

TECHNICAL PROGRESS REPORT

FIU's Support for Groundwater Remediation at SRS F/H Area

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Introduction

The Savannah River Site (SRS) was constructed during the 1950s and became one of the major producers of plutonium for the United States during the Cold War. Beginning with the implementation of the environmental cleanup program in 1981, SRS has become a hazardous waste management facility. As a hazardous waste management facility, the site is responsible for nuclear storage and remediation of contaminated soil and groundwater from radionuclides. During its production life, the F/H Area Seepage Basins received approximately 1.8 billion gallons of acidic waste containing radionuclides and dissolved heavy metals. This led to the unintentional creation of a highly contaminated groundwater plume at an acidic pH of 3-5.5. The acidity of the plume contributes to the mobility of several constituents of concern (COC) such as tritium, uranium-238, iodine-129, and strontium-90 for the F-Area plume and tritium, strontium-90 and mercury for the H-Area plume. This investigation will focus on uranium (VI), which is a key contaminant of concern in the groundwater plume.

Initially, removal of contaminants from the polluted groundwater was done by a pump-and-treat and re-inject system constructed in 1997. Downgrade groundwater within the system would be pumped to the water treatment facility and re-injected upgrade within the aquifer. The effectiveness and sustainability of this process diminished over time and it was discontinued in 2004, replaced with a funnel-and-gate process. This new process would inject sodium hydroxide directly into the gates of the F-Area groundwater to effectively raise pH levels. By raising the pH of the groundwater, a treatment zone would be created by reversing the acidic nature of the contaminated sediments and producing a negative net charge on the surface of sediment particles, enhancing the adsorption of cationic contaminants. This process resulted in a decrease in concentration of Sr and U; though there was no change in iodine concentration. The solution used for the injections contained a high carbonate alkalinity in order to overcome the surface acidic conditions and natural partitions in the groundwater system. To maintain the neutral pH in the treatment zone, systematic injections are required. The continuous use of high concentrations of a carbonate solution to raise pH could re-mobilize uranium previously adsorbed within the treatment zone, though this has not been observed in monitoring data.

FIU-ARC is conducting an investigation to evaluate replacing the carbonate base with a sodium silicate to determine if the substitute can sufficiently alkalize the acidic nature of the waste plumes. Initially, it must be determined if a silica solution with $\text{pH} \leq 10$ has sufficient alkalinity to restore the pH of the treatment zone, and whether injection of silica solution is possible without clogging the subsurface aquifer permeability. The silica solutions pH requirement of being ≤ 10 comes from regulatory constraints of high pH injections to subsurface systems. This research will also investigate binding between U(VI) and colloidal silica and synergistic effects between humic acid (HA) and colloidal silica influencing the percent removal of U(VI).

Humic substances (HS) are major components of soil organic matter with the ability to influence migration behavior and fate of heavy metals. Essentially, HS are polyfunctional organic

macromolecules formed by the chemo-microbiological decomposition of biomass or dead organic matter. Being organic substances, HS are able to interact with both metal ions and organic compounds, and based on their solubility, HS are usually divided into three fractions (Chopping, et al. 1992). The three fractions are humin, humic acid and fulvic acid. Humin is insoluble at all pH values; HA represents the fraction which is soluble at pH greater than 3.5 and fulvic acid is soluble at all pH values.

Humic acid, which carries a large number of functional groups, provides an important function in ion exchange and as a metal complexing ligand with a high complexation capacity being able to affect the mobility of actinides in natural systems (Davis, 1982; Plancque et al., 2001). Various studies have suggested that the retention of U(VI) via sorption in the presence of HA is a complex process due to HA forming organic coatings by sorbing on the surface of oxides and minerals, thus modifying the sorption capabilities of these metal ions (David, 1984; Zachara et al., 1994; Labonne-Wall et al., 1997; Perminova et al., 2002). The sorption of metal ions is considered to be enhanced at low pH and reduced at high alkaline pH (Ivanov et al., 2012). This sorption capability is also affected by the concentration of HA in the system (Chen and Wang, 2007). The U(VI) sorption onto kaolinite is influenced by the pH, U(VI) concentration, presence of inorganic carbon species and naturally occurring HA. It has also been shown that U(VI) prefers to be adsorbed onto kaolinite as a uranyl-humate complex (Krepelova et al., 2007).

This investigation will analyze any synergistic interactions between U(VI) ions, HA and colloidal silica under varying pH conditions from 3 to 8 and the presence of sediment collected from SRS FAW1. Multi-component batch systems were constructed to effectively analyze the removal behavior of U(VI).

Methodology

Removal behavior of U(VI) was studied through multi-component batch systems with a pH range from 3 to 8 in order to evaluate adsorption affected by the pH. Last year FIU/ARC investigated the synergetic effect of colloidal silica and HA on uranium removal by preparing seven batches with various combinations of Si and HA (Lagos, et al, 2014). This year only batches with HA were prepared to study the sorption behavior of uranium at a higher HA concentration (50 ppm). The results were compared to the data on the sorption behavior of U(VI) at a lower HA concentration (10 ppm) obtained last year. Sediment samples used in the experiments were collected at SRS from FAW1 at a depth of 70-90 feet and shipped to FIU-ARC. The sediment was sieved through 2 mm to remove gravel and larger sediment particles. Batch 2 contained 3.5 mM Si, 50 ppm HA, and 0.5 ppm U(VI). Batch 3 is similar to batch 2 without the inclusion of the Si; thus, being only HA and U(VI). Batch 5 would explore the capabilities of sediment in solution with 3.5 mM Si, 50 ppm HA, and 0.5 mM U(VI). Finally, the last batch, batch 6, would be similar to batch 5 though without silica in the solution and only

including HA, uranium and sediment. Control samples were prepared in triplicate containing DIW and 0.5 ppm U(VI) to account for any sorption between the uranium and container.

- **Batch 2: Si (3.5 mM) + U(VI) (0.5 ppm) + HA (50 ppm), (no sediments)**
- **Batch 3: U(VI) (0.5 ppm) + HA (50 ppm), (no Si or sediments)**
- **Batch 5: Sediments + Si (3.5 mM) + U (VI) (0.5 ppm) + HA (50 ppm)**
- **Batch 6: Sediments + U(VI) (0.5 ppm) + HA (50 ppm), (no Si)**
- **Control: U(VI) (0.5 ppm), (no SI, HA, or sediment)**

Fumed colloidal silica, silicon (IV) oxide 99%, and humic acid sodium salt (50-60% as humic acid) were obtained from Fisher Scientific. Stocks of HA and Si were prepared in deionized water (DIW) at 2000 ppm and 100 ppm, respectively. A commercial 1000 ppm uranyl nitrate stock solution in 2% nitric acid (Fisher Scientific) was used as a source of U(VI). The resulting sample mixtures were spiked with uranium to yield a concentration within a solution matrix of 0.5 ppm. Table 1 presents the amount of stock solutions needed to yield 50 ppm of HA, 3.5 mM of Si and 0.5 ppm of U(VI). Triplicate samples for each batch were prepared; uranium was added to each sample prior to adjusting the pH. The pH of the mixture was then adjusted to the required value using 0.01 M HCl or 0.1 M NaOH (Figure 1). Control samples were prepared in DIW amended with U(VI) at a concentration of 0.5 ppm U(VI) to test for U(VI) losses from the solutions due to sorption to the tube walls and caps. All volumes of solutions were prepared to initially have 20 mL of total volume in the sample tube. All control and experimental tubes were vortexed and then kept on the shaker at 100 rpm for 48 hours at room temperature.

Table 1. Experimental Matrix with Amount of Components

Batch #	Constituents					
	SiO ₂ ml	Humic Acid ml	Uranium U(VI) ml	Sediment mg	Water H ₂ O ml	Total Volume ml
Batch No. 2	2.1	10	0.01	0	7.89	20
Batch No. 3	0	10	0.01	0	9.99	20
Batch No. 5	2.1	10	0.01	400	7.89	20
Batch No. 6	0	10	0.01	400	9.99	20



Figure 1. Experimental setup.

Samples were shaken for 48 hr at 100 rpm and then centrifuged at 2700 rpm at 22°C for 30 minutes (Figure 2). All samples, after being centrifuged, were filtered using a 0.45 μm syringe filter yielding a 3-mL aliquot. Aliquots for KPA [U(VI) analysis] and ICP-OES (Fe and Si analysis) were prepared by taking a 300- μL aliquot for KPA and 500- μL for ICP-OES from the filtered solutions and doing a 10x dilution with 1% HNO_3 .



Figure 2. Shaker and centrifuge experimental setup.

Results and Discussion

pH 3

Triplicate samples at pH 3 were analyzed with KPA to determine the uranium concentration. Percent uranium removal was calculated using the uranium concentration from the control samples and Table 2 shows the average U(VI) percent removal from the triplicate samples. The percent removal of uranium for batches 2 & 3 (with no sediment) and batches 5 & 6 (amended with sediment) was found to be between 49-55% and a 79-84%, respectively. Solubility of HA is low at low pH while U(VI) is present as highly soluble uranyl ions (Krepelova, 2007a). Krepelova et al. (2007b) reported that HA enhances the U(VI) sediment uptake in acidic pH conditions. The high percent removal can be attributed to the competition of solubilizing negative functional groups (deprotonated carboxyl groups) with hydrophobic groups; at low pH, the hydrophobic group is the stronger force, causing aggregation/coagulation of the uranyl cations (Tipping, 2002). U(VI) interaction with silica colloids is found to be negligible as the average Si removal was $87.11 \pm 3.55\%$ and $84.38 \pm 0.15\%$ for batch 2 and 5, respectively. Batch 2 yielded significantly less U(VI) removal compared to batch 5 yet both have relatively similar Si removal. The presence of sediments increased the percent of U(VI) removal on average from 50% to 80%. It is possible that the sediment creates a greater number of binding sites for U(VI); the high solubility of uranium allows the cations to easily come into contact with negatively charged sediment particles and interact successfully, increasing the percent of U(VI) removal.

Table 2. Analytical Results for pH 3

Sample-Description, pH 3	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	55.17	4.00	87.11	3.55	No Sediment	
Batch 3	49.22	6.50	No Si	No Si	No Sediment	
Batch 5	83.83	1.97	84.38	0.15	0.31	0.02
Batch 6	79.16	2.90	No Si	No Si	0.37	0.07

pH 4

Resulting data for pH 4 was similar to that of pH 3, though showing slightly lower U(VI) removal for all batches. The samples prepared with sediments (batches 5 and 6) still provided a higher removal percentage than those without sediments, dropping from 70.06% removal with sediment to as low as 40.52% without sediment.

Table 3. Analytical Results for pH 4

Sample-Description, pH 4	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	53.2	3.93	82.4	1.27	No Sediment	
Batch 3	40.52	4.28	No Si	No Si	No Sediment	
Batch 5	65.36	2.39	85.61	1.65	0.3	0.06
Batch 6	70.06	0.42	No Si	No Si	0.41	0.02

pH 5 and 6

For all batches at pH 5 and 6, the samples showed similar results. For batches 2 and 3, the U(VI) removal percentage gradually decreased with an increase in pH; the average uranium removal at pH 3 was observed as 53% and was reduced to the average removal value of 35% at pH 5 and 31% at pH 6. Similar trends were observed for batches 5 and 6; uranium removal decreased from 80% at pH 3 to 50% and 44% at pH 5 and 6, respectively. At these pH values, the number of uranyl cations in solution decreases, which ultimately limits the interactions between uranium and HA. Once the pH reaches 6, the dominant species in solution is $\text{UO}_2(\text{OH})\text{HA}(\text{I})$ with minimal presence of uranyl cations and $\text{UO}_2\text{HA}(\text{II})$ (Krepelova, 2007a). Similarly, due to the increased solubility of HA, fewer binding sites are available for interactions. Liao et al. (2013) reported that the coordination number between U(VI) and humic acid increases from 1:1 to 1:2 when pH increased from 3 to 6; the data obtained in these experiments supports this theory. The coordination number suggests the number of ligands attached to the central ion, showing that greater amounts of HA is required to remove the same amount of U(VI). Similar to the lower pH results, the batches containing sediment showed higher uranium removal percentages compared to sediment-free batches.

Table 4. Analytical Results for pH 5

Sample-Description, pH 5	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	38.25	3.08	85.15	3.09	No Sediment	
Batch 3	32.98	4.12	No Si	No Si	No Sediment	
Batch 5	49.59	1.98	85.35	0.71	0.42	0.03
Batch 6	52.18	1.43	No Si	No Si	0.48	0.02

Table 5. Analytical Results for pH 6

Sample-Description, pH 6	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	30.87	5.66	77.71	4.96	No Sediment	
Batch 3	32.98	5.82	No Si	No Si	No Sediment	
Batch 5	43.08	0.94	84.14	1.75	0.48	0.03
Batch 6	45.82	0.84	No Si	No Si	0.59	0.07

pH 7

The neutral pH of 7 revealed the lowest percent uranium removal of all the batches. Uranium removal for the sediment-free batches (batches 2 and 3) was at 19.51% and 20.89%, while sediment-containing samples yielded a higher removal at 39.26% and 44.80%, respectively for batches 5 and 6. By adding sediments into the solution, a ~50% increase in U(VI) removal is seen compared to samples without sediment.

Table 6. Analytical Results for pH 7

Sample-Description, pH 7	U(VI) Avg Removal, %	Std.	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	19.51	3.64	75.67	4.02	No Sediment	
Batch 3	20.89	1.03	No Si	No Si	No Sediment	
Batch 5	39.26	1.91	84.2	0.97	0.48	0.03
Batch 6	44.80	1.66	No Si	No Si	0.68	0.18

pH 8

The alkaline pH of 8 shows a slight increase in percent of uranium removal compared to the values observed at neutral pH 7. Batches 2 and 3 resulted in a 46.14% and 34.17% removal, respectively, while batches 5 and 6 yielded a 41.57% and 43.52% removal, respectively. The uranium removal observed at pH 8 seemed to not be affected by the presence of sediments. Tipping (2002) states that, at high pH, the proton-binding sites of HA molecules are sufficiently dissociated to carry any significant charge, thus reducing any binding potential. The major species is $(UO_2)_3(OH)_8^{2-}$ a negatively charged complex limiting interaction with the dissociated functional groups of HA.

Table 7. Analytical Results for pH 8

Sample-Description, pH 8	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	46.14	2.62	68.66	4.23	No Sediment	
Batch 3	34.17	5.75	No Si	No Si	No Sediment	
Batch 5	41.57	0.54	83.57	0.5	0.46	0.03
Batch 6	43.52	1.34	No Si	No Si	0.58	0.03

Figure 3 represents the silica removal for the silica-containing batches (batches 2 and 5); the removal remains consistent for batch 5 (84-85%) and shows a slight decrease with increasing pH for batch 2 (87.11-68.66%). The presence of silica does not seem to have any significant effect. Figure 4 presents the results of U(VI) removal at 10 ppm HA; when compared to that of U(VI) removal at 50 ppm (Figure 5), the results are strikingly different. The 10 ppm HA solution showed significant removal at an alkaline pH, unlike the 50 ppm HA solution which shows a greater removal at acidic pH. It is postulated that 10 ppm HA is too low for significant interaction to occur, causing the uranium removal to be from the sediment present. However, further research is needed to test this hypothesis.

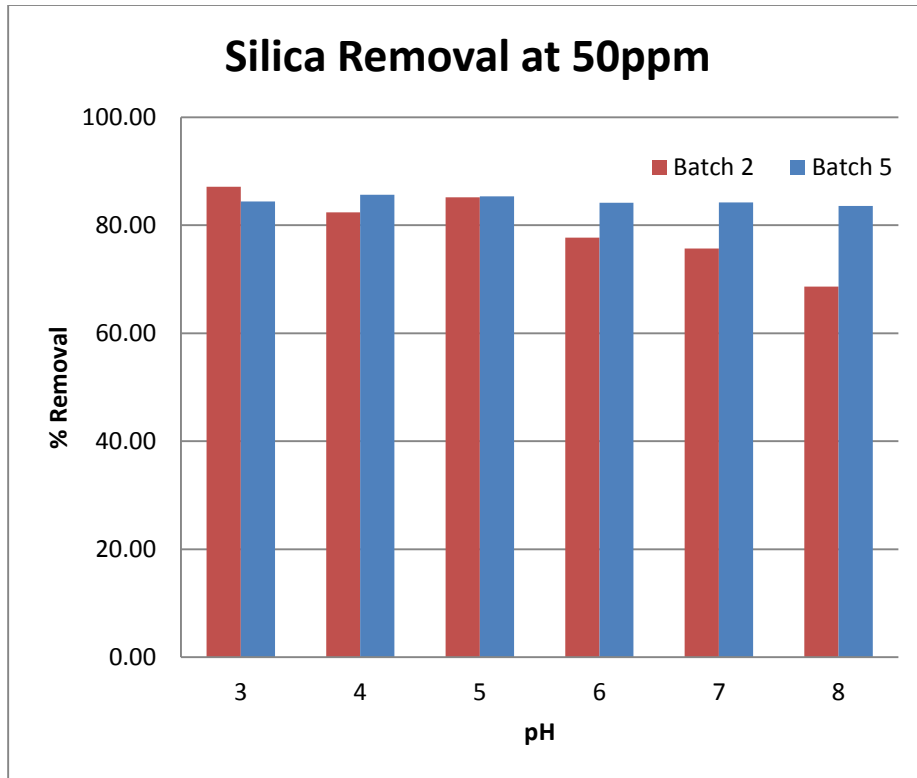


Figure 3. Silica removal at 50 ppm.

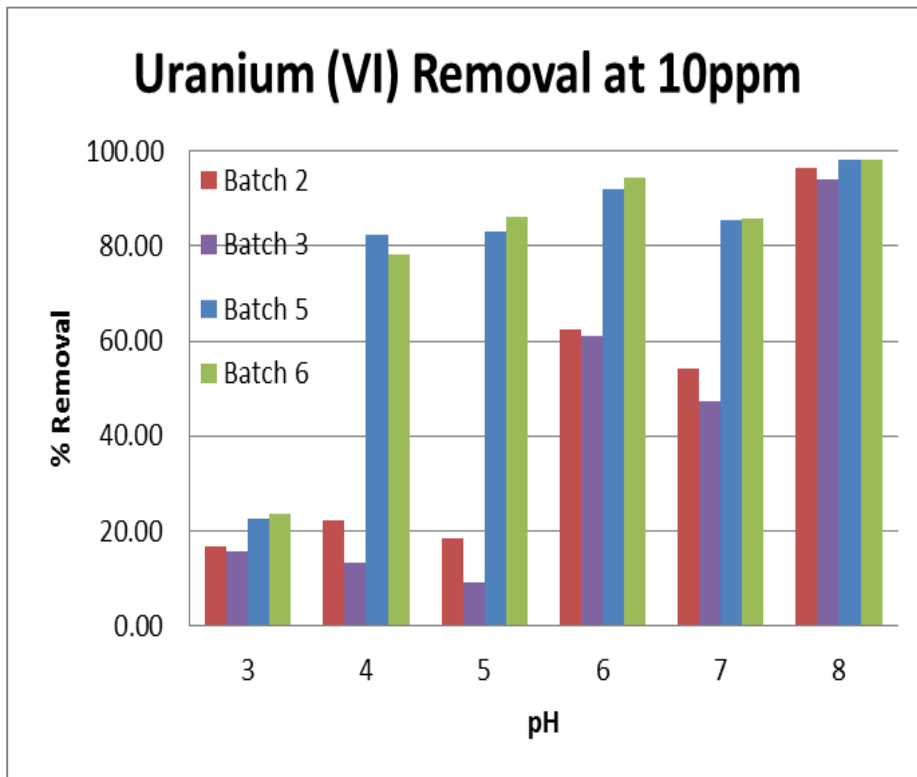


Figure 4. Uranium (VI) removal at 10 ppm HA.

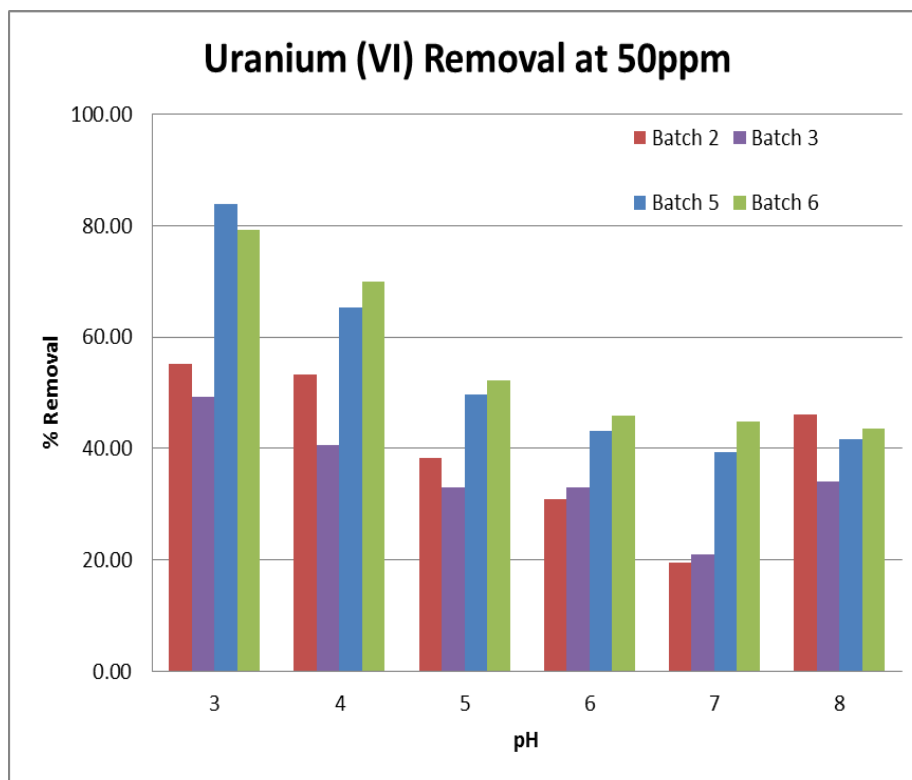


Figure 5. Uranium (VI) removal at 50 ppm HA.

The percent removal of U(VI) is directly influenced by the pH, HA and presence of sediments. Interactions of uranium with colloidal silica, HA, and sediment may be better explained by considering uranyl speciation at various pH conditions.

At acidic pH, the uranyl cation is the dominant species. As pH increases, the dominant species becomes mononuclear and polynuclear hydrolyzed uranyl ions. As the pH reaches 8, the uranyl species changes from positive to negatively charged polynuclear complexes. At pH 4.5 and below, colloidal silica particles bear little negative surface charge; so, the positively charged uranyl complexes will have little interaction (Iler, 1975). At low pH, the presence of HA significantly increases uranium removal due to the functional groups available for interaction and binding. The removal of uranium increases with the addition of sediments due to the availability of more binding sites for the uranyl cations. As pH increases from 4 to 7, the removal decreases as the primary species is not the uranyl cation but rather hydrolyzed uranyl complexes. At this pH range, the coordination number increases (1:2), requiring more HA to remove the same amount of U(VI), unlike at an acidic pH where it is 1:1. Colloidal silica does not seem to have a significant effect, though Koopal et al. (1998) reported that HA could rapidly and strongly absorb onto the silica surface. If HA is absorbing to the silica, less removal of uranium will be observed from the limited binding sites.

Table 8. Uranyl Speciation

pH	3	4	5	6	7	8
Uranyl Species	UO_2^{2+}	UO_2^{2+} $(\text{UO}_2)_2(\text{OH})_2^{2+}$	$(\text{UO}_2)_3(\text{OH})_5^+$ UO_2OH^+	$(\text{UO}_2)_3(\text{OH})_5^+$ UO_2OH^+	$(\text{UO}_2)_3(\text{OH})_5^+$ $(\text{UO}_2)_3(\text{OH})_7^+$	$(\text{UO}_2)_3(\text{OH})_8^{2-}$ $\text{UO}_2(\text{OH})_3^-$

Future Work

This investigation allowed for the comparison of 50 ppm HA data to previously obtained data at 10 ppm HA. The 10 ppm HA samples were not filtered before analysis, unlike the 50 ppm HA samples. The 50 ppm HA samples will be analyzed without filtering for a direct comparison. Samples with an intermediate concentration of 25 ppm or 30 ppm HA need to be prepared and analyzed to determine if there are any significant trends between the 10 ppm and 50 ppm batches. HA-free samples amended with Si will also be repeated in the new batches.

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