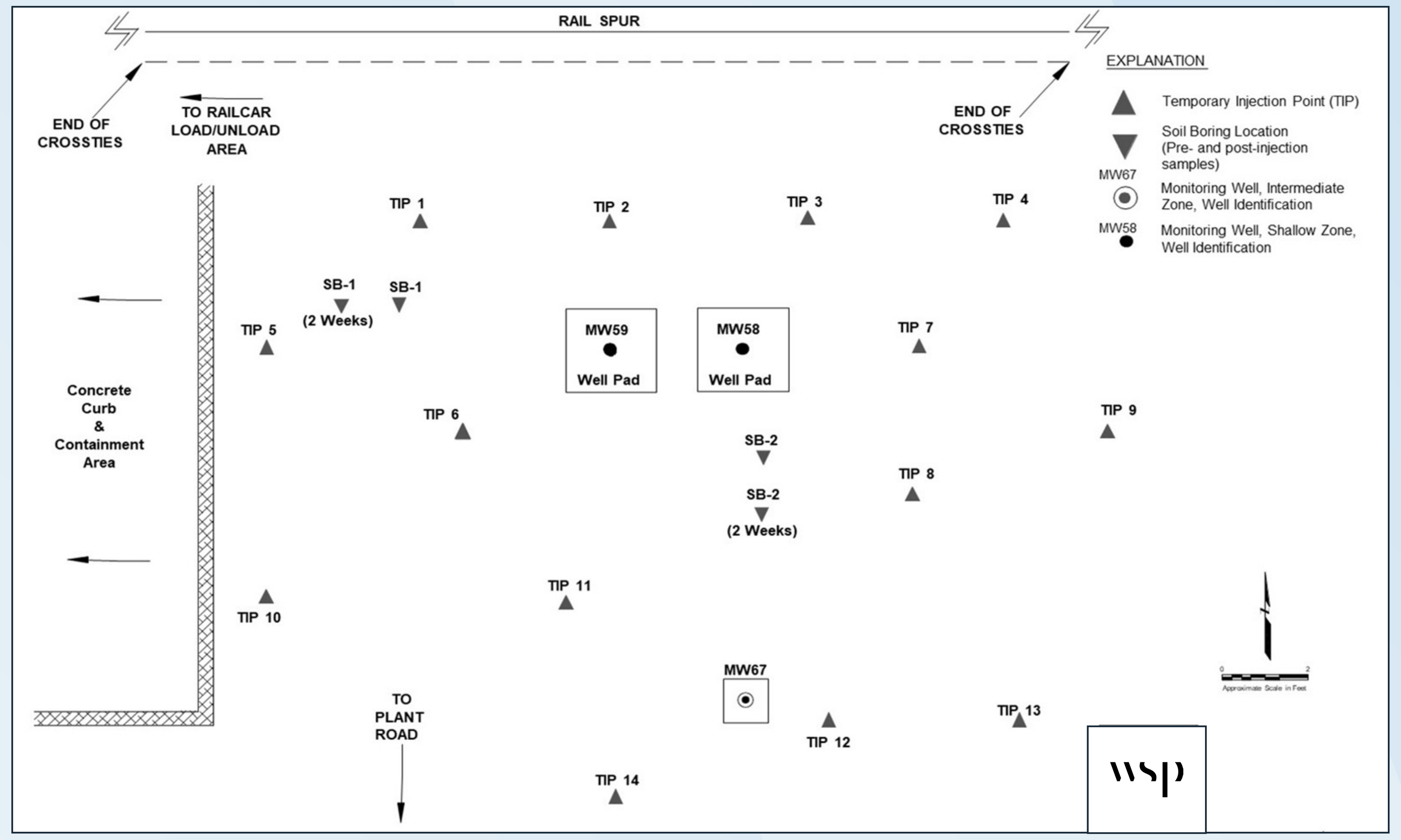
$HO_2\cdot \leftrightarrow O_2^{-}\cdot + H^+$ (pKa = 4.8) (4)

$HO_2\cdot + O_2^{-}\cdot \rightarrow HO_2^- + O_2$ (5)

APPROACH

The objective of the ISCR work plan is to assess the efficacy of applying the selected reagent solution to source areas soils and groundwater to destroy nitro-aromatic compounds primarily 2,4- and 2,6-Dinitrotoluene (DNT), as well as other associated COCs by chemical reaction. Direct chemical injection was used to introduce the reagent into the source "hot spot" area (a result of past railcar loading spills) to treat the unsaturated and saturated soil column from approximately 10 to 37 feet below grade, i.e., the base of the sand-rich shallow water bearing zone. The reagent injection methodology utilized a direct push technology (DPT) drilling rig to install temporary injection points (TIPs) to treat an area of approximately 340 square feet. Prior to and after implementing the injections, groundwater and soil samples were collected from locations within the treatment area and analyzed for site-specific nitro-aromatic compounds, nitrate, nitrite, total organic carbon, and pH. The treatment area includes two existing monitoring wells and 14 TIPs to saturate the area and assure contact with the contaminated matrix.

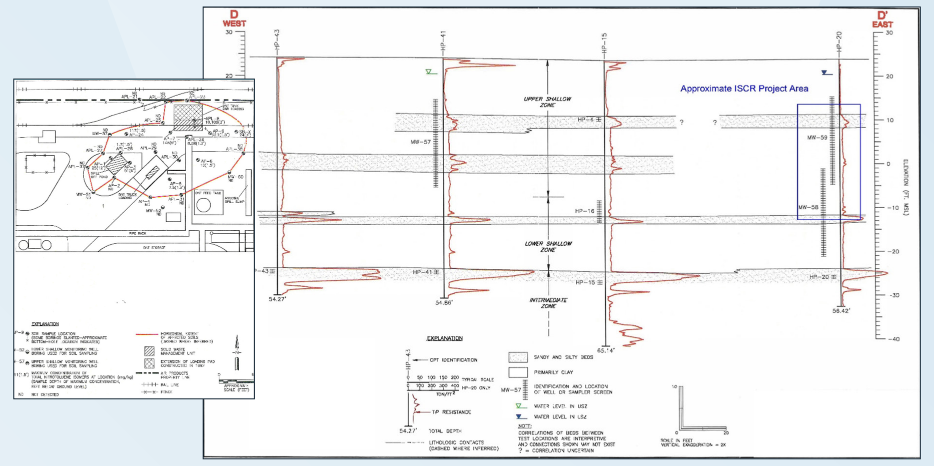
The presence of persistent GWPS exceedances has been clearly observed in groundwater samples from monitoring wells near the source area, completed in the Lower Shallow Zone (LSZ) and the Upper Shallow Zone (USZ).). It is suspected that source area DNT is present in both crystalline and colloidal forms.

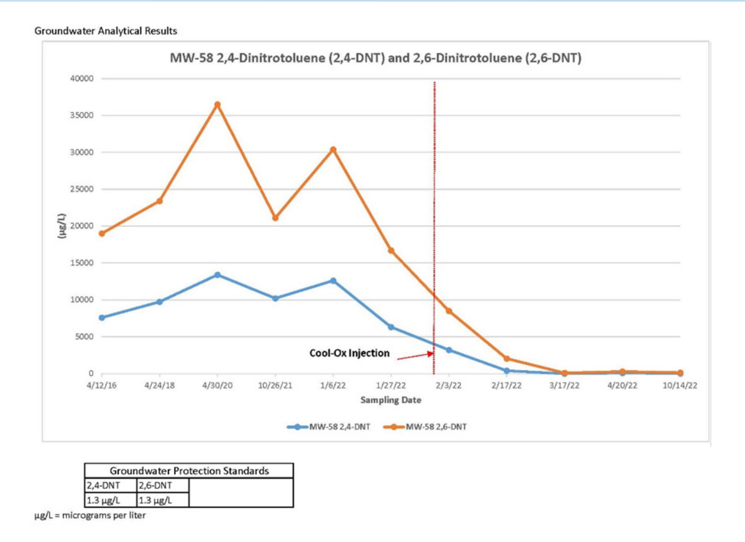


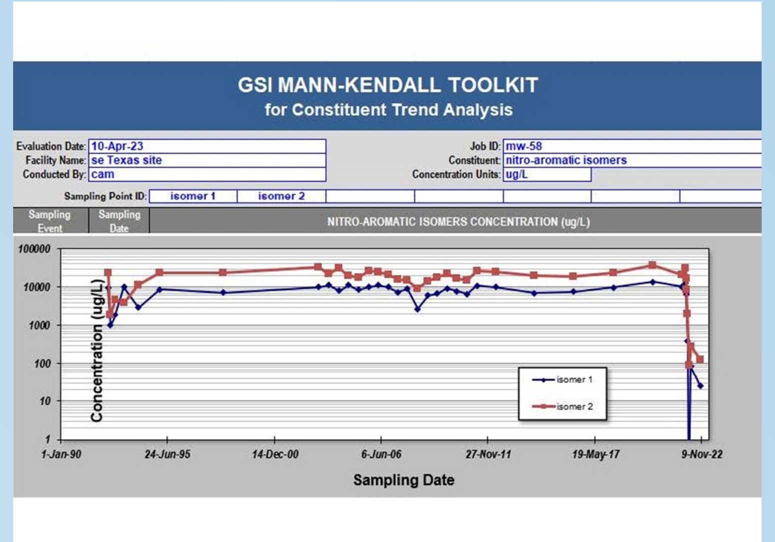
IMPLEMENTATION

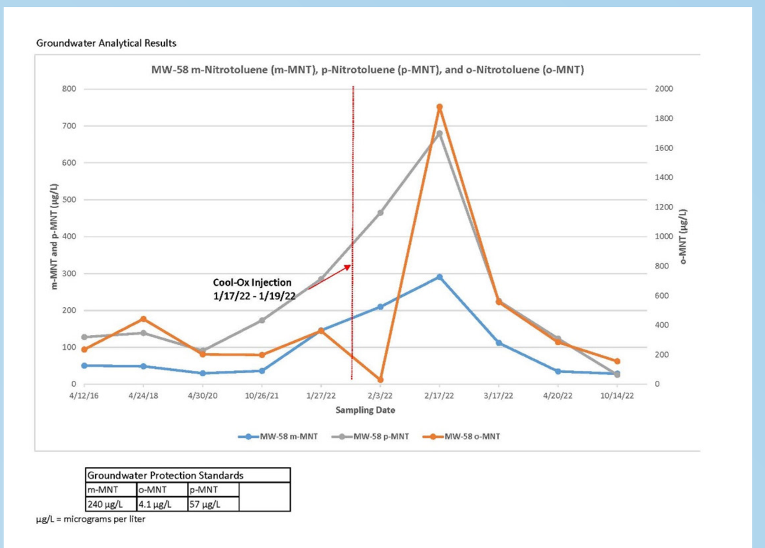
In January 2022, the Plan (approved by TCEQ) was implemented to address and evaluate the Cool-OX®-R injection effects on in situ DNT, present in the source area, the former DNT product rail car loading area.

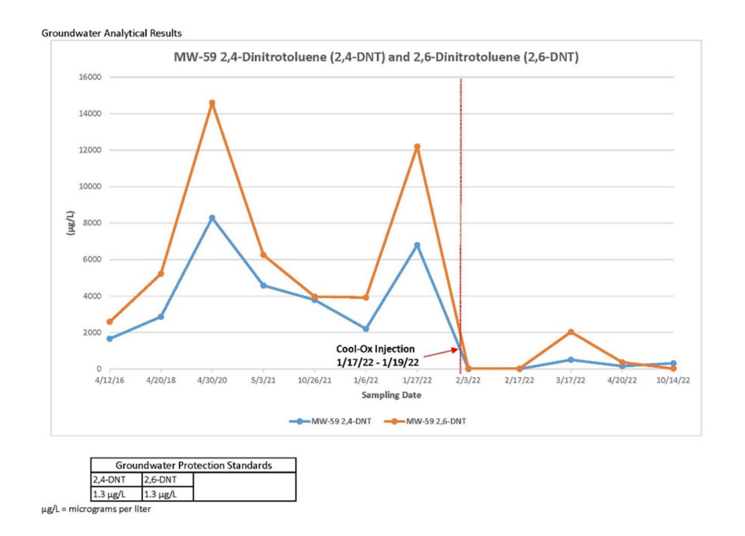
Over a three-day period, Cool-Ox®-R was injected into 14 temporary injection points (TIPs). Approximately 150 gallons of the reagent solution was injected at a rate ranging between eight to 11 gallons per minute at each TIP. A DPT rig was used to pneumatically advance hollow, threaded steel rods throughout the treatment zone (10 to 37 feet below grade).

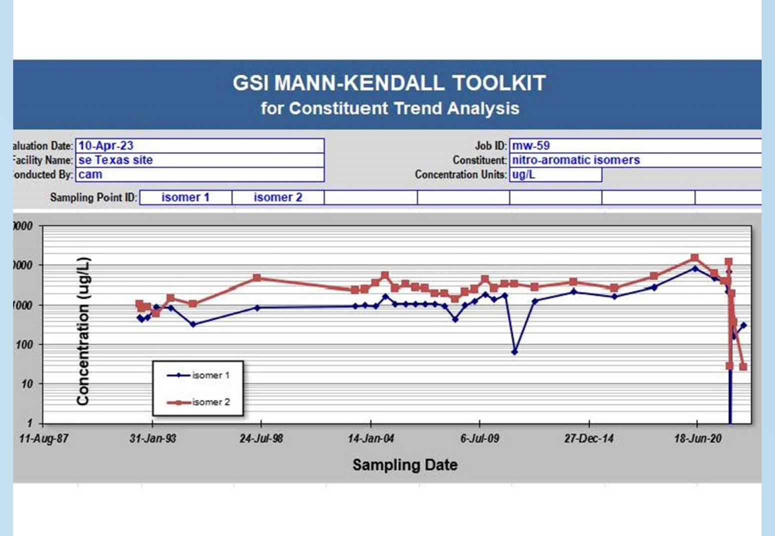


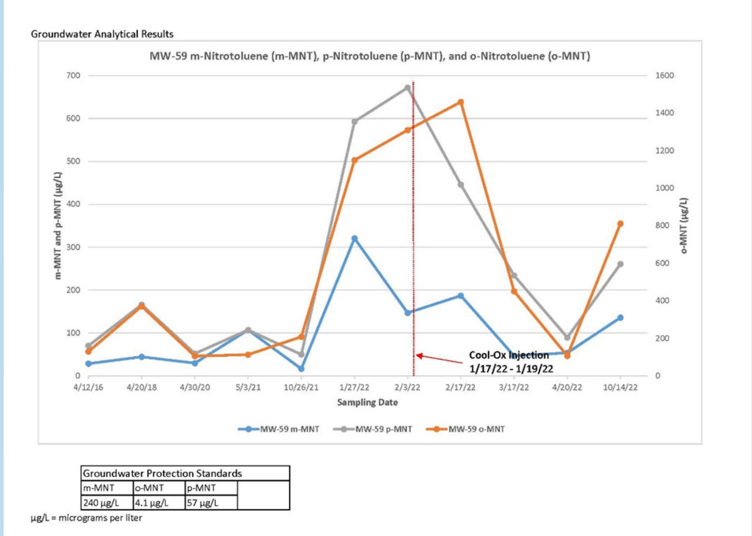


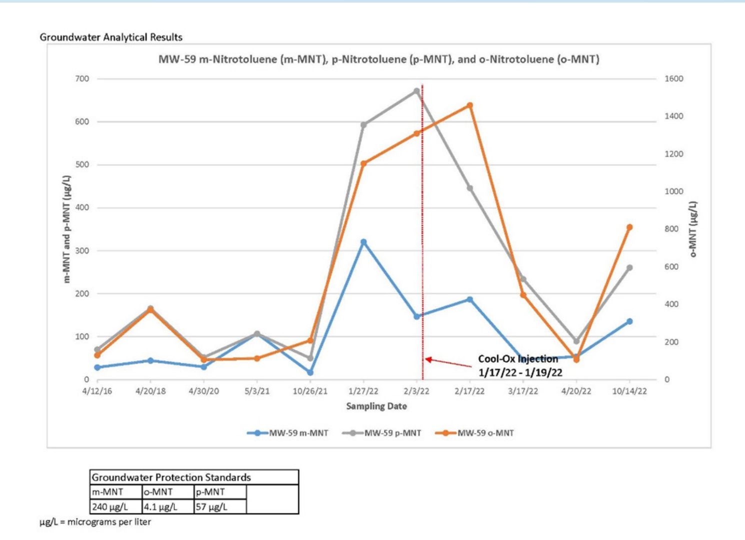


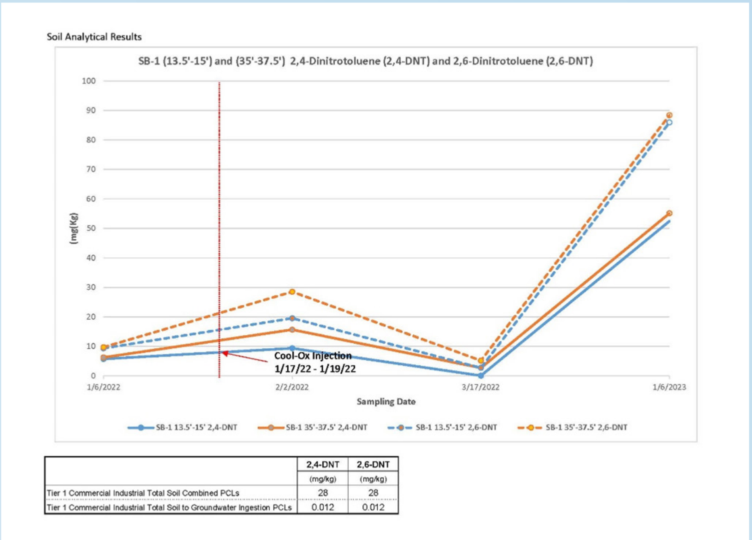


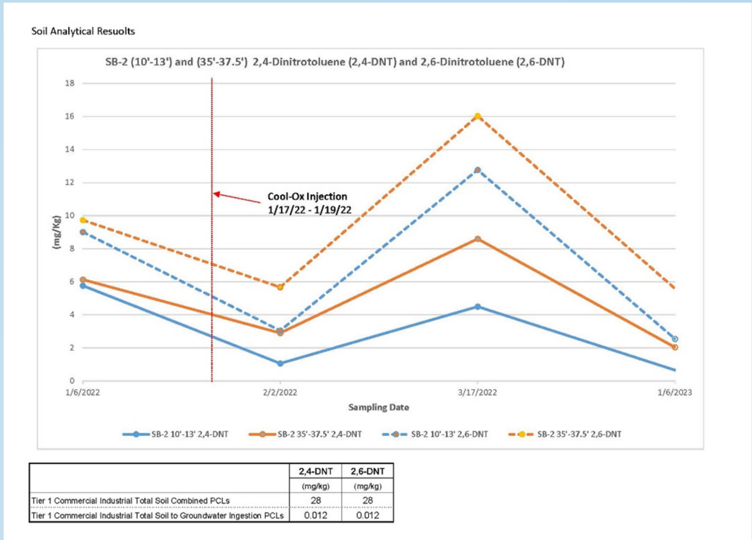












CONCLUSION

Cool-Ox ®-R (patented reagent solution) appears to have effectively promoted the reduction (i.e., destruction) of DNT groundwater. Additionally, following injection, temporary spikes in Mononitrotoluene (MNT) concentrations, as well as increased nitrate and nitrite concentrations are observed, suggesting the DNT reduction process is proceeding forward.

The effectiveness on reduction of nitro-aromatic compounds in soils through follow-up soil sampling over time, and/or inference from subsequent groundwater sampling events appears to have stabilize 12 months post injection. If continued reduction of nitro-aromatic compounds in source area and downgradient groundwater is observed, the technique may be considered for other known source areas.

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