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Applied Science Investigations to Facilitate Closure of the F-Area and H-Area Seepage Basins

Miles E. Denham, Hansell Gonzalez-Raymat, and Carol A. Eddy-Dilek

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EXECUTIVE SUMMARY

This report provides a roadmap of applied science studies that will facilitate reaching long term monitoring end state corrective actions for groundwater contamination at the F-Area Seepage Basins and the H-Area Seepage Basins at the Savannah River Site in Aiken, SC. The F-Area and H-Area Seepage Basins are waste units on the Savannah River Site in Aiken, SC at which low-level radioactive solutions were disposed into unlined basins, resulting in groundwater contamination. The current contaminants of interest in the groundwater are tritium, iodine-129, strontium-90, uranium isotopes and nitrate. Remediation at both sites has continued since 1988, consisting of closure and capping of the basins, operation of a groundwater pump-and-treat system from 1997 to 2004, and replacement of this system with a comprehensive in situ attenuation-based remedy. This report was requested by the U.S. Department of Energy – Office of Environmental Management in consultation with the Savannah River National Laboratory and Savannah River Nuclear Solutions – Area Completions Projects to provide a scientific basis for proactively addressing groundwater issues that may need to be resolved prior to final corrective actions at the F-Area and H-Area Seepage Basins.

The report is presented in two sections. The first section develops and details the scientific basis for lines of inquiry addressing unresolved technical issues related to the groundwater clean-up. The second section lists the lines of inquiry, their priority and importance, and a general approach to applied science studies to resolve the lines of inquiry. The lines of inquiry by topic area and priority are:

Wetland Geochemistry

- What are the dominant attenuation mechanisms for I-129, Sr-90, and uranium in the wetlands, how strong is attenuation, and what conditions would reverse attenuation? (High Priority)
- What is the cause of profound seasonal variation in I-129 concentrations, and to a lesser extent other contaminants, in wetland surface water? (High priority)
- What is the approximate mass of contaminants sequestered in the wetlands? (Medium Priority)
- What is the microbial involvement in the environmental fate and distribution of iodine in the wetlands? (Medium Priority)

Degradation of Basin Caps

- What processes and parameters associated with the basin caps can be monitored to detect evidence of cap degradation? (Medium Priority)

Low Permeability Zones

- Are there significant low permeability strata within the Upper Aquifer Zone (UAZ) that affect remediation and/or progress toward remedial goals? (Medium Priority)
- Are there wells screened in lower permeability zones in which apparent progress toward remedial goals is slower than in other wells and, if so, how is overall progress toward remedial goals assessed? (Medium Priority)

Vertical Movement of Contaminants

- Does differential migration of contaminants into the Lower Aquifer Zone (LAZ) have a significant influence on progress toward remedial goals? (High Priority)

- Is there significant flow of groundwater through the Tan Clay Confining Zone (TCCZ) and into the LAZ along the subsurface barrier, particularly at the troughs on top of the TCCZ? (Medium Priority)
- Where does upward flow of groundwater from the LAZ into the UAZ occur? (Medium Priority)

- Where groundwater is upwelling from the LAZ, what fraction of each contaminant in wetland surface water and Fourmile Branch is from the LAZ, how will that change with time, and will contamination from the LAZ affect progress toward remedial goals? (Low Priority)

Groundwater Flow Beneath Wetlands

- What are the patterns of groundwater flow and contaminant migration, both horizontal and vertical, beneath the wetlands and do they affect interpretation of monitoring data? (High Priority)
- How would groundwater flow and contaminant migration in the wetlands affect consideration of remedial actions in the wetlands? (Medium Priority)

Groundwater Flow Near Gates

- What are groundwater flow patterns near the gates and how do they affect monitoring and remedial actions? (High Priority)
- Are variations in concentrations of tritium, nitrate, and I-129 near the middle gate related to elevation of the water table and, if so, why? (Medium Priority)

Relative Stratification of Contaminants

- Is there vertical segregation of contaminants and is it significant enough to map? (High Priority)
- If there is significant vertical segregation of contaminants, is it solely the result of pH or do low permeability zones play a role (e.g., low permeability zones remaining acidic allowing higher concentrations of uranium and Sr-90 in groundwater)? (Low Priority)

Base Injection Optimization

- How long will it take for the pH of groundwater upgradient of the gates to reach a pH that is protective of Sr-90 and uranium attenuated in the elevated pH zone downgradient of the gates? (High Priority)
- How does the protective pH vary with time? (Medium Priority)
- What are the current pH and alkalinity needs for a base solution? (High Priority)
- Is there a base solution that would meet the requirements and not risk remobilizing uranium or Sr-90? (Medium Priority)
- Is continuation of base injection in the wetlands necessary and, if so, have base requirements changed? (High Priority)

Treatment of I-129 Optimization

- What is the speciation of I-129 currently passing through the gates? (High Priority)
- Were the high concentrations of I-129 in the gates in 2011 anomalous or will they likely reoccur? (Medium Priority)
- Is I-129 primarily confined to a limited vertical zone in the gates? (High Priority)

- What is the effect of treating I-129 in the gates on I-129 concentrations in surface water of the wetlands and Fourmile Branch? (Medium Priority)

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ACL	Alternate Concentration Limits
ACP	Area Completion Projects
CAP	Corrective Action Plan
CAR	Corrective Action Report
CPT	Cone Penetrometer Test
DOE	Department of Energy
EM	Environmental Management
ERT	Electrical Resistance Tomography
GWPS	Groundwater Protection Standard
LAZ	Lower Aquifer Zone
LBNL	Lawrence Berkeley National Laboratory
LIDAR	Light Detection and Ranging
LTM	Long-Term Monitoring
MCL	Maximum Contaminant Level
MSL	Mean Sea Level
ORWBG	Old Radioactive Waste Burial Grounds
RCRA	Resource Conservation and Recovery Act
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
TCCZ	Tan Clay Confining Zone
TZ	Transmissive Zone
UAV	Unmanned Aerial Vehicles
UAZ	Upper Aquifer Zone
UTRA	Upper Three Runs Aquifer
WSRC	Westinghouse Savannah River Company

1.0 Introduction

The purpose of this document is to identify gaps in scientific/technical knowledge that, when filled, will facilitate closure of the F-Area and H-Area Hazardous Waste Management Facilities Groundwater Units and provide a roadmap of investigations to fill these gaps. The desired end-state that would allow closure is an attenuation-based final corrective action with long-term monitoring. The waste units are referred to hereafter by the common names F-Area and H-Area Seepage Basins. The Savannah River Site (SRS) has been proactive in deploying innovative strategies to remediate contaminated groundwater. Fundamental to this proactive approach is the recognition that the enemy of innovation in remediation is the attempt to eliminate all uncertainty prior to deployment of new technologies and strategies. As remediation of sites proceeds, study of the site continues, and the conceptual model evolves. Choosing strategies that are flexible enough to accommodate the evolving conceptual model has led to the successes that SRS has achieved with this approach.

In situ attenuation-based strategies have successfully replaced pump-and-treat systems at the F-Area and H-Area Seepage Basins while concurrent field and laboratory studies, as well as continual analysis of monitoring data improves the conceptual model. As closure of the sites is considered, it becomes important to review the status of the conceptual model to identify enhancements that will facilitate the closure. This document is considered by the author, with 20 years of experience working at the F-Area and H-Area Seepage Basins, to be the starting point for this endeavor.

The challenge to closing a complex metal and radionuclide contaminated site is presenting a technically sound case to regulators and stakeholders that demonstrates that remedial goals have been or will be irreversibly achieved or that there is an alternate acceptable end-state. This requires five lines of evidence:

- A conceptual site model that is as complete as possible, with the knowledge that it may continue to evolve with time
- Demonstration that trends in contaminant concentrations, or flux, versus time indicate that remedial goals will be achieved on schedule or within a reasonable time thereafter and that trends that deviate from this path are explainable by the conceptual model
- Demonstration that remobilization of attenuated contaminants is unlikely to be reversed in the future
- Consideration of remedial contingencies, should deviations in the path toward remedial goals occur
- Development of a long-term monitoring plan to detect any conditions that might alter the path toward remedial goals

This document focuses primarily on conceptual model enhancements and remedial contingencies. Previous documents have analyzed monitoring data trends and projected times required for maximum contaminant levels (MCLs) to be achieved for primary contaminants (Denham and Amidon, 2016; Nichols and Dickson, 2019). This document does include additional trend analysis for a lower aquifer zone. Likewise, a previous document has explored a new strategy for long-term monitoring (Denham et al., 2019) at the sites that is currently under consideration by SRS. Some possible studies for improving this new strategy are also included in this document.

The document consists of two main sections. The first is a review of the conceptual model in which lines of inquiry for studies that will facilitate site closure are developed. The second is a concise discussion of those lines of inquiry and possible ways to pursue them.

2.0 Section 1: Sites Descriptions and Conceptual Site Model

2.1 Background

The description, history, and conceptual model of the contamination plume associated with the F-Area Seepage Basins has been written about extensively. There are numerous regulatory documents (e.g., permit, CARs, CAP), several published papers that discuss specific aspects of the conceptual model in detail (Killian et al., 1987a; Killian et al., 1987b; Denham and Vangelas, 2009; Xu et al., 2011; Kaplan et al., 2011; Wan et. al, 2012; Tokunaga et al., 2012), and several technical reports documenting aspects of the conceptual model that pertain specifically to plume remediation (base injection, AgCl, trends, long-term monitoring (LTM)). The brief summary here is taken primarily from Denham et al. (2019) and Denham and Amidon (2016).

2.1.1 F-Area Seepage Basins

The F-Area Seepage Basins consisted of three unlined ponds into which low level radioactive liquid waste was disposed. Disposal began in 1955 and ended in 1988, with approximately 7 billion liters disposed during this time. The waste was acidic with sodium and nitrate as the dominant constituents and contained various radionuclides associated with plutonium processing. Mobile radionuclides migrated through the vadose zone (approximately 20 meters thick), contaminating the groundwater in the saturated zone at concentrations of environmental concern. Currently the contaminants of primary concern are tritium, iodine-129, strontium-90, and uranium isotopes. The resulting contamination plume has an aerial extent of approximately 1 square kilometer and discharges into wetlands and a local stream called Fourmile Branch. The map in Figure 1 shows the location of the three basins relative to the wetlands and Fourmile Branch, with an arrow showing the general direction of groundwater flow.

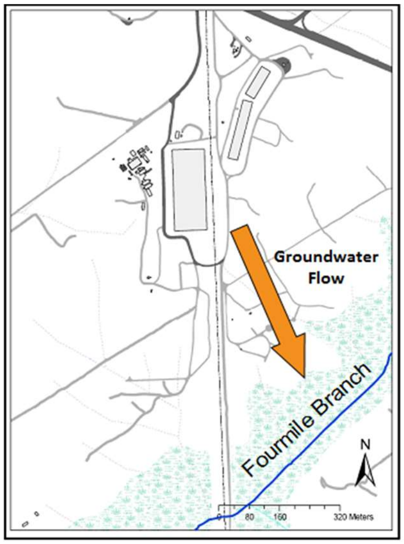

Figure 1: Map of F-Area Seepage Basins, wetlands (green patterned area), and Fourmile Branch.

2.1.1.1 Spatial Framework

The F-Area Seepage Basins are located on a topographic high at an elevation of approximately 85m MSL. The topography slopes down toward Fourmile Branch at an elevation of approximately 56 m and a distance of approximately 600 meters from the south edge of Basin 3. The seepline, a line of springs along the intersection of the water table with topography, approaches much closer to the basins as it follows small gullies eroded into the slope. The seepline comes within 400 meters of the south edge of Basin 3. The vadose zone is 22 m thick at Basin 3.

2.1.1.2 Temporal Framework

The history of the F-Area Seepage Basins is depicted in Figure 2. Disposal of waste into the basins began in 1955 and ended in 1988. Closure and installation of a low permeability cap over the basins was completed in 1991. Unlined drainage ditches surround the capped basins to collect and divert runoff from the cap to an outfall. The cap minimized infiltration through the source, allowing concentrations of radionuclides to begin decreasing in the vadose zone and ultimately in the saturated zone. The rate of drainage of the vadose zone decreased significantly between 6 and 8 years after closure of the basins, as drainage neared completion (Tokunaga et al., 2012). This approximately coincides with the start-up in 1997 of a pump-and-treat system that extracted groundwater from downgradient, removed contaminants other than tritium, and re-injected the treated water containing tritium upgradient of the basins. The pump-and-treat system was replaced in 2004 with the current remediation, a funnel-and-gate with periodic base injection in the gates and beneath the wetlands. Originally, there were two gates formed by three sections of subsurface barrier. An additional gate was added in 2011 by extending the subsurface barrier toward the northeast in two sections.

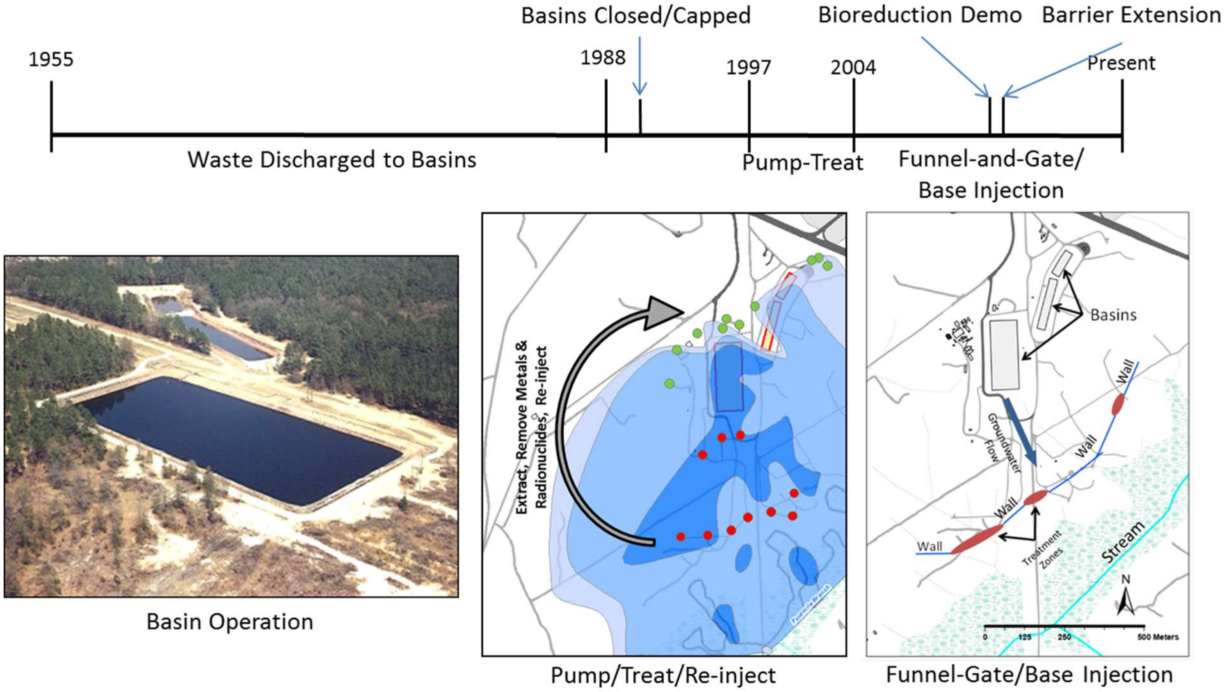

Figure 2: Timeline of major events in the history of the F-Area Seepage Basins.

The funnel-and-gate consists of a subsurface barrier that extends from near ground surface to the Tan Clay. The subsurface barrier was placed across "troughs" in the top of the Tan Clay that were preferential flow paths for contaminant migration to the wetlands and Fourmile Branch. Gaps in the subsurface barrier were left across the topographic highs of the Tan Clay and groundwater is forced by the barriers through these gaps, or gates, where in situ treatment of contamination occurs. The treatment zones have an elevated pH compared to the contaminated groundwater, causing uranium and Sr-90 to adsorb to mineral surfaces within these zones. The treatment zones are created by periodic injection of alkaline (base) fluids. Just upgradient of the base injection zones at the center gate, I-129 is treated by injection of silver chloride particles. The particles react with natural iodide and I-129 that exists as iodide to form sparingly soluble silver iodide, removing I-129 from the groundwater.

Remediation of the F-Area Seepage Basins groundwater also relies on natural attenuation of contaminants in the organic-rich soils of the wetlands associated with Fourmile Branch. Uranium and iodine, both natural I-127 and the contaminant I-129, are known to bind strongly to natural organic matter. This has been proven for I-129 in the Fourmile Branch Wetlands (Xu et al., 2011). Sr-90 is more likely bound to the relatively abundant clay-size particles in wetland soils. Wetland soils are the last opportunity for attenuation of contaminants before groundwater passes into the surface water of the wetlands and Fourmile Branch.

2.1.1.3 Hydrogeological Framework

The site is underlain by unconsolidated to consolidated, primarily Eocene, sands and clays. The lithostratigraphic and hydrostratigraphic columns are shown in Figure 3, with the yellow shaded portions indicating the section of interest. The most widespread and concentrated groundwater contamination occurs in the unconfined Upper Aquifer Zone (UAZ) of the Upper Three Runs Aquifer (UTRA). There is a downward groundwater gradient through the Tan Clay Confining Zone (TCCZ) that drove some contamination into the Lower Aquifer Zone (LAZ) of the UTRA. The TCCZ has leaky zones, and it is discontinuous across the area. There is also a smaller mass of contamination that passed through the Gordon Confining Unit into the Gordon Aquifer. Horizontal groundwater flow in the UAZ and the LAZ is toward Fourmile Branch, whereas groundwater flow in the Gordon Aquifer is northward toward Upper Three Runs, the stream into which it discharges (Figure 4).

The contamination plume occupies only a portion of the vertical extent of the UAZ – approximately 3 meters of a total saturated thickness of 10 meters. During the period of active basin use, the plume was likely more extensive vertically within the UAZ than it is now. Recharge downgradient of the basins and a downward hydraulic gradient caused the contamination to migrate downward as it moved horizontally. As a result, over much of the area between the basins and Fourmile Branch the plume moves along the top of the TCCZ.

Extensive probing of the lithology by direct push technologies, together with geophysical logs obtained from several wells allowed delineation of the top of the TCCZ. This revealed troughs in the top of the TCCZ that act as preferential contaminant flow paths both horizontally in the UAZ and vertically allowing contamination to pass into the LAZ. The vertical transport through the troughs is indicated by contaminant distribution in the UAZ shown in early plume maps (e.g., Fenimore and Horton, 1978) and current maps of the distribution of Sr-90 and gross alpha in the LAZ.

Overall, movement of groundwater in the LAZ is slower than in the UAZ. Savannah River Nuclear Solutions (SRNS) (2018) estimates the average linear velocity of groundwater to be approximately 30 ft/yr. in the LAZ and 1529 ft/yr. in the UAZ. Therefore, nonreactive contaminants are expected to be flushing from the UAZ faster than the LAZ since drainage from the vadose zone into the UAZ reached a minimum level. Tokunaga et al. (2012) estimated that almost all the drainable pore water in the vadose zone beneath Basin 3, following its closure, had moved into the saturated zone of the UAZ by 2006.

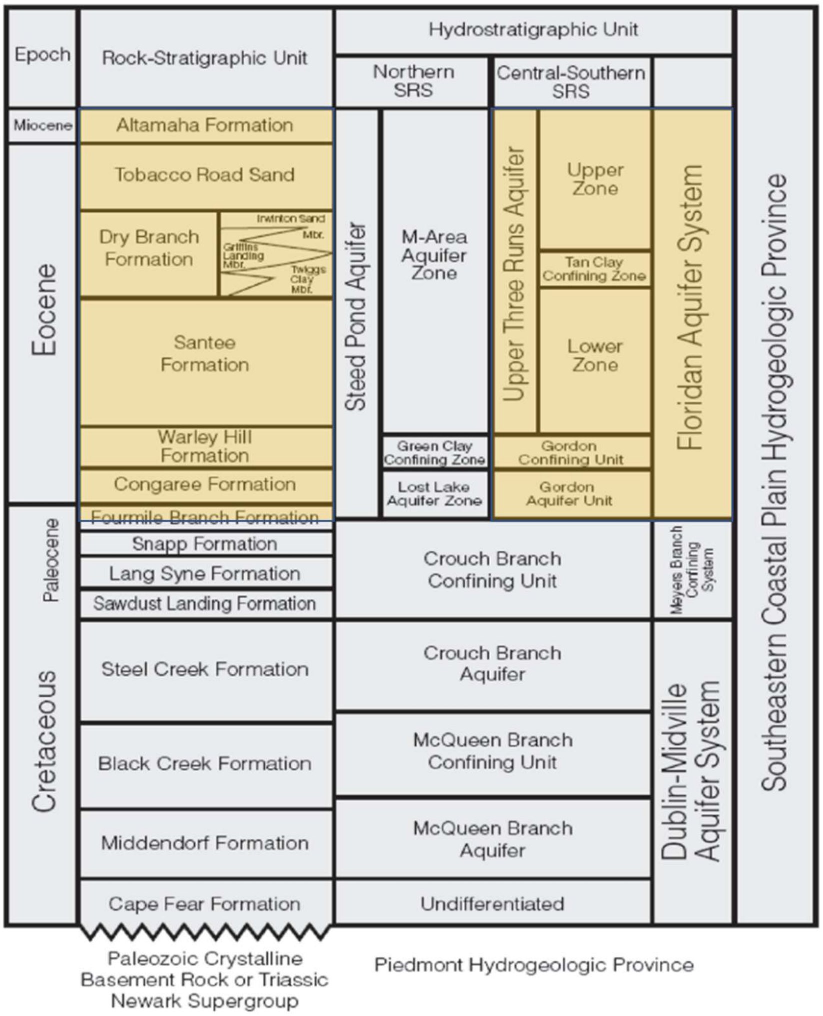

Figure 3: Lithostratigraphic and hydrostratigraphic columns with the interval of interest highlighted in yellow.

The latest contaminant distribution maps and cross-sections for the 3 pertinent aquifers are available in SRNS (2018) and estimates, by aquifer, of the total activity in groundwater of many radionuclides of concern are listed in Hiergesell and Kubilius (2016).

The Gordon Aquifer is less critical to closure of the site than the Upper Three Runs Aquifer. It does not drain into Fourmile Branch and does not affect surface water in the wetlands associated with Fourmile Branch (Figure 4). The long flow path to Upper Three Runs allows additional time for tritium to decay and provides a far greater mass of aquifer solids for other contaminants to interact with and be attenuated.

Additionally, concentrations and total mass of contaminants in the Gordon Aquifer are substantially lower than in the Upper Three Runs Aquifer. Contaminants will continue to pass from the LAZ into the Gordon Aquifer, but the rate will remain slow unless some remedial action or some other event significantly disrupts the aquifer system. For these reasons the Gordon Aquifer is not discussed any further in this document.

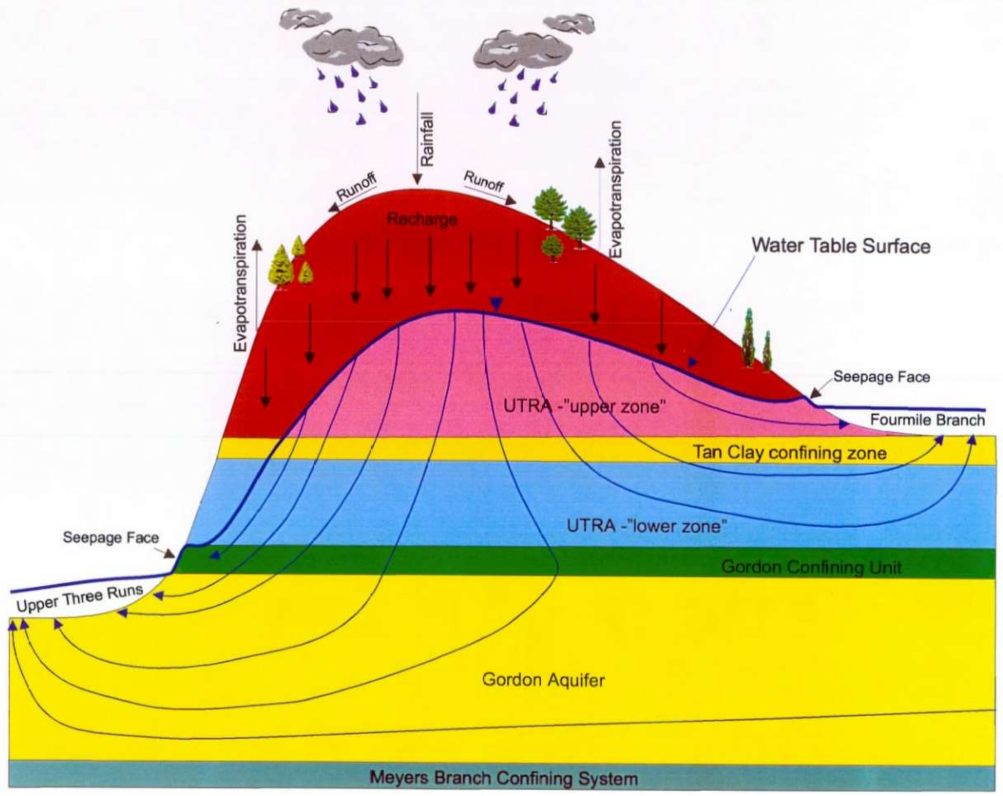

Figure 4: Conceptual model of groundwater flow below the F-Area basin.

2.1.1.4 Geochemical Framework

Natural attenuation of contaminants depends on four factors: the nature of the contaminant, the mineralogy and organic content of the sediments through which the contaminants are migrating, the chemistry of the plume, and the rate of groundwater flow. The mineralogy of the UAZ is well known. With the exception of some possible low permeability zones, the UAZ primarily consists of >95 wt.% quartz with minor kaolinite and goethite. The organic content is very low. The near-surface sediments of the wetlands have higher clay and organic contents. The mineralogy of the LAZ is less well documented but is likely similar to that of the UAZ, but with higher clay content. The chemistry of the plume is dominated by acidic conditions with current pH values as low as 3.2. The groundwater of the UAZ and LAZ is oxidizing, becoming more reducing as it encounters organic-rich sediments associated with the wetlands. Hence, attenuation of contaminants in the aquifers is dominated by their interaction with kaolinite and goethite in pH conditions that vary from acidic to basic (base injection treatment zones). Water pH is also a factor controlling attenuation in the wetlands and interaction with organic matter plays a major role.

Adsorption is the main attenuation mechanism for uranium, Sr-90, and I-129 in the vadose zone and the saturated zone upgradient of the wetlands. In the acidic conditions of untreated portions of the plume, adsorption of uranium and Sr-90 is minimal, whereas adsorption of I-129 is maximal. Figure 5 shows qualitative mobility of uranium, Sr-90 and I-129 versus pH in soils based on a composite of studies (e.g., uranium - Hsi and Langmuir, 1985; Waite et al., 1994; Barnett et al., 2002; Dong et al., 2012; Wan et al., 2011; strontium - Chen and Hayes, 1999; Small et al., 1999; Wallace et al., 2012; iodine – Yoshida et al., 1992; Fukui, 1996; Um et al., 2004; Emerson et al., 2014). In the wetlands, uranium and I-129 may be bound to organic matter and localized precipitation of uranium is possible if uranium (VI) is chemically reduced to uranium (IV).

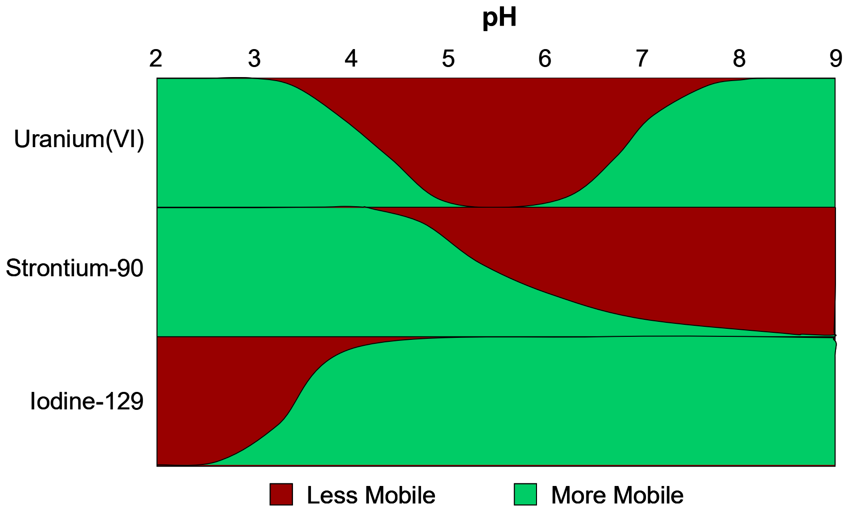

Figure 5: Qualitative depiction of the effect of pH on mobility of uranium (VI), Sr-90, and I-129 under oxidizing conditions; based on references listed in text.

2.1.1.5 Remedial Goals

The Resource Conservation and Recovery Act (RCRA) Part B Permit for the F-Area Hazardous Waste Management Facility groundwater (F-Area Seepage Basins groundwater) lists the following remedial goals.

This program shall consist of the following objectives:

Phase 1) Implementation of groundwater extraction and injection system to capture and remediate those portions of the contaminant plume delineated by the 10,000 pCi/ml tritium isoconcentration contour. Details of the groundwater extraction and injection system are contained in Section E.8.3.3 of the approved permit application. This initial phase will prevent these portions of the plumes from further migration and discharge into Fourmile Branch. The groundwater extraction and injection system are no longer operating as it is no longer mandated by regulatory requirements to operate. Phase 1 will also provide additional field data which will be used to evaluate the effectiveness of this strategy and aid in designing additional phases, as appropriate.

Phase 2) Evaluate the performance of Phase 1 including groundwater capture zones; contaminant concentrations downgradient of the Phase 1 system, downgradient of the F-Area inactive process sewer line, and at Fourmile Branch (using seepline and surface water data); treatment system effectiveness; and fate of injected water.

Provide a Phase 2A corrective action plan that will:

- 2A-1) before October 31, 2012 reduce the mass flux (Curies/year) of tritium discharging from the F-Area plume to Fourmile Branch by 70%
- 2A-2) before October 31, 2017 reduce the concentration of the remaining Appendix IVB-A constituents in Fourmile Branch (except tritium and I-129) to levels that are less than the groundwater protection standard (GWPS) as measured at Surface Water Sampling Stations FMC-002F and FMA-7U
- 2A-3) before October 31, 2025 reduce the concentration of I-129 in Fourmile Branch to levels that are less than the GWPS
- 2A-4) develop and test practicable technologies to be employed for the 2B goals (except tritium)

Provide a Phase 2B corrective action plan that will:

- 2B-1) before July 31, 2020 reduce the discharge from the F-Area plume of all Appendix IVB-A constituents in the surface water at the seepline to concentrations that are less than the GWPS (except tritium and I-129)
- 2B-2) before October 31, 2030 reduce the discharge from the F-Area plume of I-129 in the surface water at the seepline to a concentration less than the GWPS and as measured at Wetland Seepline Surface Water Sampling Locations FAS-91, FAS-92, FAS-93, FAS-96, and FAS-103 (Table E.8-6 in the approved Permit Application)
- 2B-3) consider the technical and economic feasibility of performing these remedial actions successfully

Phase 3) Three months after meeting the Phase 2 objectives or by July 31, 2020, whichever comes first, evaluate the performance of Phase 2 and submit a Phase 3 corrective action plan that, upon approval, will capture and remediate the entire contaminant plume IVB-6 of 24 above those concentrations listed in the GWPS and/or evaluate the applicability of Alternate Concentration Limits (ACL) and/or a Mixing Zone. If an ACL and/or Mixing Zone is proposed and it is determined that an ACL and/or Mixing Zone is inappropriate, then within three months, submit a Phase 3 corrective action plan that, upon approval, will capture and remediate the entire contaminant plume above those concentrations listed in the GWPS.

Evaluate the performance of the overall corrective action system and implement any modifications to the system deemed necessary to improve its effectiveness. Phase 3 will consider technical and economic feasibility of performing a successful remedial action. The schedule for implementation of the corrective action plan is included as Appendix IVB-C of this permit.

2.1.2 H-Area Seepage Basins

The H-Area Seepage Basins consisted of four unlined excavations that received low-level radioactive liquid waste from processes in H Canyon (Figure 6). Approximately 6 billion liters of liquid waste were disposed in the four basins between 1955 and 1988, however Basin 3 did not receive any after 1962. The aqueous waste was acidic with an average pH of 2.4. The radionuclides disposed were similar to those disposed in the F-Area Seepage Basins, with lower total activities of ^{129}I, ^{99}Tc, and uranium and higher activities of Sr-90 disposed in the H-Area Seepage Basins (Killian et al., 1987a; Killian et al., 1987b). The primary radioactive contaminants currently of concern are tritium and Sr-90. Tritium released to groundwater through the H-Area Seepage Basins is co-mingled with tritium from the Old Radioactive Waste Burial Grounds (ORWBG).

The hydrogeological and geochemical frameworks for the H-Area Seepage Basins are essentially the same as for the F-Area Seepage Basins. Hence, only the spatial and temporal frameworks are discussed here.

2.1.2.1 Spatial Framework

The H-Area Seepage Basins are located near the eastern corner of the Old Radioactive Waste Burial Ground (ORWBG), between the ORWBG and Fourmile Branch (Figure 6). A key aspect of the spatial framework of the H-Area Seepage Basins are their proximity to wetlands associated with Fourmile Branch and a drainage ditch due east of the basins. The seepline is highly irregular and, at its nearest point, is approximately 130 meters from Basins 4. A north-south flowing tributary to Fourmile Branch is approximately 130 meters from the eastern edge of Basin 3 and Fourmile Branch is730 meters from the southwestern corner of Basin 4. Vadose thickness beneath the basins varies from approximately 7 to 12 meters. The estimated linear velocity of groundwater in the vicinity of the H-Area Seepage Basins is 314 m/yr., slower than groundwater at the F-Area Seepage Basins (466 m/yr.). Nevertheless, the shorter travel distances in the vadose zone and to surface water at the H-Area Seepage Basins means shorter travel times for nonreactive contaminants from the bottoms of the basins to exposure in surface water.

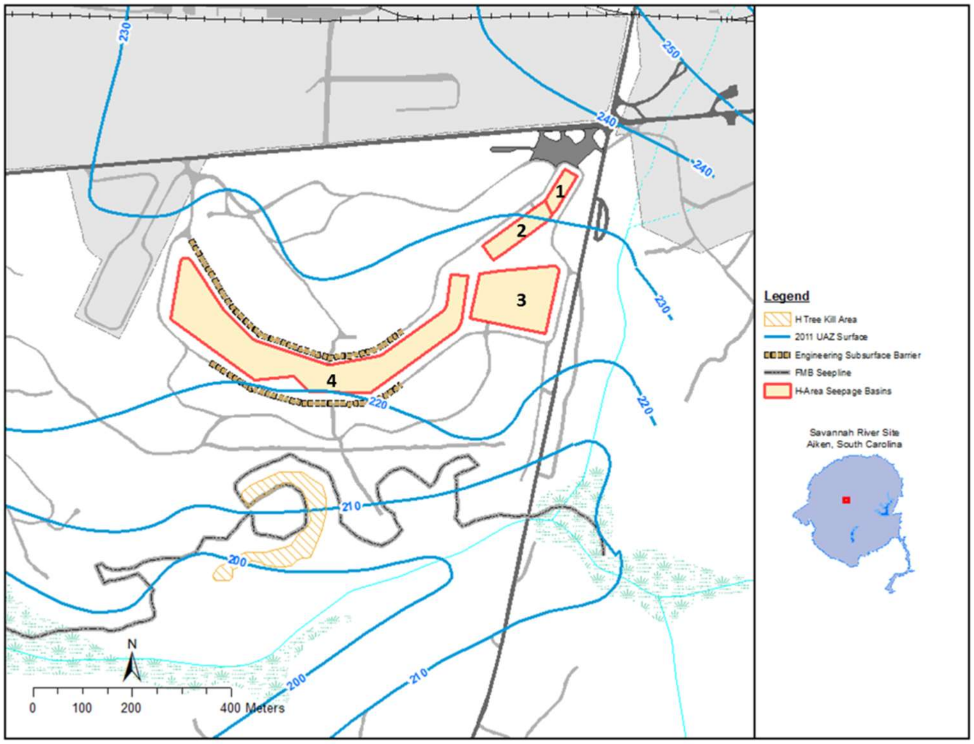

Figure 6: Map of the location of the H-Area Seepage Basins and the potentiometric surface of the water table as of 2011.

2.1.2.2 Temporal Framework

Remediation efforts and their timeline at the H-Area Seepage Basins are similar to those at the F-Area Seepage Basins. The basins were closed and capped between 1989 and 1991. A pump-and-treat system was installed in 1997 and operated until 2004. Subsurface barriers were emplaced at the upgradient and downgradient edges of Basin 4 to limit groundwater exposure to contaminants from Basin 4. These are continuous low permeability barriers, rather than a funnel-and-gate system. Periodic injection of alkaline solutions within the contaminant plume began in 2010, but only beneath the wetlands.

2.2 Considerations for Enhancing the Conceptual Model

2.2.1 Concentration Versus Time Trends: Update

Two recent documents (Denham and Amidon, 2016; Nichols and Dickson, 2019) presented concentration versus time trends to help assess the progress toward achieving regulatory goals at the F-Area and H-Area Seepage Basins. These documents presented and interpreted data from monitoring locations at the UAZ, the wetlands, and Fourmile Branch. Trends in the UAZ are not discussed in this document except for specific data that relates to the discussion of the conceptual model presented in this document.

Concentration versus time trends for monitoring wells screened in the LAZ are presented and where appropriate environmental, or effective, half-lives are reported to help assess progress toward remedial goals. The trends for all the wells analyzed appear in Appendix 1 and representative trends are presented in the main document body.

2.2.1.1 Concentration Versus Time Trends for Contaminants in the LAZ

Denham and Amidon (2016) discussed how concentration versus time trends in the UAZ evolve over time depending on the stage of evolution of the contamination plume. The summary of this discussion is that, in general, the concentration versus time trends for contaminants follow first-order decay and the decay constant changes as the plume evolves through 4 stages. The four stages are:

1. Steady-state influx of contamination from the vadose zone during basin operation
2. After capping and closure of the basins a decreasing trend in concentrations develops as the vadose zone drains
3. Once vadose zone drainage is complete, flushing of contaminants by the influx of “clean” groundwater creates a different trend
4. Once primary flushing of contaminants is complete, a new trend begins as desorption of contaminants from mineral surfaces and diffusion from low permeability zones occurs

Figure 7 shows an idealized depiction of how the concentrations versus time trends change over time. There are many influences that can complicate the real concentration versus time trends. The trends for reactive contaminants can be altered by changes in the geochemical nature of the plume, such as changes in pH. Variations in the elevation of the water table can affect the trends for all contaminants, as can remedial actions.

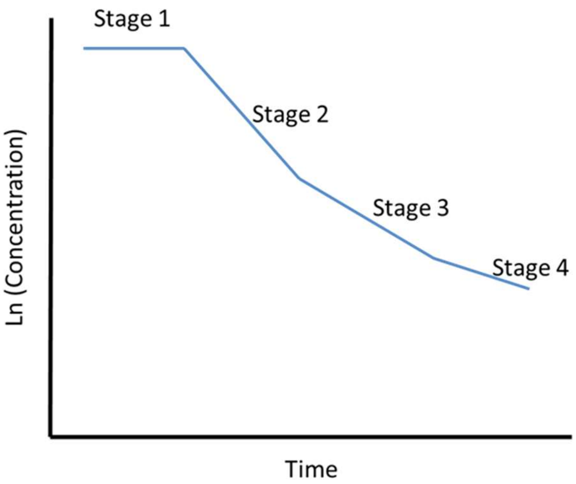

Figure 7: Idealized evolution of a concentration vs. time trend according to the conceptual model presented in Denham and Amidon (2016).

A similar conceptual model applies to the LAZ, but in the first stage the drainage is from the UAZ through the TCCZ into the LAZ. In both the UAZ and the LAZ horizontal and vertical pH gradients from the influx of acidic contamination influences the migration of reactive contaminants. These gradients had passed through the UAZ prior to any extensive and systematic monitoring of groundwater, but the effects of the pH gradients on concentrations versus time trends are observed in the LAZ. As expected, the evolution of the plume in the LAZ lags that of the UAZ. Figure 8 shows the trends for tritium at wells FSB-94DR (UAZ) and FSB-94C (LAZ). Stage 1 appears to last approximately 9 years longer in the LAZ well. The lag time varies among wells, likely because of position in the plume, thickness of the saturated zone of the UAZ, and/or effectiveness of the TCCZ as an aquitard. The other difference between the UAZ and the LAZ, apart from hydraulic characteristics, is that contamination can pass from the UAZ into the LAZ over most of the course of the plume. Influx of contamination into the UAZ is confined to the area beneath the basins and potentially in portions of the wetlands. This means the trends in the LAZ from wells downgradient of the basins are complicated by the influx of groundwater from the UAZ, be it more or less contaminated.

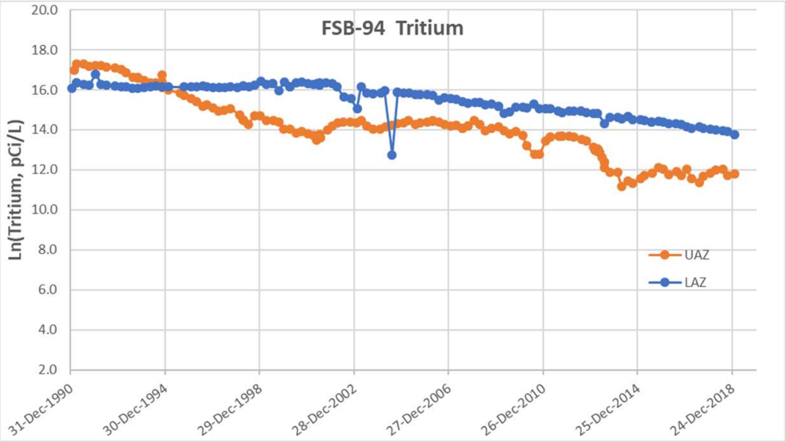

Figure 8: Concentration vs. time trend for tritium at wells FSB-94DR (UAZ) and FSB-94C (LAZ).

Table 1 lists the environmental, or effective, decay constants, the resulting environmental half-lives, and the radiological half-lives for tritium, I-129, Sr-90, and U-238 for several wells screened in the LAZ for the F-Area Seepage Basins (Figure 9). No information for wells in H-Area is listed because the tritium plume from the Seepage Basins is comingled with tritium plumes emanating from the Old Radioactive Waste Burial Grounds (Mixed Waste Management Facility). Also, the concentrations of I-129, Sr-90 and U-238 are at or below their respective MCLs in the LAZ at the H-Area Seepage Basins and, therefore, no information is included about these radionuclides.

Table 1: Decay constants (λ), environmental half-lives (Env $t_{1/2}$), and radiological half-lives (Rad $t_{1/2}$) for tritium, I-129, Sr-90, and U-238 at selected wells screened in the LAZ at the F-Area Seepage Basins site.

	Tritium			Iodine-129		
Well ID	**λ (1/day)**	**Env $t_{1/2}$ (yr)**	**Rad $t_{1/2}$**	**λ (1/day)**	**Env $t_{1/2}$ (yr)**	**Rad $t_{1/2}$ (yr)**
FSB-78C	-3.07E-04	6.2	12.3	-1.40E-04	13.6	1.60E+07
FSB-79C	-6.45E-04	2.9	12.3	NA2	-	1.60E+07
FSB-88C	-3.57E-04	5.3	12.3	NA2	-	1.60E+07
FSB-93C	-2.01E-04	9.4	12.3	-1.31E-04	14.5	1.60E+07
FSB-94C	-3.20E-04	5.9	12.3	-1.46E-04	13.0	1.60E+07
FSB-97C	-2.44E-04	7.8	12.3	-1.75E-04	10.9	1.60E+07
FSB-98C	-2.76E-04	6.9	12.3	NA2	-	1.60E+07
FSB-102C	-2.56E-04	7.4	12.3	NA2	-	1.60E+07
FSB-104C	-1.36E-04	14.0	12.3	NA2	-	1.60E+07
FSB-112C	-2.77E-04	6.9	12.3	-1.58E-04	12.0	1.60E+07

	Strontium-90			Uranium-238		
Well ID	**λ (1/day)**	**Env $t_{1/2}$ (yr)**	**Rad $t_{1/2}$ (yr)**	**λ (1/day)**	**Env $t_{1/2}$ (yr)**	**Rad $t_{1/2}$ (yr)**
FSB-78C	-2.13E-04	8.9	28.7	-9.50E-05	20.0	4.50E+09
FSB-79C	-8.96E-04	2.1	28.7	-5.62E-04	3.4	4.50E+09
FSB-88C	NA1	-	28.7	NA1	-	4.50E+09
FSB-93C	NA2	-	28.7	NA1	-	4.50E+09
FSB-94C	-2.11E-04	9.0	28.7	-2.36E-04	8.0	4.50E+09
FSB-97C	-2.68E-04	7.1	28.7	-2.02E-04	9.4	4.50E+09
FSB-98C	NA2	-	28.7	-1.80E-04	10.6	4.50E+09
FSB-102C	-2.54E-04	7.5	28.7	NA1	-	4.50E+09
FSB-104C	NA1	-	28.7	NA1	-	4.50E+09
FSB-112C	-2.04E-04	9.3	28.7	NA1	-	4.50E+09

NA1 -- Concentration low (≤ MCL)
NA2 -- Inconsistent trend

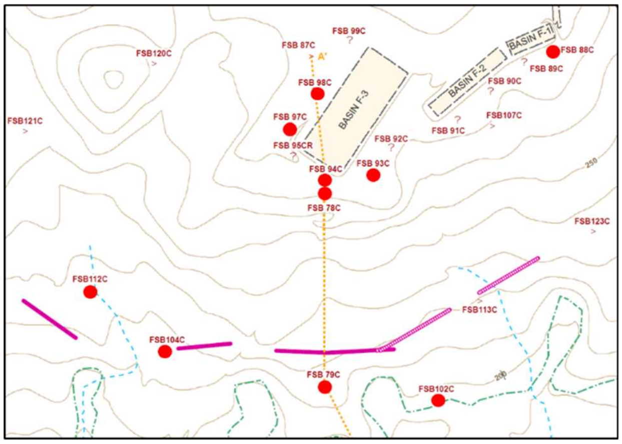

Figure 9: Map showing locations of wells listed in Table 1.

The decay constants in Table 1 were derived by applying the linear regression trend function in Microsoft Excel to the latest linear trend as shown in the examples in Figure 10. Decay constants were not calculated when concentrations were at or below the MCL (NA1) or when the trend was too inconsistent to obtain a meaningful value (NA2).

The concentration versus time trends in the LAZ show that, overall, concentrations of contaminants are decreasing and there is continued progress toward reaching MCLs in the LAZ. Nevertheless, predicting when that will occur from these trends should be approached cautiously, because of the lag in evolution of the LAZ plume. The most accurate prediction that can be made is that these trends provide the lower boundary for the range of time it will take for the concentration to reach MCL. For most cases where environmental decay constants were derived, the following general statement applies:

"Assuming the concentration versus time trend remains constant, the MCL could be reached in X years or later".

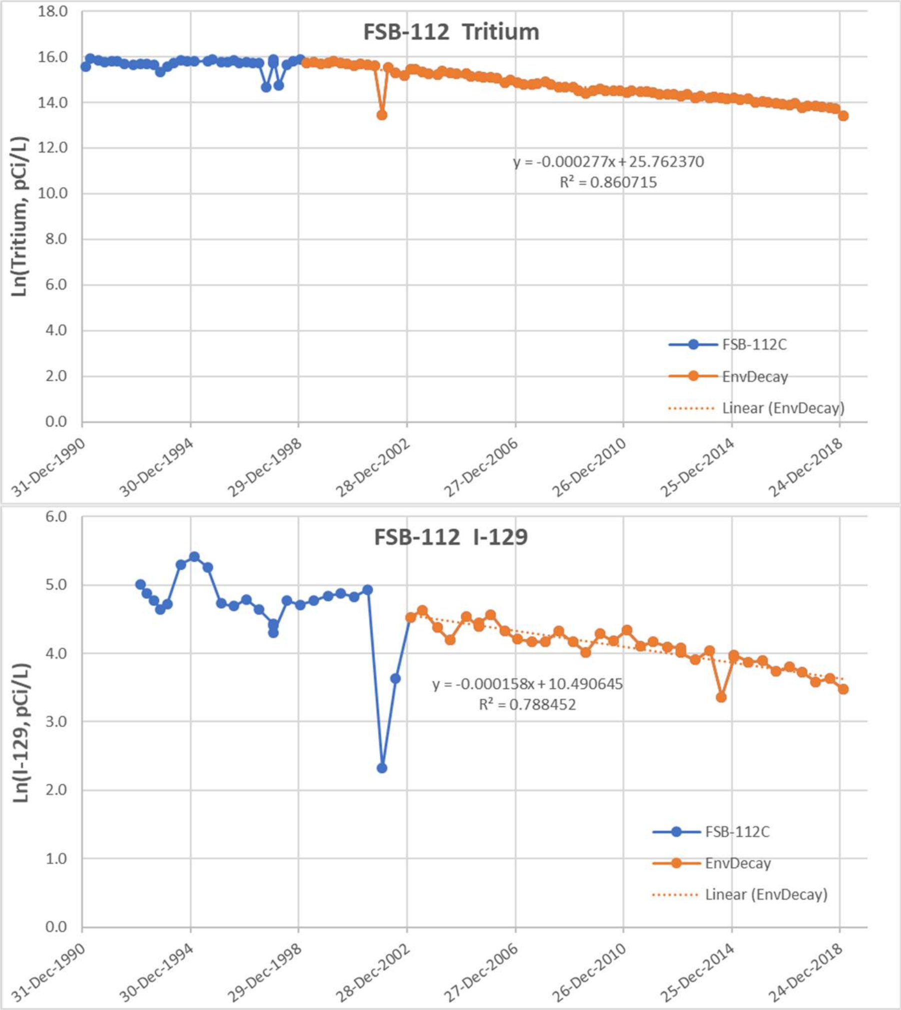

Figure 10: Concentration vs. time trends for tritium and I-129 at well FSB-112C.

Enhancing the conceptual model by adding more detail to the hydrogeological and geochemical frameworks would allow better understanding of contaminant behavior and interpretation of monitoring data. The most valuable enhancement to the geochemical framework would be to better understand geochemical processes controlling contaminant behavior in the wetlands. The degree of contaminant attenuation in the wetlands and the processes controlling attenuation and release of contaminants have direct bearing on whether regulatory agreements will be met and future remedial actions that could be taken in or near the wetlands, if necessary. Additional detail in four aspects of the hydrogeological framework would allow better understanding of contaminant behavior and interpretation of monitoring data: 1) degradation of the basin caps leading to increased infiltration through the basin soils, 2) the effects of low permeability zones within the UAZ, 3) movement of contaminants between the UAZ and the LAZ, both upgradient and downgradient of the seepline, and 4) groundwater flow within the wetlands. These aspects of the hydrogeological framework also pertain directly to any additional remedial actions that might be necessary in or near the wetlands, and their design.

2.2.2 Geochemical Processes in the Wetlands

The wetlands are a complicated and dynamic geochemical environment compared to the rest of the saturated zone. The principle geochemical process affecting contaminants upgradient of the wetlands is adsorption to mineral surfaces, controlled by pH. Speciation is an additional complication for I-129, affecting how well it is adsorbed. The same is true for uranium when it is directly exposed to the carbonate solution used in base injection. Nevertheless, pH is also a primary control on speciation of these two contaminants in groundwater associated with the F-Area Seepage Basins. In the wetlands the geochemical environment is more complicated because of the presence of abundant organic matter, vegetation, mixing with rainwater, varying seasonal temperatures, and the cycles of saturation and unsaturation that near-surface sediments experience.

Attenuation of contaminants in the wetlands is the result of natural processes and campaigns of base injection in groundwater beneath the wetlands. Contaminants have interacted with organic matter and clays in wetland soils since the contaminants initially reached the wetlands, long before any remediation activities. The base injection campaigns beneath the wetlands initially enhanced attenuation of Sr-90 and uranium, and likely released some I-129 (Denham, 2015), in deep wetland soils. Nevertheless, the processes of natural attenuation and release of contaminants have been dominant and will continue to control the behavior of contaminants in the wetlands. The varying elevation of the water table causes varying attenuation of many contaminants (Du Laing et al., 2009; Frohne et al., 2011). Wetland plants also play a role in controlling behavior of contaminants (Du Laing et al., 2009). In addition, contaminants adsorbed to soil particles can be released to Fourmile Branch by physical processes.

The dynamic nature of the wetland environment occurs on multiple time scales. There are short-term dynamic processes dominated by intense rainstorms that cause erosion of the wetland surface soils and change their chemistry. An example of the effects of these short-term processes affecting uranium mobility in Tim's Branch was detailed by Batson et al. (1996). They found that particulate-bound uranium was released from flood plain sediments to a stream at much higher masses during intense rainstorms than at baseflow conditions.

Longer term seasonal processes that include extended periods of wet and dry weather and shedding of leaves by vegetation also affect the physical and chemical processes attenuating and releasing contaminants. Seasonal effects were documented by Denham and Amidon (2016) who found that uranium and I-129 concentrations in wetland surface water increased during seasons of increased rainfall. They hypothesized that increased surface and groundwater flow during wet periods might release contaminants bound to particulate mineral and organic matter by increased suspension and transport of the particles. Nichols and Dickson (2019) correlated the oscillating nature of I-129 concentrations to warm and cool seasons, suggesting that I-129 bound to organic matter may be released at a greater rate during warm periods because of an increased rate of microbial degradation of the organic matter.

There are longer-term processes such as the climatic effects of sustained droughts and periods of sustained heavier rainfall. These result in fluctuations in the water table that can have profound effects on the configuration of the wetlands and the chemistry/microbiology of the associated soils and porewaters. The fact that the wetlands result from the water table intersecting surface topography means that the extent of water saturated soil migrates upslope as the water table rises and reverses as the water table drops (Figure 11). The saturated-unsaturated cycles likely affect redox and microbial processes that strongly influence contaminant mobility. Also important is that problematic soil contamination may be present in locations of the wetlands where there are no current groundwater seeps because seeps shift location in response to changes in the water table and surface topography.

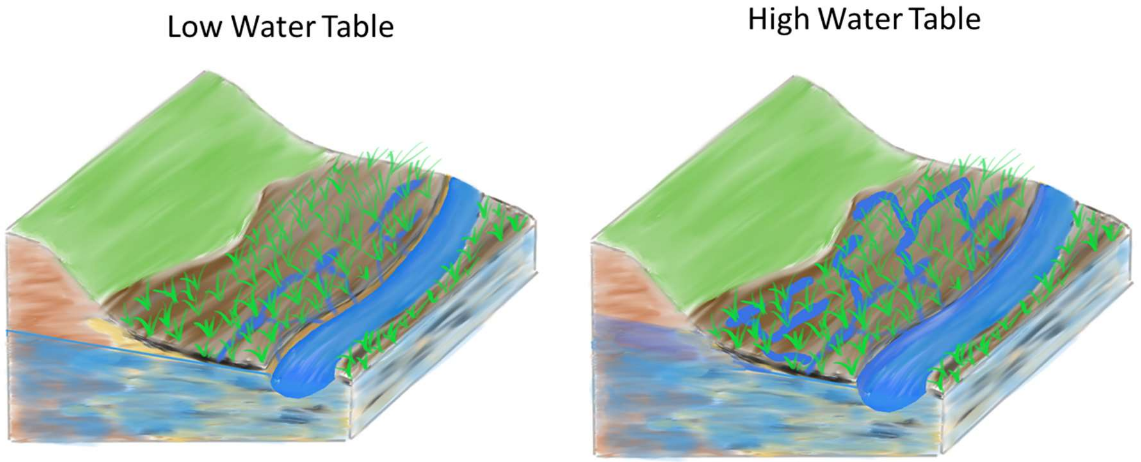

Figure 11: Wetland dynamics controlled by water table fluctuations.

It is important to understand the magnitude and cause of variations in contaminant attenuation at all time scales so that progress toward remedial goals can be assessed and monitoring data can be properly interpreted. Furthermore, if additional remedial actions are required, the understanding of natural attenuation processes in the wetlands will aid in developing enhanced attenuation strategies, as well as assessing whether remedial actions have undesirable collateral consequences.

2.2.2.1 Example of Geochemical Processes Effect on Contaminant Concentrations

Figure 12 shows I-129 concentration versus time trends for a wetland surface water sampling station (FAS-092) and two upgradient monitoring wells (FSB-130D and FSB-79). The trends show the seasonal variation of the I-129 concentrations in the wetland surface water. The green bars connect the seasonal low concentrations in the wetland with the lowest concentration of the two wells. The red bars connect the seasonal high concentration in the wetlands to the highest concentration of the two wells. The low concentrations in the wetlands are very similar to the well concentrations, but the high concentrations in the wetlands are much higher than the well concentrations. This suggests a process is releasing attenuated I-129 during the summer. It may be a geochemical, microbial, or physical process. Regardless, understanding the process may yield ways to mitigate the seasonal high I-129 concentrations or develop the necessary information to obtain an alternate concentration level or an alternate remedial goal (e.g., a flux-based measurement).

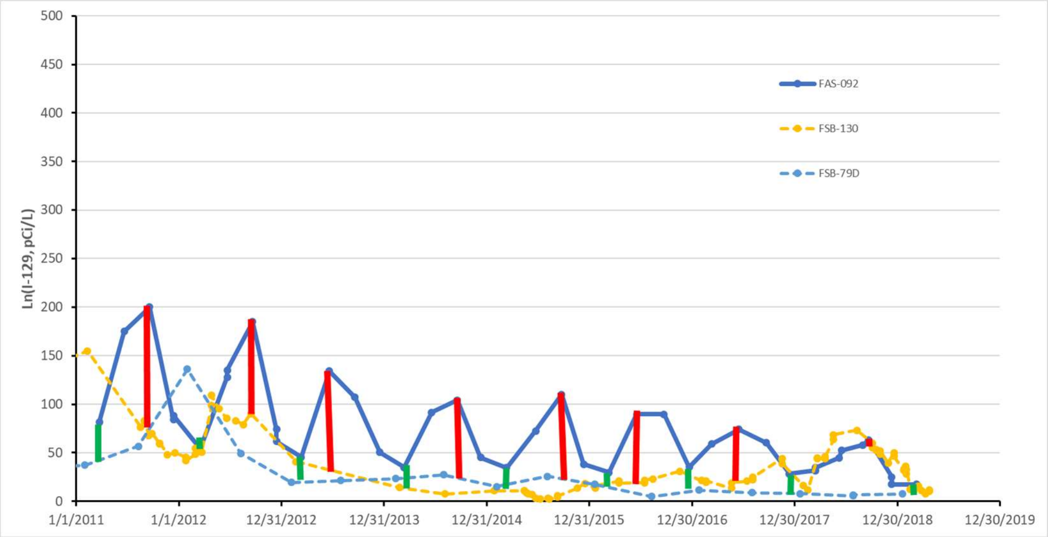

Figure 12: I-129 concentration vs. time plot for wetland sampling station FAS-092, well FSB-130, and well FSB-79D. Green bars span the difference between a seasonal low concentration at FAS-092 and the lowest concentration of the two wells, red bars span the difference in a seasonal high concentration at FAS-092 and the highest concentration of the two wells.

Lines of Inquiry for Geochemical Processes in the Wetlands

- What are the dominant attenuation mechanisms for I-129, Sr-90, and uranium in the wetlands, how strong is attenuation, and what conditions would reverse attenuation?
- What is the cause of profound seasonal variation in I-129 concentrations, and to lesser extent other contaminants, in wetland surface water?
- What is the approximate mass of contaminants sequestered in the wetlands?

2.2.3 Degradation of the Basin Caps

The low permeability caps on the basins will degrade by natural processes if left unmaintained. These degradation processes include decomposition of cap materials, subsidence leading to fractures, and penetration of the cap by plants and animals. The only way to mitigate these degradation processes is to regularly inspect/monitor the cap for any evidence these processes are active. Currently, this is done by regular walk-over inspections and surveying subsidence markers. Recent development of new technologies such as geophysical techniques and the ability to deploy powerful sensors on unmanned aerial vehicles provides an opportunity to significantly improve inspection and monitoring of the basin caps. The conceptual model would be enhanced by considering processes and parameters that will indicate early cap degradation that can be monitored by these new technologies.

Line of Inquiry

- What processes and parameters associated with the basin caps can be monitored to detect evidence of early cap degradation?

2.2.4 Effects of Low Permeability Zones Within the UAZ

There is now a considerable body of literature on how low permeability zones within an aquifer affect contaminant versus time trends at locations within the trailing edge of a plume. Primarily these publications have focused on diffusion of contaminants into and out of zones of low permeability as a plume passes through the aquifer. The "back diffusion" of contaminants into the main flow path of the trailing edge of a contaminant plume accounts for the "tailing" effect observed in many contaminants versus time trends; the tail being the decrease in the slope of the concentration degradation curve. This is discussed by Denham and Amidon (2016) in relating concentration versus time trends to a generalized conceptual model of the seepage basins.

In numerical modeling of contaminant transport, low permeability zones are often accounted for using a "dual-domain" approach that numerically simulates the effects of low permeability zones without explicitly locating them in the modeling domain. Flach (2002) and Flach et al. (2004) used this approach to simulate the transport of the tritium plumes at the F- and H-Area Seepage Basins and compared the dual domain simulations to single domain simulations. The simulations demonstrated that the dual domain approach can match the tailing observed in contaminant versus time trends better than the single domain approach. Low permeability zones can also explain the patterns of pH decrease following base injection events at the F-Area Seepage Basins (Denham, 2017). It was hypothesized that base ions (OH^-, HCO_3^-, and CO_3^{-2}) diffuse, or are forced by pressure of injection, into stagnant zones. This provides a reserve of base that can diffuse into permeable zones as they are flushed by influxing acidic groundwater between base injection events, maintaining a desirable pH for longer than expected in the absence of this base reserve. The opposite is likely true upgradient of the base injection sites, the stagnant zones contain a reserve of acid that will prolong the time it will take for the plume affected zone to return to a natural pH.

One aspect of low permeability zones that may be important for contaminant transport and interpretation of groundwater monitoring data at the F- and H-Area Seepage Basins is the case in which there are zones or strata where advection of groundwater is significant relative to diffusion, but the rate of flow is less than the bulk of the aquifer. The effect this type of low permeability zone has on bulk contaminant transport depends on the fraction of contaminant mass moving in these zones. Even if the fraction of contaminant mass moving in these zones is low, the contaminant versus concentration trends in wells screened through such zones can indicate slow contaminant migration compared to wells screened in the more permeable portion of the aquifer. This must be accounted for to understand which wells provide the most realistic indication of progress toward remedial goals.

2.2.4.1 The "AA" Horizon and Other Clay-Rich Zones

Most groundwater flow in the UAZ occurs through the so called "transmissive zone" that is bounded at top and bottom by less permeable zones. Flach et al. (1999) describe the lower permeability zone at the top of the UAZ, the "AA" horizon, as an "interbedded sequence of sands and silty sands, probably of much lower permeability than the underlying TZ (transmissive zone)". Flach et al. (1999) suggest the "AA" horizon corresponds to the bottom of the Tobacco Road Formation. The lower permeability of these sediments is indicated by the increased gamma signature on many geophysical logs marking the interface between the Dry Branch and Tobacco Road Formations (Fallaw and Price, 1995; Aadland et al., 1995). Figure 13 shows the general hydrostratigraphy of the area in which the "AA" horizon is interpreted to intersect the water table only in the upgradient portion of the F-Area Seepage Basins site.

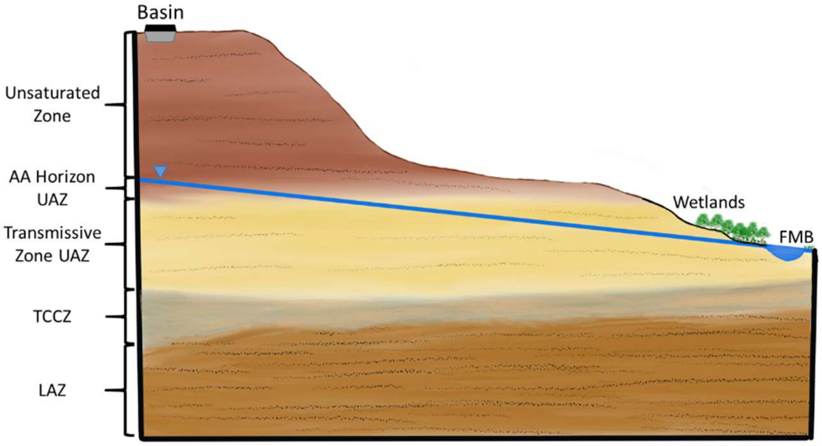

Figure 13: Generalized cross-section of the aquifer system at the F-Area Seepage Basins.

This would be consistent with the interpretation of geophysical logs of boreholes near the basins (e.g., cross-sections in WSRC-TR-99-00266 [F-Area] and WSRC-TR-98-00004 [H-Area]) that show clayey zones near the top of the present-day water table. There are likely other isolated clayey lenses within the transmissive zone.

The influence of the "AA" horizon and other clayey lenses on bulk contaminant transport at the F-Area Seepage Basins is likely to be minimal because of the greater thickness and higher permeability of the transmissive zone. Also, the downward gradient in the UAZ would tend to flush mobile contaminants from these zones as water moves downward through them. In contrast, clayey zones may contribute to maintaining low pH in the UAZ upgradient of base injection zones because of increased acidity associated with clay mineral surfaces exposed to low pH waters. For example, clayey zones near the top of the water table between the basins and the subsurface barrier may keep that portion of the UAZ acidic by desorbing acid into recharge infiltrating from the vadose zone. Similarly, in the base injection zones, the clayey horizons or lenses may help maintain an elevated pH after a base injection event by storing base in stagnant zones and on mineral surfaces.

Groundwater monitoring wells screened in or across the "AA" horizon or other clayey zones may have contaminant concentration versus time trends that differ from wells screened predominantly in the transmissive zone. The effect may be more pronounced the closer the wells are to former pump-and-treat injection locations. Injection of treated water containing tritium, but also often containing elevated concentrations of I-129, Sr-90, and nitrate (maximum allowable injection concentrations for these were greater than MCLs), were done from 1997 through 2003. Contaminants injected into the “AA” horizon may not have completely flushed from this strata and wells screened in the “AA” horizon, causing a slower rate of decrease in concentrations than is associated with near-by deeper wells.

2.2.4.2 Transition Between the TCCZ and UAZ

A lower permeability zone may also exist locally near the lower extent of the transmissive zone as it transitions into the TCCZ, or in lithostratigraphic nomenclature, the interface between the bottom of the Irwinton Sand and top of the Twiggs Clay. Some geophysical logs and cone penetrometer logs from wells and pushes near the F-Area Seepage Basins suggest the presence of a zone with higher clay content just above the top of the TCCZ (e.g., HSB-116 and HSB-119 in WSRC-TR-98-00004; FSB-79 in WSRC-TR-99-00266; and FCPT-10, FCPT-11, and FCPT-12 in WSRC-RP-2002-4090). Aadland et al. (1995) reports that the lower part of the UAZ consists of silty sand and has a lower hydraulic conductivity than reported for the bulk of the UAZ. If the rate of downward flow through this zone is substantially greater than the rate of diffusion, then this zone is unlikely to have a significant influence on contaminant transport in the UAZ upgradient of the wetlands. Within the wetlands and Fourmile Branch, where groundwater flow is upward, contaminants stored in this zone and replenished from the TCCZ and the LAZ may influence contaminant concentrations in surface water. Contaminant concentration versus time trends in monitoring wells, upgradient and near the wetlands, screened across this zone may exhibit slower rates of concentration decrease.

Example: Potential Effect of Low Permeability Zones on Contaminant Behavior

There are documented zones of clayey sand near the top of the saturated zone in the vicinity of Basin 3 that may have affected the rate of decrease in contaminant concentrations following basin closure and vadose zone drainage. Figure 14 shows a simplified version of cross-sections presented in WSRC (1999) that were based on core descriptions and geophysical logs. The information is simplified here to highlight the presence of clayey sand horizons occurring at the elevation of well screens for monitoring wells FSB-98D, FSB-94DR, and FSB-78.

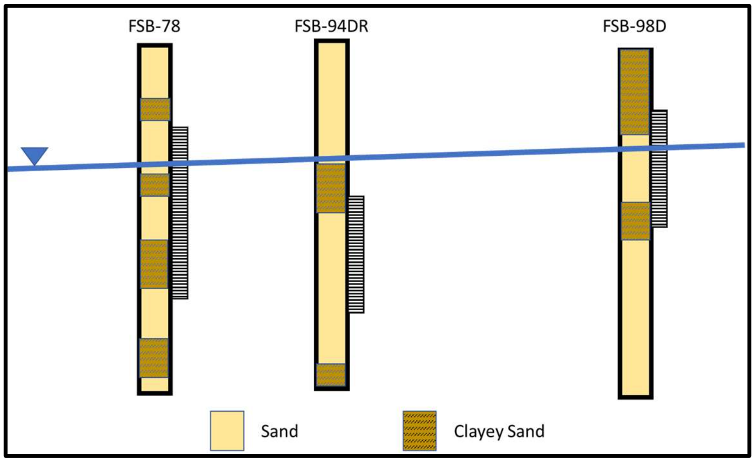

Figure 14: Idealized core sections from borings and geophysical logs for monitoring wells FSB-78, FSB-94DR, and FSB-98D near Basin 3 of the F-Area Seepage Basins (after WSRC, 1999).

These lower permeability zones may have tended to store contaminants in stagnant porosity that later diffused back into the more permeable sands. The result would be to keep concentrations of contaminants elevated longer than they would have been in the absence of the clayey sand zones. Concentration versus time trends for tritium at monitoring wells FSB-98D and FSB-87D are shown in Figure 15.

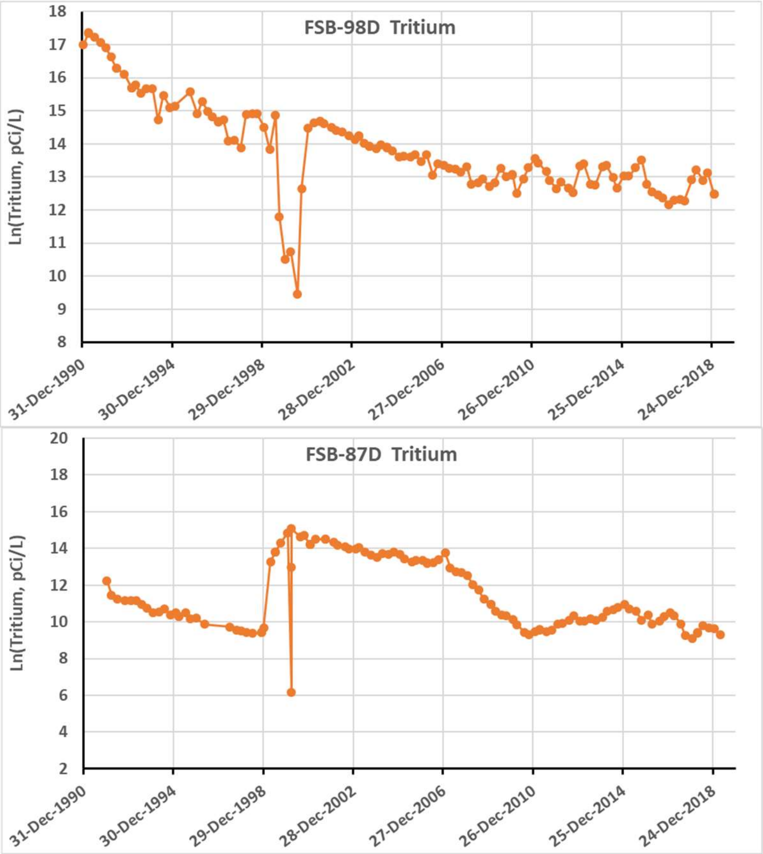

Figure 15: Tritium concentration vs. time trends for wells FSB-98D and FSB-87D.

These monitoring wells are located downgradient from injection wells that were part of the well network used to re-inject groundwater treated by the pump-and-treat system from 1997 until 2003. The two wells are close to one another, with FSB-87D closer to the injection wells. The initial trends are decreasing and typical of Stage 2 in the conceptual model. The effects of the re-injection of tritiated water are apparent in the sudden increase in tritium concentration at well FSB-87D in 1999. The effects are less apparent at well FSB-98D because of the higher pre-injection tritium concentration at this well. After the tritiated water has passed each well the tritium concentrations remain near constant from 2010 to present rather than resuming a decreasing trend. Did "back diffusion" from the low permeability zones maintain the nearly constant tritium concentrations? Do low permeability zones have a similar effect throughout the UAZ and are trends in these anomalous?

Lines of Inquiry

- Are there significant low permeability strata within the UAZ that affect remediation and/or progress toward remedial goals?
- Are there wells screened in lower permeability zones in which apparent progress toward remedial goals is slower than in other wells and, if so, how is overall progress toward remedial goals assessed?

2.2.5 Vertical Movement of Contaminants

Vertical migration of contaminants is driven by the vertical hydraulic gradients and strongly influenced by the competency of the TCCZ as an aquitard, as well as geochemistry. Throughout most of the areas around the F- and H-Area Seepage Basins, there is a downward hydraulic gradient that drives groundwater from the UAZ, through the TCCZ, and into the LAZ. This changes to an upward gradient as groundwater approaches drainage zones in the wetlands and Fourmile Branch. Thus, groundwater and mobile contaminants are moving from the LAZ into the UAZ in portions of the wetlands and beneath Fourmile. This is indicated by the drainage of the LAZ into Fourmile Branch and the absence of contamination in wells screened in the LAZ and located across Fourmile Branch from the seepage basins (FSB-115C, FSB-116C, HSB-130C HSB-131C, HSB-132C, HSB-140C, HSB-141CR, HSB-146C, and HSB-148C). Figure 16 shows the generalized groundwater flow from beneath seepage basins to Fourmile Branch. Whether passing from the UAZ into the LAZ or vice versa, groundwater and mobile contaminants pass between aquifer zones more rapidly where the TCCZ is absent, thinner, or sandier.

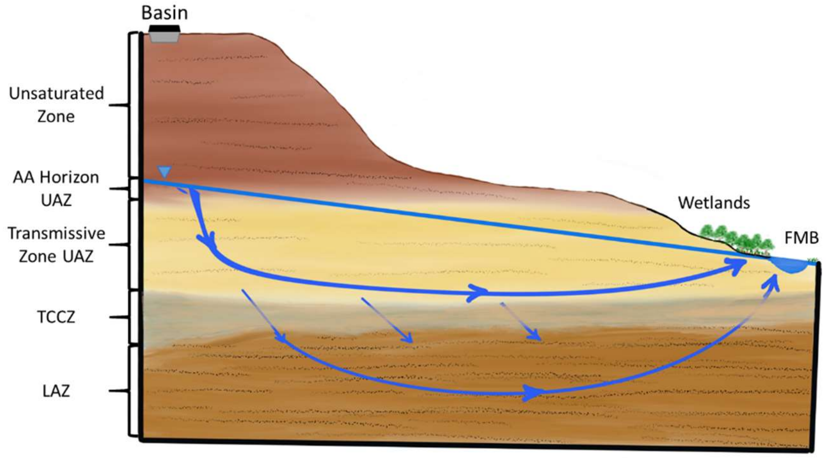

Figure 16: Cross-section showing general flow paths of groundwater in the UAZ and LAZ at the F-Area Seepage Basins.

2.2.5.1 Geochemistry and Vertical Contaminant Migration

The difference in geochemical conditions between the UAZ and the LAZ can affect the migration of I-129, Sr-90, and uranium between the two aquifer zones. As discussed previously pH is the dominant geochemical control on migration of these contaminants upgradient of the wetlands. In general, Sr-90 and uranium are more mobile at low pH values and are strongly attenuated at pH values greater than about 5. The opposite is true of I-129 that is moderately attenuated at pH<4 in F-Area Seepage Basin aquifer sediments (Emerson et al., 2014).

As acidic groundwater migrates downward, a pH gradient is established and the rate of migration of that gradient depends on the downward flow velocity and the mineralogy. The rate of migration of the pH gradient is slower through zones with elevated clay content because of lower permeability and the chemical nature of clay surfaces. Clay-sized minerals (e.g., goethite) and clay minerals (e.g., kaolinite, illite, and smectite) have a much greater capacity to buffer pH by "sorbing" acidity than siliceous sand grains. Hence, downward migration of the pH gradient is substantially slowed where it must pass through the TCCZ.

The presence of the TCCZ and the lower groundwater velocity in the LAZ may have delayed breakthrough of Sr-90 and uranium into the LAZ in the upgradient portion of the site where groundwater in the UAZ is acidic. Figure 17A shows a generalized illustration of this. I-129 is less mobile in acidic groundwater, but high I-129 concentrations in wells near the F-Area Seepage Basins suggest that it would have passed through the TCCZ ahead of the low pH gradient, impeded only by the low permeability of that zone. It is also true that the pH gradient may limit the upward migration of Sr-90 and uranium in wetland locations and near Fourmile Branch where pH is now near natural values and higher than pH values in the LAZ (Figure 17B). I-129 migration from the LAZ into the UAZ or into Fourmile Branch would only be hydraulically impeded.

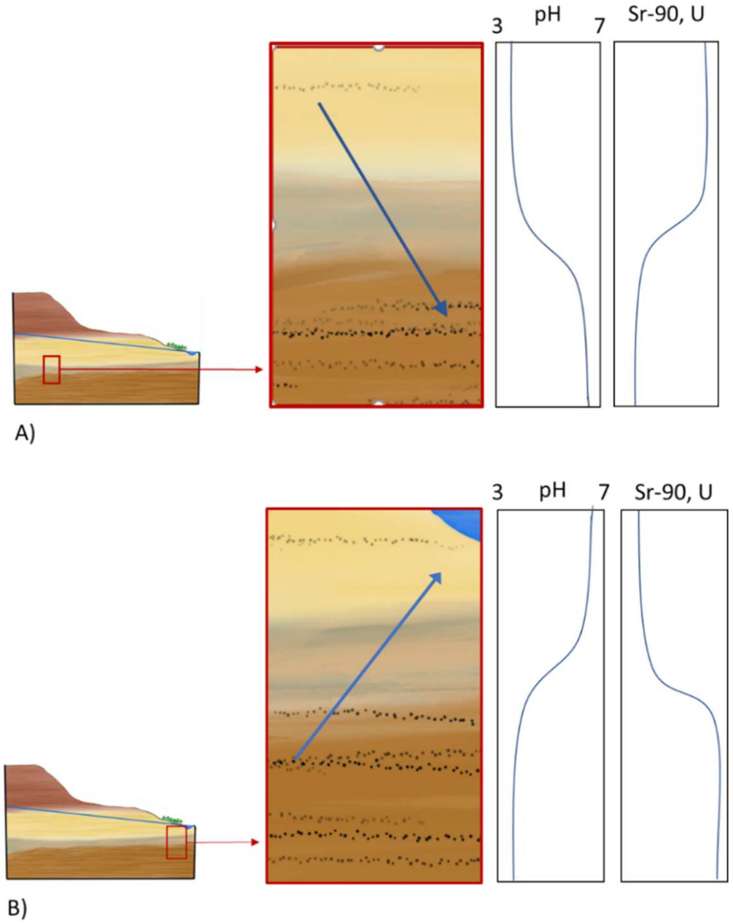

Figure 17: A) Cross-section showing downward groundwater flow from the UAZ to the LAZ and idealized pH with idealized Sr-90 and uranium concentrations; B) Cross-section showing upward groundwater flow from the LAZ to the UAZ and idealized pH with idealized Sr-90 and uranium concentrations

2.2.5.1.1 Examples of Geochemical Control on Vertical Movement

Figure 18 illustrates the issue of geochemical control on migration of reactive contaminants across the TCCZ. In the case of well cluster FSB-94, the rate of advancement of an acidic pH gradient into the LAZ controls the migration of uranium into the LAZ. In 1990, the pH in the UAZ was close to 3.0 compared to the about 4.3 in the LAZ. Thus, uranium is mobile in the UAZ, but passes more slowly into the LAZ because of the low mobility at the higher pH value. As the pH gradient moves down in the LAZ, the decreasing pH allows uranium to migrate into the LAZ. In the UAZ, uranium concentrations decrease, in part because uranium is mobile and being flushed out, and in part because uranium is beginning to adsorb as pH increases. In contrast, Sr-90 is mobile in both aquifer zones throughout the time period because the pH is below 5.5. Therefore, early in the time period, concentrations of Sr-90 are approximately the same in the two aquifer zones because Sr-90 could pass readily through the TCCZ into the LAZ.

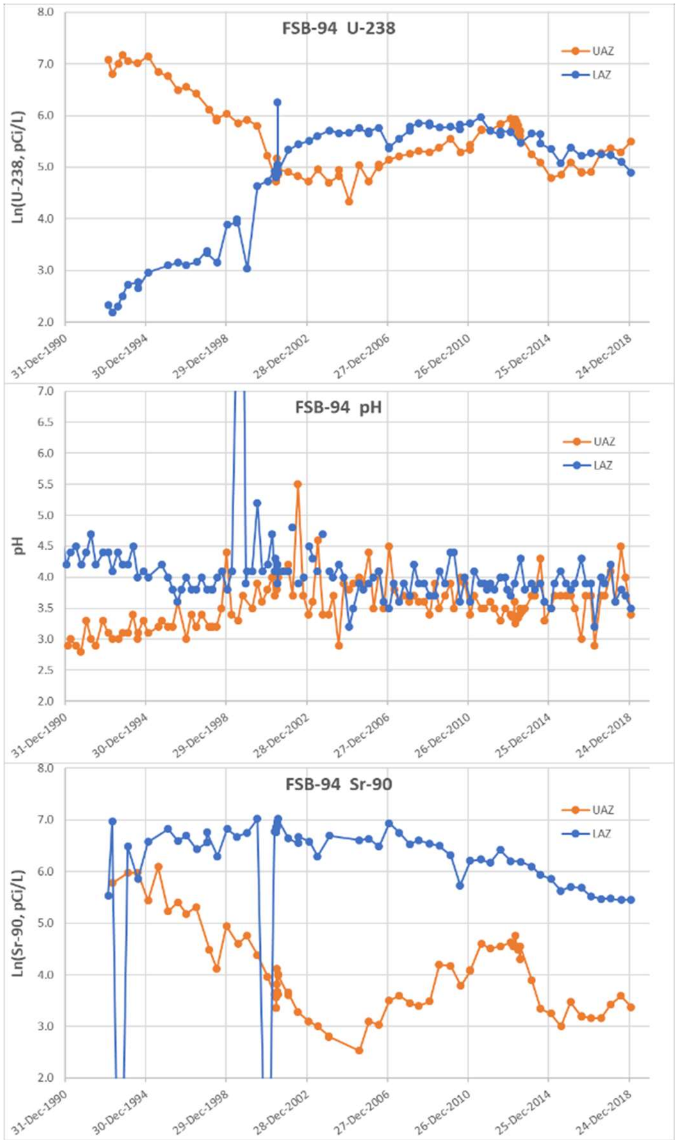

Figure 18: Concentration vs. time trends at wells FSB-94DR (UAZ) and FSB-94C (LAZ) for U-238, pH, and Sr-90.

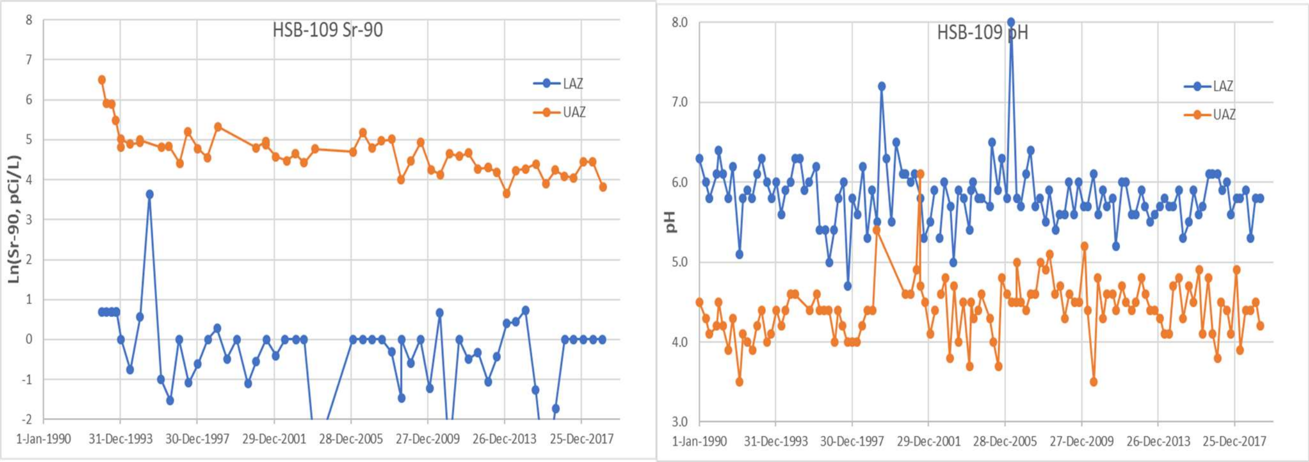

Figure 19: Concentration vs. time trends at wells HSB-109D (UAZ) and HSB-109C (LAZ) for Sr-90 and pH.

Figure 19 shows an example of the inability of Sr-90 to penetrate the LAZ at the H-Area Seepage Basins because of pH. Values of pH in the LAZ are consistently >5 and often ≥6, and thus natural attenuation has kept Sr-90 concentrations in the LAZ very low. The same is true for uranium.

Lines of Inquiry for Vertical Movement of Contaminants

- Does differential migration of contaminants into the LAZ have a significant influence on progress toward remedial goals?
- Is there significant flow of groundwater through the TCCZ and into the LAZ along the subsurface barrier, particularly at the troughs on top of the TCCZ?
- Where does upward flow of groundwater from the LAZ into the UAZ occur?
- Where groundwater is upwelling from the LAZ, what fraction of each contaminant in wetland surface water and Fourmile Branch is from the LAZ, how will that change with time, and will contamination from the LAZ affect progress toward remedial goals?

2.2.6 Groundwater Flow in the Wetlands

Groundwater flow in the UAZ is more complex in the wetlands than upgradient. At the F-Area Seepage Basins, the funnel-and-gate disrupts the groundwater flow pattern. Erosional features (ephemeral streams, gulleys, etc.) cut into the topography and form the irregular embayments of the seepline at both the F-Area and H-Area Seepage Basins. As groundwater approaches the wetlands, flow lines are strongly influenced by the presence of springs along the seepline that are drainage points for groundwater. Figure 20 shows a general conception of the directions of groundwater flow as it passes from the eastern half of the western gate into the wetlands. In addition to groundwater flowing toward drainage locations, the saturated zone of the UAZ thins as groundwater nears the wetlands with the thickness decreasing until Fourmile Branch is reached. Though there is an overall thinning in the direction of Fourmile Branch, the thickness of the UAZ in the wetlands is uneven because of the irregular topography of the top of the underlying TCCZ. In portions of the wetlands there may be upwards flow of groundwater from the LAZ into the UAZ. If there is upward flow of groundwater, the effect on contaminant concentrations in the UAZ is, in part dependent on the thickness of the UAZ.

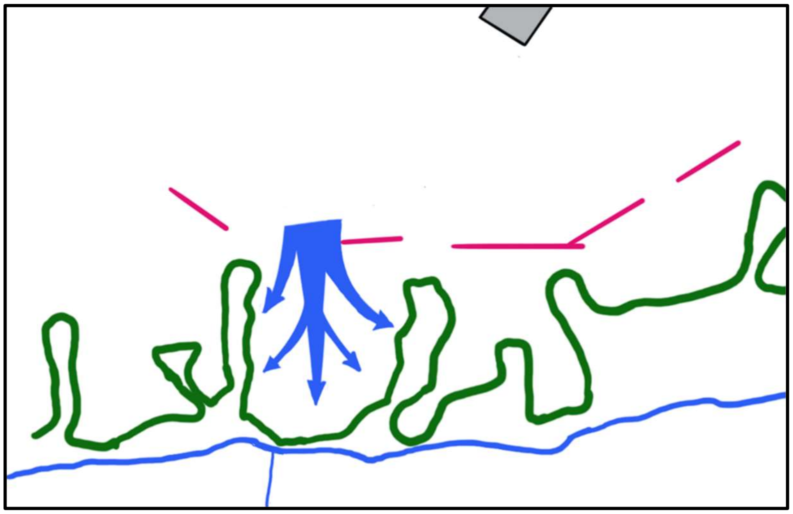

Figure 20: Map view of the downgradient portion of the F-Area Seepage Basins site with blue arrows showing idealized groundwater flow directions in the wetlands.

Hence, understanding groundwater flow in the wetlands is important to interpreting wetland monitoring data and informing decisions on potential future remedial actions in the wetlands. Knowledge of the groundwater flow in wetlands and any potential upward flow from the LAZ is particularly important in designing of future remedial actions in the wetlands.

Example: Potential Influence of UAZ Thickness in Wetlands

The thickness of the UAZ in the upgradient portion of the site strongly influences groundwater flow and contaminant migration. Presumably, the same is true in the wetlands and UAZ thickness influences contaminant migration, distribution, and monitoring.

Figure 21A is a map showing the topographic elevation of wetland sampling stations for the F-Area Seepage Basins and Figure 21B shows the estimated elevation of the top of the TCCZ beneath the stations, based on published maps. The estimated thickness of the saturated zone beneath each station (surface elevation minus top of TCCZ elevation) is posted below the station name in Figure 21B.

Stations FAS-092 and FAS-093 have a thinner saturated zone beneath them raising the question whether the thickness of the wetland sediments affects monitoring of contaminants. Concentration versus time trends for Sr-90, I-129, and tritium at the four wetland monitoring stations are shown in Figure 22 and the following observations can be made:

- Sr-90 concentrations have been consistently higher and consistently decreasing since 2011 when quarterly sampling began at the stations overlying the thinner UAZ, FAS-092 and FAS-093. At stations FAS-091 and FAS-096, overlying a thicker UAZ, concentrations of Sr-90 have been near or below the MCL, but have been slowly increasing since 2013.
- There is no pattern to the magnitude of I-129 concentrations, but concentrations have been constant to increasing at stations FAS-091 and FAS-096 since 2013, whereas seasonal high and low concentrations have been consistently decreasing at stations FAS-092 and FAS-093.

- There was a notable increase in seasonal high and low concentrations of I-129 at station FAS-091 beginning in 2016. A similar seasonal high concentration increase occurred at station FAS-096 beginning in 2017, but low concentrations have remained relatively constant since 2010. There were no similar increases observed at stations FAS-092 and FAS-093. The seasonal high and low concentration at FAS-093R did increase in 2018, but this station recently replaced FAS-093 and may not be comparable.
- There are no discernable patterns in the magnitude of the concentrations of tritium at the different stations, but tritium concentrations have been consistently decreasing since 2011.

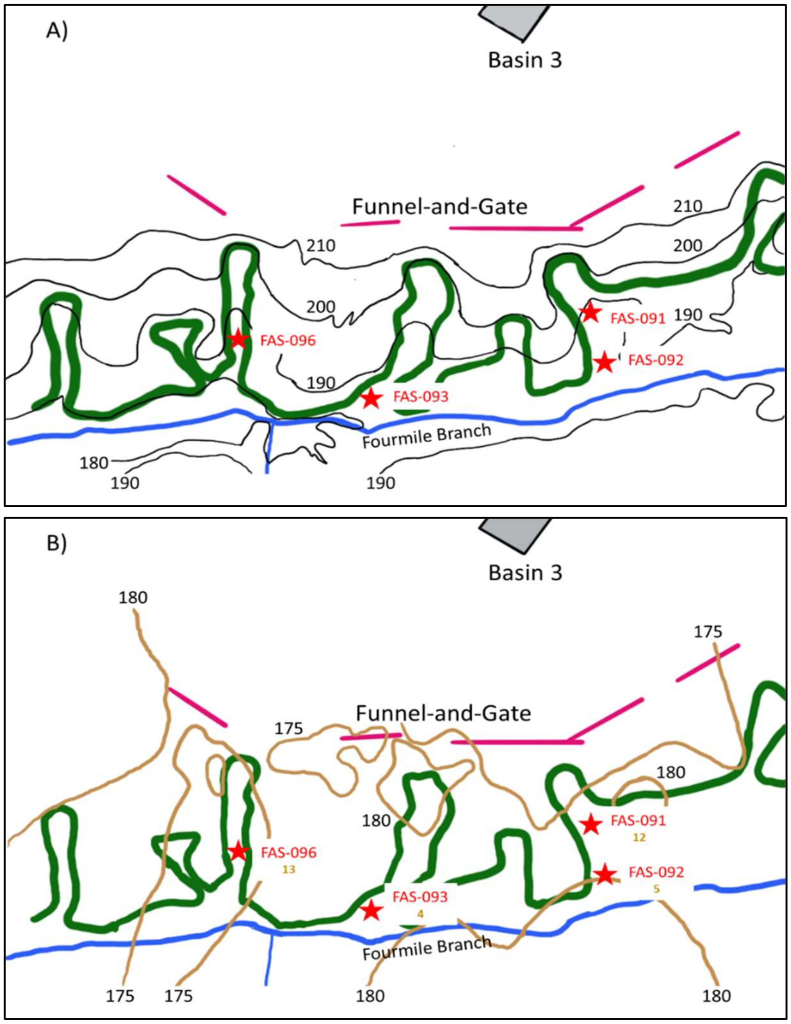

Figure 21: Map view of the downgradient portion of the F-Area Seepage Basins site showing the four wetland surface water sampling stations relative to topography (A) and the top of the TCCZ (B).

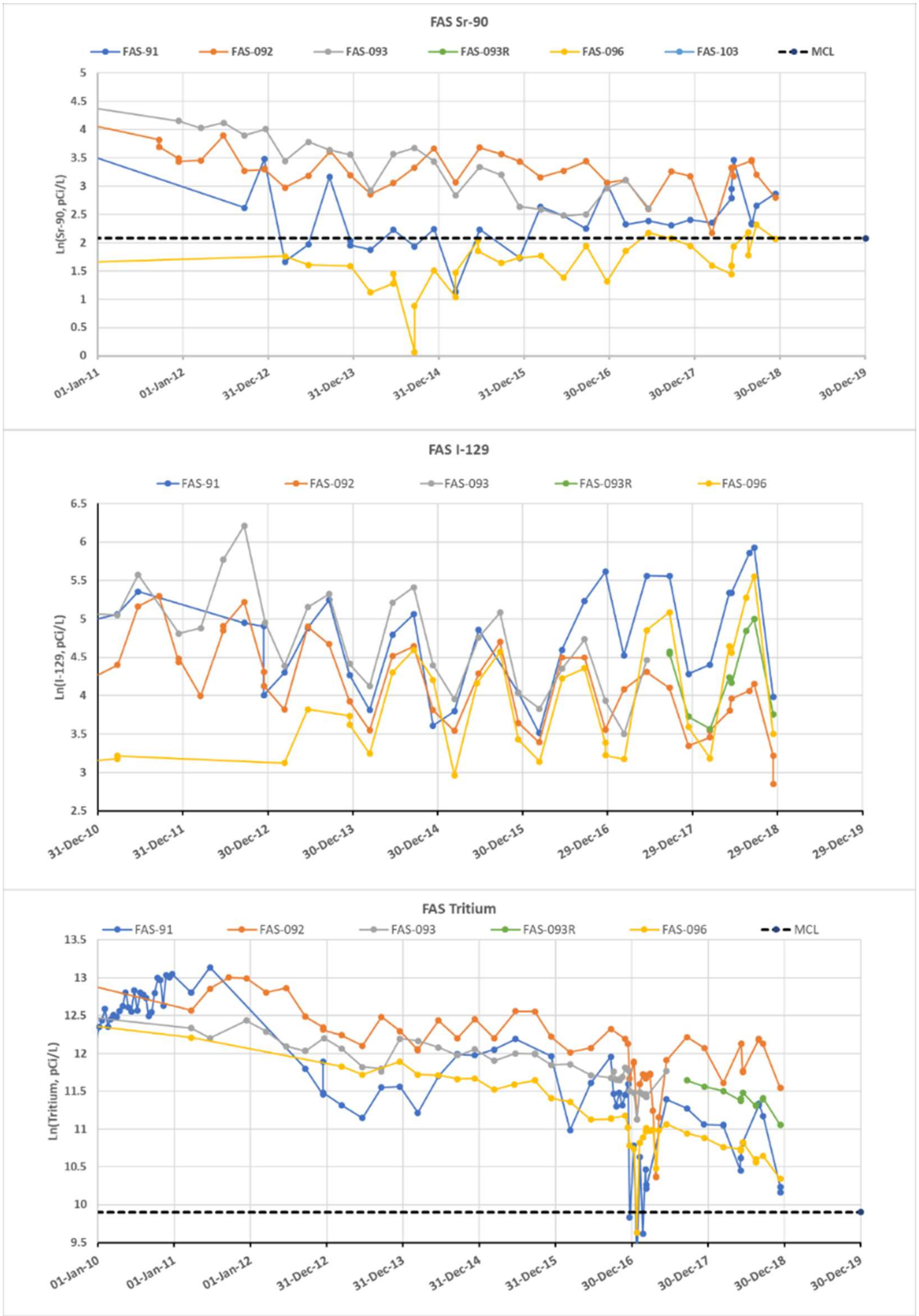

Figure 22: Concentration vs. time trends for Sr-90, I-129, and tritium at four wetland surface water sampling stations at the F-Area Seepage Basins site.

The cause of the differences in contaminant behavior observed at stations overlying thin UAZ relative to those overlying thick UAZ are unknown, and the thickness of the UAZ could be a coincidence. Regardless, the variation in thickness of the UAZ beneath the wetlands likely affects groundwater flow patterns and contaminant distribution. To fully understand the monitoring data collected in the wetlands requires understanding groundwater flow in the wetlands.

Example 2: Contaminant Flux to Fourmile Branch

Groundwater flow beneath the wetlands also controls the flux of contaminants to Fourmile Branch. There are three sources of contaminants entering Fourmile Branch: surface water flow from the wetlands, groundwater flow from the UAZ, and groundwater flow from the LAZ. The flux of a contaminant into Fourmile Branch coming from groundwater is the product of the concentration of the contaminant and the flux of groundwater containing that concentration of contaminant. Groundwater velocities in the LAZ are reportedly lower than in the UAZ (SRNS, 2018), but concentrations of some contaminants may be substantially higher in the LAZ. Hence, the LAZ may be an important source of some contaminants to Fourmile Branch. In addition, base injection into the UAZ beneath the wetlands may have affected the proportion of some contaminants coming from the UAZ relative to the LAZ.

There are three Fourmile Branch water sampling stations associated with the F-Area Seepage Basins. Station FM2-2BD located the upstream edge of the site and does not receive significant contamination from the F-Area Seepage Basins Plume. Stations FMC-002F (shown on map in Figure 23) and FM-A7U (about 900 meters downstream of FMC-002F). Station FMC-002F receives contamination from the center and eastern portion of the site, whereas station FM-A7U receives contamination from the whole site.

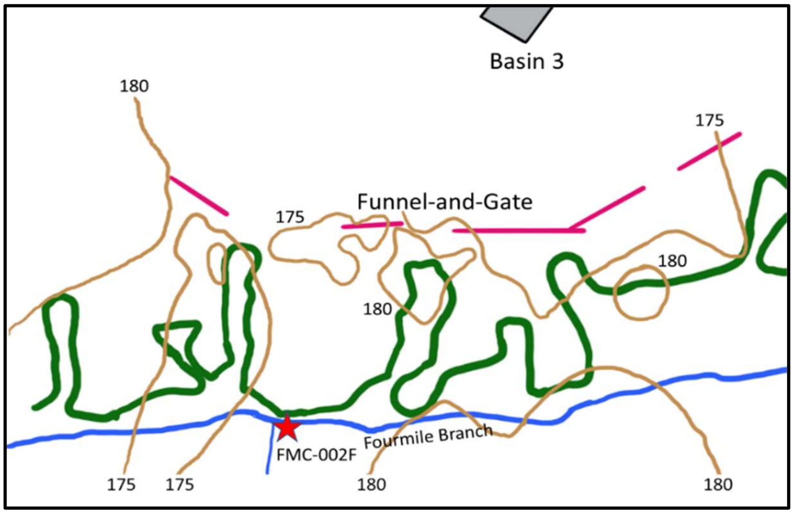

Figure 23: Map view of the downgradient portion of the F-Area Seepage Basins showing the location of Fourmile Branch sampling station FMC-002F and the underlying topography of the top of the TCCZ.

Figure 24 shows time versus concentration plots of I-129 and nitrate at Fourmile Branch sampling stations FMC-002F and FM-A7U. The concentrations of I-129 at both sites are similar and increasing until 2006. After 2006, the concentration of I-129 at the two stations remains relatively constant, given seasonal variation, until 2009 when the concentration decreases sharply at station FM-A7U while it remains unchanged at FMC-002F. The decrease in concentration of I-129 at FM-A7U is contemporaneous with the first injection of base solution into the UAZ beneath the wetlands. Thus, base injection appears to have flushed I-129 out of the UAZ in the western portion of the site, but not in the central and eastern portions of the site. One possibility is that complex flow paths in the central and eastern portions may have resulted in injectate cropping out into wetland surface water rather than flushing through the UAZ to Fourmile Branch. Another factor that should be considered in assessing the concentrations of contaminants at the two sampling stations is that FCM-002F is located on the downstream side of a culvert that collects and mixes water from the entire width of the stream, whereas FM-A7U is located on a segment of a braided portion of Fourmile Branch.

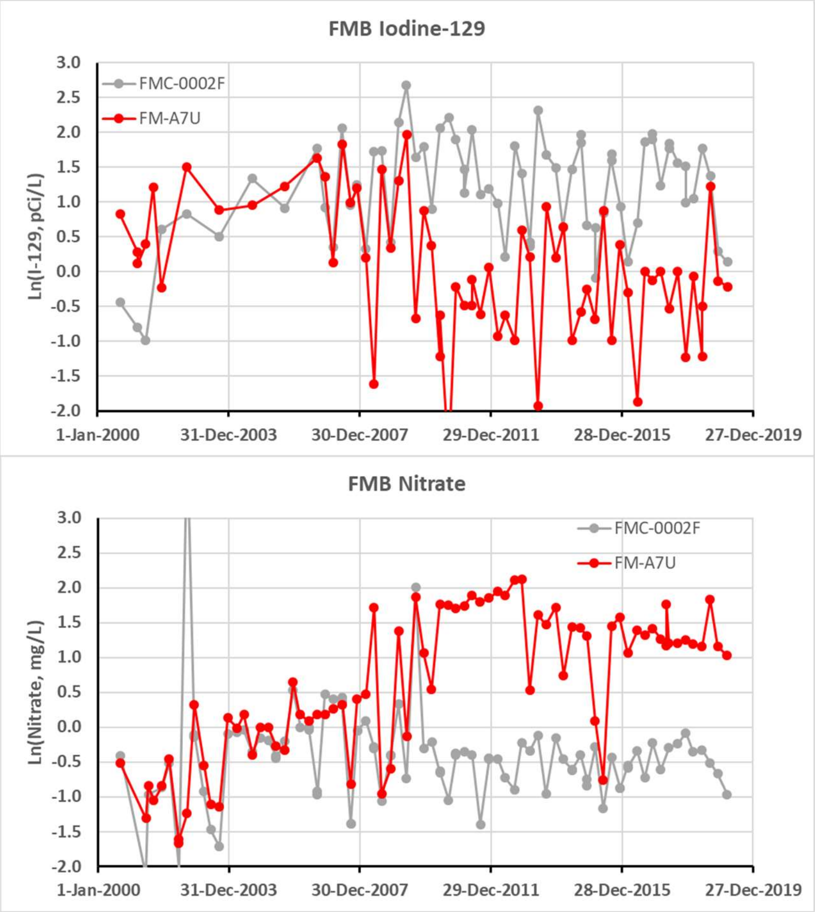

Figure 24: Concentration vs. time trends for I-129 and nitrate at the Fourmile Branch sampling stations FMC-002F and FM-A7U.

Nitrate concentrations show a different pattern with time than I-129 concentrations. The nitrate concentrations are consistent between the stations and increasing from 2001 until 2007. In 2007, the concentration of nitrate at FMC-002F reaches a maximum and remains relatively constant into 2019. In contrast, the concentration at FM-A7U continues to increase until 2012, after which it remains constant. The nitrate concentrations were apparently unaffected by base injection beginning in 2009. The patterns of nitrate are consistent with patterns in the LAZ (Figure 25). At monitoring well FSB-102C, in the eastern downgradient portion of the site, nitrate concentrations reached a maximum in 2006 and remained constant through 2019. Concentrations of nitrate in monitoring well FSB-122C, in the downgradient western portion of the site, have been consistently higher than concentrations in FSB-102C (consistent with published plume maps, e.g., SRNS, 2019). Nitrate concentration reached a maximum at well FSB-122C in 2012 and remained constant into 2019. These patterns are quite consistent with the patterns of nitrate concentrations at Fourmile Branch sampling stations FMC-002F and FM-A7U, suggesting that nitrate measured at those station came primarily from the LAZ. It is likely that the nitrate plume in the UAZ had mostly flushed through by 2000 and Fourmile Branch is now receiving the lagging LAZ plume.

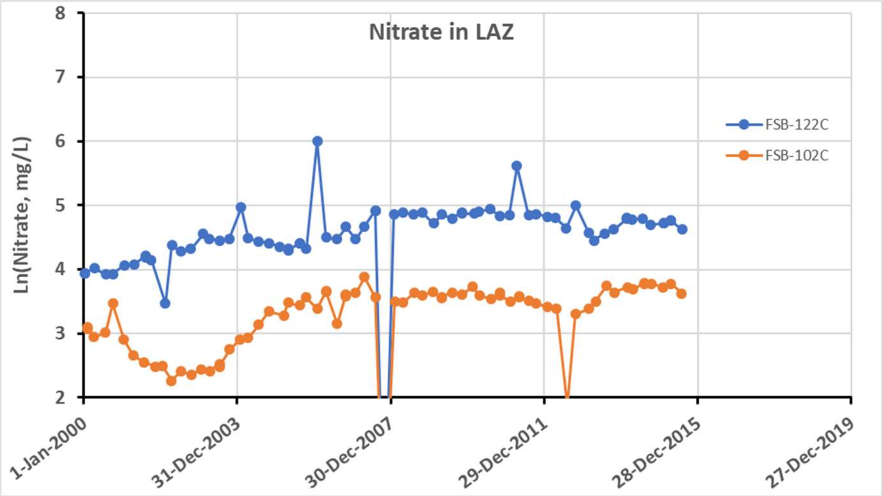

Figure 25: Concentration vs. time trends for nitrate in LAZ well FSB-122C and FSB-102C.

<u>Lines of Inquiry</u>

- What are the patterns of groundwater flow and contaminant migration, both horizontal and vertical, beneath the wetlands and do they affect interpretation of monitoring data?

- How would groundwater flow and contaminant migration in the wetlands affect consideration of remedial actions in the wetlands, including injection of base or other amendments?

2.3 Specific Conceptual Model Enhancements Related to Remediation

The general conceptual model enhancements discussed in the previous section address areas in which additional knowledge would improve overall understanding of the F-Area and H-Area Seepage Basins hydrogeology and geochemistry. This, in turn, improves overall understanding of remediation and monitoring. This section focuses on specific aspects of the conceptual model that relate directly to the enhanced attenuation remedies currently employed to treat groundwater contaminants. Some of the conceptual model aspects discussed here have been discussed in previous documents (e.g., Denham, 2011 [Appendix 2], Denham, 2013 [Appendix 3], and Denham and Amidon, 2016).

2.3.1 Groundwater Flow Near Gates

Groundwater flow near the gates is complicated. The subsurface barrier forces groundwater toward the gates. Once through the gates, groundwater near the edges tends to flow around the wall in response to the lower potentiometric surface on the downgradient side. Figure 26 depicts a generalized conception of the nature of the flow lines near the gates. There is also a vertical component of groundwater flow because groundwater moving in the troughs on top of the TCCZ is forced up and into the gates by the subsurface barriers. The troughs are preferential flow paths for the contamination plume and groundwater from the troughs likely contains higher concentrations of contaminants than other groundwater entering the gates. As discussed previously the proximity of seepline springs to the gates also influences groundwater flow as is passes through the gates. The complicated flow paths for contaminants are not fully understood. Acquiring more knowledge of these flow paths would create the opportunity to improve both remediation and monitoring of remediation.

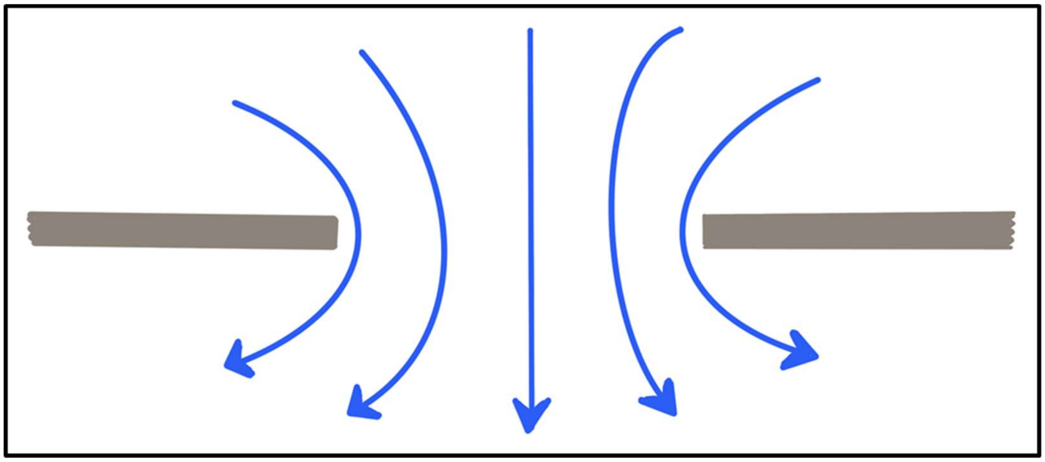

Figure 26: Idealized map view of groundwater flow lines through a gate in the funnel-and-gate.

2.3.1.1 Fluctuations in Contaminant Concentration in Gates

Denham et al. (2015) presented concentration versus time trends for I-129 in wells FSB-130D and FSB-131D, noting that the concentrations in both wells had decreased from highs >100 pCi/L in 2011 to lows <10 pCi/L since the water table began rising in 2013. A decrease in tritium concentration and specific conductance was also correlated with the rising water table. Denham et al. (2015) hypothesized that the decreases could be a function of reduced flow of contaminants from the troughs into the middle gate in response to the elevation of the water table. The thought was that when contamination moving on the top of the TCCZ in the troughs encounters the subsurface barrier most is forced up into the gates, but some may be forced downward into the TCCZ. The fraction of each vertical component may vary with the elevation of the water table, with more contamination from the troughs entering the gate during periods with a low water table. Silver chloride injections began when it appears that I-129 concentrations coming into the gate were at an anomalous high that correlated to the lowest elevation the water table had been since at least 1990. The main point raised by Denham et al. (2015) was that whatever caused the highly dynamic fluctuations in I-129 and other contaminant concentrations needs to be understood to properly target remediation both temporally and spatially.

Simple dilution does not account for the variations in concentrations of contaminants at the middle gate because contaminant concentrations do not vary proportionately. Table 2 shows the ratio of five contaminant concentrations before the increase in water table elevation to their concentrations after the increase. If dilution was the cause of concentration decrease, then the ratios should be similar. Tritium concentration varied the most followed by I-129 and nitrate. Strontium-90 and U-238 concentrations were unaffected by the increased elevation of the water table.

Table 2: Concentrations of five contaminants on two dates at well FSB-130D in the middle gate of the F-Area funnel-and-gate system and the ratio C1/C2.

Contaminant	C1 on 10/18/2012 (pCi/L)	C2 on 2/1/2017 (pCi/L)	C1/C2
Tritium	172,000	13,600	20.9
I-129	90	22	8.4
Nitrate	25.3	4.9	4.9
Sr-90	14	22	1.1
U-238	71	65	1.6

Lines of Inquiry for Groundwater Flow Near Gates

- What are groundwater flow patterns near the gates and how do they affect monitoring and remedial actions?
- Are variations in concentrations of tritium, nitrate, and I-129 near the middle gate related to elevation of the water table and, if so, why?

2.3.2 Relative Stratification of Contaminants

In the current conceptual model contamination is stratified and concentrated mostly near the bottom of the UAZ except near the source. Yet, the current conceptual model does not address the potential for stratification of contaminants relative to one another. Partial segregation of contaminants into different vertical zones could have occurred because of the pH controlled differential mobilities of the contaminants and the downward hydraulic gradient. Tritium is unaffected by pH and nitrate is minimally affected. I-129 attenuation becomes significant at pH values below approximately 3.5 (Emerson et al. 2014), whereas uranium and Sr-90 are highly mobile at such low pH values. Attenuation of uranium and Sr-90 becomes significant near pH 4.5 for uranium and 5.5 for Sr-90. As water initially left the basin soils, I-129 was free to move downward with tritium and nitrate because the low pH gradient moved more slowly than groundwater. In contrast, uranium and Sr-90 were initially attenuated and could only move downward with the acidic gradient. Currently, the acidic pH gradient has approached the base of the UAZ, and a neutralizing gradient has been established in the upper portion of the UAZ by higher pH infiltration. The vertical pH gradients could maintain a vertical segregation of the contaminants.

Vertical segregation of uranium from tritium and nitrate was observed by Wan et al. (2013) in analysis of cored materials collected by the Attenuation-Based Remedies Applied Field Research Initiative funded by the Department of Energy Office of Environmental Management (DOE-EM). Figure 27 shows the results of extraction of pore water chemistry from vertically discrete core samples. Tritium and nitrate are most concentrated near the base of the UAZ, but vertical distribution of uranium is controlled by the vertical distribution of pH.

Assessing whether vertical distribution of contaminants is significant is important to maximize effectiveness and efficiency of remediation. Whether the remedy is pump-and-treat or an in situ attenuation-based strategy, the vertical zones in which the contaminants are most concentrated should be the targets of the remediation. Likewise, monitoring should focus on the most concentrated vertical portions of the plume for each contaminant. It should also be recognized that any vertical segregation of contaminants is likely to change with time.

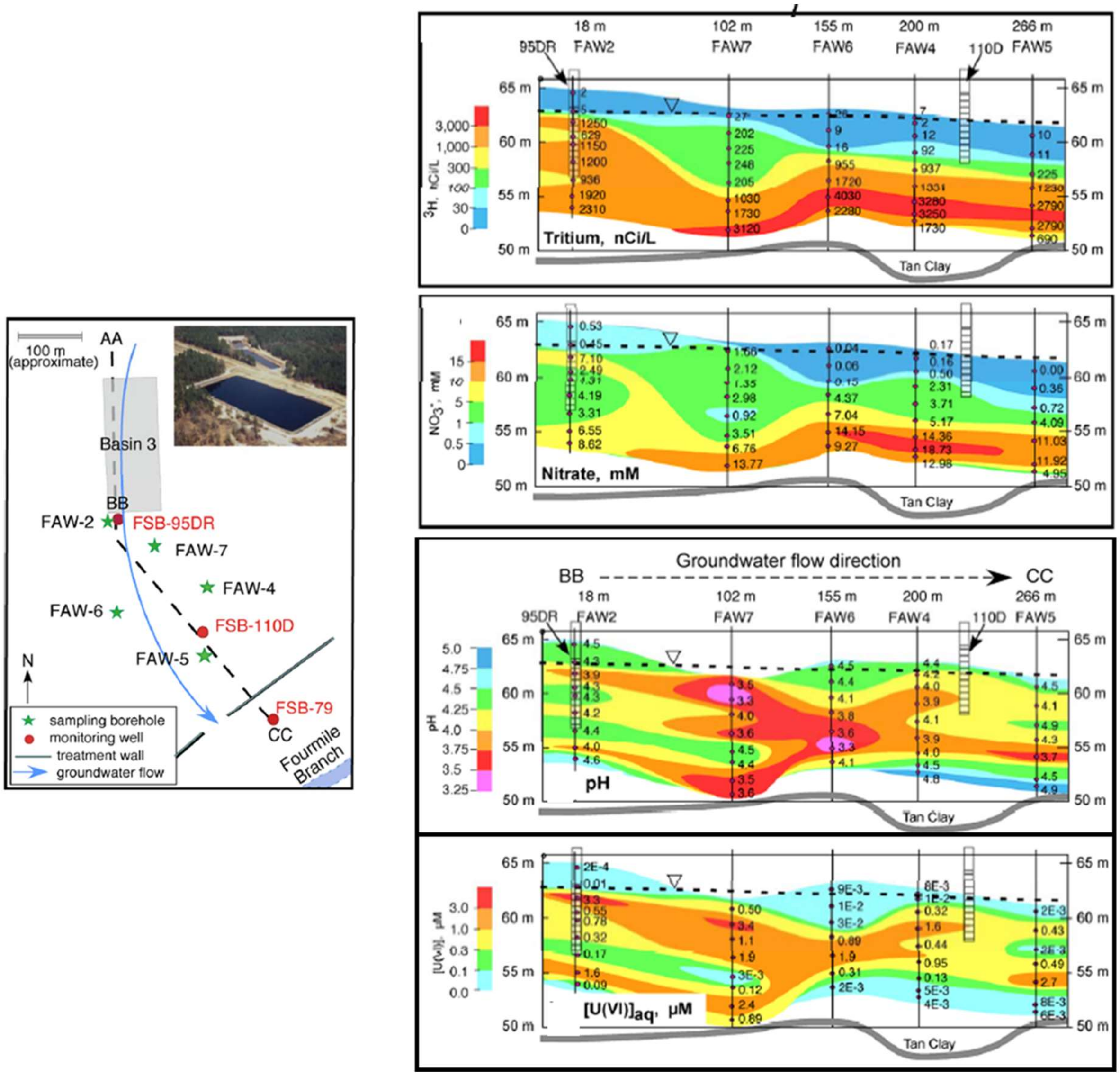

Figure 27: Figures from Wan et al. (2013) showing cross-sectional distribution of tritium, nitrate, pH, and uranium in the UAZ of the F-Area Seepage Basins site, based on depth discrete analysis of pore water composition from 5 cores.

<u>Lines of Inquiry</u>

- Is there vertical segregation of contaminants and is it significant enough to map?
- If there is significant vertical segregation of contaminants, how does this affect monitoring and remediation?
- If there is significant vertical segregation of contaminants, is it solely the result of pH or do low permeability zones play a role (e.g., low permeability zones remaining acidic allowing higher concentrations of uranium and Sr-90 in groundwater)?
- Is continuation of base injection in the wetlands necessary and, if so, have base requirements changed?

2.3.3 Base Injection Conceptual Model Enhancements

The attenuation-based strategy of base injection exploits the tendency of uranium and Sr-90 to adsorb to mineral surfaces, as well as potentially precipitate in a mineral form, at pH values greater than the acidic pH values of the contaminant plume. Monitoring data at the F-Area Seepage Basins and the extensive scientific study of uranium (VI) suggest it tends to adsorb strongly at pH values ≥4.5. Monitoring data at the site indicates Sr-90 sorbs well at pH values ≥5.5. Thus, both contaminants will be attenuated at the natural pH values of the site, approximately pH=6.

When base injection was first considered as a remedial strategy at the F-Area and H-Area Seepage Basins, the decision had to be made whether to attempt to elevate the pH of the entire contaminated portion of the aquifer or focus on a specific portion. The only way to do that would have been to expand the existing pump-and-treat system and continue to operate it for years to capture contaminants that would remain mobile (tritium) or become more mobile (I-129) during base injection. At the F-Area Seepage Basins the comprehensive attenuation-based strategy of the funnel-and-gate system was selected to both minimize the migration of tritium and treat uranium and Sr-90 by injection of base in the gates. This also allows I-129 to be treated at the gates. A periodic maintenance dose of base in the gates is required because of the influx of acidic contamination from upgradient. The upgradient acidity is slowly being neutralized by influx of clean groundwater and recharge and the periodic maintenance doses of base will continue until groundwater entering the gates has reached a pH that sustains the attenuation of uranium and Sr-90.

The conceptual model for base injection would be enhanced by understanding how long it will take for groundwater entering the gates to reach a pH that is protective of the attenuated uranium and Sr-90. An important aspect of this enhancement will be to consider how the protective pH varies with time because of the relatively short half-life of Sr-90 (28.7 years). In 100 years attenuated Sr-90 will have decayed for 3 half-lives, but essentially all the attenuated uranium will remain. Thus, over time the protective pH of groundwater flowing into the gates will be reduced from 5.5 to 4.5. This could substantially reduce the length of time required for continuing periodic maintenance doses of base at the F-Area Seepage Basins.

Previous studies have noted that the relatively high concentration of carbonate ions in the base solution that is periodically injected into the gates may remobilize some uranium attenuated downgradient of the gates (Denham, 2011; Denham, 2017; Nichols and Dickson, 2019). These studies suggested that an optimization of the base injection strategy would be to change the base solution to one with no carbonate. Bethke (2006) proposed using sodium disilicate (and other bases) to raise pH of aquifers with acidic and metal contamination. An advantage of dissolved silica is that it may cause uranium to precipitate as an insoluble silicate; a disadvantage is that the aquifer may become clogged with precipitated silica minerals. Denham et al. (2014) did a field test of humate solution to enhance attenuation of uranium, following successful laboratory studies of Wan et al. (2011). The humate solution used in these tests was meant to enhance uranium attenuation in acidic conditions and would pose a problem similar to the use of the carbonate base, initial remobilization of some attenuated uranium. Yet, more refined humate solutions may not have this problem. Szecsody et al. (2010) and Truex et al. (2018) tested ammonia gas as an amendment to raise pH in the deep vadose zone at Hanford. Thus, there are several base solutions that could potentially replace the carbonate base used currently.

Prior to investigating any new base solution, it will be important to update the conceptual model for base injection so that the solution matches the need. The original carbonate solution was selected because a high alkalinity solution with a pH ≤10 was required to neutralize the high acidity of mineral surfaces at the original groundwater pH values of approximately 3.5. Under those conditions, remobilization of uranium was not an issue because little uranium was adsorbed to mineral surfaces at pH<4. Such acidic conditions no longer exist downgradient of the gates. Hence, the conceptual model should be updated to reflect the current needs for a base solution. A solution with a lower pH and considerably lower alkalinity may be acceptable.

Base is also injected periodically into groundwater beneath the wetlands at both F-Area and H-Area. In a review of wetland base injection, Denham (2017b) recommended that base injection in the wetlands of F-Area should be reviewed in more detail and injections adjusted accordingly. The trends of uranium and Sr-90 concentrations at the time suggested that these contaminants soon be would be below MCLs without base injection. It was also observed that base injection into the H-Area wetlands had little effect on groundwater chemistry. It was recommended that H-Area wetland base injection wells be examined for silting problems that would minimize injection effects. If there are no issues with the wells, then either replacement wells in more appropriate locations should be considered or base injection into the H-Area wetlands should be discontinued.

Lines of Inquiry

- How long will it take for the pH of groundwater upgradient of the gates to reach a pH that is protective of Sr-90 and uranium attenuated in the elevated pH zone downgradient of the gates?
- How does the protective pH vary with time?
- What are the current pH and alkalinity needs for a base solution?
- Is there a base solution that would meet the requirements and not risk remobilizing uranium or Sr-90?

2.3.4 Conceptual Model Enhancements for Treatment of I-129

I-129 has the most complicated behavior of the contaminants of concern at the F-Area Seepage Basins. It was observed in an earlier section that I-129 concentrations vary greatly (with tritium and nitrate) at the middle gate and the variation seems connected to water level in the UAZ, whereas Sr-90 and uranium concentrations are unaffected. Some seasonal variation is observed in all contaminants in the wetlands (Denham and Amidon, 2016), but the variation in I-129 concentrations is the greatest and most regular (Denham and Amidon, 2016; Nichols and Dickson, 2019). The reasons for these variations are unknown, yet are important because they bear on if, when, where, and how I-129 should be treated.

Additionally, it is not known what relationship concentrations of I-129 at the gates have with concentrations of I-129 in surface water. It is possible that the high concentrations of I-129 observed at the middle gate in 2011 were anomalous, related to an unusually severe drought. It is also possible that the seasonal high concentrations of I-129 in the wetlands are the result of a process that releases attenuated I-129 and the only influence upgradient I-129 has on concentrations in surface water is how long this process will continue. In other words, I-129 concentrations in wetland surface water could remain seasonally elevated long after I-129 concentrations in upgradient groundwater have been reduced to acceptable levels. For example, the latest seasonal high concentrations at the wetland surface water stations FAS-091 (376 pCi/L) and FAS-096 (258 pCi/L) were greater than the highest concentration ever observed at the monitoring well FSB-130D (154 pCi/L), just upgradient of the middle gate.

It is also important to note that vertical stratification of contaminants may contribute to the disparity in concentrations of I-129 at monitoring well FSB-130D and wetland surface water stations. Well FSB-130D is screened in the top portion of the saturated zone at the middle gate. If I-129 is concentrated in a zone below the screen, then there may be little disparity in the observed concentrations between the wetlands and the middle gate. Regardless, understanding the vertical distribution of I-129 at the middle gate would allow precise targeting of treatment injections. This may be enhanced by depth discrete sampling in wells FSB-142D, FSB-143D, FSB-144D, FSB-145D, and FSB-146D that have screen zones extending to the TCCZ.

Finally, speciation of I-129 in groundwater must be known at both the central and western gates to design effective attenuation-based strategies for remediation. Iodine exists in some combination of iodide (I^-), iodate (IO_3^-), and organically bound iodine in groundwater associated with the F-Area Seepage Basin contamination (Kaplan et al., 2014). The proportions of each species vary with location. Thus, enhanced attenuation strategies must be designed to treat the dominant I-129 species.

The choice of injection of silver chloride to treat iodine in acidic water just upgradient of the middle gate assumed that iodide was the dominant species. It turns out this assumption was valid, but there is a significant fraction of the other two species present (Otosaka et al., 2011). The presence of the other species suggest that the silver chloride treatment is unlikely to reduce the I-129 concentration to less than the MCL of 1 pCi/L. In fact, because of speciation issues, the very low MCL, and spatial heterogeneity in treatment efficiency, it is unlikely that any attenuation-based strategy will reduce I-129 concentrations to the MCL unless the initial concentrations are near 1 pCi/L. A reasonable goal for treatment of I-129 in groundwater is to achieve concentrations at the point of treatment that are low enough for natural processes to reduce concentrations to the MCL at downgradient locations. Thus, success should be judged by the effect downgradient rather than by achievement of the MCL at the point of treatment.

Lines of Inquiry

- What is the speciation of I-129 currently passing through the gates?
- Were the high concentrations of I-129 in the gates in 2011 anomalous or will they likely reoccur?
- Is I-129 primarily confined to a limited vertical zone in the gates?
- What is the effect of treating on I-129 in the gates on I-129 concentrations in surface water of the wetlands and Fourmile Branch?

3.0 Section 2: Lines of Inquiry

This section summarizes the lines of inquiry posed in Section 1 and their importance, and briefly discusses potential investigations into these lines of inquiry. Below the title of each subsection is a reference to the page number for the beginning of the detailed discussion of the topic in Section 1. The lines of inquiry are color coded by priority:

Red = high priority
Green = medium priority
Blue = low priority

Cost and ease of investigating a line of inquiry were not considered in the prioritization. So, there are medium and low priority lines of inquiry that may be inexpensive and easy to investigate, and this may lead to their investigation before or as part of a higher priority line of inquiry.

3.1 Wetland Geochemistry

Ref: Page 26

What are the dominant attenuation mechanisms for I-129, Sr-90, and uranium in the wetlands, how strong is attenuation, can attenuation be enhanced, and what conditions would reverse attenuation?

Importance: There is evidence from soil analysis and the seasonal increases in surface water concentration of I-129, and other contaminants to a lesser extent, that wetland soils have sequestered contaminants. This is consistent with many other studies of wetlands that show strong attenuation of metals in wetland soils. Therefore, the wetlands are a zone of vulnerability as described by Denham et al. (2019); a zone that must be monitored carefully to detect any change in physical and geochemical conditions that could eventually lead to release of the attenuated contaminants. Knowing what parameters to monitor requires understanding the attenuation and release processes.

Investigations: These will consist of a combination of field and laboratory studies. The first step will be to determine the fraction of soil to which the contaminants are bound, organic matter, mineral surfaces, etc. Depth discrete samples should be analyzed to determine the vertical extent of attenuation. It should be determined if the attenuation mechanisms are microbially controlled or purely geochemically controlled. Laboratory studies will use samples from the contaminated wetlands and vary conditions within a range that is naturally occurring to measure release of contaminants from soil. Field mapping of gamma emitters may be done to determine where attenuation is occurring, or has occurred, in the wetlands.

What is the cause of profound seasonal variation in I-129 concentrations, and to lesser extent other contaminants, in wetland surface water?

Importance: The seasonal variations in I-129 concentrations in wetland surface water often result in concentrations that far exceed upgradient groundwater concentrations indicating that I-129 is being released from soils. Understanding this process may allow its mitigation or allow for alternative remedial goals for I-129 to be developed for surface water. For example, if there comes a time when the seasonal lows are below the MCL, but for a few months the concentrations are above the MCL, then the dose model may be adjustable to allow for an alternative concentration level. Likewise, the seasonal variation is a good argument for pursuing a flux-based goal.

Investigations: Adding constituents such as dissolved organic carbon, manganese, and iron to quarterly monitoring data for wetland surface water and wetland groundwater, as well as analyzing filtered and unfiltered samples may add significant insight into the mechanism of seasonal release. Analyzing seasonal speciation of I-129 will also be important. Other studies would be similar to those outlined above for general attenuation mechanisms.

What is the approximate mass of contaminants sequestered in the wetlands?

Importance: Estimating the mass of contaminants sequestered in the wetlands allows estimates of the risk to human health and the environment should conditions occur that release the contaminants.

Investigations: Investigations should begin with existing data compiled in documents such as Gonzalez-Raymat (2019). Any depth discrete analyses combined with GIS estimates of areas affected can be used to estimate contaminated volumes of wetland soil. These estimates will be improved by spectral mapping of gamma emitters. Additional soil samples may be required, guided by the gamma mapping.

What is the microbial involvement in the environmental fate and distribution of iodine in the wetlands?

Importance: Microorganisms can have an effect in the environmental fate and distribution of iodine by catalyzing its oxidation, reduction, accumulation, volatilization and incorporation into organic matter. Some studies have shown that soil bacteria can produce and emit volatile iodine species from rice paddy (Amachi et al. 2001, 2003). Volatile species such as methyl iodide can be emitted to the atmosphere where sunlight breaks down these species converting them into iodine that is deposited back to terrestrial or marine environments with precipitation.

Investigations: Experiments should focus on understand the biological processes that transform iodine species, and how these processes influence iodine volatilization and/or incorporation into organic matter.

3.2 Degradation of Basin Caps

Ref.: Page 28

What processes and parameters associated with the basin caps can be monitored to detect evidence of early cap degradation?

Importance: Current monitoring requires periodic assessment of the basin caps and this will be extended into long-term monitoring. Currently, the assessment of the caps is done by walk-overs and measuring subsidence. Significant improvements in the efficiency of the assessments can be made using advanced remote monitoring. This is particularly important in long-term monitoring.

Investigations: The following are some methods of cap monitoring that could yield valuable information on cap degradation and effectiveness.

- Electrical Resistance Tomography (ERT): ERT allows imaging of electrical conductance of sediments over a large volume of sediment using multiple electrodes and current generators and measuring electrical resistance between the electrodes. Moisture content of the sediments and dissolved salt content in the moisture affect the resistance. Therefore, it is feasible that an ERT network could be installed around or beneath the basins to detect changes in moisture content. Decreases in electrical resistance would indicate a breached cap.

  - Advantages
    - Used widely across DOE sites
    - Experts in ERT at multiple National Labs
    - May not require electrodes beneath the basin to image moisture content beneath basins
    - May also be useful for imaging injection of base solution at gates

  - Disadvantages/Unknowns
    - The magnitude of moisture content change that can be detected in SRS sediments is unknown (i.e., small scale, but important, infiltration through the waste layer beneath the caps may not be detectable.

- Neutron logging: Neutron logging detects changes in moisture content of sediments by measuring the scattered neutrons and gamma emissions resulting from exposure of the formation to a neutron source. This tool essentially measures the amount of hydrogen atoms in the formation, and hence in the absence of hydrocarbons, measures the water content in the formation. Angle boreholes cased with a neutron transparent material (aluminum casing is often used) could be installed from the edges of the basins and extending beneath them. Periodically a neutron logging tool would be lowered into the borehole and withdrawn to measure moisture content of the formation in adjacent to the basins.
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  - Advantages
    - Used for decades in the petroleum industry and more recently used extensively in other applications
    - Simple to use and interpret

  - Disadvantages
    - Requires permanent boreholes beneath the basins
    - Only provides a linear view of moisture content along the borehole, would be easy to miss small-scale cap breaches
    - Administrative hurdles to using and storing a neutron source on the SRS
    - Rare but finite possibility of having a neutron source stuck in the subsurface, creating significant administrative work

It is feasible, but uncertain, that radioactive decay of actinides trapped in the basin soils would produce sufficient helium or radon to be detected at the surface if fractures in the cap provided a pathway to the surface. These might be mappable with spectroscopic tools deployed on unmanned aerial vehicles (UAVs). The use of UAVs for long-term monitoring of the basin caps is discussed at length in Denham et al. (2019).

- Helium: Helium-4 is produced when alpha particles from radioactive decay of actinides and their daughters gain 2 electrons. Detection of anomalous concentrations of helium has long been used in exploration of uranium. The same principle might be used if the mass of radionuclides that decay by alpha emission in the basin soils is high enough to produce helium at a rate that would be detectable as an anomaly at the surface. Similarly, tritium decays to helium-3 that may be detectable as an isotopic anomaly by mass spectrometry.

    - First step is to calculate whether the rate of helium-4 and helium-3 production by radioactive decay is sufficient to pursue this method of fracture detection given the masses of actinides and tritium in the basin soils and upper vadose zone
    - If so, then a method to map concentrations of helium-4, helium-3, or the isotopic ratio of the two would need to be tested.

- Radon: Radon is a daughter of the decay of uranium and actinides, and where it is released to the surface radon daughters that are strong gamma emitters can be detected by aerial gamma surveys. If there is sufficient radon production from actinide decay in the basin soils, then the pattern of radon emanation from the surface of the cap could reveal fractures or other pathways that connect the basin soils with the surface.

    - First step is to calculate the rate of radon production in basin soils and determine if it is high enough for radon to reach the cap surface at detectable concentrations. Radon emanation modeling has been done for the high-level waste tanks and the Saltstone facility. These could potentially be used.

3.3 Low Permeability Zones

Ref.: Page 29

Are there significant low permeability strata within the UAZ that affect remediation and/or progress toward remedial goals?

Importance: If the volume of low permeability horizons in the UAZ is significant and they are distributed throughout the UAZ, then progress toward remedial goals may be hindered by "back diffusion" of contaminants and progress may be underestimated by analyzing contaminant concentration versus time trends. Numerical modeling must also account for low permeability zones if they are significant. If low permeability zones are local, for example confined to the top or the bottom of the UAZ, then their influence may be small. Additionally, the presence of low permeability zones may lengthen the time that acidic conditions are prevalent upgradient of the funnel-and-gate at the F-Area Seepage Basins.

Investigations: Initial investigation should re-analyze the abundant geophysical logs and CPT pushes to evaluate whether low permeability zones are significant and mappable units or are isolated occurrences. Other geophysical data may also be useful, for example the shallow seismic data collected by the Kansas Geological Survey, as well as the cross-hole electrical resistance tomography and shallow resistivity survey conducted by Lawrence Berkeley National Laboratory (LBNL). If the initial investigation suggests that low permeability zones are significant then additional data could be collected with geophysical logs of newer wells and additional CPT pushes.

Are there wells screened in lower permeability zones in which apparent progress toward remedial goals is slower than in other wells and, if so, how is overall progress toward remedial goals assessed?

Importance: If low permeability zones are not significant, then wells screened through or near low permeability zones that extend beyond the well may yield samples that have anomalously high concentrations of contaminants because of diffusion out of the low permeability zones between sampling periods. Any such wells should be identified and accounted for or replaced.

Investigations: The investigation into low permeability zones combined with review of contaminant concentration data from wells screened through or near low permeability zones should identify anomalous wells.

3.4 Vertical Movement of Contaminants

Ref.: Page 33

Does differential migration of contaminants into the LAZ have a significant influence on progress toward remedial goals?

Importance: The fact that contaminants may have migrated into the LAZ from the UAZ at different rates because of a vertical pH gradient means these plumes will arrive at exposure points at different times. Thus, contaminants from the LAZ may arrive at the wetlands or Fourmile Branch years after contaminants in the UAZ have flushed out, temporarily reversing long decreasing concentration trends. Contaminants may arrive at different times, following an order such as tritium/nitrate, then I-129, then Sr-90, and finally uranium.

Investigation: A modeling investigation informed by LAZ monitoring data and including geochemical controls on contaminant migration would be sufficient.

Is there significant flow of groundwater through the TCCZ and into the LAZ along the subsurface barrier, particularly at the troughs on top of the TCCZ?

Importance: If there is significant flow of contaminants through the TCCZ and into the LAZ on the upgradient side of the subsurface barrier this should be accounted for in modeling of contaminant transport and consideration of contaminant behavior in the LAZ. If flow through the TCCZ is greater in the troughs at the top of the TCCZ, that could help account for variations in contaminant concentrations in the middle gate.

Investigations: Potentiometric surface maps of the UAZ and LAZ with data concentrated along the subsurface barrier would provide an indication of enhanced downward flow at the subsurface barriers.

There are not enough wells or piezometers screened in the LAZ to accomplish this, so temporary piezometers would have to be installed or measurements made with CPT.

Where does upward flow of groundwater from the LAZ into the UAZ occur?

Importance: Knowing where upward flow from the LAZ into the UAZ occurs would improve interpretation of monitoring data. If it occurs in the wetlands, then it may influence concentrations of contaminants in UAZ screened wells and piezometers in the wetlands, and potentially wetland surface water stations.

Investigations: The bulk chemistry of groundwater in the LAZ may be sufficiently different than that of the UAZ that ratios of major dissolved ions could be used to indicate whether groundwater in the UAZ at a sampling point has a component that originated in the LAZ. This would require special sampling and analysis because major ion chemistry of groundwater is not routinely collected. If differences in major dissolved ion concentrations are not definitive, then isotopic studies designed to trace groundwater sources and pathways (e.g., stable strontium isotopes) could be investigated. An initial study with the goal of determining if and how UAZ and LAZ groundwater can be distinguished would be done. If groundwater sources can be determined, then a more extensive study would be done to determine spatial and temporal patterns of groundwater flow from the LAZ into the UAZ.

Where groundwater is upwelling from the LAZ, what fraction of each contaminant in wetland surface water and Fourmile Branch is from the LAZ, how will that change with time, and will contamination from the LAZ affect progress toward remedial goals?

Importance: The same as above, but the change with time adds a different aspect, allowing projections of future monitoring trends in the UAZ and surface water in the wetlands.

Investigation: The information on where water moves from the LAZ into the UAZ, and what fraction is from the LAZ could be integrated with concentration versus time trends from nearby LAZ wells to project how concentrations in UAZ wells will change with time.

3.5 Groundwater Flow Beneath Wetlands

Ref.: Page 36

What are the patterns of groundwater flow and contaminant migration, both horizontal and vertical, beneath the wetlands and do they affect interpretation of monitoring data?

Importance: Flow of groundwater becomes more complex as it approaches the wetlands because of a variety of factors -- discharge at the irregular seepline, thinning of the UAZ, and the irregular topography of the top of the TCCZ. Interpretation of monitoring data requires an understanding of what is actually being sampled at a monitoring point and its relation to samples from other monitoring points. Though wetland contaminant monitoring data will continue to be used primarily to assess concentrations relative to MCLs, at some point it is likely that concentrations trends that are not steadily decreasing will have to be explained. Understanding groundwater flow beneath the wetlands will be essential for this type of interpretation.

Investigations: Initial investigation can be done by focused mapping of hydraulic heads in all piezometers and wells, as well as the elevations of all known springs. There are few piezometers and wells in the wetlands that penetrate the LAZ and more may need to be added. Using natural tracers as discussed above to detect chemical signatures indicative of input of groundwater from the LAZ could be done. Survey by unmanned aerial vehicle equipped with LIDAR and other sensors can accurately map elevations of all springs. More detailed investigation could be done with a tracer test using the injection wells currently used in wetland base injection. This could be monitored using temporary screened wells or, possibly, by electrical resistance tomography if a high specific conductance tracer was used.

How would groundwater flow and contaminant migration in the wetlands affect consideration of remedial actions in the wetlands?

Importance: If remediation involving groundwater (e.g., injections, small permeable reactive barriers, etc.) beneath the wetlands is considered, it is essential to understand the flow paths of groundwater and contaminants.

Investigations: Detailed tracer tests focused on the area of remediation would be required.

3.6 Groundwater Flow Near Gates

Ref.: Page 42

What are groundwater flow patterns near the gates and how do they affect monitoring and remedial actions?

Importance: Flow paths of groundwater are perturbed by flow through the gates of the funnel-and-gate. It is important to understand these flow paths to optimize treatment of contaminants and optimize monitoring of those treatments.

Investigation: Detailed maps of hydraulic heads using all available wells and piezometers near the gates should be done. Ideally, some additional piezometers would be installed on either side of the subsurface barrier on both ends of the barrier that form a gate. Water level measurements from CPT pushes could also be used to make the water table maps.

Are variations in concentrations of tritium, nitrate, and I-129 in near the middle gate related to elevation of the water table and, if so, why?

Importance: Concentrations of I-129, tritium, and nitrate in the middle gate were at their highest when the water table was the lowest it has been since 1990. When the water table returned to more historical norms, concentrations of these contaminants decreased. It is important to understand any relationship between contaminant concentrations and water table elevation to be able to distinguish this effect on concentrations from the effects of treatment in the gates. Additionally, it is important to know whether the high concentrations were anomalous or will frequently reoccur.

Investigation: A detailed investigation of all data associated with well FSB-130D and other near-by wells such as FSB-126D and FSB-125D should be done to determine parameters that correlate with I-129, tritium, and nitrate concentrations. If it is found that water table elevation is a key control on contaminant concentrations in the gates, then an important aspect of the investigation will be to establish whether there is a critical water table elevation that triggers an increase in concentrations. This is particularly important for assessing any remedial actions proposed for upgradient of the funnel-and-gate that might lower the water table.

3.7 Relative Stratification of Contaminants

Ref.: Page 44

Is there vertical segregation of contaminants and is it significant enough to map?

Importance: If there is vertical segregation of contaminants, monitoring data from wells that are not screened across all "layers" of contaminants are not providing representative data. It has long been known that the bulk plume is vertically confined to a relatively narrow range in the saturated zone of the UAZ. This has mostly been based on measurements of tritium, pH, and specific conductance. However, the disparate geochemical behavior of contaminants suggests the possibility that some contaminants may be segregated vertically within the bulk plume. For example, the disparate behavior of I-129 and uranium with respect to pH could lead to their vertical segregation within the plume.

Investigation: The first step would be depth discrete water sampling and analysis of contaminants from wells spanning the horizontal and vertical extent of the plume. Wells with long screens, such as FSB-78, FSB-79, and FAW-5, would provide the best data. If vertical segregation of contaminants exists, then additional wells with screens spanning the UAZ saturated zone could be installed and periodic depth discrete sampling done to evaluate the vertical position of contaminants with time.

If there is significant vertical segregation of contaminants, is it solely the result of pH or do low permeability zones play a role (e.g., low permeability zones remaining acidic allowing higher concentrations of uranium and Sr-90 in groundwater)?

Importance: Understanding the cause of any vertical segregation of contaminants would improve the knowledge of how pervasive the segregation is throughout the plume. For example, there may be localized low permeability zones that maintain a lower pH than the surrounding sands. This could lead to localized vertical segregation of Sr-90 and uranium from I-129.

Investigation: If vertical segregation of contaminants is found only in a few wells, then depth discrete samples and analyses should be compared to well logs or near-by CPT pushes to see if contaminant concentrations correlate with low permeability zones.

3.8 Base Injection Optimization

Ref.: Page 46

How long will it take for the pH of groundwater upgradient of the gates to reach a pH that is protective of Sr-90 and uranium attenuated in the elevated pH zone downgradient of the gates?

Importance: Periodic base injection in the gates will need to be done until acidity of groundwater upgradient of the injections decreases and pH entering the gates is protective of attenuated Sr-90 and uranium. It is unknown how long that will be.

Investigation: The first step is to analyze the pH versus time curves for the sentry well in each gate. These curves can be viewed as in situ titration curves and may be valuable in predicting how long base injection must continue. Column studies and numerical modeling may also be done. The results of these studies will be projected pH versus time curves. In addition, this data can be used in a numerical model to predict the rate of pH increase.

How does the protective pH vary with time?

Importance: The protective pH will vary with time as Sr-90 decays. The protective pH for Sr-90 is approximately 5.5 compared to 4.5 for uranium. Therefore, in 100 years much of the attenuated Sr-90 will have decayed and the protective pH will change from 5.5 to 4.5. The time required for upgradient groundwater to reach a pH of 4.5 is shorter than the time required to reach 5.5.

Investigation: A calculation or model of the estimated mass of Sr-90 attenuated and how long it will take to decay to a point that the risk of release of remaining Sr-90 is acceptable.

What are the current pH and alkalinity needs for a base solution?

Importance: Conditions have changed since base injections began and the pH and alkalinity of the base solution can be adjusted to meet current needs. In particular, the carbonate alkalinity should be reduced to minimize mobilization of attenuated uranium by carbonate complexing.

Investigation: The first step will be geochemical modeling based on pH and acidity of groundwater entering the gates and the nature of mineral surfaces in the treatment zone. The next step would be column studies simulating the behavior of the treatment zone. It may be found that a much lower alkalinity solution could be injected more frequently to achieve remedial goals. In that case, a comparative cost analysis should be done to evaluate higher frequency, lower alkalinity injections.

Is there a base solution that would meet the requirements and not risk remobilizing uranium or Sr-90?

Importance: Ideally, it would be best to switch to a non-carbonate base solution to avoid any mobilization of attenuated uranium by carbonate complexing.

Investigation: The first step will be a literature survey of potential base solutions that would be acceptable to regulators and potentially meet remedial objectives. The second step would be geochemical modeling to assess potential performance and collateral effects. Finally, batch and column studies should be done to narrow the range of effective compositions of potential base solutions.

Is continuation of base injection in the wetlands necessary and, if so, have base requirements changed?

Importance: If base injection in the wetlands is no longer necessary, then discontinuation would be a cost savings and simplify interpretation of monitoring date in the wetlands?

Investigation: Reassess effects of base injection into wetland groundwater on contaminant concentrations in groundwater and wetland surface water using the latest monitoring data. Check the H-Area wetland injection wells to evaluate whether significant portions of the screens are blocked by silt infiltration into the wells.

3.9 Treatment of I-129 Options

Ref.: Page 47

What is the speciation of I-129 currently passing through the gates?

Importance: Silver chloride injections were designed to treat I-129 occurring as iodide and are not likely to effectively remove iodate and organo-iodide from groundwater. Initial studies suggested that the speciation of I-129 in groundwater entering the gates was dominated by iodide. However, the original data were sparse, and speciation may have changed.

Investigation: Analyze speciation of I-129 in groundwater entering the gates several times over a period of a year.

Were the high concentrations of I-129 in the gates in 2011 anomalous or will they likely reoccur?

Importance: When injections of silver chloride particles began, the concentrations of I-129 were higher than they had been at FSB-130D, the well just upgradient of the middle gate. Since then, concentrations of I-129 have decreased substantially. If the high concentration of I-129 was anomalous, the need for injections of silver chloride should be re-evaluated.

Investigation: A detailed parametric investigation of all data associated with well FSB-130D and other near-by wells such as FSB-126D and FSB-125D should be done to determine parameters that correlate with I-129 concentrations.

Is I-129 primarily confined to a limited vertical zone in the gates?

Importance: Silver chloride particle injections have been done over a wide depth range. If I-129 is mostly concentrated in a narrow depth range, then injections should target this zone. Also, vertical stratification of I-129 may, in part, explain the variations in concentration at the middle gate.

Investigation: Depth discrete samples should be obtained and analyzed for I-129 from all wells used to monitor effectiveness of the silver chloride injections. Additionally, depth discrete samples from well FAW-5 that is screened across the entire saturated zone could be obtained and analyzed for I-129.

What is the effect of treating on I-129 in the gates on I-129 concentrations in surface water of the wetlands and Fourmile Branch?

Importance: If there is no discernable effect of removing I-129 from groundwater at the gates on I-129 concentrations in surface water, then re-evaluation of the need for silver chloride injections may be warranted. If there is a sufficient mass of I-129 attenuated in the wetlands, then seasonal high concentrations exceeding the MCL may occur for a long time after I-129 ceases to enter the wetlands.

Investigation: This investigation should proceed only pending the results of the wetland geochemistry tasks and continued evaluation of the effectiveness of the silver chloride injections on removing I-129 at the gates.

4.0 References

Aadland, R.K., J.A. Gellici, and P.A. Thayer, 1995. Hydrogeologic Framework of West-Central South Carolina. State of South Carolina Department of Natural Resources, Water Resources Division Report 5. South Carolina Department of Natural Resources, Columbia, SC.

Barnett, M.O., P.M. Jardine, and S.C. Brooks. 2002. U(VI) adsorption to heterogeneous subsurface media: Application of a surface complexation model. *Environmental Science & Technology*, 36, 937-942.

Batson, V. L., P. M. Bertsch, and B. E. Herbert. 1996. Transport of Anthropogenic Uranium from Sediments to Surface Waters During Episodic Storm Events. *J. Environ. Qual.* 25:1129-1137. doi:10.2134/jeq1996.00472425002500050028x

Bethke, C.M., 2006. In Situ Treatment Process to Remove Metal Contamination from Groundwater. U.S. Patent No.: 7,141,173 B2.

Chen, C-C. and K.F. Hayes. 1999. X-ray absorption spectroscopy investigation of aqueous Co(II) and Sr(II) sorption at clay-water interfaces. *Geochimica et Cosmochimica Acta*, 63, 3205-3215.

Denham, M. and K. Vangelas, 2009. Biogeochemical gradients as a framework for understanding waste-site evolution. *Remediation*, 19, 5-17.

Denham, M. 2017a. Observations on Acidic Rebound Following Base Injection at the F-Area Central Gate. SRNL-L3200-2017-00090. Savannah River National Laboratory, Aiken, SC.

Denham, M. 2017b. Evaluation of base injection beneath Fourmile Branch wetlands. SRNL-L3200-2017-00116, Rev. 1. Savannah River National Laboratory, Aiken, SC.

Denham, M., 2011. Base Injection: An Assessment of Opportunities for Optimization. SRNL-TR-2011-00009. Savannah River National Laboratory, Aiken, SC.

Denham, M., 2013. Reassessment of Monitoring Data for I-129 Remediation by the Silver Chloride Treatment Zone. Memorandum to G. Blount, SRNL-L3200-2013-00011. Savannah River National Laboratory, Aiken, SC.

Denham, M.E. and M.B. Amidon. 2016. Analysis of Concentration Versus Time Trends for Select Contaminants in Groundwater and Wetland Surface Water Associated with the F-Area and H-Area Seepage Basins. SRNL-STI-2016-00558, Savannah River National Laboratory, Aiken, SC.

Denham, M. and K.M. Vangelas. 2008. Biogeochemical gradients as a framework for understanding waste-site evolution. *Remediation Journal*. 19, 5-17. https://doi.org/10.1002/rem.20188

Denham, M.E., C.A. Eddy-Dilek, H.M. Wainwright, J. Thibault, and K. Boerstler, 2019. A New Paradigm for Long Term Monitoring at the F-Area Seepage Basins, Savannah River Site. SRNL-STI-2019-00019. Savannah River National Laboratory, Aiken, SC.

Denham, M.E., M.B. Amidon, M.R. Millings, and R.L. Nichols, 2015. Evaluation of Contingencies and Opportunities to Optimize the Silver Chloride Technology to Treat 129I in Groundwater. SRNL-TR-2015-00214. Savannah River National Laboratory, Aiken, SC.

Denham, M.E., M.B. Amidon, M.R. Millings, K.A. Roberts, H. Gonzalez Raymat, B.B. Looney, and C.A. Eddy-Dilek, 2013. A Single Well Field Injection Test of Humate to Enhance Attenuation of Uranium and Other Radionuclides in an Acidic Plume. SRNL-STI-2014-00427, Savannah River National Laboratory, Aiken, SC.

Dong, W., T.K. Tokunaga, J.A. Davis, and J. Wan. 2012. Uranium(VI) adsorption and surface complexation modeling onto background sediments from the F-Area Savannah River Site. *Environmental Science & Technology*, 46, 1565-1571.

Du Laing, G., J. Rinklebe, B. Vandecasteele, E. Meers, and F.M.G. Tack. 2009. Trace metal behavior in estuarine and riverine floodplain soils and sediments: A review. *Science of the Total Environment*, 407, 3972-3985.

Emerson, H.P., C. Xu, Y.F. Ho, S. Zhang, K.A. Schwehr, M.Lilley, D.I. Kaplan, P.H. Santschi, and B.A. Powell. 2014. Geochemical controls on iodine uptake and transport in Savannah River Site subsurface soils. *Applied Geochemistry*, 45, 105-113.

Fallaw, W.C. and V. Price, 1995. Stratigraphy of the Savannah River Site and Vicinity. Southeastern Geology, 35, 21-58.

Flach, G.P., 2002. An Evaluation of Dual-Media Contaminant Transport for SRS Environmental Applications (U). WSRC-TR-2002-00291, Westinghouse Savannah River Company, Aiken, SC 29808.

Flach, G.P., M.K. Harris, R.A. Hiergesell, A.D. Smits, and K.L. Hankins, 1999. Regional Groundwater Flow Model for C, K, L, and P Reactor Areas, Savannah River Site, Aiken, SC. WSRC-TR-99-00248. Westinghouse Savannah River Company, Aiken, SC.

Flach, G.P., S.A. Crisman, and F.J. Molz III, 2004. Comparison of single-domain and dual-domain subsurface transport models. Groundwater, 42, 815-828.

Frohne, T., J. Rinklebe, R.A. Diaz-Bone, and G. Du Laing. 2011. Controlled variation of redox conditions in a floodplain soil: impact on metal mobilization and biomethylation of arsenic and antimony. *Geoderma*, 160, 414-424.

Fukui, M., Y. Fujikawa, and N. Satta. 1996. Factors affecting interaction of radioiodide and iodate species with soil. *Journal of Environmental Radioactivity*, 31, 199-216.

Gonzalez-Raymat, H. 2019. A Summary of Monitoring Data Collected in the Wetlands Associated with the F-Area Seepage Basins. SRNL-TR-2019-00144. Savannah River National Laboratory, Aiken, SC.

Hiergesell, R.A. and W.P. Kubilius, 2016. Radionuclide Inventories for the F- and H-Area Seepage Basin Groundwater Plumes. SRNL-STI-2016-00273, Rev. 0. Savannah River National Laboratory, Aiken, SC.

Hsi, C-K.D. and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica et Cosmochimica Acta*, 49, 1931-1941.

Kaplan, D.I., K.A. Roberts, K.A. Schwehr, M.S. Lilley, R. Brinkmeyer, M.E. Denham, D. DiPrete, H.-P. Li, B.A. Powell, C. Xu, C.M. Yeager, S.J. Zhang, P.H. Santschi. 2011. Evaluation of a radioiodine plume increasing in concentration at the Savannah River Site, *Environmental Science & Technology*, 45, 489-495.

Killian, T.H., N.L. Kolb, P. Corbo, and I.W. Marine, 1987a. Environmental Information Document: F-Area Seepage Basins. DPST-85-704. E.I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC.

Killian, T.H., N.L. Kolb, P. Corbo, and I.W. Marine, 1987b. Environmental Information Document: H-Area Seepage Basins. DPST-85-706. E.I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC.

Nichols, R.L. and J.O. Dickson, 2019. Evaluation of Constituents of Concern Above Primary Drinking Water Standards at the F- and H-Area Wetlands (Phase 2b Corrective Action Goal). SRNL-STI-2019-00234 (Revision Draft). Savannah River National Laboratory, Aiken, SC.

Otosaka, S., K.A. Schwehr, D.I. Kaplan, K.A. Roberts, S. Zhang, C. Xu, H-P. Li, Y-F. Ho, R. Brinkmeyer, C.M. Yeager, and P.H. Santschi, 2011. Factors controlling mobility of ^{127}I and ^{129}I species in an acidic groundwater plume at the Savannah River Site. *Science of the Total Environment*, 409, 3857-3865.

SCDHEC. 2017. *South Carolina Department of Health and Environmental Control Hazardous and Mixed Waste Permit, Permit Number SC1 898 008 989*, 2014 RCRA Permit Renewal for the Savannah River Site, issued on February 11, 2014, modified on August 17, 2017 and modification effective on September 2, 2017, Module IV – Groundwater Requirements, Section B, F-Area Hazardous Waste Management Facility, South Carolina Department of Health and Environmental Control, Office of Environmental Quality Control, Bureau of Land and Waste Management, Columbia, SC

Small, T.D., L.A. Warren, E.E. Roden, and F.G. Ferris. 1999. Sorption of strontium by bacteria, Fe(III) oxide, and bacteria-Fe(III) oxide composites. *Environmental Science & Technology*, 33, 4465-4470.

SRNS, 2018. Annual Corrective Action Report for the F-Area Hazardous Waste Management Facility, the H-Area Hazardous Waste Management Facility, and the Mixed Waste Management Facility (U). SRNS-RP-2018-00252. Savannah River Nuclear Solutions, Aiken, SC.

Szecsody, J.E., M.J. Truex, L. Zhong, M.D. Williams, C.T. Resch, J.P. McKinley, 2010. Remediation of Uranium in the Hanford Vadose Zone Using Gas-Transported Reactants: Laboratory-Scale Experiments. PNNL-18879. Pacific Northwest National Laboratory, Richland, WA.

Tokunaga, T., J. Wan, and M. Denham. 2012. Estimates of Vadose Zone Drainage from a Capped Seepage Basin, F-Area, Savannah River Site. *Vadose Zone Journal*. 11. 10.2136/vzj2011.0131

Truex, M.J., J.E. Szecsody, C.E. Strickland, D.A. St. John, M.M Snyder, C.T. Resch, M.D. Miller, Z. Wang, S.A. Saslow, M.E. Bowden, S.R. Baum, I.I. Leavy, B.N. Gartman, R.E. Clayton, W.L. Garcia, and E.C. Gillispie, 2018. Deep Vadose Zone Treatability Test of Uranium Reactive Gas Sequestration for the Hanford Central Plateau: Final Report. PNNL-27773. Pacific Northwest National Laboratory, Richland, WA.

Um, W., R.J. Serne, and K.M. Krupka. 2004. Linearity and reversibility of iodide adsorption on sediments from Hanford, Washington under water saturated conditions. *Water Research*, 38, 2009-2016.

Wallace, S.H., S. Shaw, K. Morris, J.S. Small, A.J. Fuller, and I.T. Burke. 2012. Effect of groundwater pH and ionic strength on strontium sorption in aquifer sediments: Implications for 90Sr mobility at contaminated nuclear sites. *Applied Geochemistry*, 27, 1482-1491.

Wan, J., T. Tokunaga, W. Wong, M. Denham, and S. Hubbard, 2012. Persistent source influences on the trailing edge of a groundwater plume, and natural attenuation timeframes: The F-Area Savannah River Site. *Environmental Science & Technology*, 46, 4490-4497.

Wan, J., Tokunaga, T. K., Dong, W., Denham, M. E., and Hubbard, S. S. 2012. Persistent Source Influences on the Trailing Edge of a Groundwater Plume, and Natural Attenuation Timeframes: The F-Area Savannah River Site. *Environmental Science & Technology*. 5735.

Wan, J., W. Dong, and T.K. Tokunaga, 2011, Method to attenuate U(VI) mobility in acidic waste plumes using humic acids. *Environmental Science & Technology*, 45, 2331-2337.

WSRC, 1998. H-Area Hazardous Waste Management Facility Corrective Action Report (U), Third and Fourth Quarter 1997, Volume 1. WSRC-TR-98-00004. Westinghouse Savannah River Company, Aiken, SC.

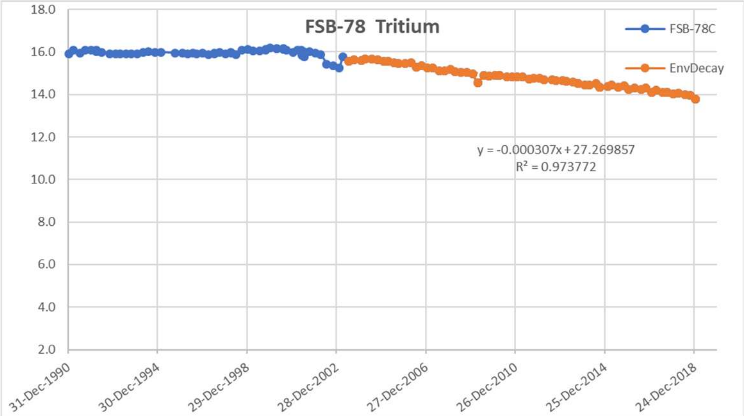
WSRC, 2000. F-Area Hazardous Waste Management Facility Corrective Action Report(U), Third and Fourth Quarter 1999, Volume 1. WSRC-TR-1999-00266. Westinghouse Savannah River Company, Aiken, SC.

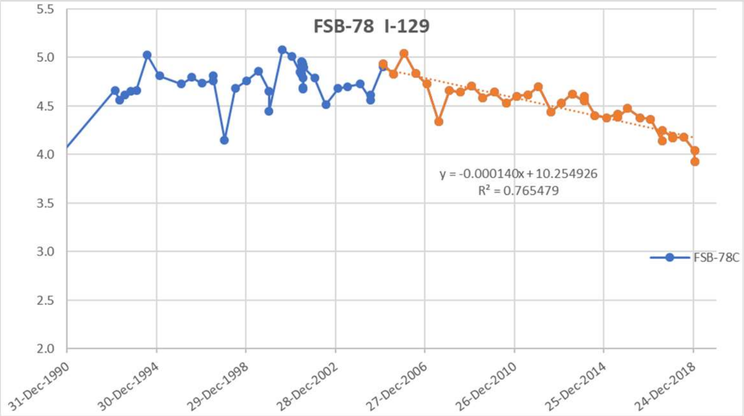
WSRC, 2002. Technical Report for Vertical Extent Characterization at the S- and H-Area Seepage Basins(U). WSRC-RP-2002-4090, Rev. 0. Westinghouse Savannah River Company, Aiken, SC.

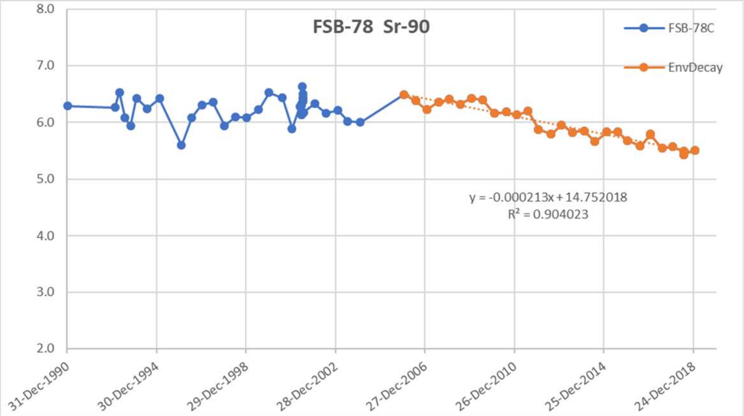
Xu, C., S. Zhang, Y-F. Ho, E.J. Miller, K.A. Roberts, H-P. Li, K.A. Schwehr, S. Otosaka, D.I. Kaplan, R. Brinkmeyer, C.M. Yeager, and P.H. Santschi. 2011. Is Soil natural organic matter a sink or source for mobile radioiodine (^{129}I) at the Savannah River Site?. Geochimica et Cosmochimica Acta, 75, 5716.

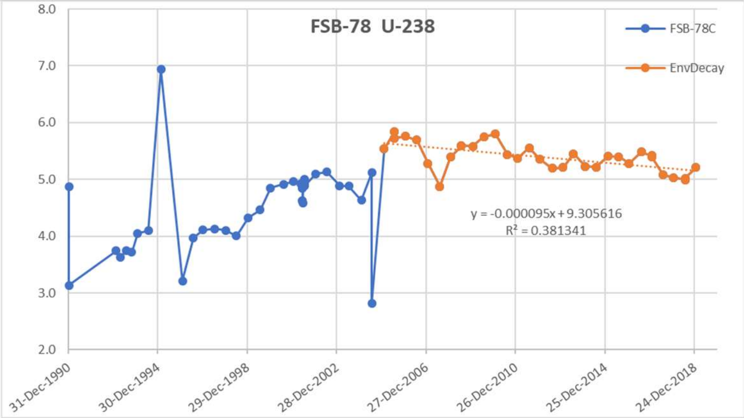
Yoshida, S., Y. Muramatsu, and S. Uchida. 1992.. *Water Air and Soil Pollution*, 63, 321. https://doi.org/10.1007/BF00475499.

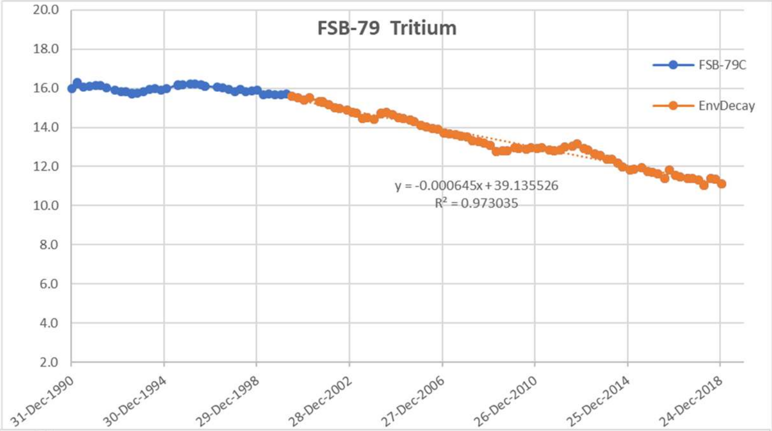
5.0 Appendix 1: Concentrations Versus Time Trends for the LAZ

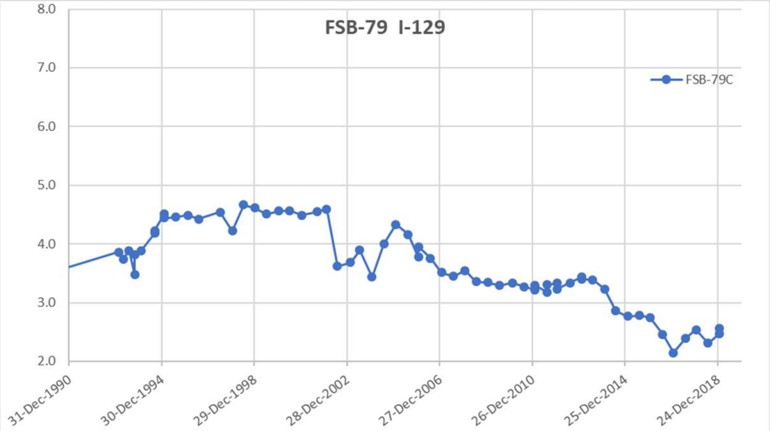









FSB-79 Tritium
FSB-79C
EnvDecay
y = -0.000645x + 39.135526
R² = 0.973035
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018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FSB-79C
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7.0
6.0
5.0
4.0
3.0
2.0
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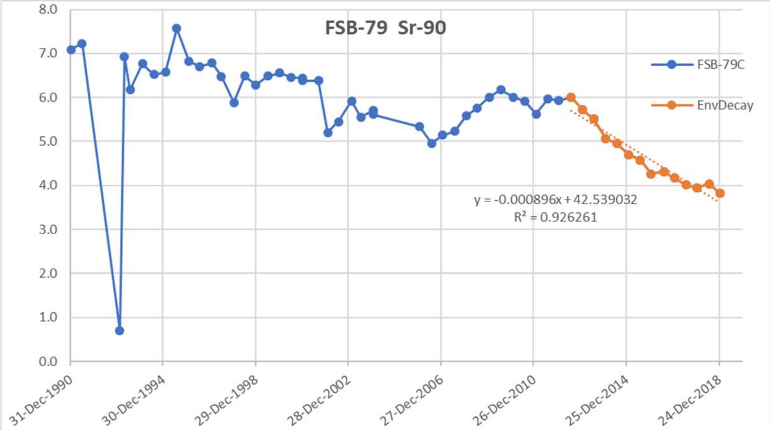
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-79 Sr-90
FSB-79C
EnvDecay
y = -0.000896x + 42.539032
R² = 0.926261
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
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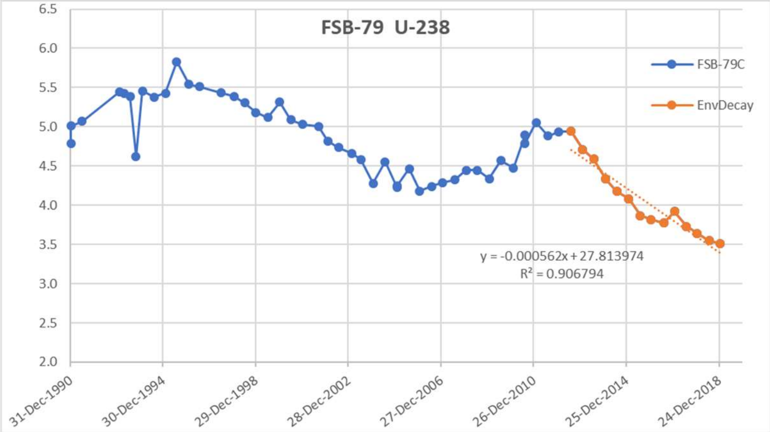
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-79 U-238
FSB-79C
EnvDecay
y = -0.000562x + 27.813974
R² = 0.906794
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
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26-Dec-2010
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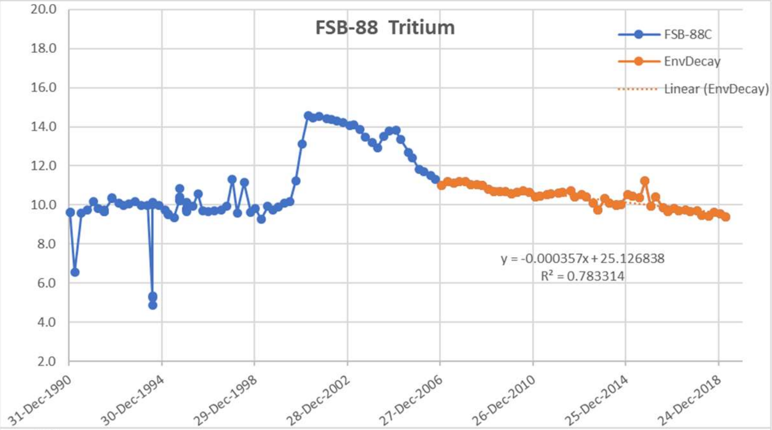
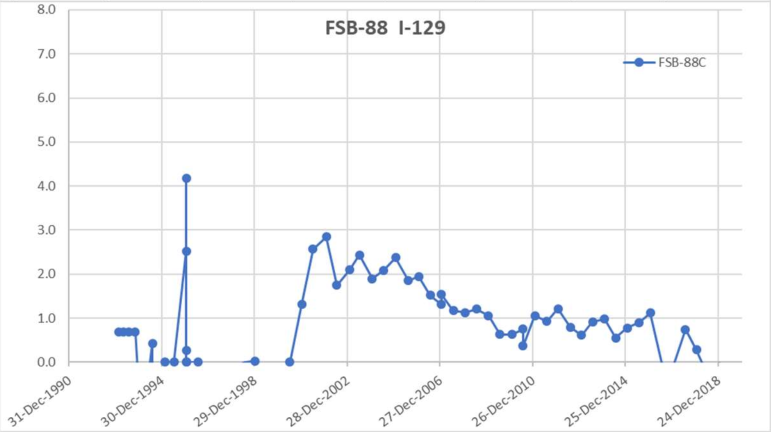
24-Dec-2018


FSB-88 Tritium
FSB-88C
EnvDecay
Linear (EnvDecay)
y = -0.000357x + 25.126838
R² = 0.783314
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-88 I-129
FSB-88C
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
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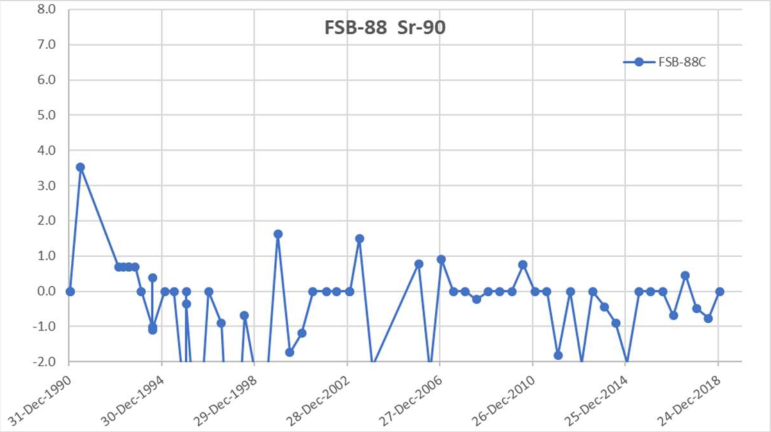
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-88 Sr-90
FSB-88C
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
31-Dec-1990
30-Dec-1994
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28-Dec-2002
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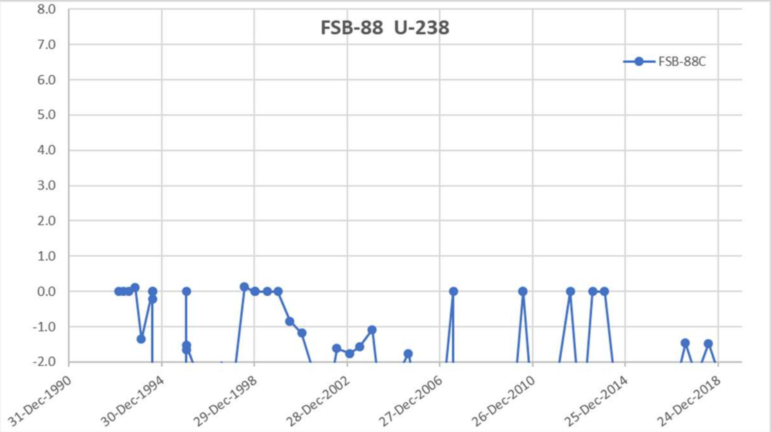
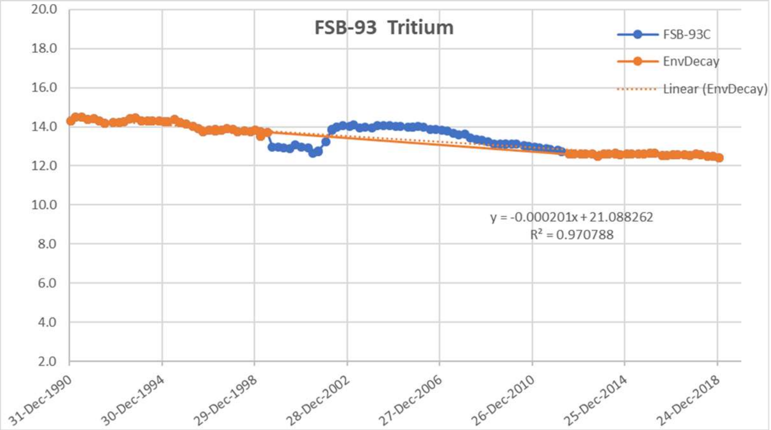
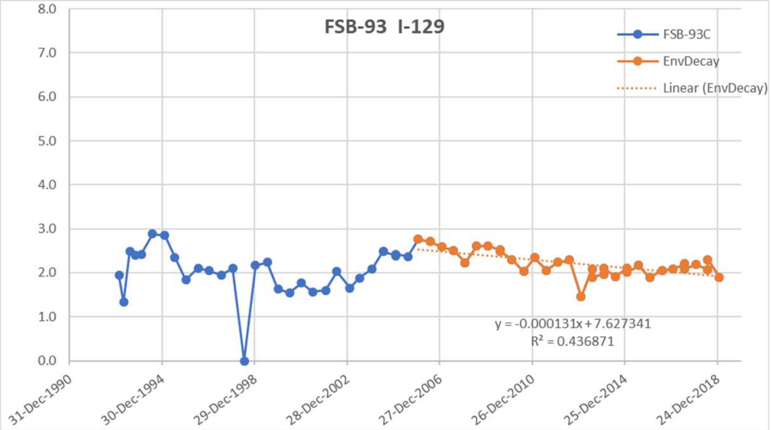
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-88 U-238
FSB-88C
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-93 Tritium
FSB-93C
EnvDecay
Linear (EnvDecay)
y = -0.000201x + 21.088262
R² = 0.970788
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-93 I-129
FSB-93C
EnvDecay
Linear (EnvDecay)
y = -0.000131x + 7.627341
R² = 0.436871
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
31-Dec-1990
30-Dec-1994
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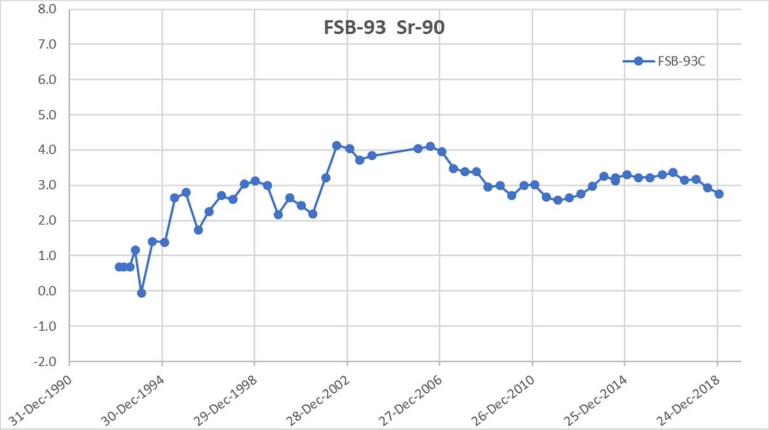
24-Dec-2018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FSB-93C
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6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
31-Dec-1990
30-Dec-1994
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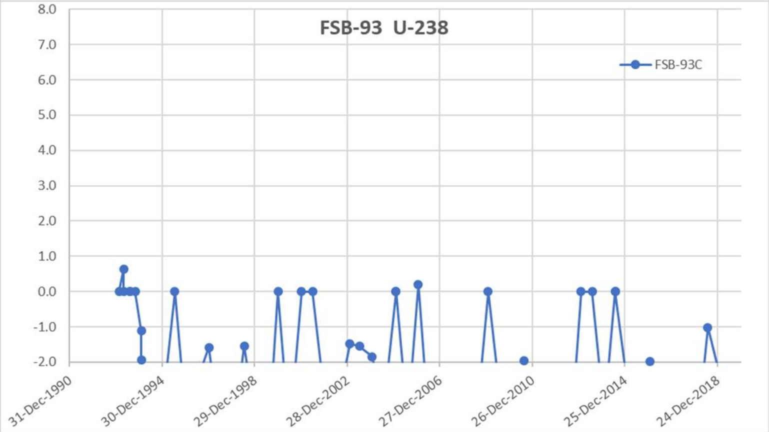
25-Dec-2014
24-Dec-2018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FSB-93C
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
31-Dec-1990
30-Dec-1994
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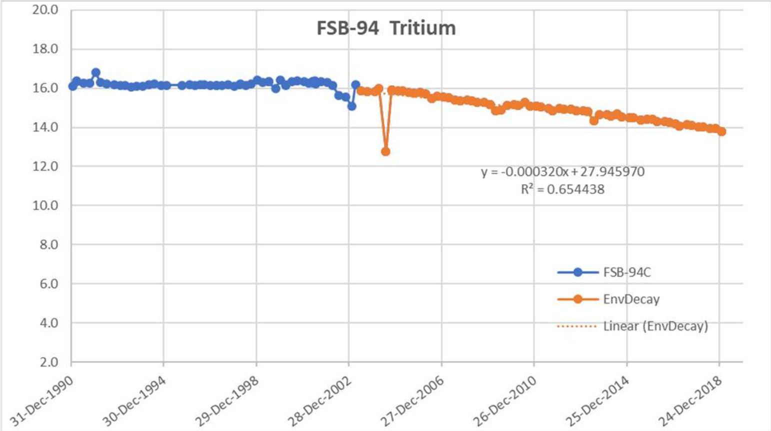
24-Dec-2018


FSB-94 Tritium
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18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
y = -0.000320x + 27.945970
R² = 0.654438
FSB-94C
EnvDecay
Linear (EnvDecay)
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30-Dec-1994
29-Dec-1998
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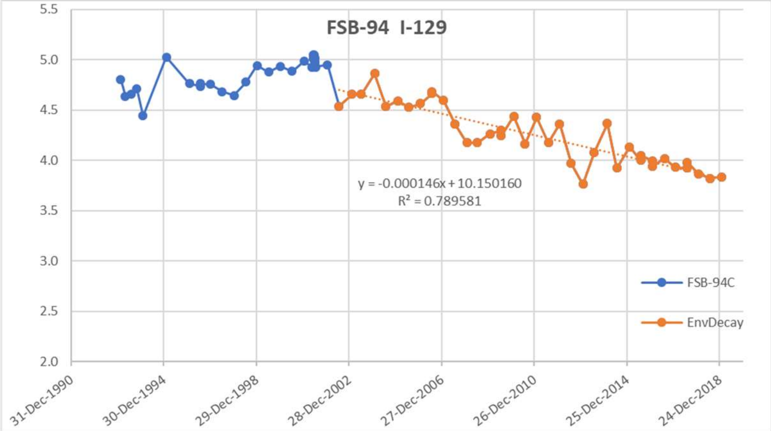
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-94 I-129
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
y = -0.000146x + 10.150160
R² = 0.789581
FSB-94C
EnvDecay
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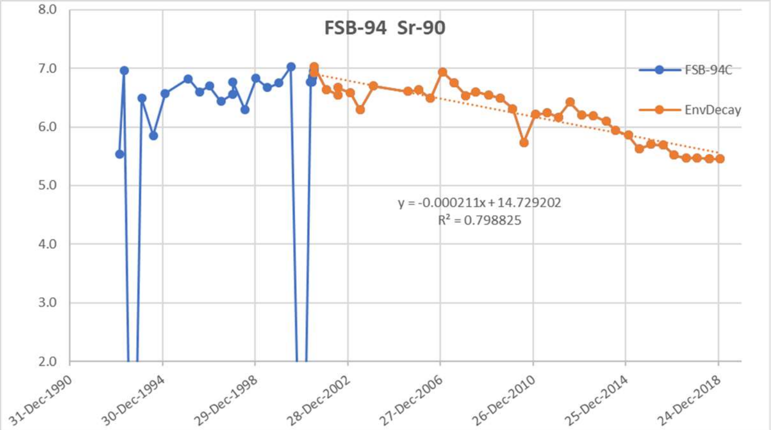
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-94 Sr-90
8.0
7.0
6.0
5.0
4.0
3.0
2.0
y = -0.000211x + 14.729202
R² = 0.798825
FSB-94C
EnvDecay
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30-Dec-1994
29-Dec-1998
28-Dec-2002
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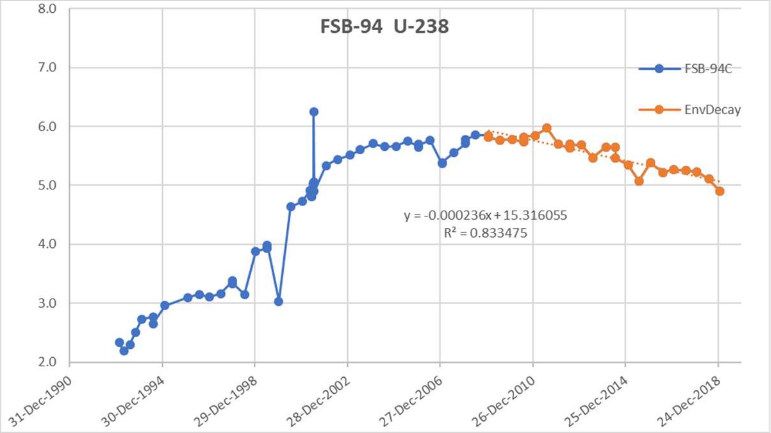
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7.0
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5.0
4.0
3.0
2.0
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R² = 0.833475
FSB-94C
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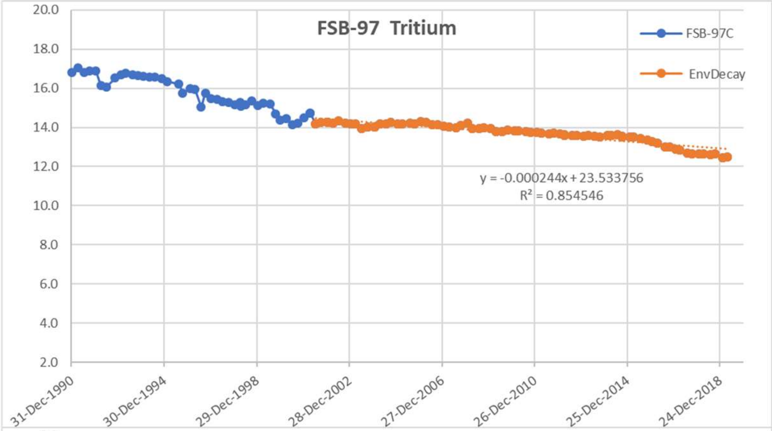
25-Dec-2014
24-Dec-2018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FSB-97C
EnvDecay
y = -0.000244x + 23.533756
R² = 0.854546
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18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
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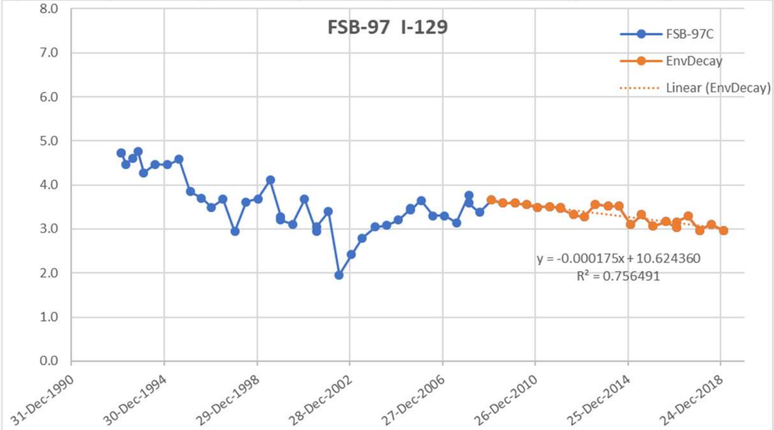
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FSB-97C
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Linear (EnvDecay)
y = -0.000175x + 10.624360
R² = 0.756491
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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30-Dec-1994
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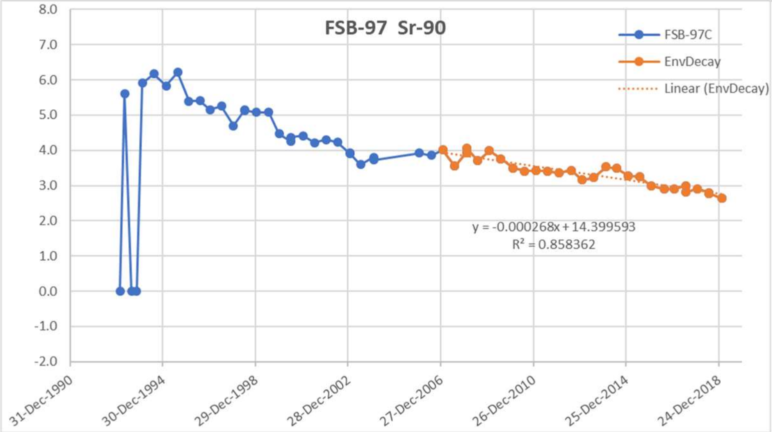
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FSB-97C
EnvDecay
Linear (EnvDecay)
y = -0.000268x + 14.399593
R² = 0.858362
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
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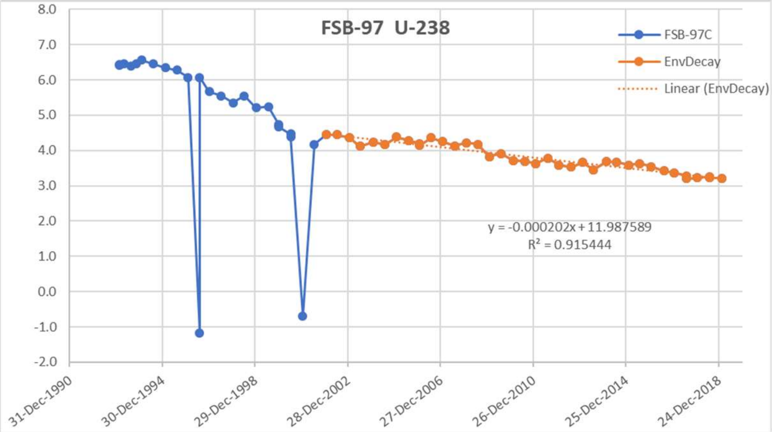
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FSB-97C
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Linear (EnvDecay)
y = -0.000202x + 11.987589
R² = 0.915444
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6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
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30-Dec-1994
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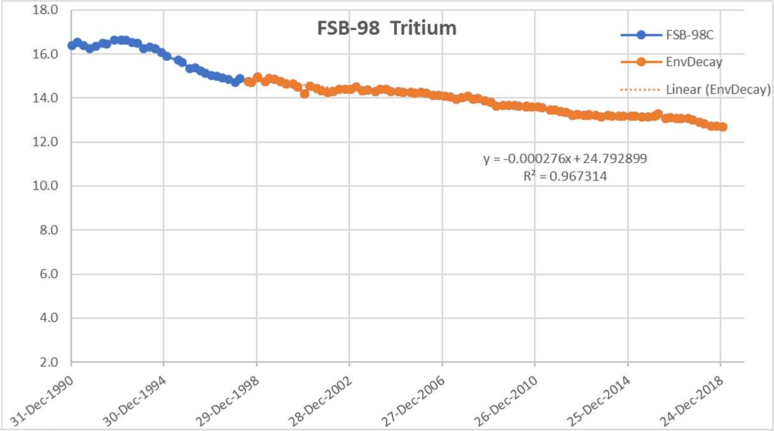
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FSB-98C
EnvDecay
Linear (EnvDecay)
y = -0.000276x + 24.792899
R² = 0.967314
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
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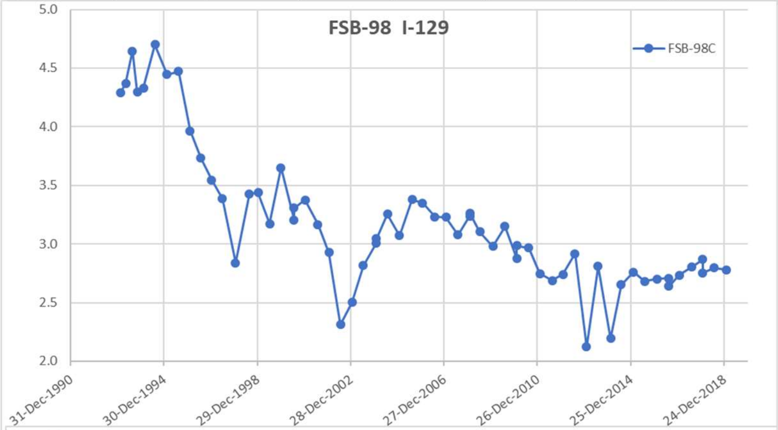
25-Dec-2014
24-Dec-2018


FSB-98 I-129
FSB-98C
5.0
4.5
4.0
3.5
3.0
2.5
2.0
31-Dec-1990
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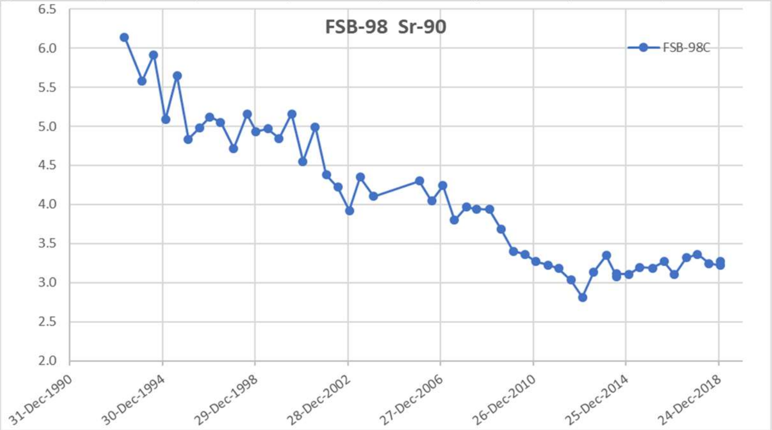
25-Dec-2014
24-Dec-2018


FSB-98 Sr-90
FSB-98C
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
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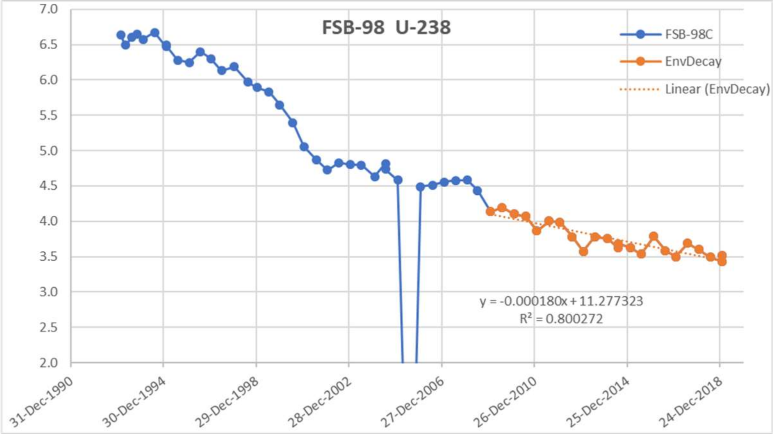
24-Dec-2018


FSB-98 U-238
FSB-98C
EnvDecay
Linear (EnvDecay)
y = -0.000180x + 11.277323
R² = 0.800272
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
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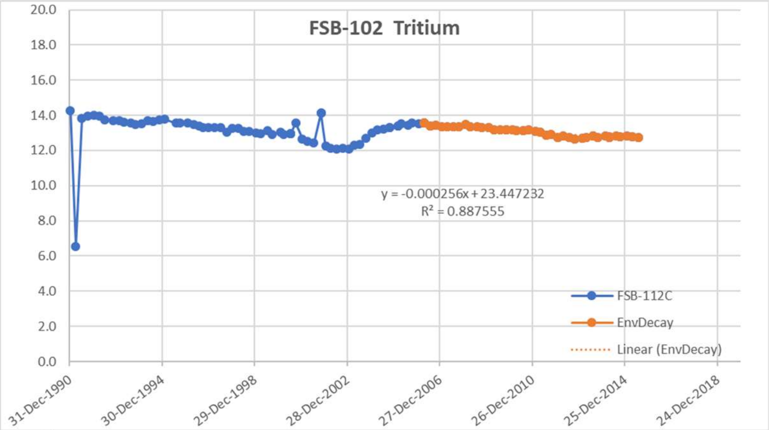
24-Dec-2018


FSB-102 Tritium
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
y = -0.000256x + 23.447232
R² = 0.887555
FSB-112C
EnvDecay
Linear (EnvDecay)
31-Dec-1990
30-Dec-1994
29-Dec-1998
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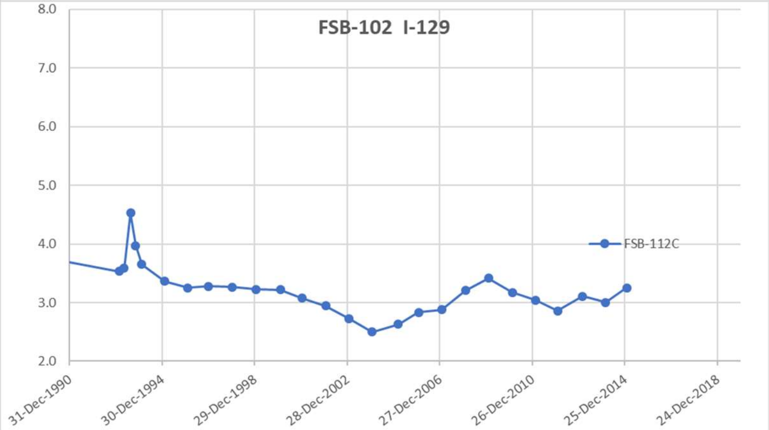
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-102 I-129
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7.0
6.0
5.0
4.0
3.0
2.0
FSB-112C
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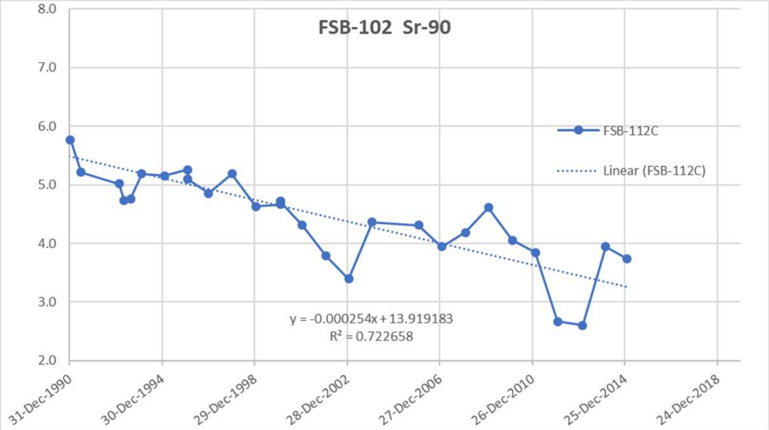
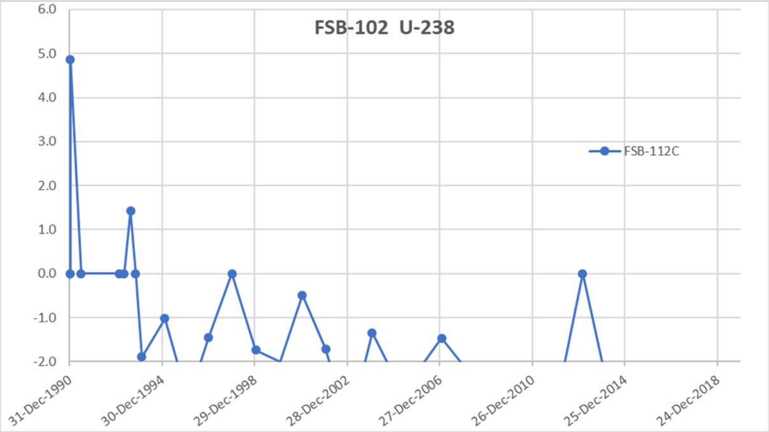
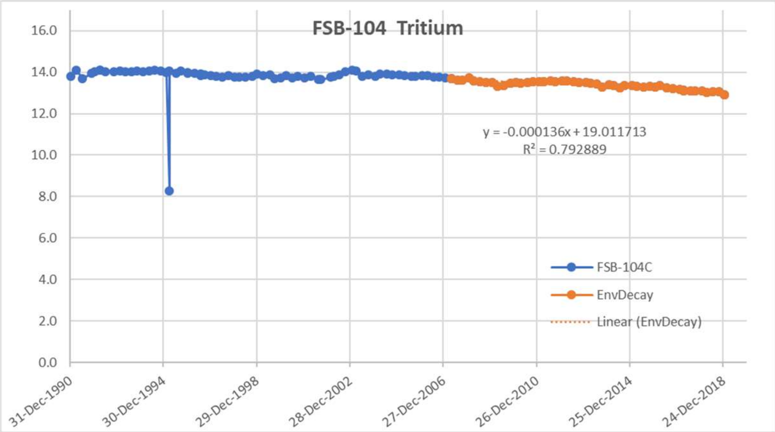
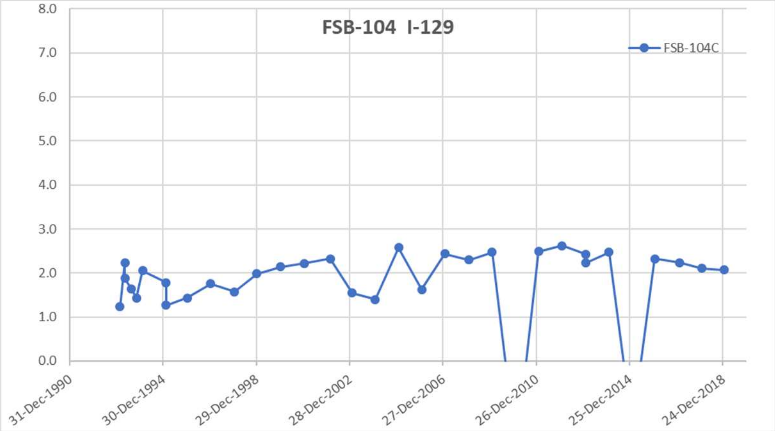
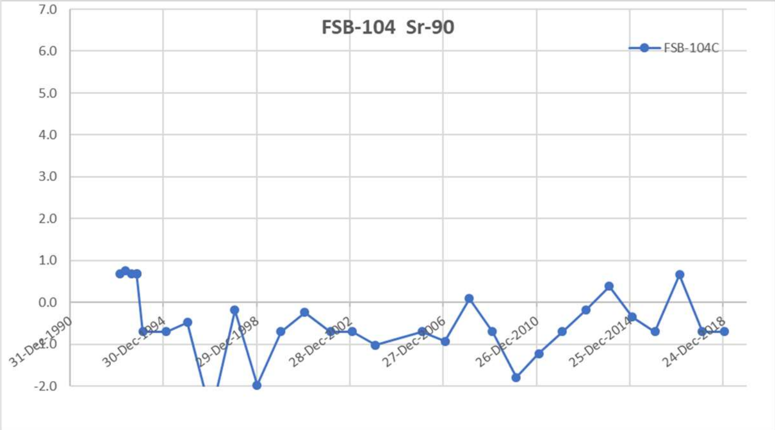
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018

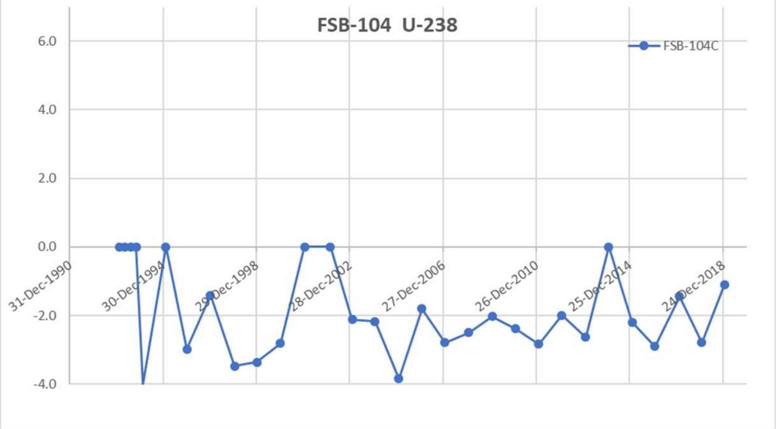

FSB-102 Sr-90
8.0
7.0
6.0
5.0
4.0
3.0
2.0
FSB-112C
Linear (FSB-112C)
y = -0.000254x + 13.919183
R² = 0.722658
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018

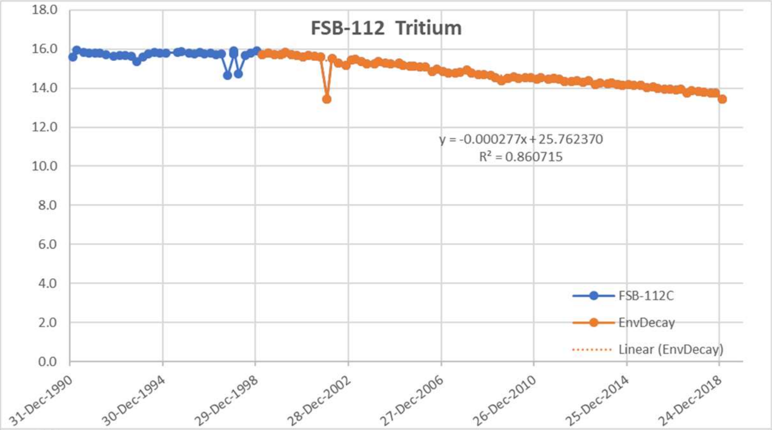

FSB-102 U-238
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
FSB-112C
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-104 Tritium
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
y = -0.000136x + 19.011713
R² = 0.792889
FSB-104C
EnvDecay
Linear (EnvDecay)
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018

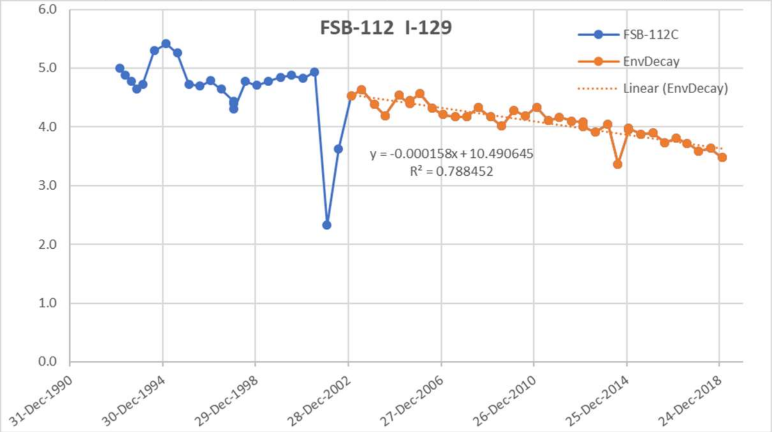

FSB-104 I-129
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
FSB-104C
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018


FSB-104 Sr-90
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
FSB-104C
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018

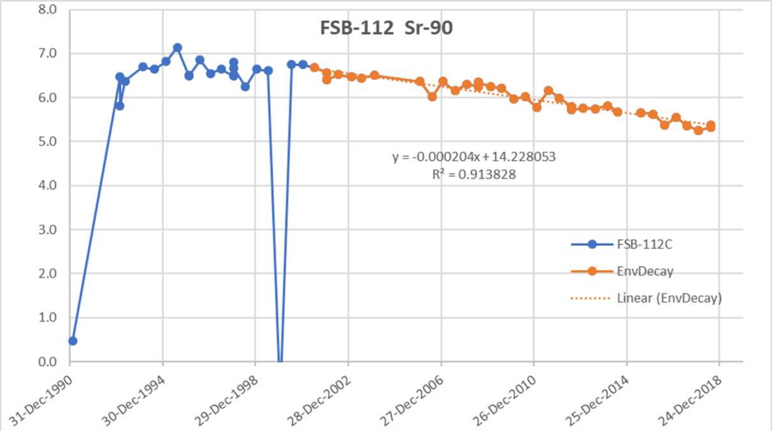

FSB-104 U-238
6.0
4.0
2.0
0.0
-2.0
-4.0
FSB-104C
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018



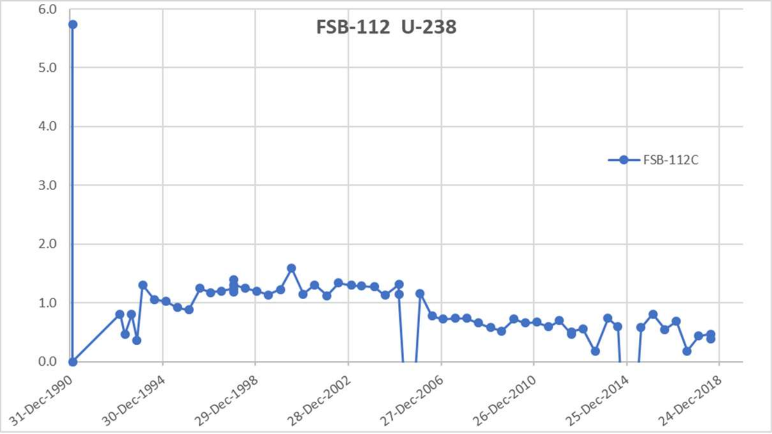
FSB-112 Tritium
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
y = -0.000277x + 25.762370
R² = 0.860715
FSB-112C
EnvDecay
Linear (EnvDecay)
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018



FSB-112 I-129
6.0
5.0
4.0
3.0
2.0
1.0
0.0
FSB-112C
EnvDecay
Linear (EnvDecay)
y = -0.000158x + 10.490645
R² = 0.788452
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018



FSB-112 Sr-90
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
y = -0.000204x + 14.228053
R² = 0.913828
FSB-112C
EnvDecay
Linear (EnvDecay)
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018



FSB-112 U-238
6.0
5.0
4.0
3.0
2.0
1.0
0.0
FSB-112C
31-Dec-1990
30-Dec-1994
29-Dec-1998
28-Dec-2002
27-Dec-2006
26-Dec-2010
25-Dec-2014
24-Dec-2018

6.0 Appendix A: Denham (2011)

Base Injection: An Assessment of Opportunities for Optimization

Executive Summary

At the request of Area Completions Projects, SRNL has performed a general assessment of base injection performance at the F-Area Seepage Basins and examined potential opportunities for optimizing performance. Analysis of soil borings in the base injection treatment zone of the middle gate indicates that a treatment zone of elevated pH has been successfully created and it is operating according to the original conceptual model. Groundwater monitoring data confirm this.

Groundwater monitoring data also show that U-238 and Sr-90 concentrations generally remain below drinking water standards between base injection events, indicating that the elevated pH in the treatment zone is attenuating these contaminants. There is tenuous evidence that some uranium may be mobilized during base injection events by carbonate complexing. However, concentrations of U-238, corrected for dilution, are lower than would be expected if large fractions of the sequestered uranium were mobilized.

Some potential opportunities for optimization have been identified. These are:

- Installing injectors that extend to near the top of the Tan Clay Confining Zone
- Changing the pH trigger value for turning off the base injection system from 10 to 9
- Reducing alkalinity of the base, taking advantage of the fact that between pH 6 and 9 small amounts of base cause large changes in pH
- Investigating alternative bases – this is currently being done by SRNL under a project funded by DOE EM-32.

Introduction

The purpose of this study, funded by Area Completion Projects, was to provide a re-examination of base injection after 5 years and look for any opportunities to optimize performance and cost effectiveness. This was done using existing monitoring data, analysis of samples obtained from 4 soil borings, and integration of data obtained in a separate study funded by DOE EM-32.To examine the effectiveness of base injection we focused on the area downgradient of the "Middle Gate". Figure A1 is a map of the location of the gate, the injectors and three wells of interest. The wells are FSB-131D – the sentry well for base injection, FSB-130D – a background well, FPZ-4A, and FSP-12A. FPZ-4A and FSP-12A are progressively downgradient of the gate and illustrate the downgradient effects of base injection. We used time trends of concentrations of Sr-90 and U-238 compared to those of tritium, pH, specific conductance, and water level to assess chemical effects of base injection on the contaminants and to evaluate mobilization of uranium by the carbonate base.

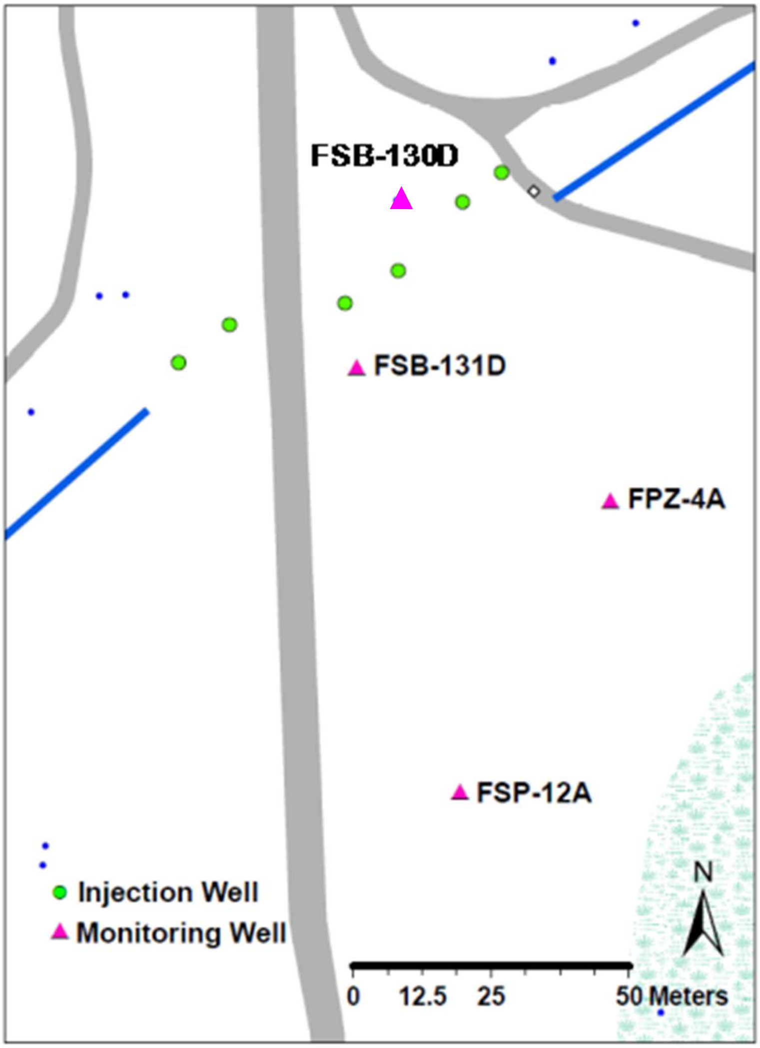


Figure A1: Map of Middle Gate area showing the barrier wall (blue line), monitoring wells (red triangles), and injection wells (green circles).

The first objective of the study was to determine if a treatment zone with elevated pH had been established and if the treatment zone was behaving according to the conceptual model. Figure A2 shows the conceptual model for the treatment zone. Initial injection of base neutralizes surface acidity associated with aquifer minerals. When base injection is stopped, acidic groundwater bearing Sr-90 and uranium migrates into the zone of elevated pH. The pH of the acidic groundwater is neutralized by adsorption of hydrogen ions to mineral surfaces. Likewise, adsorption of Sr-90 and uranium attenuates their migration. The influent of acid groundwater between base injection events erodes the buffering capacity of the treatment zone and at some point, the pH at the sentry well decreases to the value that triggers re-injection of base. After re-injection of base stops, the erosion of the treatment zone buffering capacity begins again. There are other reactions that influence pH, such as precipitation and dissolution of aluminum, but once the treatment zone has been established, they have a negligible effect on operations.

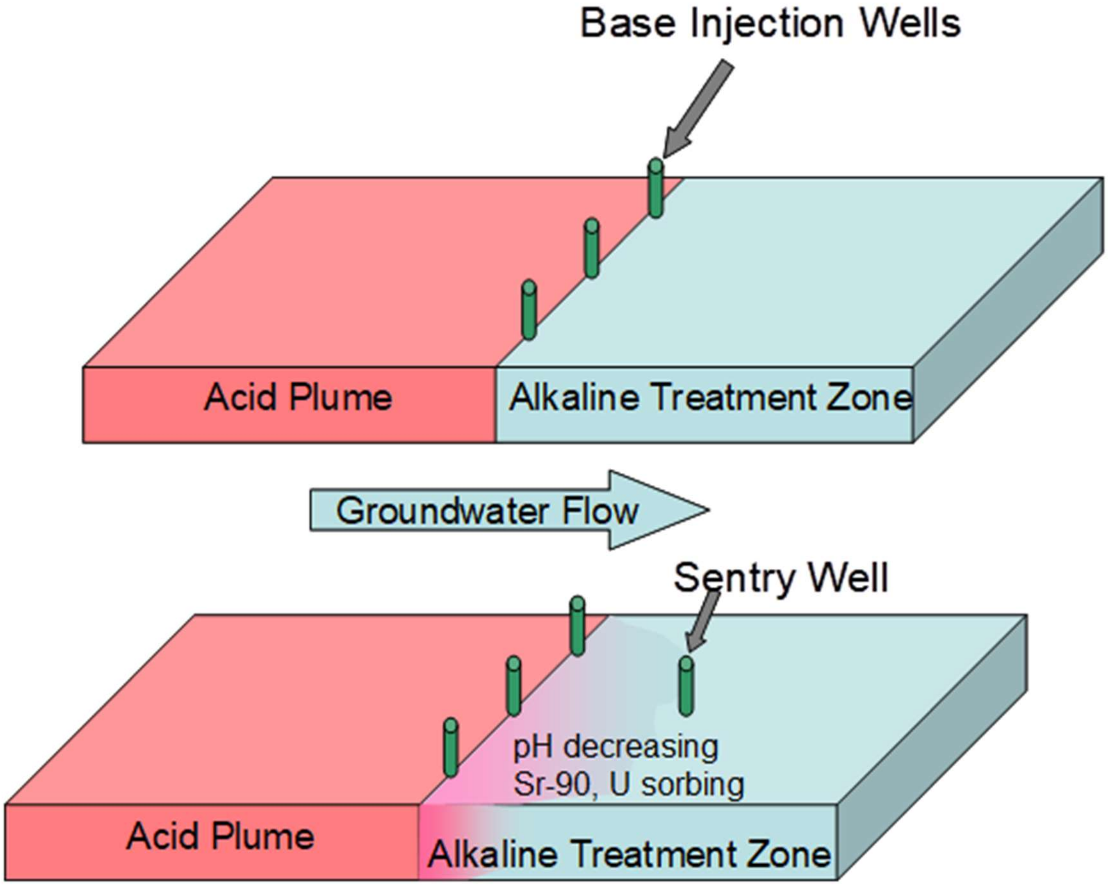


Figure A2: Conceptual model of base injection treatment zone.

Analysis of Soil Borings from Treatment Zone

Four soil borings were obtained in the area of the Middle Gate – one upgradient of base injection and three progressively downgradient in the treatment zone. The locations of the soil borings are shown in Figure A3. Measurements of soil pH were done over depth profiles of each boring using EPA Method 9045D in which pH is measured in a 1:1 slurry of soil and distilled-deionized water.

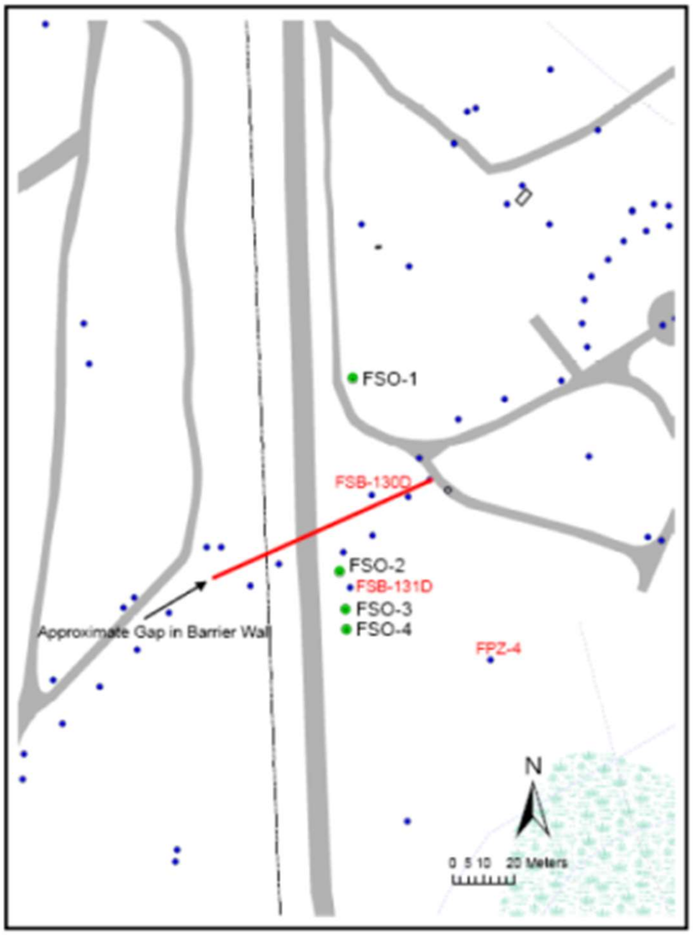


Figure A3: Map of soil boring locations (green circles) in base injection treatment zone associated with the Middle Gate in the barrier wall.

The results (Figure A4) show that an elevated pH treatment zone has been successfully created. In the background pH profile, boring FOS-1, the pH values are mildly acidic with samples from below 180 ft. MSL being slightly more acidic. This is as expected. Soil pH values of sub-surface soil samples from the study area are rarely as acidic as corresponding groundwater samples. The lower pH values at depth are consistent with profiles of pH in groundwater obtained from wells in the study area (Figure A5). They show that pH of groundwater is stratified, with the most acidic portion of the plume extending from an elevation of 185 ft. MSL down to the top of the Tan Clay Confining Zone (TCCZ). In the FOS-4 soil pH profile – the boring furthest downgradient from the line of base injection wells, pH values exceed 8 except for one (pH=6.2) at an elevation of 176 ft. MSL. In the FOS-3 pH profile – just upgradient, the top three pH values exceed 8, but pH decreases with depth beginning with the sample at 187 ft. MSL. Yet, the minimum pH of 6.8 remains less acidic than the background pH values. The samples in the upper portion of the FOS-2 pH profiles are more acidic than those from the upper portions of the two downgradient profiles, but less acidic than the background profile. Below an elevation of 185 ft. MSL the pH values are similar to those in the lower portion of the background profile.

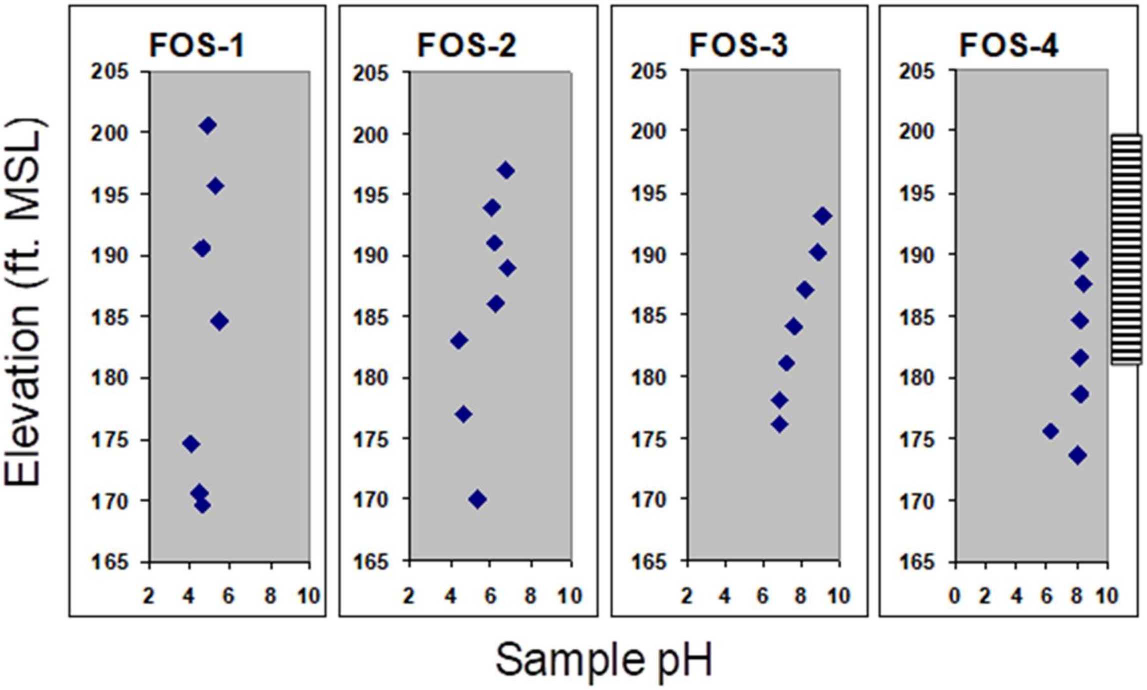


Figure A4: Depth profiles of soil pH in each of the 4 soil borings obtained from the base injection treatment zone associated with the Middle Gate; screen zone of injectors shown on the right side of the FOS-4 profile.

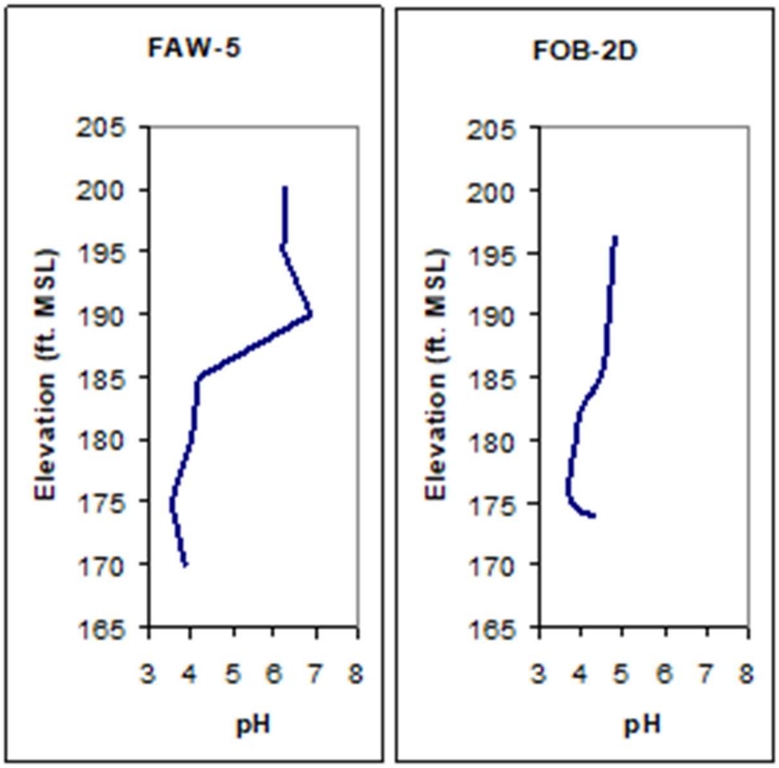


Figure A5: Depth profiles of pH in groundwater from wells FAW-5 and FOB-2D.

The pattern of the pH profiles indicates that the treatment zone is behaving according to the conceptual model. Near the line of injection wells the buffering capacity of the treatment zone has been depleted by incoming acidic groundwater. The degree of buffering capacity depletion reflects the pH stratification in the groundwater. In the lower portion, buffering capacity is completely depleted, but it is only partially depleted in the upper portion. Degradation of buffering capacity is less downgradient in the treatment zone and at FOS-4 depletion of buffering capacity is minimal.

Selected samples were analyzed for the presence of amorphous aluminum hydroxide using an extraction procedure similar to that used by Dayton and Basta (2005). The results, shown in Appendix A, are inconclusive. The extractable aluminum varies with total aluminum in the sample, but there are no correlations with sample location. The reasons for this could be multiple:

- Amorphous aluminum hydroxides or sulfates are likely to only precipitate in the upgradient portion of the treatment zone and were re-dissolved by incoming acidic groundwater

- The amount of natural amorphous aluminum may be significantly greater than that precipitated in the treatment zone

- The method may dissolve some kaolinite that masks the presence of amorphous aluminum

Analysis of Groundwater Monitoring Data

The behavior of the treatment zone is also evident in time trends of constituents in groundwater from the sentry well FSB-131D. There were four base injection events since 2005 that are evident from the time trends of specific conductance and pH (Figure A6). Specific conductance reflects the breakthrough of the injected base better than tritium because the alkaline ions that make up the base are attenuated relative to tritium. Hence, peaks in specific conductance align well with sharp rises in pH produced by the base breakthrough. After pH rises to a maximum and base injection is stopped, it decreases slowly as incoming acidic groundwater degrades the buffering capacity. The patterns of pH change with time are almost identical for the first two base injection events. The third event is unusual and is followed by what appears to be much slower decay of pH. However, this may be an apparent effect rather than a real change in the pH decay rate that may be related to the water table elevation.

An artifact of pH stratification in the aquifer is that a sample taken from a well is a mixture of low pH water from the bottom of the screen zone and higher pH water from the upper part of the screen. At times of an elevated water table the sample mix will consist of more water from the upper portion of the screen zone resulting in a higher pH sample. The time trend in the elevation of the water table reflects the base injection events with a rising water level for each event. However, between the third and fourth base injection events the water table rose approximately 1 foot. This is during the time that the pH decay rate seems to be slower than after the previous two base injection events. The pH decay rate may have actually been similar to the previous two events but appeared slower because of the elevated water table.

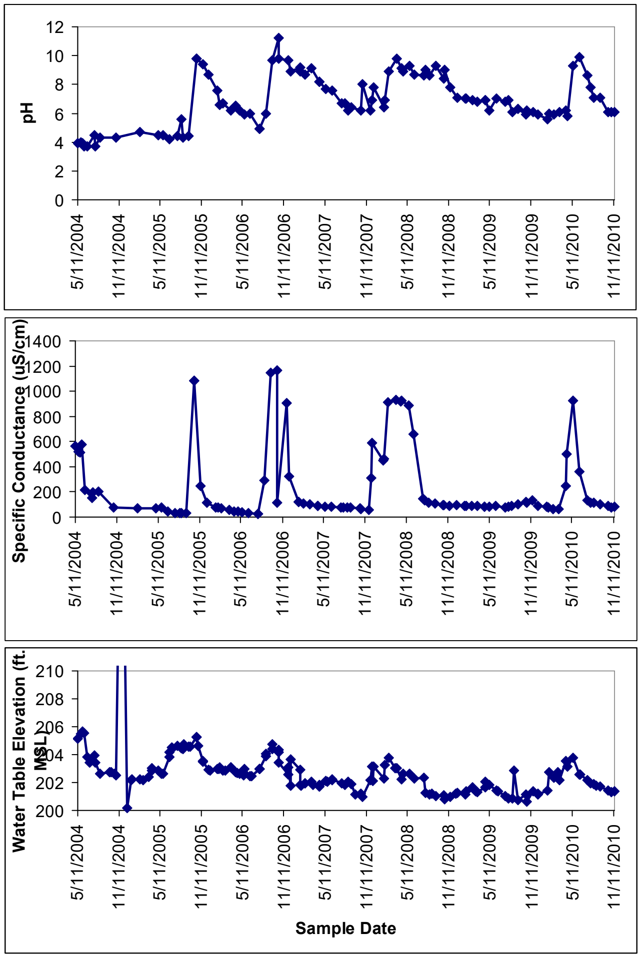


Figure A6: Time trends of pH, specific conductance, and water table elevation for well FSB-131D.

The effects of the barrier wall and base injection on the contaminants of concern is shown by the comparison of time trends for Sr-90 and U-238 concentrations in wells FSB-130D, FSB-131D, FPZ-4A, and FSP-12A (Figure A7). Quantitative comparisons of concentrations are not valid because the wells are not along a direct flow path, screen placements are not directly comparable, and other hydraulic effects occur as groundwater moves downgradient. Nevertheless, the qualitative comparison of concentrations shows that the system has caused Sr-90 and U-238 concentrations to decrease to near or less than the pertinent drinking water standards.

With the exception of one sample obtained on 2/1/2008, Sr-90 concentrations have remained greater than the drinking water standard of 8 pCi/L in samples from well FSB-130D, the background well. Samples from FSB-131D, in the treatment zone, have had concentrations <8 pCi/L except for the most recent. Samples from the wells downgradient of well FSB-131D have had Sr-90 concentrations very near or <8 pCi/L since the beginning of 2006. Likewise, uranium concentrations downgradient of the base injection system have been consistently near or less than the 10 pCi/L drinking water standard.

Much of the decrease in contaminant concentrations can be attributed to the physical effects of the barrier wall. This is illustrated by the time trends of tritium concentrations in samples from well FSB-131D. Figure A8 shows the time trend at two different vertical scales. After installation of the wall, tritium concentrations decreased from 1460 pCi/ml to near 100 pCi/ml. Since 2005, concentrations of tritium rise and fall in response to base injection events (shown in gray). Importantly, concentrations of Sr-90 and U-238 have remained low even as tritium concentrations have increased, indicating enhanced attenuation caused by the chemical effects of base injection.

Effects of Base Injection on Uranium

One of the objects of this study was to examine the potential effect of carbonate complexing on uranium sorbed within the treatment zone. At elevated pH uranium will form dissolved complex ions with carbonate, enhancing its mobility. Hence, injection of a base with a relatively high concentration of carbonate could mobilize uranium previously sorbed within the treatment zone. Figure A9 shows the aqueous speciation of uranium calculated for the carbonate concentration of the base used in base injection. The speciation is dominated by uranium-carbonate complexes. Hence, it is worth assessing the effects of the carbonate on uranium concentrations as recorded in the groundwater monitoring data.

There are small peaks in uranium concentrations in the time trends for wells FPZ-4A and FSP-12A. Some of these may be related to mobilization by injected base, others are not. Figure A10 shows the time trends of three parameters and U-238 for samples from well FPZ-4A located approximately 55 meters from the injector line. From the fall of 2005 to the present there were 5 peaks in the U-238 concentration time trend. One occurred during a base injection event and the other four occurred approximately 3 months after the end of a base injection event. Those that occurred following a base injection event may be related to mobilization of uranium by carbonate, but that would suggest a retardation factor for the mobilized uranium of 2-3. If that is the case, then the peak that occurred during a base injection event is not related to mobilization by carbonate.

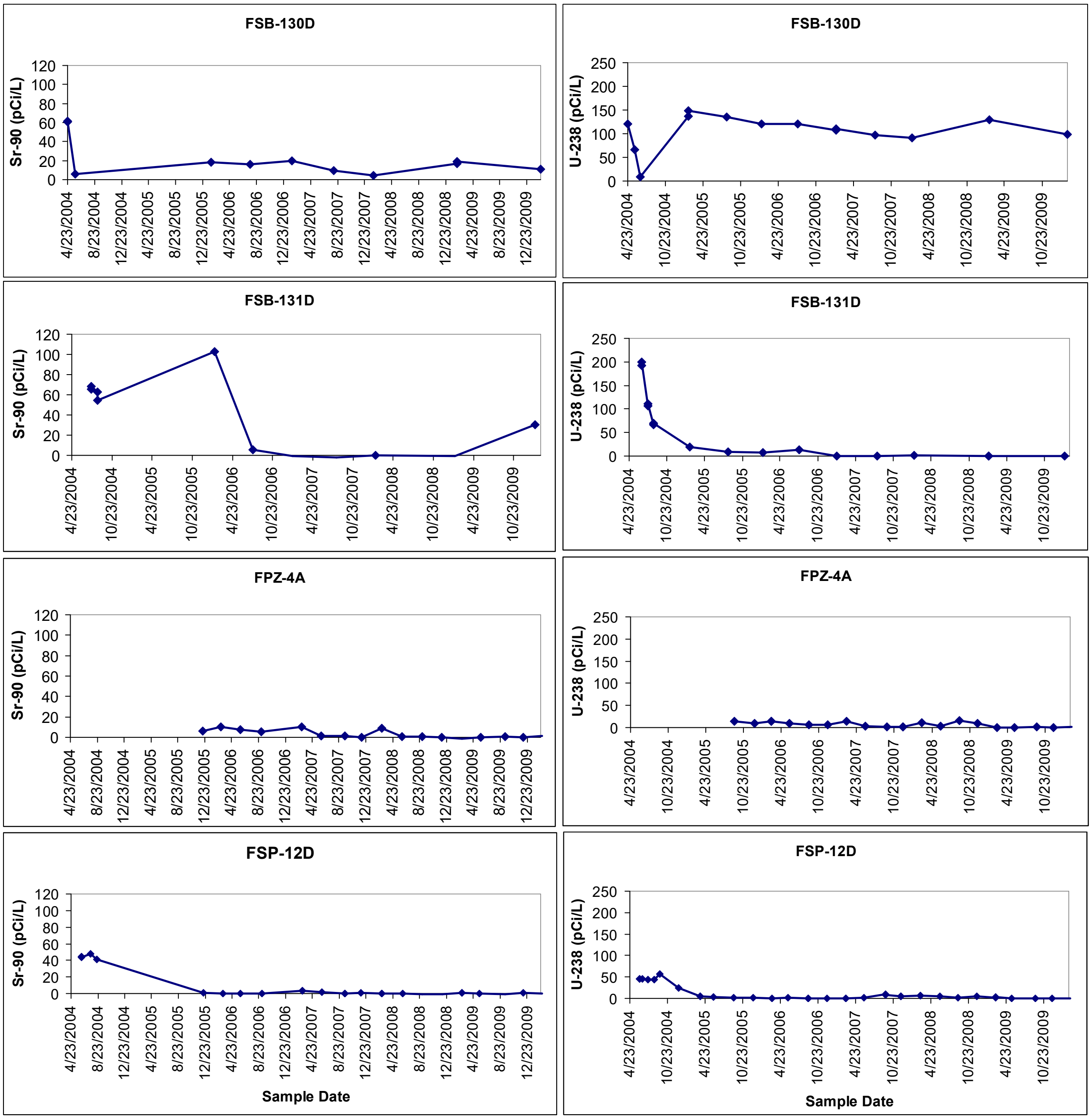


Figure A7: Time trends of concentrations of Sr-90 and U-238 in samples from wells FSB-130D, FSB-131D, FPZ-4A, and FSP-12A.

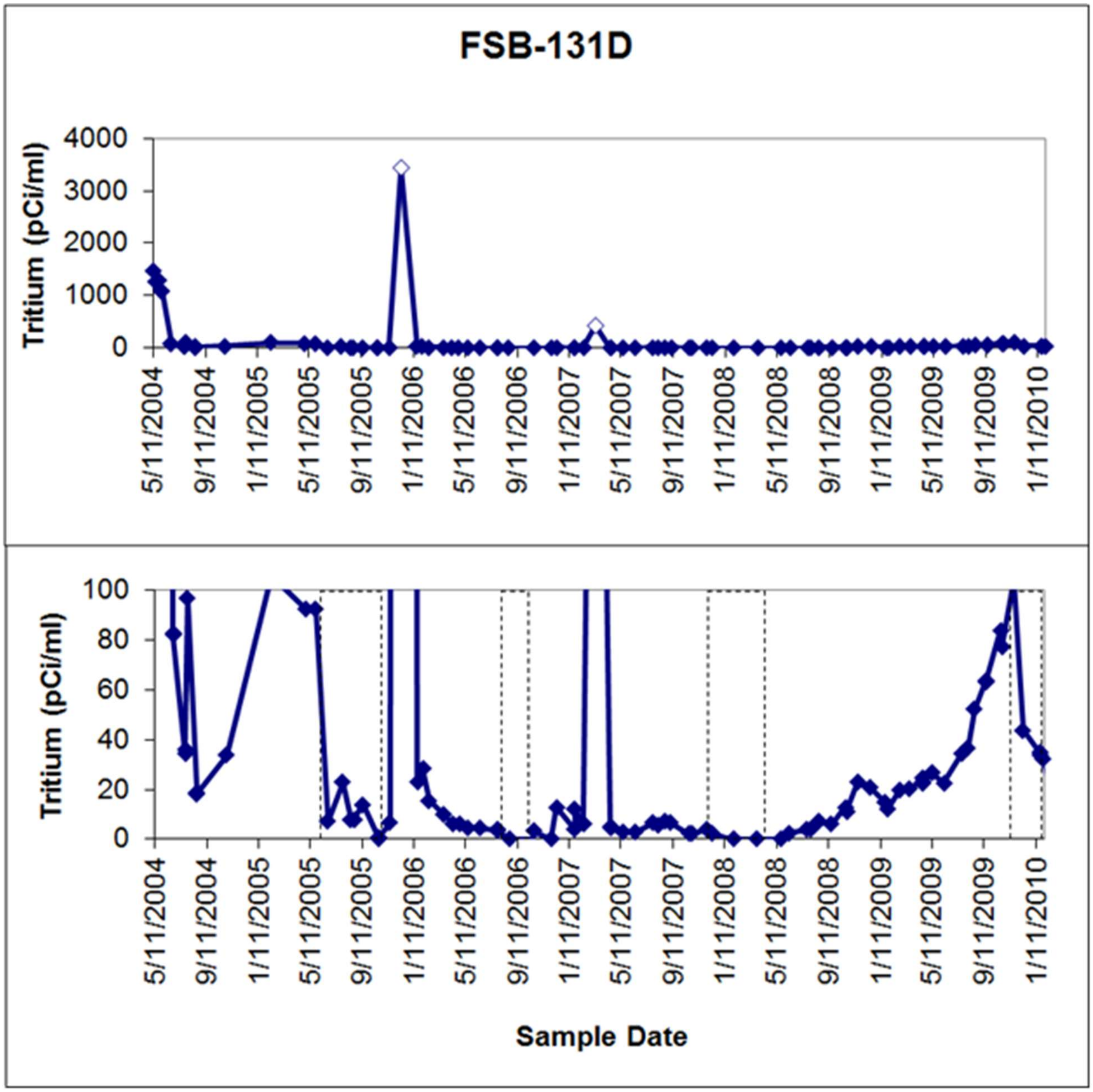


Figure A8: Time trend for concentrations of tritium in samples from well FSB-131D; top shows large vertical scale, bottom shows small vertical scale with dashed lines representing approximate periods of base injection.

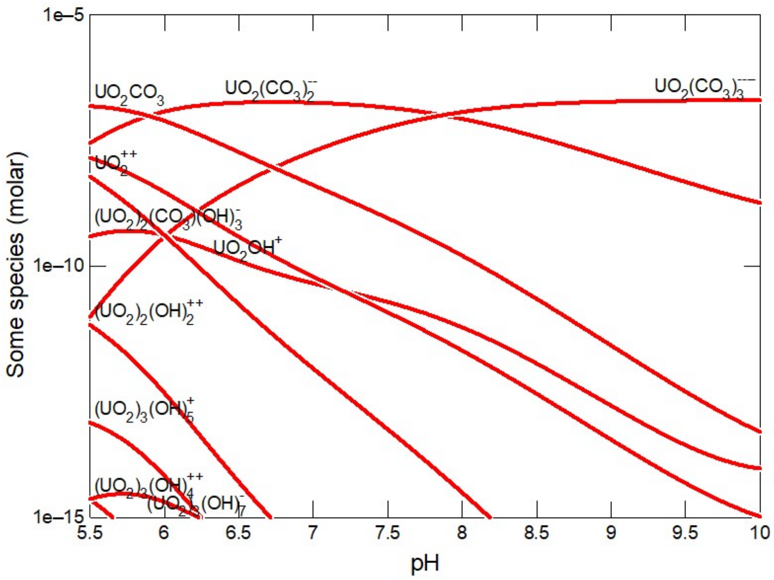


Figure A9: Aqueous speciation versus pH of uranium at a total carbonate concentration of 3.7 x 10-3 M – approximately that used for base injection (calculated using The Geochemist's Workbench®; Bethke, 2005).

The peak concentrations of U-238 are not high. However, the highest concentration occurs during a low in tritium concentration, suggesting that it may be diluted by the base injection event. The other peaks occur at times of relatively high tritium concentration and thus are not substantially diluted. Table A1 shows the U-238 and tritium concentrations and what the U-238 concentration would be after correcting for dilution – all assuming a background tritium concentration of 100 pCi/ml. The highest "dilution corrected" concentration of U-238 is 250 pCi/L. This suggests that uranium mobilization by injected carbonate may be occurring, but if it is assumed that 100% of the sequestered uranium was removed by the 2008 injection, then 10% or less was removed by the other injections. Interestingly, the period between the 2008 and 2010 injections was the longest period between injections and the longest period of uranium sequestration (measured as U-238 concentrations <2 pCi/L) – nearly 15 months. Hence, if a substantial fraction of uranium accumulated in the treatment zone were removed by injection of base, the uranium peak following the 2010 injection should be much larger than the others.

Figure A11 shows time trends U-238 concentration compared to those for tritium concentration, specific conductance and water table elevation for well FSP-12A. There are only two peaks in U-238 concentration that could be effects of base injection. The peak concentrations are less than those observed for well FPZ-4A. Substantial mobilization of uranium by carbonate complexing is not observed in groundwater sampled from well FSP-12A.

Table A1: Observed concentrations of U-238 and tritium and a calculated "Dilution Corrected" U-238 concentration in samples from well FPZ-4A.

Peak Year	**U-238 Observed (pCi/L)**	**Tritium Observed (pCi/ml)**	**"Dilution Corrected" U-238 (pCi/L)**
2006	15	71	21
2007	14	51	27
2008	15	6	250
2010	9	88	10

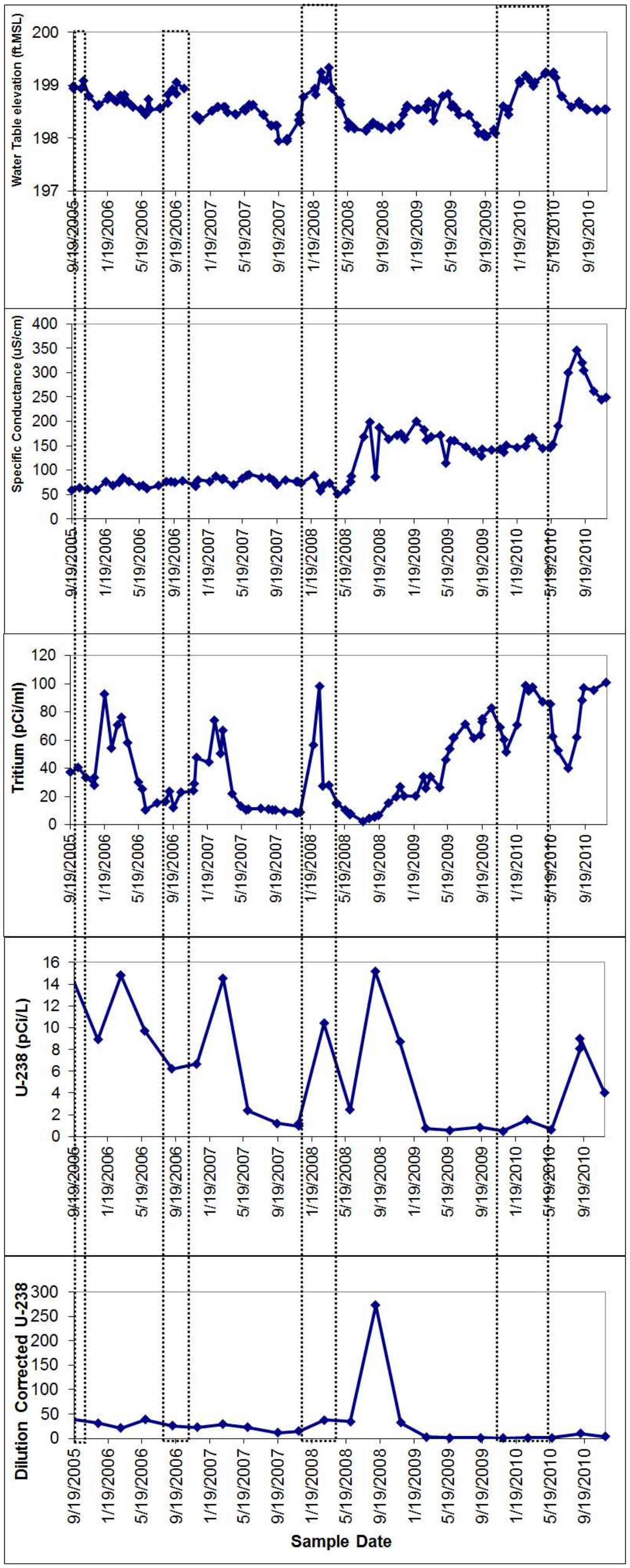


Figure A10: Time trends of U-238 and tritium concentrations, specific conductance, and water table elevation for well FPZ-4A; dashed lines show approximate periods of base injection.

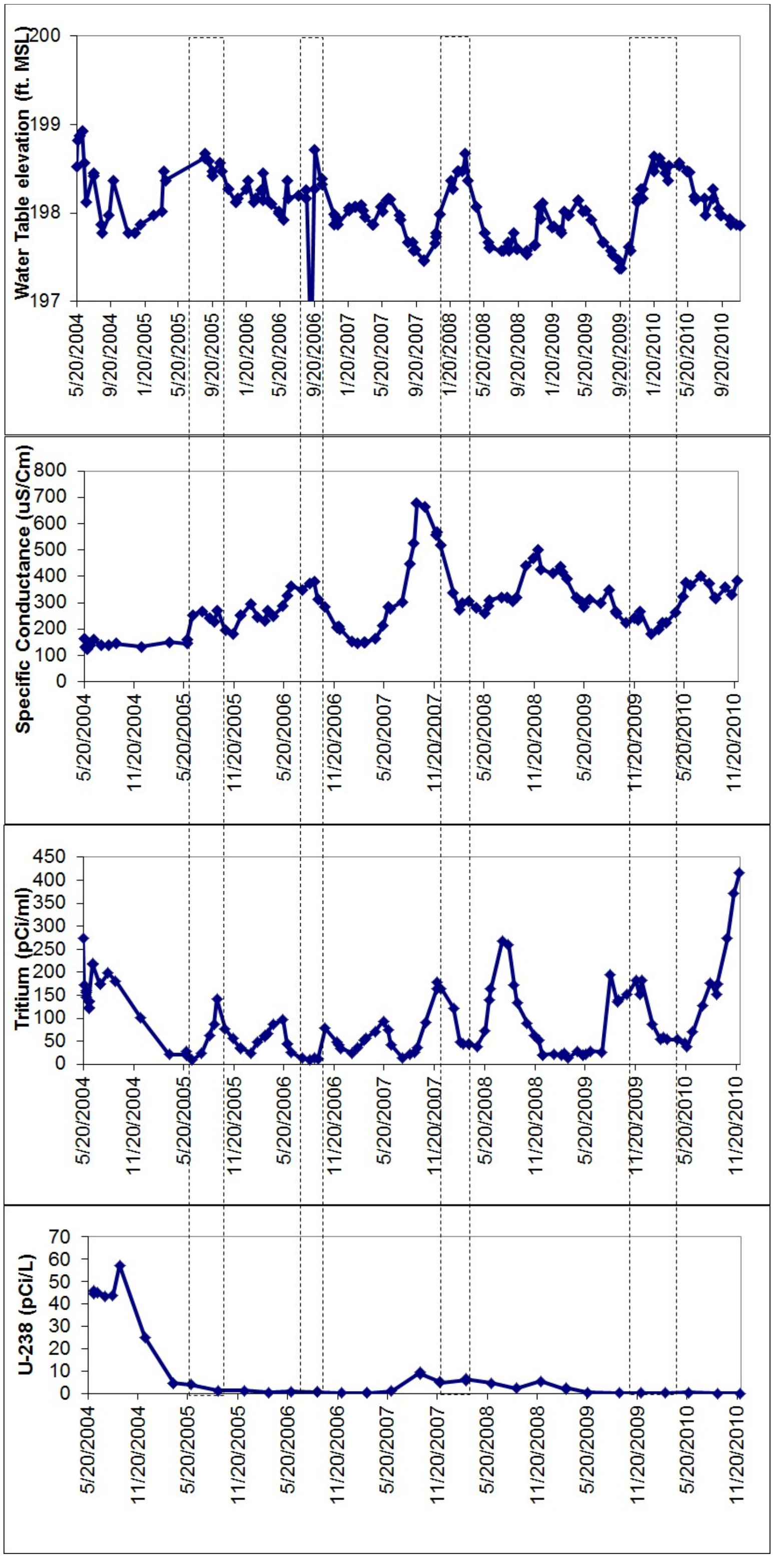


Figure A11: Time trends of U-238 and tritium concentrations, specific conductance, and water table elevation for well FPS-12A; dashed lines show approximate periods of base injection.

Preliminary unpublished data from an ongoing study funded by DOE EM-32 suggests that sorption of uranium onto F-Area sediments, even at acidic pH, may be difficult to remove completely by a carbonate solution. Diffusion samplers containing sediment from the Irwinton Sand were deployed in a well within the plume for 3 months. After retrieval, the sediments were leached twice with a bicarbonate solution comparable to injected base. This leaching removed less than 20% of the sorbed uranium. It is possible that desorption is much slower than adsorption or that the uranium precipitates in relatively insoluble minerals.

One possibility, currently under investigation is that uranium concentrations are controlled by the solubility of uranium silicates. Kaolinite, the dominant clay mineral in the Irwinton Sand, dissolves incongruently in acid with preferential leaching of aluminum. This potentially leaves behind an amorphous silica coating on minerals exposed to the acidic F-Area plume. Amorphous to chalcedonic silica has been observed in thin-sections of the deepest samples from soil boring FOS-1 (Figure A12). Whether this is the result of acid leaching or predates the plume is unclear.

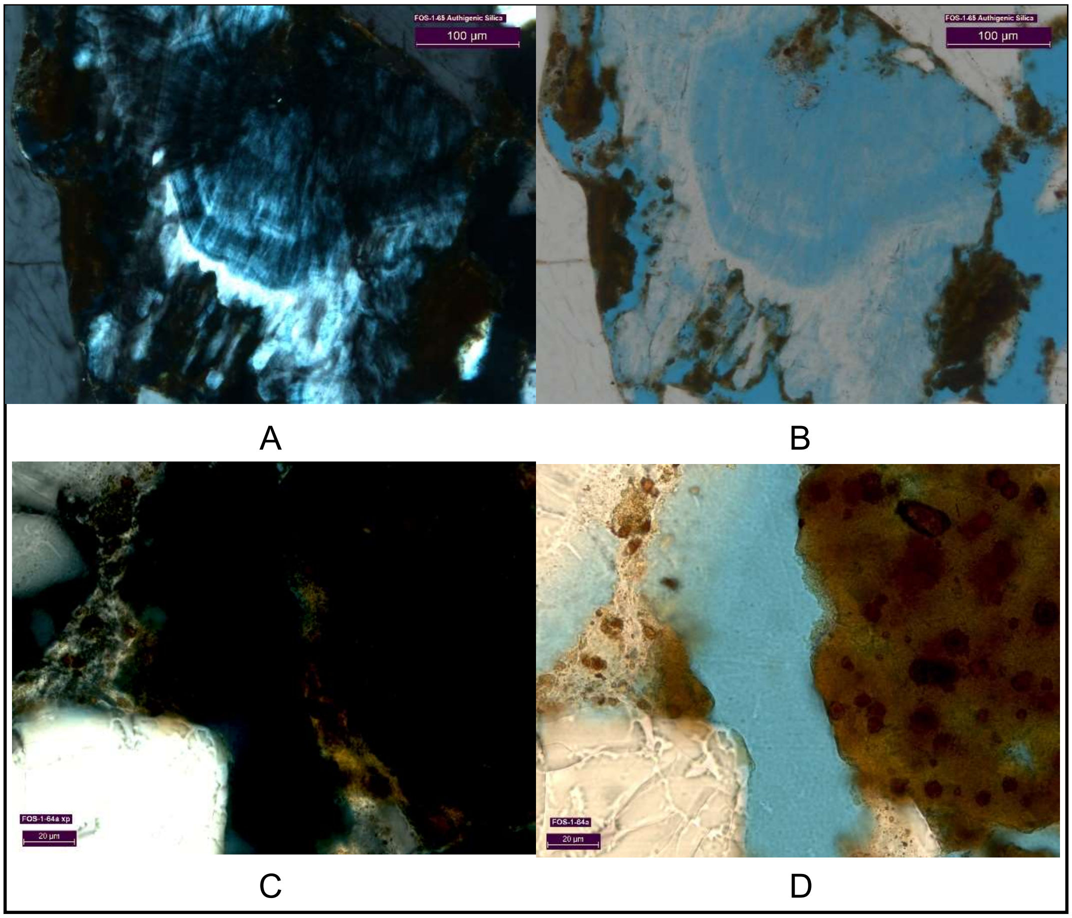


Figure A12: Thin-section photomicrographs showing amorphous to chalcedonic silica replacing clay matrix in samples from soil boring FOS-1; A) sample from 65 feet – crossed polars, B) sample from 65 feet – plane polarized light, C) sample from 64 feet – crossed polars, D) sample from 64 feet – plane polarized light.

Amorphous silica would be reactive and could form silicates with uranium. Figure A13 is a stability diagram for the mineral soddyite [$(UO_2)_5Si_2O_9.6H_2O$] showing concentrations of uranium and pH of groundwater samples from 29 wells in the F-Area Seepage Basin plume sampled in July 2010. The sample data from acidic portions of the plume plot along the boundary of the soddyite stability field. This does not mean that uranium concentrations are controlled by soddyite precipitation, but the data are consistent with this hypothesis. Figure A14 is a stability diagram for soddyite and uranophane [$Ca(UO_2)_2Si_2O_7.6H_2O$] at carbonate concentrations similar to those used in base injection. It suggests that it is possible that even during the injection of the carbonate-bearing base, uranophane could control the solubility of uranium to less than 10 pCi/L. Again, much more study is required to demonstrate this, but it remains a possibility for explaining why uranium concentrations don’t increase much more than observed following base injection.

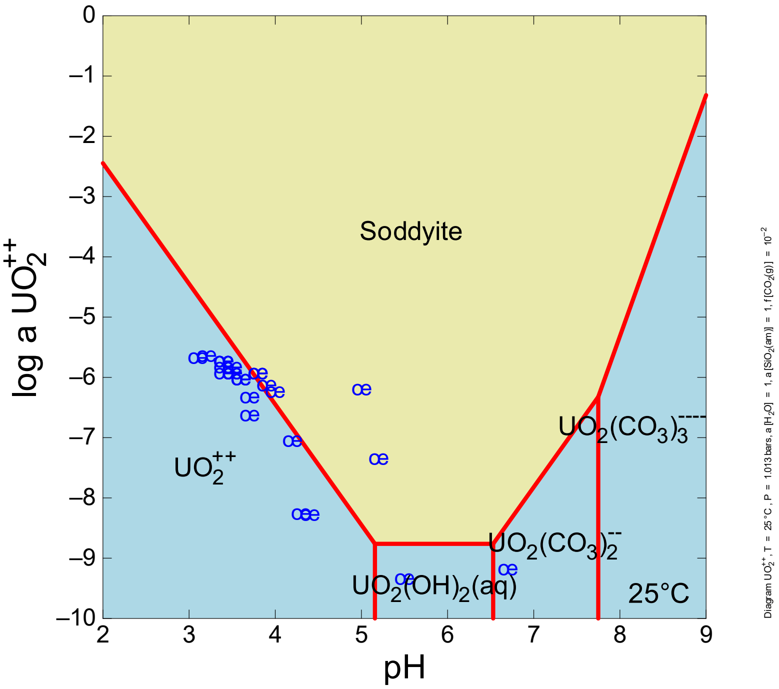


Figure A13: Stability field of soddyite in equilibrium with amorphous silica and a PCO2 of 10-2 atm.; uranium vs. pH data for 29 samples obtained from the F-Area Seepage Basins plume in July 2010; calculated with The Geochemist’s Workbench® (Bethke, 2005).

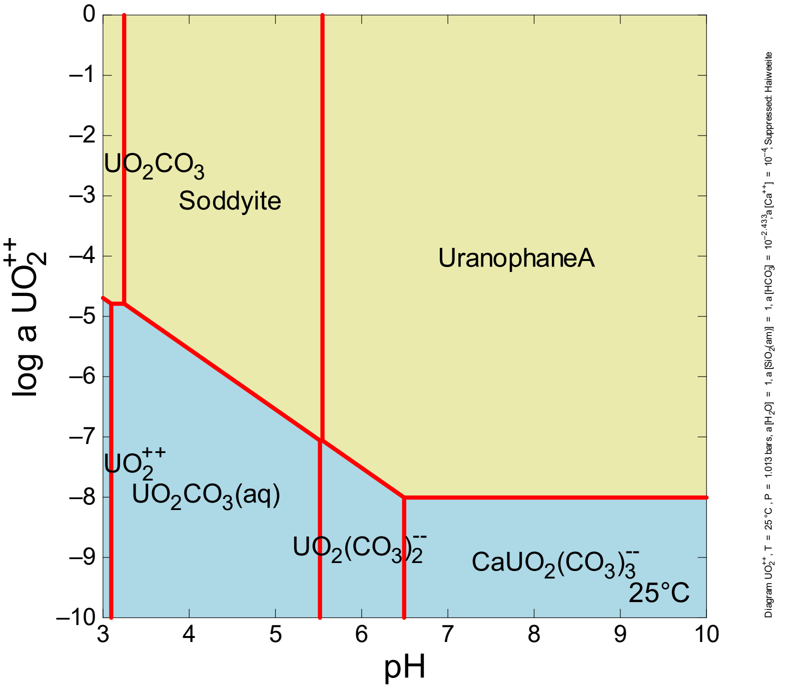


Figure A14: Stability fields for uranyl carbonate, soddyite, and uranophane in equilibrium with a total carbonate concentration of 3.69x10-3 moles/liter, a calcium concentration of 1x10-4 moles/liter, and amorphous silica; calculated with The Geochemist's Workbench® (Bethke, 2005); thermodynamic data for uranophane from Perez et al. (2000).

Titrations of Soil Samples

Acid-base titrations and closely spaced x-ray fluorescence (XRF) analyses were done on samples from soil boring FAW-5 located 120 meters upgradient of FSB-131D. The XRF analyses (Figure A15) show that iron is most abundant in the top of the soil boring and at the bottom near the TCCZ. The mineral goethite [FeOOH] is responsible for much surface acidity that base injection seeks to neutralize. Therefore, higher concentrations of iron means that more base is required to bring a sample to an elevated pH. This is reflected in the titration curves (Figure A16).

The shapes of the curves also give some insight into potential areas of optimization. Between pH values of 6 and 9 small changes in the amount of base result in large changes in pH. This provides the opportunity to potentially reduce the alkalinity of the base. This would reduce the cost of chemicals but would also reduce the amount of carbonate in the base. Between pH values of 9 and 10 silica, as quartz or amorphous silica, begins to dissolve by a reaction such as:

$$SiO_2 + 2OH^- = H_2SiO_4^{-2}$$

The reaction consumes base and may account for much of the base added between pH values of 9 and 10. Figure A17 shows calculated titrations of soil with goethite in the presence or absence of SiO_2 as either quartz or amorphous silica. The presence of amorphous silica requires the use of 54% more base to reach a pH of 10, than if no amorphous silica were present. Yet, if the titration is stopped at pH=9, the presence of amorphous silica requires the use of only and additional 7% of base. Hence, it would make sense to stop base injection when the sentry well reaches a pH of 9 rather than 10. This would save on the use of base and would also minimize dissolution of amorphous silica that may be contributing to attenuation of uranium.

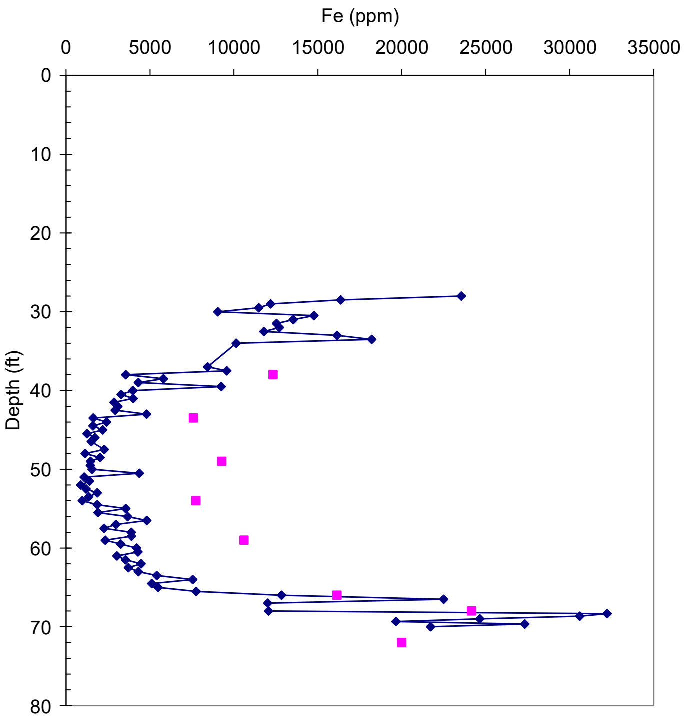


Figure A15: X-ray fluorescence data for soil boring FAW-5; red squares correspond to titrated samples in Figure 16.

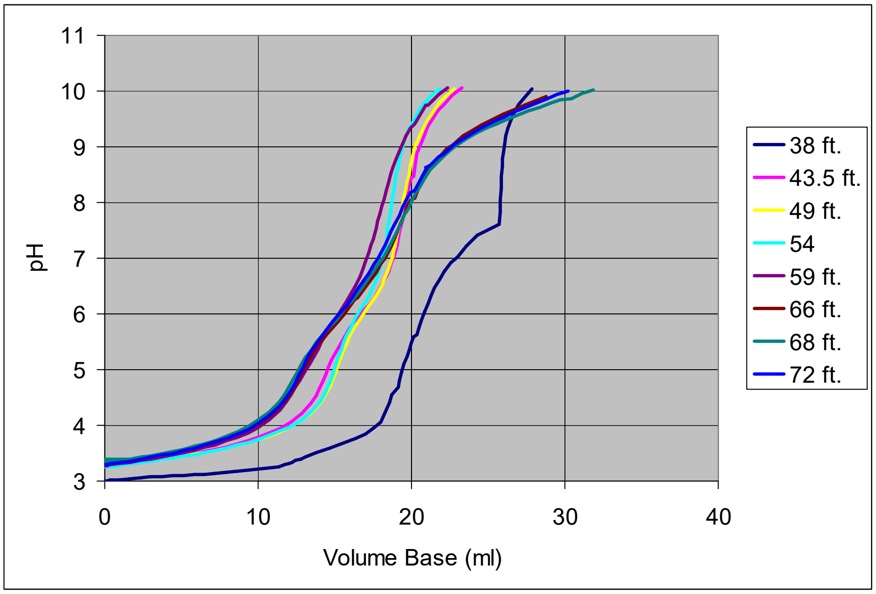


Figure A16: Titration curves for soil samples from FAW-5; base used 0.01N NaOH, 13 gram samples.

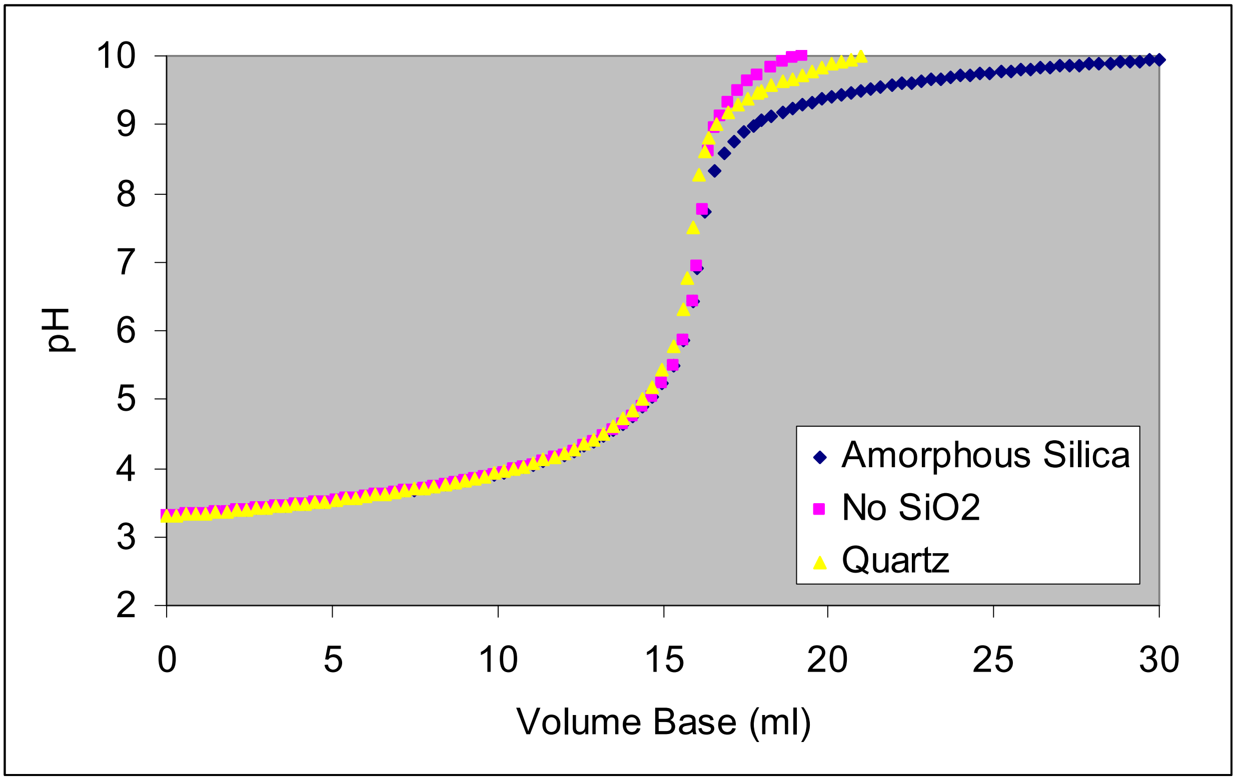


Figure A17: Calculated titration curves for a system similar to the samples of FAW-5 showing the effect of the presence of amorphous silica and quartz; calculations done with the Geochemist's Workbench (Bethke, 2005).

Conclusions

Five years after the first base injection campaign, monitoring data indicate that the system is operating as predicted in the original conceptual model. A treatment zone with elevated pH has been established downgradient of the injectors. Between injection periods, degradation in the upgradient portion of the treatment zone by influent acidic groundwater water was observed. Groundwater monitoring data show that there was a large effect on contaminant concentrations by the physical processes that occur at the barrier wall. Smaller, but definitive, chemical effects of base injection on Sr-90 and U-238 concentrations were observed. With the exception of occasional isolated peaks, Sr-90 and U-238 concentrations have remained below their respective drinking water standards.

The U-238 peaks may be due to increased mobility during base injection events caused by carbonate complexing. However, these don't represent mobilization of large fractions of the uranium sequestered in the treatment zone between base injection events. Desorption of uranium may be a slower process than adsorption or it is feasible that uranium concentrations are solubility limited. The conditions in the treatment zone would favor precipitation of uranium silicates. This is being examined by SRNL as part of a DOE EM-32 funded project.

Opportunities for Optimization

1. The screen zones of the injectors do not completely intersect the contamination plume. The lowest pH groundwater occurs near the top of the TCCZ. Additional injectors could be installed and screened to a lower elevation to better address this contamination. In addition, there is more clay near the top of the saturated zone. More base is required to raise the pH in more clayey zones.

Hence, the top of the screens for any additional injectors could be located below this clayey zone. No loss of performance would be expected because contamination passing through the upper portion of the saturated zone is minimal compared to lower zones.

2. The trigger pH for turning off base injection could be lowered from 10 to 9. Above a pH of 9 much of the base is being used to dissolve quartz and possibly amorphous silica. This would result in a minimal loss of buffering capacity in the treatment zone, while saving on base use.

3. Base concentration could be reduced in alkalinity because acid-base titrations indicate that between pH values of 6 and 9 a small amount of base produces a large change in pH. This would lower the carbonate concentration and save some costs of chemicals.

4. Use of a base other than one containing carbonate would eliminate any concerns associated with uranium mobilization during base injection events. SRNL is currently studying two alternative bases as part of a DOE EM-32 project. One is disodium silicate the other is solid magnesium hydroxide.

Disodium silicate was proposed by Bethke (2006) to provide alkalinity as a silicate ion. This has the advantage of not containing carbonate that tends to increase mobility of several metals including uranium. In addition, it would provide silicate for potential precipitation of uranium silicates. The amorphous silica that precipitates as the pH decreases also provides potential sorption sites for other contaminants. The potential issues with disodium silicate are precipitation of too much silica in the aquifer and achieving a high enough alkalinity at a pH acceptable to regulators.

Magnesium hydroxide is also advantageous because it contains no carbonate, but also because it is a solid. The advantage of a solid is that it stays in the injection area and provides long-lasting buffering capacity. A further advantage is that it can potentially be used in the vadose zone to neutralize acidic pore water. The disadvantages are that large areas can be difficult to treat because of the limited travel distance of an injected solid and that magnesium could potentially mobilize sequestered Sr-90 by ion exchange.

Bench-scale experiments on these potential bases will be conducted this spring, with small-scale field test planned in the future.

References

Bethke, C.M., 2006, In Situ Treatment Process to Remove Metal Contamination from Groundwater. U.S. Patent No.: 7,141,173 B2.

Bethke, C.M., 2005, The Geochemist's Workbench® (geochemical modeling software), Release 6.0, University of Illinois.

Dayton, E.A. and N.T. Basta, 2005. A method for determining the phosphorus sorption capacity and amorphous aluminum of aluminum-based drinking water treatment residuals. J. Environ. Qual., 34, 1112-1118.

Pérez, I., I. Casas, M. Martin, and J. Bruno, 2000. The thermodynamics and kinetics of uranophane dissolution in bicarbonate test solutions. Geochim. Cosmochim. Acta, 64, 603-608.

Appendix A.1 – Results of extractions from FSO soil boring samples.

Sample Name	weight soil (g)	volume extractant (mL)	Concentration in Extraction Solution		
			Al (ug/g)	Fe (ug/mL)	U (ug/mL)
FOS-1-44-	1.17	15	3.17	7.09	0.0261
FOS-1-44-	1.09	15	2.58	5.01	0.0211
FOS-1-60-	1.37	15	7.39	10	0.137
FOS-1-60-	1.36	15	4.8	7.94	0.0863
FOS-2-36-	1.01	15	1.37	3.83	0.0447
FOS-2-36-	1.04	15	4.79	7.93	0.0861
FOS-2-38-	1.15	15	2.47	15.3	0.00854
FOS-2-38-	1.27	15	2.29	14	0.00654
FOS-2-41-	1.16	15	2.47	5.49	0.0892
FOS-2-41-	1.08	15	2.53	6.31	0.0888
FOS-2-44-	1.02	15	6.47	6.05	0.103
FOS-2-44-	1.35	15	7.85	7.65	0.139
FOS-2-50-	1.72	15	103	57.4	0.0855
FOS-2-50-	1.05	15	69.2	36	0.0521
FOS-3-33-	1.49	15	7.38	5.22	0.0997
FOS-3-33-	1.17	15	6.18	4.04	0.0773
FOS-3-39-	1.46	15	2.49	15.1	0.0643
FOS-3-39-	1.68	15	3.11	25.9	0.075
FOS-3-42-	1.32	15	3.02	5.6	0.0535
FOS-3-42-	1.34	15	2.82	10.2	0.0421
FOS-3-45-	1.08	15	2.74	1.85	0.0332
FOS-3-45-	1.28	15	2.2	1.88	0.028
FOS-4-39-	1.55	15	3.03	29.7	0.207
FOS-4-39-	1.67	15	3.82	15	0.36

7.0 Appendix B: Denham (2013)

Reassessment of Monitoring Data for I-129 Remediation by the Silver Chloride Treatment Zone

Environmental Compliance & Area Completion Projects (EC&ACP) requested that SRNL evaluate data monitoring effectiveness of the I-129 treatment zone emplaced near the middle gate of the F-Area Seepage Basins barrier wall. The treatment consisted of injection into the aquifer of submicron silver chloride particles suspended in water. The injections were done over the depth profile of the water table aquifer using direct push technology (SRNS, 2011). Figure B1 shows the locations of the injection pushes and the wells used to monitor effectiveness. Table B1 shows the depth range of the injections, the screen zones of the observation wells, and the average elevation of the water table at each well during the monitoring period.

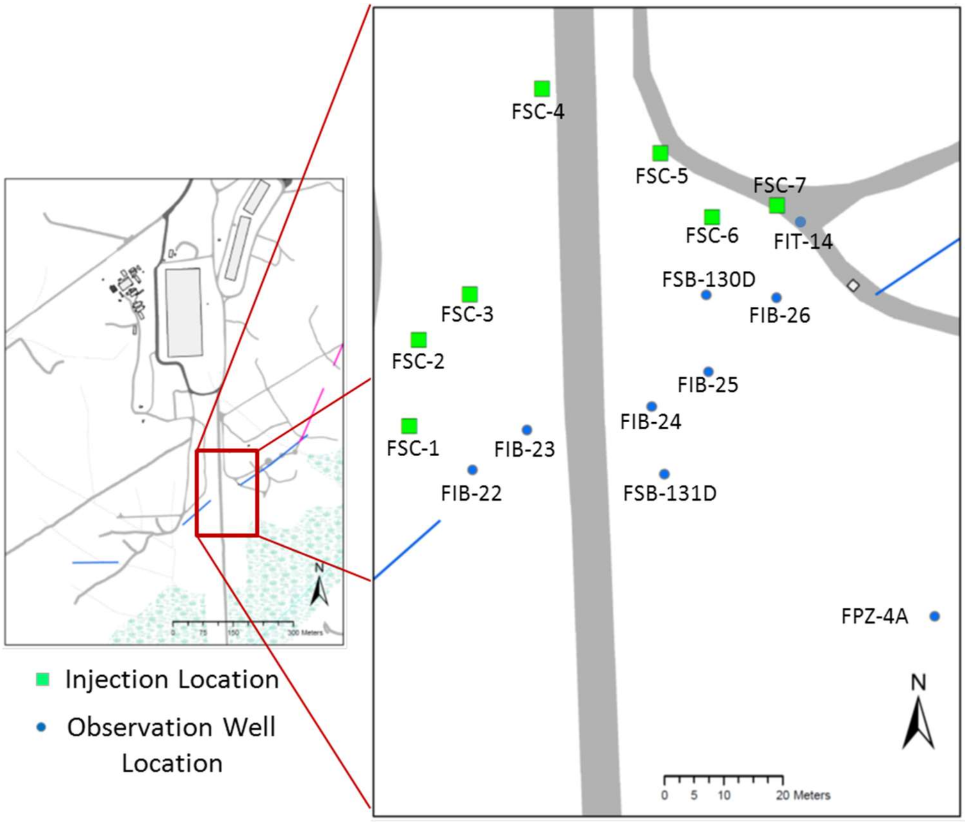


Figure B1: Location of injection pushes and observation wells.

Table B1: Depth intervals of silver chloride particle injections, screen zones of observation wells, and water table elevation in observation wells.

Injection/Well ID	Function	Injection/Screen Top Elev. (ft. MSL)	Injection/Screen Bottom Elev. (ft. MSL)	Water Table Elev. (ft. MSL)
FSC-1	Injection	204	179	NA
FSC-2	Injection	206	181	NA
FSC-3	Injection	207	182	NA
FSC-4	Injection	208	183	NA
FSC-5	Injection	207	185	NA
FSC-6	Injection	208	183	NA
FSC-7	Injection	207	187	NA
FIB-22	Observation	194	179	201
FIB-23	Observation	194	179	202
FIB-24	Observation	198	183	201
FIB-25	Observation	200	185	201
FIB-26	Observation	199	184	201
FIT-14	Observation	200	185	200
FSB-130D	Observation	200	190	201
FSB-131D	Observation	201	191	200

In the absence of strategically placed background wells upgradient from the treatment zone, the best way to assess the performance of the silver chloride injections is to analyze time trends in concentration of I-129 at the observation wells. For a short time, the injections themselves can cause a decrease in the I-129 concentration because of dilution by the injectate fluid. To discern decreases in I-129 concentration due to dilution from those due to removal by silver chloride, I-129 concentration can be compared to other constituents that would not be affected by the silver chloride. Here, I-129 concentrations are compared to specific conductance (a measure of total dissolved solids) and tritium. Yet, even when dilution is not an issue, a decrease in I-129 concentrations alone is not diagnostic of removal by the silver chloride. This is because the nature of plume dynamics causes concentrations of constituents to vary as source releases vary, attenuation varies, or the plume shifts. Hence, to evaluate the performance of the silver chloride treatment zone, the time trends in concentrations of I-129 must be compared with those of constituents like specific conductance and tritium.

The only observation well that shows a definitive effect on I-129 by the silver chloride treatment zone is FSB-130D.

Figure B2 shows the time trend data for I-129 at FSB-130D compared with the data for specific conductance and tritium. Over the time period between 2/10/2009 and 2/10/2011 the I-129 concentration averaged 135 pCi/L. Shortly before the silver chloride injections began, the I-129 the concentration had dropped to 77 pCi/L. When the injections began, the I-129 concentration decreased and there were corresponding small decreases in specific conductance and tritium concentration. With time the concentration of I-129 continued to decrease, whereas specific conductance and tritium concentration increased. This suggests strongly that the decrease in I-129 concentration was the result of removal by the injected silver chloride. The minimum concentration reached was 46 pCi/L and the concentration was stable for at least 6 months. At 7 months post-injection, the I-129 concentration increased to 99 pCi/L. The I-129 concentration remained between 109 and 79 pCi/L over the final five months of monitoring.

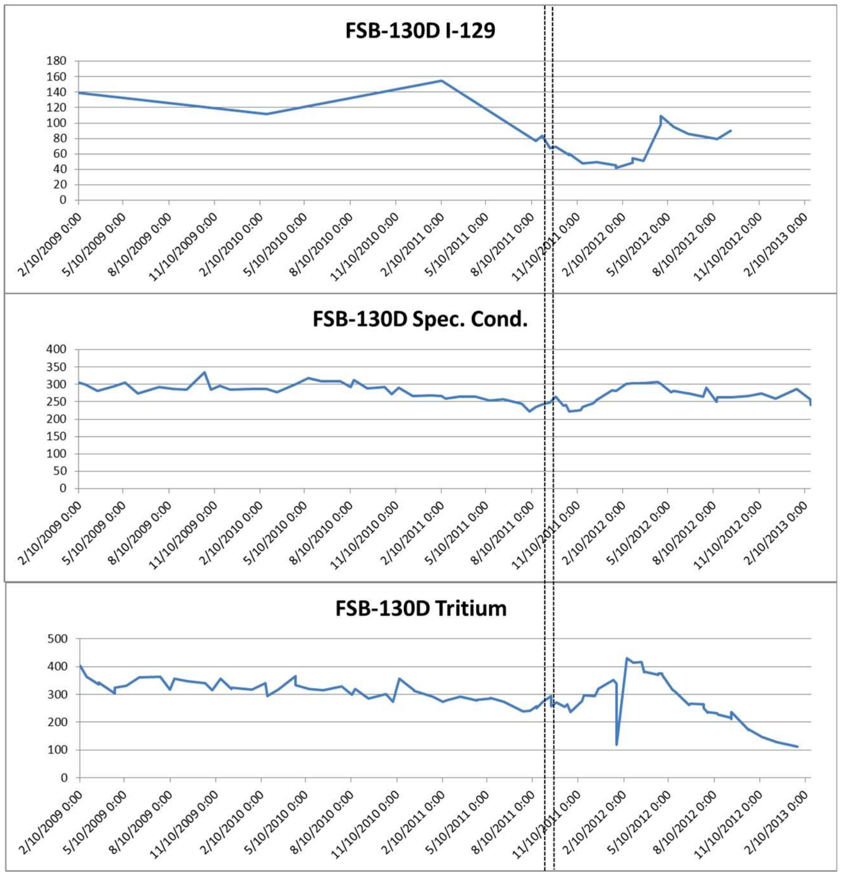


Figure B2: Time trends of I-129 concentration (pCi/L), specific conductance (uS/cm), and tritium (pCi/ml) in observation well FSB-130D; dotted lines denote the period of silver chloride injection.

The data from observation well FSB-131D are ambiguous (

Figure B3). I-129 concentration decreased during the injection period and remained constant for approximately one month. I-129 and tritium concentrations, as well as specific conductance then increased for three months. This was followed by a decrease in all parameters. It is possible that the initial decrease in I-129 concentration reflects the effects of the silver chloride treatment zone and that a subsequent change in the plume reduced those effects. However, the data do not support a definitive interpretation.

Data from the other observation wells appear compromised by local well effects. Specific conductance and tritium concentrations in wells FIB-22, FIB-24, FIB-25, and FIB-26 are uncharacteristically low for groundwater within this plume. For some, tritium concentrations are similar to rainwater. I-129 concentrations are also very low. A reasonable explanation is that water entering the well casings during sampling is predominantly from the top few feet of water in the water table and thus has a composition similar to recharge. This could be caused by reduced permeability in the lower part of the aquifer or by clogging of the lower part of the screen. Just prior to the silver chloride injections the I-129 concentration in water from well FIB-23 was very low (11 pCi/L). It increased throughout the monitoring period reaching 452 pCi/L by the final sampling event. The increase in I-129 concentration was accompanied by general increases in specific conductance and tritium concentration. There is no indication of effects of the silver chloride, but the unusual time trend in I-129 concentration suggests well FIB-23 may not provide representative data.

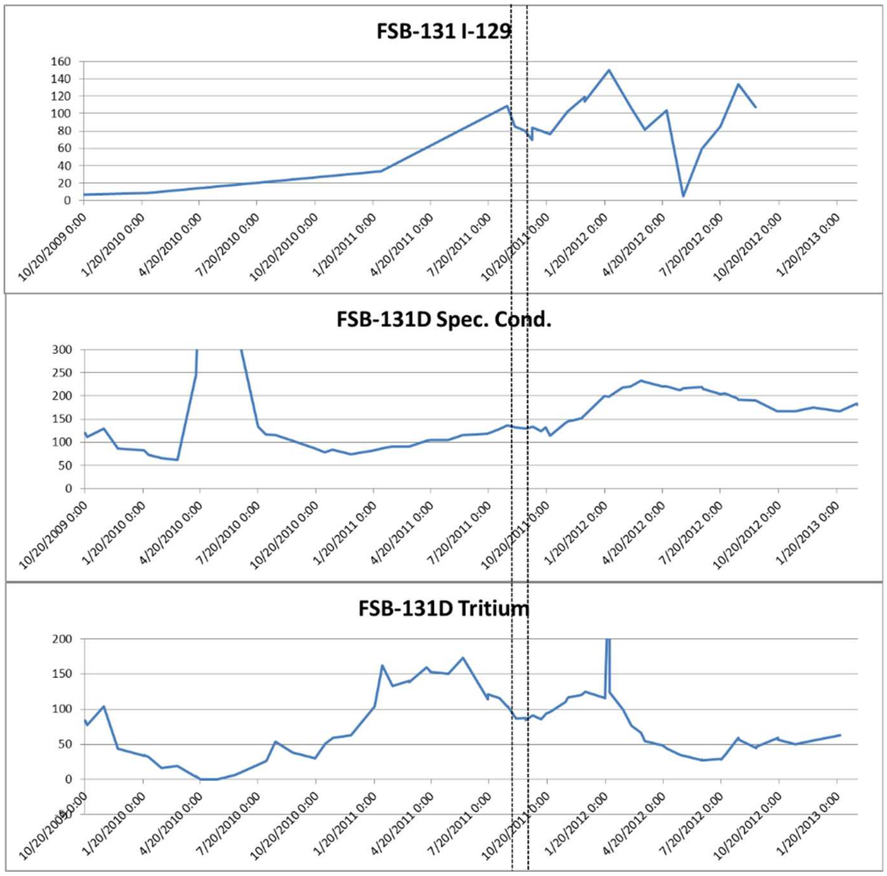


Figure B3: Time trends of I-129 concentration (pCi/L), specific conductance (uS/cm), and tritium (pCi/ml) in observation well FSB-131D; dotted lines denote the period of silver chloride injection.

Likewise, well FIT-14 has an unusual time trend. The concentration of I-129 decreased significantly from 164 pCi/L prior to injection to 31 pCi/L one year later. However, tritium concentration decreased in a similar manner with time. Specific conductance also decreased. These time trends suggest that any effects of the silver chloride were masked by some other plume dynamic.

Monitoring of the silver chloride treatment zone is complicated by unknown flow paths and unknown distribution of the injected particles. Groundwater flow within the gates is likely to be complex because groundwater that is forced into the gates by the walls intersects groundwater flowing from upgradient of the gates. Hence, observation wells that appear to be directly downgradient of injection locations, based on flow paths prior to the wall construction, may not be. If this is the case, water sampled from these wells may not have contacted silver chloride particles.

Another complexity is that the distribution of injected silver chloride particles is not homogenous. Even in a perfectly homogenous aquifer the concentration of particles will be substantially higher closer to the injection point, resulting in much lower concentrations toward the edge of the radius of influence. In a real aquifer, some increased deposition of particles along preferential pathways is likely, resulting in greater heterogeneity in particle distribution. The heterogeneity in particle distribution can be reflected in apparent short-lived effects of the silver chloride, because water being sampled has only contacted low concentrations of particles that become completely reacted in a short time. Nevertheless, short-lived effects may also be real, caused by reaction product coatings on the particles that render them inert.

In summary, data from one observation well shows removal of I-129 by the injected silver chloride particles. Data from another observation well shows very short-lived effects. The other wells appear to be compromised. If the compromised wells could be restored, a clearer picture of the effectiveness of the silver chloride injections would emerge.

Reference

SRNS, 2011. Field Summary for the Injection of Silver chloride for the Treatment of Iodine-129 in Groundwater at the F-Area Hazardous Waste management Facility. SRNS-RP-2011-01481, Savannah River Nuclear Solutions, Aiken, SC 29808.