

**The Use of Subsurface Barriers to Support Treatment of Metals and Reduce the Flux of Tritium to Fourmile Branch at the Savannah River Site in South Carolina - 13358**

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**ABSTRACT**

The Savannah River Site (SRS) produced tritium, plutonium, and special nuclear materials for national defense, medicine, and the space programs. Acidic groundwater plumes containing metals, metallic radionuclides, non-metallic radionuclides and tritium sourced from the F and H Area Seepage Basins have impacted the surface water of Fourmile Branch on SRS. Tritium releases from Fourmile Branch have impacted the water quality within areas of the Savannah River adjacent to the SRS, and this circumstance has been an ongoing regulatory concern.

The F and H Area Seepage Basins operated until 1988 for the disposition of deionized acidic waste water from the F and H Separations Facilities. The waste water contained dilute nitric acid and low concentrations of non-radioactive metals, and radionuclides, with the major isotopes being Cs-137, Sr-90, U-235, U-238, Pu-239, Tc-99, I-129, and tritium. The tritium concentration in the waste water was relatively elevated because there is not a practicable removal method in water. The acid content of the waste water during the operational period of the basins was equal to 12 billion liters of nitric acid. The seepage basins were closed in 1988 and backfilled and capped by 1991.

The plumes associated with the F and H basins cover an area of nearly 2.4 square kilometers (600 acres) and discharge along ~2,600 meters of Fourmile Branch. The acidic nature of the plumes and their overall discharge extent along the branch represent a large challenge with respect to reducing contaminant flux to Fourmile Branch. The introduction of nitric acid into the groundwater over a long time effectively reduced the retardation of metal migration from the basins to the groundwater and in the groundwater to Fourmile Branch, because most negatively charged surfaces on the aquifer materials were filled with hydrogen ion.

Two large pump and treat systems were constructed in 1997 and operated until 2003 in an attempt to capture and control the releases to Fourmile Branch. The operating cost, including waste disposal, for the two systems was ~\$1.3M/month. Both systems employed reinjection of tritiated water up gradient of the extraction, and produced large quantities of waste from non-tritium isotopes and metals removal prior to reinjection. Both systems were determined to be ineffective and potentially detrimental with respect to limiting the flux of contaminants to Fourmile Branch.

After it became apparent that there was very little benefit to continued operation of the systems, and the staggering cost of operations was recognized by the SRS and regulators, a new remedy was developed. The new system uses vertical subsurface barriers to redirect groundwater flow to limit the transport of contaminants to the stream. The barriers were constructed of acid resistant grout using deep soil mixing techniques. The grout mixture used low swelling clay, fly ash, and sodium hydroxide to form a pozzolan material with low permeability and low strength. The SRS and regulators agreed to a series of remedial goals, with the first goal to reduce tritium flux to the stream by 70% and bring constituents other than tritium to groundwater protection standards.

At the F Area Seepage Basins the subsurface barriers extend to 18 meters (60 feet) below the surface, and form a funnel and gate system 1,036 meters (3,400 feet) long. The system contains three gates that have openings set in the upper portion of the water table, which promotes water movement mostly in the top of the stratigraphic section. The gates also contain a base injection system to neutralize nitric acid and cause the precipitation of metals onto aquifer materials.

At the H Area Seepage Basins the subsurface barriers extend to 27 meters (90 feet) below the surface and have a cumulative length of 1,005 meters (3,300 feet). The barriers are positioned up gradient (length of 610 meters (2,000 feet)) and down gradient (length of 400 meters (1,300 feet)) of the largest seepage basin (H-4). The barriers create a “step-down” configuration from up gradient of the basins to down gradient of the basins adjacent to Fourmile Branch, with a large reduction in groundwater gradient within each of the steps. The reduction in gradient is used to reduce the flux of contaminants to the stream.

Construction of the subsurface barriers was completed in 2005; a 70% reduction in tritium flux was achieved in 2011. SRS has implemented several base injection campaigns in the gates and down gradient of the barriers to work toward achieving standards in Fourmile Branch for all constituents other than tritium. It is believed that achieving groundwater protection standards for radioactive metals will be achieved soon. SRS is currently evaluating a passive reactive treatment for I-129 in one of the gates at the F Area Seepage Basins.

## **INTRODUCTION**

At the F and H Area Seepage Basins approximately 12 billion liters of acidic aqueous waste from nuclear processing facilities was disposed of in unlined basins from 1955 until 1988. The belief was that most of the radionuclides would be bound in the soils beneath the basins and would not significantly pollute groundwater. This was true for many radionuclides, including plutonium isotopes and Cs-137, but many such as Sr-90, uranium isotopes, I-129, Tc-99, and tritium migrated to groundwater resulting in significant plumes that discharge to a surface water stream.

Figures 1, 2, and 3 show the location of the Savannah River Site, the F and H Area Seepage Basins plumes, and photographs of the basins during operation and following closure.

### **Hydrogeologic Setting**

A large percentage of the groundwater contamination occurs within the Irwinton Sand of the Upper Aquifer Zone, with less in the Lower Aquifer Zone. The Tan Clay Confining Zone separates the two zones and is also contaminated. Both the Upper and Lower zones comprise the Upper Three Runs Aquifer which is the water table aquifer. Figure 4 illustrates the lithologic and hydrostratigraphic units and nomenclature.

The Upper Aquifer Zone occurs predominantly within the Irwinton Sand. The Irwinton Sand consists of tan, yellow and orange, moderately-sorted quartz sand, with interlaminated and interbedded clay abundant in places. Pebbly layers are present, as are zones of abundant clay clasts, which are of the Twiggs Clay/Tan Clay lithology. Interlaminations and thin beds of silt and clay are present within some sections of the Irwinton Sand. The Tan Clay at SRS is locally considered to be a leaky confining unit.

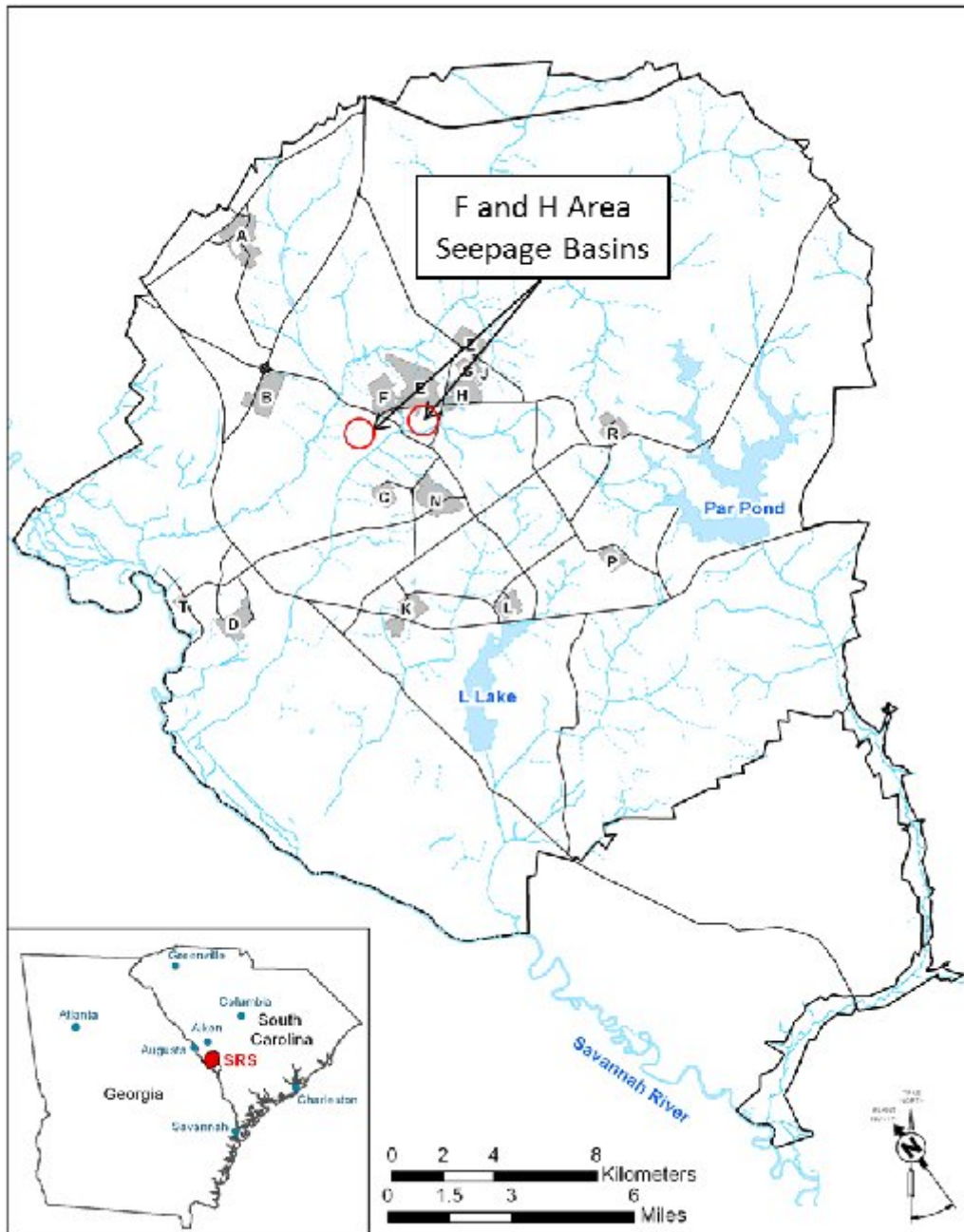


Figure 1. Location of the F and H Area Seepage Basins at the Savannah River Site.

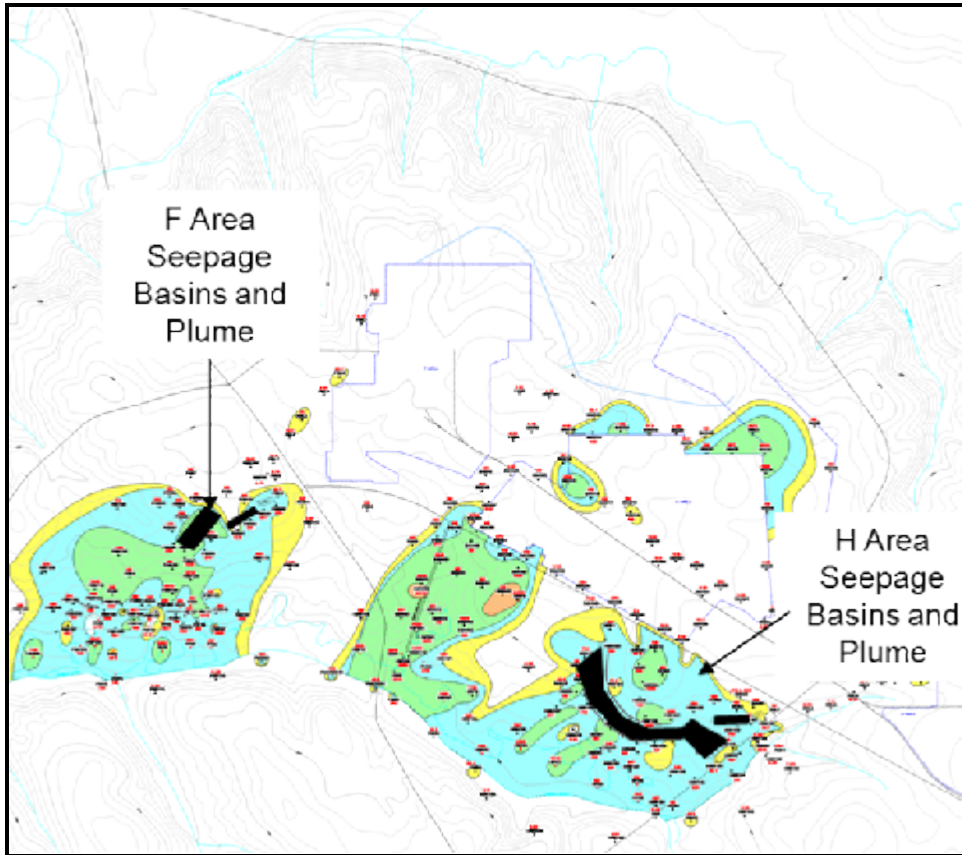


Figure 2. F and H Area Seepage Basins Tritium Groundwater Plumes.





Figure 3. F Area Seepage Basins During Operations (top) and After Closure (bottom).

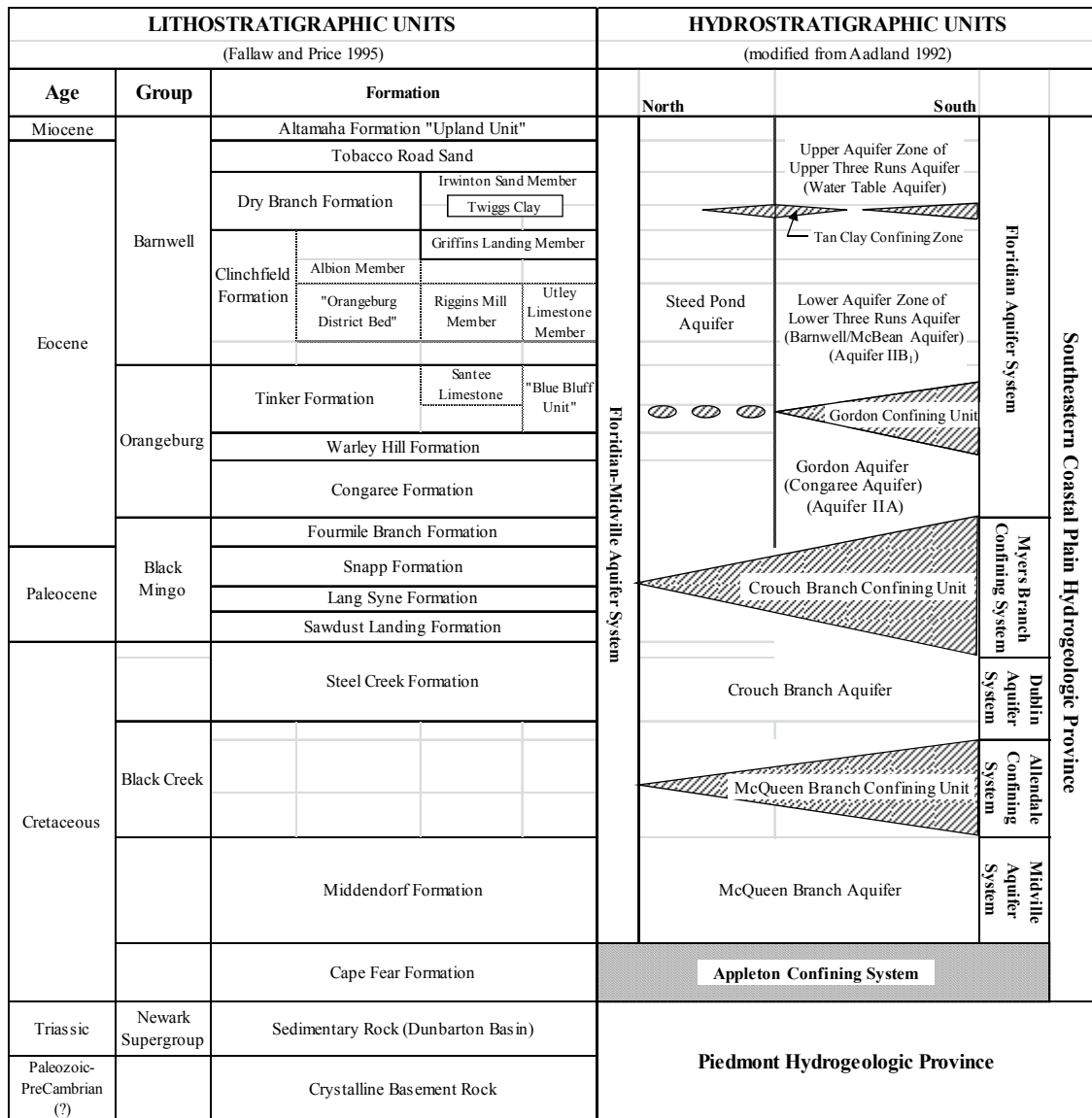


Figure 4. Lithologic and Hydrostratigraphic Units at the F Area Seepage Basins.

The depth to groundwater ranges from 21 meters (70 feet) near the basins to 6 meters (20 feet) near the wetlands adjacent to Fourmile Branch. The thickness of the Upper Aquifer Zone ranges between 6 to 12 meters. Portions of the Irwinton Sand have hydraulic conductivities as high as 27 meters/day (90 feet/day) and groundwater velocities upward of 300 meters/year (1,000 feet/year). Groundwater flow is from the source area at the basins to Fourmile Branch. The plume outcrops at seeps within the wetlands and directly into the stream.

**Original Remedial Strategy**

In 1992, SRS entered into a RCRA Part B permit for the cleanup of groundwater contamination from the F and H Area Seepage Basins. The corrective action strategy was a phased approach with the initial remedial action focused on capturing the most contaminated portions of the plume

(known as the Phase 1 capture zones) and reducing the discharge of tritium to Fourmile Branch. In 1998, SRS began full time operation of two large pump and treat systems to capture and remediate the portions of the tritium plumes greater than 10,000 pCi/mL.

The treatment systems consisted of extraction wells, a wastewater treatment facility, and injection wells. The plume was captured by the extraction network prior to discharging at the wetlands. Collected water was treated using reverse osmosis, flocculation and clarification, and ion exchange processes. The treated water, still containing tritium, was injected up gradient of the seepage basins allowing for additional radioactive decay before being recaptured by the extraction wells. The pump and treat systems operated at flow rates up to 760 liters/minute (200 gallons/minute) and treated approximately 3.2 billion liters (850 million gallons) of groundwater during operation.

The pump and treat systems operated for nearly five years after which time the effectiveness of the corrective action was evaluated. The treatment units were effective at removing many of the metals and metallic radionuclides, but created large amounts of low level waste (over 400 cubic meters annually) that was difficult and expensive to dispose of due to I-129. The capture efficiency of the extraction network was estimated at up to 72 percent of groundwater originating within the Phase 1 capture zone and was even less (50 percent) for recapture of treated injected water. Also, the capture efficiency was predicted to further degrade over time due to the effects of natural infiltration and groundwater inflow from up gradient of the system.

The second phase of the corrective action originally was to expand the pump and treat systems (by adding many more extraction wells) to capture and remediate all contaminated groundwater. Given the high operating costs associated with the phase 1 treatment system and the inefficiencies with plume capture and injected water recapture, it was deemed not desirable to continue with operation of a pump and treat corrective action. A new solution was needed, one preferably less energy intensive. And the key steps toward a passive corrective action were re-characterization of the groundwater contamination and renegotiation of the clean-up goals.

### **Road to a New Remedial Strategy**

At the F Area Seepage Basins the Tan Clay Confining Zone is a convenient marker bed to map using cone penetrometer characterization methods. Over 200 new cone penetrometer locations were pushed to re-characterize the groundwater plumes. Based on the new data it was discovered that a relatively large aerial depression exists in the top of the Tan Clay Confining Zone in the vicinity of the basins, extending down gradient toward Fourmile Branch. The deepest portion of the depression occurs between the basins and Fourmile Branch, with trough-like features connecting the depression to Fourmile Branch. The permeable sand portion of the Upper Aquifer Zone is thicker within the depression and troughs, and interlaminations and beds of silt and clay seem to increase in number in the depression. The increased thickness of the overlying sand indicates that the depression was formed at the time of deposition of the sand.

The new data also indicated that the highest tritium concentrations were located at the base of the Upper Aquifer Zone on top of the Tan Clay Confining Zone. In particular, the highest concentrations were stored within the depression and the troughs. More than twelve years later the concentration of tritium in the depression was similar to that observed throughout the aquifer in the early 1990s, shortly after releases to the basins ceased. The existence of this “hot zone” is probably a result of lower hydraulic conductivity and effective porosity in the relatively thin lenses and stringers of fine-grained materials located immediately above the Tan Clay Confining

Zone. These low permeability strata are serving as a secondary contaminant source which will continue to release contaminants over a long period of time through diffusion.

In the vicinity of the seepage line along Fourmile Branch, the depression in the Tan Clay Confining Zone forms three linear troughs that coincide with local gullies in the surface topography. The troughs crop out at the seepage line and correspond to the locations of tree kill zones and locations where groundwater with high tritium concentrations and low pH discharges to the seepage line. These releases comprise a large fraction of the contamination being released to Fourmile Branch. It is estimated that approximately 80% of the tritium flux at the seepage line is discharged through these troughs. A thickness map of tritium concentrations greater than 2,000 pCi/mL (Figure 5) illustrates the location of the bulk of the contaminant mass and the flow paths discharging to the branch.

This additional characterization work led to a new understanding of the groundwater system, a detailed nature and extent of contamination (updated 10 years after the initial characterization), and a revised phase 2 corrective action goal. A key finding was identifying that the bulk of the tritium was discharging to Fourmile Branch across a small cross-sectional area relative to the entire plume. In other words, only a small area of the plume would have to be managed in order to impart a large reduction in flux to Fourmile Branch. This realization led to a revised phase 2 corrective action goal of a 70% reduction in the activity flux of tritium to Fourmile Branch. The next step was to design and construct a passive barrier system to achieve the new goal.

## **SUBSURFACE BARRIERS**

For phase 2 of the corrective action, the objectives shifted from hydraulic capture of the plume to reducing the contaminant flux to Fourmile Branch and reducing the concentration of other contaminants in the surface water. Tritium is the most pervasive contaminant reaching Fourmile Branch. Other contaminants (including low pH, metals, and radioactive constituents) are commingled with the tritium so that a system designed for tritium remediation also needs to be applicable for the other contaminants.

Based on the revised understanding of the contaminant plumes, a funnel and gate system was designed and constructed across the high concentration troughs to contain the groundwater plume and increase the flow path length to Fourmile Branch. The longer flow path lengths allow for greater radioactive decay (most effective for tritium) and retardation of metal contaminants in the aquifer. The barriers are located down gradient of the majority of the tritium contamination and include gates in the walls where treatment is performed to adjust the pH of the acidic plume. Figure 6 shows the configuration of the funnel-and-gate system and the base injection areas at the F Area Seepage Basins. A conceptual cross section illustrates the installation of barriers across the trough areas (Figure 7).

The key design criteria for the barriers were a nominal thickness of 0.15 meters (6 inches) and a permeability less than  $1 \times 10^{-6}$  cm/sec. The walls were constructed by mixing in-situ native soil with a proprietary blend of an acid-resistant pozzolanic cement and attapulgite clay using a large-diameter auger technique. Attapulgite clay was specifically selected because it resists cation exchange under the high ionic strength of the groundwater plume, is stable in low pH conditions, and has a low diffusion rate. Three counter rotating augers were used to mix 45% by volume grout slurry with the native soils. Over 4,500 cubic meters of grout slurry were used to construct the barriers at F Area Seepage Basins. Figure 8 illustrates the configuration of the equipment used to construct the barrier system.



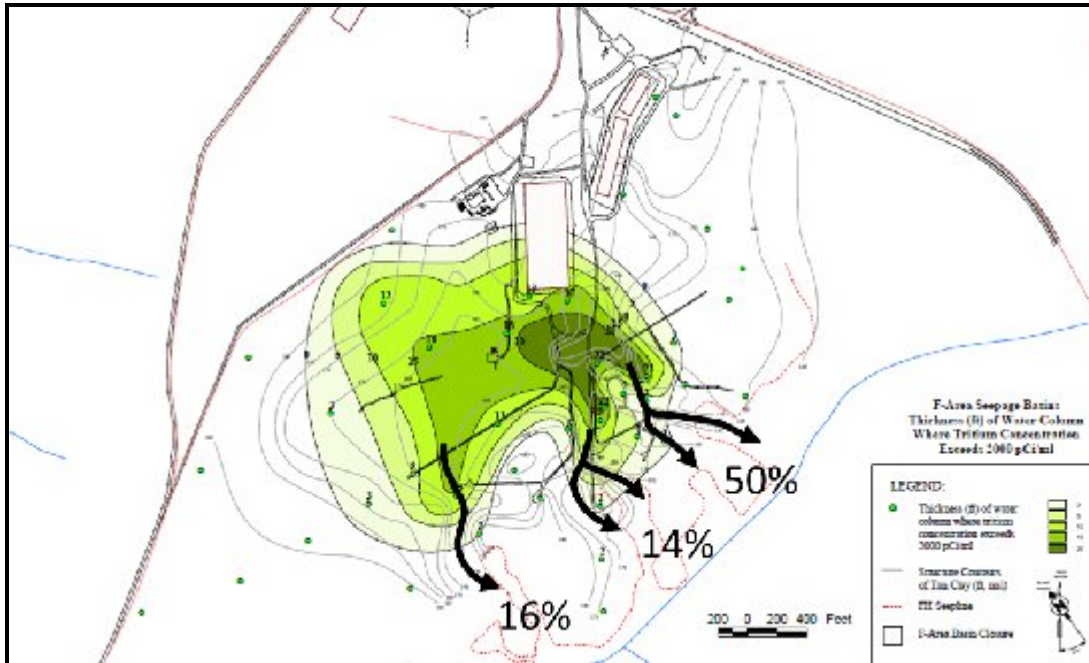


Figure 5. Tritium Hot Spot, Discharge Pathways, and Estimated Tritium Flux to Fourmile Branch.

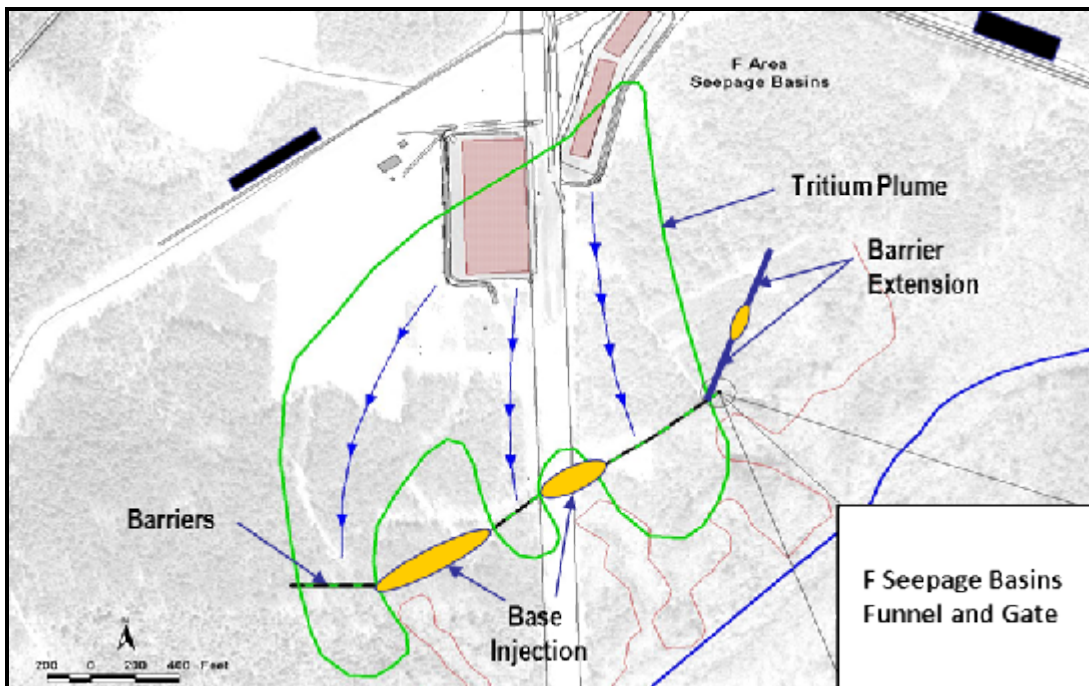


Figure 6. Constructed Groundwater Funnel-and-Gate System with Base Injection at the F Area Seepage Basins.

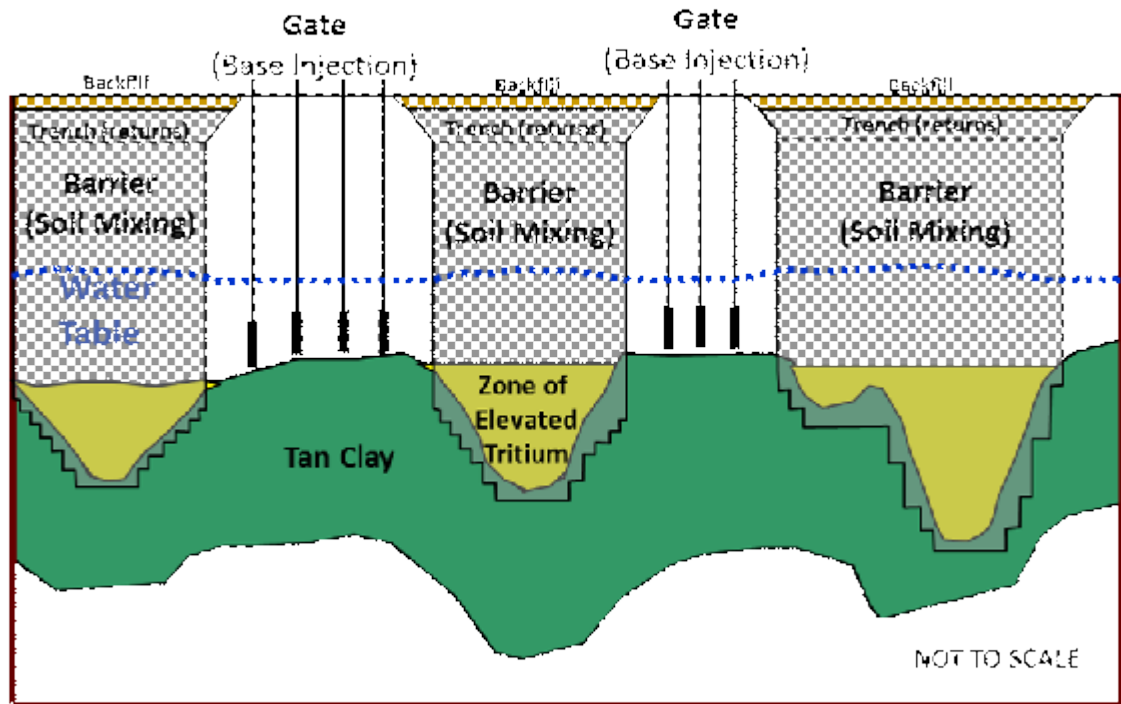


Figure 7. Cross Section Conceptual Model of Barriers Placed Across Contaminant Pathways.



Figure 8. Soil Mixing Equipment Used to Construct the Groundwater Barriers.

Continuity of the wall was achieved by overlapping and re-drilling the previous hole with the outer auger of the three mixing augers. The walls average 0.9 meters in thickness and have an average permeability on the order of  $1 \times 10^{-7}$  cm/s. The walls were installed to a depth of about 20 meters and key into the Tan Clay layer at the bottom of the aquifer. Approximately 730 linear meters of barrier wall were installed in four segments, forming three gates.

Waste management during construction was achieved by excavating a trench in the vadose zone atop the barrier alignment. Soil mixing was performed starting at the base of the trench and any contaminated soil returns (estimated up to 35% the volume of the wall) accumulated inside the trench. The spoils were then covered with clean fill and graded to reduce infiltration. This technique saved considerably on the cost of managing contaminated soils.

The barriers have had a pronounced effect on the groundwater flow as well as on contaminant discharges to Fourmile Branch. After a year following completion of the barriers, the groundwater system had stabilized. Installation of the walls has resulted in a flattening of the water table up gradient and down gradient of the barriers. Due to this flattening, hydraulic gradients have been reduced resulting in lower groundwater velocities and increased travel times. These effects result in reduced transport of contaminants to the surface water and seepage line and increase the time for radioactive decay of tritium.

The funnel-and-gate system has been effective at managing contaminant releases to Fourmile Branch including reducing the activity flux of tritium by over 70 percent. Table I illustrates the measured tritium flux to Fourmile Branch and the reduction achieved since the baseline in year 2000.

**Table I. F Seepage Basins Tritium Flux to Fourmile Branch**

Year*	Tritium Flux (Ci/yr)	Reduction
2000	660	NA
2003	352	47%
2004	352	47%
2005	254	61%
2006	177	73%
2007	173	74%
2008	168	74%
2009	115	82%
2010	240	64%
2011	117	82%

\*Flux was not measured in 2001 and 2002.

## BASE INJECTION

During the 33 years of operation, the F Area seepage basins received over 6 billion liters of acidic wastewater, with an average pH 2.9. The consequence is that the aquifer sediments and groundwater within the contaminant plumes are acidic. Acidity in groundwater has the effect of causing metals to solubilize and desorb from the formation that otherwise might stay in a sorbed state. Desorption is likely occurring, not only in the coarse grained aquifer material, but also within finer grained layers which have the capacity to store significantly greater volumes of contaminants.

The ability of the aquifer to sorb contaminants can be controlled, in part, by pH because it affects the surface charge of aquifer minerals. The strength of cationic sorption to aquifer sediments is generally positively correlated to pH because low pH imparts a stronger positive charge to important sorption surfaces. Thus, increasing pH of the groundwater will tend to decrease the positively charged surfaces and increase the ability of cationic species to sorb to aquifer sediments.

Strontium-90 is an example of a constituent that is sourced from the original waste stream and exists predominantly as a cationic species in groundwater and for which sorption is the dominant interaction with aquifer sediments. Studies at SRS have shown that control of pH influences the rate at which cations like Sr-90 migrate through the aquifer. Thus, artificial adjustment of the plume pH (2.9) back to natural levels (5-6 pH) would reduce aqueous concentrations of most cationic contaminants.

Within the gates of the funnel-and-gate system groundwater pH is adjusted by periodically injecting a dilute base solution. The injection system consists of a domestic water supply, concentrate chemical storage tank, chemical mixing system, distribution piping and 24 injection wells. The concentrate solution consists of sodium bicarbonate (baking soda) mixed with sodium hydroxide. The solution is injected at a rate that, after mixing with the groundwater, the concentration of sodium bicarbonate does not exceed 5% saturation and pH does not exceed 11. Monitoring is performed to assure that groundwater pH down gradient of the treatment zone is maintained at natural levels between 5.0 and 6.0. Base injection is performed as needed to maintain natural pH levels. After an initial treatment dose is completed, groundwater is monitored to determine when more alkaline solution needs to be injected. Continuous injection is not required. The middle gate treats the most acidic part of the plume and requires the most frequent injections, which have occurred once per year on average.

Injection of the alkaline solution establishes treatment zones for uranium and Sr-90 for approximately 30 meters down gradient of the gates. The base neutralizes the acidity of the plume and aquifer mineral surfaces causing sorption of the contaminants and possible precipitation of uranium silicates. For each injection campaign between 5.7 and 13.2 million liters (1.5 to 3.5 million gallons) of alkaline solution are injected per gate. An injection campaign takes about two months to complete. Since 2005, 132 million liters (35 million gallons) have been injected at all three gates. The gate areas comprise about 306 linear meters of the funnel-and-gate system.

Treatment at the gates has been effective at reducing aqueous concentrations of most metal and metallic radionuclide contaminants. Figure 9 shows the reduction in concentration achieved by adjusting the pH at the gates. The contamination reduction factor ( $C_o/C_f$ ) was determined by comparing the initial concentration ( $C_o$ ) with the minimum concentration measured as a result of the base injection ( $C_f$ ). Due to the large volume of alkaline solution, the effect of diluting the contaminants rather than neutralization was a concern. The effect of dilution was determined using tritium because it is a non-reactive contaminant. The effect of dilution corresponded to a contaminant reduction factor of 1.5 and is shown on Figure 9.

Base injection has been effective at treating most metals and radioactive contaminants. Although operation of the base injection system is not entirely a passive corrective action, active operations are needed only a few months out of the year and the time between injections is increasing as the plume pH slowly rises naturally.

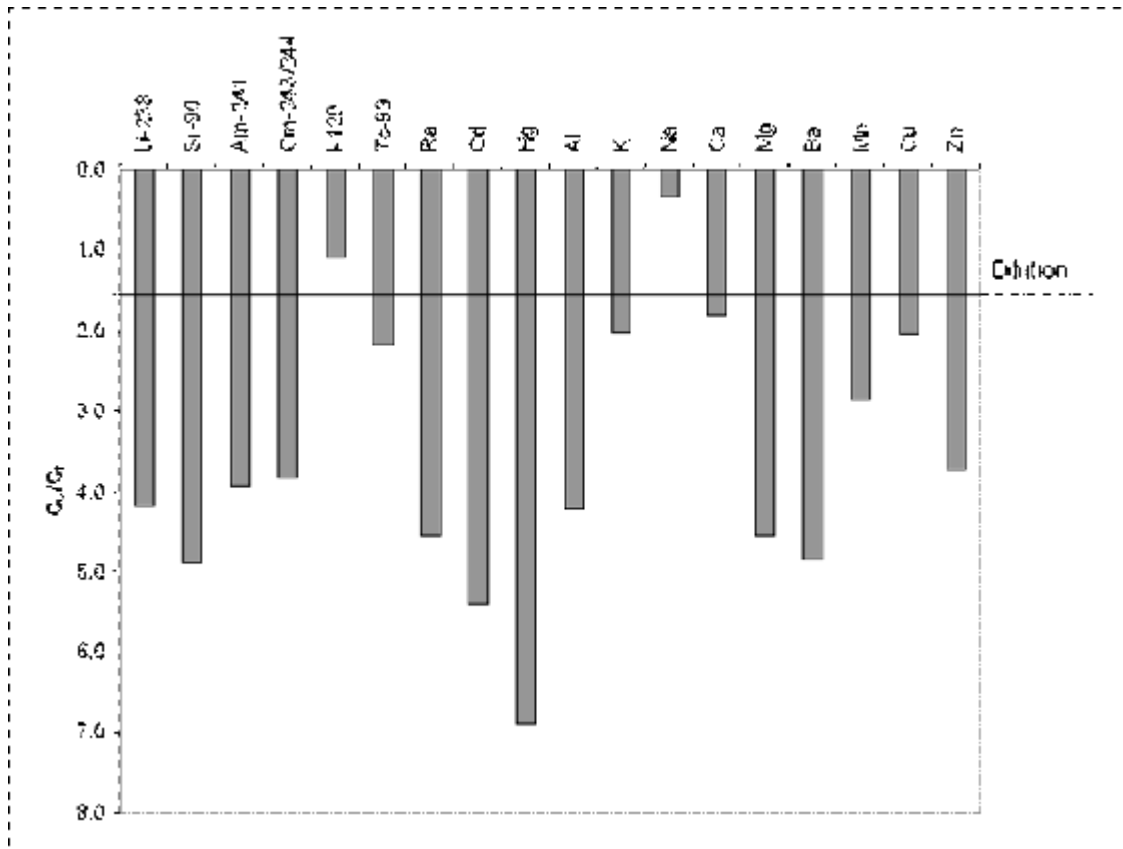


Figure 9. Effectiveness of Base Injection Treatment at the Gates.

## CONCLUSIONS

The corrective actions for the F and H Area Seepage Basins metals and radionuclides plumes have transitioned from active pump and treat systems to passive groundwater barriers with intermittent injection of amendments for pH adjustment. Detailed re-characterization of the plumes led to a revised conceptual model of the contaminant problem and development of new corrective action goals. The key opportunities supporting the transition and the results are summarized below.

- An updated characterization of the groundwater plumes, over 10 years after the seepage basins were closed, identified vertical and lateral contaminant “hot spots” and located subsurface geologic features that control the release of contaminants to surface water in the wetlands and Fourmile Branch.
- Groundwater barriers were constructed across structural lows in the basal clay layer to cut-off the release of contaminant hot spots to Fourmile Branch. Gates between the barriers are located at the structural highs and allow cleaner water at the top of the aquifer to be released to the seeps at the wetlands.
- Treatment for metals and metallic radionuclides passing through the gates is achieved by injecting an alkaline solution into the aquifer. Operation of the injection is as needed and currently occurs once per year. The pH adjustment is effective for many of the plume constituents.



- The new passive corrective actions have been effective at reducing the concentration of contaminants in Fourmile Branch and reducing by 70% the activity flux of tritium to Fourmile Branch. Currently only I-129 is detected in Fourmile Branch above 1 pCi/L and the flux reduction for tritium is nearly 80%.