

Influences on Effective Decay Rates of Radionuclides in Groundwater: F-Area Seepage Basins, Savannah River Site – 17149

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ABSTRACT

Effective decay rates for radionuclides incorporate all attenuation mechanisms and are useful for assessing the progress of natural or enhanced attenuation. If a concentration versus time trend at a given monitoring well behaves according to first-order decay, then an effective decay constant can be calculated from the slope of the linear trend. It is important to view time trends in terms of all possible processes that can affect them prior to evaluating effective decay rates, because changes to groundwater flow and attenuation processes influence the rate at which contaminant concentrations decrease. In addition, other factors can lead to apparent changes in the effective decay rate. Groundwater associated with the F-Area Seepage Basins at the Savannah River Site in South Carolina provides an excellent case study for examining processes that affect concentration versus time trends and some of the pitfalls in evaluating effective decay rates. The site has an extensive groundwater monitoring database and its history is well known. The objective of this case study is to highlight the importance of viewing a site holistically in any evaluation of effective decay rates, because what is obvious at the F-Area Seepage Basins may not be obvious at sites with sparser monitoring data and more obscure histories.

INTRODUCTION

Analysis of effective first-order decay rates in the concentration of constituents in a contamination plume is a valuable tool for assessing remediation. Newell et al. (2002)[1] demonstrated this by using first-order exponential decay rates to assess natural attenuation and predict times required to reach remedial goals. They stress the importance of spatial variation within a contamination plume and the necessity to consider contaminant versus time trends at several locations. Tardiff and Katzman (2007)[2] demonstrated that information about retardation of a non-conservative constituent can be derived by comparing its first-order decay rate to that of a conservative tracer. Both [1] and [2] discuss uncertainty and limitations to analyzing time trends for predictive purposes. A primary caution to using this approach is that contaminant versus time trends can be misleading if they are analyzed without considering information on events or processes that may influence the trends.

The contamination plume in groundwater associated with the F-Area Seepage Basins at the Savannah River Site provides an excellent case study on how events and processes can influence effective first-order decay rates. Throughout the evolution of the site there have been several events and changes in processes that

are well characterized. Groundwater monitoring data are available throughout the history of the site that document the changes in the contaminant concentration versus time trends. Here we examine log concentration versus time trends to highlight the importance of viewing a plume holistically when attempting to derive information from first-order exponential decay rates. It also follows that changes in the first-order effective decay rate of a contaminant may indicate an important change has occurred in the factors influencing contaminant migration.

F-Area Seepage Basins History

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. The mobile radionuclides, tritium, uranium, I-129, and Sr-90 migrated through the vadose zone, contaminating groundwater in the saturated zone at concentrations of environmental concern. The resulting contamination plume has an areal extent of approximately 1 square kilometer and discharges into wetlands and a local stream called Fourmile Branch. The map in Fig. 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.

The contamination plume occupies only a portion of the vertical extent of the saturated zone – approximately 3 meters of a total thickness of 10 meters for the saturated zone. During the period of active basin use, the plume was likely more extensive vertically than it is now. Recharge downgradient of the basins and a downward hydraulic gradient caused the contamination to migrate downward from the basins toward a semi-permeable stratigraphic layer at the bottom of the aquifer, referred to as the Tan Clay. Interpretation of concentration data is complicated by the fact that monitoring well screens do not all penetrate the same vertical portion of the plume and highlights the necessity of understanding the vertical distribution of contamination.

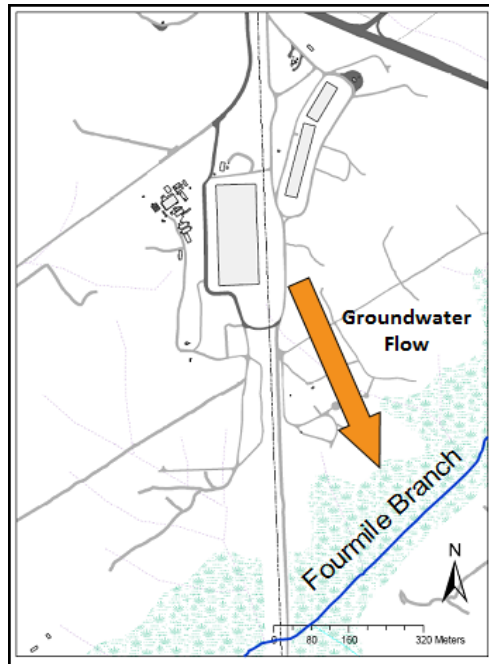


Fig. 1. Map of F-Area Seepage Basins, wetlands (green patterned area), and Fourmile Branch.

The history of the F-area Seepage Basins is depicted in the timeline in Figure 2. Disposal of waste into the basins began in 1955 and ended in 1988. During basin operation, the concentration of radionuclides entering the basins varied considerably, but these variations were dampened by mixing in the basins and by processes that occurred during migration through the vadose zone. Closure and installation of a low permeability cap over the basins was completed in 1991 and 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 [3]. This approximately coincides with the start-up in 1997 of a pump-and-treat system that extracted groundwater from downgradient, removed most of the radionuclides except tritium, and re-injected the treated water upgradient of the basins. The pump-and-treat system was replaced in 2004 with the current remediation, a funnel-and-gate with base injection in the gates. 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 enhanced adsorption of uranium and Sr-90 to mineral surfaces within these zones. The treatment zones are

created by periodic injection of alkaline fluids. In 2010, a small zone of elevated pH was created on the east side of Basin 2 by a DOE funded demonstration of a bioreduction technology to treat uranium and Tc-99 [4]. The most recent major event in the history of the F-Area Seepage Basins was installation of an eastern extension of the funnel and gate system, completed in 2011.

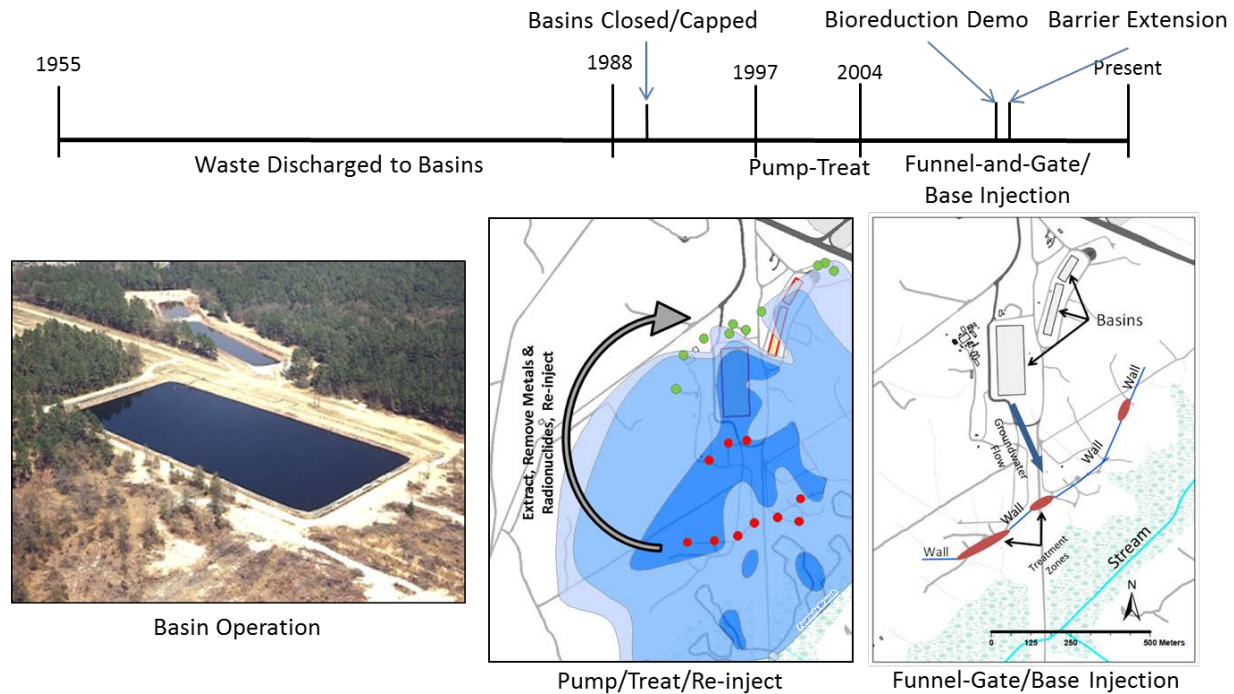


Fig. 2. Timeline of events in the history of the F-Area Seepage Basins.

CONCENTRATION VERSUS TIME TRENDS

The variation in concentration with time for first order decay can be expressed:

$$C_t = C_0 \times e^{-kt} \quad (\text{Eq. 1})$$

where C_t =concentration at time t , C_0 = initial concentration, and k =the decay constant. This relation is linearized as follows:

$$\ln(C_t) = -kt + \ln(C_0) \quad (\text{Eq. 2})$$

where the negative of the decay constant (k) is the slope of $\ln(C_t)$ plotted versus time (t). Various authors have demonstrated that concentration versus time trends for contaminants in a shrinking plume for which the source has been depleted or is diminishing often follow first order decay at a given monitoring point (e.g., [1], [2]). The decay constant derived from this behavior is referred to here as the effective decay constant to distinguish it from the radioactive decay constants of the contaminants of concern at the F-Area Seepage Basins. The effective decay constant incorporates multiple attenuation processes responsible for the decay of

contaminant concentrations. Hence, a change in the rate of any of these processes can result in a change in the effective decay constant. In addition, artifacts of well screen placement and shifts in plume flow can result in a calculated effective decay constant that could be mistaken for changes in plume attenuation. The following examples from the F-Area Seepage Basins monitoring data illustrate why it is imperative to have a holistic understanding of a contaminant plume prior to using an effective decay constant to derive attenuation information about a plume.

Artifacts of Well Screen Placement

The stratified nature of the contaminant plume associated with the F-Area Seepage Basins can result in apparent trends in contaminant concentrations caused by the fluctuation of the water table in relation to the well screen. Fig. 3 is a depiction of a stratified contaminant plume with two monitoring wells, A and B, and the effects caused by a high (top diagram) and a low water table (bottom diagram). The screen for well A is placed across the entire vertical extent of the contaminant plume and

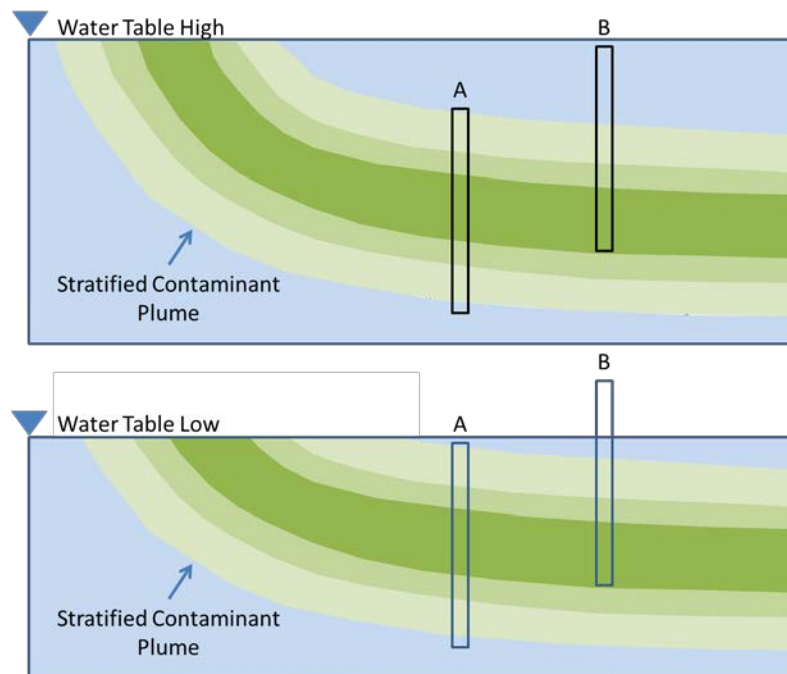


Fig. 3. Diagram illustrating the effects of well screen placement and a fluctuating water table on apparent contaminant concentrations.

does not straddle the water table. The screen for well B extends into the top portion of the contaminant plume and, at times, the screen does straddle the water table. When the water table is high, the screen for well B is exposed to a significant amount of relatively clean groundwater that dilutes the contaminated water entering the screen. In contrast, when the water table is low there is little clean

groundwater entering the screen to dilute the contaminated groundwater. Thus, a rising water table results in an apparent decreasing trend in contaminant concentrations and vice versa. Water table fluctuations do not affect the contaminant trends associated with well A, because of its placement relative to the plume and the water table.

In groundwater associated with the F-Area Seepage Basins apparent trends in contaminant concentrations caused by a fluctuating water table are observed in several wells. Fig. 4 shows two of these wells and a well that is unaffected by the fluctuating water table. The green vertical lines on the contaminant versus time plots show the elevation of the well screens and the red lines show the variation in the elevation of the water table with time. At all three wells, tritium concentrations follow first-order decay until August of 2011 when concentrations at wells A and B increase, corresponding to an abrupt decrease in the water table elevation. For the remainder of the monitoring period, the tritium concentrations vary inversely with the elevation of the water table. As the water table rises the tritium concentrations decrease and vice versa. The effect of the water elevation on tritium concentrations is muted at well C. The difference is that the screens for wells A and B are at a higher elevation than the screen for well C. Significant portions of the screens for wells A and B are always above the water table and they intersect less of the stratified plume than the screen for well C. The apparent trends in tritium concentrations in wells A and B could be mistaken for changes in plume behavior if well screen placement and the fluctuating water table were not considered.

Another question is raised by the relationship of the tritium concentrations to the water table elevation. Is the decay constant that could be derived from the first-order decay between the beginning of monitoring and August 2011 truly representative of the effective decay in tritium concentrations? The water table elevation steadily decreases throughout this time period, which should cause an apparent increase in tritium concentrations, at least in wells A and B. It is possible that this effect is partially offsetting the actual decrease in tritium concentrations and the actual decay constant is higher than would be calculated from the concentration versus time trends.

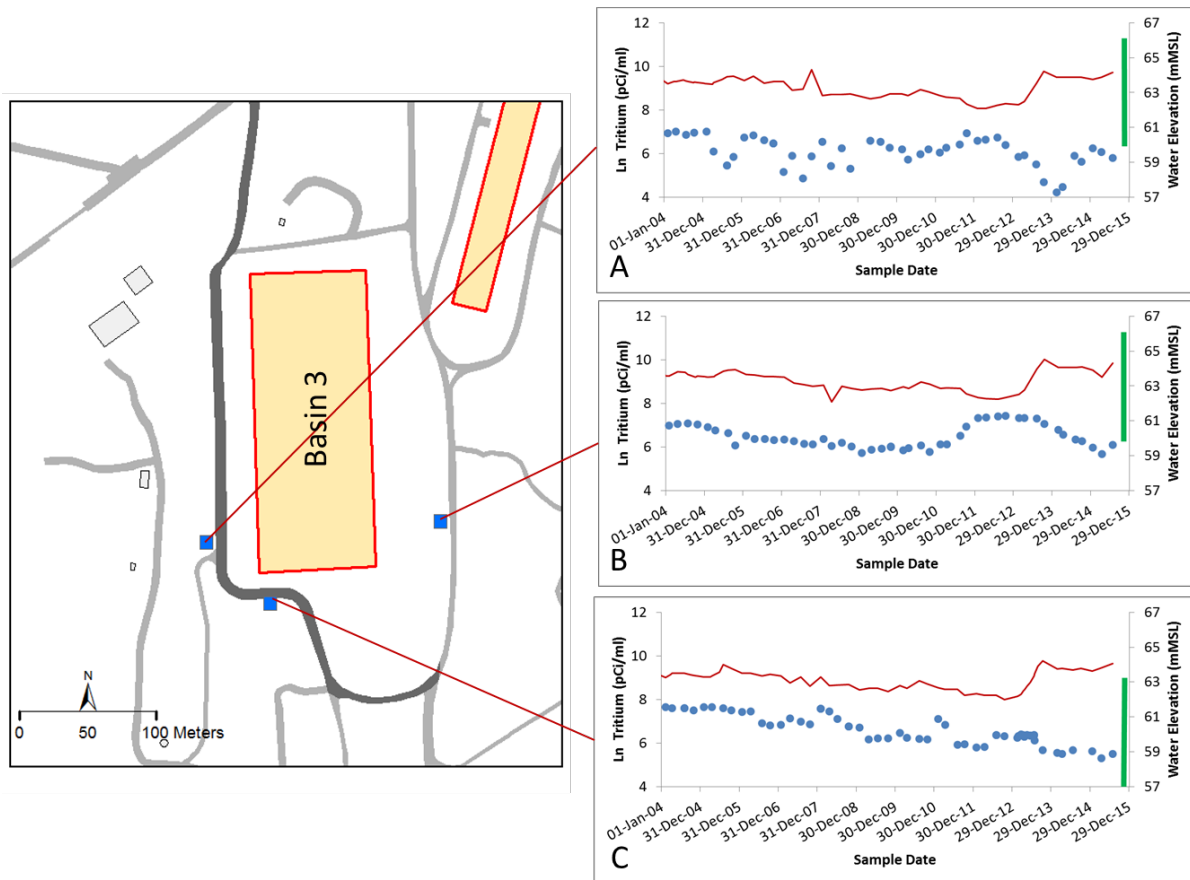


Fig. 4. Natural log of tritium concentrations (blue circles) and the water table elevation (red line) for 3 monitoring wells; green line shows well screen location.

Shifting Plume Flow Lines

Various events can cause a mature contaminant plume to shift flow direction and this, in turn, can cause an apparent change to the rate of concentration decrease at a given location. Variations in water balance, such as changes in local recharge or installation of nearby pumping or injection wells are the most common cause of shifting plume flow lines. Other causes include installation of in situ remediation infrastructure and changes in hydraulic conductivity in response to remediation or plume induced diagenesis. At the F-Area Seepage Basins there are two examples of shifting flow lines caused by remediation activities.

Pump-Treat-Reinject

The pump-treat-reinject remediation system caused shifting flow lines downgradient where groundwater was extracted and upgradient where treated groundwater was re injected. The slope of the overall hydraulic gradient at the site increased during this phase of remediation. In addition, there were local effects near extraction and injection wells. Fig. 5 shows an example of a contaminant

versus time trend influenced by the change in flow near two extraction wells (red circles). Note that the subsurface barrier (dotted line) was not in place at the time the pump-treat-reinject system was operating, so that both extraction wells had an influence on the monitoring well shown (blue square). Extraction of groundwater began in 1997 and ended in 2003 and this is reflected in the lowering of the water elevation in the monitoring well shown in Fig. 5. The tritium concentration at this monitoring well was nearly constant until 1998 when groundwater with lower tritium concentrations began entering the well. This was in response to the extraction wells pulling less contaminated portions of the plume toward the monitoring well. When extraction ceased in 2003, the water elevation rose in the monitoring well accompanied by increasing concentrations of tritium. This was interrupted by installation of the subsurface barrier of the funnel-and-gate system.

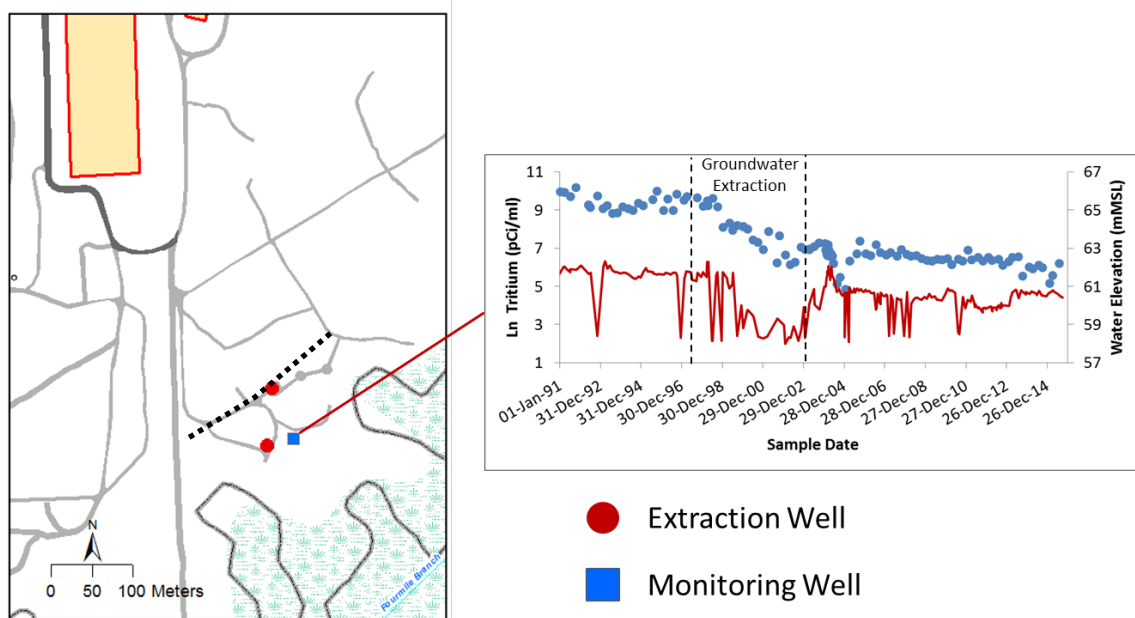


Fig. 5. Effect of pump-treat-reinject system on tritium concentrations (blue circles) and water elevation (red line) at a monitoring near two extraction wells.

Installation of Funnel-And-Gate System

Fig. 5 also illustrates the effect installation of the subsurface barrier portion of the funnel-and-gate system had on tritium concentrations and the water elevation. The purpose of the subsurface barrier was to change groundwater flow, so that contaminated groundwater would be blocked from flowing along preferential pathways and forced to flow to the gates. Prior to installation of the subsurface barrier, alkaline solutions were injected into the aquifer along the planned path of the barrier. The sharp decrease in tritium concentrations in 2004 at the monitoring well in Fig. 5 reflects the dilution of the plume caused by the injections. By 2005

the subsurface barrier was completed and tritium concentrations began to decrease according to a different effective decay constant than previously observed.

A more obvious example of the plume flow lines shifting because of remediation infrastructure is shown in Fig. 6. An extension to the subsurface barrier was installed in 2011, shown as the green line on the map in Fig. 6. The tritium concentrations at monitoring well A were unaffected and remained constant with time. Well D is located near the intersection of the original subsurface barrier and

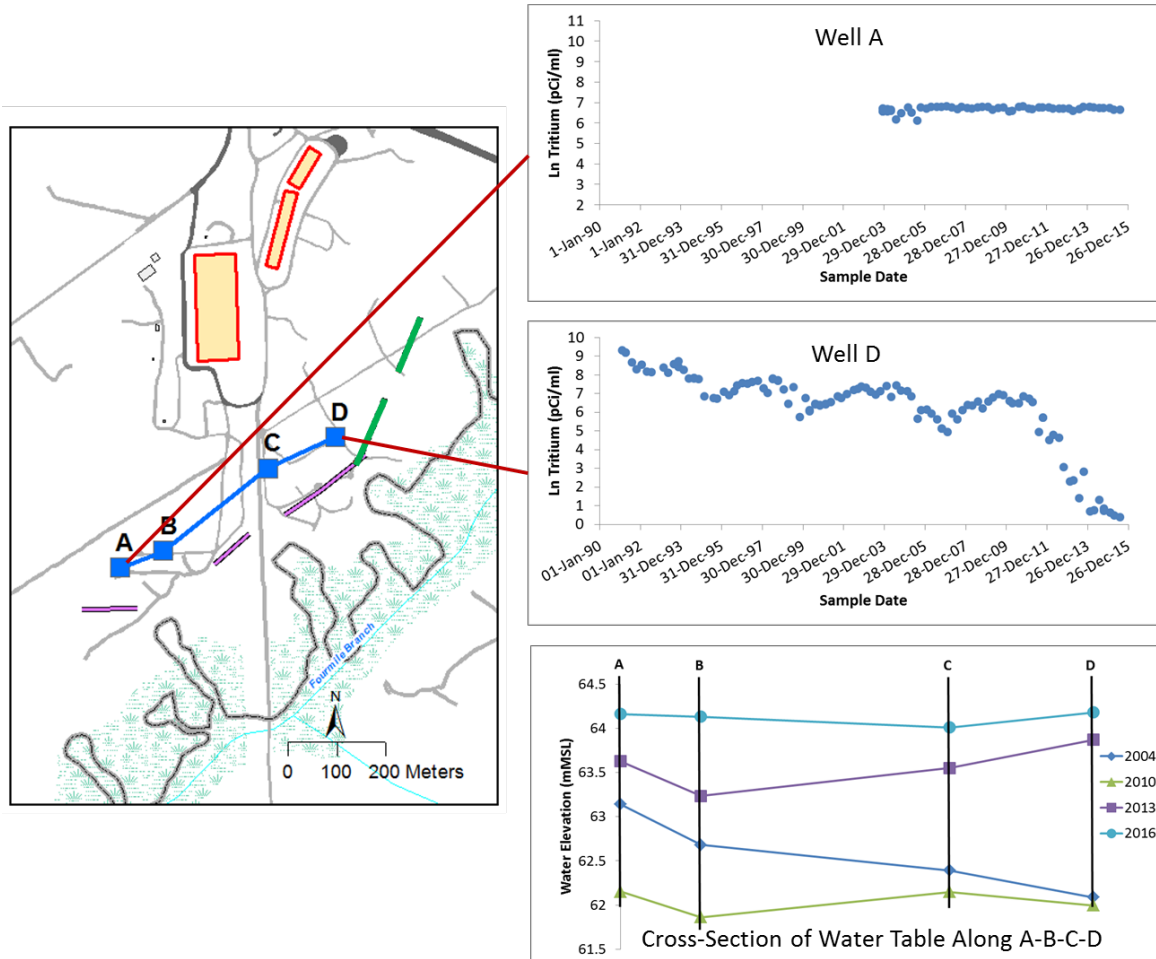


Fig. 6. The effect of extension of the subsurface barrier on tritium concentrations and the hydraulic gradient.

the extension. Tritium concentrations at well D were decreasing at a relatively constant slope until 2011, though not along a smooth trend. After the subsurface barrier extension was completed, the tritium concentrations decreased at a much faster rate until they reached background concentrations. The reason for the rapid decrease in tritium concentrations is that well D was near the edge of the plume

and the subsurface barrier extension forced groundwater that had been moving southeastward to move south westward. The change in plume flow lines moved the edge of the plume from east of well D to west of well D, so that well D now samples relatively clean water. The cross-section of the water table along A-B-C-D shows the hydraulic gradient dipping from well C toward well D prior to the barrier extension (2004 and 2010) and the dip reversing after the barrier was extended (2013 and 2016).

Changes in Contaminant Source

When tritium was reinjected upgradient of the seepage basins, it created a new source that was recorded differently in concentration versus time trends at different wells. Fig. 7 shows the concentration versus time trends at three monitoring wells and the

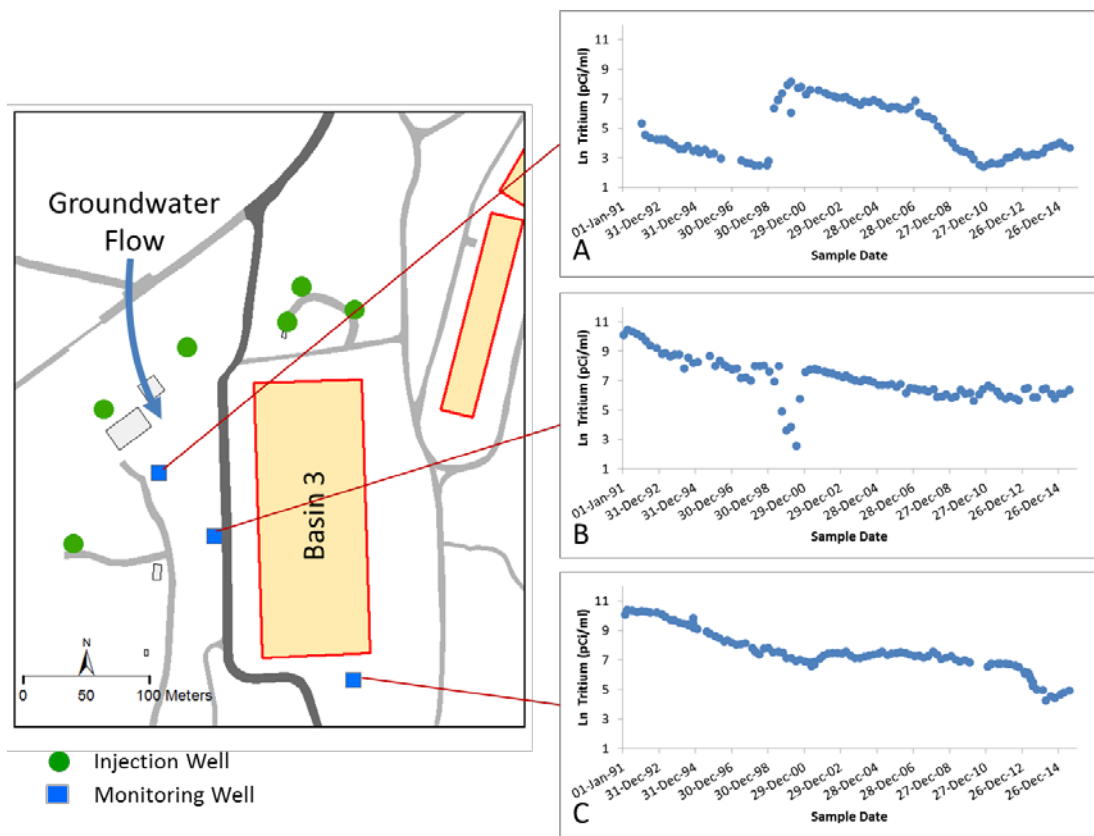


Fig. 7. The effect of injections of tritium-bearing water into the aquifer at 3 monitoring wells and the location of the monitoring wells relative to the injection wells.

location of the monitoring wells relative to the injection wells. At well A, closest to injection wells, tritium concentrations were decreasing linearly until they abruptly increased approximately 1 year after upgradient injections of treated water began in 1997. The elevated tritium concentration continued for approximately 6 years

after injections ceased in 2003, reflecting the input of groundwater to well A from two injection wells at different distances from the monitoring well. At well B, tritium concentrations decreased linearly until 1999, after which they decreased rapidly. The cause of the rapid decrease in tritium concentrations is not known, but it is observed in other monitoring wells adjacent to the basins. The decrease does not correlate directly to water table elevation, but the water table was elevated during this time. It is also possible it reflects completion of vadose zone drainage following basin closure [3]. Nevertheless, within a year of the decrease, the injected tritium arrived at well B, increasing tritium concentrations to near the levels that were injected. In well C, the only evidence of the tritium injections is a minor change in slope of the concentration versus time trend when the injected tritium arrived at the well.

Chemical Changes

Changes in the chemistry of a contamination plume can also cause changes to the concentration versus time trends of contaminants. The chemistry near one monitoring well at the F-Area Seepage Basins was temporarily altered by a demonstration of bioreduction to treat uranium and Tc-99 in groundwater [4]. The pH of the acidic groundwater was increased and the oxidation-reduction potential was decreased during the demonstration. The effect on the concentration versus time trends for the target contaminants, uranium and Tc-99, are shown in Fig. 8. The concentrations of

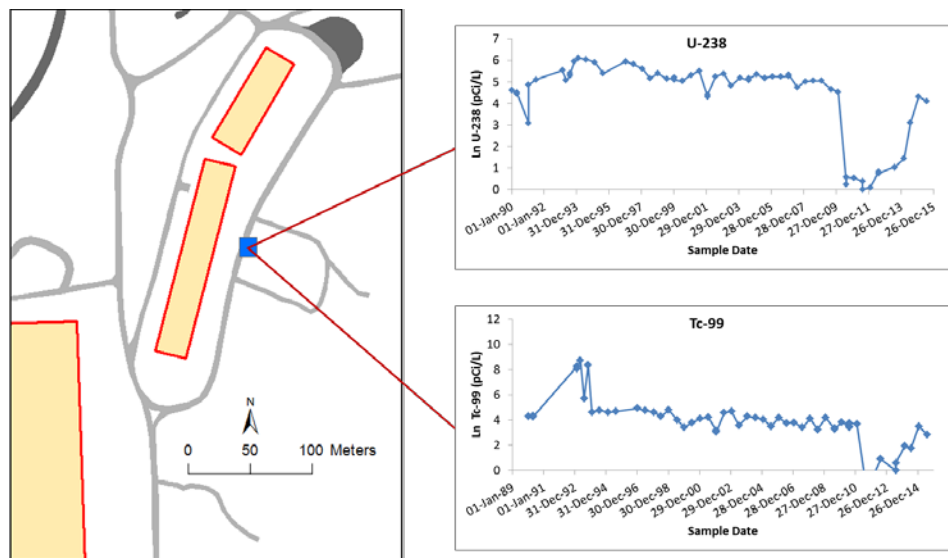


Fig. 8. Effect of variations in oxidation-reduction potential and pH on concentration versus time trends for U-238 and Tc-99 during demonstration of bioreduction technology.

both contaminants were decreasing according to first-order decay until the beginning of the demonstration. The change in chemical conditions caused an

abrupt decrease in concentrations. The effect on Tc-99 was caused by reduction of soluble Tc(VII) to low solubility (Tc(IV)) as intended by the demonstration. Both the decrease in oxidation-reduction potential and the increase in pH could have contributed to the decrease in uranium concentrations. Nonetheless, the concentrations increased as contaminated groundwater from upgradient passed through the demonstration site and returned the geochemical conditions to those of the contaminant plume. Three years after the demonstration, the concentrations of uranium and Tc-99 had returned to the first-order decay trend established prior to the demonstration.

The change in pH also caused interruption of the first-order decay trends of Sr-90 and I-129 as shown in Fig. 9. Adsorption of Sr-90 was enhanced by the increase in pH and concentrations decreased. Desorption occurred as pH returned to the original value. As expected, desorption of I-129 occurred as pH increased. Interestingly, as pH decreased again, the concentration of I-129 decreased to values below the original first-order decay trend.

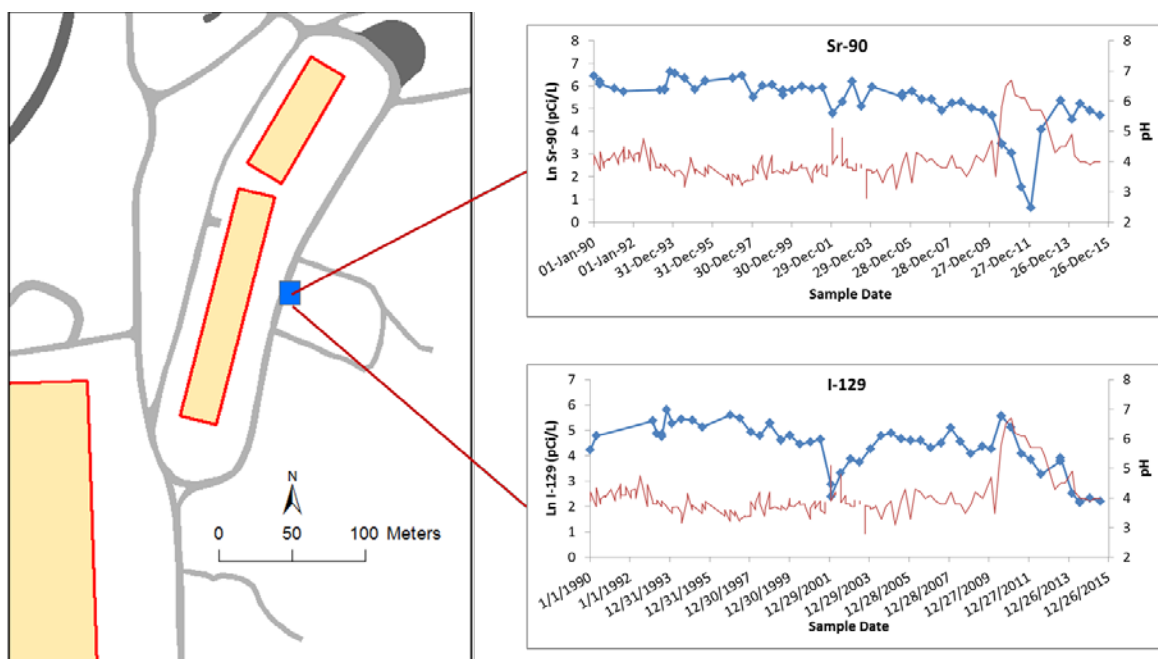


Fig. 9. Effect of variations in pH on concentration versus time trends for Sr-90 and I-129 during demonstration of bioreduction technology.

CONCLUSIONS

The F-Area Seepage Basins at the Savannah River site provide an excellent example of how different processes or variations in subsurface conditions influence effective first-order decay in contaminant concentrations. The example highlights the importance of viewing a site holistically when using first-order decay trends to derive information about remediation progress or attenuation processes. At the F-Area Seepage Basins the changes in processes and subsurface conditions are substantial and abrupt, resulting in abrupt changes to concentration versus time trends for contaminants that are related to known events. This is not true at many sites where changes are subtle, the history is not well known, or monitoring periods are relatively short. At these sites, changes to the system may manifest as changes to effective decay rates that can lead to erroneous conclusions about natural or enhanced attenuation.

The general examples presented here occur commonly at waste sites with contaminated groundwater. For example:

- *Artifacts of Well Screen Placement:* At many waste sites it is not known how vertical placement of well screens relate to the vertical extent of the plume or whether the plume is stratified. The spatial relation of monitoring well screens installed when the plume was first discovered may change over time. At many sites, particularly in arid climates, mineral deposits that contain leachable contaminants may form in the capillary fringe and rising water tables that intersect these may result in contaminant release [5]. Hence, it is important to be aware of any relation of contaminant concentrations to water levels in monitoring wells.
- *Shifting Plume Flow Lines:* Contaminant plumes shift flow directions in response to changes in conditions governing groundwater flow, including localized changes such as a leaking water line or dewatering of an excavation at a nearby construction site. To be certain that concentration decay rates are real requires an understanding of groundwater flow directions throughout the monitoring period.
- *Changes in Contaminant Source:* Co-mingling of contaminant plumes from distinct sources or from a single source from which contamination entered the saturated zone at multiple distinct locations will affect concentration versus time trends. As shown in Fig. 7, this can result in abrupt changes or subtle shifts in effective decay rates. Multiple contaminant sources should be one of the hypotheses considered to explain changes to effective decay rates.
- *Chemical Changes:* When a contaminant plume has a different chemical composition than the natural groundwater there will be changes to the chemistry of the plume throughout its evolution. The chemical evolution of a plume can cause variation in contaminant attenuation rates, and thus, effective decay rates. The result can be that derivation of effective decay

rates from monitoring data covering one time period may not be applicable to another time period. Hence, chemical evolution of a plume should be considered when using effective decay rates to assess remediation progress or natural attenuation.

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