Large-Scale Implementation of Recirculation Systems for In-Situ Treatment of Hexavalent Chromium in Groundwater in Hinkley CA – 17338

Margy Gentile *, Frank Lenzo *, Kevin Sullivan**, Iain Baker**
* ARCADIS US, Inc., **Pacific Gas and Electric Company

ABSTRACT

In-situ remediation using recirculation systems is being used to treat hexavalent chromium (Cr[VI]) in groundwater within the plume core at the Pacific Gas and Electric Company Hinkley Compressor Station in Hinkley, California (the Site). In-situ Reactive Zones (IRZs) are currently treating an area of 0.8 kilometers (km, one-half of a mile) by 1.6 km (a mile) to target treatment of the core of the Cr(VI) plume, where concentrations of Cr(VI) range from 10s of micrograms per liter (μg/L) to several milligrams per liter (mg/L). Following pilot testing from 2004-2006, large scale implementation of in-situ remediation began in late 2007 and has been on-going. Implementation of the recirculation systems has been successful in remediating Cr(VI) in groundwater at a large scale. Through Third Quarter 2015, in-situ remediation had removed over 44 percent of the mass in the target treatment area. Within the IRZs, concentrations are rapidly reduced within the timeframe of weeks to a few months. Downgradient of the IRZs, treatment has been observed at distances over 915 meters (3,000 feet). This presentation will focus on the design, operation, adaptive management and results of this effort.

INTRODUCTION

Pacific Gas and Electric (PG&E) is conducting assessment and cleanup of hexavalent chromium (Cr[VI]) in groundwater related to industrial activities that took place at the PG&E Hinkley Compressor Station in Hinkley, California (the Site). The Facility began operating in 1952 and disposed of cooling water containing Cr(VI), used as a corrosion inhibitor, to unlined ponds until 1964. Cr(VI) bearing water percolated through soil to the water table, creating the Cr(VI) plume in groundwater. Cooling water was treated to remove chromium prior to disposal in ponds from 1964 to 1966. A different non-chromium based additive was substituted in 1966 and cooling water was pumped to lined evaporation ponds starting in 1972.

PG&E has been remediating chromium-impacted groundwater at the Site through a series of interim remedial actions. Prior to 2004, initial remedial activities included groundwater extraction and treatment via agricultural application. Since 2004, PG&E began implementing several key remediation components, including the following:

- Hydraulic containment through operation of a network groundwater extraction wells and agricultural treatment units and a freshwater injection system.
- In-situ treatment of Cr(VI) through operation of three In-Situ Reactive Zones (IRZs)

In December 2015, a Cleanup and Abatement Order was issued which established cleanup requirements for the site, including cleanup timeframes for the southern plume to reach 50 micrograms per liter (μg/L) across 90% of the 50 μg/L plume by 2025 and to reach 10 μg/L across 80% of the 10 μg/L plume by 2032 at specified monitoring wells.

This paper focuses on the design, operation, adaptive management and results of the IRZ systems implemented at the Site to date.

DESCIPTION

Conceptual Site Model within the IRZ Area

IRZ treatment is being implemented at the site across an area of approximately 0.8 kilometers (km, one-half of a mile) by 1.6 km (a mile) to target treatment of the core of the Cr(VI) plume, where concentrations of Cr(VI) range from 10s of μg/L to several milligrams per liter (mg/L). Within this area, the Cr(VI) plume in groundwater resides within the Upper Aquifer, above a confining unit referred to as the Blue Clay. The sediments of the Upper Aquifer are heterogeneous deposits from historic flows of the Mojave River. Depth to groundwater in this area currently ranges from approximately 24 to 30 meters (m), or 80 to 100 feet, below ground surface and saturated thickness ranges from 9 to 21 m (30 to 70 feet). Groundwater velocities range from 0.3 to 1.2 m per day (1 to 4 feet per day). For purposes of monitoring the Upper Aquifer, it has been separated into a shallow zone and a deep zone; however, there is no defining aquitard that separates these layers within the IRZ area. The inferred baseline chromium distribution prior to large scale IRZ implementation is shown in Fig. 1.

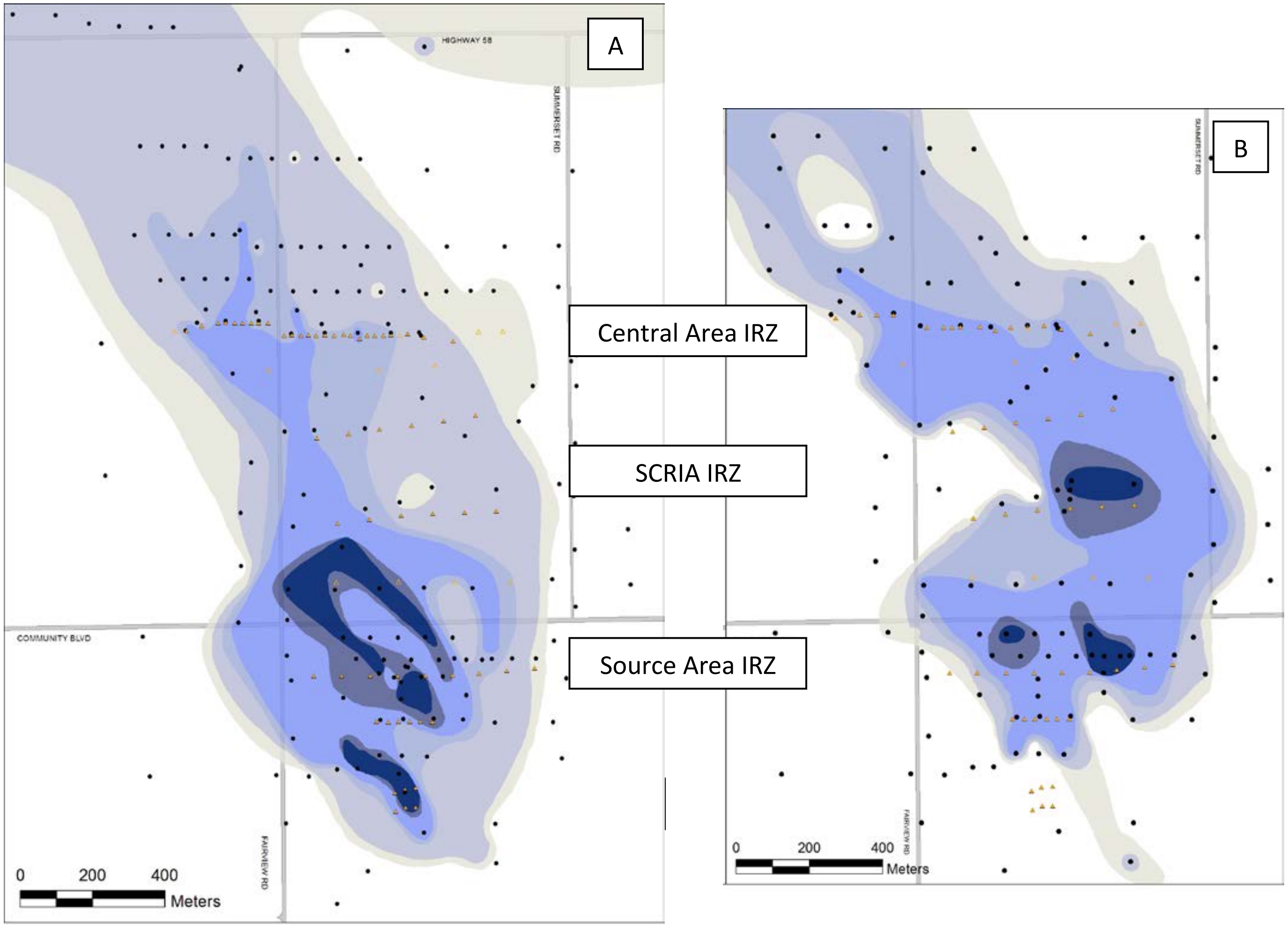

Fig. 1. Baseline distribution of Cr(VI) in groundwater inferred from maximum concentrations before or 6 months following the start-up of the three IRZ systems prior to arrival of treated water. Panel A depicts the distribution in the shallow zone of the Upper Aquifer and Panel B depicts the distribution in the deep zone of the Upper Aquifer. Closed orange triangles represent in-situ injection wells, open orange triangles depict recirculation extraction wells and closed black circles represent monitoring well locations. Plume contours are defined in Fig. 2.

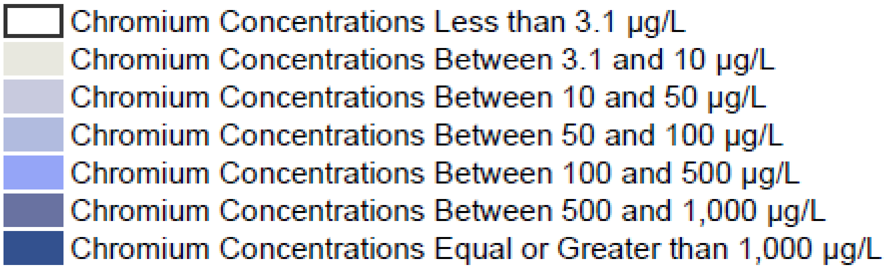

Fig. 2. Definition of plume contour coloration used throughout this paper.

System Description

The in-situ remedy includes delivery of an organic carbon substrate (lactate or ethanol, in this case) to groundwater using a recirculation system. Groundwater is extracted, amended with the organic carbon substrate and re-injected into the aquifer. The distribution of the organic carbon substrate within the aquifer results in generation of IRZs within which Cr(VI) is reduced to trivalent chromium (Cr[III]) and forms sparingly soluble precipitates via biological and chemical processes.

There are three IRZ systems at the Site (Fig. 1): the Central Area IRZ located on the north end of the treatment area, the South Central Re-injection Area (SCRIA) IRZ located south of the Central Area IRZ, and the Source Area IRZ between the south end of the Cr(VI) plume and the SCRIA. Various aspects of the design, recirculation system layout, well spacing, and well design, have been implemented over time to fit the purpose of each system and to adapt operations in response to performance data collected over time. Table I summarizes the designs and operations for each system as they were expanded and adapted over time.

TABLE I. IRZ System Design and Operational Summary

Operating Period	**Recirculation Design**	**Injection Well Spacing**	**Injection Wells**	**Extraction Wells**	**Volume of Water Recirculated**
Central Area IRZ					
November 2007 to November 2012	Alternating injection and extraction wells perpendicular to groundwater flow	45 m (150 ft)	6	6	454 ML (120 MG)
November 2012 to present[2]	Extraction exterior to IRZ transect, injection along transect perpendicular to groundwater flow	deep zone 46 m (150 ft) shallow zone 23 m (75 ft)	27	6	816 ML (216 MG)
South Central Area IRZ					
October 2009 to May 2015	Extraction over 1,200 m (4,000) feet north for plume containment, injection along two IRZ transects perpendicular to groundwater flow	88 m (290 ft)	12	5	594 ML (157 MG)
May 2015 to present[2]	Additional injection wells added to southeastern transect	37 to 49 m (120 to 160 ft)	18	5	268 ML (71 MG)
Source Area IRZ					
April 2008 to April 2011	Extraction downgradient (north), injection along transections upgradient (south)	29 to 30.5 m (95 to 100 ft)	12	4	208 ML (55 MG)
April 2011 to April 2015	Extraction downgradient (north), injection along transections upgradient (south)	30.5 to 79 m (100 to 260 ft)	21	4	363 ML (96 MG)
April 2015 to present[2]	Extraction downgradient (north), injection along transections upgradient (south)	27 to 46 m (90 to 150 ft)	33	4 to 18	204 ML (54 MG)

Notes:

1. Sodium lactate was used from November 2007 to August 2008. Ethanol was used from August 2008 to present.
2. Data presented is through September 30, 2016.

Abbreviations: ft – feet, m- meters, MG- million gallons, ML- million liters

DISCUSSION

Overview of Treatment

Once organic carbon has been distributed within the aquifer by injection, rapid development of reducing conditions suitable for Cr(VI) reduction have been observed. Fig. 3 presents characteristic concentration trends for monitoring wells within the IRZ footprint of carbon distribution in the Central Area IRZ (Panel A) and Source Area IRZ (Panel B). Both locations demonstrate that following arrival of Total Organic Carbon (TOC) from the injections, nitrate and metal reducing conditions develop and Cr(VI) is rapidly reduced, as indicated by declining nitrate concentrations and increasing dissolved iron concentrations. The reduction of Cr(VI) is likely mediated by direct chemical reduction from ferrous iron produced by iron reduction given the rapid kinetics of that reaction, although biological reduction may also be occurring.

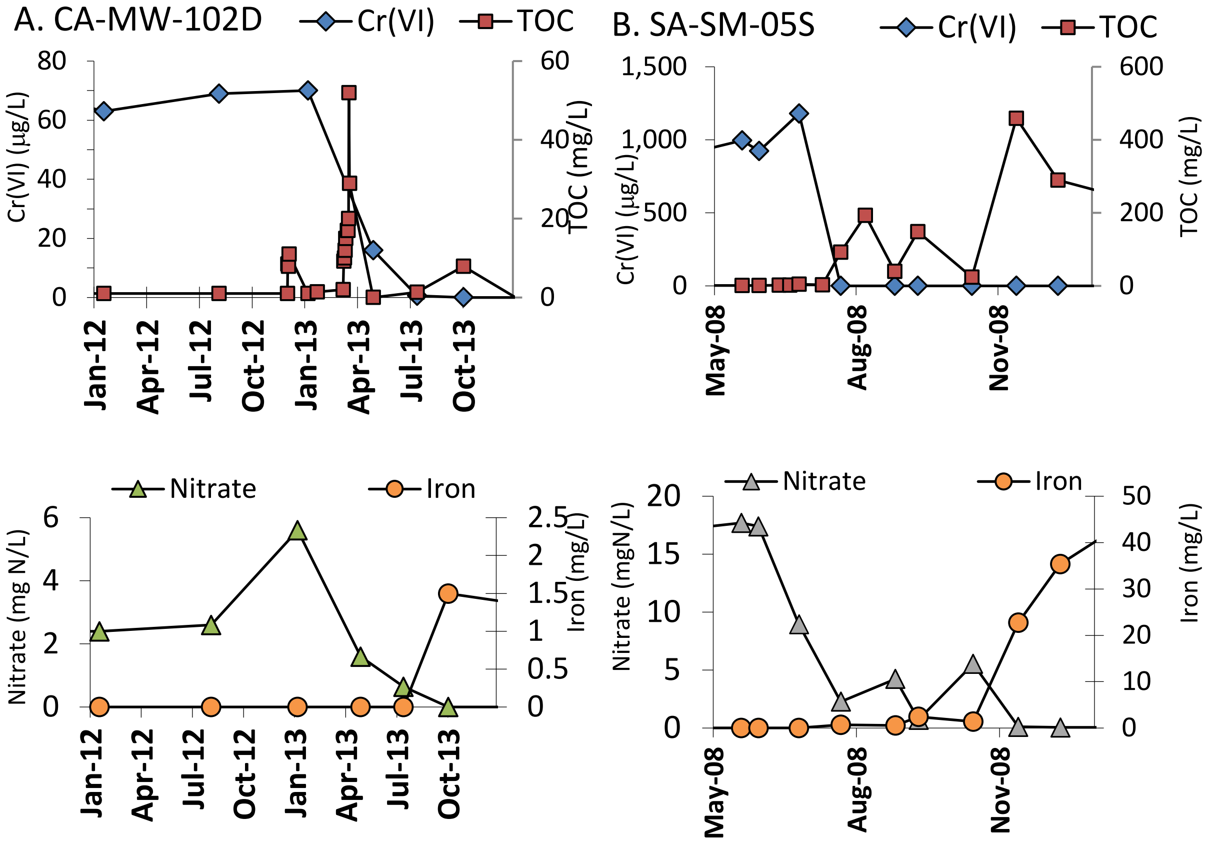

Fig. 3. Geochemical trends from characteristic monitoring wells within the carbon footprint. Panel A- Central Area IRZ, Panel B- Source Area IRZ

Downgradient of the carbon footprint, concentrations decline as treated water from the IRZ flushes through the aquifer. Fig. 4 presents characteristic declines in Cr(VI) concentrations downgradient of the in-situ systems. Nitrate is used as a secondary indicator to verify that downgradient trends are a result arrival of treated water from the in-situ systems.

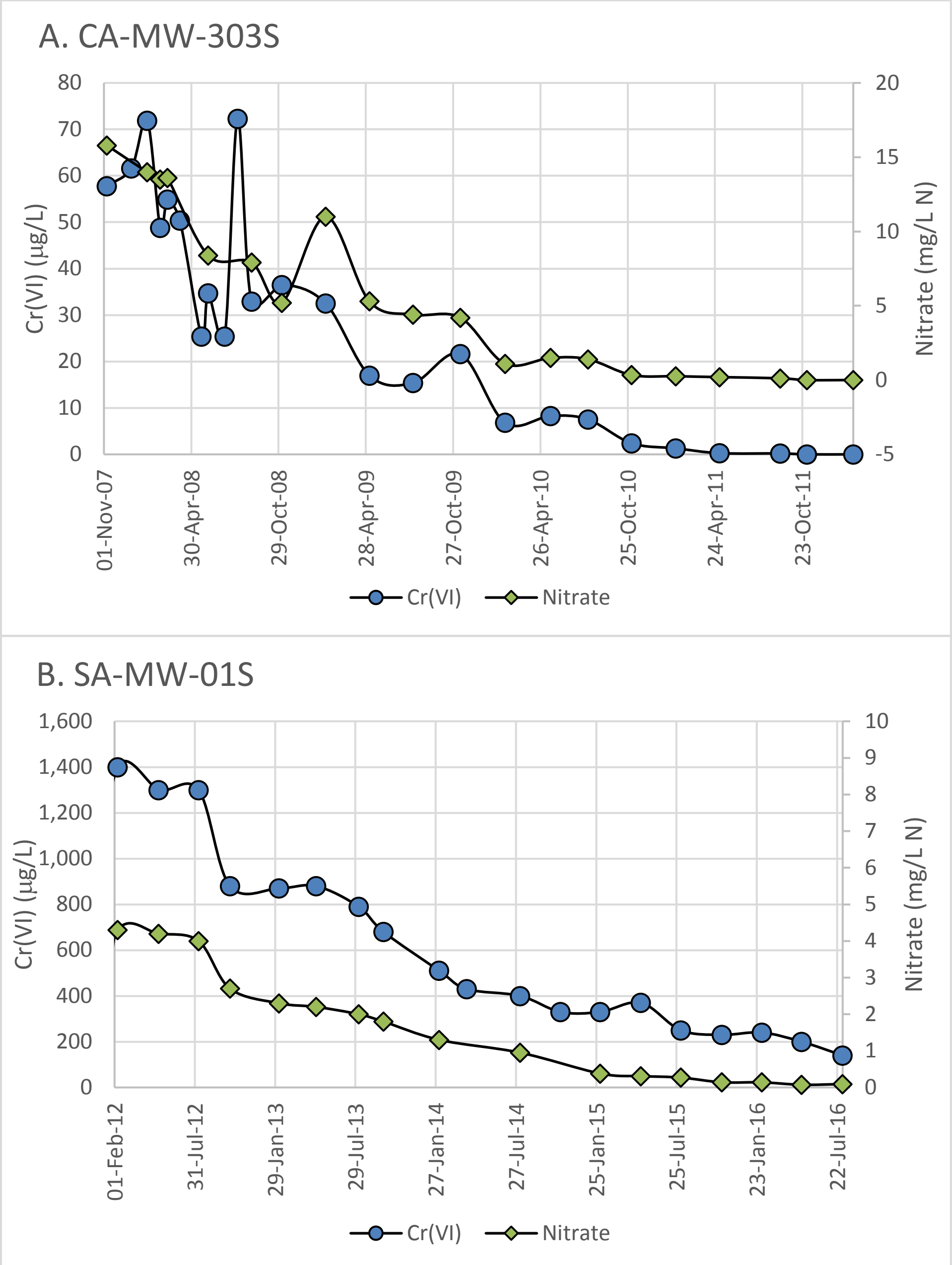

Fig. 4. Characteristic Cr(VI) and nitrate trends downgradient of the carbon footprint. Panel A- Central Area IRZ 137 m (450 feet) downgradient of the IRZ, Panel B- Source Area IRZ 61 m (200 feet) downgradient of the IRZ

Adaptive Management

Distribution of organic carbon substrate in the subsurface is critical to the success of in-situ remediation, particularly when working at the large scale of the Site. Performance monitoring data is continually used to evaluate substrate distribution and make operational and design adjustments to achieve adequate distribution to stimulate the microbial processes necessary for treatment. As detailed in Table I, several different configurations of extraction and injection wells for groundwater recirculation have been implemented in the three IRZs at the Site, including recirculation within a line of recirculation wells oriented perpendicular to groundwater flow, recirculation cells oriented along the direction of groundwater flow, and injection into a network of wells with groundwater extracted from a downgradient area of the site.

Three case studies demonstrating adaptive management of the system follow.

Case Study 1. Central Area Recirculation Transect

In 2007, the Central Area IRZ system was designed as a line of recirculation dipoles, with 12 alternating injection and extraction wells spaced 45 m (150 feet) apart in a transect perpendicular to groundwater flow. To establish a complete IRZ across the transect with a dipole configuration requires distribution of the organic carbon from injection well to the extraction well. However, it is difficult to perfectly balance the dosing of organic carbon and recirculation rates to achieve complete distribution from injection to extraction well without extracting organic carbon. During operation of the Central Area IRZ dipoles, it was observed that extraction of organic carbon at the extraction well resulted in growth of biofilms within the recirculation piping and a reduction in achievable recirculation rates, as shown by the data presented on Fig. 5.

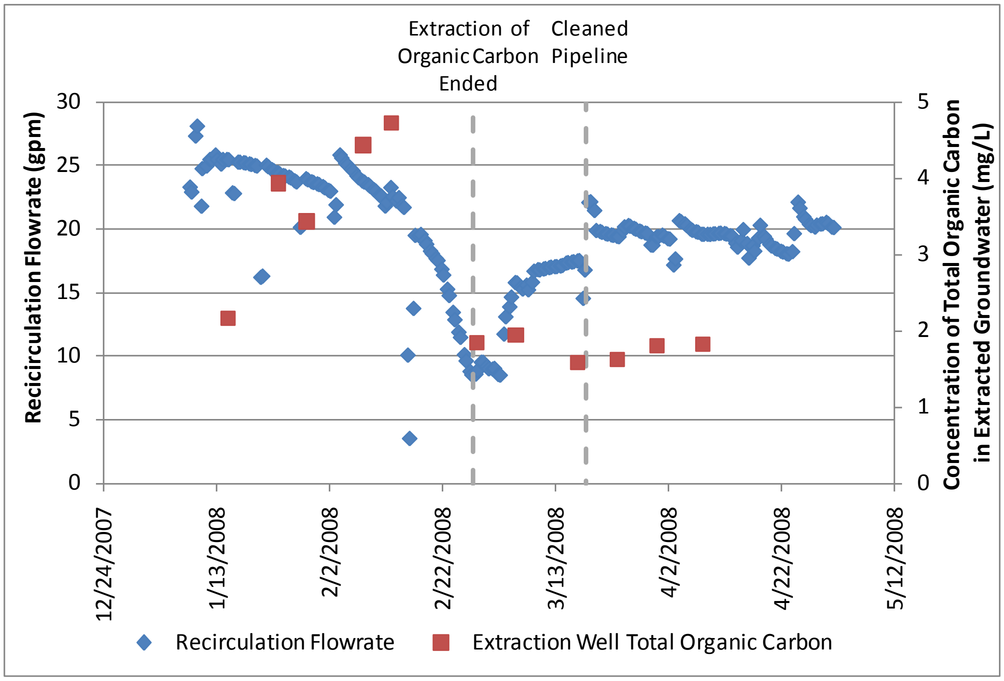

Fig. 5. Panel A- Recirculation rate of a Central Area IRZ dipole and concentration of

TOC in the extracted groundwater.

Based on the observed constraints on performance of recirculation dipoles in the early operation of the Central Area IRZ, recirculation system designs were modified. Subsequent designs used transects of injection wells within the target treatment areas with recirculation water sourced either at the edges of the transect, downgradient of the injection transect, or from another area of the site.

Case Study 2: Targeted Screened Intervals and Well-Spacing in Source Area Expansion

The aerial extent of organic carbon substrate distribution that can be achieved with injection wells is a function of the configuration of the recirculation system, local hydrogeological conditions, and achievable injection rates. The evaluation of performance of an expanded Source Area IRZ system installed in 2011 demonstrates the influence of well-spacing on achieving sufficient reagent distribution to stimulate Cr(VI) reduction. In 2011, the Source Area IRZ was expanded to target treatment of an area of the deep zone of the Upper Aquifer where the highest concentrations of Cr(VI) at the Site had been observed at SA-MW-05D ranging from 3,060 to 9,030 μg/L from 2008 to 2011 (Fig. 6A). A transect of injection wells spaced approximately 79 m (260 feet) apart were installed to target treatment in this area and operations began in Spring 2011. Well SA-RW-04 was installed in 2008 as one long screened injection well injecting across the entire saturated interval. Injection well SA-RW-19 was installed in 2011 with discreet screens in the shallow and deep zones of the Upper Aquifer and injection began in 2011 with injection into the deep interval only. After three years of injections (Second Quarter 2014), treatment had not been observed at SA-MW-05D or SA-MW-20D located 38 m (125 feet) downgradient of the injection system (Fig. 6A).

A nested pair of monitoring wells was installed to the east (SA-MW-29S/D) and west (SA-MW-30S/D) of SA-MW-05D. Analytical results indicated arrival of treated groundwater at SA-MW-29S/D and SA-MW-30S, with Cr(VI) concentrations ranging from less than 0.02 µg/L to 1.6 µg/L (Fig. 6B). Low or non-detect concentrations of nitrate and/or sulfate and detections of dissolved metals (for example, dissolved iron greater than 0.25 mg/L and dissolved manganese greater than 1 mg/L were also present at SA-MW-29D and SA-MW-30S. Cr(VI) concentrations persisted at SA-MW-30D (2,600 µg/L). These results indicated that injections into SA-RW-04S/D (located southwest of SA-MW-05S/D and south of SA-MW-30S/D and screened continuously from 21 to 43 m [70 to 140 feet] below ground surface), resulted in preferential flow into and treatment of the shallow zone of the Upper Aquifer, rather than the targeted deep zone. Conversely, observing treatment in both the shallow and deep zone at SA-MW-29S/D suggested that dual-screened injection wells such as SA-RW-19S/D, which was operated from 2011 to 2013 with injections into the deep zone only, more effectively treated Cr(VI) in the deep zone in this part of the Source Area IRZ. The results also indicated that additional wells could improve treatment in the vicinity of SA-MW-05D.

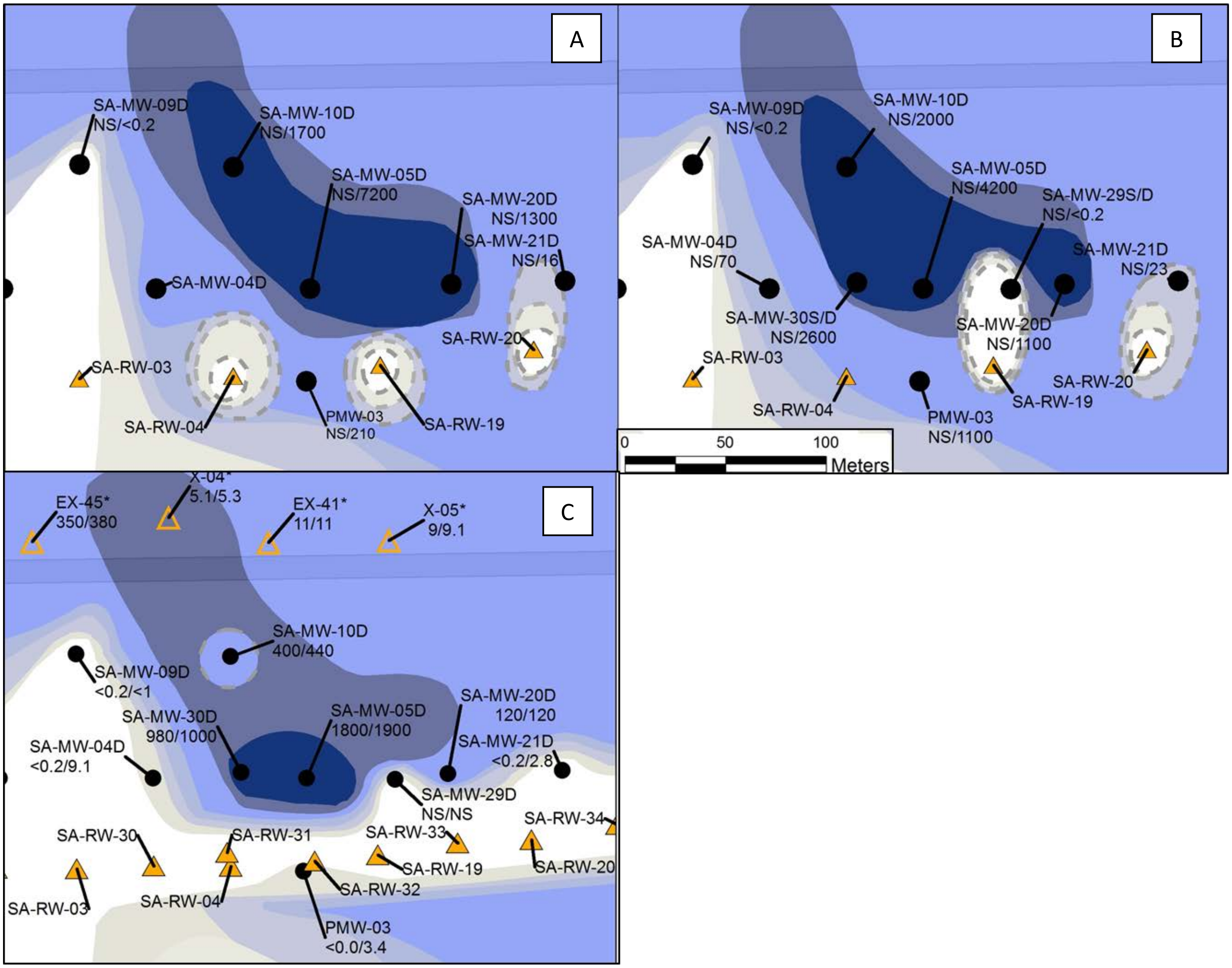

Fig. 6. Cr(VI) concentration distribution near SA-MW-05D in the deep zone of the Upper Aquifer. Closed triangles represent IRZ injection well locations (black-active, grey- inactive during sampling event). Closed circles represent monitoring well locations. Data is total dissolved chromium/Cr(VI) concentrations in µg/L. Panel A- Second Quarter 2014, Panel B- Fourth Quarter 2014, Panel C- Third Quarter 2016. The plume contours are defined in Fig. 2.

The system was adapted in 2015 to add injection wells at a tighter spacing of 40 m (130 feet) or less in this area with the installation of SA-RW-32 and SA-RW-33. Injection into SA-RW-32 and SA-RW-33 the depth intervals for treatment of the deep zone began in October 2015. Within four months, by February 2016, treatment was observed at SA-MW-05D. Cr(VI) concentrations declining from 5,300 ppb in August 2015 to 1,800 ppb in August 2016 and at SA-MW-20D with concentrations decreasing from 1,300 ppb in August 2014 to 120 ppb in August 2016, as shown in Fig. 6C.

Case Study 3: Central Area Deep Zone Operation

A new set of injection wells were installed in the Central Area IRZ in 2012 to target the deep zone of the Upper Aquifer. Injections began in Fourth Quarter 2012. By April of 2014, robust treatment had been observed at six of the eight dose response monitoring wells in the deep zone of the Upper Aquifer, with the exception of CA-MW-107D and CA-MW-109D (see Fig. 7) on the west end of the injection transect. Treatment was observed in the shallow intervals at these locations, CA-MW-107S and CA-MW-109S (data not shown), although injections were being conducted in deep zone injection well CA-RW-19; and despite the boring logs indicating similar lithology near CA-RW-19 to the other injections locations where treatment was achieved in the deep zone. Two operational adjustments were made: the shallow screen interval was opened for injection in both the shallow and deep screen interval and the dosing of organic carbon substrate was doubled. Following these two adjustments, treatment was established by early 2015 and continued to improve, with Cr(VI) reaching non-detect concentrations.

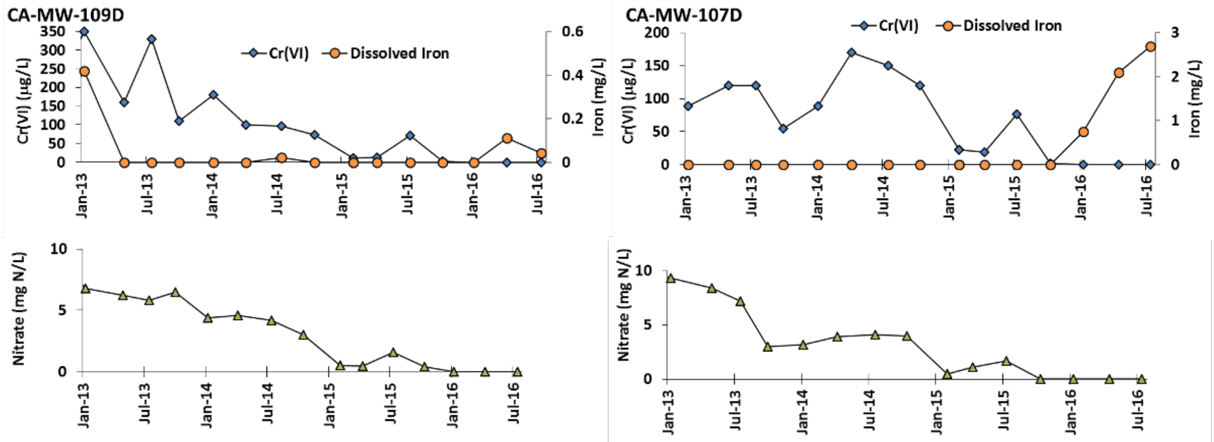

Fig. 7. Cr(VI) and geochemical indicator concentrations from CA-MW-109D and CA-MW-107D

CONCLUSIONS

The remedial progress through Third Quarter 2016 is shown Fig. 8. The figure shows the development of reactive zones within the vicinity of the system injection wells and the downgradient migration of treated water from the IRZs, as shown by the white and grey shapes on Fig. 8 that depict areas with Cr(VI) concentrations that are less than the interim background value of 3.1 µg/L and the California maximum contaminant level of 10 µg/L, respectively. The arrival of treated water has been observed over 915 m (3,000 feet) downgradient of the IRZs in the shallow zone of the Central Area. To estimate overall mass removal, the Cr(VI) mass at baseline (Fig. 1) and in the Fourth Quarter 2015 (Fig. 8) were estimated from digitization of the plume contours. In the Fourth Quarter 2015, it was estimated that approximately 44% of the mass within the IRZ area has been removed by in-situ treatment.

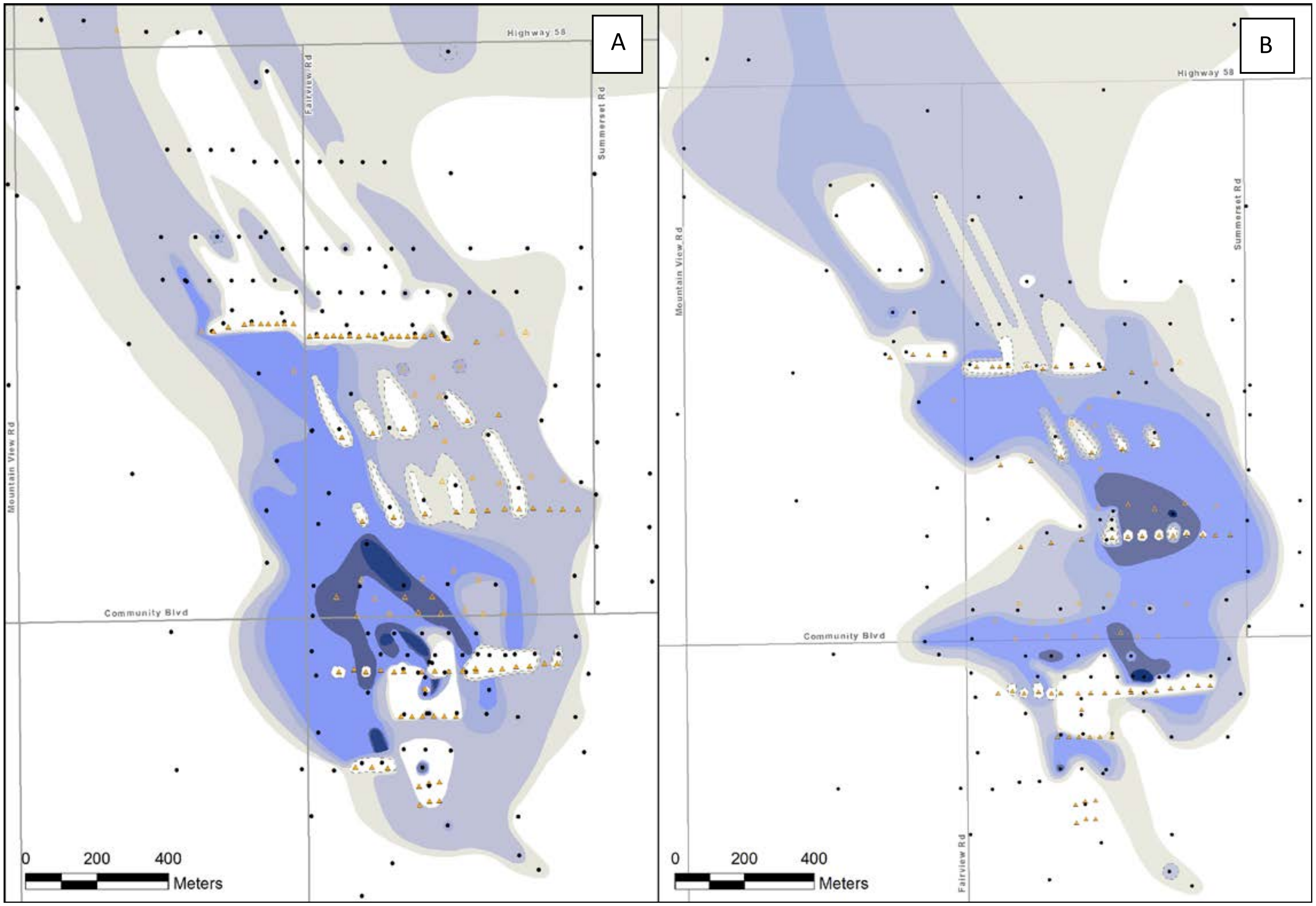

Fig. 8. Distribution of Cr(VI) in groundwater Third Quarter 2016. Panel A depicts the distribution in the shallow zone of the upper aquifer and Panel B depicts the distribution in the deep zone of the upper aquifer. Closed orange triangles represent in-situ injection wells, open orange triangles depict recirculation extraction wells and closed black circles represent monitoring well locations. Plume contours are defined in Fig. 2.

The results to date demonstrate the effectiveness of recirculation systems for the in-situ remediation of Cr(VI) at large spatial scales. The case studies presented herein illustrate the heterogeneity that can be encountered when working at large scales within complex geologic systems and the importance of adaptively managing the remedial systems over time to improve performance. The next steps for the project are to build out in-situ recirculation systems into the remaining areas that require treatment to continue the progress made to date.