Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

SRNL-STI-2014-00427

Single Well Field Injection Test of Humate to Enhance Attenuation of Uranium and Other Radionuclides in an Acidic Plume

September 2014

Prepared for: The U.S. Department of Energy (DOE) Office of Environmental Management
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Technical content and coordination for this effort was provided by the Savannah River National Laboratory in conjunction with Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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U.S. Department of Energy

A Single Well Field Injection Test of Humate to Enhance Attenuation of Uranium and Other Radionuclides in an Acidic Plume

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Prepared for

U.S. Department of Energy Office of Environmental Management

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Executive Summary

This report documents research conducted as part of the Attenuation-Based Remedies for the Subsurface Applied Field Research Initiative (ABRS AFRI) at the Savannah River Site that is funded by the Department of Energy Environmental Management Office of Soil and Groundwater Remediation (EM-12). This applied research initiative is focused on developing and bringing to maturity science-based approaches to Cleanup Sites contaminated with combinations of metals, radionuclides, and recalcitrant organic compounds. A key activity in this program is to develop tools and approaches for attenuation-based remedies, in this case, to investigate and validate the use of humate for subsurface stabilization of metals in contaminated groundwater plumes. A preliminary report was completed in 2013 which documented the successful field campaign that demonstrated the viability of dissolving and then injecting low cost agricultural humate into the subsurface. This report documents the impact of the injected humate on targeted contaminants over a period of 4 months and suggests it is a viable attenuation-based remedy for uranium, potentially for I-129, but not for Sr-90. Future activities will focus on issues pertinent to scaling the technology to full deployment.

A single well injection test was conducted in the acidic portion of the groundwater contamination plume associated with the F-Area Seepage Basins on the Savannah River Site to evaluate whether humate is a viable amendment to enhance attenuation of uranium and other radionuclides. The humate, a mixture of organic anions of humic acid, was an inexpensive unrefined form typically used as an organic farming fertilizer. The humate fertilizer was dissolved and a relatively concentrated solution of humate was injected into an existing monitoring well in the heart of the F-Area plume. The geochemical conceptual model is that the injected humate sorbs to mineral surfaces in the injection volume, thereby creating a subsurface treatment zone. After the injection, groundwater was sampled from the injection well at regular intervals to determine the composition of groundwater that had passed through the treatment zone, in particular to evaluate the sorption of contaminants within the treatment zone.

The post-injection monitoring data showed that uranium attenuation was enhanced in the treatment zone. Uranium concentrations decreased by 32% compared to pre-test concentrations, even when accounting for a natural decrease associated with a regional water table rise during the test. An estimated 30-40 pore volumes of groundwater passed through the 1-meter wide treatment zone during the test. A full deployment with a much wider treatment zone would achieve sufficient uranium removal to achieve regulatory standards. An outstanding question left to be resolved is how long this impact could be sustained, and whether repeated humate injections are beneficial. Radioiodine attenuation was complicated by changing speciation during the test. In the early portion of the test, when pH was still elevated by the humate injection, the dominant inorganic species was iodate and enhanced attenuation was observed. As pH decreased, the dominant species became iodide and a significant decrease in enhanced attenuation was observed. Sr-90 was not significantly attenuated by the humate treatment zone.

Selected results of experiments on humate sorption to aquifer sediments are reported here to support interpretation of the results of the humate injection field test. They show that humate is strongly sorbed to the aquifer sediments at acidic pH. Humate desorption curves suggest that a substantial fraction of humate will remain sorbed to the sediments over long-periods of time.

Ongoing studies by the ABRS AFRI and Florida International University support development of the humate technology. The culmination of these studies will be the understanding of what DOE sites will benefit from the humate technology and how best to deploy it at different types of sites.

1.0 Introduction

The conceptual approach of using derivatives of natural humic substances to enhance the attenuation of contaminant metals and radionuclides evolved from the studies of the tendency of metals to bond with organic matter leading to the formation of ore deposits in natural systems. The association of uranium with natural organic matter has long been recognized (Breger and Deul, 1959; Haji-Vassiliou and Kerr, 1972; Breger, 1974; Adams and Saucier, 1981). Similarly, organic matter may play a role in formation of other metal ores (Jackson and Beales, 1967; Pering, 1973, Macqueen, 1979). Paralleling studies of metal accumulation with organic matter were studies demonstrating the effect of humic substances on metal behavior in natural waters (Bertha and Choppin, 1978; Davis and Leckie, 1978; Kerndorff and Schnitzer, 1980; Davis, 1984; Ho and Miller, 1985; Jardin et al., 1989). A primary conclusion of most of these studies was that humic substances sorb strongly to mineral surfaces under certain natural geochemical conditions and enhance sorption of several metals from water.

This observation suggests that an in-situ approach for remediation of groundwater plumes could be based on the injection of humic amendments into the aquifer thereby enhancing attenuation of some metals in the subsurface. Petrović et al. (1999) suggested humic substances could be used to mobilize some metals and could be used to enhance the sorption of other metals. Oeste and Kempfert (1996) describe a method for creating a permeable reactive barrier in a two-step process by first precipitating injected dissolved humic acid followed by a subsequent injection of acid. To avoid the subsequent injection, a method of creating humic derivatives that adhere more strongly to soil or other substrates under a variety of conditions was described by Perminova et al. (2011). However, under the acidic groundwater conditions typical of many metal and radionuclide contaminant plumes, humic substances sorb well to mineral surfaces. In such cases, acid injections or specialized humic derivatives may not be necessary to create a subsurface treatment zone for many metals. Wan et al. (2011) demonstrated that laboratory grade humic acid, when sorbed to Savannah River Site soils, enhanced the sorption of uranium under acidic conditions (pH=3.0 to 4.5).

A potential challenge to the use of soluble humic substances is the cost of the materials. Most groundwater contamination sites will require several thousand kilograms of concentrated humic substance to remediate a plume. Processing and purifying commercial sources of humic substances increases their cost. Hence, we identified an inexpensive commercial humic product, an amendment used in organic farming that could be used as a cost effective, injectable amendment at the appropriate scale. Our hypothesis is that in an acidic groundwater plume, sufficient humic material will be sorbed to aquifer minerals to provide an effective treatment zone without having to add acid or use derivatives that are processed to enhance adherence of humics to mineral surfaces. To test this hypothesis, a pilot field test funded by the DOE Office of Environmental Management (EM-12) was done at the F-Area Seepage Basins at the Savannah

River Site. For the pilot test, a concentrated humate solution was injected into the acidic portion of groundwater contamination plume using a single well to create a treatment zone around the well bore. We then extracted samples from the well over a period of four months to collect water from the contamination plume that had passed through the treatment zone. Groundwater samples were analyzed for numerous parameters including uranium, Sr-90, and I-129. The post-injection results were compared with the pre-injection values to determine the effect of the humate treatment zone on contaminant concentrations. In the remainder of this report, we will refer to the humic substances in this product as humate, because collectively they can be considered a mixture of weak acid anions of humic acid.

2.0 F-Area Seepage Basins

Site Background and Operational History

The F-Area Seepage Basins consist of three basins that were originally unlined, earthen surface impoundments used to dispose of effluents from the F-Area Separations facility. From 1955 through 1988, these unlined basins received approximately 1.8 billion gallons (7.1 billion liters) of low-level waste solutions originating from the processing of uranium slugs and irradiated fuel (Figure 1). The effluents were acidic (wastewater with nitric acid) and low activity waste solutions containing a wide variety of radionuclides and dissolved metals (Killian et al., 1987; Cummins et al., 1991). The wastewater was allowed to evaporate and to seep into the underlying soil. The purpose of the basins was to take advantage of the interaction with the basin soils to minimize the migration of contaminants to exposure points. Though the seepage basins essentially functioned as designed, the acidic nature of the basin influent caused mobilization of some metals and radionuclides resulting in the formation of groundwater contaminant plumes.

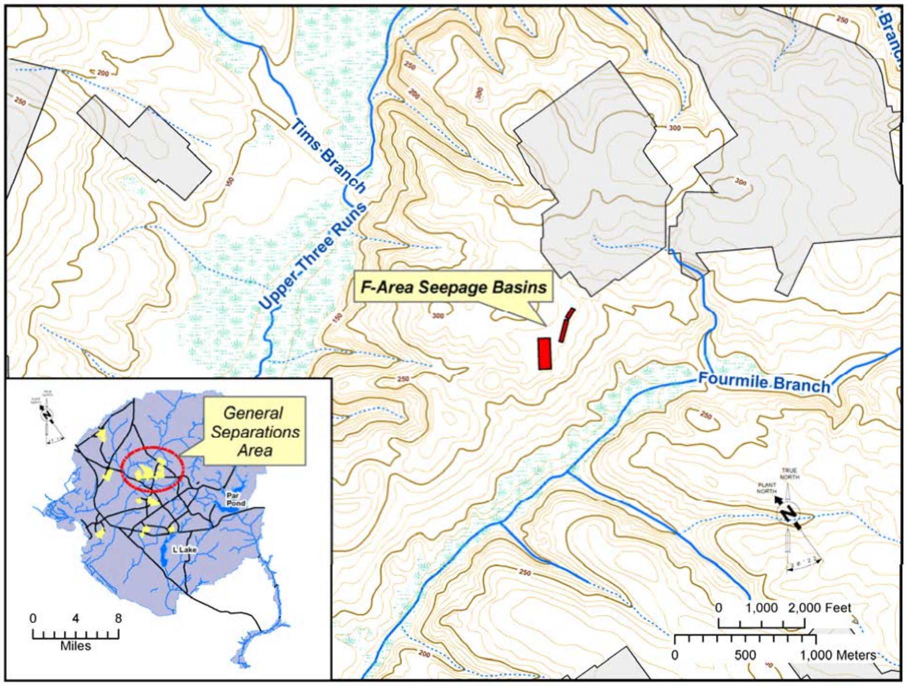


Figure 1: Location of the F-Area Seepage Basins at the Savannah River Site

Processed liquid effluent from the Separations Facilities was disposed into the seepage basins from 1955 until 1988. In 1986, the determination was made that the basins should be regulated under the Resource Conservation and Recovery Act (RCRA) as hazardous waste disposal facilities, and closure plans were initiated. Closure actions included dewatering, physical and chemical stabilization of the remaining sludge, and isolation with a protective multilayer system to reduce rainwater infiltration. These actions were completed in 1991. Groundwater downgradient of the basin was contaminated with constituents including strontium-90 (Sr-90), uranium isotopes, iodine-129 (I-129), technetium-99 (Tc-99), and tritium. In addition, the groundwater remains acidic, with pH as low as 3.2 near the basins increasing to a pH of approximately 5 down gradient. Prolonged exposure to low pH groundwater altered the mineralogy and texture of the impact sediments.

In 1997, SRS designed and installed a pump-treat-and-re-injection system that coupled a water treatment unit with an upgradient reinjection; the system was designed to trap the untreatable tritium in a continuous loop by extracting groundwater from downgradient, removing contaminants other than tritium from the water, and re-injecting the treated water upgradient of the seepage basins. The water treatment system consisted of precipitation/flocculation, reverse osmosis, and ion exchange. The pump-and-treat system operated as designed, but had significant drawbacks; most notably, it was very expensive to operate and resulted in the production of large amounts of radioactive solid waste. As a result, SRS sought another more efficient way to treat the groundwater contaminant plume. Operation of the water treatment unit began in 1999 (WSRC, 2000) and was suspended in 2003 (WSRC, 2005).

In 2004, the pump-and-treat system was replaced by a hybrid funnel-and-gate system installed about 300 meters from the stream (WSRC, 2005; SRNS, 2012). The purpose of the funnel-and-gate is to slow migration of contaminated groundwater and to funnel contaminated water through in situ treatment zones at the gates. Extensive geologic characterization showed that much of the plume migrated along “troughs” at the top of the clay layer that confines the lower aquifer. The walls (or engineered subsurface barriers) were installed across these features to slow contaminant migration and force it through the gates. The treatment zones at the gates attenuate migration of uranium, Sr-90, and I-129 by sorption or precipitation. Tritium migration is slowed by the walls and additional decrease in tritium concentrations is achieved when the stratified plume mixes with less contaminated groundwater as it migrates up through the gates.

Treatment zones for uranium and Sr-90 at the gates are maintained by neutralizing acidity of the groundwater and mineral surfaces with injections of an alkaline solution. This causes sorption of the contaminants and/or precipitation of uranium phases. Periodic injections are performed with the frequency at each gate dictated by sentry monitoring wells located downgradient.

Monitoring of the performance of the funnel-and-gate with base injection since it was installed indicates that it has functioned as planned. Analysis of subsurface cores collected downgradient of the middle gate shows that an elevated pH treatment zone has been established. Monitoring of groundwater indicates that tritium flux has been reduced to target levels and regulatory limits on concentrations of Sr-90 and uranium have been achieved downgradient of the treatment system.

In 2009, a pilot study was initiated to evaluate the removal of I-129 by the injection of particles of solid silver chloride (SRNS, 2012). Contaminant I-129 and natural I-127 react with the silver chloride to form insoluble silver iodide, removing I-129 from the groundwater. In 2011, a modification to the RCRA permit was approved to deploy silver chloride technology at the middle gate as part of the corrective action. The treatment zone was from the top of the water table down to the tan clay confining zone (25 to 50 feet below ground surface). Injection was performed starting at the bottom of the aquifer and proceeded upward pumping a specific volume of amendment into each zone at 2.5 foot intervals. Evaluation of the performance of the silver chloride treatment zones continues. Figure 2 provides 2011 plume maps for Sr-90 and U-238.

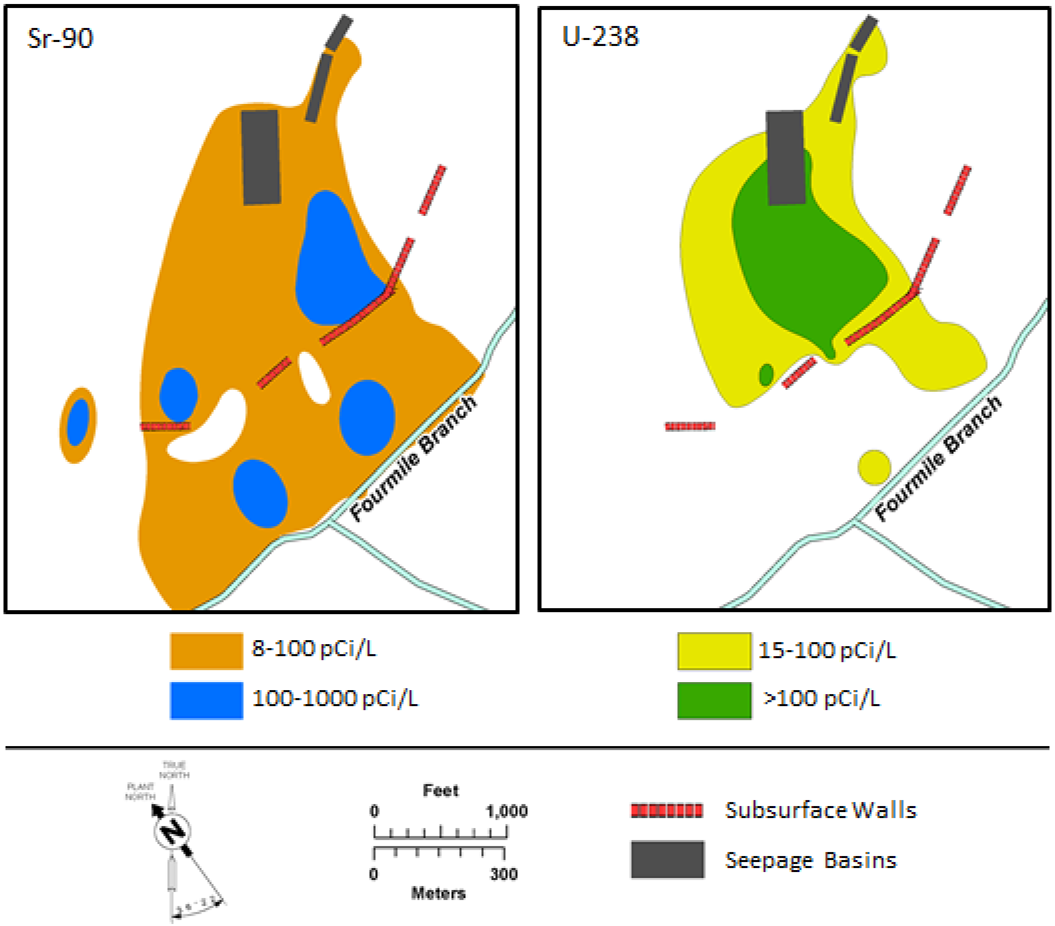


Figure 2: Distribution Map for Sr-90 and Uranium concentrations in 2011. Black rectangles show the outline of the seepage basins and red lines show the funnel and gate system.

3.0 Description of the Pilot Injection Test

The idealized conceptual model for the single well injection test of humate is that as the humate solution is injected into the subsurface, the humate will sorb to sediments in the affected volume around the injection well screen. After the injection is complete, the contaminated plume water will begin to flow back through the upgradient portion of the affected volume, or treatment zone. An idealized diagram of the concept is shown in Figure 3. As the groundwater moves through the injection zone, contaminants that have an affinity for humate sorb to the humate bound on minerals surfaces, thereby lowering the concentrations of the contaminant in the impacted groundwater. Over time, the upgradient portion of the treatment zone becomes saturated with contaminants, and concentrations of contaminants in the well bore will increase. This is the simplest of field tests with two goals: 1) to determine if the humate solution can be injected into the subsurface without clogging the well, and 2) to determine if the treatment zone created by sorbed humate enhances sorption of contaminants.

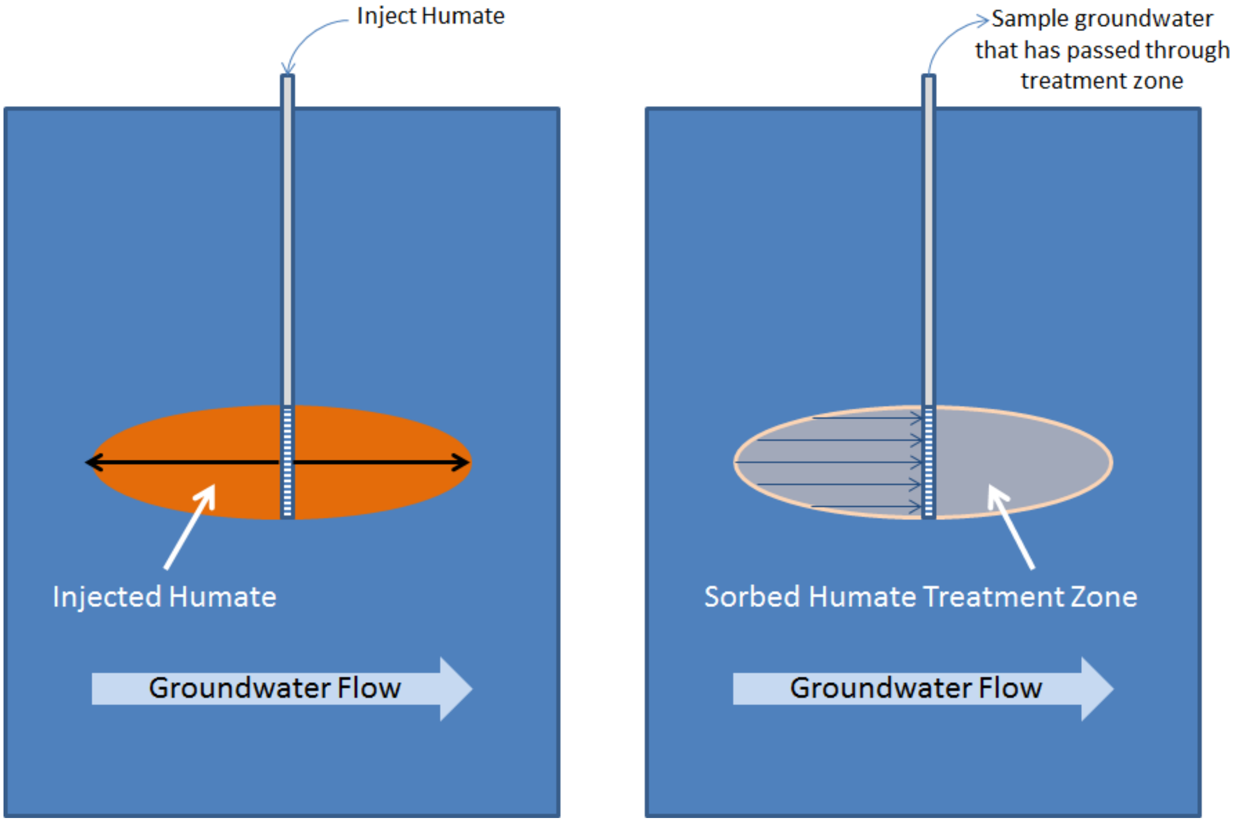


Figure 3: Idealized conceptual model of the single well humate injection test.

Additional information can be derived if the field test is supplemented with laboratory tests on sorption of the humate used in the field test. This is important because sorption of the humate injected into an acidic plume is complex. Humate sorption to sediment minerals varies with pH, sorbing more strongly at low pH than high (Tipping, 1981; Davis, 1982). The humate solution has a pH that approaches 10, whereas the aquifer at F-Area typically has a pH of approximately 3.2. As the humate solution is injected, a pH gradient is established that moves away from the borehole until injection is complete. This can result in varying sorption across the injection volume as suggested by Figure 4.

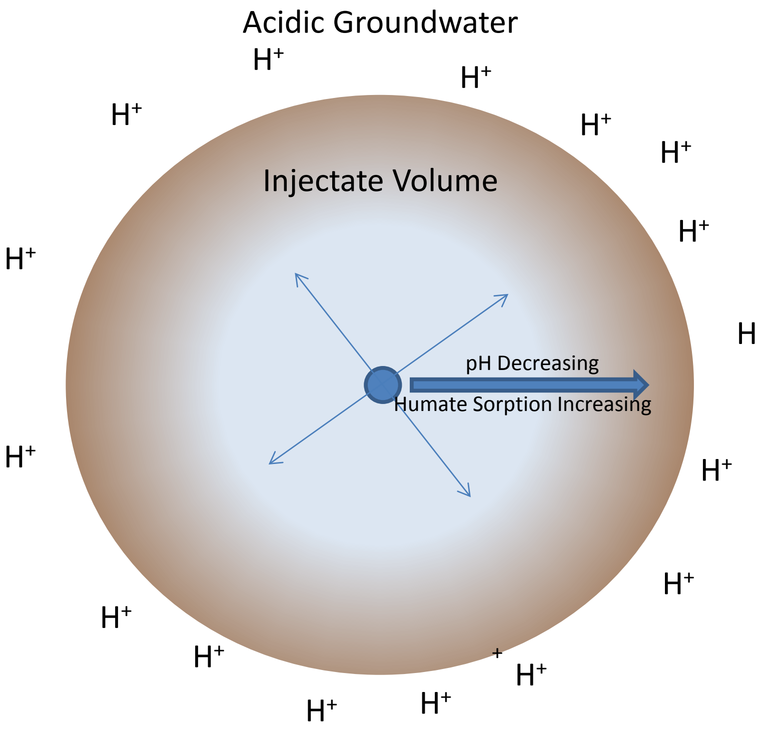


Figure 4: Conceptual Model (planar view) during injection of the humate solution into an acidic plume. The pH decreases away from the well bore (blue circle) leading to increased sorption of humate at the edges of the treatment zone.

Description of the Humate Amendment

For an applied research test, it was important to choose a relatively inexpensive and commercially available product to demonstrate whether the humate technology could be a realistic remedial option for large groundwater plumes typical of DOE sites. For this field study, Huma K© was chosen as the humate amendment because of its ease of use with the dry flake as well as existing data and experience with the amendment (Millings et al., 2008; Millings et al., 2013).

Huma K© is a commercially available, dry flake, organic amendment manufactured by Land and Sea Organics. The amendment is high in humic and fulvic compounds and is just one of several brands produced for large scale use as soil conditioners to boost productivity in organic agriculture. It is certified by the organic materials review institute (OMRI) for use in organic farming based on a number of stringent criteria including low concentrations of trace metals.

Huma K$^{©}$ is made from leonardite, a natural organic rich material, by extracting the raw leondardite with a potassium hydroxide base solution and then drying it. The high pH solubilizes the humic acid molecules and generates a dark-brown highly-concentrated solution, rich in humic acid, which can be diluted for use. Importantly, while such solutions are commonly called *soluble humic acid*, they are actually basic with pH greater than 7. Land and Sea Organics offers a soluble humic acid 12% solution known as TriHumic$^{©}$ or the dry flake material, Huma K$^{©}$.

Description of the Wells for the Pilot Field Test

A detailed discussion of the selection of the test well, as well as upgradient and downgradient wells can be found in Millings et al. (2013). Briefly, well FOB-16D was chosen as the test well because it is in the heart of the plume both laterally and vertically. Another important factor was that it is not regularly sampled for regulatory compliance purposes. Therefore the test could be performed in FOB-16D without interfering in any site operations. The upgradient wells, FSB-95DR and FSB-94DR, and the downgradient well, FSB-126D, were chosen because they are located approximately along a flow path from Basin 3 through the test well. Table 1 provides construction details of all of the wells used in the test and Figure 5 shows the locations of the wells.

Table 1: Description of Wells Used in the Pilot Test

Well ID	Top of Screen (ft msl)	Screen Length (ft)	Ground Elevation (ft msl)	Reference Elevation (ft msl)	Total Depth (ft)	Well Diameter (inches)	Well Material	Pump Type	Install Date
FOB 16D	183.7	20	251.7	254.5	90.6	2	PVC	VARIABLE SPEED PUMP	Jan 2004
FSB 94DR	203.4	20	278.4	281.3	97.2	4	PVC	SINGLE SPEED PUMP	Oct 1990
FSB 95DR	207.0	20	282.0	284.4	97.1	4	PVC	SINGLE SPEED PUMP	Sept 1990
FSB 126D	183.1	10	236.9	239.8	66.4	2	PVC	VARIABLE SPEED PUMP	Dec 2003

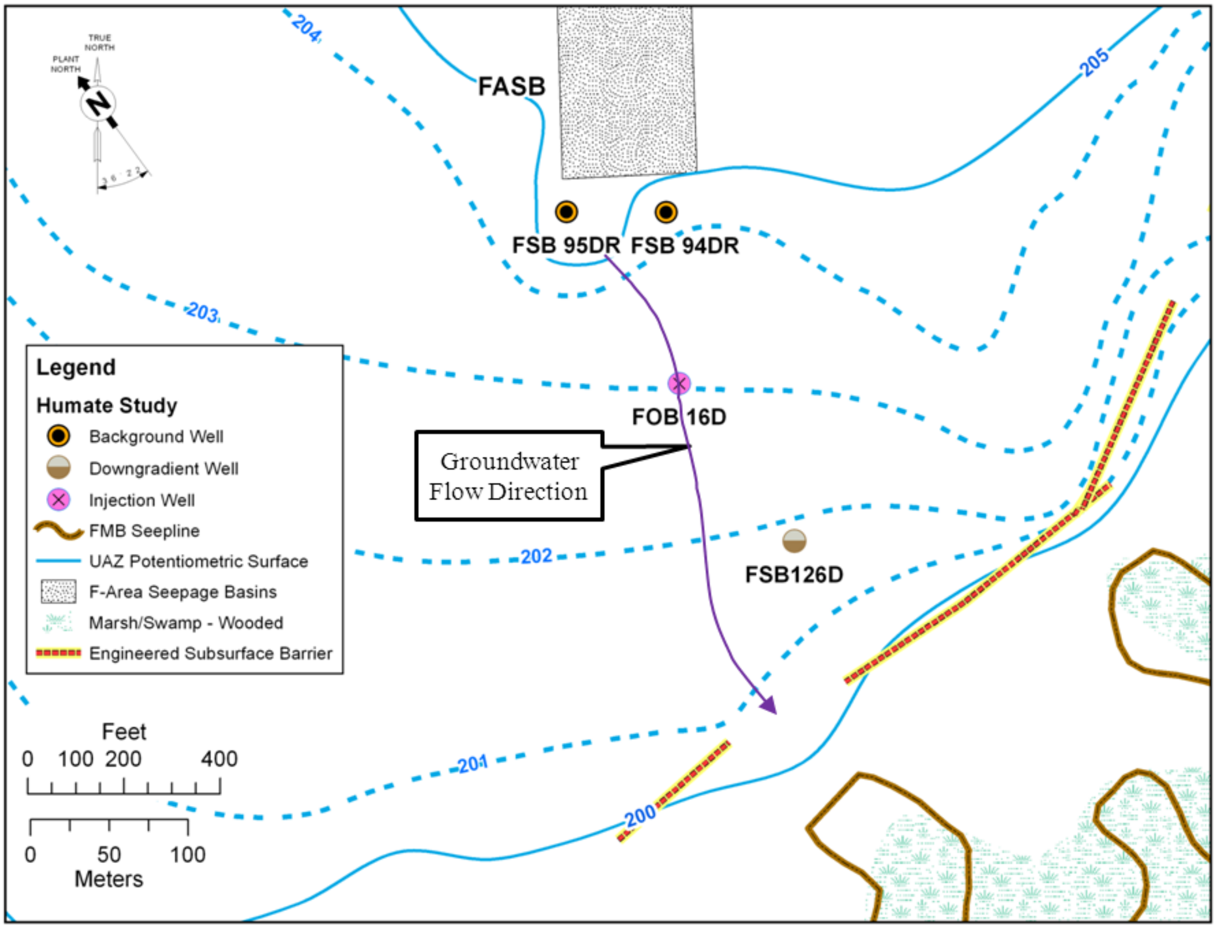


Figure 5: Map showing location of the wells used in the pilot test. The potentiometric surface of the upper aquifer is shown in blue, and the general direction of groundwater flow is indicated with the purple arrow.

Description of the Injectate Solution

The injectate solution consisted of 2,000 L (528 gal) of water, 20 kg of Huma K$^{©}$ brand humate, and 0.2 kg of sodium bromide. The sodium bromide was added to act as a tracer during the test to evaluate the rate of movement of the injectate with the groundwater. These materials were mixed into two equal batches using a 330 gal, aluminum framed, plastic tote. Mixing was initially conducted with a paddle oar to wet all of the materials followed by the use of a drum pump to facilitate thorough mixing.

The injectate solution contained approximately 10,000 mg/L Huma K$^{©}$ which is equal to 3200 mg/L organic carbon. The pH and specific conductance of the injectate solution were measured periodically during injection using a YSI sonde. The mean pH was 9.9 and the specific conductance was 1840 uS/cm.

Figure 6 provides a layout schematic of the injection. A large volume peristaltic pump was used to transfer the injectate from the totes to the screen zone of the well. The injectate was not pressurized but rather allowed to flow under a gravity feed. The tote tank was connected to the peristaltic pump via a valved outlet on the tote. A 100 micron filter was connected to the outlet side of the peristaltic pump to remove any large humate debris in an effort to prevent clogging of the well.

At the well, the injectate flowed through a 1-inch schedule 40 PVC casing with a 5 ft screen attached at the bottom. This screen was set within the screen zone of the well at the desired elevation in order to accurately emplace (as much as possible) the material during injection. Monitoring of the water level in the well was conducted to evaluate the amount of head placed on the injectate. Mixing and injection took place over the course of seven hours on Monday, April 29, 2013.

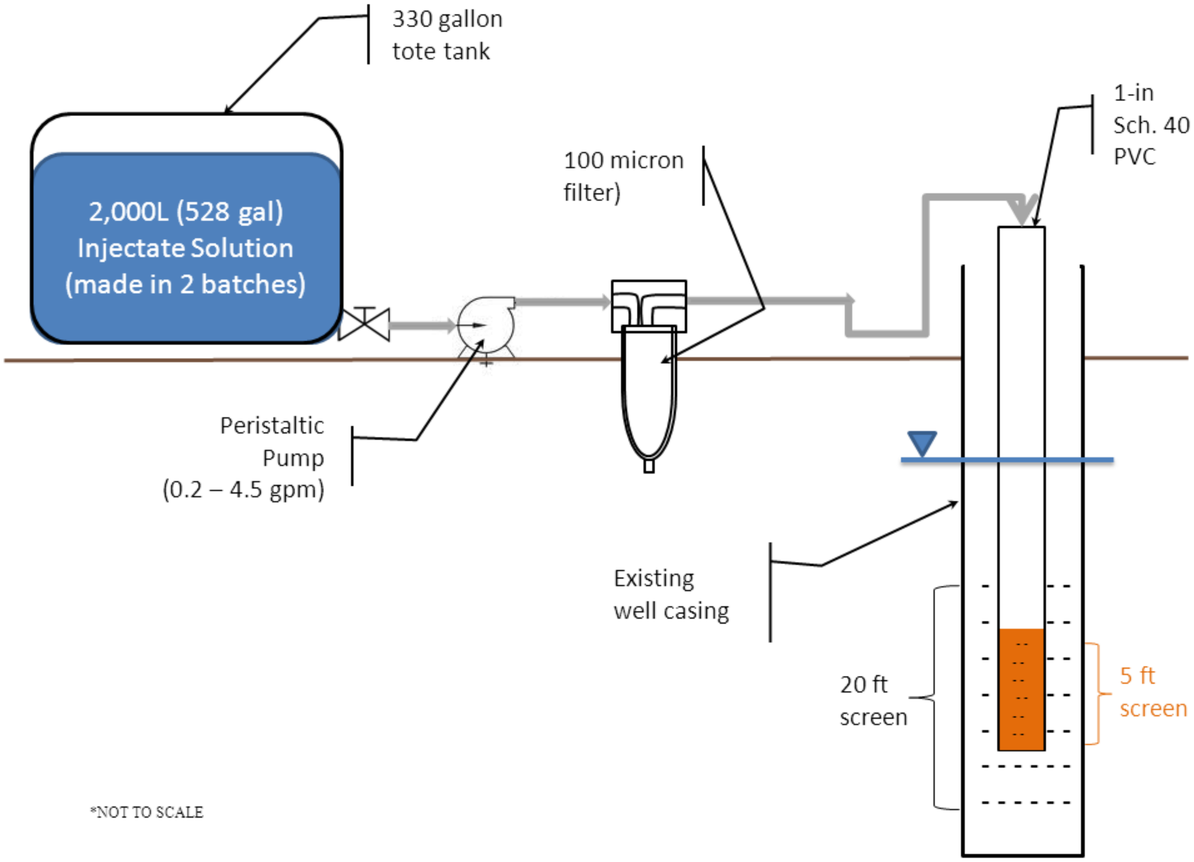


Figure 6: Schematic of Injection Setup

Analytical Methods

Standard field parameters, specifically, pH, Specific Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, and Temperature were measured during sampling using a YSI sonde with a flow through cell. Cations, anions, Sr-90, tritium, uranium isotopes, and total organic carbon were analyzed by an E.P.A. Certified laboratory using the methods listed in Table 2. Iodine-129 and I-127 speciation analyses were done at the Savannah River National Laboratory.

Table 2: Analytical methods used for analysis of cations, anions, Sr-90, tritium, uranium isotopes, and total organic carbon

Analyte	Method
Cations	EPA 6020A
Chloride, bromide	EPA 300
NO_3-NO_2 as Nitrogen	EPA 353.1
Tritium	EPA 906.0 MOD
Uranium Isotopes	A-01-RMOD
Sr-90	DOE SR-03-RCMOD
Total Organic Carbon	EPA 9060

4.0 Results & Discussion

Post-Injection Monitoring Results

Natural variations in contaminant concentrations must be considered to assess the effectiveness of injected humate for enhancing sorption of contaminants since other factors such as seasonal variations in groundwater levels can impact concentrations of constituents. Simply comparing pre- and post-injection concentrations is not sufficient. Pre- and post-injection concentrations must be compared to other plume constituents that can reasonably be expected to co-vary with the contaminants in the plume, but not be affected by sorbed humate. Tritium, nitrate, and specific conductance are parameters that potentially serve this purpose. Figure 7 shows long-term trends in tritium and nitrate compared to specific conductance in samples from the background well FSB-94DR. Nitrate (measured as nitrate-nitrite as nitrogen) co-varies with specific conductance because it is a primary contributor to the electrical conductivity of the groundwater. Yet, there is significantly more short-term variation in the concentration of nitrate.

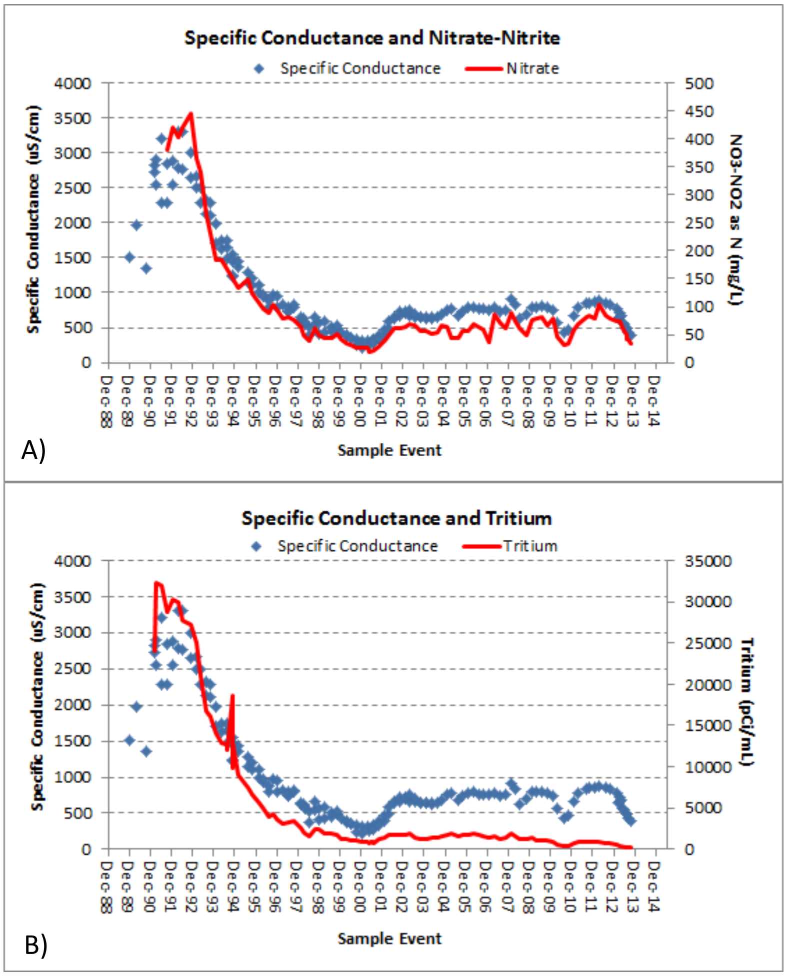
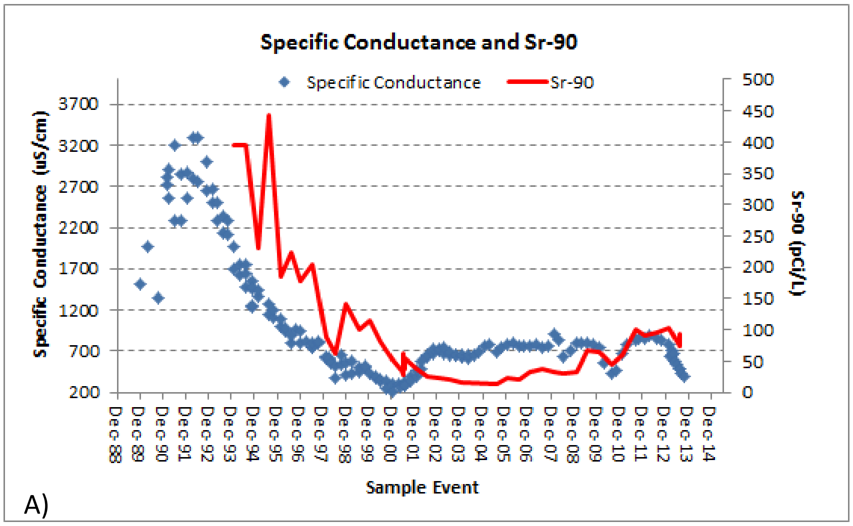


Figure 7: Time trends of concentrations of NO_3-NO_2 as N_2 (A) and tritium (B) versus specific conductance of groundwater from well FSB-94DR.

This is because specific conductance is a reflection of the contributions to electrical conductivity of all dissolved ionic species, and it is less sensitive to analytical error. In contrast to nitrate, tritium concentrations have consistently decreased relative to specific conductance since 2001.

Specific conductance was chosen as the baseline parameter to account for natural variation in contaminant concentrations because it reflects the bulk behavior of ionic constituents in the plume. The long-term trend in specific conductance in FSB-94DR samples also matches those of Sr-90 and U-238 since 2001 (Figure 8). Furthermore, specific conductance is unlikely to be affected significantly by interaction with the humate treatment zone. To maintain electrical neutrality in the groundwater, ions that are sorbed in the treatment zone must be counterbalanced by desorption of an equivalent charge of ions. This tends to "buffer" specific conductance from changes due to sorption.



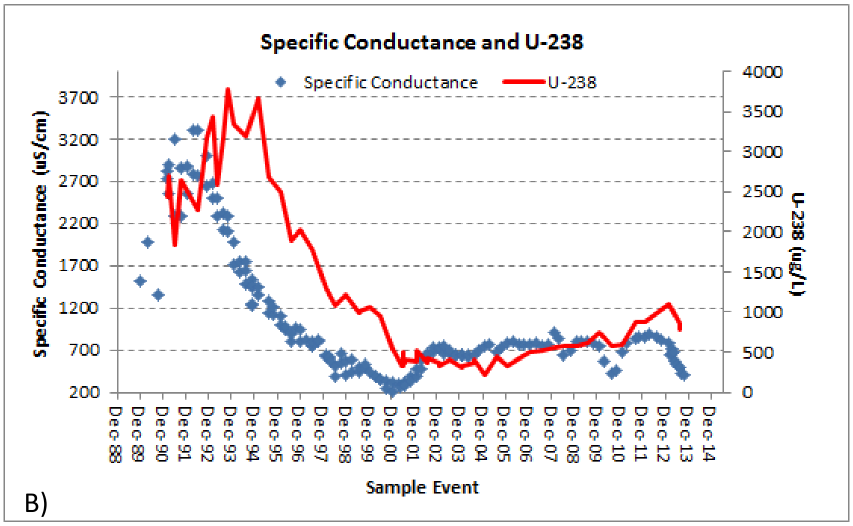


Figure 8: Time trends of concentrations of Sr-90 (A) and U-238 (B) versus specific conductance of groundwater from well FSB-94DR.

Specific conductance, as well as nitrate and tritium, decreased throughout the time period of the field test (Figure 9). This is consistent with the decrease in specific conductance measured in groundwater from well FSB-94DR shown during 2013 in Figure 8. The decrease in specific conductance is likely due to a rising water table during the test period. Figure 10 shows the rise in the water table at the injection-extraction well, FOB-16D, with the dotted lines showing the water table elevations at wells FSB-95DR (green) and FSB-94DR (purple).

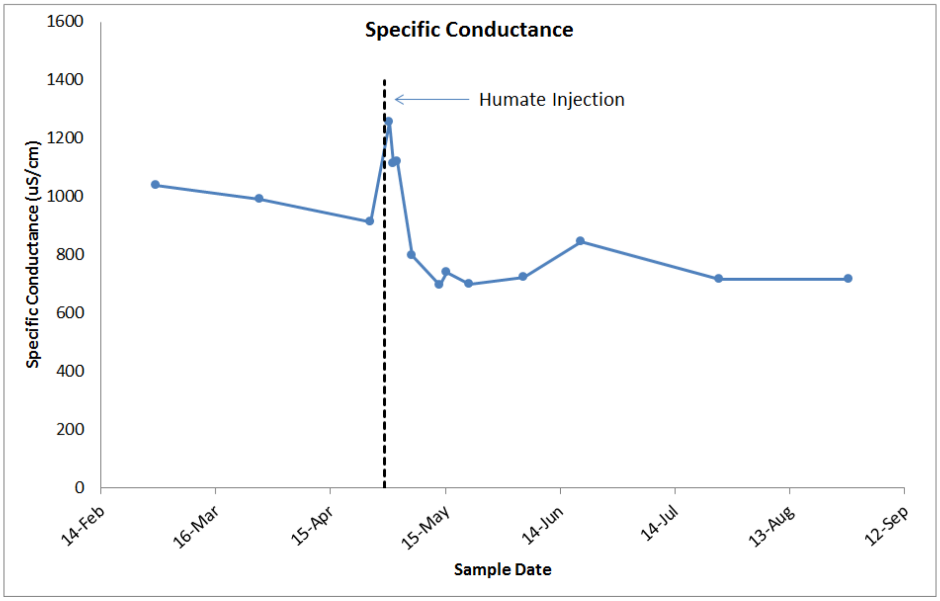


Figure 9: Specific conductance values in groundwater extracted from the injection well during the humate injection field test.

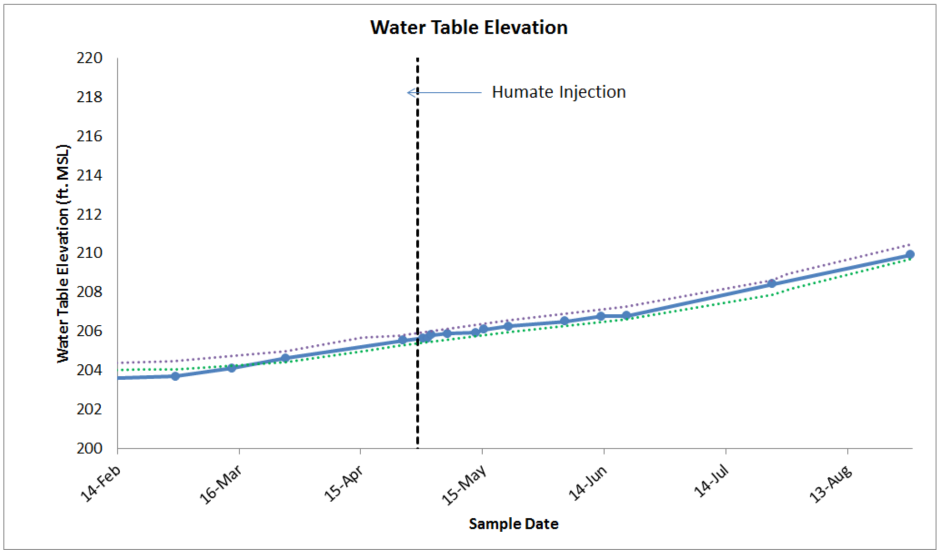


Figure 10: Water table elevation at test well, FOB-16D, during humate injection field test; dotted lines are water table elevations at wells FSB-94DR (purple) and FSB-95DR (green).

To test whether using specific conductance to predict baseline (untreated) contaminant concentrations is reasonable, we can apply the correction to chloride, another constituent that is unlikely to preferentially sorb to the humate treatment zone. The correction factor was calculated as a ratio using of the final specific conductance measurement, made on 8/28/2013, to the average of the pre-injection measurements. This was then multiplied by the average of the 3 pre-injection chloride concentrations. The results are shown in Figure 11. The blue line and data points are the values measured during the test and the orange square is the baseline value predicted from specific conductance. The agreement between the two indicates that using specific conductance to account for natural variation in the baseline contaminant values is reasonable.

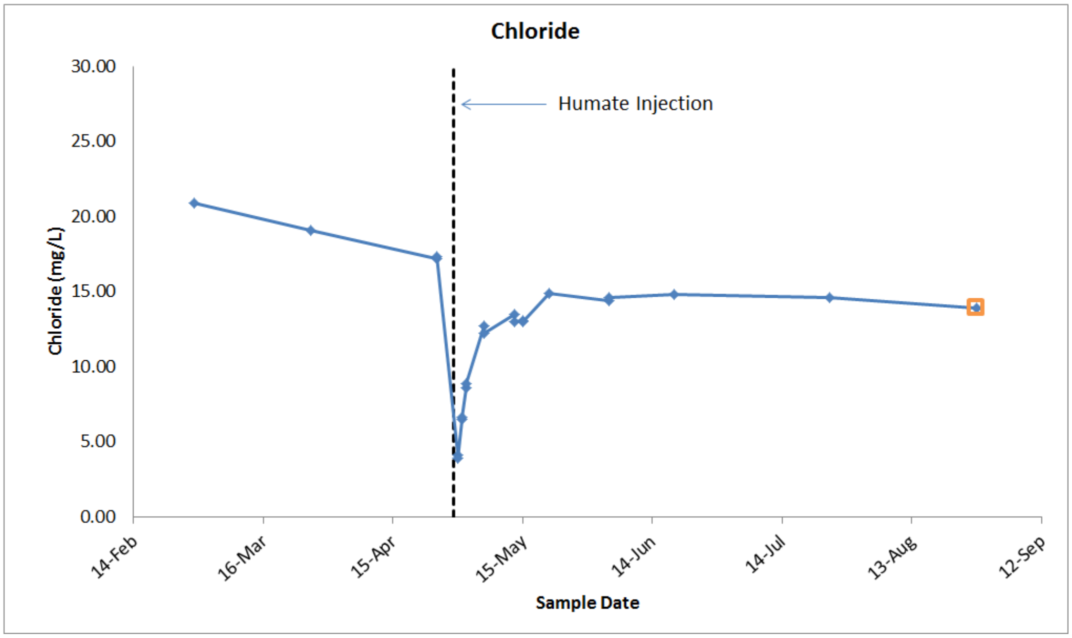


Figure 11: Comparison of the final measured chloride concentration in well FOB-16D, the injection well, to the concentration predicted using specific conductance.

The pattern of chloride concentration during the test is typical of constituents that are present in the contamination plume in concentrations that are high relative to those in the humate solution and that are minimally sorbed in the treatment zone. The concentrations decrease because of dilution and displacement of groundwater from the injection of the humate, and then increase as contaminated groundwater flushes through the treatment zone. Tritium and nitrate show similar patterns (Figure 12). In all, there is a rapid increase in concentration for the first several days, followed by slower increase until the constituent returns to its pre-test concentration (adjusted for the overall natural decreasing trend). All non-reactive constituents have reached their adjusted pre-test concentrations by the 6/19/2013 sampling event or 21 days after injection.

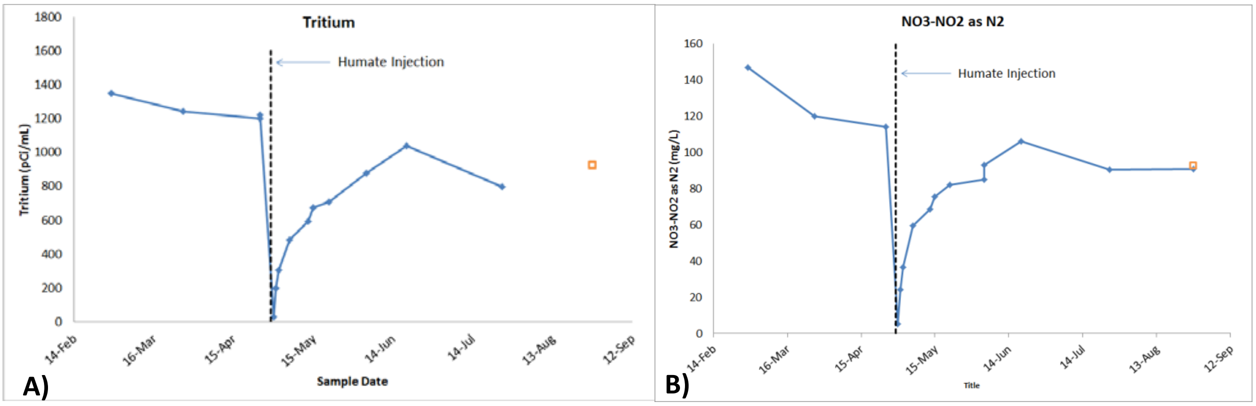


Figure 12: Concentrations of tritium (A) and nitrate-nitrite as nitrogen (B) during humate field test; orange squares are the projected final concentrations based on specific conductance.

Bromide

Bromide was added to the humate injectate solution as a tracer, anticipating minimal reaction with the treatment zone. Figure 13 shows the bromide concentrations in groundwater samples from the test well after injection of the humate solution. Over the first 7 days following injection, there was rapid decrease in bromide concentration. That was followed by slower decrease, with bromide remaining in the treatment zone at 51 days after injection. At an estimated groundwater flow velocity of 0.3 meters/day, a pore volume should flush through the treatment zone every 3-4 days. That bromide remained in the system for greater than 51 days suggests that either bromide was attenuated in the treatment zone or there is significant heterogeneity in hydraulic conductivity within the treatment zone. Since tritium and nitrate rebounded to their pre-test concentrations at the same rate (corrected for the decreasing overall trend), this suggests that heterogeneity is the more likely explanation for the slow bromide flushing from the treatment zone.

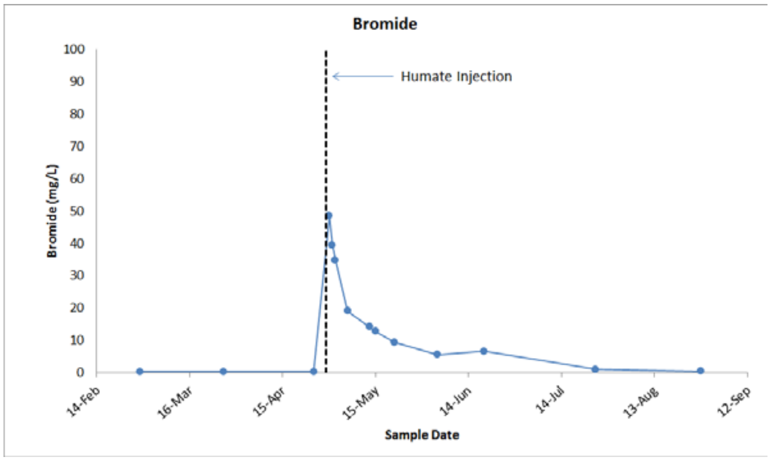


Figure 13: Bromide concentrations in groundwater from the test well, FOB-16D, following injection of the humate solution.

pH

The value of pH during the test is important because uranium and Sr-90 sorption in the absence of humate is dependent on pH. Figure 14 shows the pH values in groundwater extracted during the test. The injection of the alkaline humate solution brought the pH from 3.3 to near 10. As acidic groundwater flushed through the treatment zone the pH decreased, but at the end of the test the pH was 3.6 rather than the pre-test value of 3.3.

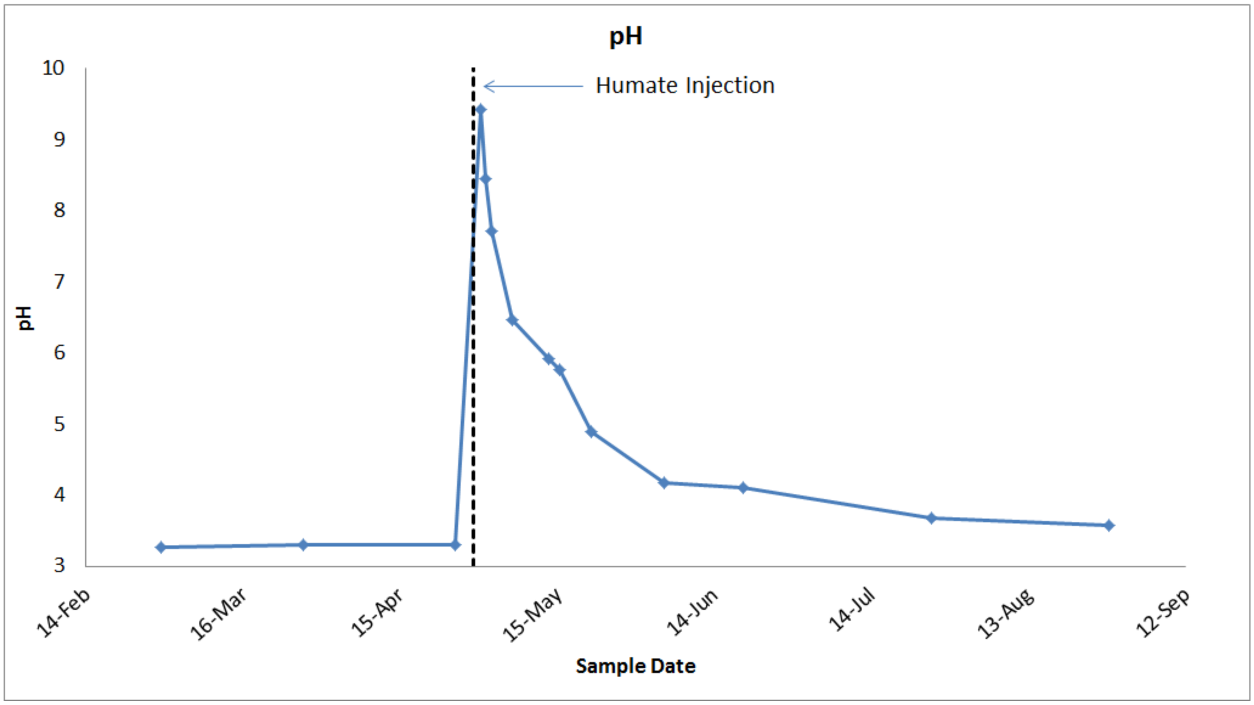


Figure 14: Values of pH during the humate injection field test.

Strontium-90

Figure 15A shows the concentration of Sr-90 in groundwater from the injection test well, FOB-16D, during the humate injection field test. The pattern is similar to the non-reactive constituents, and by the last sampling event, the Sr-90 concentration is equal to that projected using specific conductance. This indicates that there was minimal sorption of Sr-90 within the humate treatment zone. Nevertheless, when the rebound of Sr-90 concentrations is compared to the projected rebound based on rebound of tritium and nitrate, there does appear to be minor sorption of Sr-90 (Figure 15B). However, the sorption capacity of the treatment zone for Sr-90 was low, and the concentration is back to the projected plume concentration by the last sampling event on 8/28/2013.

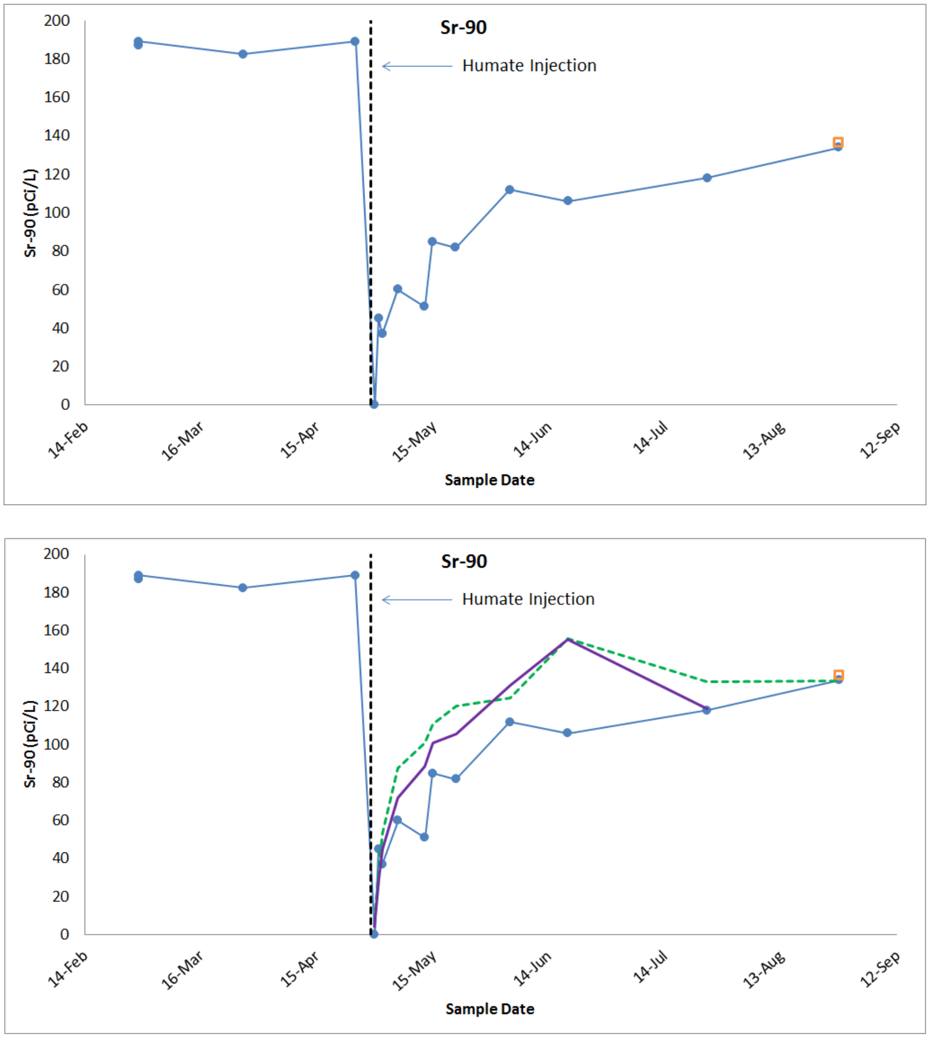


Figure 15: A) Sr-90 concentrations in groundwater from injection well FOB-16D during the humate injection field test (orange square is concentration in plume projected using specific conductance); B) Sr-90 concentrations compared to projected Sr-90 concentrations based on tritium (purple) and nitrate (green dashed) rebound curves.

The sorption of Sr-90 by the humate treatment zone may have been suppressed during the early portion of the test by the presence of relatively high concentrations of calcium and stable strontium in the injected humate solution. Figure 16 shows the calcium concentrations in groundwater from the injection well throughout the test. Analysis of Huma K$^{©}$ solutions by Millings et al. (2008) indicate there should be approximately 57 mg/L Ca in a 10,000 mg/L solution. This is consistent with the maximum concentration observed during the humate injection test. The maximum concentration of stable strontium observed during the injection test was 0.2 mg/L, approximately 6 times the background concentration. Elevated concentrations of calcium and stable strontium would suppress sorption of Sr-90 because of their similar – identical in the case of stable strontium – chemical behavior.

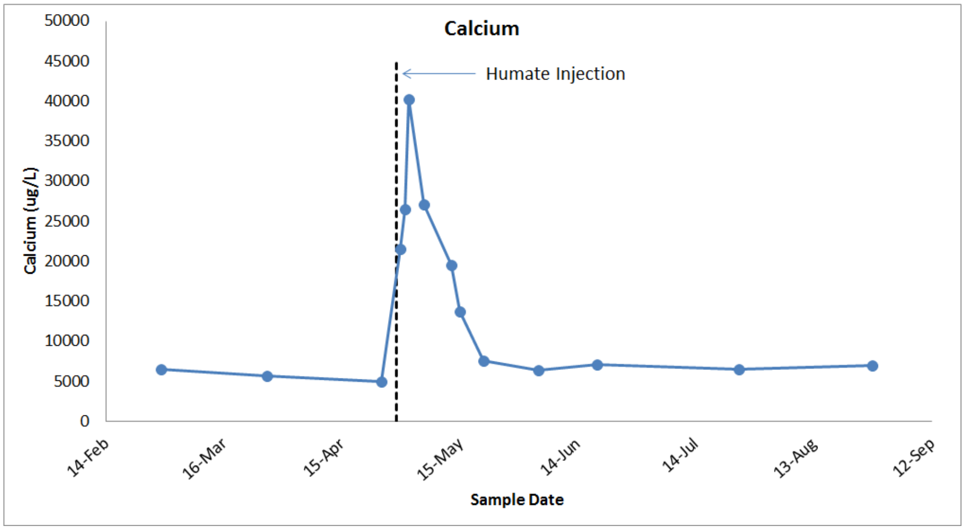


Figure 16: Calcium concentrations in groundwater from the injection well, FOB-16D, during the humate injection field test.

In contrast to Sr-90, uranium concentrations in groundwater sampled from the injection test well suggest significant enhanced attenuation in the humate treatment zone. Figure 17 shows the uranium concentration throughout the test period. The mean background concentration was 1033 ug/L and the concentration at the final sampling event on 8/28/2013 was 509 ug/L. The projected concentration that accounts for the natural decreasing concentration trend using specific conductance was 753 ug/L. Hence, the uranium concentration at the end of the test was 49% of the mean pre-test concentration and 68% of the projected concentration. This suggests that uranium sorption was significantly enhanced in the humate treatment zone and that the enhanced sorption had some longevity. If a pore volume takes 3-4 days to flush through the treatment zone then enhanced sorption of uranium was still occurring after 30-40 pore volumes.

Uranium

The effect of pH must be considered before attributing all of the enhanced sorption of uranium to humate. As shown in Figure 14 (pH curve), after injection of humate the pH had not returned to the pre-test value. It remained at 3.6 at the end of the test compared to the pre-test value of 3.3. Figure 18, from Dong et al. (2012), shows measured uranium sorption curves in sediments from the same aquifer as the humate injection test and near the same location. The conditions of the experiments simulated the F-Area Seepage Basins contamination plume and no humate was added. Sorption is higher at low pH in the sediment used in their “a” figure. At pH=3.3 just approximately 12% of the uranium is sorbed, whereas approximately 20% is sorbed at pH=3.6. The difference in sorption at pH 3.3 versus 3.6 suggests that the higher pH at the end of the test compared to the pre-test pH may account for some of the sorption. However, the pH difference cannot account for most of the sorption.

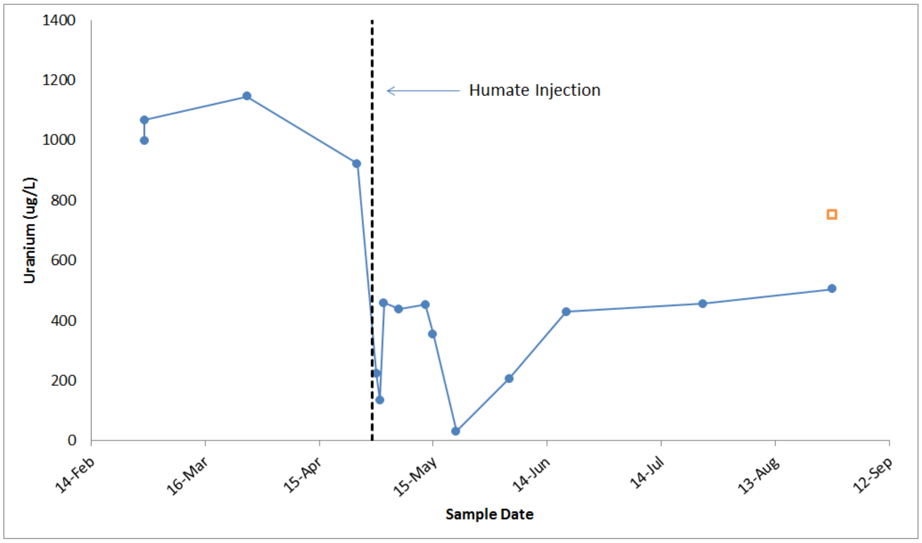


Figure 17: Uranium concentrations in groundwater from the injection well, FOB-16D, during the humate injection field test; the orange square is the projected concentration using the decreasing trend in specific conductance.

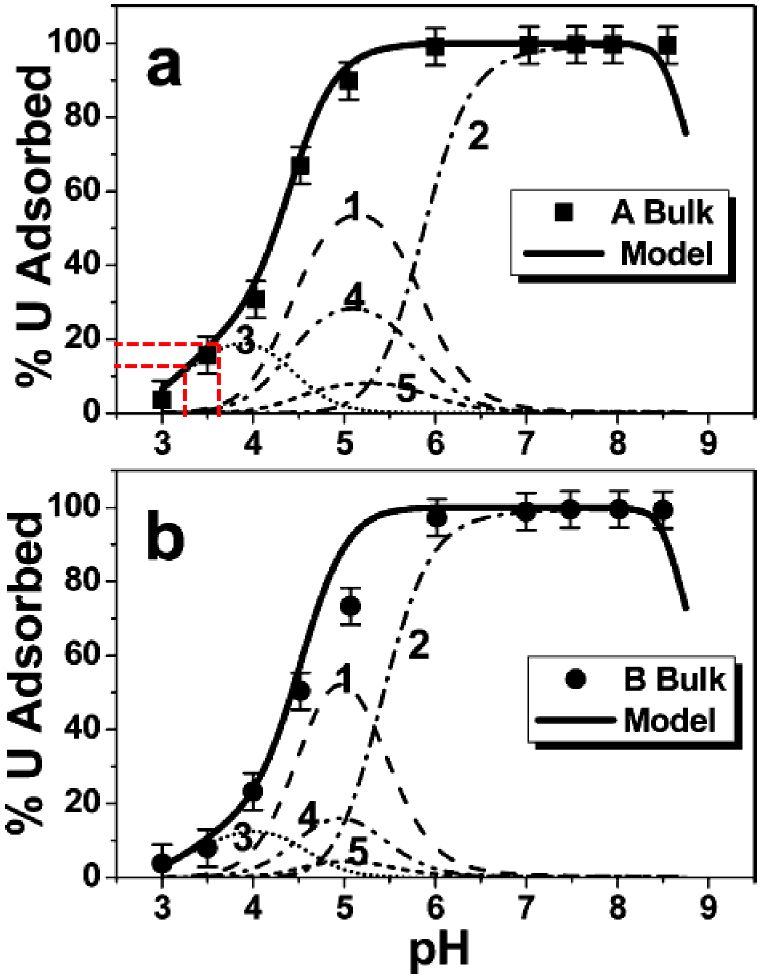


Figure 18: Uranium adsorption curves from Dong et al. (2012) on sediment from same site as humate injection test(symbols are measured data, solid line is modeled sorption, dashed/dotted lines are surface complexation species; added red dashed lines in "a" show difference in sorption at pH=3.3 versus pH=3.6.

In Figure 19, the measured uranium rebound curve is compared to projected rebound curves calculated from the rebound of tritium and nitrate. This indicates that enhanced sorption of uranium was greater earlier in the test and was decreasing with time. The uranium concentrations in the early portion of the test have an interesting pattern that is different than other constituents. The concentration decreases from the injection, but 3 days after the injection increases from 135 ug/L to 458 ug/L. The concentration remains essentially the same until 14 days after the humate injection, when it begins to decrease. It decreases to 31 ug/L at 22 days after injection and then begins to increase, with the rate of increase slowing at 51 days.

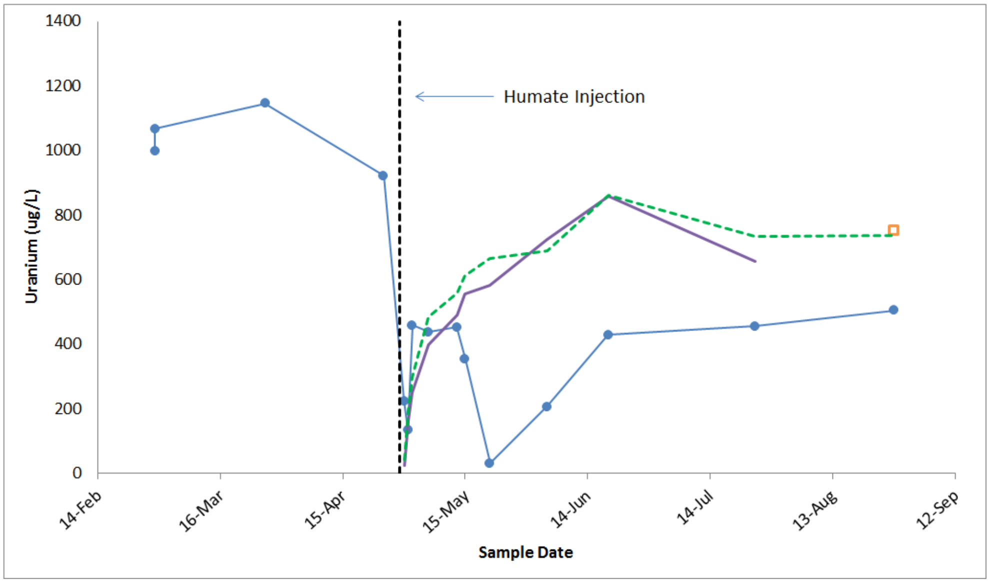


Figure 19: Uranium concentrations in groundwater from the injection well, FOB-16D, during the humate injection field test compared to projected rebound concentrations calculated from tritium (purple) and nitrate (green dashed) rebound curves.

The cause of the unusual pattern of uranium concentrations is unclear, but may be the result of aqueous complexing of uranium by dissolved humate. Total organic carbon (TOC) concentrations measured during the injection test are plotted with uranium concentrations in Figure 20. The magnitude of the TOC values are low and analytical error is suspected. Nevertheless, the pattern of TOC concentrations is very similar to those measured using visible light spectroscopy (Millings et al., 2013) and the pattern is suggestive of a relationship between uranium concentrations and TOC early in the test. The maximum TOC concentration sampled occurs 3 days after injection and there is a concomitant increase in uranium concentration. The elevated uranium concentrations last until the TOC concentration has decreased to less than 10% of its maximum. When there is very little TOC in the groundwater, the uranium concentration drops to the lowest concentration observed during the test. The behavior of uranium suggests complexing by dissolved humate in the early portion of the test when dissolved humate concentrations are high. When dissolved humate concentration decreases to a certain level, pH becomes a dominant control on dissolved uranium concentration. When uranium reaches the minimum observed concentration of 31.4 ug/L on 5/21/2013, the pH is 4.89 and there is little humate in solution. The pH of the sample taken on 6/4/2013 was 4.2 and uranium concentration was 206 ug/L. This is consistent with the experiments of Wan et al. (2011) on uranium sorption to humate coated minerals. They found a sorption edge at a pH near 4, below which uranium sorption onto humate coated minerals decreased. The increasing uranium concentration in samples after 5/21/2013, as pH decreases to 3.6 in the final sample, likely reflects this sorption edge. Yet, even at this point, a significant fraction of uranium is sorbed to the humate coated minerals.

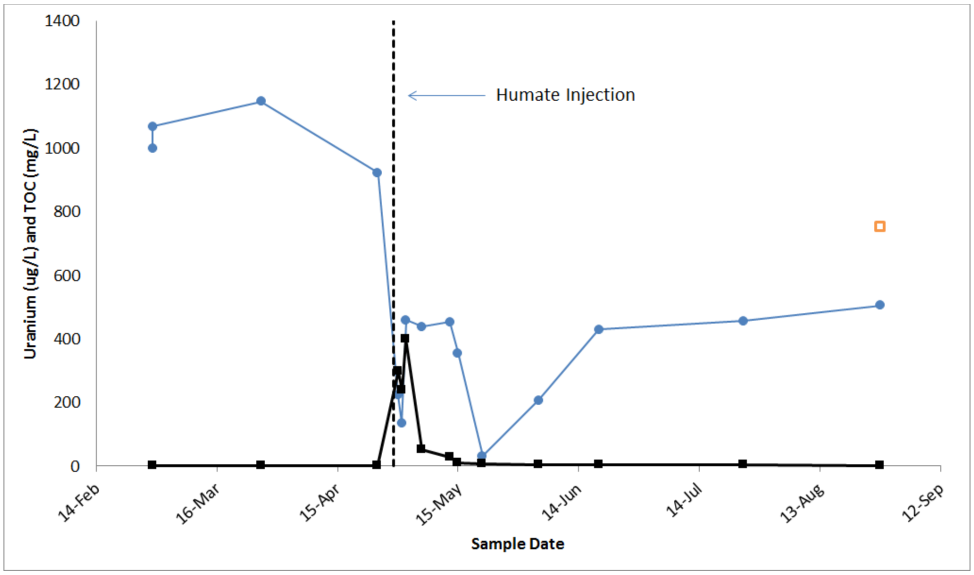


Figure 20: Uranium concentrations in groundwater from the injection well, FOB-16D, during the humate injection field test compared to total organic carbon (TOC) concentrations.

Iodine-129

In general, iodine concentrations in groundwater from the extraction well behaved similarly to other constituents during the humate injection field test. Stable iodine-127 and radioactive I-129 were measured, but I-129 data are still under review. Figure 21 shows the behavior of I-127 during the field test. Iodine can exist in multiple species with inorganic species dominated by iodide (I-) and iodate (IO3-). Figure 21 shows the concentrations of both iodate and total inorganic iodine, which is the sum of iodate and iodide concentrations. The inorganic speciation of pre-test I-127 was dominated by iodide, but as rebound of I-127 began after the injection of humate, the inorganic speciation was dominated by iodate. In a study of iodine speciation in the F-Area Seepage Basins plume, Otosaka et al. (2011) observed that in acidic portions of the plume the dominant inorganic iodine species was iodide, but in the portions downgradient of the base injection, where pH was elevated, the dominant species was iodate. In the humate injection field tests, it is likely that the elevated pH introduced by the humate injection controlled speciation of I-127, favoring iodate. As the pH decreased below 6.5, the fraction of iodide increased. At pH below 5.8, iodide became the dominant species again. During early rebound, when speciation was dominated by iodate, there was minor attenuation relative to the rebound curves projected using rebound of tritium (purple) and nitrate (green dashed). Once iodide was the dominant species, attenuation was minimal.

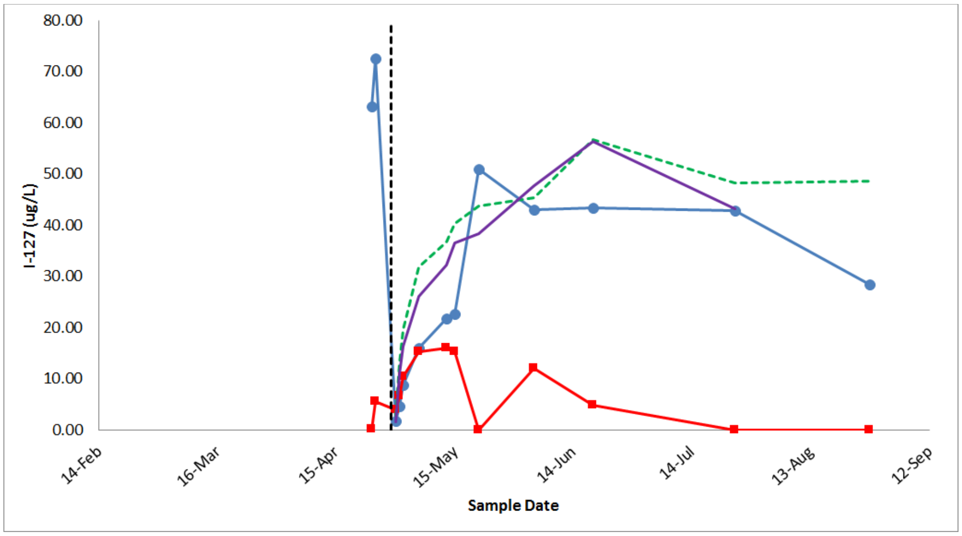


Figure 21: Total inorganic I-127 (blue circles) and iodate I-127 (red squares) concentrations in groundwater from the injection well, FOB-16D, during the humate injection field compared to rebound curves projected using tritium (purple) and nitrate (green dashed).

Humate Sorption Laboratory Studies

A key to developing a field-scale application of humate injection to enhance sorption of contaminants is understanding sorption of the humate to aquifer minerals. Preliminary experiments to develop humate isotherms and desorption curves were done. More detailed reporting of these tests will appear in a subsequent report, but some general aspects pertinent to the humate field injection test are reported here.

A Langmuir isotherm fit the data for 3 of the 4 samples used in the experiments. The equation for a Langmuir isotherm reported in Sposito (1989) is:

$$Cs = \frac{bKCw}{1+KCw}$$

Where Cs = concentration sorbed to soil, Cw = equilibrium concentration in water, b = maximum concentration adsorbed to the solid, and K is the equilibrium constant for the sorption reaction. This can be rearranged to provide a linear equation:

$$\frac{Cw}{Cs} = \frac{Cw}{b} + \frac{1}{bK}$$

To determine the maximum concentration adsorbed to the solid $(\frac{1}{b})$ and the equilibrium constant (K), $\frac{Cw}{Cs}$ is plotted versus Cw. This is shown for two of the samples having different fines content in Figure 2. Table 3 shows the parameters b and K for each sample and the estimated fine (silt + clay) fraction.

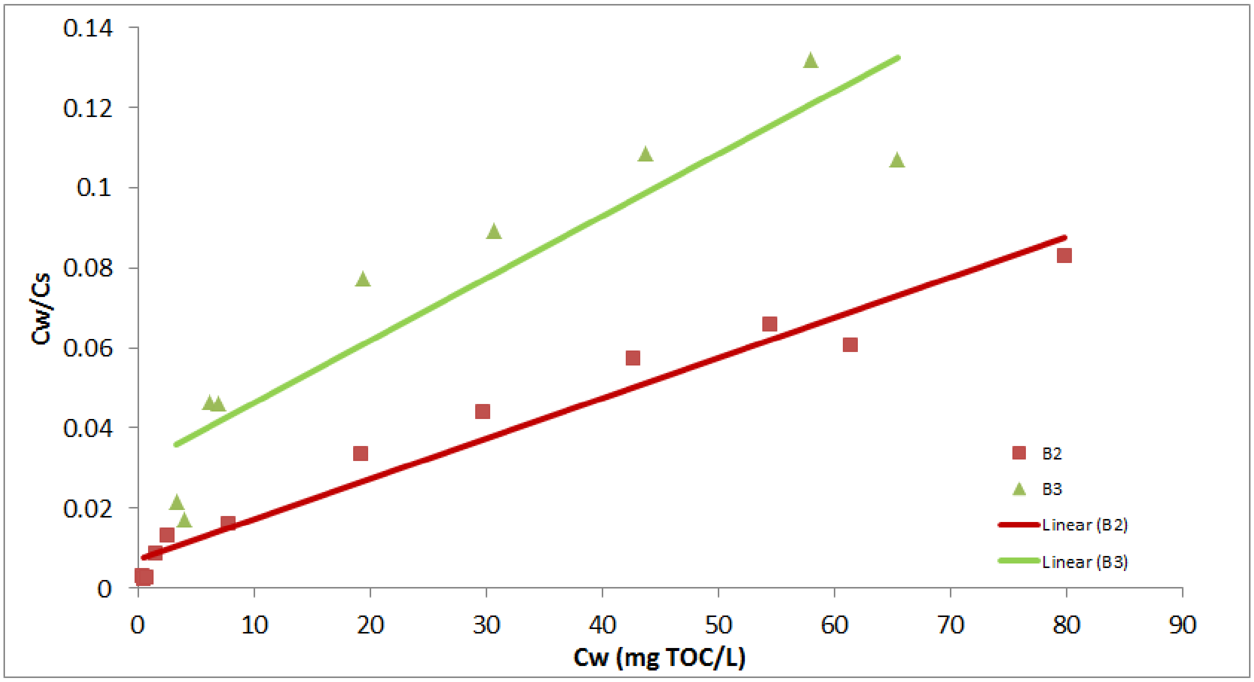


Figure 22: Linearized plots of the Langmuir isotherm equation for humate sorption onto two aquifer sediments from the F-Area Seepage Basins plume.

Table 3: Langmuir isotherm parameters for two aquifer sediment samples plotted in Figure 22.

Sample	Fine Fraction (wt.%)	b (mgTOC/kg)	K (L/kg)
B2	7.2	1000	1.4×10^5
B3	4.9	625	2.0×10^4

The results of the humate desorption experiment with sediment B2 in terms of the percent TOC lost from the sediment with each desorption batch or elution are shown in Figure 23. After 4 elutions, the amount of humate lost from the sediment is minimal. Desorption of humate in the first 2-3 elutions may contribute to the pattern of elevated uranium concentrations occurring shortly after humate injection. More importantly, the desorption experiments suggest that during a full-scale deployment, a large fraction of humate originally sorbed to aquifer sediments will remain sorbed for a long time.

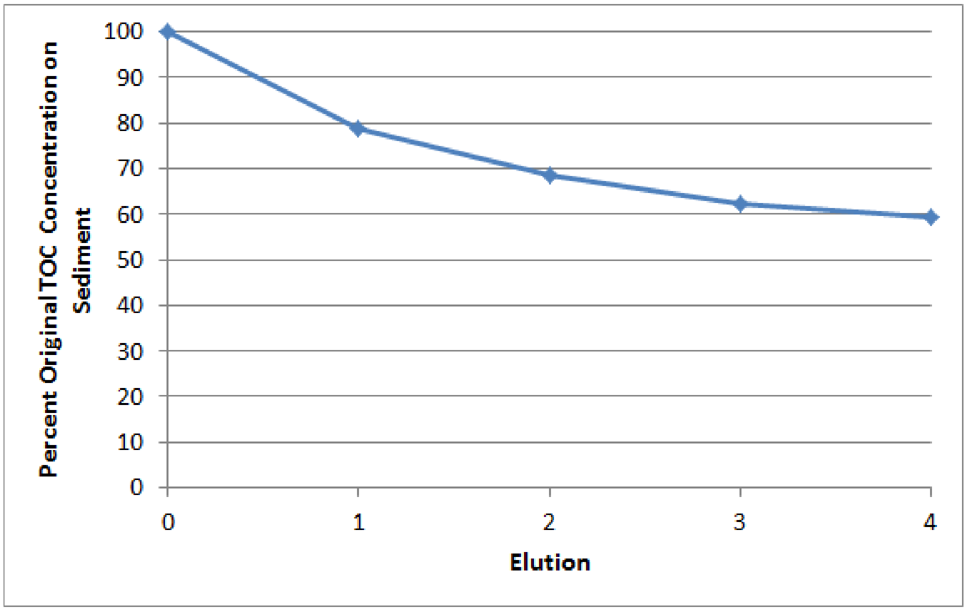


Figure 23: Results of desorption experiment on aquifer sediment B2 in terms of the percent of humate remaining on sediment after each elution.

Implications for Full-Scale Deployment

The goal of a full-scale deployment of humate would be to create a treatment zone with a groundwater travel path of tens of meters in length in which a large fraction of the surface area of aquifer minerals is covered with sorbed humate. The humate must effectively enhance the sorption of target contaminants, and there must be sufficient sorption capacity to minimize the frequency of re-injection. Likewise, the humate must remain sorbed for long periods of time

The humate injection field test demonstrated that a concentrated solution of unrefined humate can be injected into an acidic aquifer with little difficulty. The injection of 2000 liters through a 5 foot screen was completed by gravity feed in less than 8 hours. There was no indication of formation or well screen clogging. It is anticipated that much larger injections, as required in a full-scale deployment, could be done with no issues.

Humate sorption studies indicate that humate strongly sorbs to mineral surfaces at a pH of 4. Desorption studies indicate that a large fraction of the humate injected would remain sorbed for long periods of time. At the maximum loading of 1000 g humate per kilogram sediment, it would require approximately 34 metric tons of Huma K to create a treatment zone 3 meters vertically, 100 meters orthogonal to the plume, and 20 meters along the plume axis.

The treatment zone would be effective for uranium, less so for I-129, and ineffective for Sr-90. Even though only 32% of the uranium in groundwater was sorbed in the humate injection field test treatment zone, the treatment zone was only 1 meter wide. A treatment zone that was 10-20 meters wide would decrease uranium concentrations to regulatory limits.

Remaining Questions About Humate as an Enhanced Attenuation Amendment

The single well humate injection field test answered the critical questions of whether a concentrated solution of humate can be injected into an acidic aquifer and the effectiveness of humate at enhancing sorption of uranium, Sr-90, and I-129. Yet, there are additional questions that should be answered with laboratory studies prior to designing field deployments. These are listed below. Some of these questions will be addressed in fiscal year 2015 and later years by the ABRS AFRI.

- What is the sorption capacity for uranium of aquifer sediment amended with humate? The humate injection field test provides a minimum sorption capacity for the conditions of the test, but the duration of the test did not allow for an estimate of the maximum sorption capacity.
- What is the envelope of conditions (pH, mineralogy, etc.) for which humate injection is a viable technology? The field injection test was done in an acidic aquifer with a silicate mineralogy. The contaminated aquifers at many DOE sites have a neutral to alkaline pH and a mineralogy with a substantial fraction of calcite.
- Are subsequent humate injections useful when the sorption capacity for uranium or other contaminants of a humate amended aquifer is exceeded? The humate field injection test suggests that subsequent injections may mobilize some fraction of the uranium immobilized by the first humate injection. Is mobilizing this fraction an acceptable risk?
- Is the apparent speciation change of radioiodine from iodide to iodate when humate is injected microbially mediated and can it be expected to occur elsewhere? Does the apparent enhanced sorption of iodate imply that humate will be an effective treatment for I-129 when the dominant species is iodate?
- Is the rate of microbial degradation of sorbed humate significant to its use as an enhanced attenuation amendment?

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