

In situ Precipitation of Radionuclides in Groundwater at US DOE Savannah River Site – 14559

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ABSTRACT

A field demonstration of an in-situ groundwater remediation technology, enhanced anaerobic reductive precipitation (EARP)/enhanced reductive dechlorination (ERD)/enhanced denitrification, was conducted at the US DOE's Savannah River Site (SRS). EARP/ERD had previously been used to remediate a wide variety of constituents including chromium, chlorinated solvents, and nitrate (NO_3^-). The SRS demonstration applied the technology to isotopes of uranium (U); technetium (Tc) and other key radionuclides in a mixed-waste plume. The technology entails injection of a cost-effective, food-grade carbohydrate substrate into groundwater to stimulate an indigenous microbial population, precipitate metals and radionuclides, and reduce NO_3^- . In some cases, ferrous iron and sulfate are added to generate iron sulfide minerals that co-precipitate, sorb, and/or encapsulate the precipitates to protect them from reoxidation. A successful demonstration entails not only a reduction in contaminant concentrations, but evidence that the precipitated metals and radionuclides remain in insoluble forms after aerobic conditions are reestablished in the treated zone. In the field-scale test, geochemical zones ranging from aerobic to methanogenic were established in a plume pattern emanating from a line of molasses injection wells. Eighteen months after the last reagent injection, the reactive zone was gradually rebounding to ambient, less reducing conditions. Groundwater data showed decreases in concentrations of U-233/234, U-238, Tc-99, NO_3^- and strontium-90 (Sr-90) to below treatment targets. Monitoring results 30 months after the end of active treatment show continued precipitate stability.

INTRODUCTION

A commercially available in-situ remediation technology, EARP/ERD, was applied in a field-scale demonstration to a mixed-waste groundwater plume containing radionuclides, metals and nitrate. Prior to this demonstration, EARP/ERD had already been used for a wide variety of metals, energetic materials, chlorinated solvents and nitrate, and uranium at one site. Geochemical laboratory measurements and limited field tests have shown that EARP/ERD can be applied to other key radionuclides and to mixed-waste plumes. At SRS, the efficacy of the EARP technology was assessed for the treatment of three key contaminants (uranium, technetium, and nitrate) and secondarily for additional radionuclides/alkaline earth metals (including Sr-90) and other metals. The demonstration was funded under US DOE's Advanced Remediation Technologies (ART) Program in an effort to identify cost-effective groundwater remediation for US DOE High Level Waste Sites.

EARP involves the use of a food-grade carbohydrate substrate, which serves as a supplemental food source for microbiological processes in the subsurface. By injecting this substrate into the subsurface, an aerobic or mildly anoxic aquifer can be altered to a highly anaerobic reactive zone. This in-situ reactive zone (IRZ) creates suitable conditions for the precipitation of certain metals in insoluble forms or for biodegradation of chlorinated solvents. However, once the carbohydrate additions end and geochemical conditions return to oxidizing, the insoluble radionuclides may resolubilize. The demonstration targets long-term stability by enhancing the creation of reduced mineral forms in and around the precipitated radionuclides to act as both a redox buffer for oxidizing groundwater and as a sorptive medium for any dissolved uranium and technetium.

Specific goals of the application at SRS F-Area were to demonstrate the following: effective distribution of reagents to the targeted aquifer; achievement of sustained sulfate-reducing biogeochemical conditions for a treatment period of 18 months; achievement of treatment goals for key contaminants within two years in the

central area of the reactive zone; the presence of precipitated uranium and technetium in insoluble forms following treatment; and limited spatial impact of transient water quality impacts attributable to the technology.

Background: Principles Upon Which EARP is Based

Reducing conditions created in the IRZ provide the biogeochemical environment necessary to convert dissolved metals in the groundwater to insoluble compounds that precipitate and are immobilized in the soil matrix. These EARP mechanisms are primarily biologically-driven co-metabolic processes. The indigenous microbes use organic carbon as a primary substrate for obtaining energy. The organic carbon (typically food-grade molasses, corn syrup, or whey) serves as an electron donor and is oxidized during this process. Cationic metals serve as electron acceptors and are subsequently reduced and precipitated in hydroxide, carbonate or sulfide forms of limited solubility. Oxygen, nitrate, iron, manganese, sulfate, and carbon dioxide also serve as electron acceptors and are consumed sequentially in these reactions, making the aquifer progressively more anaerobic and reducing. The process does not need to proceed all the way to methanogenic conditions to be effective for metals precipitation. However, as a practical matter, under predominantly sulfate-reducing conditions, some methanogenesis will occur. Processes for treatment of uranium, technetium and strontium are briefly discussed below.

The treatment will promote microbial sulfate-reducing conditions in order to facilitate uranium precipitation as well as formation of sparingly soluble technetium phases incorporated into iron sulfide and other biogenic iron minerals. A key to sustained treatment is the establishment of a mass of minerals within the treatment zone capable of consuming incoming oxidants (present in the naturally oxic aquifer) as well as the creation of sorptive mineral phases for long-term stabilization.

To summarize, in order for this in-situ technology to be successful in the long term, the precipitated uranium must not be re-dissolved at an unacceptable rate once groundwater geochemical conditions return to their pretreatment state (which is often aerobic and near-neutral pH). The technology is intended to prevent uranium remobilization not only by the kinetics of the uranium oxidation reaction but also by preferential oxidation of other reduced compounds, preferential consumption of oxidants by sulfide minerals, and sorption of desorbed uranium to freshly formed amorphous iron oxides and sorption of desorbed uranium to iron sulfide minerals.

The process will immobilize technetium upon return of oxic conditions by preferential oxidation of other reduced compounds, preferential consumption of oxidants by sulfide minerals, stabilization of technetium in the sulfide minerals, and sorption of any oxidized technetium to freshly formed amorphous iron oxides and iron sulfide minerals. The amount of iron sulfide formed during the sulfate reduction process can be adjusted to provide a redox buffer to stabilize the reduced technetium precipitate by maintaining reduced conditions and by providing an iron source as oxidizing conditions are reestablished over time to provide a sorption capacity far in excess of the naturally available sorption capacity of the aquifer.

Strontium's form in the environment is independent of reduction potential (Eh), and the sulfate form (SrSO_4) is a stable mineral under near-neutral conditions. The EARP process introduces sulfate as part of the molasses and additional sulfate can be added. EARP might therefore be expected to produce effective stabilization of aqueous strontium as the sulfate as long as the pH can be kept near neutral. However, there is considerably less bench-scale literature on the biological immobilization of strontium than there is for uranium and technetium.

Background: SRS F-Area Site

Groundwater at the SRS F-Area contains persistent levels of radionuclides, metals and nitrate in an area extending nearly a mile from the source area.

The targeted groundwater horizon for the demonstration was the water table aquifer, known as the Upper Aquifer Zone of the Upper Three Runs Aquifer (UAZ of the UTRA). The depth to the water table in the demonstration area is approximately 20 to 21 meters (65 to 70 feet) in the demonstration area, and the saturated thickness of the UAZ is approximately 7.6 meters (25 feet).

The UAZ consists predominantly of fine sand and clayey sand with minor interbeds of clay and sandy clay [1]. The estimated hydraulic conductivity (K) of the UAZ in the F-Area is 3.2×10^{-2} cm/s (92 feet/d) and horizontal groundwater velocity is 270 m/y (890 feet/y) [2]. Underlying the water table aquifer is a semi-confining clay unit.

The demonstration took place in the vicinity of an existing mid-plume monitoring well, FSB-90D, with a long monitoring record. Concentrations of the constituents of particular interest to the demonstration at FSB-90D prior to the demonstration, and their respective cleanup goals (Groundwater Protection Standards [GWPS]), are provided in Table I. Baseline ranges of geochemical parameters are listed in Table II. Groundwater in the target zone was acidic and aerobic at the beginning of the demonstration.

TABLE I. Baseline concentrations of constituents of interest at target well FSB-90D

Constituent/parameter	Baseline concentration at well FSB-90D, June 2009	GWPS
Uranium-233/234	3.96 Bq/L (107 pCi/L)	0.56 Bq/L (15 pCi/L)
Uranium-238	5.07 Bq/L (137 pCi/L)	0.56 Bq/L (15 pCi/L)
Technetium-99	1.08 Bq/L (29.2 pCi/L)	1.85 Bq/L (50 pCi/L)
Strontium-90	5.03 Bq/L (136 pCi/L)	0.30 Bq/L (8 pCi/L)
Nitrate-nitrite as N	31.3 mg/L	10 mg/L

Bq/L – Becquerels per liter
 pCi/L – picoCuries per liter
 mg/L – milligrams per liter

METHODS

Injection and monitoring wells were installed in two phases in the vicinity of target well FSB-90D. In the first phase, wells were installed with 20-foot screens to span the majority of the 7.6-m (25-foot) saturated thickness of the aquifer. Baseline discrete-interval testing of groundwater samples showed vertical variability in target constituents and geochemistry parameters. Thus, in the second phase of well installations, a subset of injection and monitoring wells were screened across the top half (3 m [10 feet]) of the saturated thickness of the UAZ to match the effective screen interval for FSB-90D. For this reason, data are presented separately for shallow wells (top half of the UAZ) and long-screened wells (full UAZ thickness). Soil cores exhibited silty fine sands with little visible variability in grain size over the saturated interval of the UAZ.

A tracer test was conducted using combined sodium chloride salt and fluorescein dye tracers gravity-fed into injection well IP-2. In-well vertical profiling of specific conductance (source strength approximately 3,500 microsiemens/centimeter [uS/cm] vs. background of ~200 uS/cm) indicated that the salt tracer was distributed non-uniformly in the vertical as well as the horizontal dimension. The salt tracer was only

lightly evident at FSB-90D (maximum 774 uS/cm), but was measured at nearly full strength (>3,000 uS/cm) at a more distant monitoring well, PMW-5. Dye tracer was observed at only one monitoring well (PMW-5), months later than the salt tracer.

TABLE II. Baseline concentrations of geochemical parameters at target well FSB-90D

Parameter	Baseline at well FSB-90D, July 2009
pH	3.77
Redox potential	266 mV
Dissolved oxygen	1.3 mg/L
Total organic carbon	0.529 mg/L
Dissolved organic carbon	0.572 mg/L
Nitrate	28.1 mg/L
Nitrate-nitrite as N	31.3 mg/L
Manganese, total	399 ug/L
Manganese, dissolved	390 ug/L
Iron, total	149 ug/L
Iron, dissolved	52 ug/L
Sulfate (at PMW-11 and PMW-12)	<2 mg/L
Methane	0.16 ug/L
CO ₂	88.8 mg/L

mV – millivolts

ug/L – micrograms per liter

Carbohydrate reagent was made in 9,500-L (2,500-gallon) batches using by mixing 38 L (10 gallons) of molasses (0.4% by volume) in supplied (treated) water which was then dosed with sodium hydroxide to reach a pH of 7.0 to 7.5. Due to the presence of fairly high concentrations of iron during reagent injections, no additions of ferrous iron or sulfate were required for this application. The reagent was gravity-fed into the four injection wells, followed by a small slug of clean water. Nine injections were completed at approximately one-month intervals between April 2010 and January 2011. Injection wells were redeveloped after the third injection to reverse declining injection well performance. Injection well IP-2, the best-performing well, received the highest reagent volume (48 to 74% of each reagent batch). The spatial distribution of the molasses reagent, measured as total organic carbon (TOC), took on a typical plume pattern which expanded with time. This distribution differed substantially from that of either of the tracers.

Periodic groundwater monitoring took the form of process monitoring to assess and modify the injection strategy as the test proceeded, and performance (full biogeochemical) monitoring to assess the remedial system performance and to provide in-depth understanding of groundwater geochemistry. Performance monitoring samples were collected using low-flow methods, with a bladder pump, Teflon tubing and a flow-through cell for measurement of stabilization parameters. SRS' FSB wells were sampled by SRS personnel in accordance with standard operating procedures for the site. The most recent monitoring data represented in this report are for mid-2012 through mid-2013, 18 to 30 months after the last reagent injection.

RESULTS

Potentiometric data indicates that in the demonstration area, groundwater in the water table aquifer flows to the south (Figure 1), with a horizontal gradient of 0.004 m/m. On average, K is higher for the lower half of the UAZ than for the upper half. Average K for the full saturated portion of the UAZ, based on slug testing, is 4.2×10^{-3} cm/s (12 feet/d). Horizontal velocity, based on tracer and reagent arrivals, ranged from 45 m/y (146 feet/y) for the upper half of the UAZ to 156 m/y (511 feet/y) for the full UAZ, also suggesting that permeability is highest in the lower half of the UAZ.

The major results of the demonstration are discussed below in terms of the specific project goals.

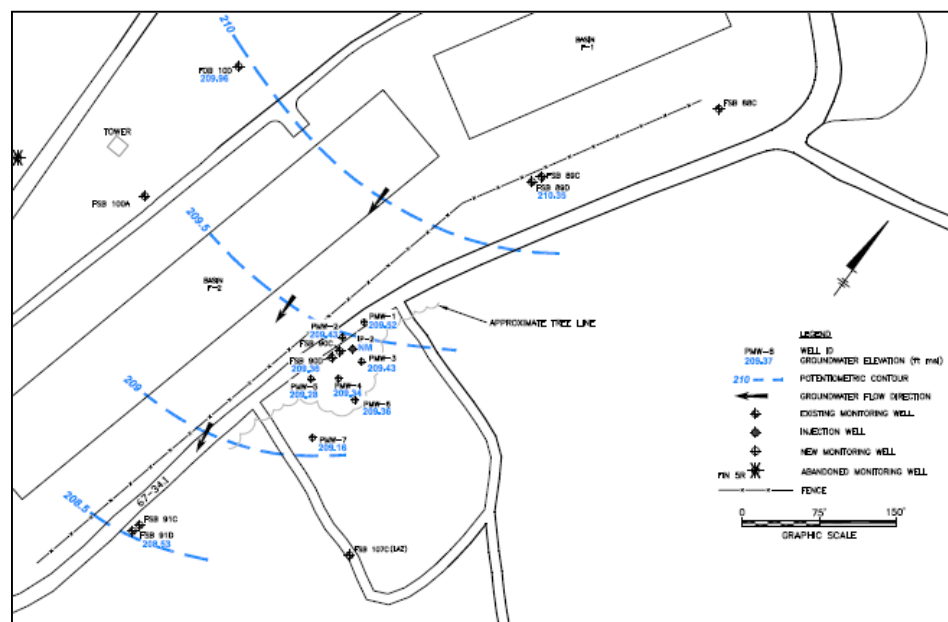


Fig. 1. Demonstration Area with Seepage Basins, Wells and Potentiometric Surface.

Effective Distribution of Reagents

The separation and uneven distributions of the salt and dye tracers were enigmatic since both were expected to be conservative tracers. This topic will be discussed more in a subsequent publication. Tracer testing indicated substantial anisotropy in the flow field, but the molasses reagent distributed in a more symmetrical configuration. The reagent distribution at two time periods, represented as TOC, is shown in Figure 2. The TOC plume reached the downgradient end of the well field (PMW-9; approximately 210 feet from injection wells) by December 2011, after eight monthly injections of reagent. After reagent injections ended, concentrations of TOC greater than a typical treatment target value of ~100 mg/L receded within a few months. During the period from 6 to 18 months after the last injection (from July 2011 to July 2012), low levels of supplied TOC (greater than approximately 2 mg/L) have persisted within the wellfield but have continued to recede spatially.

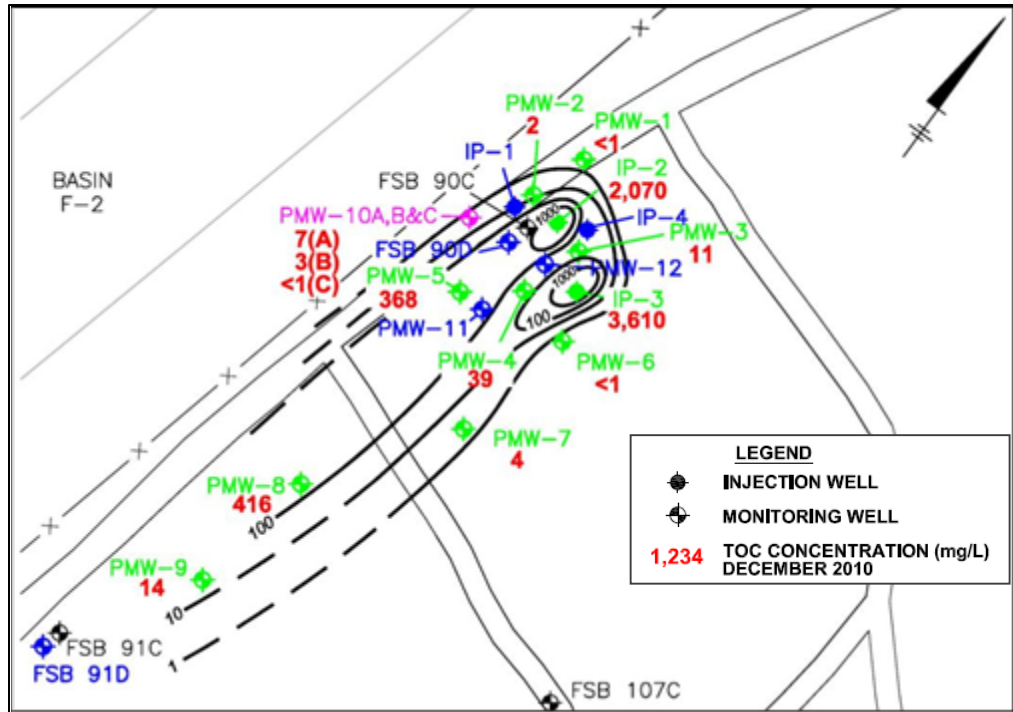


Fig. 2a. TOC Distribution, Long-Screened Wells, December 2010 (8 Months after First Injection).

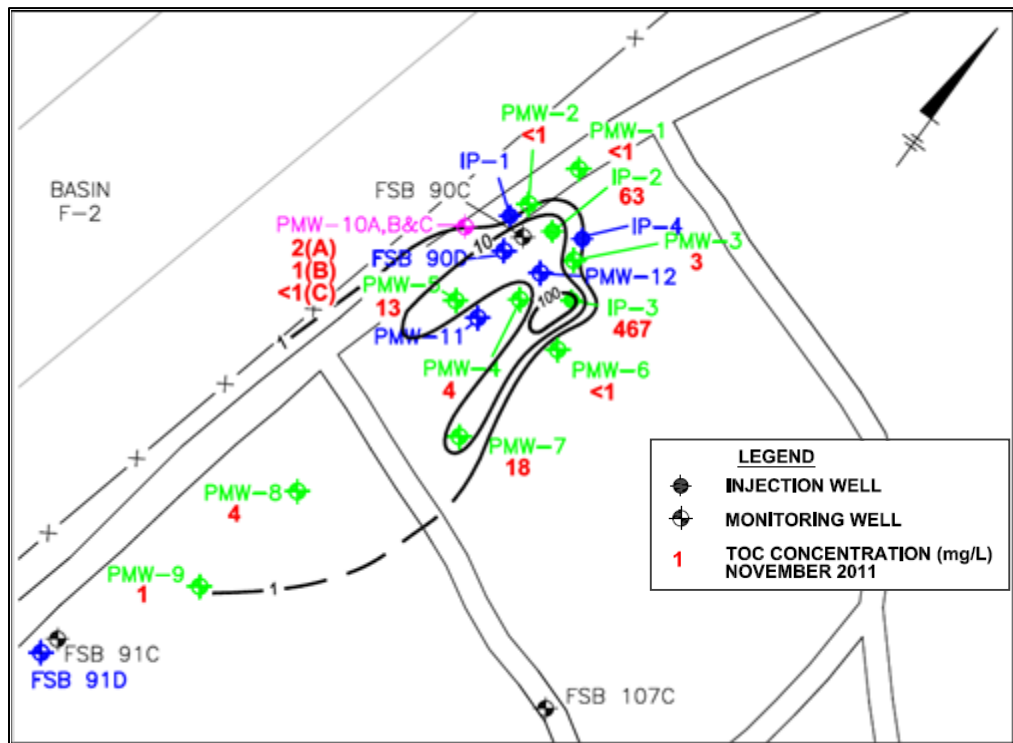


Fig. 2b. TOC Distribution, Long-Screened Wells, November 2011 (19 Months after First Injection).

Achievement of Sustained Reducing Biogeochemical Conditions

By the end of active treatment, redox zones ranging from aerobic to methanogenic were established in a plume pattern emanating from a line of injection wells. Approximate redox zonation in the wellfield at two time periods is shown in Figure 3. Elevated methane concentrations in groundwater of up to 36 mg/L were observed within the reactive zone. At the target date of eighteen months after the last reagent injection, the reactive zone was gradually rebounding to less reducing conditions, but still exhibited methane concentrations in groundwater of up to 4 mg/L, suggesting that sulfate-reducing conditions were also still present in the reactive zone.

Achievement of Treatment Goals for Key COCs within Two Years in the Central Area of the Reactive Zone

Trends in concentrations of key COCs in groundwater at target well FSB-90D relative to cleanup goals are shown in Figures 4 through 8. Data are available for this well through July 2013, 30 months after the last reagent injection. Concentrations of U-233/234, U-238, NO_3^- , Tc-99, and Sr-90 decreased dramatically within a few months after treatment began. Concentrations of each of these constituents fell below GWPS during treatment at target well FSB-90D, and remained below GWPS through at least January 2012, 12 months after the last reagent injection. Figure 8 shows that the Sr-90 reductions may be attributable mainly to the effect of pH adjustment on particle surfaces. In this hypothesis, as pH in the treated area returned to baseline levels, Sr-90 decreases attributable to the increased cation exchange capacity at lower pH reversed. Sr-90 tied up in stable precipitates would not be expected to re-dissolve so rapidly. Continued monitoring at FSB-90D is necessary to determine the longevity of reduced concentrations of uranium and technetium.

Concentration trends for the same constituents along the axis of the pilot test are shown in Figures 9 through 12, with three graphs depicting baseline, 5 months and 15 months after the first injection. At 5 months, concentrations had decreased at wells as far downgradient from the injection wells as PMW-5 (48 feet). At 15 months, the nitrate profile indicates that treatment effects had reached PMW-9 (110 feet).

Presence of Precipitated Uranium and Technetium in Insoluble Forms following Treatment

Continued long-term groundwater monitoring at SRS will provide an indirect indication of whether uranium and technetium have been adequately immobilized. In a successful demonstration, after aerobic conditions are reestablished in the treated zone, the precipitated uranium and technetium will not be re-dissolved at an unacceptable rate (i.e., at a rate producing concentrations above cleanup standards) once groundwater geochemical conditions return to their original redox state. At the SRS site, the most recent data at 2.5 years after the last injection indicate that certain biogeochemical indicators (pH, nitrate-nitrite as N) have returned to background levels, indicating a reestablishment of pre-treatment conditions. At the same time, U-233/234, U-238 and Tc-99 have remained at low, post-treatment levels, suggesting that sorptive mineral phases have provided continuing treatment of these constituents.

Limited Spatial Impact of Transient Water Quality Impacts of the EARP Technology

Iron is expected to be mobilized during reducing in-situ treatment processes. The maximum iron concentrations detected during the demonstration were 18 mg/L before treatment, 412 mg/L during reagent injections; and 62 mg/L 18 months after treatment (in the remaining reactive zone); as expected, iron concentrations were generally decreasing post-treatment. Due to the presence of fairly high concentrations of iron during reagent injections, additional ferrous iron (as ferrous sulfate) was not added to the pilot test area. The secondary MCL for iron is 0.3 mg/L. The maximum concentration of sulfate during the demonstration was below the secondary MCL of 250 mg/L.

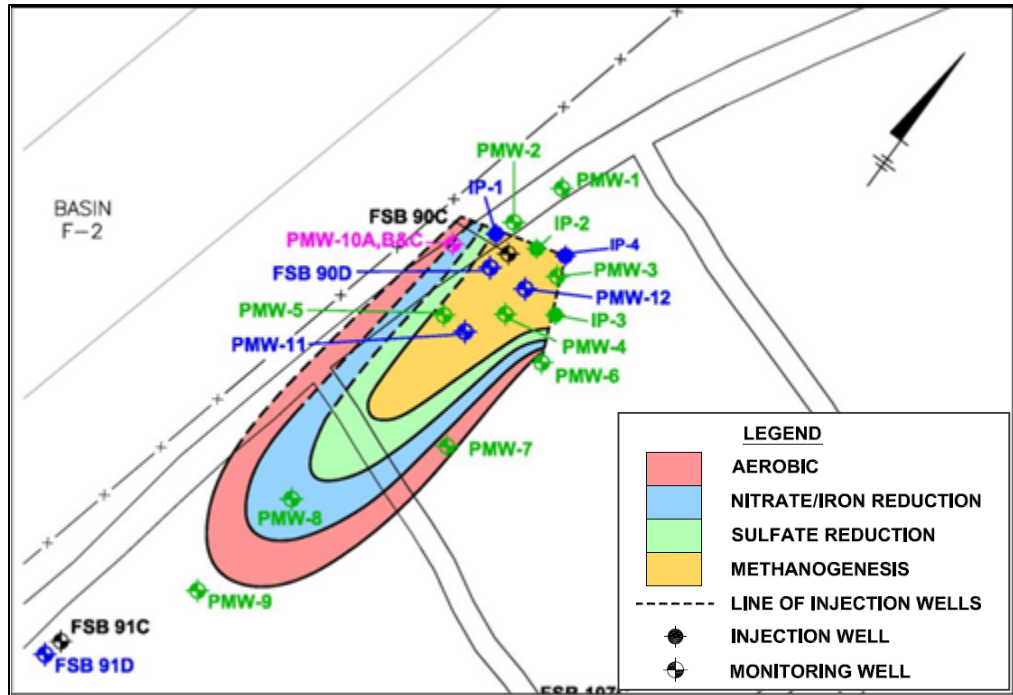


Fig. 3a. Redox Zones, Long-Screened Wells, December 2010 (8 Months after First Injection).

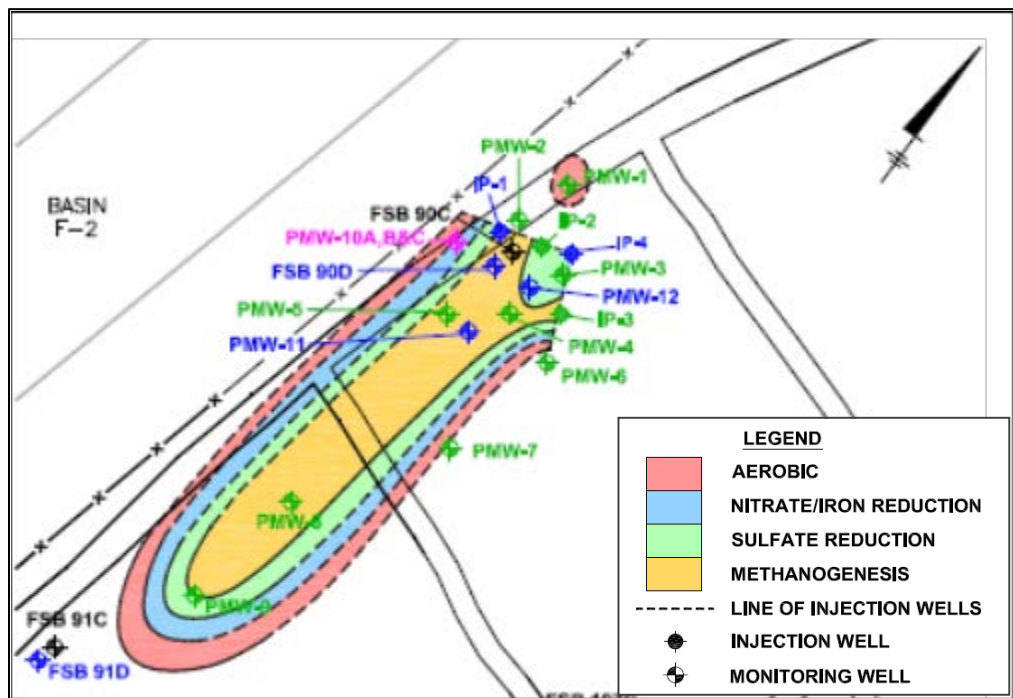


Fig. 3b. Redox Zones, Long-Screened Wells, July 2011 (15 Months after First Injection).

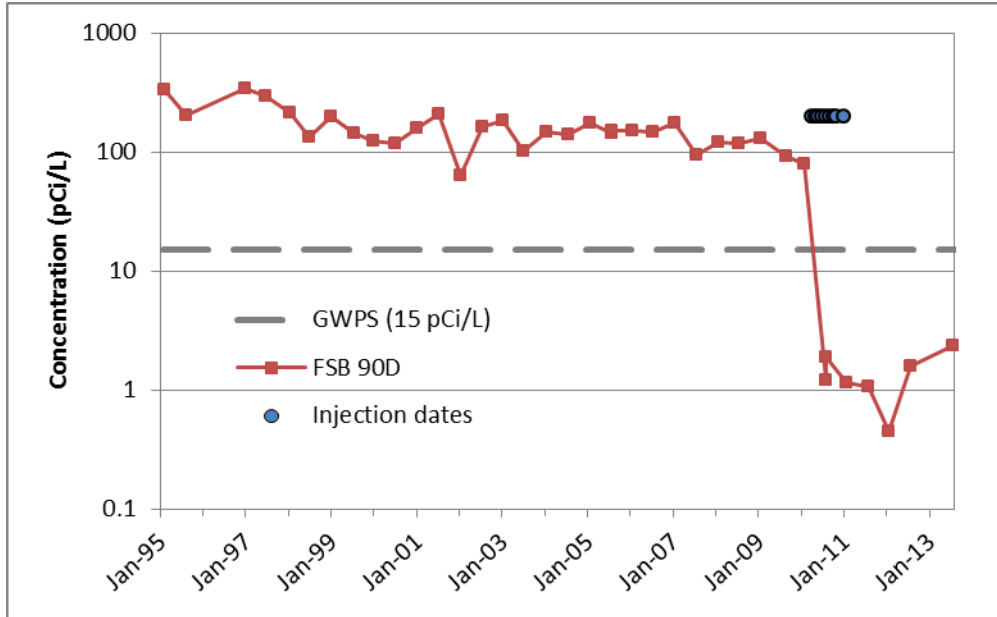


Fig. 4. Long-Term Trend for U-233/234 at Well FSB-90D (Data through July 2013, 30 Months After Last Reagent Injection).

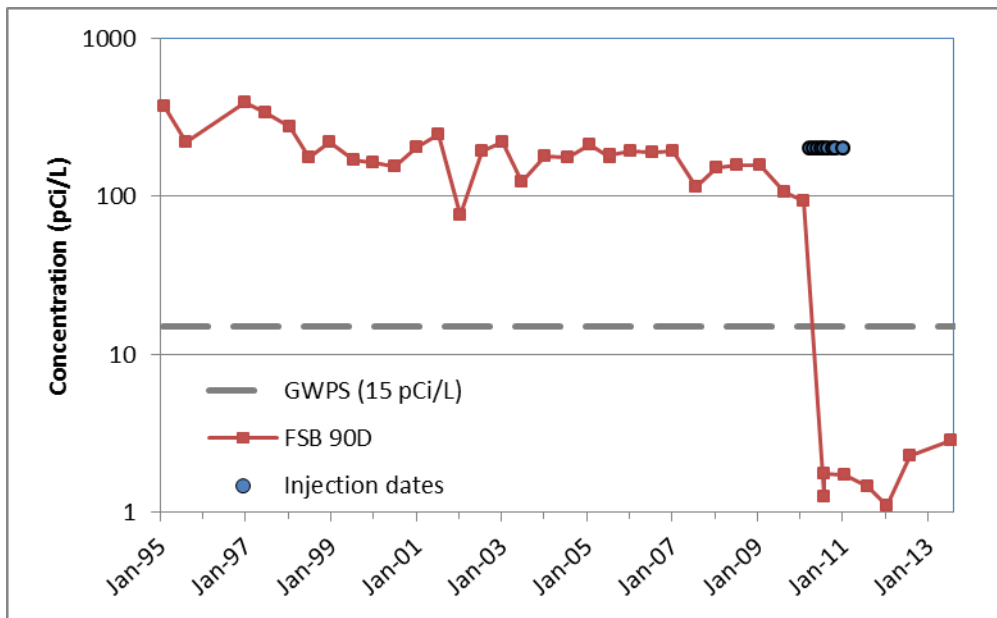


Fig. 5. Long-Term Trend for U-238 at Well FSB-90D (Data through July 2013, 30 Months After Last Reagent Injection).

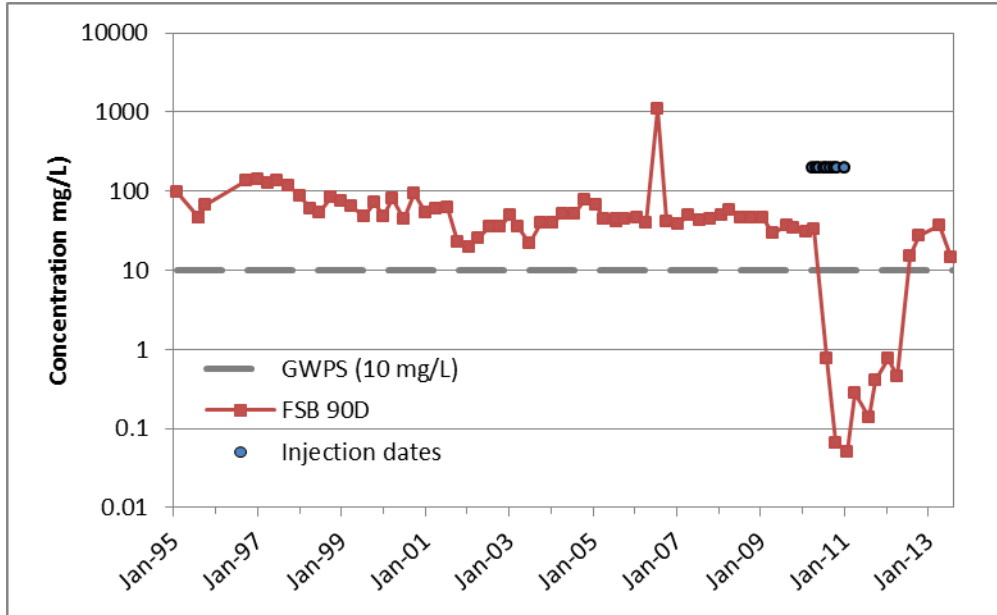


Fig. 6. Long-Term Trend for Nitrate-Nitrite as N at Well FSB-90D (Data through July 2013, 30 Months After Last Reagent Injection).

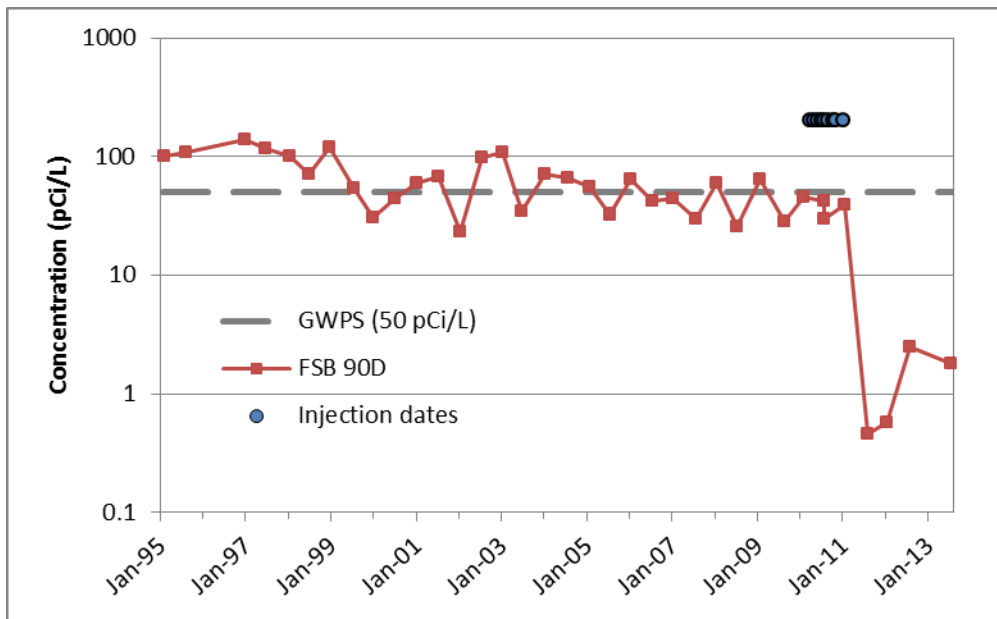


Fig. 7. Long-Term Trend for Tc-99 at Well FSB-90D (Data through July 2013, 30 Months After Last Reagent Injection).

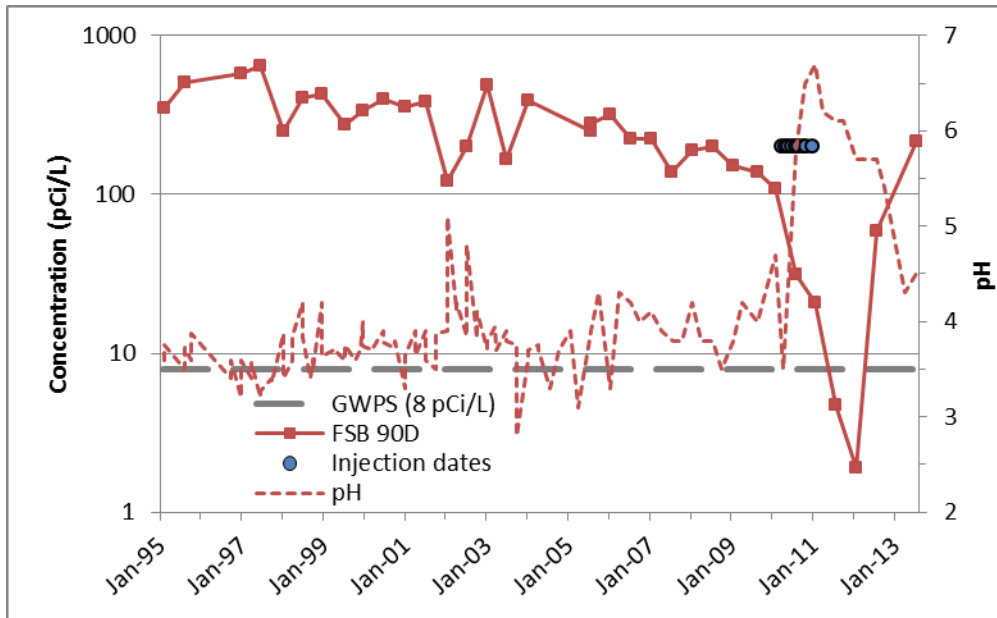


Fig. 8. Long-Term Trends for Sr-90 and pH at Well FSB-90D (Data Through July 2013, 30 Months After Last Reagent Injection).

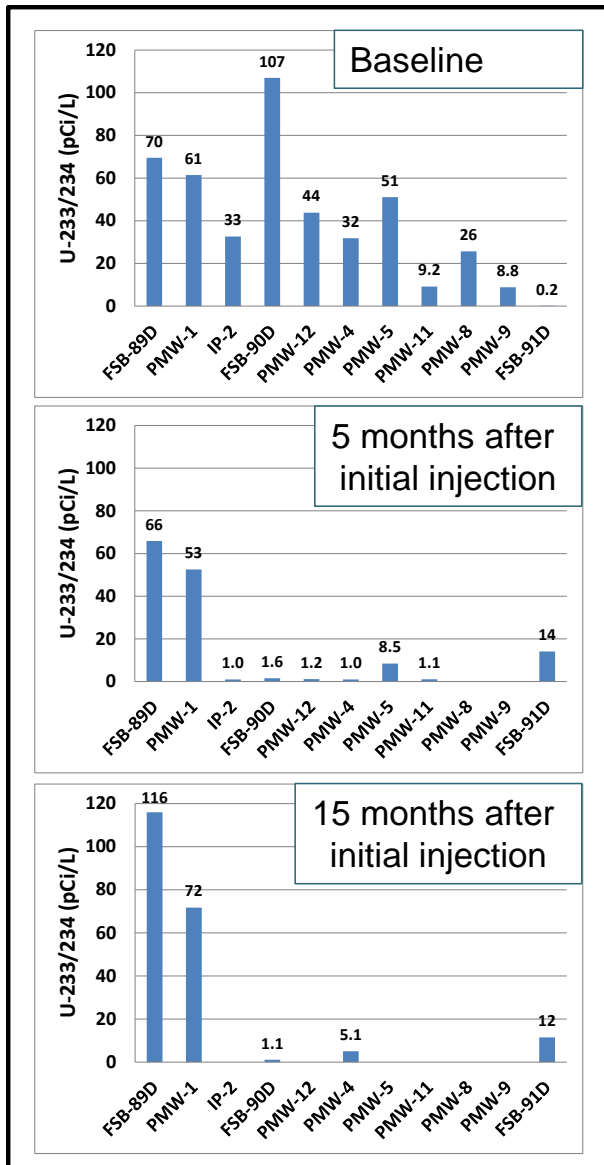


Fig. 9. Uranium-233/234, 0.56 Bq/L (15 pCi/L) Site Standard, Concentrations in Groundwater, Arranged Generally from Upgradient (FSB-89D) to Downgradient (FSB-91D).

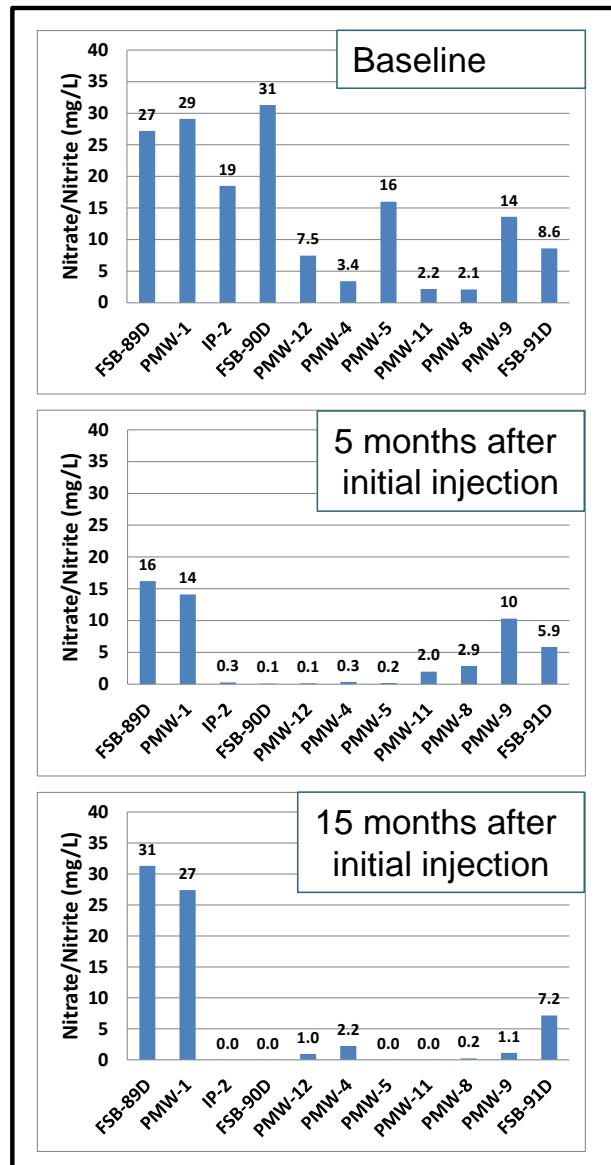


Fig. 10. Nitrate-Nitrite as N, 10 mg/L site Standard, concentrations in Groundwater, Arranged Generally from Upgradient (FSB-89D) to Downgradient (FSB-91D).

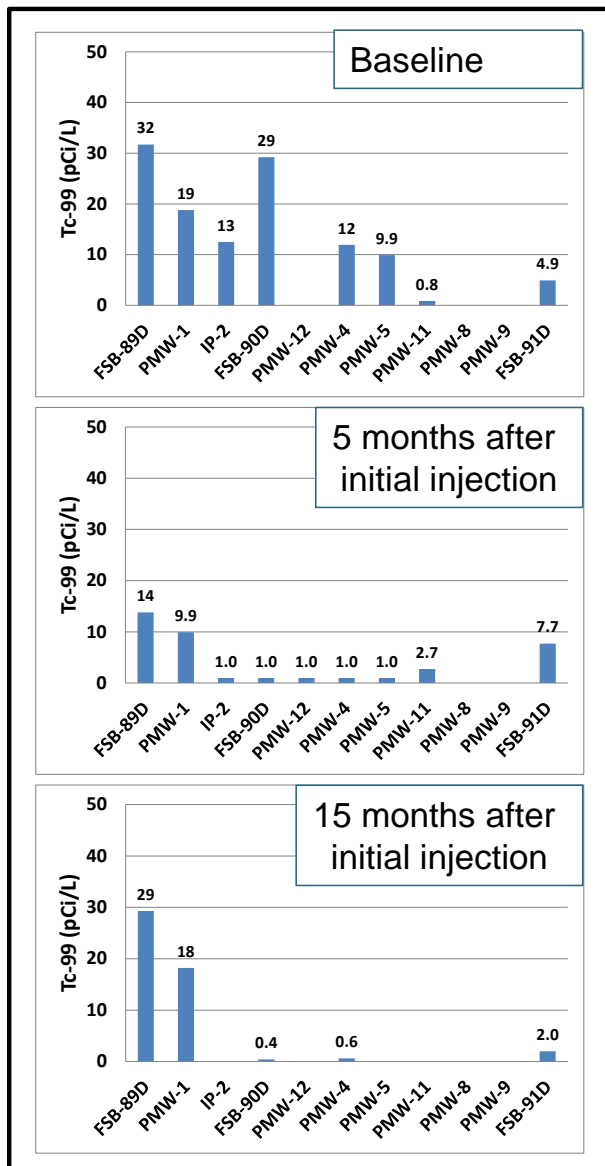


Fig. 11. Technetium-99, 1.85 Bq/L (50 pCi/L) Site Standard, Concentrations in Groundwater, Arranged Generally from Upgradient (FSB-89D) to Downgradient (FSB-91D).

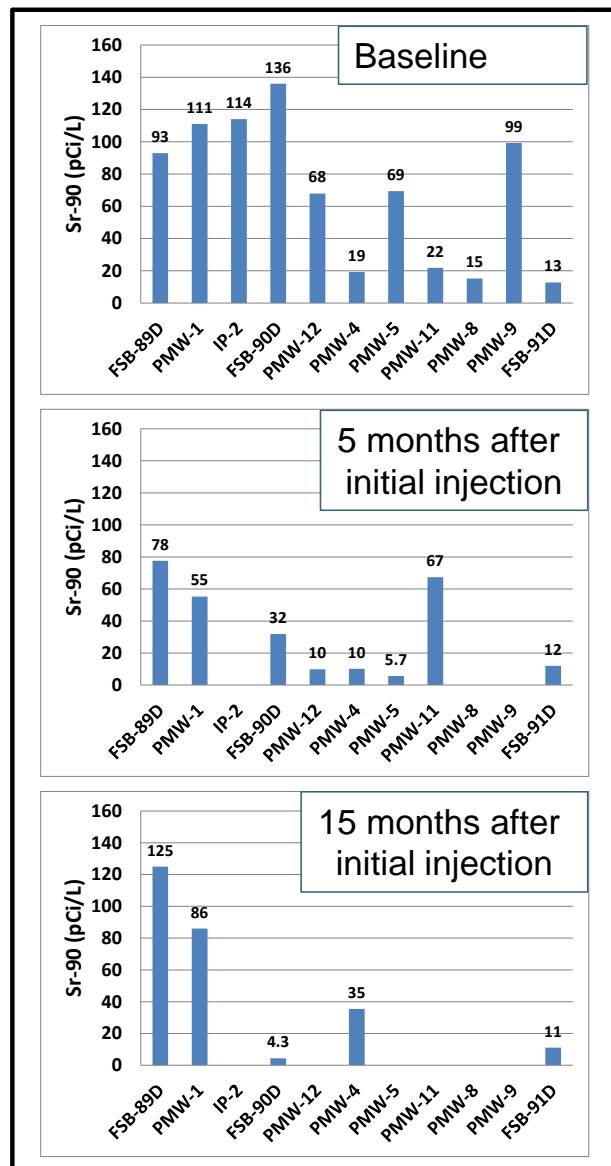


Fig. 12. Strontium-90, 0.30 Bq/L (8 pCi/L) Site Standard, Concentrations in Groundwater, Arranged Generally from Upgradient (FSB-89D) to Downgradient (FSB-91D).

CONCLUSIONS

The EARP/ERD/enhanced denitrification demonstration met project goals (distribution, sustained reducing conditions, achievement of cleanup goals within two years, evidence of precipitate stability and limited water quality impacts). Treatment goals for the key COCs were met very soon after the reagent was introduced, with dramatic reductions in concentrations of U-233/234, U-238, nitrate, and Tc-99. Temporary reductions in Sr-90 appear to have been primarily attributable to changes in pH. Treatment of uranium and technetium has been sustained over a period of 2.5 years of available data, and appears to have been ongoing even after reestablishment of background biogeochemical conditions. This suggests that sorptive mineral phases have provided continuing treatment of these constituents. The application has demonstrated the practicality of the EARP/ERD/enhanced denitrification technology at the SRS F Area and provides confidence that it can be successfully applied toward remediation of other mixed-waste plumes including US DOE High Level Waste Sites.

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