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Title: Large-Scale Plume, Nano-Scale Solution: Remediation of CVOC Using Sodium Persulfate and Ozone Nanobubbles

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Key Topic: Innovative Remediation Technologies

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Client Name: Confidential

Project Name: Confidential

Project Location: São Paulo, Brazil

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ABSTRACT

Background/Objectives:

The project's area of concern comprises two neighbouring industrial sites located in a mixed-use zone in the State of São Paulo, Brazil. There are two known primary sources of contamination: i) a former underground tetrachloroethene (PCE) tank in site A, removed in 2013; and ii) a portion of site B used as a waste disposal area until the 1990s. The combination of both sources created a chlorinated volatile organic carbon (CVOC) groundwater plume affecting the local sedimentary aquifer over a thickness of 15 m and a length of over 100 meters, reaching sensitive residential and commercial areas downgradient from site B. A remediation strategy was designed using an innovative *in-situ* chemical oxidation (ISCO) approach to destroy contaminant mass in the unsaturated and saturated zones of the hotspots in both sites to allow for future residential use.

Approach/Activities:

Preparation for remediation started in April 2018, with bench-scale tests for *in-situ* bioremediation (ISB) and ISCO, using groundwater from the source areas in sites A and B. While biostimulation-based ISB was ineffective in the bench test due to the absence of PCE-degrading microbes (confirmed by genetic testing), ISCO using an innovative technique combining sodium persulfate and nanoscale ozone bubbles (smaller than 300 nanometers) showed significant mass reduction of CVOCs, in addition to a tenfold increase of dissolved oxygen which can be explained by the high internal pressure and high mass transfer rate of the nanobubbles. In April 2019, pilot tests of bioaugmentation-based ISB and ISCO using sodium persulfate and ozone nanobubbles were performed in site A, and ISCO again proved most effective in the former PCE tank source area. Informed by the aforementioned tests and geological model of the sites, as well as MiHPT and historical analytical data, a network of 69 injection wells was designed, distributed in both source areas comprising 23 wells targeting the vadose zone (depths from 4 to 15 meters below ground surface [mbgs]), 32 wells in the shallow aquifer (depths from 16 to 22 mbgs) and 14 wells targeting the intermediate aquifer (depths from 23 to 26 mbgs). In December 2020, a baseline groundwater monitoring event was carried out with a network of 60 monitoring wells distributed along both sites. Five injection events are planned to occur between February and August 2022, with groundwater sampling occurring in-between injection events.

Results/Lessons Learned:

To date, five injection events have been completed and the sixty (final one) is scheduled for August 2022. In the first five events, over 72,300 kg of sodium persulfate was used to prepare 857 m^3 of oxidant solution, also containing 3% (v/v) ozone gas. After the first injection event, groundwater monitoring evidenced increases in PCE concentrations in both hotspots, indicating residual mass transfer from the vadose zone to the aquifer and from the adsorbed phase to the dissolved phase. To

contain this mobilization, the second injection event more strongly targeted the vadose zone and shallow aquifer, with increases to both oxidant concentration and oxidant solution volume, in the areas with highest PCE concentration. The third, fourth, and fifth campaigns were focused on the hot spots, areas with concentrations above the remediation goals. After these 5 events, reductions in PCE concentration of on average 85% were observed in the former PCE tank source area. In this source area, the redox potential (Eh) increased by up to 150 mV and dissolved oxygen was raised by 2 mg/L in relation to the baseline. The combination of sodium persulfate and ozone nanobubbles presents itself as a powerful technique to treat CVOC groundwater plumes. Compared to traditional injection of millimeter-sized ozone bubbles, the nanobubbles offer greater stability and larger specific surface area, leading to a better penetration factor, which is desired particularly in aquifers containing low-permeability layers.

Aspect of Work that Relates to Sustainability:

ISCO usually is not the preferred remediation technique related to sustainability. But in this case, after the development of Treatability Tests and Pilot Tests, a sustainable assessment was done and ISCO became the first option (against soil excavation, bioremediation). Therefore, this paper is a paradigm break related to the use of ISCO for chlorinated solvents. Also, the nano-scale application (using a patent registered supplier) is contributing to a more successfully remediation on this complex site.