LIMITED SCALE AQUIFER STORAGE AND RECOVERY (LSASR) OKLAHOMA DEPARTMENT OF ENVIRONMENTAL QUALITY APPLICATION

City of Ada

Pontotoc County, Oklahoma

FINAL

November 2021

Revised April 2022

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I. Statement of Interest

The following proposed Limited Scale Aquifer Storage and Recovery Pilot Project is a collaborative venture by the City of Ada, the Chickasaw Nation, East Central University and the USEPA Kerr Lab to develop technical means and methods for future full-scale Aquifer Storage and Recovery (ASR) using managed aquifer recharge (MAR) methods. Tests proposed in this document and seeking permitting fall squarely in the description of activities that should seek permitting as Limited Scale Aquifer Storage and Recovery (LSASR) pilot projects in the LSASR permit application guidance document provided by Oklahoma Department of Environmental Quality: these tests will help City of Ada determine the feasibility of a prospective full-scale ASR project and will provide aquifer flow characteristic data for research purposes for collaborators from academia and the USGS. Activities seeking permitting in this application consist of up to 3 tracer tests using a natural recharge structure (e.g. a sinkhole) and subsequent groundwater and springflow monitoring that will help characterize the impacts of storm-driven recharge on Arbuckle-Simpson Aquifer (ASA) groundwater. These tests will achieve several goals of the project partners, listed here in order of priority:

1. Satisfy the information needs required for the eventual submission of a full-scale ASR application to ODEQ by obtaining necessary detail about aquifer properties and identifying that planned future ASR activities in the region pose no threat to groundwater resources.
2. Broadly benefit understanding of advective flow and its implications for bio-attenuation in the fractured carbonate/karst matrix of the Arbuckle-Simpson aquifer in the Byrds Mill Spring capture zone.
3. Provide information on aquifer characteristics that can be incorporated into the USGS Arbuckle-Simpson Aquifer Phase II Groundwater Model update.

II. Proposed Location & Site Description

Geography

The City of Ada MAR (Managed Aquifer Recharge) site is located in south-central Oklahoma approximately 5.1 km (3.2 mi) southwest of Fittstown in Pontotoc County, Oklahoma on land owned and operated by the City of Ada, OK (Figure 1 and Figure 2). Roughly situated along the eastern edge of the Arbuckle-Simpson Aquifer, a sinkhole is located at 34°35’11.3”N 96°40’47.1”W and is found along a ravine that runs into a small pond which periodically overflows into the sinkhole. The PLSS location of the site is the SE ¼ NW ¼ S4 T1N R6E. The area of the pond under normal conditions is roughly 1,800 m^2 (5,900 ft). The elevation of the area which includes the sinkhole and the pond sits between 340-345 m (1,115-1,132 ft) above mean sea level. Byrds Mill Spring is located northeast 1.5 km (0.95 mi) from the sinkhole and the Blue River is located 1.5 km (0.91 mi) west of the sinkhole. The immediate land in the area is made up of tall grass prairie and forest.

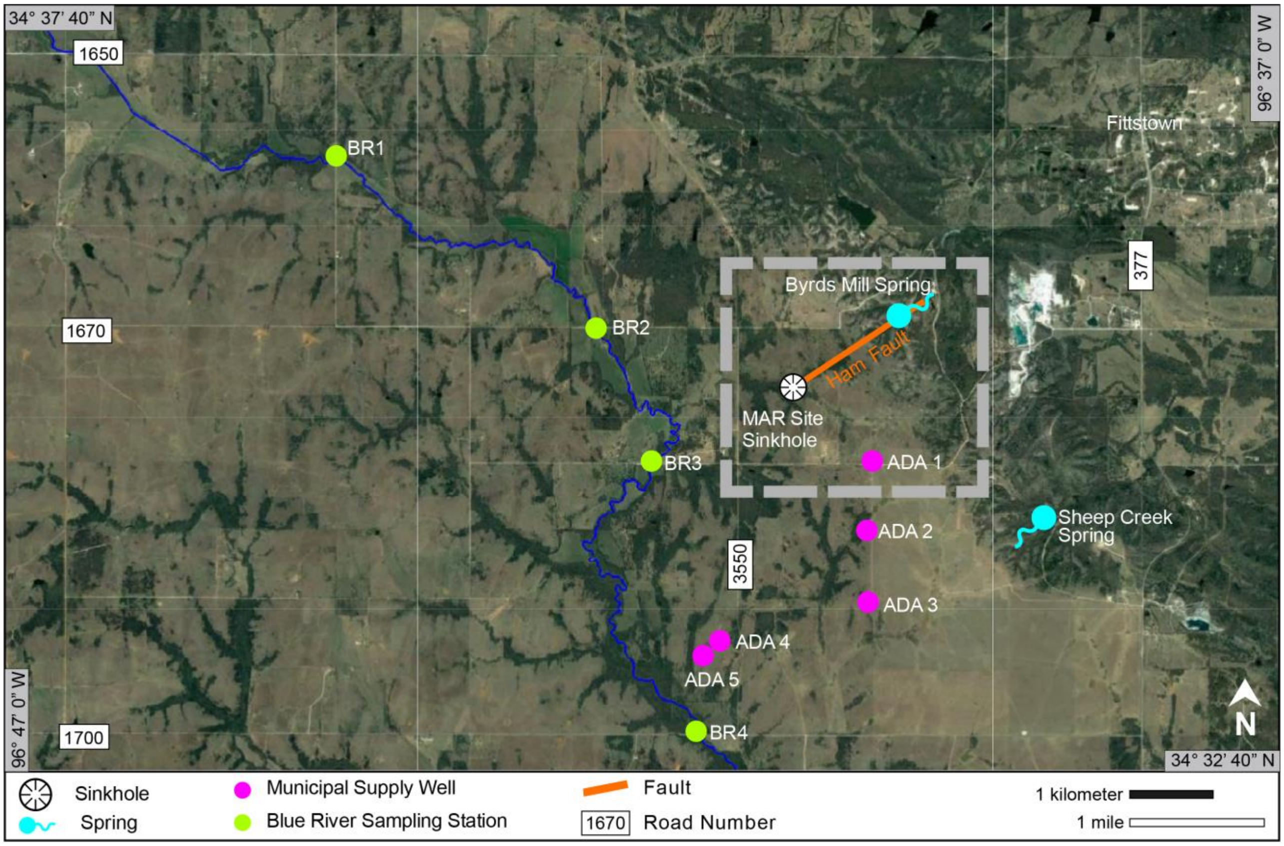


Figure 1: Regional-scale map of City of Ada MAR Research Site. Inset site map (gray, dashed rectangle) shown in Figure 2.

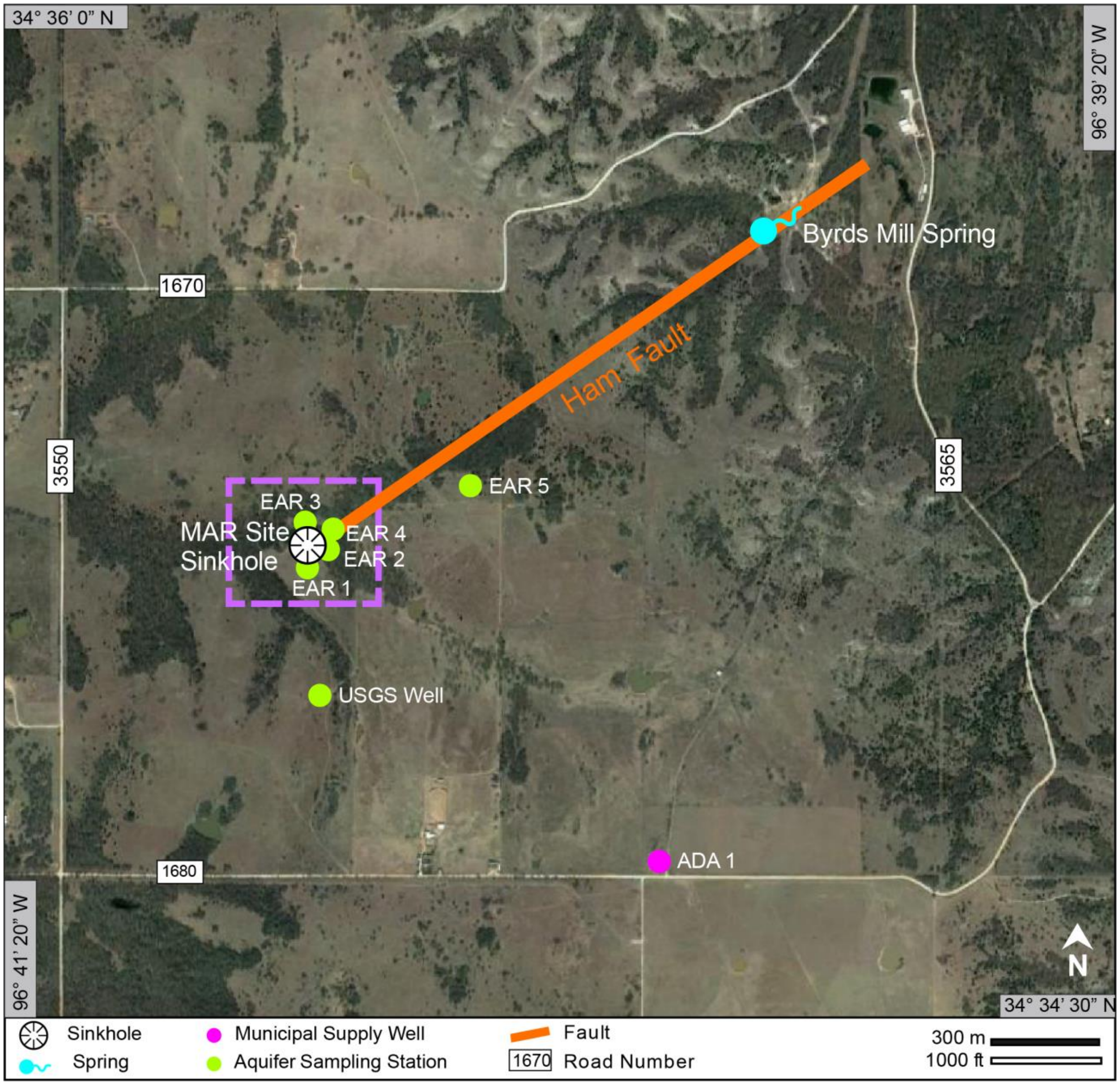


Figure 2: City of Ada MAR Research Site Map. Distance from the sinkhole intended for use as an enhanced recharge feature is approximately one mile from Byrds Mill Spring. Pink rectangle shows approximate extent of City of Ada MAR Research Facility.

Climate

Climate data are collected and reported by Oklahoma Mesonet and Oklahoma Climatological Survey which are operated jointly by the University of Oklahoma and Oklahoma State University (Oklahoma Climatological Society, 2017). Like much of the state, this area is within the Köppen climate classification of humid subtropical climate. Temperatures for Fittstown, OK average a maximum of 22.8°C (73°F), a minimum of 10°C (50°F), and an annual of 16.7°C (62°F) (Oklahoma Climatological Society, 2017). Annual precipitation averages 1046 mm (41 in) annually with historical extremes of 1625 mm (64 in) and 595.4 mm (23 in). Fittstown experiences 76 days a year with precipitation along with 50 thunderstorm days (Oklahoma Climatological Society, 2017). Weather data are collected automatically every 5 minutes at the Fittstown Mesonet weather station located at 34° 33’ 7” N, 96° 43’ 4” at an elevation of 350 m (1148 ft). The research site also has two weather stations collecting a range of meteorological data.

Geology

This site sits on top of the Ordovician Arbuckle group, specifically, the West Spring Creek Formation, which is principally karstified dolomite with minor sandstone beds (Figure 3). The area is located at the eastern edge of the Hunton Anticline. Subsurface faults generally trend to the northeast and northwest. It is suspected that numerous unidentified faults likely follow the same directional trend of the identified faults. The geology has been mapped as surficial geology by Ham et al. (1954), revised by Johnson et al. (1990), and discussed in Fairchild et al. (1990). A large-scale project was conducted by a consortium of researchers in the 2000s that resulted in a 3D geologic model of the Hunton anticline region (Faith, et al., 2010). The project also resulted in a database of hydrogeologic publications and reports related to the Arbuckle Simpson aquifer.

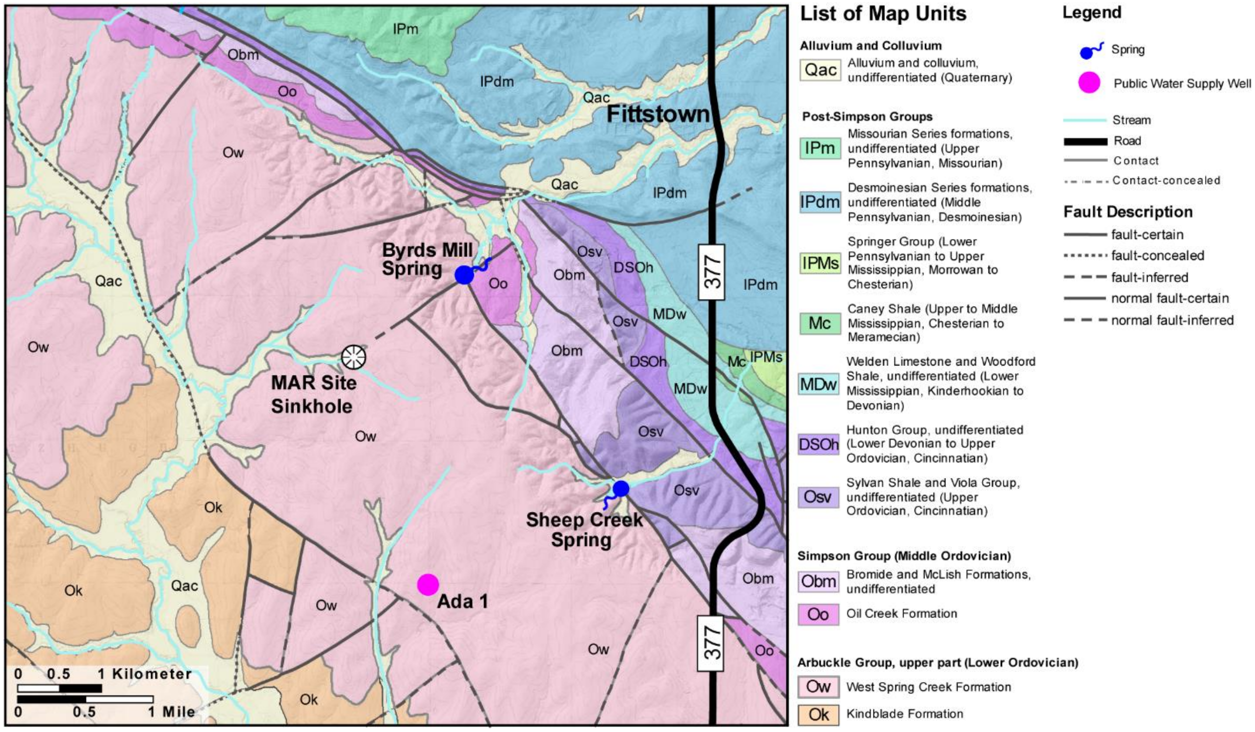


Figure 3: Geological map of the region surrounding the research site. (After Lidke & Blome, 2017).

Hydrogeology

The regional scale hydrogeology of the City of Ada MAR site is part of the Eastern Arbuckle Simpson aquifer which is the aquifer name for the Hunton Anticline structural portion of the aquifer. The regional scale system was modeled in MODFLOW by the USGS and while a fractured, karstic system, it does model well on the regional scale as a continuum flow system (Christenson, et al., 2011). The system is not well differentiated vertically as the well logs do not have significant features to correlate laterally, except the “brown zone” which can be distinguished in cores and geophysical well logs.

The regional system is unconfined in the shallow portion and changes aquifer type with depth (Rahi & Halihan, 2013). The aquifer becomes semiconfined at depths of 100-200 m (330-660 ft) and fully confined at deeper depths. Regional-scale faults and fractures generate vertical anisotropy that causes the aquifer to be nearly isothermal with depth (Swinea, 2011) and to require the MODFLOW model to include vertical flow to allow calibration (Christenson, et al., 2011). The regional water table at the research site has a flow direction from the south to the southeast (Fairchild, Hanson, & Davis, 1990).

The water table at the research site is approximately 30 m (100 ft) deep. A long-term monitoring well installed in 1958 by the USGS (USGS Fittstown Well, USGS ID 343457096404501) is available to evaluate long-term aquifer conditions (Figure 2). The site also has five constructed aquifer monitoring locations called EAR1 – EAR5. These monitoring locations, as well as the location of the USGS well, are detailed in Figure 2 and Table 1. There are multiple piezometers of varying depth installed at each location to monitor aquifer conditions near the site sinkhole. Individual piezometers at each of locations EAR 1-4 can be observed in Figure 4. The list below details completed or planned piezometer installations at each monitoring location. Their depths are identified in Table 2. Note that wells EAR-1D and EAR-5D are planned but are not yet constructed. Also note that a geophysical logging of the USGS well is planned but has not yet been performed. The USGS website identifies a well depth of 121 m (396 ft) and a hole depth of 520 m (1707 ft), but there is reason to believe that the hole was abandoned below 121 m (396 ft).

- EAR-1 Location: Wells EAR-1, EAR-1S, EAR-1I, *EAR-1D* (Proposed, but not yet constructed)
- EAR-2 Location: Wells EAR-2, EAR-2S
- EAR-3 Location: Wells EAR-3, EAR-3S
- EAR-4 Location: Wells EAR-4, EAR-4S
- EAR-5 Location: Wells EAR-5, EAR-5I, *EAR-5D* (Proposed, but not yet constructed)

It is expected that all of the already-constructed wells, including the USGS well, will be used for tracer test monitoring. EAR wells were constructed for the purpose of monitoring tracer tests, but the USGS well pre-dates this study and was constructed for other purposes. Deep wells that are not yet constructed may be used for tracer test monitoring if constructed in time, but are more intended for other aquifer characterization tasks.

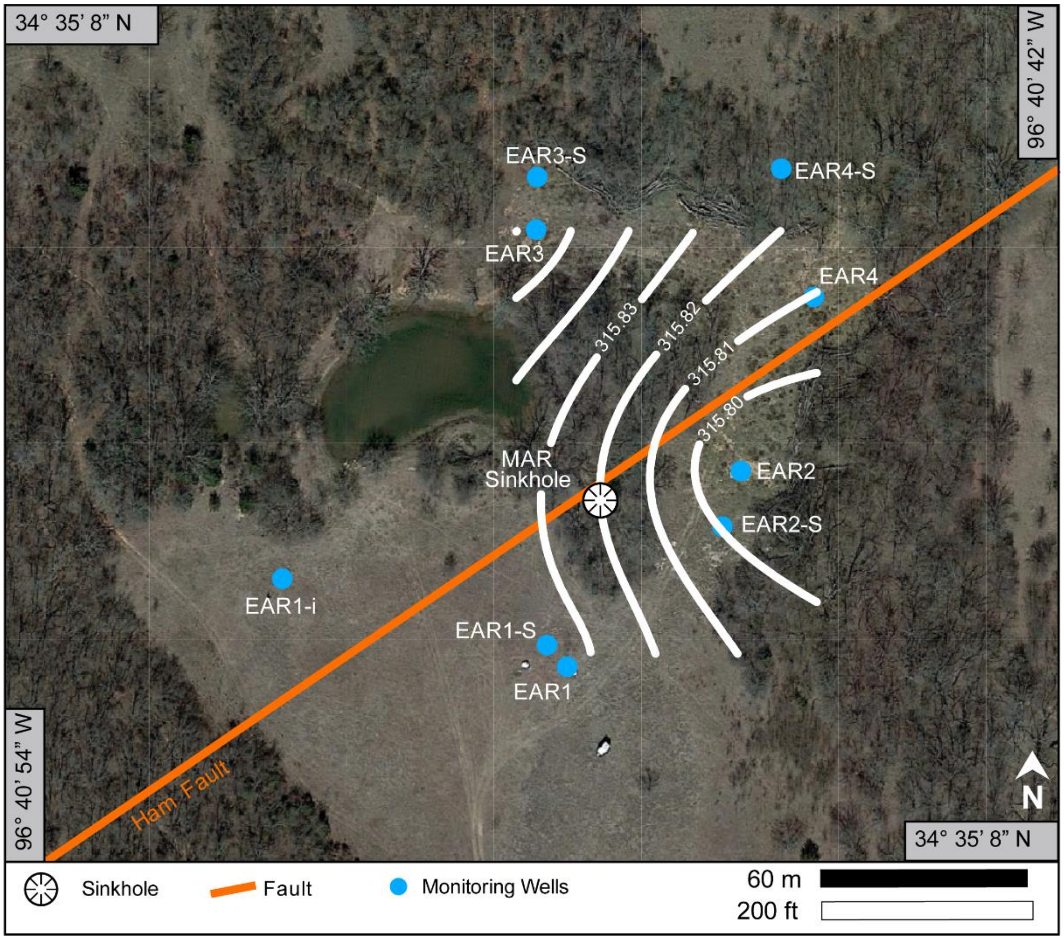
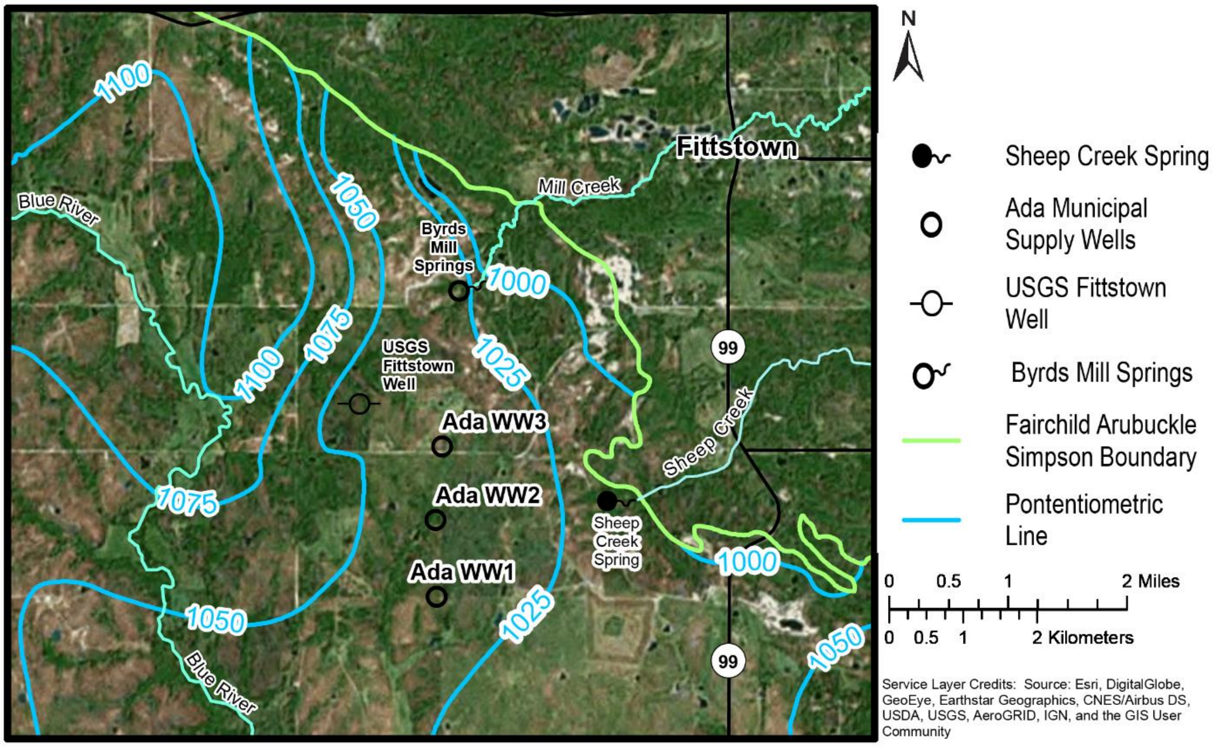


Figure 4: Potentiometric surface developed from existing monitoring well water levels that shows hydrologic gradient from approximately northwest down to southeast.

Two nearby springs are available for monitoring as well. Byrds Mill Spring is located a mile to the northeast of the sinkhole along the Ham Fault. Sheep Creek Spring is located to the southeast of the site (Figure 1). Monitoring stations also exist on the Blue River to the west of the site at bridge crossings. The research site is north of the City of Ada wellfield which consists of five deep production wells (Ada1 – Ada5) (Figure 1). These wells are plumbed to Byrds Mill Spring and are only pumped when the flow at Byrds Mill Spring is low.

Under most conditions groundwater flows in the southerly direction towards the USGS Fittstown Well or Ada Well 3. During storm events, geophysical data suggest when the water table rises, the flow direction potentially changes and groundwater flows to the northeast towards Byrds Mill Spring along the Ham Fault in a conduit that exists largely above the base water table elevation. A regional potentiometric surface is shown in Figure *5*, and a local potentiometric surface measured in the vicinity of the MAR sinkhole is shown in Figure 4. Water chemistry displays calcium-magnesium bicarbonate type water (Christenson, Hunt, & Parkhurst, 2009).



Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 5: Potentiometric map of the Arbuckle-Simpson aquifer. Flow is toward the east-southeast direction (Pickens, 2018).

Table 1: List of monitoring well locations at the City of Ada MAR Research Site.

Aquifer Monitoring Location Name	Northing (Y) UTM meters	Easting (X) UTM meters	Elevation (Z) TOC meters
EAR 1	3829587.58	712796.21	346.15
EAR 2	3829644.34	712845.16	342.87
EAR 3	3829712.30	712784.14	343.04
EAR 4	3829695.10	712866.28	342.53
EAR 5	3829821.83	713241.71	348.67
USGS	3829235.11	712837.11	351.31

Details on the construction of monitoring wells with no suffix and suffix “S” are available in Section B.1.1 of Appendix C-1, a Quality Assurance Project Plan for an EPA study at this site (Beak & Ross, 2020). Another document is presented as Appendix C-9 that details the well completion information for wells with suffix “I” and “D” in Table 2. Table 2 details their total depth and screened/open depth interval.

Table 2: Total depth and screened/open interval of existing and proposed wells at research site. Rows highlighted in gray are not yet constructed. Adapted from (Beak & Ross, 2020).

Well Name	**Top of Open Interval m (ft) below land surface**	**Total Well Depth m (ft) below land surface**
EAR-1	9 (30)	46 (150)
EAR-2	9 (30)	46 (150)
EAR-3	9 (30)	46 (150)
EAR-4	9 (30)	46 (150)
EAR-1S	24 (80)	30 (100)
EAR-2S	24 (80)	30 (100)
EAR-3S	24 (80)	30 (100)
EAR-4S	24 (80)	30 (100)
EAR-1I	61 (200)	76 (250)
EAR-5I	61 (200)	76 (250)
EAR-1D	76 (250)	305 (1000)
EAR-5D	76 (250)	230 (750)
USGS 343457096404501	-	121 (396)

III. Purpose and Scope

The City of Ada, the Chickasaw Nation, East Central University and the USEPA Kerr Lab are currently implementing an Managed Aquifer Recharge (MAR) research project with three phases, detailed below:

- **Phase 1:** Seeking permitting through this LSASR application. Tracer tests using native recharge features to characterize the aquifer and gather data for Phase 2 and a full-scale ASR permit application submission to ODEQ.
- **Phase 2:** Will seek permitting through a full-scale ASR permit application submission to ODEQ. Construction of multiple proposed retention structures on ephemeral drainages in a single watershed and monitoring to determine success of system in recharging aquifer.
- **Phase 3:** Construction of retention structures on ephemeral drainage throughout the watershed to provide recharge to the ASA.

The City of Ada's MAR approach involves overland flow from significant rainfall events being captured by small, serial retention structures on ephemeral drainages and allowed to infiltrate rather than runoff. The net effect, within a delineated ground water/surface water basin, is the conversion of stormflow to baseflow. The long-term impacts are more persistent ground water and surface water resources and enhanced springflow and baseflow during dry periods.

By the ODEQ definition of Aquifer Storage and Recovery (ASR), the MAR activities proposed in this project are considered to be a form of ASR, and fall under the scope of ASR permitting protocols. They are referred to as ASR activities in the remainder of this report, accordingly. Phase 1 of this project is currently underway, and includes four injection tests, three of which are seeking permitting through this LSASR Pilot Project application. Results from Phase 1 are expected to supply local and regional scale aquifer process characterization to the final system design for Phase 2 and 3 implementations, and provide critical information needed for eventual full-scale ASR applications that will be submitted to ODEQ to permit later phases. Key research objectives that will benefit proposed full-scale system design and the full-scale ASR application include determinations of attenuation rates for chemical and biological stressors and evaluation of particulate transport in fractured rock aquifers. Additionally, current and future management of ASA ground water resources would benefit from an improved understanding of (1) local hydrogeologic gradients and groundwater velocities/fluxes within the Byrds Mill Spring capture zone; (2) lateral and potentially vertical solute and particulate travel times and associated hydrologic parameters within the representative formations that comprise the ASA; and (3) effective solute/particulate travel times between recharge features and Byrds Mill Spring. All these characterization needs will be improved significantly through the planned multi-phase and multiple-constituent tracer test to be implemented as part of Phase 1.

In Phase 1, a native recharge structure (sinkhole) located at the City of Ada's MAR facility is being studied to evaluate the quality and quantity impacts of storm driven recharge to the Arbuckle-Simpson Aquifer (ASA) on hydraulically connected springflow. The project team proposes to evaluate and compare traditional chemical tracer methods and fluorescent magnetic particulate (250 nm) tracer methods, in the context of ongoing bacteriological and physical/chemical characterizations. The tests are designed so that particle tracer tests will be tied to results from chemical tracer tests, yielding a more complete understanding of the karst pathway sizes and the possibility for colloidal transport. Defined concentrations and volumes of chemical and chemical/particle tracer mixtures (see Section "Raw Water Characterization") will be introduced through the sinkhole at the MAR facility. The project team will utilize magnetic and visual filter collection approaches to address the tracer sample collection challenges associated with diffuse spring discharge and monitoring wells. The project team will compare the arrival time and concentration profile of fluorescent magnetic particles and some conservative chemical tracers (NaCl) to seasonal variations in aquifer recharge and bacterial assessment of water quality at monitored locations. An on-site weather station will record precipitation during the duration of the tests. Nearby Oklahoma Mesonet meteorology stations provide additional atmospheric and groundwater information. A nearby USGS groundwater monitoring point provides long term data for the chemical analysis (nonreactive tracer concentration and nano-particle detection) and reactive transport modeling.

The hypothetical full-scale ASR activities that this small-scale study will support will benefit baseflow and springflow in the region and represent an innovative water management adaptation strategy. Tracer tests executed as part of this phase are vital due diligence to ensure, prior to site-scale or full-aquifer-scale ASR implementation, that aquifer processes are fully understood and that activities associated with future project phases will be successful: specifically that future phase activities will increase baseflow and springflow magnitudes and that they will not negatively impact groundwater quality. If successful, tracer tests will offer evidence that ASR-supplied water will not have the capability to introduce pathogens to groundwater via fracture flow. Additional results from these tracer tests have a separate benefit of providing hydrogeologic parameters that will be used to inform parts of the planned USGS Phase II model in this region. Finally, the project also achieves the science goal of testing a nano-particle tracer as a biological particulate surrogate that has the potential to become a standard tool for water system managers and water resource professionals to evaluate risks associated with surface activities in spring capture zones in other systems, though this is lower priority and not necessary for the eventual submission of a full-scale ASR permit application to ODEQ.

IV. Tracer Test Workplan

Sub-test 1 of Phase 1 has already been permitted by submission of a letter to ODEQ requesting permission to perform the test, and has been completed. This test was designed to optimize logistics of subsequent tracer tests by injecting a slug of potable water with no additional tracer material. The slug of groundwater was thermally distinct from (at a higher temperature than) ASA groundwater at the time of injection in order to identify optimal well locations for monitoring. Sub-test 1 is summarized below:

1. Operation test of tracer slug delivery utilizing test-site infrastructure. Potable water (18.9 m^3 /5,000 gallons, Arbuckle-Simpson Aquifer-sourced, unprocessed and acquired from natural flow at Byrds Mill Spring) stored in two 9.5 m^3 (2,500 gallon) tanks was delivered using a pump and discharge hose to the major sinkhole at the MAR facility. The objective was to test delivery components and determine sustainable discharge rates that the sinkhole is capable of conveying. Data logging pressure transducers in monitoring wells were used to record pressure head, temperature and conductivity data to determine local scale impacts from the slug release as described in the section Post-deployment Monitoring Activities. The correspondence requesting permission for the test that was submitted by City of Ada to ODEQ and the permission letter received from ODEQ by City of Ada are included in this document as Appendix D. Results from sub-test 1 are included in Appendix A. Sub-test 1 showed that operational components are functional, and allowed for the determination that the conveyance rate of the slug delivery system, 16 l/s (250 gpm), could be accommodated by the natural recharge feature for the length of the tracer release.

Sub-test 2 is a deployment of a tracer slug consisting of a nonreactive chemical tracer (NaCl) and thermally distinct water. Sub-test 3 is the deployment of a tracer slug consisting of Groundwater Tracing Particles (GTPs), a nonreactive chemical tracer and thermally distinct water. Details about the composition, toxicity characteristics and production of GTPs are provided in Appendix B. If the sampling frequency used for sub-test 3 does not adequately capture the breakthrough of the GTPs because of rapid travel times, team personnel will consult on performing sub-test 4. Activities associated with sub-tests 2-4 from the Phase 1 workplan that are seeking permitting through this application are outlined in more detail below. Science activities and data collection and analysis tasks detailed here will adhere to the QA/QC plan detailed in Appendix C.

Summary of Sub-tests Seeking Permitting

2. Slug deployment of nonreactive chemical tracer(s) and thermally distinct water into sinkhole. A proposed principal NaCl tracer (250 mg/l as Cl^- initial concentration solution) will be deployed in a 18.9 m^3 (5,000 gal) slug of potable water from on-site storage tanks. At this point, short-term monitoring following this subtest will proceed as identified below in the section Post-deployment Monitoring Activities. Collected groundwater samples will only be analyzed to determine Cl^- concentration. Details on the preparation of the NaCl tracer, including the approximate mass of NaCl added to raw water, are provided in the section Raw Water Characterization.

3. Slug deployment of Groundwater Tracing Particles (GTP), nonreactive chemical tracer(s) and thermally distinct water into sinkhole. Sub-test 3 will not begin until detectable parameter (pressure, temperature, conductivity) perturbation, in the monitoring wells nearest the natural

recharge feature, has ended or decreased to near background levels. The GTPs, the NaCl nonreactive chemical tracer(s) and thermally distinct water will be deployed in a 18.9 m^3 (5,000 gallon) slug of potable water from on-site storage tanks. At this point, short-term monitoring following this subtest will proceed as identified below in the section Post-deployment Monitoring Activities. Collected groundwater samples will be analyzed to determine Cl^- concentration, the amount of magnetic material present and the amount of fluorescent material present. Details on the preparation of the NaCl and GTP tracer are provided in the section Raw Water Characterization.

4. Second slug deployment of GTPs, nonreactive chemical tracer(s) and thermally distinct water into sinkhole. Sub-test 4 will not begin until detectable parameter (pressure, temperature, conductivity) perturbation, in the monitoring wells nearest the natural recharge feature, has ended or decreased to near background levels. A second release of the GTPs, the NaCl nonreactive chemical tracer(s) and thermally distinct water will be deployed in a 18.9 m^3 (5,000 gallon) slug of potable water from on-site storage tanks. At this point, short-term monitoring following this subtest will proceed as identified below in the section Post-deployment Monitoring Activities. Collected groundwater samples will be analyzed to determine Cl^- concentration, the amount of magnetic material present and the amount of fluorescent material present. Details on the preparation of the NaCl and GTP tracer are provided in the section Raw Water Characterization.

Post-deployment Monitoring Activities

Baseline monitoring was performed before Sub-test 1 occurred. Baseline monitoring involved sampling for specific ions used in tracer tests and water quality to provide a baseline dataset for comparison after sub-tests have been performed.

Short-term monitoring described below is expected to occur between sub-tests and for 6 months following the final sub-test. Short-term monitoring will provide all the data that is needed for the aquifer characterization that is expected to inform the full-scale ASR application submitted at the onset of Phase 2. Long-term monitoring, including occasional groundwater sampling, will occur at the site for 2 years following the completion of the final sub-test as part of further science activities for aquifer characterization – these results are not anticipated to be necessary for submission of the full-scale ASR application.

Short-term (6 month) monitoring activities will occur during and after slug release for each of the above sub-tests. These activities consist of data collection and data analysis that will constrain flow paths and identify any particulate preferential flow in the aquifer, determine local hydrogeologic gradients and groundwater velocities/fluxes in the aquifer as well as hydrologic parameters of representative ASA formations, and identify solute/particulate travel times from recharge areas in the Byrds Mill Spring capture zone to the spring itself. Overall, these tests are intended to confirm that aquifer characteristics are well understood and that ASR activities in this area will not impair groundwater resources. Protocols for all science activities described in this section are detailed in Appendix C.

After each sub-test, the project team plans to perform short-term monitoring and sampling for tracers in monitoring wells and at Byrds Mill Spring. Based on estimated hydrologic properties of the ASA, initial breakthroughs in on-site monitoring well locations 1-4 near the natural recharge feature are anticipated within hours to days. Particulate travel times to proposed mid-path monitoring well 5 and to Byrds Mill Spring are anticipated to be in the range of 4-8 days. Monitoring in all subtests is based (primarily) on continuous monitoring data from in-situ pressure, temperature, and conductivity loggers. Data from loggers will be collected weekly to monthly depending on location and subtest activity. In addition, Electrical Resistivity Imaging (ERI) will be used in Subtests 2 and 3. ERI data collection (in locations associated with EAR 1-4) is real time and will occur for short durations up to days immediately after the release of the tracer material in Subtests 2 and 3.

Monitoring wells will be sampled for chemical tracers (Sub-tests 2 and 3) and for fluorescent/magnetic particles (Sub-tests 3). The frequency and duration of sampling for sub-test 2 will vary based on location. The frequency of groundwater sampling for chemical and fluorescence monitoring is predicted to range from daily for 2 weeks following subtests in near wells, to monthly during short- and long-term monitoring at BMS. As tracer breakthrough is observed in any of the monitoring well screens, tracer monitoring will be extended to additional down-gradient locations as available. The sampling frequency will be increased in the locations where breakthrough was observed until tracer breakthrough can be defined adequately to support hydrogeologic analysis. Following observation of breakthrough in any location, hydrogeologic analyses will be completed to determine the optimum sampling frequency to define the tracer breakthrough profile. The necessity for continued sampling will be evaluated periodically. Sampling practices will be the same for sub-test 3 as for sub-test 2, unless the project team identifies that there is a need to modify sampling plans based on the outcome of sub-test 2.

Sub-test 4, as identified above, would consist of a subsidiary tracer deployment with modified protocols to better capture breakthrough based upon findings. Aspects of the deployment and subsequent monitoring that may be modified in this case include the sampling frequency, sampling locations, and the proportions of tracer slug components.

The schedule detailed here is also provided in Table 1 of Appendix A.

Proposed Source of Water

The water delivered to the aquifer via the on-site sinkhole will be unprocessed Arbuckle-Simpson aquifer water, acquired from natural flow at Byrds Mill Spring and transported to the MAR facility. Water will be delivered as a 18.9 m^3 (5,000 gallon) slug for each of Sub-tests 2-4. This water originates in the aquifer and should be chemically similar to that in the aquifer. Byrds Mill Spring water quality and more details about water used for injection are provided in the section Raw Water Characterization.

Use of Recovered Water

Instead of storing treated water via injection and then recovering it at the same location later for human use, water introduced into the aquifer at the sinkhole (in Phase 1) and, in proposed future phases, via infiltration behind small impoundment structures on surface drainage pathways (planned Phases 2 and 3) will recharge the Arbuckle Simpson Aquifer for the purpose of increasing local springflow and baseflow in rivers. None of the water released in this pilot project will be recovered for use from the recharge locations. Some of the water may be recovered at City of Ada municipal water wells or at the Byrds Mill Spring intake for City of Ada municipal water supply after it migrates through the aquifer.

Proposed Method of Recharge

In this phase, 18.9 m^3 (5,000 gallon) slugs of water will be delivered from two on-site 9.5 m^3 (2,500 gallon) tanks directly into an aquifer-connected sinkhole using a pump and discharge hose. The aquifer-connected sinkhole is a natural recharge feature for the aquifer. The location of on-site storage tanks that will be used to hold the water before delivery is approximately at the sinkhole location identified in Figure 1. Figure 6 and Figure 7 depict the storage tanks and hoses used for storage of water and conveyance of that water to the natural recharge feature. These images were taken during the completion of sub-test 1.

In sub-tests 2-4, water will be conveyed from the storage tanks through the same hoses to the natural recharge feature. Water will be conveyed simultaneously from both tanks, and the approximate discharge into the natural recharge feature will be 16 l/s (250 gpm). During sub-test 1, it was confirmed that this discharge could be delivered with the existing conveyance infrastructure and that the natural recharge feature is capable of conveying this discharge for the duration of a single test. For more details on the results of sub-test 1, see Appendix A.

Area of Hydrologic Effect

The recharge structure is known to be in the capture zone of Byrds Mill Spring. Regional groundwater flow in this region is generally to the south towards the USGS Fittstown well (Fairchild et al., 1990). Local site conditions indicate the flow direction may head towards the north and east towards Byrds Mill Spring when it encounters a conduit along the Ham Fault that appears to be most weathered above the base elevation of the groundwater table. Accordingly, the area of hydrologic effect may vary and will be better defined from these tracer tests, but it approximately consists of an arc from the northeast to the south of the test facility. The introduction of a large volume of water as part of a tracer test may shift the groundwater flow direction more towards the northeast and Byrds Mill Spring. Monitoring to other potential orientations during storm and base flow conditions will be utilized to evaluate the system response. For more information on the hydrogeology of this area, see the Section “Hydrogeology”.

Existing Wells, Springs, Seeps and Wetlands

The two major springs in the vicinity of the MAR facility are Byrds Mill Spring and Sheep Creek Spring, as shown in Figure 1. Other than the MAR and USGS monitoring wells at the research site (shown in Figure 2), nearby City of Ada municipal supply wells located in the vicinity of the MAR facility are shown in Figure 1.

Notice of Filing Plan

City of Ada and the rest of the project team will publish notice of the filing of this LSASR application in local newspaper *The Ada Evening News* concurrently with their submission to ODEQ, giving any parties ample time to provide comment on the application.

Tracer Tests

This LSASR application is seeking permitting of three tracer tests. For all tracer tests, water will be thermally distinct from (e.g. hotter than) ASA groundwater. Additionally, in each of these tracer tests, tracer materials will be added to and mixed (via electric paint mixers) with raw water in the storage tanks before conveyance begins, altering the composition of the raw water. The slug water will be contained in two 2500-gallon storage tanks, which deliver water in parallel. The material that will be added for each sub-test is detailed below:

- Sub-test 2 – **Chemical Tracer**: Enough NaCl will be added to raw water to create a chemical tracer solution with a concentration of ~250 mg/L. According to Table 3, the Dissolved Na^+ concentration in Byrds Mill Spring is about 3.7 mg/L and the Cl^- concentration in Byrds Mill Spring is about 3.3 mg/L. Based on these concentrations, about 7.8 kg of NaCl (3.9 Kg to each 2500-gal tank) will be added to the raw water. With the addition of this NaCl to create the chemical tracer, the Dissolved Na^+ Concentration will likely be about 160 mg/L and the Cl^- concentration will be just less than 250 mg/L.
- Sub-test 3 – **Chemical Tracer + GTP**: Enough NaCl will be added to raw water to create a chemical tracer solution with a concentration of 250 mg/L. According to Table 3, the Dissolved Na^+ concentration in Byrds Mill Spring is about 3.7 mg/L and the Cl^- concentration in Byrds Mill Spring is about 3.3 mg/L. Based on these concentrations, about 7.8 kg of NaCl (3.9 Kg to each 2500-gal tank) will be added to the raw water. With the addition of this NaCl to create the chemical tracer, the Dissolved Na^+ Concentration will likely be about 160 mg/L and the Cl^- concentration will be just less than 250 mg/L. Additionally, a to-be-decided mass of Groundwater Tracing Particle (GTP) not to exceed 10 kg (5 Kg to each 2500-gal tank) will be added to raw water. Details about the composition, toxicity characteristics and production of GTPs are provided in Appendix B. The amount of GTP that the project team uses will ultimately be based on an analysis of results from sub-test 2. The concentration of chemical tracer detected in monitoring wells in sub-test 2 will help the project team identify what mass of GTP needs to be added to the tracer slug in sub-test 3 to reach detection limit concentrations for GTP in monitoring well samples.
- Sub-test 4 – **Chemical Tracer + GTP:** Enough NaCl will be added to raw water to create a chemical tracer solution with a concentration of 250 mg/L. According to Table 3, the Dissolved Na^+ concentration in Byrds Mill Spring is about 3.7 mg/L and the Cl^- concentration in Byrds Mill Spring is about 3.3 mg/L. Based on these concentrations, about 7.8 kg (3.9 Kg to each 2500-gal tank) of NaCl will be added to the raw water. With the addition of this NaCl to create the chemical tracer, the Dissolved Na^+ Concentration will likely be about 160 mg/L and the Cl^- concentration will be just less than 250 mg/L. Additionally, a to-be-decided mass of Groundwater Tracing Particle (GTP) not to exceed 10 kg (5 Kg to each 2500-gal tank) will be added to raw water. Details about the composition, toxicity characteristics and production of GTPs are provided in Appendix B. In the event that GTP is not detected in monitoring wells in sub-test 3, the project team may opt to increase the mass of GTP deployed in the tracer slug in sub-test 4.

Water will be discharged into the aquifer through a natural recharge feature at a rate of approximately 16 l/s (250 gpm). It will be pumped from the two on-site storage tanks to the natural recharge feature through two hoses, which will be situated so that they discharge directly into the natural recharge feature. Each subtest will involve the delivery of 18.9 m^3 (5,000 total gallons) of raw water from two 9.5 m^3 (2,500 gallon) storage tanks. After the completion of sub-tests 2-4, a total volume of water of 57 m^3 (15,000 gallons) will have been discharged into the aquifer. The composition of this water will not vary based on discharge rate and discharge rate will be held constant across tests as long as the conveyance equipment continues to function as expected.

Figure 6: Image of two black, 9.5 m^3 (2,500-gallon) storage tanks located at site taken during Subtest 1. Blue hoses used to convey water to natural recharge feature are shown in foreground.

Figure 7: Image of two blue hoses used to convey water from storage tanks to natural recharge feature taken during Subtest 1.

V. Raw Water Characterization

Raw water being used in this LSASR project will be natural discharge from Byrds Mill Spring. Spring discharge comes directly from the aquifer, so the raw water that will be injected into the aquifer during LSASR activities will have the same composition as water in the aquifer. The composition of this water is detailed based on results from four recent water samples in Table 3. This water will not be sampled specifically for this project, but sampling of this water is performed regularly by City of Ada to ensure that it can be used for public supply. BMS water is representative of water quality parameters for ground water sampled from shallow and intermediate well in the LSASR test area.

Table 3: Results from four recent water samples taken at Byrds Mill Spring.

Parameter	Units	Quantitation Limit	MDL	Sample ID			
				Byrds Mill Spring	**Byrds Mill Spring**	**Byrds Mill Spring**	**Byrds Mill Spring DUP**
Date	-	-	-	2/3/2021	4/30/2021	6/16/2021	6/16/2021
Temp	ºC	-	-	17.2	17.4	17.6	17.6
SPC	mS/cm	-	-	0.624	0.628	0.616	0.616
SPC	µS/cm	-	-	624	628	616	616
TDS	mg/L	-	-	403	410	403	403
DO	mg/L	-	-	6.77	6.31	5.90	5.90
pH	-	-	-	7.08	7.04	7.16	7.16
ORP	mV	-	-	258.4	64.2	127.3	127.3
Eh	mV	-	-	458.4	264.2	327.3	327.3
pE	-	-	-	7.74	4.46	5.53	5.53
Turbidity	NTU	-	-	0.84	1.33	2.41	2.41
Alkalinity	mg $CaCO_3$/L	-	-	288	290	260	260
Total Hardness	mg $CaCO_3$/L	-	-	548	330	270	270
Fe^{2+}	mg Fe^{2+}/L	0.10		0.18	-----	<0.10	<0.10
H_2S	mg S/L	0.10		<0.10	-----	<0.10	<0.10
Water Type	-	-	-	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3
Anion-Cation Balance	%	-	-	5.3	7.1	6.1	4.9
Dissolved Hardness (Calc)	mg CaCO3/L	-	-	337.526	139.017	401.016	399.842
Br	mg/L	0.03	0.20	0.03	<0.20	0.03	0.02
Cl	mg/L	0.02	1.00	3.33	3.39	3.32	3.36
SO_4	mg/L	0.15	1.00	9.06	8.56	8.81	8.44
F	mg/L	0.01	0.20	0.07	0.08	0.08	0.08
I	µg/L	0.83	10.0	2.8	2.13	4.31	2.51
DOC	mg/L	0.13	0.50	0.22	0.40	0.23	0.18
DIC	mg/L	0.05	1.00	84.7	82.9	80.8	83.0
TOC	mg/L	0.13	0.50	0.16	0.25	0.22	0.17

Parameter	Units	Quantitation Limit	MDL	**Sample ID**			
				Byrds Mill Spring	**Byrds Mill Spring**	**Byrds Mill Spring**	**Byrds Mill Spring DUP**
TIC	mg/L	0.05	1.00	84.8	83.2	81.5	83.5
H2CO3	mg H_2CO_3/L	-	-	62	66	51	52
CO2 aq	mg CO_2/L	-	-	44	47	36	37
HCO3	mg HCO_3^-/L	-	-	369	356	360	370
CO3	mg CO_3^{2-}/L	-	-	0.22	0.19	0.26	0.26
$NO_3 + NO_2$	mg N/L	0.01	0.10	0.89	0.93	0.89	0.92
NH_3	mg N/L	0.03	0.10	<0.02	<0.10	<0.05	<0.05
TKN	mg N/L	0.07	0.10	0.09	0.83	0.93	0.96
TON	mg N/L	-	-	0.09	0.83	0.93	0.96
TN	mg N/L	-	-	0.97	1.76	1.82	1.88
PO_4	mg P/L	0.002	0.050	<0.050	0.025	0.025	0.021
Total P	mg P/L	0.002	0.100	<0.100	0.020	0.016	0.018
Dissolved Ag	µg/L	0.5	1	<1	-----	-----	-----
Dissolved Al	µg/L	1	5	<5	-----	-----	-----
Dissolved As	µg/L	0.5	1	1.0	-----	-----	-----
Dissolved B	µg/L	160	500	<500	<500	<500	<500
Dissolved Ba	µg/L	0.5	1	51	51	49	49
Dissolved Be	µg/L	0.5	1	<1	-----	-----	-----
Dissolved Ca	mg/L	0.05	0.50	75.4	76.9	73.8	73.6
Dissolved Cd	µg/L	0.5	1	<1	-----	-----	-----
Dissolved Co	µg/L	0.5	1	<1	-----	-----	-----
Dissolved Cr	µg/L	0.5	1	<1	-----	-----	-----
Dissolved Cu	µg/L	0.5	1	<1	-----	-----	-----
Dissolved Fe	µg/L	50	100	<100	<100	<100	<100
Dissolved K	mg/L	1.00	1.00	1.50	1.37	1.29	1.33
Dissolved Li	µg/L	10	50	<50	<50	<50	<50
Dissolved Mg	mg/L	0.05	0.50	36.4	35.7	37.3	37.4
Dissolved Mn	µg/L	0.5	1	<1	-----	-----	-----

Parameter	Units	Quantitation Limit	MDL	Sample ID			
				Byrds Mill Spring	Byrds Mill Spring	Byrds Mill Spring	Byrds Mill Spring DUP
Dissolved Mo	µg/L	0.8	1	1.6	-----	-----	-----
Dissolved Na	mg/L	0.18	2.00	3.91	3.74	3.54	3.63
Dissolved Ni	µg/L	0.5	1	0.5	-----	-----	-----
Dissolved Pb	µg/L	0.5	1	<1	-----	-----	-----
Dissolved Sb	µg/L	0.5	1	<1	-----	-----	-----
Dissolved Se	µg/L	1	5	1	-----	-----	-----
Dissolved Si	mg/L	0.10	1.00	5.02	5.39	5.45	5.46
Dissolved Sr	µg/L	1	10	154	154	145	146
Dissolved Th	µg/L	0.5	1	0.6	-----	-----	-----
Dissolved Ti	µg/L	5	10	<10	<10	<10	<10
Dissolved Tl	µg/L	0.5	1	<1	-----	-----	-----
Dissolved U	µg/L	0.5	1	1.3	-----	-----	-----
Dissolved V	µg/L	0.5	1	0.9	-----	-----	-----
Dissolved Zn	µg/L	50	100	<100	<100	<100	<100
Total Ag	µg/L	40	100	<120	-----	-----	-----
Total Al	µg/L	40	500	<580	-----	-----	-----
Total As	µg/L	200	200	<230	-----	-----	-----
Total B	µg/L	160	500	<580	<580	-----	-----
Total Ba	µg/L	0.5	1	53	53	-----	-----
Total Be	µg/L	50	100	<120	-----	-----	-----
Total Ca	mg/L	0.05	0.50	76.9	77.3	-----	-----
Total Cd	µg/L	50.0	10	<60	-----	-----	-----
Total Co	µg/L	50.0	10	<60	-----	-----	-----
Total Cr	µg/L	5.0	10	<10	-----	-----	-----
Total Cu	µg/L	10.0	100	<120	-----	-----	-----
Total Fe	µg/L	50	100	<120	<120	-----	-----
Total K	mg/L	1.00	1.00	1.33	1.84	-----	-----
Total Li	µg/L	10	50	<60	<60	-----	-----
Total Mg	mg/L	0.05	0.50	33.8	36.6	-----	-----
Total Mn	µg/L	50.0	100	<120	-----	-----	-----
Total Mo	µg/L	10.0	50	<60	-----	-----	-----
Total Na	mg/L	0.18	2.00	3.82	3.77	-----	-----
Total Ni	µg/L	10.0	50	<60	-----	-----	-----

Parameter	Units	Quantitation Limit	MDL	**Sample ID**			
				Byrds Mill Spring	**Byrds Mill Spring**	**Byrds Mill Spring**	**Byrds Mill Spring DUP**
Total Pb	µg/L	100.0	100	<120	-----	-----	-----
Total Sb	µg/L	50.0	50	<60	-----	-----	-----
Total Se	µg/L	100	100	<120	-----	-----	-----
Total Si	mg/L	0.10	1.00	4.89	5.57	-----	-----
Total Sr	µg/L	1	10	16	160	-----	-----
Total Th	µg/L	0.5	1		-----	-----	-----
Total Ti	µg/L	5	10	<10	<10	-----	-----
Total Tl	µg/L	100.0	100	<120	-----	-----	-----
Total U	µg/L	20.0	50	<60	-----	-----	-----
Total V	µg/L	10.0	20	<20	-----	-----	-----
Total Zn	µg/L	50	100	<120	<120	-----	-----
La	ug/L	0.001	0.020	0.002	-----	-----	-----
Ce	ug/L	0.002	0.020	0.002	-----	-----	-----
Pr	ug/L	0.003	0.020	<0.020	-----	-----	-----
Nd	ug/L	0.003	0.020	<0.020	-----	-----	-----
Sm	ug/L	0.002	0.020	<0.020	-----	-----	-----
Eu	ug/L	0.002	0.020	<0.020	-----	-----	-----
Gd	ug/L	0.003	0.020	<0.020	-----	-----	-----
Tb	ug/L	0.002	0.020	<0.020	-----	-----	-----
Dy	ug/L	0.003	0.020	<0.020	-----	-----	-----
Ho	ug/L	0.002	0.020	<0.020	-----	-----	-----
Er	ug/L	0.002	0.020	<0.020	-----	-----	-----
Tm	ug/L	0.003	0.020	<0.020	-----	-----	-----
Yb	ug/L	0.001	0.020	0.001	-----	-----	-----
Lu	ug/L	0.001	0.020	<0.020	-----	-----	-----
Hg	µg/L	0.2	0.2	<0.25	<0.25	<0.25	<0.25
$\delta^{18}O$	‰	-	-	-5.24	-5.31	-----	-----
$\delta^{2}H$	‰	-	-	-29.33	-29.14	-----	-----

VI. References

Beak, D., & Ross, R. (2020). *Quality Assurance Project Plan for Evaluation of Enhanced Aquifer Recharge Using Hydrogeologic, Geophysical (Surface and Borehole) and Geochemical Mehtods in the Arbuckle-Simpson Aquifer* . US EPA.

Christenson, S., Hunt, A. G., & Parkhurst, D. L. (2009). *Geochemical investigation of the Arbuckle-Simpson aquifer, South-central Oklahoma, 2004–06: U.S. Geological Survey Scientific Investigations Report 2009–5036.*

Christenson, S., Osborn, N. I., Neel, C. R., Faith, J. R., Blome, C. D., Puckette, J., & Pantea, M. P. (2011). *Hydrogeology and simulation of groundwater flow in the Arbuckle-Simpson aquifer, south-central Oklahoma.* U. S. Geological Survey.

Fairchild, R. W., Hanson, R. L., & Davis, R. E. (1990). *Hydrology of the Arbuckle Mountains area, south-central Oklahoma.* Oklahoma Geological Survey.

Faith, J. R., Blome, C. D., Pantea, M. P., Puckette, J. O., Halihan, T., Osborn, N., . . . Pack, S. (2010). *Three-Dimensional Geological Model of the Arbuckle-Simpson Aquifer, South-Central Oklahoma: Open-File Report 2010-1123.* U. S. Geological Survey.

Hamm, W. E., & McKinley, M. E. (1954). *Geologic Map and sections of the Arbuckle Mountains, Oklahoma: Oklahoma Geological Survey Map A-2, scale 1:72000.* Oklahoma Geological Survey.

Johnson, P., Stanley, C. C., Kemblowski, M. W., Byers, D. L., & Colthart, J. D. (1990). A practical approach to the design, operation, and monitoring of in situ soil-venting systems. *Groundwater Monitoring and Remediation, 10*(2), 159-178.

Keller, A. A., Garner, K., Miller, R. J., & Lenihan, H. S. (2012). Toxicity of Nano-Zero Valent Iron to Freshwater and Marine Organisms. *PLOS ONE*.

Lidke, D. J., & Blome, C. D. (2017). *Geologic map of the Fittstown 7.5′ quadrangle, Pontotoc and Johnston Counties, Oklahoma: U.S. Geological Survey Scientific Investigations Map 3371.*

Oklahoma Climatological Society. (2017). *The Climate of Pontotoc County*. Retrieved October 18, 2021, from https://climate.ok.gov/county_climate/Products/County_Climatologies/county_climate_pontotoc

Pickens, C. M. (2018). *A Comparison Between Model and Field Diesel Mass Recovery in Dolomite Karst .* MSc Thesis, Oklahoma State University.

Rahi, K. Y., & Halihan, T. (2013). Identifying Aquifer Type in Fractured Rock Aquifers using Harmonic Analysis. *Groundwater, 51*(1).

Swinea, T. (2011). *Thermal controls on springs in the eastern Arbuckle-Simpson aquifer system.* MSc Thesis, Oklahoma State University.

Zhang, M., Yi, K., Zhang, X., Han, P., Liu, W., & Tong, M. (2020). Modification of zero valent iron nanoparticles by sodium alginate and bentonite: Enhanced transport, effective hexavalent chromium removal and reduced bacterial toxicity. *Journal of Hazardous Materials*.

Appendix A: Results from Sub-test 1 – Conveyance System Test

Tracer Study Systems Test 1 (ST-1) Report

This report outlines the objectives and results of ST-1 of the Joint BIA/CN/ECU/OSU/City of Ada advanced tracer study which was conducted in support of the ongoing Limited Scale Aquifer Storage and Recovery (LS-ASR) project, and the City of Ada and US-EPA's Enhanced Aquifer Recharge (EAR) research project.

Tracer Study Overall Scope of Work: Chemical tracers are often used to evaluate subsurface fluid flow and transport. However, fractured rock systems pose a challenge to the appropriate use of traditional chemical tracers for the evaluation of biological contaminant risk. Particulate preferential flow may occur through fractures and exceed the rates predicted by chemical tracers. Particulate tracers could be more effective predictors of transport rates from larger, connected fractures, thus being more representative of the risks associated with particulate contaminants, such as bacteria and viruses. Groundwater Tracing Particles (GTPs) address the challenges associated with collecting samples in diffuse discharge spring systems and the limits of detection for chemical tracers. Recent experiments with thermal water slugs and resistivity-based geophysical techniques suggest that the introduction of GTPs with a thermal slug could allow for additional characterization of subsurface transport.

Project Timeline and SubTests:
Table 1

Sub-Test	Time Period	Description	Monitoring	Performed By
Baseline Monitoring	Preceding ST 1	WQ monitoring	SIA, WQ	Oka Institute/USEPA
ST 1	July & August 2021	System Test*/Thermal*	P,T,C*	Oka Institute/USEPA/City of Ada/OSU
ST 2 and Short-Term Monitoring	First Quarter after permit award	Tracer*/Thermal	P,T,C SIA	Oka Institute/USEPA/City of Ada/OSU
ST 3 and Short-Term Monitoring	Second Quarter after permit award	GTP*/Tracer/Thermal	P,T,C SIA, MF	Oka Institute/USEPA/City of Ada/OSU
ST 4 (optional) and Short-Term Monitoring	Third Quarter (if needed) after permit award, monitoring until up to Fifth Quarter	GTP/Tracer/Thermal	P,T,C SIA*, MF*	Oka Institute/USEPA/City of Ada/OSU
Long-Term Monitoring	Up to 2 full years after completion of ST 3/4	Periodic sample/data collection	P,T,C SIA, MF	Oka Institute/USEPA

**Supporting ERI (electrical resistivity imaging) site characterization activities will be conducted throughout the project period.*

System Test (ST): Qualitative and Quantitative testing of slug delivery system and flow rate.
Tracer: NaCL non-reactive tracer addition.
Thermal: Storage tank supplied potable water at above or below formation water temperature.
GTP: groundwater tracing particles.
P,T,C: Data logger based pressure, temperature and conductivity monitoring.
SIA: Chemical analysis of ground water samples for specific ions (Cl^-, Br^-).
MF: Fluorescence detection of magnetically treated/collected ground water samples.
WQ: nitrate/nitrite, ammonia, total phosphorus, BacT (ODEQ approved methods)

Work Plan: System Test 1

I. **Objectives**:
   1. **Test water delivery system components** (e.g., tanks, pumps, valves, suction hose, discharge hose). Field personnel will monitor to ensure that system integrity is maintained and evaluate both the set-up time and break-down time needed for the test.
   2. **Determine discharge rate** (gal/min). Time will be recorded from start of discharge pumps to the point where flow is interrupted due to low tank levels (functionally empty). Average flow rate = 2500 gal/pump time.
   3. **Determine temperature differential**. A handheld infrared thermometer will be used to continuously monitor and record discharge water temperature.
   4. **Evaluate potential temperature and water table elevation changes in the monitoring well network**. Currently deployed HOBO data logger will be recovered and downloaded, after the system test, to evaluate recorded temperature and pressure data.

II. **Narrative**:

The duplicate (2x) 2500 gallon storage tanks will be filled with freshly collected (native) Arbuckle-Simpson Aquifer ground water, discharging from Byrds Mill Spring, utilizing a City of Ada (potable) water truck. Each filled storage tanks will be connected to a new, dedicated, general purpose 2-Inch centrifugal water pump with a maximum rate capacity of 164 GPM. The pumps will be linked to the storage tanks through 20’ quick-connect 2” vacuum hoses. The discharge side of the pump will be connected to 300’ of 2” quick-connect discharge hose, which will deliver water to the EAR site sinkhole (Lat. 34.586397°, Long. -96.679695°, 1131’ MSL). Data loggers (HOBO: temperature, pressure) will be deployed in nearby monitoring wells and will be utilized to detect any potential changes in aquifer conditions resulting from the introduction of 5000 gallons of Byrds Mill Spring water.

III. **Site and Test Conditions**:

a. **Discharge Water**. The discharge water will be essentially native ground water, reintroduced through the test site sink hole. No amendments are planned for the Stage 1 System Test. We expect a ~30°F temperature differential between the reintroduced water (expected discharge temperature ~90°F) and the *in-situ* conditions found in the Arbuckle

Simpson Aquifer (approximately 60°F year-round). We expect to see, at most, transient temperature impacts of a few degrees in the nearby monitoring wells, as *in situ* mixing equilibrates the reintroduced and native aquifer water. A transient 30°F or less degree temperature differential will have little impact on native microorganisms.

b. **Aquifer Water**. The ground water at the EAR test site (and Byrds Mill Spring) is consistent with the calcium magnesium bicarbonate waters found in the eastern part of the Arbuckle-Simpson Aquifer (1).

Results

ST1-a: Test date 7/12/21. We decided to test the system components while we wait for ODEQ approval. Focus of the test was to ensure physical components of system were functioning. Tanks were drained sequentially starting with Tank 1(eastern tank). Pumps were run at full speed, 200' of discharge hose was used to deliver flow to land surface south of EAR pond. ***No discharge was allowed to reach the sinkhole.***

Tank 1 emptied in 22 min, 38 seconds. Tank 2 emptied in 21 min, 21 seconds. All connections, vacuum hose and discharge hose worked as expected. Surface layer in tanks before test registered in 105 to 118 °F range. Water at the discharge point ranged from 81- 87 °F.

ST1-b: Test date 8/17/21. We received ODEQ approval for Subtest 1 (ST1b). Focus of the test was to ensure physical components of system were functioning when discharging to the sinkhole. Pressure/temperature data logger were recovered next week and any detectable change in water table elevation or temperature will be reported when analysis of these data is completed. However, we feel it is unlikely to indicate clear impacts. We will be incorporating new pressure/temperature/conductivity logger into the monitoring well network prior to sub-test 2. These sensors will be set at a much faster sampling rate to hopefully catch short-term transient impacts to pressure/temperature/conductivity. In addition, the EPAs ERI system should also be available.

Tanks were drained concurrently. Pumps were run at full speed, and 300' of discharge hose (each) was used to deliver flow to the EAR sinkhole. Discharge from the tanks did not accumulate in the sinkhole indicating the recharge capacity was not exceeded. Pumps were started at 2:40 pm local time. Tank 1 was emptied by 2:57 pm and Tank 2 by 3:02 pm. Discharge temperature (at the end of the delivery hose) from Tank 1 averaged 89.9 °F and from Tank 2 averaged 87.5 °F. Average delivery rate for the system was calculated to be 227 gallons per minute.

References

1. Christenson, S., A.G. Hunt, and D.L. Parkhurst. 2009. Geochemical Investigation of the Arbuckle-Simpson Aquifer, South-Central Oklahoma, 2004–06. Scientific Investigations Report2009–5036. U.S. Department of the Interior U.S. Geological Survey.

Appendix B: Groundwater Tracing Particles

1. Groundwater Tracing Particles Introduction

This study will attempt a groundwater tracer experiment using groundwater tracing particles (GTP) to gain an understanding of karst groundwater connections at the managed aquifer recharge (MAR) site near Byrds Mill Spring (Holmbeck Pelham et al., 2000; Laskoskie, 2013). The GTP that are to be deployed in this study are intended to provide a degradable particle that has low toxicological risk for use in groundwater tracing. The planned particles are composed of:

1) sodium alginate (food grade gel carrier for the particles),
2) calcium chloride dihydrate (reacts with sodium alginate to form gel),
3) uranine dye (common fluorescent groundwater tracer),
4) borosilicate glass bubbles (to provide neutral buoyancy),
5) and powdered magnetite (to allow magnetic capture of particles).

These GTP are to be released in a sink hole that is located approximately 1 mile southwest of Byrds Mill Spring that is of interest due to its potential to facilitate MAR. The GTP will allow for investigation into any larger groundwater connections that may be present between the MAR sink hole and Byrds Mill Spring that can cause sediment and colloidal particles to migrate from the sinkhole through the aquifer. Hydrogel tracer beads made of sodium alginate, similar to those being utilized in this study, have been used previously for the purpose of surface water tracing (Laskoskie, 2013). The present study will deploy nontoxic GTP into the groundwater system to characterize fate and transport of recharge to the sinkhole and aquifer. Unlike previously used hydrogel tracer beads, the GTP in this study will include magnetite. The magnetite will allow for the capture of the GTP via magnets deployed in wells and at the spring. The GTP include a fluorescent ingredient, uranine, for identification purposes in wells or at springs which can be carried out via blacklight. The GTP used in this study, in conjunction with the salt tracer tests, will allow a well calibrated fate and transport model to be developed for the spring system.

2. GTP Ingredient Toxicity

As previously stated, the GTP to be deployed in this present study are composed of 1) sodium alginate, 2) calcium chloride dihydrate, 3) borosilicate glass bubbles, 4) uranine dye, and 5) powdered magnetite. The toxicity of each ingredient will be discussed based on literature for the ingredients as the researchers involved in the tracing tests are not toxicologists. The Material Safety Data Sheet (MSDS) and a representative paper from the literature is included at the end of this appendix as a zip file named “Appendix B_MSDS Sheets and Papers.zip”.

2.1 Sodium Alginate

Sodium alginate is a non-toxic substance that is derived from the cell walls of brown algae (Laskoskie, 2013). Sodium alginate is a widely used material in a number of industries including food, pharmaceuticals, cosmetic, dentistry, and more. It is used to create food products and is thus available for human consumption from ordinary stores. Sodium alginate is also utilized for drug delivery (Sachan et al., 2009). It is classified as Generally Recognized as Safe (GRAS) by the U.S. Food and Drug Administration (https://www.fda.gov/food/food-additives-petitions/food-additive-status-list#ftnC).

> From US FDA:
> Sodium alginate - STAB, GRAS/FS, Cheeses and Rel Prods - Part 133; Froz Desserts - Part 135; Art Sw Fruit Jelly - 150.141; Art Sw Fruit Pres and Jams - 150.161; GRAS - 184.1724; BC, REG, Comp of boiler water additive -173.310

2.2 Calcium Chloride Dihydrate

Calcium chloride dihydrate ($CaCl_2(H_2O)_x$) is what acts as a curing solution for the sodium alginate to make the GTP. Calcium chloride dihydrate is the hydrated form of calcium chloride. Calcium chloride is a highly soluble salt used for dust control, calcifying aquarium water, increasing hardness in swimming pools, and as a food additive. The use in food production indicates the suitability for use in GTP production (Dean et al., 2020). It is classified as Generally Recognized as Safe (GRAS) by the U.S. Food and Drug Administration (https://www.fda.gov/food/food-additives-petitions/food-additive-status-list#ftnC).

> From US FDA:
> Calcium chloride - MISC, GRAS/FS, 184.1193, Parts 131, 133, 150, 155 & 156 in Evaporated Milk; Cheese & Cheese Products; Part 133; VET, REG, For use in mastitis formulations for treating dairy animals - 526.820

2.3 Borosilicate Glass

Borosilicate glass bubbles are included in the GTP in order to make them buoyant. To traverse the groundwater system, the particles will be formed as neutrally buoyant particles. Borosilicate glass is commonly used in glassware for cooking and food storage as it is lead and BPA-free. It is also used in reagent bottles and flasks and is sold under various tradenames. The material is also used to decrease the weight of material by adding small glass bubbles filled with air. The product used for this experiment is a 3M™ glass bubble that allows the borosilicate glass to float. When included in the GTP, the particles will maintain neutral buoyancy. If consumed, it would be like passing a well-rounded grain of sand (El-Kady et al., 2020).

2.4 Uranine Dye

Uranine ($C_{20}H_{10}O_5Na_2$) will also be included in the GTP to impart fluorescent properties to the particles. Uranine is the water soluble form of fluorescein and has a bright green color in concentrated form. The GTP need to be fluorescent so they can be more easily identified upon their arrival at a well or at Byrds Mill Spring using fluorescent light detection. This dye is commonly used as a tracer in surface and groundwater systems. It has previously undergone intensive evaluation for toxicological and ecotoxicological effects (Behrens et al., 2001; Gombert et al., 2017).

2.5 Magnetite

The GTP in this study are unique because they will include a magnetic material, powdered magnetite (Fe_3O_4). The magnetite, like the uranine, is being added for ease of collection. If the particles are magnetic, magnets can be used in observation wells and springs to facilitate collection. The powdered magnetite that will be used to make the GTP is also used in children's toys and administered for biomedical applications (Ruiz et al., 2016).

3. GTP Production

Hydrogel beads made of sodium alginate have been utilized in previous studies in surface water settings. The procedure for the formation of the GTP used in this study is taken from Laskoskie, 2013. The powdered magnetite is a new addition that is unique to the present study.

The procedure for GTP production is expected to be (taken from Laskoskie, 2013 for a 3% alginate solution):

Step 1: Make 3% sodium alginate solution

The 3% alginate solution must be prepared at least 24 hours prior to particle production. For a 3% sodium alginate solution, dissolve 3.0 grams sodium alginate into 100 grams of deionized (DI) water.

1. Begin with a clean 400 mL beaker. Place the beaker on the scale and tare the scale. Once the scale is tared, weigh 100 grams of DI water. Remove from scale and set aside.
2. Place a plastic petri dish and weighing paper on the scale and tare the scale. Once the scale is tared, weigh 3.0 grams of sodium alginate.
3. Add the sodium alginate to the DI water in the 400 mL beaker.
4. Place a large stir bar into the sodium alginate and DI water mixture, and cover the beaker with parafilm.
5. Place the covered beaker on a stir plate. Set stir plate to 200-400 rpm. Leave to stir until the solution is homogeneous.
6. Once the solution is homogeneous, store in refrigerator. Mold will begin to grown in solution after mixing if left at room temperature for extended periods.

When homogeneous, the 3% sodium alginate solution will form a highly viscous gel. (We are experimenting with 1.5-3.0% solutions to reduce the GTP size from the current 2 mm sand size.)

Step 2: Add uranine dye, 3M glass bubbles, and powdered magnetite

1. Place an empty 50 mL centrifuge tube into a Styrofoam holder and place it on the scale. Tare the scale.
2. Add an arbitrary amount of 3% sodium alginate solution to the centrifuge tube. Record the mass.
3. From the recorded mass of 3% sodium alginate solution, determine amounts needed to add 1% uranine dye, 3M glass bubbles, and powdered magnetite.
    a. For example, if the 3% sodium alginate solution is 20 grams, add 0.2 grams of all three additives.
4. Using the plastic petri dish and weighing paper, weigh out the needed amounts of uranine dye, 3M glass bubbles, and powdered magnetite.
5. Cap the centrifuge tube and mix using Vortex mixer until homogeneous.

The GTP may be split 50/50 between powdered magnetite and uranine dye. Further testing is needed to know how these two additives interact. 3M glass bubbles will be included in all particles to provide buoyancy. (We anticipate utilizing half particles without magnetite and half with magnetite to evaluate transport and detection properties.)

Step 3: GTP production

1. Prepare the calcium chloride dihydrate curing solution. The curing solution can range from 0.1 to 1 M depending on the batch size that is desired.
    a. Large batch: dissolve 14.78 grams calcium chloride dihydrate in 1 L DI water
    b. Small batch: dissolve 1.48 grams calcium chloride dihydrate in 100 mL DI water
2. Place prepared amount of during solution on stir plate. Set stir plate to 100 rpm. Do not allow a tornado to form.
3. Fill a 30 mL plastic syringe with the 3% sodium alginate and additives mixture. Place a needle on the syringe.
    a. The gauge of the needle determines the overall particle size. The larger the gauge the larger the particle and vice versa.
    b. 30, 25, and 18 gauge needles are being tested to determine which needle size forms the ideal GTP.
4. Add the sodium alginate mixture to the curing solution dropwise.
    a. This can be done manually or with a syringe pump. We will be using a syringe pump.
    b. Syringe pump is set to 1 mL per hour rate.
5. Let GTP cure for a least 1 minute.
6. Store produced GTP in curing solution in refrigerator.

The 3% sodium alginate solution is a highly viscous gel that when placed in the curing solution forms a spherical particle that has a consistency similar to that of a gummy bear. Once cured, the GTP will not be flowing gel, but a solid particle.

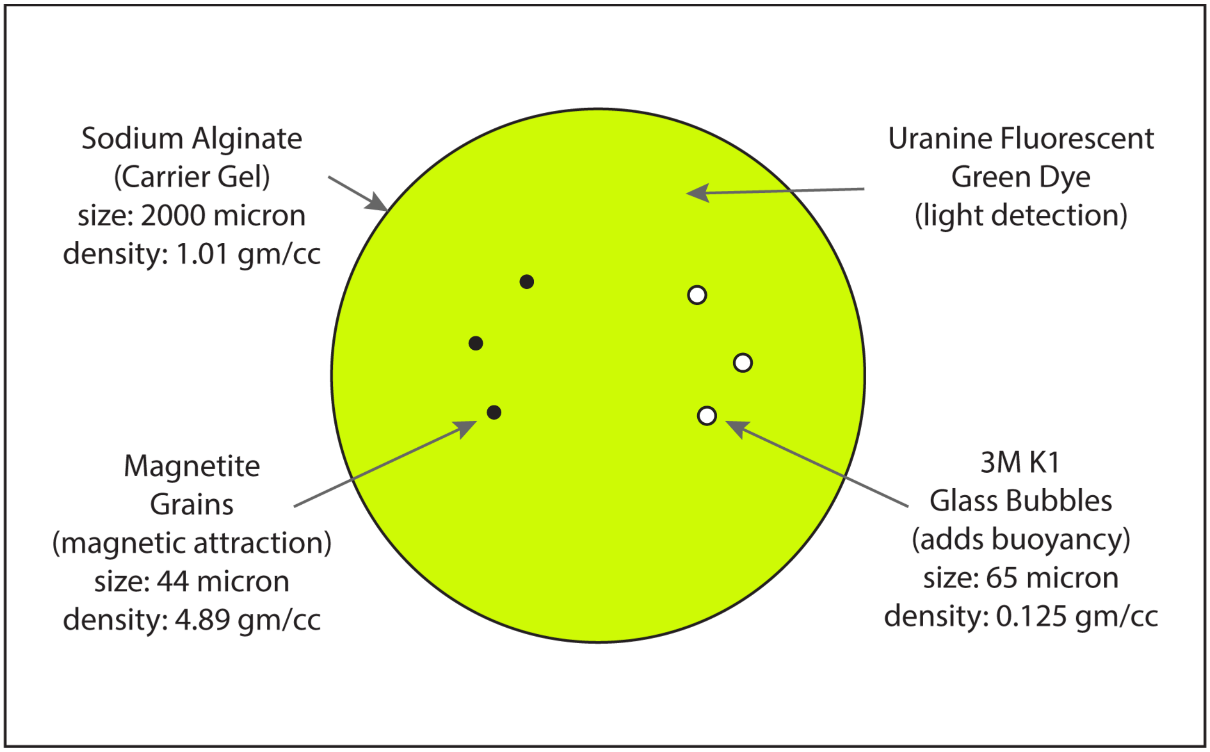


Figure B.1. GTP schematic illustrating the primary components of the tracer particle. Further development will aim at reducing the size of the particle by altering the production of the sodium alginate carrier gel as it is converted to a particle from sand size to silt size if possible.

A finished GTP will be composed of a composite of the smaller magnetite and borosilicate glass particles and the sodium alginate carrier dyed with uranine (Figure B.1). The particles will be manufactured at Oklahoma State University in the School of Geology laboratories. If the addition of magnetite makes the particle not fluoresce detectably, then two types of particles will be generated, fluorescing green dye particles and black magnetic particles. The shelf-life of the particles is over a year if they are refrigerated in the calcium chloride, and approximately 6 months in room temperature solution (Laskoskie, 2013). When injected into the aquifer, the particles should be detected in a period of days to weeks and be dissolved or consumed by microbial activity within a year. The remaining material will be borosilicate glass particles and magnetite particles.

4. GTP References

Behrens, H. et al., 2001, Toxicological and ecotoxicological assessment of water tracers, *Hydrogeology Journal 9*, p. 321-325, doi 10.1007/s100400100126.

Dean, Gillian H. et al., 2019, A simple, non-toxic method for separating seeds based on density, and its application in isolating *Arabidopsis thaliana* seed oil mutants, *Applications in Plant Sciences,* vo. 8, n. 4, p. 1-8, doi 10.1002/aps3.11332.

El-Kady, A. M. et al., 2020, Controlled delivery of therapeutic ions and antibiotic drug of novel alginate-agarose matrix incorporating selenium-modified borosilicate glass designed for chronic wound healing, *Journal of Non-Crystalline Solids,* p. 1-21.

Gombert, P. et al., 2017, Toxicity of fluorescent tracers and their degradation byproducts, *International Journal of Speleology,* vol. 46, no. 1, p. 23-32.

Holmbeck-Pelham, S. et al., 2000, Regulation of Injected Ground Water Tracers, *Ground Water*, v. 38, no. 4, p. 541-549.

Laskoskie, A., 2013, Development of hydrogel tracer beads and comparative tracer tests to better understand contaminant fate and transport in karst systems, Master's thesis, West Virginia University, Morgantown, West Virginia, 108 p.

Ruiz, A. et al., 2016, Dose-Response Bioconversion and Toxicity Analysis of Magnetite Nanoparticles, *IEEE Magnetics Letters,* v. 7.

Sachan, Nikhil K. et al., 2009, Sodium alginate: the wonder of polymer for controlled drug delivery, *Journal of Pharmacy Research,* v. 2, no. 7, p. 1191-1199.

End of Appendix B

Appendix C: Project QA/QC Plan

Appendix C: Quality Assurance/Quality Control (QAQC) Plan

QAQC protocols will be in place during this test to ensure that tests conform to established best practices and, separately, that they are suitable for incorporation into the USGS Phase II groundwater model update for the Arbuckle-Simpson Aquifer. The QA/QC plan involves adhering to several prepared or published protocols for data collection and analysis, and performing quality control activities detailed in Section B.4.1 Quality Control Samples of the attached document C-1 (Beak & Ross, 2020). Protocols and associated data collection/analysis tasks are detailed in the following sections.

Groundwater/Byrds Mill Spring Sampling Standard Operating Procedure

Groundwater sampling from monitoring wells will follow USEPA protocols, as detailed in Section B.2.2 Groundwater Sampling of the attached document C-1 (Beak & Ross, 2020). Sampling of Byrds Mill Spring will follow USEPA protocols for runoff sampling, as detailed in Section B.2.1 Runoff Sample Collection of the attached document C-1 (Beak & Ross, 2020). Quality control samples will be collected for groundwater samples and spring samples, as detailed in Section B.4.1 Quality Control Samples of the attached document C-1 (Beak & Ross, 2020).

Sampling of wells and springs for groundwater tracing particles (GTPs) will follow protocols detailed in document C-7 “Groundwater Tracing Particle Sampling Protocol”.

Electrical Resistivity Imaging Standard Operating Procedure

Electrical Resistivity Imaging will be performed in tandem with each subtest as part of short-term monitoring activities. Any Electrical Resistivity Imaging data collection will follow USEPA protocols as detailed in the attached document C-2 “K-GCRD-SOP-3756-1: SOP for Electrical Resistivity Field Data Acquisition for Subsurface Investigations” (Ross & Fields, 2021). Retention of data files from ERI activities will follow the protocol laid out in Section A.6.5 Electrical Resistivity Image Surveys Files of the attached document C-1 (Beak & Ross, 2020).

Temperature, Pressure and Conductivity Monitoring Standard Operating Procedure

Monitoring of temperature, pressure and conductivity will be performed with automatic data loggers as described in Section A.4 Project Description and Section B.1.1 Subsurface Monitoring of the attached document C-1 (Beak & Ross, 2020). Temperature data will be collected as part of ongoing monitoring activities in accordance with USEPA protocols, as detailed in the attached document C-3. Document C-3 details EPA Method 170.1 from “EPA 600/4-79-020 Methods for Chemical Analysis of Water and Wastes” (United States Environmental Protection Agency, 1983). Conductivity data will be collected as part of ongoing monitoring activities in accordance with USEPA protocols, as detailed in the attached document C-4. Document C-4 details EPA Method 120.1 from “EPA 600/4-79-020 Methods for Chemical Analysis of Water and Wastes” (United States Environmental Protection Agency, 1983). Pressure data will be used to determine water level, and will be collected as part of ongoing monitoring activities in accordance with USEPA protocols, as detailed in the attached document C-5 “K-GCRD-SOP-1134-0: SOP for Water Level Monitoring Using Automated Pressure Transducer/Data Loggers” (Acree, 2010).

Chemical, Fluorescence and Magnetic Analysis of Samples Standard Operating Procedure

Chemical analysis of groundwater and spring samples to detect the presence of chloride or bromide will follow USEPA protocols, as detailed in Section B.1.2 Specific Target Analytes of the attached document C-1 (Beak & Ross, 2020). The SOP identified for chloride and bromide analysis is EPA Method 9056A from “EPA SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods”, which is provided in document C-6 (United States Environmental Protection Agency, 2015).

Sampling and analytical methods used to detect the presence of GTPs in wells and springs will follow the protocols identified in Document C-7 “Groundwater Tracing Particle Sampling Protocol”.

Tracer Test Documentation Standard Operating Procedure

Tracer Test Documentation will adhere to USGS Tracer Test Documentation requirements, detailed in the attached document C-8 “USGS Tracer Test Documentation Memo” (Mashburn & Lockmiller, 2021). This document also details how analyses to quantify hydrogeologic characteristics will be performed using results from tracer tests.

References

Acree, S. D. (2010). *K-GCRD-SOP-1134-0: Standard Operating Procedure for Water Level Monitoring Using Automated Pressure Transducer/Data Loggers.* US EPA.

Beak, D., & Ross, R. (2020). *Quality Assurance Project Plan for Evaluation of Enhanced Aquifer Recharge Using Hydrogeologic, Geophysical (Surface and Borehole) and Geochemical Mehtods in the Arbuckle-Simpson Aquifer .* US EPA.

Mashburn, S., & Lockmiller, K. (2021). *USGS Tracer Test Documentation and Methods Memo for the EARs Site.* USGS.

Ross, R., & Fields, J. (2021). *K-GCRD-SOP-3576-1: Standard Operating Procedures for Electrical Resistivity Field Data Acquisition for Subsurface Investigations.* US EPA.

United States Environmental Protection Agency. (1983). *Methods for Chemical Analysis of Water and Wastes.* Washington, DC: USEPA.

United States Environmental Protection Agency. (2015). Method 9056A: Determination of Inorganic Anions by Ion Chromatography. In *EPA Publication SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd Edition.*

Document C-1: Quality Assurance Project Plan for Evaluation of Enhanced Aquifer Recharge Using Hydrogeologic, Geophysical (Surface and Borehole) and Geochemical Methods in the Arbuckle-Simpson Aquifer

QUALITY ASSURANCE PROJECT PLAN

Office of Research and Development
Center for Environmental Solutions & Emergency Response
Groundwater Characterization & Remediation Division

Evaluation of Enhanced Aquifer Recharge Using Hydrogeologic, Geophysical (Surface and Borehole) and Geochemical Methods in the

EPA Project Lead:

EPA Project Co-Lead: Doug Beak

EPA Project Co-Lead: Randall Ross
Environmental Measurements

QA Category B

Intramural

Revision Number: 0

Date: 08/03/2020

Prepared By:

Randall Ross & Doug Beak

ORD Research Program

SSWR

QA Track ID:

K-GCRD-0032739-QP-1-1

Approval Page

QA Project Plan Title:	Evaluation of Enhanced Aquifer Recharge Using Hydrogeologic, Geophysical (Surface and Borehole) and
QA Activity Number:	K-GCRD-0032739-QP-1-1
If Intramural or Extramural, EPA Project Approvals	
Name: EPA Project Co-Lead: Doug Beak	Signature/ Date: DOUGLAS BEAK Digitally signed by DOUGLAS BEAK Date: 2020.08.04 08:38:50 -05'00'
Name: Co-Lead's Supervisor: Rick Wilkin	Signature/ Date: RICHARD WILKIN Digitally signed by RICHARD WILKIN Date: 2020.08.04 07:54:24 -05'00'
Name: QA Manager: Mustafa Bob	Signature/ Date: MUSTAFA BOB Digitally signed by MUSTAFA BOB Date: 2020.08.04 12:12:29 -05'00'
Name: EPA Co-Lead: Randall Ross	Signature/ Date: RANDALL ROSS Digitally signed by RANDALL ROSS Date: 2020.08.03 15:48:41 -05'00'
Name: Co-Lead's Supervisor: Kelly Dipolt	Signature/ Date: KELLY DIPOLT Digitally signed by KELLY DIPOLT Date: 2020.08.04 07:57:49 -04'00'
Name:	Signature/ Date:
If Extramural, Contractor Approvals	
Name:	Signature/ Date:
Name:	Signature/ Date:
Name:	Signature/ Date:
Name:	Signature/ Date:

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Acronyms/Abbreviations

AESTUS – Subcontractor to ERG
amsl – above mean sea level
ASA – Arbuckle-Simpson aquifer
ASR – aquifer storage and recovery
ASRF – analytical service request form
bgs – below ground surface
bls – below land surface
CCB – continuing calibration blank
CCV – continuing calibration verification standard
CESER – Center for Environmental Services and Emergency Response
cm – centimeter
cm/s – centimeter per second
CN – Chickasaw Nation
COC – chain of custody
DIC – dissolved inorganic carbon
DO – dissolved oxygen
DOC – dissolved organic carbon
EAR – enhanced aquifer recharge
EC – electrical conductivity
ECU – East Central University
ERG – Technical Support Contractor for ORD
ERI – Electrical Resistivity Imaging
ft – feet
GCRD – Groundwater Characterization and Remediation Division
gpm – gallons per minute
HNO_3 – nitric acid
H_2SO_4 – sulfuric acid
HASP – Health and Safety Plan
ICB – initial calibration blank
ICP-OES – inductively coupled plasma-optical emission spectroscopy
ICP-MS – inductively coupled plasma-mass spectroscopy
ICS – interference check standard
ICV – initial calibration verification standard
L – liter
L/min – liters per minute
LCS – laboratory control standard
MB – method blank
MDL – method detection limit
mg/l – milligrams per liter
µm – micrometer
µS/cm – micro Siemens per centimeter

min – minute
mL – milliliter
mV – millivolt
MS – matrix spike
MSD – matrix spike duplicate
N – normal
NA – not applicable
NTU – Nephelometric Turbidity Units
ODEQ – Oklahoma Department of Environmental Quality
ORD – Office of Research and Development
ORP – oxidation reduction potential
OSU – Oklahoma State University
OWRB – Oklahoma Water Resources Board
PE – performance evaluation
‰ – per mille
PL – project lead
QA – quality assurance
QAPP – quality assurance project plan
QL – quantification limit
REE – rare earth elements
RL – reporting limit
RPD – relative percent difference
RSKERC – Robert S. Kerr Environmental Research Center
SOP – standard operating procedure
SPC – specific conductivity
SSWR – Safe and Sustainable Water Resources
TD – technical directive
TDS – total dissolved solids
TSA – technical system audit
TSCD – Technical Support Coordination Division
TOC – top of casing
TOS – top of screen
USEPA – U.S. Environmental Protection Agency
USGS – U.S. Geological Survey
VOC – volatile organic compound

SECTION A – PROJECT MANAGEMENT

A.1 Distribution List

Name	Organization	Work	E-mail
Doug Beak	CESER/GCRD	580-436-8813	beak.doug@epa.gov
Randall Ross	CESER/TSCD	580-436-8611	ross.randall@epa.gov
David Burden	CESER/GCRD	580 436-8606	burden.david@epa.gov
Steve Acree	CESER/GCRD	580-436-8609	acree.steve@epa.gov
Cherri Adair	CESER/GCRD	580-436-8969	adair.cherri@epa.gov
Mustafa Bob	CESER/GCRD	580 436-8565	bob.mustafa@epa.gov
Cody Holcomb	City of Ada	580-559-9471	cody.holcomb@adaok.com
Guy Sewell	City of Ada/ECU	580-421-3440	gsewell@ecok.edu
Wayne Kellogg	Chickasaw Nation	580-272-5076	wayne.kellogg@chickasaw.net
Shana Mashburn	USGS/OKWRD	405-664-6557	shanam@usgs.gov
Rick Wilkin	CESER/GCRD	580-436-8874	wilkin.rick@epa.gov
Todd Halihan	AESTUS/ERG	405-744-9248	todd.halihan@okstate.edu
Jon Fields	CESER/GCRD	580-436-xxxx	fields.jon@epa.gov

Quality Assurance (QA) Project Plans and Standard Operating Procedures (SOPs) shall be controlled (through documented approvals) as required by Section 5.3 of the Office of Research and Development (ORD) Quality Management Plan. The project lead will be responsible for distribution of the current signed approved version of the QA Project Plan to project participants shown in Section A.1. Signed approved versions of SOPs will be available to project staff through the ORD@Work SOP intranet site. Signature approved electronic copies of this QA Project Plan, SOPs, and any associated QA assessment reports, will also be maintained in ORD QA Track.

The project lead (PL) will also be responsible for timely communications with all involved participants and will retain copies of all management reports, memoranda, and correspondence between research task personnel.

A.2 Project/Task Organization

Table 1 lists the project participants and a generalized organizational chart is given in Figure 1. The PLs will serve as the organizational primary point of contact. Other project participants will keep the PLs informed whenever significant developments or changes occur.

Communication among project participants may be in person conversations, electronic mail, phone conversations, conference calls, and periodic face-to-face meetings as appropriate. All written communication between U.S. Geological Survey (USGS) and U.S. Environmental Protection Agency (USEPA) must copy the IAs USEPA Project Officer, David Burden. Verbal communications and other meetings between USGS and USEPA should also include the Project Officer but can occur without the Project Officer at the Project Officers discretion. The PLs are responsible for tracking laboratory and field activities, ensuring that monitoring data and samples are received, working with the laboratories to address issues with sample analysis and QA, and ensuring that data reports and raw data are received. The USEPA QA Manager, reviews and approves the Quality Assurance Project Plan (QAPP) and may independently undertake Technical System Audits (TSA) of the field and laboratory activities.

Table 1. Project participants, organizations, contact info, title and responsibility in project.

Name	Organization	Phone	Role	Responsibility	Distribution List
R. Ross	EPA ORD	580-436-8611	Project Lead	Project management, hydrology, borehole geophysical logging, ERI surveys, QAPP development and management, hydrologic testing	Yes
D. Beak	EPA ORD	580-436-8813	Project Co-Lead	Geochemistry, sampling, analysis, QAPP development and management	Yes
M. Bob	EPA ORD	580-436-8565	QA Manager	Oversight of QA program implementation	Yes
S. Acree	EPA ORD	580-436-8609	Hydrologist	Hydrogeology, hydrologic testing	Yes
D. Burden	EPA ORD	580 436-8606	Project Officer	Coordinate contracts/IAG	Yes
M. White	EPA ORD	580 436-8709	Chemist	Chemical Analysis coordination	Yes
R. Wilkin	EPA ORD	580-436-8874	Geochemist	Chemical analysis, participant	Yes
S. Mashburn	USGS	405-664-6557	Hydrologist	Surface water monitoring	Yes
C. Holcomb	City of Ada	580-436-8001	City Engineer	Property Access	Yes
G. Sewell	City of Ada / ECU	580-559-5547	Microbiologist	Coordination of activities with ECU and City of Ada	Yes
W. Kellogg	Chickasaw Nation	580-272-5076	Geologist	Weir design	Yes
C. Adair	EPA ORD	580-436-8969	SHEM	Health and safety	Yes
J. Fields	EPA ORD	580-436-xxxx	Hydrologist	Hydrogeology, hydrologic testing, ERI surveying	Yes
T. Halihan	AESTUS (ERG Subcontractor)	405-744-9248	Geophysicist	Electrical Resistivity Imaging,	Yes

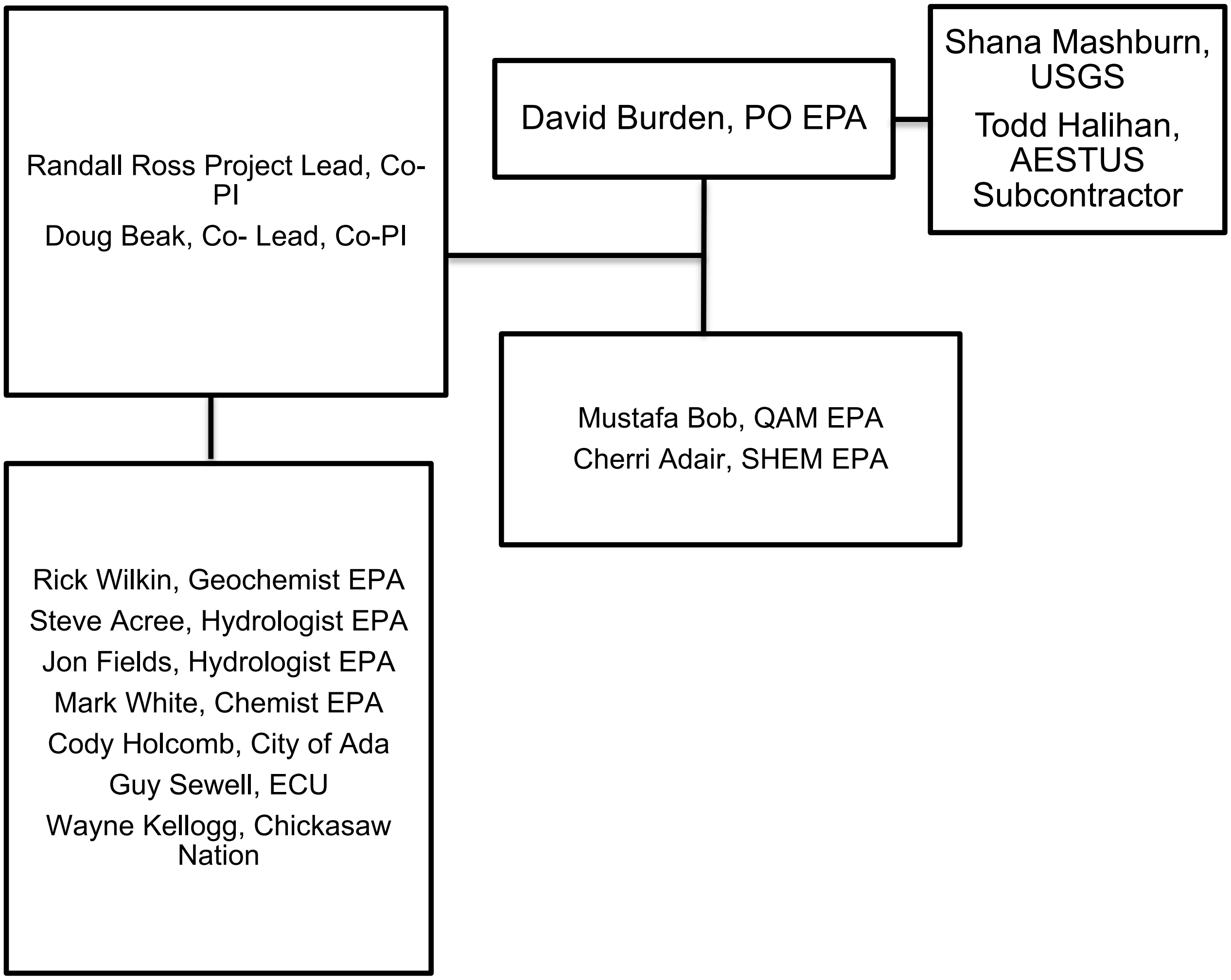


Figure 1. General organizational flowchart for project participants.

A.3 Problem Definition/Background

This project is part of the Enhanced Aquifer Recharge (EAR) research and development effort of the USEPA ORD's Safe and Sustainable Water Resources (SSWR) research program. The Arbuckle-Simpson aquifer (ASA) is the sole source of drinking water for many people in southcentral Oklahoma. The Robert S. Kerr Environmental Research Center (RSKERC) has been involved in projects related to the ASA for over five decades. RSKERC has worked with the city of Ada, Oklahoma, Chickasaw Nation (CN), Oklahoma Water Resources Board (OWRB), Oklahoma Department of Environmental Quality (ODEQ), USGS and other entities on issues related to ASA water quality and quantity. Over the last several years, the state of Oklahoma has implemented a permitting process for aquifer storage and recovery (ASR). The ASA has been identified as a candidate for ASR. Under the SSWR program RSKERC will evaluate the impact of EAR on groundwater quality and quantity in the ASA. This effort will build on current collaborations with the USGS, Chickasaw Nation, Oklahoma State University (OSU) and the city of Ada, Oklahoma.

EAR is a variant of ASR, where surface water runoff is temporarily stored as a surface water body (i.e., pond) and allowed to recharge via a large karst feature (i.e., sinkhole). Conceptually, the recharged water will cause a rise in groundwater levels, resulting in increase in spring flow and stream base flow.

The full project involves EAR implementation, monitoring and assessment. It will assess the impact of the recharge of rural surface water run-off on groundwater quality and quantity, assess subsurface water movement, assess the impact on spring water quality and quantity and support community education and outreach efforts regarding the benefits of sustainable water resource management.

The project will be conducted at a rural area in Pontotoc County, Oklahoma that has been delineated as part of the groundwater shed of Byrds Mill Spring. The primary study area is owned by the city of Ada, Oklahoma. This allows controlled access and security to the site and monitoring instrumentation. The city of Ada and the CN are interested in the use of EAR to enhance groundwater supplies but are also concerned about potential groundwater quality degradation.

A.4 Project Description and Objectives

The study will focus on an area in the eastern portion of the ASA, which consists primarily of Arbuckle group carbonates, approximately one mile southwest of Byrds Mill spring, the largest spring in Oklahoma and water source for most of Pontotoc county. Previous studies indicate the unsaturated epikarst zone may be capable of storing a significant volume of groundwater (Halihan, et al., 2009). The conceptual site model is that rainfall infiltrates through the vadose zone and is temporarily stored in the epikarst zone as it drains into the underlying aquifer. The EAR process may be able to take advantage of the storage capacity to increase recharge to groundwater. The nature of the connection between the shallow and deep groundwater will be investigated during the study.

The primary objectives of this proof-of-concept study are to determine the magnitude and impact of direct recharge of overland surface runoff on groundwater quality in a rural karst setting. Rural settings are inherently different from urban settings in terms of water quality and are not well represented in current literature. Groundwater quality will be examined before, during and after significant recharge events. The secondary objective is to evaluate the use of relatively simple and easily transferable hydrogeologic methods and geophysical techniques to estimate the overall contribution of the enhanced recharge to groundwater. Data logging pressure transducers will be used to monitor water level, temperature and electrical conductivity changes in surface water and groundwater resulting from overland flow events. A series of tracer tests will be conducted by the City of Ada, Chickasaw Nation and Oklahoma State University in an effort to better understand the contribution of recharge via the sink hole to groundwater discharge at Byrds Mill Spring. These tests will provide an opportunity to evaluate the movement of water through the unsaturated epikarst zone to groundwater using transient electrical resistivity imaging surveys. When coupled with measurements of inflow and outflow from the system, the study will provide a comparison of qualitative and quantitative estimates of recharge rates of surface runoff to groundwater.

Field research conducted by EPA/ORD is designed to assess 1) the water quality impacts of recharged surface runoff on groundwater by analyzing the spatial and temporal variability of groundwater and surface water parameters from monitoring wells in the ASA and selected springs before, during and after surface runoff recharge events, 2) the utility of hydrogeologic methods and geophysical techniques to estimate the contribution of enhanced aquifer recharge to groundwater.

Table 2. Proposed schedule for field activities.

	2020				2021				2022			
	1	2	3	4	1	2	3	4	1	2	3	4
Project Initiation	X											
Prepare HASP		X										
Prepare QAPP			X	X								
Install Shallow Wells				X	X	X						
Install Intermediate Wells					X	X						
Install Deep Wells					X	X						
Groundwater/Surface Water Sampling				X	X	X	X	X	X?	X?	X?	X?
Long Line (Deep) ERI Survey			X									
Purchase/Install Short ERI Lines			X	X								
Characterize Serial Dam Area							X					
Install Transient ERI Lines				X								
Sample/Survey Overland Flow Event				X	X	X	X	X	X?	X?	X?	X?
Initiate Thermal/EC Tracer Study				X								
Initiate Magnetic Fluorescent Nano Particle Tracer Study						X						
Data analysis and summary								X	X			
Report									X	X	X	

A.5 Special Training/Certification

N/A

A.6 Documents and Records

Research activities must be documented according to the requirements of ORD QA Policies titled *Scientific Recordkeeping: Paper*, *Scientific Recordkeeping: Electronic*, and *Quality Assurance/ Quality Control Practices for ORD Laboratory and Field-Based Research*, as well as requirements defined in this QA Project Plan. The ORD QA Policies require the use of research notebooks and the management of research records, both paper and electronic, such that project research data generation may continue even if a researcher or an analyst participating in the project leaves the project staff.

Electronic Records shall be maintained in a manner that maximizes the confidentiality, accessibility, and integrity of the data. ORD PPM Section 13.6 provides guidance on the maintenance of electronic records for ORD.

A.6.1 Data Storage

The Project Leads will maintain all original versions of field data sheets and entries into field notebooks. Scanned electronic copies of the paper documents will be generated and stored as PDF files in the project folder on the ORD/CESER intranet network drive (OneDrive – Environmental Protection Agency (EPA)\EAR Project), accessible by all project collaborators. Electronic file naming conventions that will be used are described below.

A.6.2 Field Notes

Hand-written notes and observations that are recorded in a field notebook will be digitally scanned to produce an electronic file in PDF. The digitized field notes file will be assigned a name that identifies the location, month-year, field note identifier (“FN”) and date (year-month-day) the PDF file was generated (e.g., EAR_Jun2020_FN_20200601).

A.6.3 Borehole Geophysical Log Files

Digital files generated with the Century Geophysical, Inc. logging rig and tools will use the Century format which included the well name, date the well was logged, logging tool used, data collection interval (e.g., 0.1 ft) depth of ending and beginning of log (e.g., EAR1_06-01-20_9510C_.10_7.00_92.20.ORIG.log).

A.6.4 Depth to Water Measurements

Depth to water measurements for monitoring wells will be recorded in field notebooks and transferred to a master spreadsheet that will calculate water level elevations by subtracting the depth to water measurements for specific dates from the top of casing elevations. The spreadsheet will be named EAR_water_level_and_survey_master.xlsx.

A.6.5 Electrical Resistivity Image Surveys Files

Digital ERI files generated with the Advanced Geosciences Inc. (AGI) SuperSting will be assigned a name that identifies the location, month-day-year, orientation, number of electrodes and electrode spacing (e.g., EAR_ERI1_July-04-2020_NS_56_4.stg). These files will be transferred from the SuperSting to a field computer and stored as indicated above.

A.6.6 Records retention

Records that are generated under this research effort will be retained in accordance with EPA Records Schedule 1035, and as required by Section 5.1 of the ORD Quality Management Plan for QA Category B Projects.

SECTION B – DATA GENERATION & AQCUISITION

B.1 EXPERIMENTAL DESIGN

This research effort will evaluate water movement and changes in water quality influenced by EAR. To achieve this, a series of wells will be installed by EPA, contractors and/or City of Ada. The study will also utilize traditional hydrogeologic techniques and surface and borehole geophysical methods to estimate the amount of recharge through known karst features and potential storage capacity of the unsaturated epikarst zone.

B.1.1 Subsurface monitoring

Figure 2 shows the location of existing wells and the proximity of the site to Byrds Mill spring and the Ada well field. Figure 3 illustrates locations of the proposed shallow, intermediate and deep monitoring wells. In addition, surface water samples, runoff samples, and discharge from springs will be sampled when possible to understand the natural inputs to the system and outputs from the system. Wells EAR-1, EAR-2, EAR-3 and EAR-4 have surface casing from land surface depths of approximately 30 ft and are open-hole construction to depths of approximately 150 ft below land surface. Three wells (EAR-1S, EAR-3S and EAR-4S) with screened intervals of approximately 80 to 100 ft bls will be constructed adjacent to EAR-1, EAR-3 and EAR-4. Additionally, three deep wells (EAR-1D, EAR-5D and EAR-6D) will be drilled to 1000 ft, 750 ft and 750 ft, respectively, and completed as open-hole wells from 250 ft bls to total depth. The deep and intermediate depth wells will be installed with tremie grouted surface casing from land surface to depths of 250 ft and 200 ft, respectively. These wells will have open boreholes from the bottom of surface casing to the total depth of the borehole. Construction details are included in Table 4. New shallow and intermediate well locations were selected to be complementary to existing wells and provide head data for determining vertical hydraulic gradients, as wells as horizontal hydraulic gradients. Horizontal hydraulic gradients will be determined from elevation corrected pressure transducer data incorporated into the spreadsheet tool 3PE (Beljin, et al, 2014).

This design will not only allow for the collection of data for chemistry but will also allow for continuous monitoring of water levels. This design will provide a means to understand the infiltration of water from the recharge point through the vadose zone into the saturated zone as well as groundwater movement in the aquifer. Finally, the data collected will be used to better understand the fate and transport of chemicals in the subsurface as well as provide an understanding of the biogeochemical processes that affect groundwater quality. The proposed list of analytes is presented in Table 3. The proposed schedule for field activities is provided in Table 2. Based on results and available funding, additional sampling may continue after 2022.

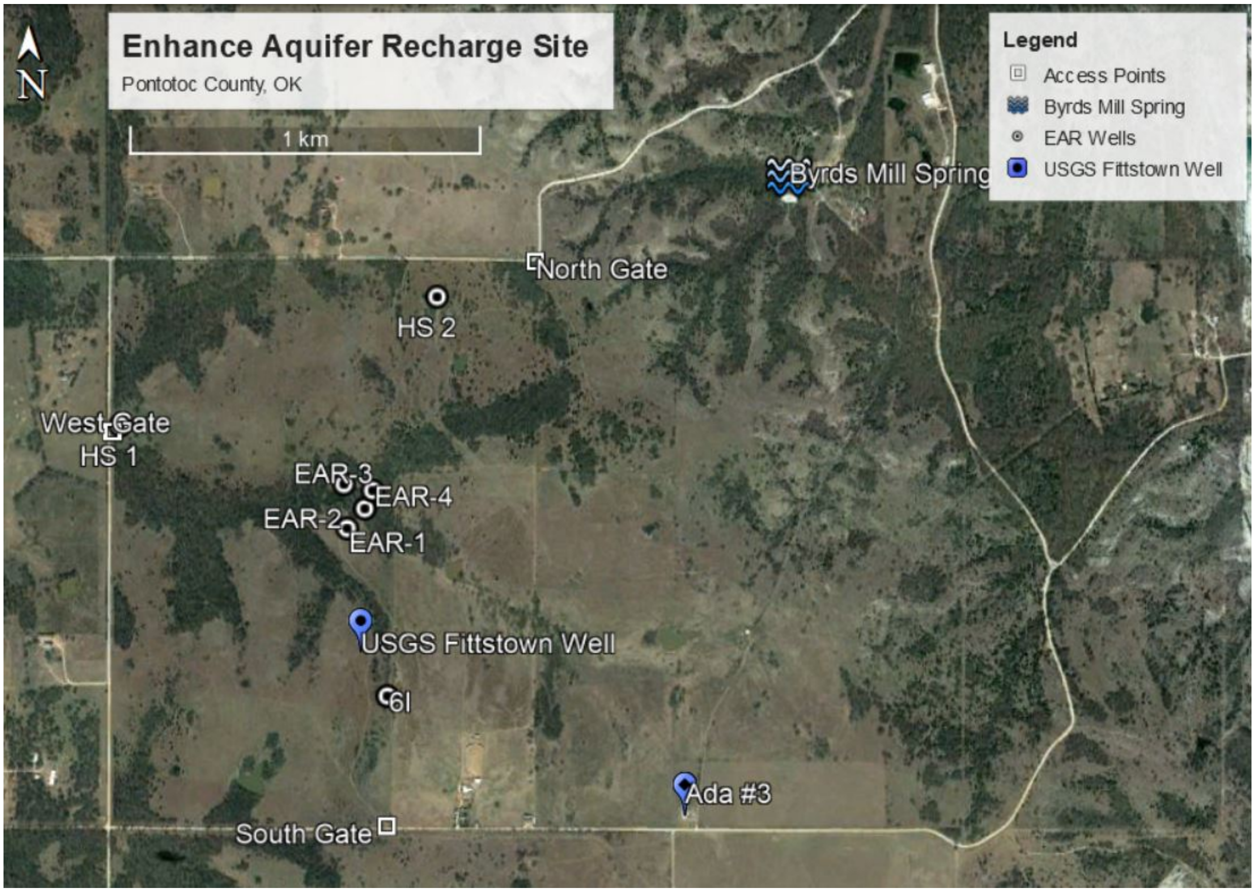


Figure 2. Location of existing EAR wells in relation to Byrds Mill spring, USGS Fittstown well, and Ada #3, the northern most well in the Ada well field. HS1 and HS2 are relic homestead wells available for water level measurements; Ada#3 is a production well for the city of Ada; 6I is a water supply well constructed during installation of current USGS Fittstown well.

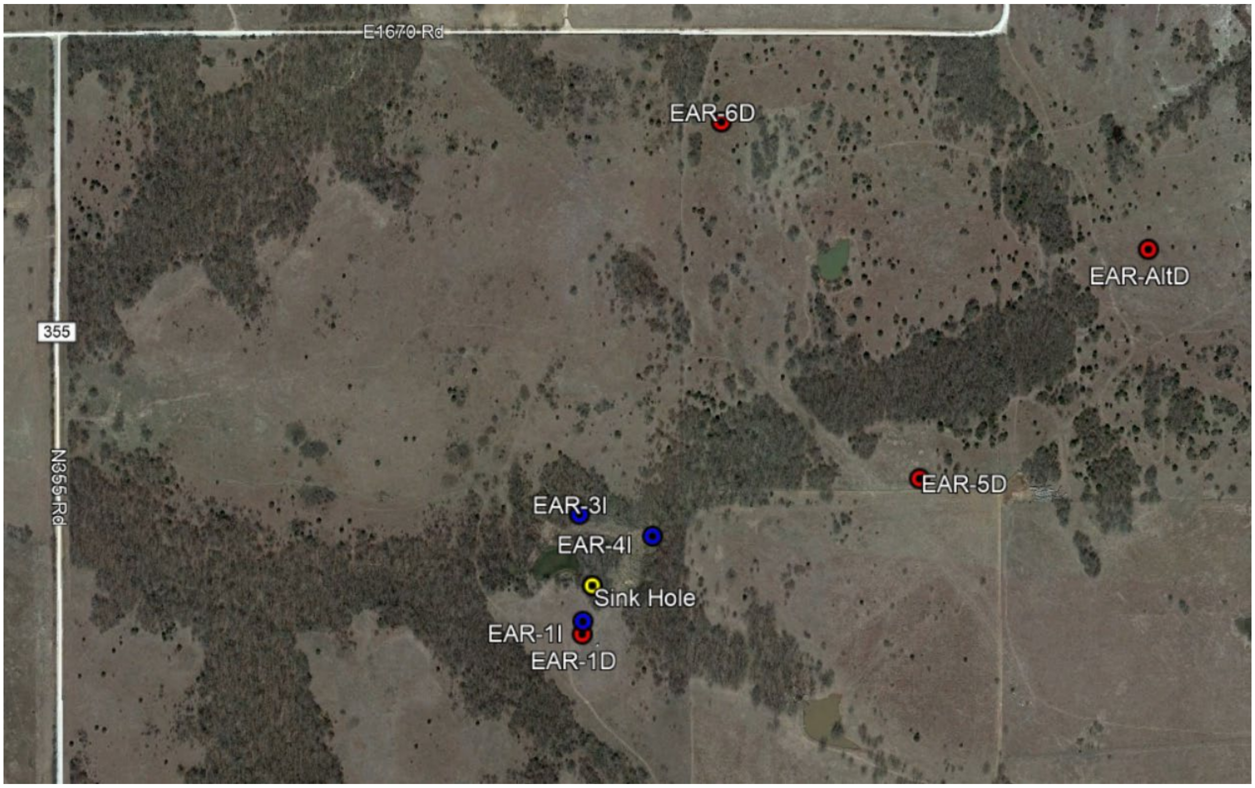


Figure 3. Locations of proposed monitoring wells associated with EAR site. Depths of wells described in text.

B.1.2 Specific target analytes

Table 3 lists the specific target analytes, analytical methods, and laboratory performing the analysis for this project.

Table 3. Specific target analytes, analytical methods, and laboratory performing analysis of water samples for the Arbuckle-Simpson geochemical characterization study.

Analyte	**Analytical Method**	**Laboratory Performing the Analysis**
Field Parameters		
pH	EPA Method 150.2	Field Measurement/GCRD
Temperature	EPA Method 170.1	Field Measurement/GCRD
Specific Conductivity	EPA Method 120.1	Field Measurement/GCRD
ORP	No EPA Method	Field Measurement/GCRD
Alkalinity	SM 2320B (Hach method 8203)	Field Measurement/GCRD
Nutrients		
Nitrite+Nitrate Nitrogen	EPA Method 353.2, rev. 2.0 (K-GCRD-SOP-1151-0)	GCRD
Ammonium Nitrogen	EPA Method 350.1 (K-GCRD-SOP-1151-0)	GCRD

Orthophosphate Phosphorus	EPA Method 365.1, rev. 2.0 (K-GCRD-SOP-1151-0)	GCRD
Metals		
ICP-OES Total Metals[2,3]	EPA Method 200.7 (K-GCRD-SOP-1154-0, K-GCRD-SOP-1089-4)	GCRD
ICP-OES Dissolved Metals[2]	EPA Method 200.7 (K-GCRD-SOP-1154-0)	GCRD
ICP-MS Total Metals[3,4]	EPA Method 200.8 (K-GCRD-SOP-1156-0, K-GCRD-SOP-1089-4)	GCRD
ICP-MS Dissolved Metals[4]	EPA Method 200.8 (K-GCRD-SOP-1156-0)	GCRD
ICP-MS Rare Earth Elements[5]	K-GCRD-SOP-1158-0	GCRD
Mercury[6]	Under development	GCRD
Anions		
Bicarbonate	Calculated[7]	GCRD
Bromide	K-GCRD-SOP-3329-0	GCRD
Chloride	EPA Method 9056A (K-GCRD-SOP-3329-0)	GCRD
Fluoride	EPA Method 9056A (K-GCRD-SOP-3329-0)	GCRD
Iodide	K-GCRD-SOP-1097-2	GCRD
Sulfate	EPA Method 9056A (K-GCRD-SOP-3329-0)	GCRD
Stable Isotopes		
O, H Stable isotopes of water	K-GCRD-SOP-1137-0	GCRD
Sr Isotopes	Method in Development	GCRD
Sulfur Isotopes	Method in Development	GCRD
Dissolved Carbon, Organic and Inorganic		
DOC	EPA Method 9060A (K-GCRD-SOP-1165-0)	GCRD
DIC	EPA Method 9060A (K-GCRD-SOP-1165-0)	GCRD
Organic Analytes		
Volatile Organic Compounds (VOC)[6,8]	K-GCRD-SOP-3445-0	GCRD

[1] *TDS (mg/L) = SPC (µS/cm) × 0.65*

[2] *Al, B, Ba, Ca, Fe, K, Li, Mg, Na, Si, Sr, Ti, Zn results will be reported.*

[3] *Total metals only analyzed for runoff, surface water, and spring samples.*

[4] *Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, and V.*

[5] *La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu will be reported.*

[6] *Continuation of mercury and VOC analysis will be made after first year of sampling.*

[7] *Calculated based on the DIC concentration and pH using AqQA or using an Excel spreadsheet calculator for carbonate speciation.*

[8] *For list of VOCs analyzed see method.*

Table 4. Current and Proposed Well Construction Details

Well Name	Total Depth (Feet below land surface)	Screened/Open Interval (Feet below land surface)
EAR-1	150	30-150
EAR-2	150	30-150
EAR-3	150	30-150
EAR-4	150	30-150
EAR-1S*	100*	80-100*
EAR-2S*	100*	80-100*
EAR-3S*	100*	80-100*

EAR-4S*	100*	80-100*
EAR-1I*	250*	200-250*
EAR-3I*	250*	200-250*
EAR-4I*	250*	200-250*
EAR-1D*	1000*	250-1000*
EAR-5D*	750*	250-750*
EAR-6D*	750*	250-750*

*Indicates proposed well, total depth and open/screened interval.

Based on the experimental design up to 20 locations including wells, springs, surface runoff and surface water will be sampled during any sampling round in addition to QC samples (field and equipment blanks, temperature blanks, duplicate samples, spiked samples (if method requires), and matrix spike duplicate samples (if method requires). Field and equipment blanks will be collected at minimum once per day, and temperature blanks will be one per cooler. A trip blank will be included in each ice chest with VOC samples. A duplicate sample will be collected for every ten samples or one sample per matrix.

B.1.3 Soil/ Sediment Characterization

Soils/ sediments from wells will be collected from each 20-foot section into large plastic bottles or plastic core tube in the field, kept on ice and shipped back to the GCRD lab. The soils/ sediments at the GCRD lab will follow the SOP for storage and disposal (K-GCRD-SOP1146-1). The soil samples will be dried in the laboratory atmosphere and gently ground with a mortar and pestle to pass through a 2-mm sieve. The soil particle fractions larger than 2-mm will be weighed and recorded. The sieved samples (smaller than 2-mm) will be mixed and subsamples will be used for a variety of analyses including soil texture using the hydrometer method (Gee and Or, 2002), pH in water and 0.01 M calcium chloride (Thomas, 1996), electrical conductivity (Rhoades, 1996), cation exchange capacity (Sumner and Miller, 1996), total carbon/inorganic carbon (Nelson and Sommers, 1996), total metals (EPA method 200.7; EPA Method 200.2; K-GCRD-SOP-1090-5), as well as mineralogy using x-ray diffraction (Moore and Reynolds, 1997; K-GCRD-SOP-1107-1) and electron microscopy (K-GCRD-SOP-1745-0). Depending on the outcome of the soil/sediment characterization Fourier transform infrared and Raman spectroscopy (Johnston and Aochi, 1996) and synchrotron analysis (Fendorf and Sparks, 1996) may be performed. Additional analysis may be added depending on needs for the project.

B.1.4 Borehole Geophysical Logging

Electromagnetic induction and natural gamma properties of the aquifer materials will be logged using geophysical tools in monitoring wells EAR1, EAR2, EAR3, EAR4 and any other wells in the area using standard operating procedure K-GCRD-SOP-1157-0 and the Century Geophysical, Inc., logging trailer and sonde (9510C) owned by GCRD. Natural gamma and electromagnetic induction logs are industry standard tools designed to aid in the interpretation of site stratigraphy. The selected wells and piezometers provide full horizontal and vertical coverage of the site. These data will be used to define the geologic framework and describe lithologic variation within the aquifer. All data sets generated during the geophysical logging will be backed up to a flash drive prior to leaving the site.

Additional borehole geophysical tools will be used at the site as SOPs become available. It is anticipated that this will include acoustic televiewer, resistivity (e-log), electromagnetic borehole flow meter, fluid properties and possibly other tools.

B.1.5 Electrical Resistivity Imaging

Electrical properties of aquifer materials are often correlated with differences in lithology. Electrical resistivity imaging (ERI) techniques will be applied at this site using a SuperSting R8 unit manufactured by Advanced Geosciences Inc., to better define the local stratigraphy and potential areas of variability within the aquifer. Methodology for the ERI investigation will follow standard operating procedure K-GCRD-SOP-1139-0. The ERI results will be compared with boring logs to identify possible differences in lithology and target areas for additional hydrogeologic investigation. All data sets generated during the investigation will be backed up from the SuperSting unit to a flash drive prior to leaving the site.

In order to better understand the connectivity between the shallow portions of the aquifer and the deeper zones that likely contribute most of the flow to Byrds Mill spring, five long-line ERI surveys will be performed. The orange lines on Figure 4 indicate the locations of approximately 1.1 km long ERI lines with 5 m electrode spacing that will provide a survey depth of approximately 225 meters below land surface, which should allow the identification of conductive zones. These surveys will be used to identify locations for deep monitoring wells (e.g., 200 m). This will be followed by an ERI survey on portions of the same lines with 6 m electrode spacing to provide greater resolution of any geologic features present in the subsurface. The subcontractor conducting the 1.1 km long ERI survey will be provided a copy of the K-GCRD-SOP-1139-0 and will be required to follow that SOP.

EPA will conduct ERI surveys as indicated by the red lines on Figure 4. These lines indicate the approximate locations of ERI lines in the vicinity of the large karst recharge feature. These ERI survey lines will have electrode spacing of 4 meters, allowing a vertical penetration of approximately 45 meters. The lines will be buried in a shallow trench with each electrode in direct contact with the strata using a conductive bentonite paste. Burial of the cable and electrodes will prevent damage to the cable by vermin and more importantly ensure consistent contact of the electrodes with the sediments/rock over time. These surveys lines are intended to capture the movement of water through fractures and solution openings in the unsaturated karst strata into the saturated zone. This will be accomplished by imaging the profile under dry conditions and after overland recharge events. The images will be differenced using AGI software. The image differencing will indicate changes in resistivity between surveys indicating water transport through the subsurface.

B.1.6 Hydrologic Testing

B.1.6.1 Slug Tests

Slug tests will be used to estimate the transmissivity and saturated hydraulic conductivity of the aquifer in monitoring wells and piezometers located at the site. The methodology for performing slug tests will follow K-GCRD-SOP-1104-1, if the hydraulic conductivity is below 0.01 cm/s, and K-GCRD-SOP-1103-1, if the hydraulic conductivity is equal to or greater than 0.01 cm/s. When tests will be performed in multiple wells using the same slugs and transducers, slugs and transducers will be rinsed with potable water between each well/piezometer. All electronic data files will be backed up to a portable flash drive prior to leaving the site.

B.1.6.2 Electromagnetic Borehole Flowmeter Tests

The distribution of groundwater flow to a monitoring well under pumping/non-pumping conditions and the saturated hydraulic conductivity of geologic materials adjacent to the well screen will be estimated using a Tisco/QE electromagnetic borehole flowmeter as detailed in procedure K-GCRD-SOP-1092-1. Electromagnetic borehole flowmeter tests will be utilized at existing monitoring wells to better define aquifer heterogeneity and refine estimates of bulk hydraulic conductivity derived from slug tests. All electronic data files will be backed up to a portable flash drive prior to leaving the site.

B.1.6.3 Surface water flow measurements using weirs

Surface water flow into the retention pond will be measured using a weir located adjacent to the pond (Figure 5). Similarly, the volume of water flowing out of the pond will be measured using weirs located on the pond spillway and at the entrance to the large sinkhole. The weirs are designed by the Chickasaw Nation and will be installed by the City of Ada as in-kind contributions to the project.

Flow rates over the weirs will be calculated using the following equation:

$$Q = 3.33\, H^{3/2}\, (L-0.2H)$$

Where Q is discharge (ft^3/sec), L is width of weir (ft), and H is height of water above weir in feet (USBR, 1997), which will be measured and recorded using a datalogging pressure transducer installed upstream of the weir.

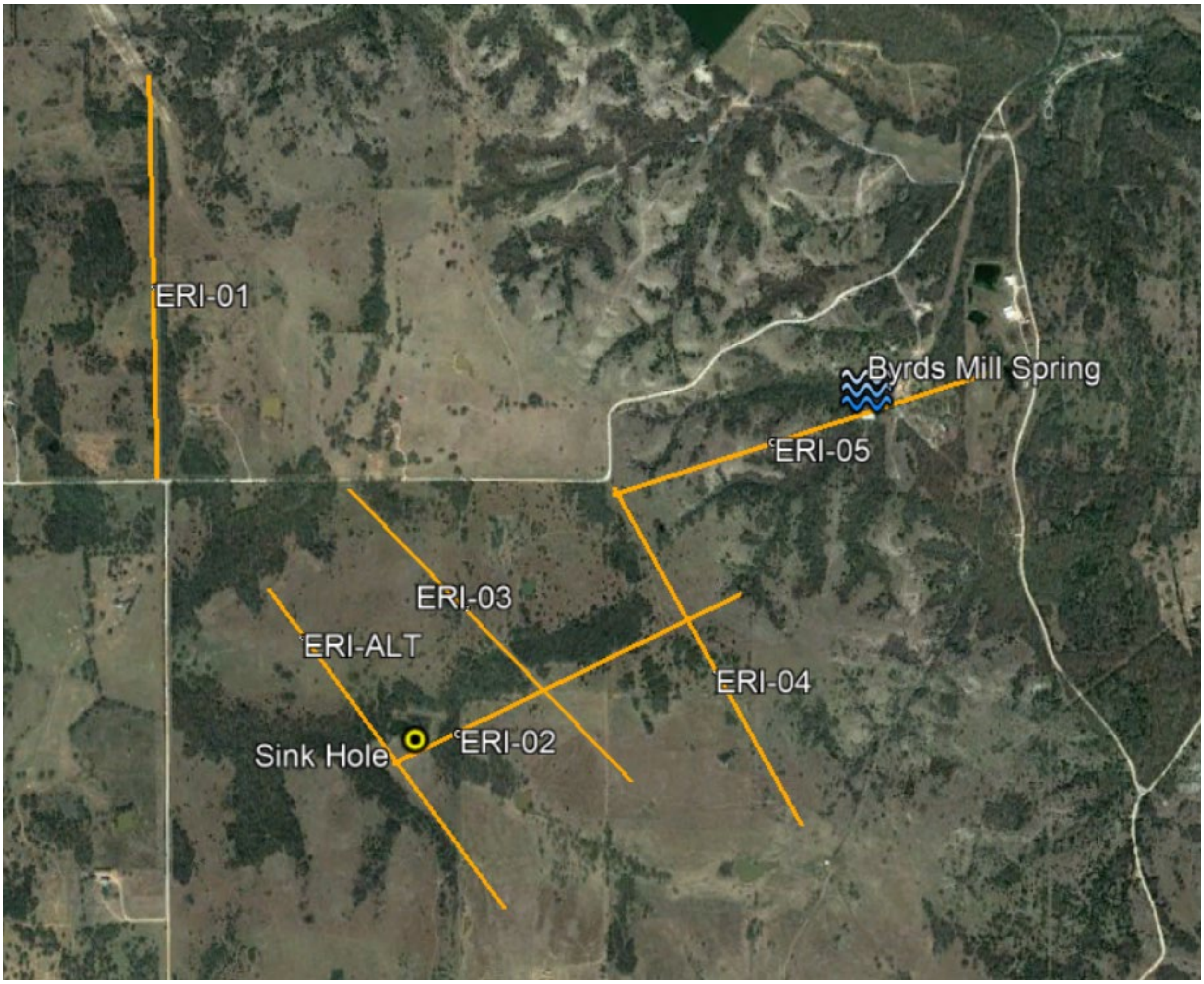


Figure 4. Potential locations of ERI lines in relation to karst feature (sink hole) and Byrds Mill Spring.

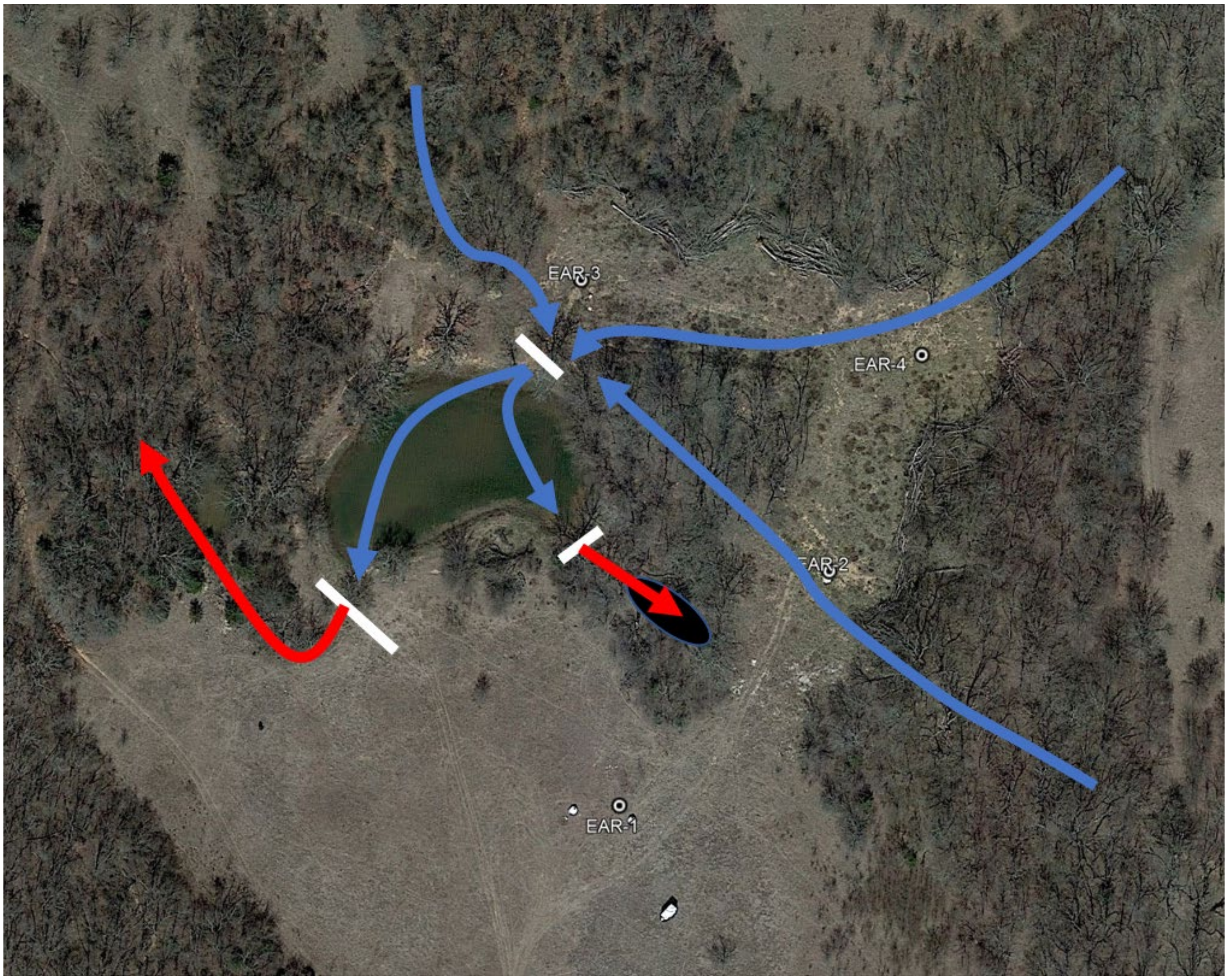


Figure 5. General surface water flow lines into and through (Blue) the pond. Red lines indicate general flow paths out of the retention pond. Weir locations are indicated by white rectangles to quantify flow out of the pond via the spillway or via the sinkhole

B.2 SAMPLING PROCEDURES

B.2.1 Runoff Sample Collection

Four to six refrigerated-automated samplers equipped with data logger, at minimum will be deployed at the site during the study and will be used to measure and log stage and initiate collection of stormwater runoff for chemical analysis of water samples to characterize stormwater runoff events. The samplers will be located 1) within the sink hole, 2) in the pond, 3) in the dry channel leading to the pond, 4) at Byrds Mill Spring and potentially two other locations to be specified later. The data loggers will record stage data in 15-minute intervals when no runoff is occurring. Depending on availability and configuration of the autosampler, additional sensors and measures may be added (e.g. velocity sensor, precipitation). During runoff events, the data-recording frequency for stage and any other added sensors will be increased to 1-minute intervals when a stage measurement in the channel leading to the pond exceeds 5 cm (increased data-recording data threshold) needed to completely submerge the stage and velocity sensors. The data logger program will enter sampling mode when a stage measurement of 15 cm (sampling threshold) is reached. The peristaltic pump in the automatic sampler will be used to draw stormwater through a 1 cm inside by 1.3 cm outside diameter Teflon-lined sample tubing. The tubing intake line will be positioned to draw water from storm runoff pipe or drainage ditch from a catch basin. The tubing-intake will be sloped down gradient into the pipe or drainage ditch so water will not collect in the tubing.

The automated sampler will be programmed to perform three field rinses through tubing up to the peristaltic-pump head before collecting a sample. The automated sampler will be equipped with 14 1-L sample bottles or alternatively a 10-L sample bottle. Samples will be collected using 14 1-L or ten 1-L pump cycles collected in 5-minute intervals, however these sampling intervals could be varied to meet specific sampling needs. The automated sampler will be calibrated onsite to deliver 1-L for each pump cycle. The data logger will receive and log a signal from the sampler for each completed pump cycle and will record pumped sample volume during a runoff event. Once in sampling mode, the data logger will trigger samples based on a preset time until all sample bottles have been collected or 10-L of sample is collected when the 10-L sample bottle is used, or the stage falls below the sampling threshold. All data and sampling thresholds can be adjusted within the data logger program at the monitoring station through remote communication using wireless cellular communication, data logger access, and reprogramming capabilities. After the composite sample has been collected, the data logger will continue to collect stage and precipitation data in 1-minute intervals until stage falls below the 5 cm data threshold. When stage falls below 5 cm the data-recording frequency will revert to 15-minute intervals. When lower than expected sample volume is collected, system will be reset with clean bottles (1-L bottles) or the existing composite sample (10-L bottles) will be flagged in the data and processed like a whole sample at the discretion of the PL based on the ability to meet quality criteria for the analytes desired.

The automated sampler will have remote access and retrieval of data through off-site monitoring of system status, notification when a sample event is occurring, or when equipment service is required. Upon retrieval of the sample after a runoff event, the sample will be removed from the automated sampler and data recorded by the data logger will be downloaded. The composite sample will be split in subsamples for specific chemical analysis.

B.2.1.1 1-L Sample Bottle Carrousel

The 14 1-L sample bottle carrousel will be used to collect runoff and spring samples. The advantage of using this sampling technique is that time interval samples can be collected during a runoff or precipitation event to provide insight into patterns of constituent concentrations and concentrations of constituents in springs following the event. Alternatively, samples can be composited based on times intervals (multiple bottles combined) or as a whole sample (to be determined by professional judgement). The method for collecting the subsamples will be described next.

1. Remove sample carrousel from the automated sampler.

2. If samples are to be composited, group the sample bottles by the appropriate time intervals to be composited, taking care to label bottles in correct chronological order. If bottles are to be analyzed as single samples, label each bottle as 1 – 14 ensuring that the numbers correspond to the correct chronologic order.

3. For composite samples pour the contents of the individual bottles for a sample time interval into a clean 5-gallon bucket and mix the sample using a clean mixing rod. For single bottles thoroughly mix the sample in the sample bottle.

4. Once the sample has been mixed pour off 200 mL of sample into an appropriately sized container for measuring field parameters: alkalinity, Fe^{2+}, sulfide, temperature, specific conductivity (SPC), total dissolved solids (TDS), dissolved oxygen (DO), pH, and oxidation reduction potential (ORP).

5. Measure the field parameters and record values in the field notebook.

6. Once field parameters have been recorded, a series of unfiltered samples will be collected into pre-labeled sample bottles using a peristaltic pump using clean tubing and pump tubing as follows.

    a. Three 40-ml amber glass VOA bottles will be collected without headspace, for VOC analysis using K-GCRD-SOP-3445-0. Sulfuric acid (H_2SO_4) will be added to the VOA vial after collection to obtain a $pH < 2$ as a preservative. The samples will be stored and shipped on ice to the GCRD Laboratory for GC-MS analysis.

    b. A 125-mL plastic bottle will be collected for metals analysis will be filled for the analysis of total metals concentrations. Analysis of these samples will be by ICP-OES (EPA Method 200.7) and by ICP-MS (EPA Method 200.8). These samples will be preserved using concentrated nitric acid (HNO_3) to a $pH < 2$ (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to GCRD Metals Lab for analysis. The total metal samples will be microwave digested in accordance to the method outlined in K-GCRD-SOP-1089-4.

    c. A 60 ml plastic bottle will be collected for total nitrogen and total phosphorous analysis using K-GCRD-SOP-1151-0. Samples will be preserved with H_2SO_4 to a $pH < 2$ (pH test strips will be used as spot checks on samples to confirm that the sample pH is < 2). The samples will be stored and shipped on ice to GCRD Metals Lab for analysis.

7. After the unfiltered samples have been collected a high-capacity ground-water filter (0.45µm, Pall Corporation, or equivalent manufacturer) will be placed on the end of the

pump tubing and filtered samples will be collected into pre-labeled sample bottles. First, approximately 100 mL of ground water will be filtered and sent to waste and next the following series of samples will be collected.

a. One 60-mL clear plastic bottle for sulfate, chloride, bromide and fluoride using ion chromatography (K-GCRD-SOP-3329-0). Iodide analysis will be analyzed using K-GCRD-SOP-1097-2. Orthophosphate phosphorous using EPA Method 365.1 (K-GCRD-SOP-1151-0). No preservative will be added. The samples will be stored and shipped on ice to the GCRD general parameters lab.

b. A 125-mL plastic bottle will be filled for the analysis of dissolved metals, rare earth element (REE), mercury concentrations and Sr isotope ratios. Analysis of these samples will be by ICP-OES (EPA Method 200.7) and ICP-MS (EPA Method 200.8, and for REE by K-GCRD-SOP-1158-0). Strontium isotopes and mercury analysis will be conducted using SOPs that are currently under development. These samples will be preserved using concentrated HNO_3 to a pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to the GCRD Metals Lab for analysis.

c. One 40-mL glass VOA vials will be collected for analysis of dissolved inorganic carbon (DIC) also filtered and analyzed using EPA Method 9060A (K-GCRD-SOP-1165-0. No preservative will be added to these samples. The samples will be stored and shipped on ice to the GCRD general parameters lab.

d. One 40-mL glass VOA vials will be collected for analysis of dissolved organic carbon (DOC) also filtered and analyzed using EPA Method 9060A (K-GCRD-SOP-1165-0). The samples will be stored and shipped on ice to the GCRD general parameters lab.

e. A 20-mL glass VOA will be collected for analysis of $\delta^{18}O$ and $\delta^{2}H$ of water using cavity ring-down spectrometry using K-GCRD-SOP-1137-0. The sample will be stored and shipped on ice o the GCRD general parameters lab.

f. One 60-mL clear plastic bottle for nitrate + nitrite, and ammonia also filtered and analyzed using EPA Method 353.2 and EPA Method 350.1 (K-GCRD-SOP-1151-0). This sample will be preserved with H_2SO_4, pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to the GCRD lab.

B.2.1.2 10-L Bottle

The subsampling of the 10-L sampler bottle will be described below.

1. Remove sample carrousel from the automated sampler.

2. Empty the contents of the 10-L sampler bottle into a clean 5-gallon bucket and mix the sample using a clean mixing rod.

3. Follow steps 4 – 7 including all sub steps in section B.2.1.1 until all subsamples have been collected.

B.2.2 Groundwater Sampling

Wells and piezometers will be used to sample groundwater as part of this study. The type of pump that will be used for sampling of wells and piezometers is a submersible pump (e.g. Proactive pump or similar type of pump). A bladder pump (QED or equivalent bladder pump) could potentially be used when needed.

The following methods will be used for sampling monitoring wells.

1. Water level measurements will be taken prior to placing the pump in the well or pumping the well. The water level measurements will follow the K-GCRD-SOP-1132-0 standard operating procedure. Water levels will be recorded in the field notebook or purge log prior (Attachment 1) to sampling.

2. A dedicated piece of tubing for each well or piezometer (stored in large plastic bag placed inside storage unit at the site when not being used for sampling) will be connected to the pump and the pump will be lowered into the well to the desired depth within the well screen. The pump will then be powered on. The initial pump rate will be at the pumps maximum pumping rate, likely between 3.5 – 7.5 L/min depending on depth to water at the time of the sampling. The initial pump rate will be maintained until 3 well volumes has been pumped from the well. The rate of pumping will be determined by measuring the water volume collected after approximately 1 min into a calibrated container. The well volume will be calculated using the equation for a cylinder (e.g., $v = \pi r^2 h$). Once the three well volumes have been pumped, the pumping rate will be lowered to a lower pumping rate for sampling; the desirable pumping rate for sampling will be less than 0.5 L/min. Once the rate of pumping has been determined, the other end of the tubing will be connected to a flow cell equipped with an YSI 5600 multiparameter probe (or equivalent probes). The YSI probe (or equivalent probes and electrodes) will be used to track the stabilization of pH, oxidation-reduction potential (ORP), specific conductance (SPC), dissolved oxygen (DO), and temperature. In general, the guidelines in Table 4 will be used to determine when parameters have stabilized. These criteria are initial guidelines; professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs. The values for parameter stabilization will be recorded to the purge log at approximately 2 min intervals until parameter stabilization has been reached. Water levels will be taken following sampling to confirm the drawdown caused by pumping.

3. Once stabilization occurs, the final values for pH, ORP, SPC, DO, and temperature will be recorded on the purge log.

4. After the values for pH, ORP, SPC, DO, and temperature have been recorded, the flow cell will be disconnected. A series of unfiltered samples will be collected into pre-labeled sample bottles as follows:

    a. A 1-L plastic beaker or glass jar will be filled for selected analyses to be conducted in the field. Field measurements will consist of turbidity, alkalinity, ferrous iron, and dissolved sulfide (Table 5). Turbidity (EPA Method 180.1) will be measured using a HACH 2100Q portable turbidimeter (or equivalent instrument). Alkalinity will be measured by titrating ground water with 1.6N H_2SO_4 to the bromcresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to Standard Method 2320B for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH DR/2010 spectrometer, HACH method 8146, equivalent to Standard Method 3500-Fe B for wastewater). Dissolved sulfide will be measured using the methylene blue colorimetric method (HACH DR/2010 spectrometer; HACH method 8131, equivalent to Standard Method 4500-S^{2-} D for wastewater).

    b. Three 40-ml amber glass VOA bottles will be collected without headspace, for VOC analysis using K-GCRD-SOP-3445-0. H_2SO_4 will be added to the VOA vial after collection to obtain a pH < 2 as a preservative. The samples will be stored and shipped on ice to the GCRD Laboratory for GC-MS analysis.

    c. A 125-mL plastic bottle will be collected for metals analysis will be filled for the analysis of total metals concentrations. Analysis of these samples will be by ICP-OES (EPA Method 200.7) and by ICP-MS (EPA Method 200.8). These samples will be preserved using concentrated HNO_3 to a pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to GCRD Metals Lab for analysis. The total metal samples will be microwave digested in accordance to the method outlined in K-GCRD-SOP-1089-4

    d. A 60 ml plastic bottle will be collected for total nitrogen and total phosphorous analysis using K-GCRD-SOP-1151-0. Samples will be preserved with H_2SO_4 to a pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is < 2). The samples will be stored and shipped on ice to GCRD Metals Lab for analysis.

5. After the unfiltered samples have been collected a high-capacity ground-water filter (0.45µm, Pall Corporation, or equivalent manufacturer) will be placed on the end of the pump tubing and filtered samples will be collected into pre-labeled sample bottles. First,

approximately 100 mL of ground water will be filtered and sent to waste and next the following series of samples will be collected.

a. One 60-mL clear plastic bottle for sulfate, chloride, bromide and fluoride using ion chromatography (K-GCRD-SOP-3329-0). Iodide analysis will be analyzed using K-GCRD-SOP-1097-2. Orthophosphate phosphorous using EPA Method 365.1 (K-GCRD-SOP-1151-0). No preservative will be added. The samples will be stored and shipped on ice to the GCRD general parameters lab.

b. A 125-mL plastic bottle will be filled for the analysis of dissolved metals, REEs, mercury concentrations and Sr isotope ratios. Analysis of these samples will be by ICP-OES (EPA Method 200.7) and ICP-MS (EPA Method 200.8, and for REE by K-GCRD-SOP-1158-0). Strontium isotopes and mercury analysis will be conducted using SOPs that are currently under development.. These samples will be preserved using concentrated HNO_3 to a pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to the GCRD Metals Lab for analysis.

c. Sulfur isotopes may also be collected. Method and sampling details will be provided

d. One 40-mL glass VOA vials will be collected for analysis of dissolved inorganic carbon (DIC) also filtered and analyzed using EPA Method 9060A (K-GCRD-SOP-1165-0). No preservative added will be added to these samples. The samples will be stored and shipped on ice to the GCRD general parameters lab.

e. One 40-mL glass VOA vials will be collected for analysis of dissolved organic carbon (DOC) also filtered and analyzed using EPA Method 9060A (K-GCRD-SOP-1165-0). The samples will be stored and shipped on ice to the GCRD general parameters lab.

f. A 20-mL glass VOA will be collected for analysis of $\delta^{18}O$ and $\delta^{2}H$ of water using cavity ring-down spectrometry using K-GCRD-SOP-1137-0. The sample will be stored and shipped on ice to the GCRD general parameters lab.

g. One 60-mL clear plastic bottle for nitrate + nitrite, and ammonia also filtered and analyzed using EPA Method 353.2 and EPA Method 350.1 (K-GCRD-SOP-1151-0). This sample will be preserved with H_2SO_4, pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to the GCRD lab.

B.2.2.1 Discreet Sampling with Century "Bomb" Samplers

The following methodology will be used to acquire groundwater samples from intervals of interest identified during geophysical logging of the deep wells.

1) The logging trailer will be used to lower the bomb sampler (Century Geophysical Corporation Fluid Sampler, 1 liter, 303 SS, model # 9751 plus a series of 304 SS vessels) through the well opening and to the desired depth within the screened interval. A series of valves will be used to attach 500 mL vessels and two 150 mL stainless steel sampling vessels (Swagelok, 150 mL, 304L SS, part #304L-HDF4-50a). This series of sampling vessels will used to collect groundwater in one sampling pass.
2) Once at the desired depth, the bomb sampler will be activated from the surface and groundwater will fill the bomb sampler and attached sample vessels.
3) Once the bomb sampler is allowed to fill, the downhole valve on the bomb sampler will be closed and the sampling vessels will be retrieved.
4) Once at the surface, samples will be collected after first expelling the contents of the bomb sampler into an appropriate sized plastic reservoir. A peristaltic pump will be used to pump water from the reservoir through polyethylene tubing into pre-labeled sample bottles.
5) A 200 mL unfiltered sample will be collected for field measurements. Field measurements will consist of temperature, SPC, TDS, DO, pH, ORP, alkalinity, ferrous iron, and dissolved sulfide.
6) Once field measurements have been collected a series of unfiltered and filtered samples will be collected as outlined in section B.2.2.

The procedure described above for deploying the bomb-sampler may be used on the deep and intermediate depth monitoring wells.

Table 5. Geochemical parameter stabilization guidelines.

Parameter	Stabilization Criteria	Calibration Standards
pH	≤0.02 pH units/min	pH 4, 7, and 10 buffers
Oxidation Reduction Potential (ORP)	≤ 1 mV/min	231 mV Zobell's Solution
Specific Conductance (SPC)	≤ 1 %/min	1413 µS Conductivity Standard
Dissolved Oxygen (DO)	≤ 0.25 mg/L/min	

Table 6. Field analytical methods to be used in this study.

Analyte	Method	Equipment
Alkalinity	Standard Method 2320B; HACH method 8203	HACH Model AL-DT Digital Titrator (or equivalent device)
Dissolved Ferrous Iron	Standard Method 3500-Fe B; HACH Method 8146	HACH DR890 Portable Colorimeter (or equivalent device)

Analyte	Method	Equipment
Dissolved sulfide	Standard Method 4500-S^{2-} D; HACH Method 8131	HACH DR890 Portable Colorimeter (or equivalent device)
Turbidity	EPA Method 180.1	HACH 2100Q Portable Turbidimeter
pH	EPA Method 150.2	YSI 556MP or equivalent combination of meters and probes
Dissolved Oxygen	EPA Method 360.1	YSI 556MP or equivalent combination of meters and probes
Temperature	EPA Method 170.1	YSI 556MP or equivalent combination of meters and probes
Specific conductance	EPA Method 120.1	YSI 556MP or equivalent combination of meters and probes
ORP	No EPA Method	YSI 556MP or equivalent combination of meters and probes
TDS[1]	No EPA Method	YSI 556MP or equivalent combination of meters and probes

[1] A calculated value from the YSI 556MP based on the specific conductance measurement.

B.2.3 Surface Water Sampling

Samples will be collected using a peristaltic pump with the tubing attached to a painter's extension pole that extends to 12 feet and an attached roller frame (6-inch roller). This will keep the end of the tubing above the bottom sediment to reduce any capture of sediment into the sampling bottles. The locations of the sampling sites will be recorded with a handheld GPS device. General observations will be recorded in a field notebook. The analytes sampled for will be the same as in the groundwater sampling section (Section B.2.2).

The following methods will be used for sampling surface water.

1. Attach the roller frame to the painter's extension pole and extend the pole to its maximum reach.

2. Attach two C-clamps to the grip end of the painter's extension pole so that the screw portion of the c-clamps point towards the ground (point of the roller frame will point upwards) and are approximately 45° from a level horizontal plane (see Figure 5). The C-clamps will help keep the painter's extension pole from moving and ensure that the tubing points away from the bottom sediment.

3. Attach one end of a clean piece of 3/8 in × 1/2 in × 1/16 inch poly tubing to the roller frame using three plastic wire ties (see Figure 6).

4. Once the tubing has been attached to the roller frame at approximately 2-foot intervals, tape the poly tubing to the painter's extension pole.

5. Carefully place the tubing and painter's extension pole assembly in the desired sampling location in the surface water and ensure that only the tubing that is to be placed in the water goes in the water. Assure that the end of the tubing that is in the water is pointing away from the bottom sediment and that it is underwater. If not adjust until these criteria are meet (see Figure 7).

Figure 6. Surface water sampling. A) is the entire set up. B) is a close up showing the placement of the c-clamps.

Figure 7. Close up of how the tubing is connected to the roller frame and top of the painter's extension pole.

6. Using a hand-held GPS record the position of the end of the painter's extension pole along the shoreline of the surface water body. Record this position.
7. Unroll the poly tubing until you reach the desired sample collection location where the peristaltic pump is located. Cut the tubing.

8. Obtain the Masterflex tubing and cut approximately 2 feet of this tubing.

Figure 8. Positioning of the sampling tube attached to the roller frame and painter is extension pole showing the inlet for the sampling tube above the bottom sediments.

9. Connect the Masterflex tubing to the poly tubing from the sampling assembly.
10. Cut another approximately 4-foot piece of poly tubing and connect it to the other end of the Masterflex tubing. This piece of poly tubing will be used to fill bottles and connect to the in-line filter.
11. Place the Masterflex tubing in the peristaltic pump head and secure the tubing.
12. Turn on the peristaltic pump and verify that the pump direction is such that the water from the surface water body will be pumped to the shore and sample collection location.

If not reverse the pump direction. It can take several minutes for the water to pump to the sample collection location.

13. Once the water arrives at the sample collection location, adjust the pump rate so that the flow of sample is < 1 L/min.
14. Allow several liters of water to purge before collecting samples as described in Section B.2.2.

B.2.4 Sample containers and sample volumes

The sample containers and sample volumes needed are given in Table 7. Note that parameters for field analysis are not included since these will be measured in the field during sampling.

Table 7. Sample containers, volumes, preservation and holding times for the lab analytes sampled in this study for water samples.

Parameter	**Analysis Method**	**Sample Bottles/# of bottles**	**Preservation/Storage**	**Holding Time**
Total Metals	EPA Method 200.7, EPA Method 200.8, and K-GCRD-SOP-1089-4	125-ml plastic bottle/1	HNO_3, pH < 2; room temperature	6 months
Dissolved Metals	EPA Method 200.7 and EPA Method 200.8	125-ml plastic bottle/1	HNO_3, pH < 2; room temperature	6 months
Dissolved Rare Earth Elements	K-GCRD-SOP-1158-0			
Strontium Isotopes	Under Development			
Mercury	Under Development			
Total Nitrogen	K-GCRD-SOP-1151-0	60 mL plastic/1	H_2SO_4, pH<2; refrigerate <6°C	28 days
Total Phosphorous				
Nitrate + Nitrite	EPA Method 353.2 (K-GCRD-SOP-1151-0)	60 mL plastic/1	H_2SO_4, pH<2; refrigerate ≤6°C	28 days
Ammonia	EPA Method 350.1 (K-GCRD-SOP-1151-0)			
Bromide	K-GCRD-3329-0	60 mL plastic/1	Refrigerate≤6°C	28 days
Chloride				
Fluoride				
Sulfate				
Iodide	K-GCRD-SOP-1097-2			
Orthophosphate	EPA Method 365.1 (K-GCRD-SOP-1151-0)			24 hrs
O, H Stable isotopes of water	K-GCRD-SOP-1137-0	20 mL glass VOA vial/1	Refrigerate at ≤6°C	Stable
Sulfur Isotopes	K-GCRD-SOP-3830-0	TBD	Refrigerate at ≤6°C	Stable
DOC	EPA Method 9060A	40 mL clear glass VOA vial/1	refrigerate ≤6ºC	7 days
DIC	EPA Method 9060A	40 mL clear glass VOA vial/1	refrigerate ≤6°C	14 days

Parameter	Analysis Method	Sample Bottles/# of bottles	Preservation/Storage	Holding Time
Volatile Organic Compounds (VOC)	K-GCRD-SOP-3445-0	40 ml glass VOA /3	$H_2SO_4 \underline{<} 2$ refrigerate $\underline{<}4$°C (no headspace)	14 days

B.2.5 Sample Preservation and Holding Times.

Sample Preservation and holding times are listed in Table 7.

B.2.6 Sample Labeling

Samples collected from each sampling location will include the unique label, the date, the initials of the sampler, and designation of the sample type, e.g., “metals” and preservation method (when applicable). This information will be recorded onto labeling tape, using water-insoluble ink, affixed to each sample bottle. Samples will be labeled as follows. Samples will be labeled EARGWxx. The first three letters, EAR will be the same for all sample collected as part of this study since it will be the code for this project. The next two letters will be for the sample type, GW for groundwater, RO for runoff sampler samples, SP for spring samples, and SW for surface water. The xx will move in sequence (i.e., 01, 02, etc.). If the same points are sampled in subsequent trips, the number designation will remain the same (linked to the site). Duplicate samples will be marked by dup following the label above. Samples collected for use in spikes will be marked by Spike following the label above. Equipment blanks will be labeled EqBlank XX, where XX will move in sequence. Similarly, Field Blanks will use the same system, but the EqBlank will be replaced with FBlank.

B.2.7 Procedures for packing and shipping samples

Samples collected from each analytical parameter will placed together in a sealed Ziploc plastic bag. The bags will be placed on ice in coolers. Glass bottles will be packed with bubble wrap to prevent breakage. It is anticipated that samples will be brought back by the sampling crew to GCRD after each day of sampling. The coolers will in addition to samples contain analytical service request forms (ASRF), which will also serve as the chain of custody form (COC). However, if labs other than GCRD labs are used the coolers will be sent via using overnight services to the appropriate lab with chain of custody COC forms, ASRF (if applicable) and custody seal will be affixed to the outside of each cooler.

At least 1 week prior to collecting samples, a technical directive (TD) must be submitted to the lab. The lab will assign a TD number and this number must be placed on all ASRF (Attachments 2) and COCs for samples shipped to GCRD to ensure that the proper analysis will be performed on the samples. The individual PL or their designee will be responsible for submitting a TD to the GCRD labs. A TD will need be submitted to the General Parameters Laboratory and a separate TD will need to be submitted to the Metals Laboratory and onsite contractor (Pegasus) for VOC analysis. Upon receipt at GCRD, all samples shall be logged-in using K-GCRD-1152-1, *Sample Receipt and Log-in Procedures for GWERD, Ada, OK*. Ice chests are then opened, the temperature blank is located to take the temperature and it is noted whether or not ice is still present. ASRFs, and samples are removed. Samples are checked against the COC (ASRF). The observations concerning temperature, if ice was not present, and any sample discrepancies are noted on the COC and the sample custodian signs the form. A copy of the COC/ASRF is distributed to the PL and the GCRD general parameters lab retains a copy. The PL should be notified immediately if samples arrive with no ice and/or if the temperature recorded from the temperature blank is > 6 ºC. Samples can only be received Monday – Friday during normal business hours with the exception of holidays. Samples cannot be received on holidays.

B.3 MEASUREMENT PROCEDURES

B.3.1 Analytical methods

Most of the analytical methods to be used in this study have already been listed previously. In addition to these methods, water level measurements (K-GCRD-SOP-1132-0) and hydrologic testing (K-GCRD-SOP-1092-1, K-GCRD-SOP-1103-1, K-GCRD-SOP-1104-1, and K-GCRD-SOP-1134-0) will be used.

B.3.2 Calibration Procedures

For the GCRD laboratories the calibration procedures, including calibration frequency, linearity checks, and initial and continuing calibration checks are described in GCRD SOPs. Detection and quantitation limits are included in the GCRD analytical reports.

Field instruments (meters for pH, specific conductance, ORP, DO, and temperature) are calibrated (per manufacturer's instructions) or checked for calibration daily prior to use, mid-day, and at the end of the day after the last sample measurement. Calibration standards shall be NIST traceable, if available, and verified that all dated calibration standards are not beyond their expiration date and will not expire during the field trip. Prior to deployment, each test meter will be checked that it is in good working order. Calibration data will be recorded in bound waterproof notebook and personnel making entries will adhere to the established notebook policy. Calibration of instruments will be performed daily prior to initiation of sample collection and will be performed according to manufacturer's instructions and will be recorded in the field notebook. In addition, calibration checks will be performed using known standards or buffers before use, mid-day and at the end of the day. With the exception of pH, all checks must be within ± 10 % of known concentrations and in the case of pH must be within ± 0.2 pH units. Dissolved oxygen calibration will be checked at the end of the day using a saturated air check and must be within in the range of 90- 110 %. These calibration checks will be recorded in the field notebook. If a calibration check fails, this will be recorded in the field notebook and the possible causes of the failure will be investigated, corrective action taken, and the instrument recalibrated. Samples taken between the last good calibration check and the failed calibration check will be flagged to indicate there was a problem. Duplicate field measurements are not applicable to measurements in flow through cell (K-IO-SOP-1260-1, *Field Analytical QA/QC*).

Hach spectrophotometers (ferrous iron and sulfide) and turbidimeters (turbidity) will be inspected prior to going to the field and their function verified. These instruments are factory-calibrated and will be checked in the lab prior to going to the field per the manufacturer's instructions. For the Hach spectrophotometers, this will consist of checking the accuracy and precision for that method. The ferrous iron accuracy will be checked by measuring a 1 mg Fe^{2+}/L standard and the results should be between 0.90 -1.10 mg Fe^{2+}/L. Similarly, the precision will be tested using the standard performing the measurement three times on this solution. The single operator standard deviation should be no more than ± 10%. Turbidity will be checked against turbidity standards supplied by Hach. In addition, blanks (deionized water) will be run at the beginning of the day, midday, and at the end of the day. The values for the blanks will be recorded in the field notebook and any problems associated will be recorded. Turbidity blanks will have detectable concentrations (typically < 1 NTU). If turbidity is > 2 NTU then the sample cells will be decontaminated, and a new blank will be run. This process will continue until the turbidity blank is < 2 NTU. Standards for redox sensitive species such as sulfide and ferrous iron are difficult to use in the field because once exposed to atmospheric oxygen their concentrations can change. Similarly, calibration standards for alkalinity are sensitive to atmospheric carbon dioxide. Alkalinity measurements will use a 1.6N H_2SO_4 solution to titrate samples and standards in the field. The titrator will be checked using a 250 mg/L standard made from Na_2CO_3. The analyzed value should be in the range of 225- 275 mg/L. Duplicates will be performed once a day. Duplicates acceptance criteria are Relative Percent Difference (RPD) $\leq$ 15%. The values obtained for each duplicate sample will be recorded in the field notebook and RPD will be calculated and recorded in the field notebook. If the duplicate samples fail an additional duplicate sample will be taken and reanalyzed. If the additional duplicate samples fail to meet the QC criteria, then the instruments will be checked, and corrective action taken. The corrective actions will be recorded in the field notebook. Samples collected between the last valid duplicate sample and the failed duplicate sample will be flagged.

B.3.3 Non-direct measurements

Non-direct measurements (also known as existing data or secondary data) are data from sources other than those collected directly for this study (primary data). Existing data may be needed for an understanding local groundwater quality and variability in groundwater quality to compare with the study data and determine if there are significant differences. Sources of existing data may include federal, state, and local databases, and peer reviewed literature.

As described elsewhere in the QAPP, primary data have criteria that must be met to be usable for this project. Likewise, existing data must also be evaluated to ensure it meets project requirements. Whether or not these data are acceptable to use for this case study is dependent upon these evaluation criteria: (1) the organization that collected the data has a quality system in place, (2) data were collected under an approved Quality Assurance Project Plan or other similar planning document, (3) analytical methods used are comparable to those used for the primary data, (4) the laboratory has demonstrated competency (such as through accreditation) for the analysis they performed, (5) the data accuracy and precision are within limits similar to that for the primary data, (6) the MDLs and QLs are comparable to those associated with the primary data or at least adequate to allow for comparisons, and (7) sampling methods are comparable to those used for the primary data.

To be able to evaluate these criteria, metadata (data or information about the data) associated with the data sources will be reviewed by the PLs. If the data does not meet project requirements, or metadata is not available to provide for a complete evaluation of the data quality based on the criteria above, the data would need to be qualified or rejected. If this action removes much of the background data needed to make comparisons, it will not be possible to determine if there have been significant changes to water quality. Instead of taking this action, these data will be used with the understanding that they are of an indeterminable quality relative to the project requirements.

B.4 METHOD PERFORMANCE METRICS

B.4.1 Quality Control Samples

Quality control samples, acceptance criteria and corrective actions for water samples collected in the field are listed in Table 8.

Table 8. Field QC Samples to be collected for water samples.

QC Sample	Purpose	Method	Frequency	Acceptance Criteria/ Corrective Actions
Equipment Blanks	Assess contamination from field equipment, sampling procedures, decon procedures, sample container, preservation, and shipping.	Apply only to samples collected via equipment, such as filtered samples: Reagent water is filtered and collected into bottles and preserved same as filtered samples.	One per day of sampling	< QL: Sample will be flagged if > QL and analyte concentration < 10x concentration in blank.
Field Duplicates	Represent precision of field sampling, analysis, and site heterogeneity.	One or more samples collected immediately after original sample.	One in every 10 samples, or if < 10 samples collected for a water type (ground or surface), collect a duplicate for one sample[1]	Report duplicate data: RPD $\leq$ 30% for results greater than 5 x QL. The affected data will be flagged as needed.
Temperature Blanks	Measure temperature of samples in the cooler.	Water sample that is transported in cooler to lab.	One per cooler.	≤6° C Record temperature; condition noted on COC form[2]

QC Sample	Purpose	Method	Frequency	Acceptance Criteria/ Corrective Actions
Field Blanks	Assess contamination introduced from sample container with applicable preservation.	In the field, reagent water is collected into sample containers with preservatives.	One per day of sampling	< QL: Sample will be flagged if > QL and analyte concentration < 10x concentration in blank.
Trip Blanks (VOC only)	Assess contamination introduced to sample during transport and sample collection	In the Lab, reagent water is collected into sample containers with preservatives	One per cooler containing VOCs.	< QL: Sample will be flagged if > QL and analyte concentration < 10x concentration in blank.

[1] At least two per sampling event if >12 samples are collected.

[2] The PL should be notified immediately if samples arrive with no ice and/or if the temperature recorded from the temperature blank is greater than 6° C. These samples will be flagged accordingly.

For analytical methods performed at the GCRD General Parameters laboratory the QC samples, and acceptance criteria for water samples analyzed are listed in Table 9.

Table 9. GCRD General Parameters Laboratory QC Requirements.

Analyte	Blanks (Frequency)	Calibration Checks AC* (Frequency)	Second Source Standard AC* (Frequency)	Lab Duplicates AC* (Frequency)	Matrix Spikes AC* (Frequency)
SO_4, Cl, F, Br	< MDL; except Br, < 0.3 mg/L (Beginning and end of each sample queue)	90-110 % Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits, if other than PE, 90-110% Rec. (One per sample set)	RPD ≤ 10 % (every 15 samples)	80-120 % Rec. (one per every 20 samples)
Iodide	<½ QL (Beginning and at the end of each set of samples.)	90- 110 % of known value (At beginning of each analytical run. Every tenth sample and at end of analytical run.)	90-110 % of known value (Beginning of sample set and every 20 samples)	RPD < 10 % (Every 20 samples)	80 – 120 % Recovery (Every 20 samples)/ LCS: 80 – 120% (If matrix spike fails)
DOC/DIC	<MDL (Beginning and at the end of each set of samples.)	90-110 % of known value (after initial calib., every 10 samples, and at end)	90-110 % of known value (One per sample set)	RPD ≤ 10 % (every 10 samples)	80-120 % Rec. (one per 20 or every set
Stable Isotopes of Water	NA	≤1.5‰ for δ^2H;	NA	≤1.5‰ for δ^2H; ≤0.3‰ for $\delta^{18}O$	NA

Analyte	Blanks (Frequency)	Calibration Checks AC* (Frequency)	Second Source Standard AC* (Frequency)	Lab Duplicates AC* (Frequency)	Matrix Spikes AC* (Frequency)
		≤0.3 ‰ for $\delta^{18}O$ (Beginning and end of sample set and every 20 samples)		(Beginning and end of sample set and every 20 samples)	
Orthophosphate	< low calibration standard (Beginning and end of each sample set)	90-110 % Rec. (Beginning, end, and every 10 samples)	90-110 % of known value (One per sample set)	RPD< 10 % (every 10 samples)	80-120 % Rec. (one per every 20 samples)
Total Nitrogen	< low calibration standard (Beginning and end of each sample set)	90-110 % Rec. (Beginning, end, and every 10 samples)	90-110 % of known value (One per sample set)	RPD< 10 % (every 10 samples)	80-120 % Rec. (one per every 20 samples)
Total Phosphorous	< low calibration standard (Beginning and end of each sample set)	90-110 % Rec. (Beginning, end, and every 10 samples)	90-110 % of known value (One per sample set)	RPD< 10 % (every 10 samples)	80-120 % Rec. (one per every 20 samples)
Nitrate + Nitrite	<½ lowest calib. std. (Beginning and end of each sample set)	90-110 % Rec. (Beginning, end, and every 10 samples)	90-110 % of known value (One per sample set)	RPD< 10 % (every 10 samples)	80-120 % Rec. (one per every 20 samples)
Ammonia	<½ lowest calib. std. (Beginning and end of each sample set)	90-110 % Rec. (Beginning, end, and every 10 samples)	90-110 % of known value (One per sample set)	RPD<10 % (every 10 samples)	80-120 % Rec. (one per every 20 samples)

Table Notes: This table only provides a summary; SOPs should be consulted for greater detail. Corrective actions are outlined in the SOPs. *AC = Acceptance Criteria. MDL = Method Detection Limit. QL = Quantitation Limit. PE = Performance Evaluation. NA= not applicable. LCS = Laboratory Control Spike

For sample analysis conducted by the GCRD Analytical Laboratory (for total and dissolved metals using EPA Method 200.8, ICP-MS by K-GCRD-SOP-1156-0) the QC samples, and acceptance criteria for water samples analyzed are listed in Table10.

Table 10. GCRD Laboratory QC Requirements for ICP-MS.

QC Type or Operation	**Acceptance Criterion**	**Frequency**
Instrument Calibration	The acceptance criterion for the initial calibration correlation coefficient is r≥0.99.	Daily before sample analysis.
Initial Calibration Verification (ICV)	90-110 % Recovery	Following instrument calibration for each mass used.
Initial Calibration Blank (ICB)	≤ RL	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification (CCV)	90-110 % Recovery	For each mass used, at a frequency of at least after the ICV, every 10 samples, and at the end of each run.
Low Level Quantitation Limit Standard (LLQLS)at the RL	70-130 % Recovery	At beginning of each run.
Continuing Calibration Blank (CCB)	≤ RL	At a frequency of at least after every 10 samples, and at the end of each run. Performed immediately after the last CCV.
Interference Check Sample (ICSA and ICSAB)	For solution AB, ±20 % of the analyte's true value except Al & Mo which are above calibration range; for solution A < RL except for interfering elements and Al.	At the end of the run
Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 50 above the RL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10 % of the original determination after correction for dilution.	Every 20 samples.
Preparation or Method Blank (MB)	≤ RL	Every 20 samples.
Laboratory Control Sample (LCS)	85-115 % Recovery	Every 20 samples.
Matrix Spike (MS), digested	70-130 % Recovery (Recovery calculations are not required if concentration of the spiked analyte is < 30 % of the native analyte concentration in the sample.)	Two samples for every 20 samples.
Post-Digestion Spike	70-130 % Recovery per 6020A	For each time Matrix Spike.
Matrix Spike, undigested	70-130 % Recovery	Two for every 20 samples.
Duplicate Sample, digested	RPD ≤20 % for sample values ≥ 5x RL; Or, limits are +/-RL for sample values <5xRL	Two for every 32 samples.
Duplicate Sample, undigested	RPD ≤ 15 % for sample values ≥ 5 x RL;	Every 10 samples.

QC Type or Operation	**Acceptance Criterion**	**Frequency**
	Or, limits are +/-RL for sample values < 5 x RL	
HR-ICP-MS Tune	Low resolution mass signal must be > 3x10^6 cps for ^{7}Li, 2.5x10^7 cps for ^{115}In, and 2.5x10^6 cps for ^{238}U. The %RSD < 2.5% for ^{238}U. Medium resolution mass resolution between Fe and ArO is > 4000. High resolution mass resolution between K and ArH > 9000.	Prior to calibration
Internal Standards	The absolute response of any one internal standard in a sample must not be < 60 % or > 125 % of the response in the calibration standard.	Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

For sample analysis conducted by the GCRD Metals Laboratory (for total and dissolved metals using EPA Method 200.7 (K-GCRD-SOP-1154-0), ICP-OES) the QC samples, and acceptance criteria for water samples analyzed are listed in Table 11.

Table 11. GCRD Laboratory QC Requirements for ICP-OES

QC Type	**Acceptance Criteria**	**Frequency**
Instrument Calibration	Criteria not given in 200.7. Ensure that the new calibration is within about 10% of the previous calibration based on the standard slopes for all elements and wavelengths.	Daily before sample analysis.
Initial Calibration Verification (ICV)	95-105 % Recovery	Immediately after calibration.
Initial Calibration Blank (ICB)	$\leq$ RL	Analyzed at the beginning of the run.
Low-Level Quantitation Limit Standard (LLQLS)	70-130 % Recovery	Analyzed at the beginning of the run after the ICV

QC Type	Acceptance Criteria	Frequency
Continuing Calibration Verification (CCV)	90-110 % Recovery	At beginning and end of run; every 10 samples during analytical run.
Continuing Calibration Blank (CCB)	≤ RL	Analyzed immediately after every Continuing Calibration Verification (CCV); at beginning and end of run and every 10 samples during an analytical run.
Interference Check Sample	For solution AB, ±20 % of the analyte's true value; for solution A ± 20% of the interferent's true value, for all other analytes within ±2 times the RL of the analyte's true value.	At the beginning of the run after the ICB but before the CCV and at the end of the run.
Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10 % of the original determination after correction for dilution.	Every 20 samples.
Digestion or Preparation Blank (PB)	≤ RL	Two for every 32 samples.
Laboratory Control Sample (LCS)	85-115 % recovery	Two for every 32 samples.
Matrix Spike (MS) (digested and undigested)	75-125 % Recovery (Recovery calculations are not required if sample concentration >4x spike added.)	Every 10 samples.
Matrix Spike Duplicate (MSD) (undigested)	RPD ≤ 15 % for sample values ≥ 5x RL; for sample values < 5x RL, control limit = RL	Every 10 samples
Post-Digestion Spike	85-115 % Recovery	For each digested MS.
Duplicate Sample (digested)	RPD ≤ 20 % for sample values ≥ 5x RL; for sample values < 5x RL, control limit = RL	Two for every 32 samples.

For sample analysis conducted by the GCRD Metals Laboratory for Rare Earth Elements (for dissolved elements using K-GCRD-SOP-1158-0) the QC samples and acceptance criteria for water samples analyzed are listed in Table 12.

Table 12. GCRD Laboratory QC Requirements for REE Analysis.

QC Type or Operation	**Acceptance Criterion**	**Frequency**
Instrument Calibration	Acceptance criterion not given due to use of forced zero.	Daily before sample analysis.
Initial Calibration Verification (ICV)	90-110 % Recovery	Following instrument calibration for each mass used.
Initial Calibration Blank (ICB)	$\leq$ RL	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification (CCV)	90-110 % Recovery	For each mass used, at a frequency of at least after the ICV, every 10 samples, and at the end of each run.
Low Level Quantitation Limit Standard (LLQLS) at the RL or QL	70-130 % Recovery	At the beginning of the run.
Continuing Calibration Blank (CCB)	$\leq$ RL	At a frequency of at least after every 10 sample, and at the end of each run. Performed immediately after the last CCV.
Interference Check Samples (ICS1, ICS2, and ICS3)	80-120 % Recovery of primary elements (Pr, Nd, Eu, Sm, Gd, and Tb) ICS1: Eu < RL ICS2: Gd(Pr), Tb(Nd), Er(Nd), and Tm(Eu) < RL ICS3: Dy(Sm), Ho(Sm), Er(Gd), and Lu(Tb) < RL	At the end of the run.
Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 50 above the RL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10 % of the original determination after correction for dilution.	Every 20 samples.
Preparation or Method Blank (MB)	$\leq$ RL	Every 20 samples.
Laboratory Control Sample (LCS)	85-115 % Recovery	Every 20 samples.
Matrix Spike (MS) digested	70-130 % Recovery (Recovery calculations are not required if concentration of the spiked analyte < 30 % of the native analyte concentration.)	Every 20 samples.

QC Type or Operation	Acceptance Criterion	Frequency
Post-Digestion Spike	70-130 % Recovery	One for each pre-digestion Matrix Spike.
Matrix Spike (MS) undigested	70-130 % Recovery (Recovery calculations are not required if concentration of the spiked analyte < 30 % of the native analyte concentration.)	At least 2 samples per every 20 samples.
Duplicate Sample digested	RPD $\leq$ 20 % for sample values $\geq$ 5x RL Or, limits are +/-RL for sample values < 5x RL	Every 20 samples.
Duplicate Sample undigested	RPD $\leq$ 15 % for sample values $\geq$ 5x RL Or, limits are +/- RL for sample values < 5x RL	At least 2 samples per every 20 samples.
HR-ICP-MS Tune	Low resolution mass signal must be > 3x10^{6} cps for ^{7}Li, 2.5x10^{7} cps for ^{115}In, and 2.5x10^{6} cps for ^{238}U. The %RSD <2.5 % for ^{238}U. Medium resolution mass resolution between Fe and ArO is > 4000. High resolution mass resolution between K and ArH > 9000.	Prior to calibration
Internal Standards	The absolute response of the internal standard in a sample must not be < 60 % or > 125 % of the response in the calibration standard.	Internal standard shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

For sample analysis conducted by the GCRD Contract Laboratory for VOCs (for VOCs using K-GCRD-SOP-3445-0) the QC samples and acceptance criteria for water samples analyzed are listed in Table 13.

Table 13. QC requirements for VOC analysis.

QC Type	Acceptance Criteria	Frequency
Instrument Performance Check	Meet ion ratio criteria for p-bromofluorobenzene (8260 c/D).	Prior to initial calibration; beginning and end of the sample que, and after every 20 samples.
Water Blank	No target analytes are found in the method blank.	At the beginning of the sample que before the method blank.
Initial Calibration (ICAL)	For linear or quadratic regression model: $R^2 \geq 0.99$; Lower standard (LLOQC) recalculation (refit) is	Prior to analyzing samples, and as needed if continuing performance criteria cannot be met

QC Type	Acceptance Criteria	Frequency
	within ± 50% of true value; other standards > LLOQ withing ± 30% of the true value.	
Second Source Verification (SSV)	Calculated concentration of target analytes are with in ± 20% of expected value.	After each initial calibration and prior to analyzing samples (after the CCV at beginning of que.
Continuing Calibration Verification (CCV)	Calculated concentration of target analytes are with in ± 20% of expected values.	Following the method blank, every 20 samples and end of each sample que. (At least one CCV should be same concentration as the MS to allow for comparison).
Method Blank (MB)	Target analyte concentrations in MB < ½ LLOQ or ≤ 10% of concentration found in field blanks.	Analyze a MB at the beginning and end of sample que, and after every 20 samples.
Lab Duplicate (LD) of a sample	RPD < 20% when the calculated concentration is > 5*QL.	One per each set of 20 samples.
Matrix Spike (MS) of a sample	%R of spiked compounds should be in the range of 70 – 130%.	One per each set of 20 samples.
Laboratory Control Spike (LCS)	%R of spiked compounds should be in the range of 70 – 130%.	Along with the MS and MSD (at least one CCV should be at same concentration as MS to allow for comparison).
Surrogate (Sur) Standards	%R of Sur peak area should be in the range of ± 20% compared to response ratios in IS/Sur in the initial calibration standards.	Every HS vial except the WB. A control chart of the Sur %R is plotted for all analyzed standards and samples.
Internal Standard (IS)	IS peak area should be -50% to +100% of average peak areas found in the initial calibration standards	Every HS vial except WB. A control chart of the % change of the IS peak area is plotted for all analyzed standards and samples
Performance Evaluation (PE) Sample	Quantitative values should be within acceptance range specified by PE vendor.	Before SOP is approved and biannually.

For sample analysis conducted by the GCRD Metals Laboratory for Strontium Isotopes (for using K-GCRD-SOP-xxxx-x, under development) the QC samples and acceptance criteria for water samples analyzed are listed in Table 14.

Table 14. QC requirements for Strontium isotope analysis.

QC Type	Acceptance Criteria	Frequency
TBD	TBD	TBD

For sample analysis conducted by the GCRD Metals Laboratory for Mercury analysis (for using K-GCRD-SOP-xxxx-x, under development) the QC samples and acceptance criteria for water samples analyzed are listed in Table 15

Table 15. QC requirements for Mercury analysis.

QC Type	Acceptance Criteria	Frequency
TBD	TBD	TBD

For sample analysis conducted by the GCRD Metals Laboratory for Sulfur Isotope analysis (for using K-GCRD-SOP-3830-0) the QC samples and acceptance criteria for water samples analyzed are listed in Table 16.

Table 16. QC requirements for Sulfur Isotope analysis.

QC Type	Acceptance Criteria	Frequency
Blanks	Mass 64 and mass 66 responses will be 50 mV or less.	At beginning and end of each sequence.
Calibration verification	The difference between the true and measured $\delta^{34}S \leq 0.5‰$.	In the middle and end of sample sequence.
Sample Duplicates	The difference between the mean value of the original and duplicate sample ≤ 0.5‰.	Every 10 samples.

Soil/sediment samples for X-ray diffraction will follow the methods outlined in K-GCRD-1107-1 and the QA/QC outlined in this SOP. The performance of the diffractometer will be evaluated on a quarterly basis by collecting a silicon powder (SRM 640b) diffraction pattern. The Si (111) peaks centroid has a reported position of 35.965 °2θ. The acceptance criteria is a peak position within ± 0.02 °2θ. If the acceptance criterion is not met, then the goniometer will need to be realigned.

For soil/sediment sample analysis preformed at GCRD the QC samples, and acceptance criteria for are listed in Table 17.

Table 17. QC requirements for soil/sediment analysis.

Analyte	**Blanks (Frequency)**	**Calibration Checks AC* (Frequency)**	**Second Source Standard AC (Frequency)**	**Lab Duplicates AC (Frequency)**	**Matrix Spikes AC (Frequency)**
pH	NA	≤0.5 pH units (After calibration; Every 10 samples; at the end of analysis)	≤0.5 pH units (At beginning of a batch of samples)	≤0.5 pH units (After calibration; Every 10 samples)	NA
pH, 0.01 M $CaCl_2$	NA	≤0.5 pH units (After calibration; Every 10 samples; at the end of analysis)	≤0.5 pH units (At beginning of a batch of samples)	≤0.5 pH units (After calibration; Every 10 samples)	NA
Electrical Conductivity	NA	± 10% of calibration Standard (After calibration; Every 10 samples; at the end of analysis)	± 10% of second Source Standard (At beginning of a batch of samples)	RPD ≤ 30 % (After calibration and every 10 samples thereafter)	NA

*AC = Acceptance Criteria

B.4.2 Additional QA objectives

The computer program AqQA (RockWare Inc., version 1.1.1) will be used as a check on the quality of solute concentration data. The method will be to calculate the charge balance for each solution. This is done by summing and comparing the net positive and negative charge from the measured concentrations of anions and cations. The agreement should be within 15%. Poor agreement would suggest that some major solute(s) is not accounted for in the analytical measurements. At the discretion of the PL, discrepancies in this manner will be either flagged or the identity of other sample components and/or reason(s) for poor agreement will be investigated.

SECTION C – ASSESSMENT AND OVERSIGHT

C.1 Assessments and Response Actions

For QA Category B projects, QA audits are conducted at the discretion of management and/or the QA Manager. QA audits will be conducted in accordance with ORD QA Policy titled *Audits of Technical and Quality Systems*.

Draft publications resulting from this project will undergo ORD clearance in STICS prior to dissemination as required by ORD Policy titled *ORD Clearance Policy and Procedures* and CESER SOP titled *Standard Operating Procedure for Product Clearance*.

C.2 Reports to Management

Results of QA audits will be reported in accordance with ORD QA Policy titled *Audits of Technical and Quality Systems*. Implementation of corrective actions for audit findings will be verified by the QA Manager, and status of implementation tracked through closure.

Required approvals for draft publications undergoing ORD clearance is documented in STICS.

SECTION D – DATA VALIDATION AND USABILITY

D.1 Data Review and Verification

The PLs is responsible for maintaining data files, including their security and integrity. All files (both electronic and hard copy) will be labeled such that it is evident that they are for this project. This will be done in accordance with the ORD PPM 13.2, *Scientific Recordkeeping: Paper, ORD PPM 13.6, Scientific Recordkeeping: Electronic,* as well as EPA Records Schedule 1035, *Environmental Programs and Projects*.

Data will be submitted to the PLs as either hard copies (field notes), or electronically (laboratory data) on CD or DVD or via email. Data in hard copy form will be entered into Excel spreadsheets on the PLs computer or designated staff. The data will be saved on a local server. The local server is automatically backed up nightly. The PLs, technicians, post-docs, or students will conduct this task. Data will be spot-checked by the PLs to ensure accuracy. If errors are detected during spot-checks, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100 % check of the data set being entered at that time if multiple errors are found.

Data in electronic form shall be electronically transferred to the spreadsheets. Data will be spot-checked by the PLs to ensure accuracy of the transfer. If errors are detected during the spot-check, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100 % check of the data set if multiple errors are found.

An Excel workbook consisting of multiple spreadsheets will be compiled for each sampling round. A standard format for the Excel spreadsheets will be developed for all of data. The Excel spreadsheets will be utilized as the electronic data deliverable (EDD) for downloading the data into a database if needed.

Criteria that will be used to accept, reject, or qualify data will include specifications presented in this QAPP, including the methods used and the measurement performance criteria presented in Tables 7-16. In addition, sample preservation and holding times will be evaluated against requirements provided in Table 6.

D.1.1 % Recovery or Accuracy

$$\%\mathrm{REC}=\frac{\mathrm{m}}{\mathrm{n}}\times 100$$

Where m = measurement result

n = True Value (a certified or known value) of standard or reference

D.1.2 Precision

Precision is described by Relative Percent Difference (RPD) as previously defined. The Relative Percent Difference (RPD) is calculated based on the following:

$$\text{RPD}=\frac{2(\text{a-b})}{\text{a+b}}\times 100$$

where, a = sample measurement and b = duplicate sample measurement and a > b.

For duplicate samples collected in the field, the RPD will only be calculated where analyte concentrations for both samples (primary and duplicate) are >5 times the quantitation level. RPDs are expected to be less than or equal to 30%. If RPDs are greater than 30%, actions will be taken to better understand the reason and data will be flagged. The duplicate samples will be used for the purposes of determining reproducibility. In all cases, results reported in prepared reports or publications will be based on the primary sample. Results for duplicate samples will be reported in QA appendices or supporting material. Analytes detected in various blank samples will be evaluated and flagged, if appropriate, in presentations of data. Generally, blank contamination will be evaluated for significance when blank contaminants are above reporting limits. Samples will be flagged if their concentrations are less than 10 times that in the associated blank and greater than the QL.

D.1.3 Matrix Spike Recovery

Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results.

$$\%\text{Recovery}=\frac{\text{spiked sample concentration-native sample concentration}}{\text{spiked sample concentration}}\times 100$$

D.1.4 Data Validation

Data validation will consist of initial and final review of data. Initial review will include continuous oversight during field collection and lab analysis of data by the PL to avoid common transcription errors associated with recording of data. Final review will include evaluation of all collected data for suitability in data interpretation. It will include but is not limited to the following activities: (1) assessment of data completeness, (2) review of logbooks and forms used for data logging, and (3) review of calibration and standard checks.

Data reports are reviewed by the PL for completeness, correctness, and conformance with QAPP requirements. All sample results are verified by the PL to ensure they meet project requirements as defined in the QAPP and any data not meeting these requirements are appropriately qualified in the data summary prepared by the PL. See Table 17 for the Data Qualifiers. The Contract

Laboratory Program guidelines on organic methods data review (USEPA, 2008) is used as guidance in application of data qualifiers.

D.2 Verification Methods

Data verification will evaluate data at the data set level for completeness, correctness, and conformance with the method. Data verification will be done by those generating the data. This will begin with the analysts in the laboratory and the personnel in the field conducting field measurements, monitoring the results in real-time or near real-time. For the GCRD Labs at RSKERC, data verification includes peer analysts in the labs and the team leader. The GCRD Labs process goes beyond the verification level, as they also evaluate the data at the analyte and sample level by evaluating the results of the QC checks against the SOP performance criteria. For field measurements, the PL will verify the field data collected to ensure they meet requirements as defined in the QAPP.

Table 18. Data qualifiers

Qualifier	Definition
U	The analyte was analyzed for but was not detected above the reported quantitation limit (QL).
J	The analyte was positively identified. The associated numerical value is the approximate concentration of the analyte in the sample (due either to the quality of the data generated because certain quality control criteria were not met, or the concentration of the analyte was below the QL).
B	The analyte is found in a blank sample above the QL and the concentration found in the sample is less than 10 times the concentration found in the blank.
H	The sample was prepared or analyzed beyond the specified holding time. Sample results may be biased low.
*	Relative percent difference of a field or lab duplicate is outside acceptance criteria.
R	The data are unusable. The sample results are rejected due to serious deficiencies in the ability to analyze the sample and/or meet quality control criteria. Sample results are not reported. The analyte may or may not be present in the sample.
Data Descriptors	
Descriptor	**Definition**
NR	Not Reported by Laboratory or Field Sampling Team
NS	Not Sampled
Note:	If the analyte concentration was less than the Quantitation Limit (<QL), then the B qualifier was not applied.
	If both an analyte and an associated blank concentration are between the MDL and QL, then the sample results are reported as <QL and qualified with U.

D.3 Reconciliation with User Requirements

The PL shall analyze the data, as presented below. Depending on the data collected additional analysis may be added at a later date. The PL shall use the results from the data verification and validation process to assess whether or not the data quality has met project requirements and thereby the user requirements.

For concentration data below the MDL, a value of ½ the MDL will be used. However, this approach should only be followed in cases where detections above the MDL are available for 50 % or more of the concentration values in a data series to be used for calculating statistical parameters (USEPA, 2010). This guideline will be followed, and any exceptions will be noted.

Analysis of primary and secondary data will also be carried out using the Geochemist's Workbench software package. Geochemical calculations will be performed to estimate the saturation state of ground water and surface water with respect to naturally occurring minerals (e.g., calcite, gypsum). The software is analogous to other packages (e.g., MinteqA2 and Phreeq-C). Major ion data (e.g., Ca, Mg, Na, K, Cl, SO_4, HCO_3, pH) and temperature are entered into a user interface. The software uses the Debye-Hückel equation to estimate ion activity coefficients and a selectable thermodynamic database in order to calculate mineral saturation indices for minerals that may be undersaturated, at equilibrium, or oversaturated in the prescribed system (Bethke, 1996). The Lawrence Livermore National Laboratory database (thermo.com.v8.r6) will be used for calculating aqueous speciation and mineral saturation. This software may also be used to construct activity-activity diagrams, such as Eh-pH diagrams. Such diagrams can be helpful in describing processes that impact the concentration of redox-sensitive elements, like iron and manganese.

Geostatistics can be used to aid in the understanding of geospatial distributions of parameters measured during the study. Geostatistical analysis will be accomplished using Rockworks, GS+ or other appropriate software packages. The geospatial distributions can be overlaid onto GIS software such as Arc GIS or Google Earth.

Statistical calculations, such as determinations of the mean, median, and standard deviation will be carried out using MS Excel, SYSTAT software, or Statistica software packages using standard statistical methods. The descriptive statistics could be used in summary tables or could be used on graphical projections of the data. Additional parametric or nonparametric summary statistics could be reported depending on the data distribution that will need to be determined after several data collection events. These additional summary statistics, if needed, will be added at a later date.

Statistical calculations, such as analysis of variance and other non-parametric tests will be carried out using MS Excel, SYSTAT, ProUCL, Statistica or similar software packages using standard statistical methods. Statistical significance will be determined once several data sets have been collected and the data distribution is better understood. It is likely that the level of significance will be either $\alpha = 0.05$ or $\alpha = 0.10$. In addition, several statistical methods for determining geogenic background and showing differences between geogenic background have been proposed by Matschullat et al. (2000) and Reimann et al. (2008). These methods include 2σ, iterative 2σ, 4σ outlier test, calculated distribution function, and the inflection point methods. These techniques could potentially be used in this project.

REFERENCES

Aller, L., T.W. Bennett, G. Hackett, R.J. Petty, J.H. Lehr, H. Sedoris, D.M Nielsen, and J.E. Denne, 1991. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells, EPA/600/4-89/034-REV. U.S. Environmental Protection Agency, Las Vegas, NV.

American Society of Testing and Materials (ASTM), 1998. Standard Test Method D 4101 (Analytical Procedure) for Determining Transmissivity of Nonleaky Confined Aquifers by Overdamped Well Response to Instantaneous Change in Head (Slug Tests). In the Annual Book of ASTM Standards Vol. 04.08 Soil and Rock (I): D420 4914. ASTM, West Conshohocken, PA.

American Society of Testing and Materials (ASTM), 1999a. Standard D 5521 Guide for Development of Ground-Water Monitoring Wells in Granular Aquifers. In the Annual Book of ASTM Standards Vol. 04.09 Soil and Rock (II): D 4943 - latest; Geosynthetics. ASTM, West Conshohocken, PA.

Beljin, M., R. Ross, and S. Acree, 2014. 3PE: A Tool for Estimating Groundwater Flow Vectors. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-14/273, 2014.

Fendorf, S. and Sparks, D.L. 1996. X-ray absorption fine structure spectroscopy. In: Methods of Soil Analysis, Part 3- Chemical Methods. Soil Science Society of America. Madison. 377-416.

Gee, G.W. and Or, D. 2002, Particle–size analysis, in Methods of Soil Analysis Part 4-Physical Methods, Soil Science Society of America, Inc., Madison, Wisconsin, USA.

Halihan, T., J. Puckette, M. Sample, and M. Riley, 2009, Electrical resistivity imaging of the Arbuckle-Simpson aquifer: Final report submitted to the Oklahoma Water Resources Board, Oklahoma State University School of Geology, 92 p.

Johnston, C.T.; and Aochi, Y.O. 1996. Fourier Transform Infrared and Raman Spectroscopy. In: Methods of Soil Analysis, Part 3- Chemical Methods. Soil Science Society of America. Madison. 269-322.

K-GCRD-SOP-1089-4. Total Nitric Acid Extractable Metals from Aqueous Samples by Microwave Digestion. 15 p.

K-GCRD-SOP-1090-5. Standard Operating Procedure for Total Nitric Acid Extractable Metals from Solids and Sludges by Microwave Digestion. 11 p.

K-GCRD-SOP-1092-1. Standard Operating Procedure for Estimation of Hydraulic Conductivity Distribution Using the Tisco/Quantum Engineering (Tisco/QE) Electromagnetic Borehole Flowmeter. 12p.

K-GCRD-1097-2. Determination of Iodide in Water Samples Using 0.2 M Potassium Hydroxide Carrier with Lachat Flow Injection Analysis, 11 pp.

K-GCRD-SOP-1103-1. Standard Operating Procedure for Performance of Slug Tests in Saturated Porous Media Using Pneumatic Techniques. 9p.

K-GCRD-SOP-1104-1. Standard Operating Procedure for Performance of Slug Tests in Saturated Porous Media Using Solid Slugs. 8p.

K-GCRD-1107-1. SOP for X-ray Diffraction Analysis Using the Rigaku Miniflex Diffractometer. 18 p.

K-GCRD-SOP-1134-0. Water Level Monitoring Using Automated Pressure Transducer/Data Loggers.

K-GCRD-SOP-1137-0. Determination of Stable Hydrogen and Oxygen Isotope Ratios in Water Samples using a Picarro L2120i Cavity Ring-Down Spectrometer (CRDS), 30 pp.

K-TSCD-SOP-1139-0. SOP for Electrical Resistivity Field Data Acquisition. 9 p.

K-GCRD-SOP-1146-1. GCRD In-House Soil/Sediment Tracking System: Collecting/Receiving Domestic Soil, Storing Domestic Soil, and Transferring/Disposing of Domestic soil. 31 p.

K-GCRD-SOP-1151-0. GWERD SOP for Quality Control Procedures for General Parameters Analyses Using Lachat Flow Injection Analyzers (FIA), 12 p.

K-GCRD-SOP-1152-1. Sample Receipt and Log-in Procedures for GWERD, Ada, OK, 10 p.

K-GCRD-SOP-1154-0. Standard Operating Procedure for Operation of the Perkin Elmer Optima 8300 DV ICP-OES. 90 p.

K-GCRD-SOP-1156-0. SOP for Operation of the Thermo Scientific Element XR HR-ICP-MS. 42 p.

K-TSCD-SOP-1157-0. Data Acquisition with the Downhole Induction Logging Tool. 12 p.

K-GCRD-SOP-1158-0. SOP for the Determination of Rare Earth Elements using HR-ICP-MS. 39 p.

K-GCRD-SOP-1159-0. SOP for Low Flow Sampling of Ground Water. 14 p.

K-GCRD-SOP-1165-0. Determination of Various Fractions of Carbon in Aqueous Samples Using the Shimadzu TOC-VCPH Analyzer. 15 p.

K-GCRD-SOP-1745-0. Standard Operating Procedure for Operation of the TESCAN Vega3 Scanning Electron Microscope and Element EDAX Energy-Dispersive X-Ray Spectrometer. 19 p.

K-GCRD-SOP-3329-0. SOP for the Determination of Inorganic Anions in Aqueous Samples Using the Dionex ICS-2100 Ion Chromatography System. 21 p.

K-GCRD-SOP-3445-0. Determination of Volatile Organic Compounds (Fuel Oxygenates, Aromatic, and Halogenated Hydrocarbons) in Water using Automated Headspace GC/MS. 51 p.

Moore, M.M. and Reynolds, Jr., R.C. 1997. X-ray diffraction and the identification and analysis of clay minerals. Oxford University Press, Inc. Oxford. 378p.

Nelson, D.W. and Sommers, L.E. 1996. Total carbon, organic carbon and organic matter. In: Methods of Soil Analysis, Part 3- Chemical Methods. Soil Science Society of America, Madison. 961-1010.

Rhoades, J.D. 1996. Salinity: Electrical Conductivity and Total Dissolved Solids. In: Methods of Soil Analysis, Part 3- Chemical Methods. Soil Science Society of America, Madison. 417-436.

K-IO-SOP-1260-1. Field Analytical QA/QC.9 p.

Standard Method 3500-Fe B Fe Iron (Colorimetric). Standard Methods for the Examination of Water and Wastewater.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, 4500-N Nitrogen, pp 4-99- 4-100.

Standard Method 4500-S^{2-}D for Wastewater. Standard Methods for the Examination of Water and Wastewater.

Sumner, M.E. and Miller, W.P. 1996. Cation exchange capacity and exchange coefficients. In: Methods of Soil Analysis, Part 3- Chemical Methods. Soil Society of America. Madison. 1201-1230.

Thomas, G.W. 1996. Soil pH and soil acidity. In: Methods of Soil Analysis, Part 3- Chemical Methods. Soil Society of America. Madison. 475-490.

U.S. Department of the Interior, Bureau of Reclamation. Water Measurement Manual. 1997. 3ed.

U.S. Environmental Protection Agency (US EPA) Method 360.1 (1971). Oxygen, Dissolved (Membrane Electrode), 2 pp.

U.S. Environmental Protection Agency Method 170.1 (1974). Temperature, 1 pp.

U.S. Environmental Protection Agency Method 310.1 (1978). Alkalinity (Titrimetric, pH 4.5), 3 pp.

U.S. Environmental Protection Agency Method 353.1 (1978). Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Hydrazine Reduction), 5 pp.

U.S. Environmental Protection Agency Method 120.1 (1982). Conductance (Specific Conductance, umhos at 25°C), 3 pp.

U.S. Environmental Protection Agency Method 150.2 (1982). pH, Continuous Monitoring (Electrometric), 3 pp.

U.S. Environmental Protection Agency Method 180.1 (1993). Determination of Turbidity by Nephelometry, 10 pp.

U.S. Environmental Protection Agency Method 350.1 (1993b). Determination of Ammonia Nitrogen by Semi-Automated Colorimetry, 15 pp.

U.S. Environmental Protection Agency Method 200.7 (1994). Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, 58 pp.

U.S. Environmental Protection Agency Method 200.8 (1994). Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry, 57 pp.

U.S. Environmental Protection Agency Method 9060a (2004). Total Organic Carbon, 5 pp.

U.S. Environmental Protection Agency (2013). ProUCL, Version 5.0.00. U.S. Environmental Protection Agency, Atlanta, GA

U.S. Environmental Protection Agency (2013), ProUCL Version 5.0.00 User Guide, EPA/600/R-07/041, 2013. http://www.epa.gov/osp/hstl/tsc/ProUCL_v5.0_user.pdf

REVISION HISTORY

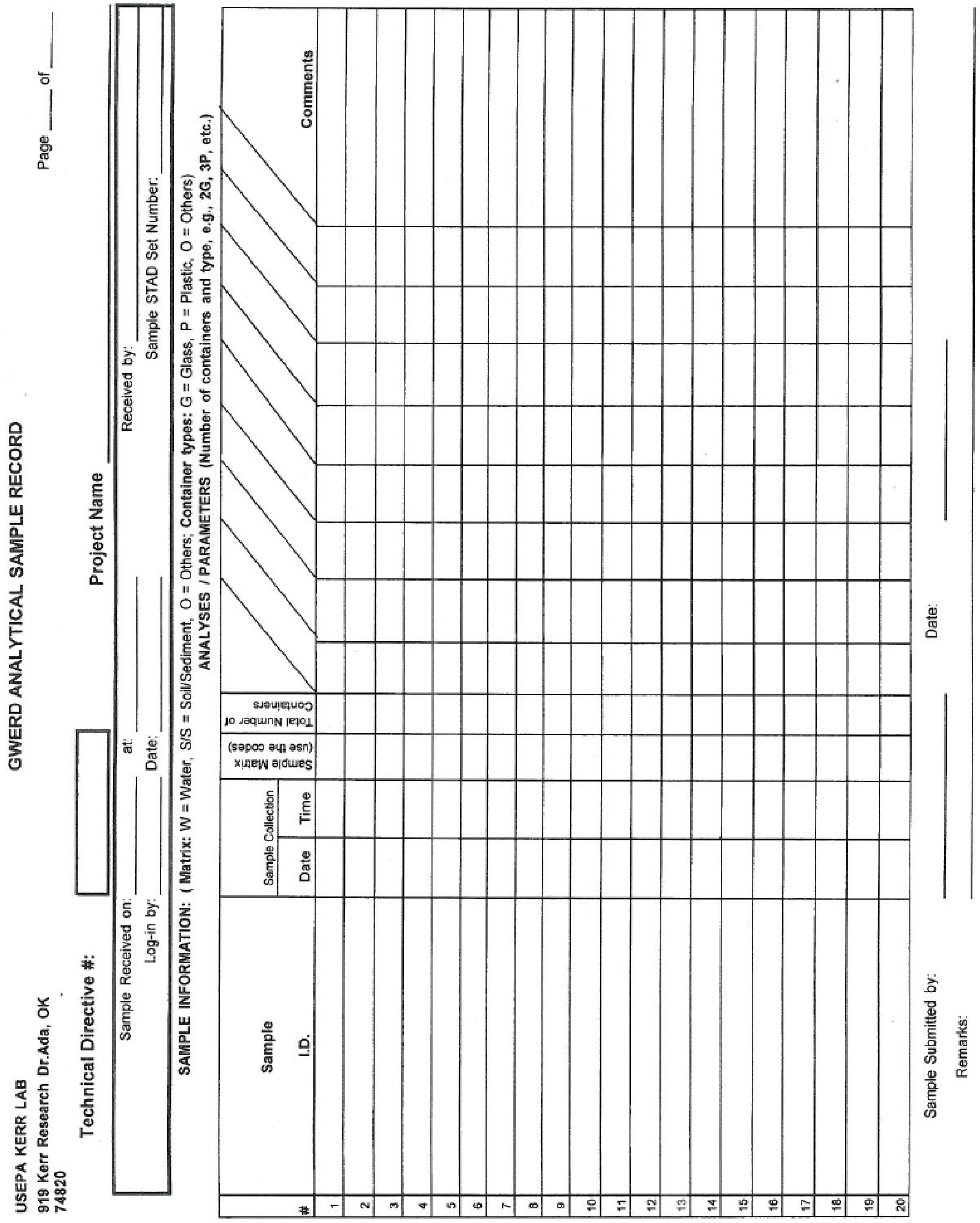
Revision #	Description	Effective Date
0	Initial Version	Date of Approval

Attachment 1. Groundwater Purge Log Form.

Project			
Sample ID		Date	
Pump Placement Depth (Generally MW or GW wells) (ft)			
Initial Water Level		Final Water Level	
Start Purge Time		Purge Rate	
End of Purge Time		Pump Off Time	
Weather Conditions			

Time	**Temp (ºC)**	**Specific Conductivity (mS/cm) [≤ 1 %/ min]**	**TDS (g/L)**	**DO (mg/L) [≤ 0.25 mg/L/ min]**	**pH [≤ 0.02 pH Units/ min]**	**ORP (mV) [≤ 1 mV/ min]**	**Comments**

Attachment 2. Analytical Service Request Form



USEPA KERR LAB
919 Kerr Research Dr.Ada, OK
74820

GWERD ANALYTICAL SAMPLE RECORD

Page ______ of ______

Technical Directive #:

Project Name ______________

Sample Received on: ______________ at: ______________ Received by: ______________

Log-in by: ______________ Date: ______________ Sample STAD Set Number: ______________

SAMPLE INFORMATION: (Matrix: W = Water, S/S = Soil/Sediment, O = Others; **Container types:** G = Glass, P = Plastic, O = Others)

ANALYSES / PARAMETERS (Number of containers and type, e.g., 2G, 3P, etc.)

#	Sample I.D.	Sample Collection Date	Sample Collection Time	Sample Matrix (use the codes)	Total Number of Containers									Comments
1														
2														
3														
4														
5														
6														
7														
8														
9														
10														
11														
12														
13														
14														
15														
16														
17														
18														
19														
20														

Sample Submitted by: ______________ Date: ______________

Remarks: ______________

Document C-2: K-GCRD-SOP-3756-1: SOP for Electrical Resistivity Field Data Acquisition for Subsurface Investigations

CESER

Standard Operating Procedure (SOP)

Title:	**Standard Operating Procedures for Electrical Resistivity Field Data Acquisition for Subsurface Investigations**
Applicable To: **[*CESER-Wide, Division or Staff*]**	GCRD/Field Staff
SOP Number:	**K-GCRD-SOP-3576-1**
Former SOP Number: (if applicable)	G-GWERD-SOP-3576-0
Effective Date:[1]	Date of Management Approval
SOP Author(s)	
Primary Author (Must be EPA employee) (Name/Affiliation): Randall Ross/EPA/ORD/CESER/TSCED	
Author (Name/Affiliation): Jon Fields/EPA/ORD/CESER/GCRD	
Author (Name/Affiliation):	
Author (Name/Affiliation):	
Author (Name/Affiliation):	
QA Approval	
Name: Mustafa Bob	Signature/Date: Bob, Mustafa Digitally signed by Bob, Mustafa Date: 2021.10.20 09:54:45 -05'00'
SHEM Approval	
Name: Jennifer Tant	Signature/Date. JENNIFER TANT Digitally signed by JENNIFER TANT Date: 2021.10.20 07:48:04 -04'00'

Management Approval	
Name: Ann Keeley	Signature/Date: AZADEH AZADPOUR-KEELEY Digitally signed by AZADEH AZADPOUR-KEELEY Date: 2021.10.20 10:13:39 -05'00'

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[1] The effective date of the SOP is the date of management approval unless otherwise specified.

Table of Contents

1 INTRODUCTION

This SOP documents field procedures for data acquisition using the GCRD Electrical Resistivity Imaging (ERI) system consisting of the Advanced Geoscience, Inc (AGI) SuperSting™ R8/IP Earth Resistivity System (SuperSting) and PowerSting External High-Power Transmitters.

The ERI method is used to measure the electrical resistivity of the subsurface. There are several variations of the method but the basic ERI measurement requires four grounded electrodes. Two of the electrodes form a dipole used to inject low frequency alternating electrical current into the ground. The other two electrodes form a second dipole used to measure the resulting electric field (Figure 1). Various combinations of electrode positions enable the user to image the subsurface based on geometric principles. For example, greater depths of investigation are achieved by increasing the distance between electrodes, but it bears mentioning that resolution generally decreases with increasing depth of investigation. There are no theoretical limits on the maximum depth of investigation for ERI but in practice the method is most appropriate for imaging of depths of a few hundred meters or less. The tutorial written by Loke (2010) provides a detailed description of the electrical resistivity method and was used in the preparation of this document. Figure 2 provides a diagram of equipment typically used for performing ERI.

The electric field measured at the Earth's surface is distorted by subsurface regions containing anomalous bodies or strata of differing conductivities. ERI measurements are especially sensitive to saturated pore spaces. With the exception of conductive rock such as ore bodies, most earth materials in the near surface under dry conditions are typically resistive; therefore, propagation of current in the shallow subsurface is primarily achieved via movements of ions within the pore water. For this reason, ERI data are often useful for groundwater and environmental applications. ERI techniques can also potentially provide information for general site characterization, such as the depth and attitude of geological contacts and faults. Like other geophysical techniques, ERI produces non-unique results. Resistivity measurements should be used in conjunction with data acquired via boreholes and monitoring wells. Resistivity results may also be integrated with data from other geophysical methods. There are many case study and theoretical papers detailing various aspects of the electrical resistivity available in the scientific literature. Specific papers used in preparing this document include Miller, et al (2008), Zonge, et al. (2005), Zhou, et al. (2001), Ramirez, et al. (1995) and Lane, et al. (1995).

2 SCOPE

This SOP has been prepared for the GCRD field staff to use the GCRD Electrical Resistivity Imaging system, the AGI SuperSting™, R8/IP. It is a weatherproof, ruggedized instrument for earth resistivity and induced polarization (IP) field work. This SOP does not include IP. The implementation of this SOP will ensure that the data collected by the ERI technician will be of adequate quality and provide information on materials encountered in the subsurface. This SOP documents field procedures for acquisition of electrical resistivity data using galvanically-coupled electrodes. In general, the data collected will be used to better understand subsurface stratigraphy and identify potential preferential pathways that may impact groundwater flow and contaminant transport. Depth of investigation for GCRD's ERI system is approximately 64 meters using the 5-meter electrode spaced cables.

This procedure is based on the American Society of Testing and Materials (ASTM) standard guide describing the usage of this type of geophysical testing including Standard G57-06 (2006), Standard D6431-99 (2010), and Standard D6429-99 (2006). This method of geophysical imaging is commonly referred to as direct current (DC) resistivity, electrical resistance tomography (ERT), electrical resistivity imaging (ERI), or simply as the resistivity method. For the purposes of this document, the method will be referred to as ERI. Procedures for detailed analysis and modeling/imaging of electrical resistivity data are not within the scope of this document.

3 DEFINITIONS

Term	**Definition**
Resistivity (Res)	The property of a material that resists the flow of electric current, Ohm-M (ASTM D6431-99, 2010)
Electrode	Stainless steel rod in direct contact with soil through which electrical current is injected and/or measured
ERI	Electrical Resistance Imaging
ERT	Electrical Resistance Tomography
IP	Induced Polarization

4 ROLES AND RESPONSIBILITIES

This SOP applies to all GCRD field staff for use of the GCRD ERI system. Only personnel that have been properly trained on the safe operation of the ERI system (i.e., ERI technician) will be permitted to operate the system. The ERI technician is responsible for ensuring that the procedures of this SOP are followed by all personnel. All personnel performing these procedures must have a complete understanding of the operation of the SuperSting™ instrument, the SuperSting Manual, the procedures described within this SOP, and receive specific training regarding these procedures. Personnel receiving training must demonstrate competency performing this procedure before they can acquire data independently. This may be done by the trainer observing the trainee’s operation of the system and data collection. Competency must be documented by the trainer using the ORD Certification Statement for Demonstration of Capability form available at https://intranet.ord.epa.gov/quality-assurance/qa-forms.

5 PROCEDURES

5.1 Method Summary

Prior to conducting the ERI investigation, a survey plan should be developed. If buried utilities are suspected, then these should be flagged at the site by the appropriate authorities. Known interferences should be identified, such as metal fences and power lines. Locating these on a map prior to the investigation will allow for efficient use of time while on site. On the day of the ERI investigation, the layout of the map can be confirmed, and the survey plan can be finalized. The instrument is set up and electrodes are inserted into the ground at planned locations. Cables are attached to the electrodes and instrument. Contact resistance is checked before beginning the measurements. Once this first survey transect is complete, the cables and electrodes are moved to the next survey transect location. This is repeated until the on-site data acquisition is completed. Data is saved to another device, such as a thumb drive, and returned to the laboratory for analysis.

5.2 Sample Preservation, Containers, Handling, and Storage

No physical samples are collected, preserved, contained, handled, or stored with this geophysical tool.

5.3 Health and Safety Precautions

Consult the EPA Cincinnati/Ada Field Safety Manual for additional information. All staff should read, understand, and sign the project specific HASP for necessary safety information prior to performing any field work.

1. Electrical resistivity equipment is designed to deliver electrical current at high voltages and presents an electrocution hazard to workers and bystanders. All personnel on site shall be informed of these potential hazards.
2. Always use a "Danger High Voltage" warning cover on each electrode.
3. During data acquisition, assume all electrodes are "hot" and never touch electrodes or wires while measurements are being made.
4. Use safe practices when setting up the survey transect by following this sequence:
    a. Place any metal electrodes (stakes, aluminum foil or any sheet metal) into the ground before laying out the electrode cable.
    b. Place the electrode switch/take-out on the stake, without touching any metal.
    c. Once the switch/take-out is in contact with the stake, attach the switch/take-out with the stainless-steel spring.
    d. This procedure ensures that the electrode take-out is grounded as you attach the take-out to the stake.
5. If batteries are used to power the equipment, it is preferable to use gel-cell or sealed batteries and to store all batteries in vented non-conductive (e.g. plastic) containers.
6. Personal protective equipment and procedures, as defined in the site-specific health & safety plan, should be used at all sites.
7. All researchers using the SuperSting system shall receive electrical safety training compliant with 29 CFR 1910.332 as well as instrument specific training.

5.4 Interferences

- Overhead powerlines.
- Buried Powerlines or pipelines
- Cathodically protected structures
- Other grounded metallic objects (e.g. above ground pipelines, fences)
- Anisotropy of the subsurface geologic structure
- Electrical storms
- Heavy rain and/or snow

Buried utilities shall be located by the appropriate authorities prior to the ERI survey. If possible, to minimize interference, lay out the survey transect perpendicular to linear interference sources, such as metal fences or pipelines. Do not conduct ERI surveys during electrical storms. Heavy rain will affect surveys resulting in a noisy image as the water percolates through the subsurface. Wait a at least a day after heavy rains to conduct a survey.

5.5 Reagents and Supplies

- Tape measure (meters)
- Electrical tape
- Hammer
- Field notebook and pen
- Assorted hand tools
- Salt water
- Fuel for generator

5.6 Equipment/Apparatus

- SuperSting R8 Control box
- Switch box
- 4 each, 16 electrode cables or 4 each, 14 electrode cables or 2 each, 28 electrode cables, depending on the application
- Connector cables for multielectrode cables (e.g., connect high and low ends of electrode cables to switch box; share similar number of "pins" as the multielectrode cables)
- Power box
- Power Supply - Generator (e.g., Honda EU2000i generator) or two deep cycle marine batteries
- Power cords x2 (e.g., Power cord from generator to power box; power cord from power box to SuperSting).
- Field Computer
- PC Serial Communications cable (e.g., connects SuperSting and field computer)
- Extension cord
- Awning/tent
- 56 or 64 stainless steel stakes (depending upon configuration) and connectors (e.g., springs or cable ties)
- SuperSting Test Box
- Office Power Cord (e.g., for running diagnostic tests using residential power outlets)
- ERI Data Acquisition Form (e.g., for noting field conditions, site map, and contact resistance values; see Appendix C)

Warning

Do not use a 12V auto battery installed in a vehicle. Metallic tools or electrodes touched to both terminals of a battery will cause the battery to arc. Battery terminals should be covered during transport and operations to minimize this hazard.

5.7 Miscellaneous Equipment

Miscellaneous equipment needs are site and equipment specific but commonly used items are listed below.

- Electrode cables (GCRD's unit consists of four (4), 16 passive electrode cables with 5-meter electrode spacing, and two (2), 28 passive graphite electrode cables with 4-meter electrode spacing).
- Stainless steel stakes
- Survey/Pin flags or wooden stakes
- Survey equipment (i.e., Topcon CTS-2 total station, closed traverse survey equipment)
- Tape measure (meters)
- Computer cables (e.g., data download)
- Waterproof and bound field notebook
- Two-way radios for large scale surveys
- Rubber work gloves
- Site map with planned survey locations
- Field computer with data acquisition software (AGI SuperSting™ Administrator)
- Handheld digital multi-meter (voltage, resistance, current)
- Wire hook-up accessories (electrical tape, alligator clips, banana plugs)
- Calculator
- Hand tools (hammer, shovel or trowel, wire strippers, etc.)
- Tarps or ground cloths
- Tent or rain canopy
- Fuel (e.g., for generator)
- Drip pad for generator/fuel

5.8 Procedure

5.8.1 Planning

Planning is important to ensure a successful survey. See ASTM D6431-99 for good guidance on planning. The objectives of the survey should be discussed in the QAPP for the field site. Both the survey objectives and site characteristics should be considered for planning and design of the survey. Factors to consider include the geology, topography, access, and depth of investigation. The presence of potential interferences (e.g., metal fencing, buried pipes, etc.), natural obstacles (e.g., trees, thick vegetation, water bodies, etc.), and impervious surfaces (e.g., concrete, geologic outcrops, etc.) need to be determined. Information on the site needs to be collected prior to designing the survey and deploying to the site. The use of aerial photos, topographic maps, and, if feasible, a preliminary site visit will help with the planning. Identify preliminary locations of the survey transects using the maps or photos. Locations of boreholes or monitoring wells for control data need to be considered in the design. The survey transect should lie along as straight a line as possible as well as flat as possible. Site preparation (e.g., clearing vegetation, drilling holes, etc.) may be required and thus add significant time to data collection. Ensure the instrument is in good working order before taking it to the field. See 5.9.2 for tests to perform.

5.8.2 Conducting the Survey

1. Inventory equipment to ensure that all necessary components are on site.
2. Assemble equipment according to the manufacturer's SuperSting Manual.

Caution

Equipment should be placed on dry ground and protected from precipitation and extreme heat or direct sunlight to avoid damage to sensitive electrical components.

3. Measure and mark the electrode locations with the tape measure and survey flags along the first survey transect based on the plan. Electrode locations shall be equally spaced and in a straight line.
4. Install steel stakes at appropriate locations along the first survey transect based on the plan. Stakes are hammered in the ground to a depth of 4 to 8 inches. Ensure they are firmly in the ground. Orientation of the stakes should be as perpendicular to the surface as possible, but deviations to this are allowed to ensure the stake is adequately covered.

Warning

Field sites often contain underground utilities. Attempting to insert stakes in the vicinity of underground utilities could potentially result in injury. Coordinate with the appropriate site manager to have utilities located and marked before commencing with electrode installation.

5. Layout the multielectrode cables in sequential order starting with electrode 01 until the highest numbered electrode is deployed at the opposite end.
6. Connect each electrode to the corresponding steel stake with a springs or cable ties.
7. Connect the multielectrode cables to the Switch box, the Switch box to the SuperSting, the SuperSting to the Power box, and the Power box to the Power Supply (Figure 2).

Caution

Most cables have a matching number of pins to ensure proper connection. To avoid damaging the sensitive pins, do not force a connection together. Instead, ensure the plug and socket of the equipment match before proceeding.

8. Note locations of any possible sources of interference in the logbook and provide a brief description (e.g. length, azimuth, and distance from survey location) and include these locations in a site map (if not included during the planning phase), which are provided in the ERI Data Acquisition form (see Appendix C).
9. Measure the contact resistance of all electrodes. See p. 49 of the SuperSting Manual and Section 5.10.2.1.
10. For electrode pairs with significantly higher contact resistance, check connections between those electrodes and stakes, and between the corresponding stakes and soil, and if necessary wet the ground in the immediate vicinity of the stakes using a dilute saltwater solution. See Section 5.10.2.1. for further instruction.
11. Begin measurement cycle. See Appendix A for the list of recommended operational settings.
12. For each measurement, the SuperSting records the magnitude and frequency of the source current, electrode locations, electrical self-potential, and electrical potential.
13. Carefully observe any real-time analog or digital displays available on the equipment during the measurement cycle. Watch for null or erratic readings (error codes HVOVL, INOVL, or TXOVL; or consistent ERR% > 10) which may indicate a broken wire or other equipment error. When possible, correct any deficiencies and reacquire the data prior to proceeding with the survey. See the SuperSting™ Manual for further instruction.
14. If electrodes are moved to another location, repeat from step 3. If the next measurements will be part of the same survey transect, allow sufficient overlap of electrode locations to ensure continuous subsurface coverage along the profile.
15. Begin data download. See Appendix B for the list of steps.
16. At the end of the day, copy data to another media, such as a flash drive, as a backup copy.

5.9 Calculations

1. The electrical resistivity method does not measure true resistivity but rather measures apparent resistivity. Apparent resistivity (ρ_a) is the resistivity value of homogeneous ground that will give the same resistance value for the same electrode arrangement. Conversion between apparent resistivity values and true resistivity values requires inverse modeling and is not within the scope of this document. Apparent resistivity is given by the following expression:

$$\rho_a = k\frac{\Delta\phi}{I},$$

   where k is the geometric factor for the measurement (length units), $\Delta\phi$ is the measured electrical potential (Volts) and I is the magnitude of the source current (Amperes). Assuming the geometric factor is calculated using distances in meters, the apparent resistivity will have units of Ohm-meters.

2. The geometric factor (k) is calculated based on distances (meters) between the current (source) electrodes (C1,C2) and the potential (measurement) electrodes (P1,P2). Figure 3 is a sketch indicating the distances used in the calculation. The inverse of the geometric factor gives an indication of the voltage that would be measured between the P1 and P2 potential electrodes, i.e.

the larger the geometric factor, the smaller the potential that will be measured between P1 and P2. The geometric factor is given by the following expression:

$$k = \frac{2\pi}{\left(\frac{1}{r_{C1P1}} - \frac{1}{r_{C2P1}} - \frac{1}{r_{C1P2}} + \frac{1}{r_{C2P2}}\right)}$$

5.10 Quality Assurance/Quality Control

5.10.1 Data Recording

1. Field data should be recorded on the ERI Data Acquisition form (Appendix C) and transcribed or pasted in a bound, waterproof notebook. The recorded data should include:
    - Project Name, lead, and co-lead.
    - Date and time of collection
    - Name of person/s performing the collection
    - Location and sketch of site
    - Description of field conditions (e.g., approximate temperature, humidity, wind speed and direction, and recent precipitation totals if available)
    - Survey orientation (e.g., West to East, South to North, etc.)
    - GPS location of the first and last electrodes (i.e., degrees or UTM)
    - Survey transect name/number (and segment number if more than one segment is used)
    - Electrode spacing
    - Survey total length
    - Command file used
    - Cable addresses for the low and high ends
    - Electrode location of the Switch box

    - Whether or not the survey is a Roll-along
    - Contact Resistance Test results for each electrode pair (see Section 5.10.2.1. for acceptable results)
    - Measurements times and voltages as dictated in Section 5.8
    - Notes concerning any conditions that may significantly affect test results (such as those in Section 5.4)
2. All electronic data files should be backed up on suitable media (e.g., flash drive, portable hard drive, compact disk) on a daily basis, prior to returning to the laboratory.

5.10.2 Instrument Testing

5.10.2.1 Contact Resistance Test

This test is performed in the field. See p. 49 of the SuperSting Manual. Resistivity measurement signal to noise ratio is highly sensitive to electrode contact resistance. Contact resistance shall be measured and recorded when electrodes are first set up and each time the electrodes are moved, prior to beginning each measurement cycle. If an electrode has contact resistance significantly higher than the others (e.g, greater than about 2,000 ohm-m), use salt water to wet soil around the electrode(s). It also may help to push the electrode deeper into the ground. Re-run the test after attempting to make corrections. Consult AGI if the problem persists.

5.10.2.2 Receiver Test

This test should be done prior to mobilizing to the field. See p. 50 of the SuperSting Manual (Appendix G). Also see Appendix D for a more detailed presentation of this test. All eight values should read 500 mohm (+/-5%). Acceptable range is 475 – 525 mohm. If not, see Appendix D. If the receiver test passes, conduct the relay test.

5.10.2.3 Switchbox Relay Test

This test should be done prior to mobilizing to the field. See p. 51 of the SuperSting Manual (Appendix G). See Appendix E for a more detailed presentation of this test.

5.10.2.4 Cable Test

This test should be done prior to mobilizing to the field. See p. 49-50 of the SuperSting Manual (Appendix G).

5.10.3 Replicates

The default factory setting is 2 cycles. The instrument will display the average and standard deviation. The default setting for maximum error is 2%. If the standard deviation is not lower than the maximum error after running all the cycles, the instrument will automatically repeat those measurements. See Section 5.1.6.1 in the SuperSting Manual.

The program performs reciprocal measurements for each electrode configuration where the current dipole and potential dipole are switched.

5.10.4 Calibration

Factory calibration of the SuperSting is recommended once a year. Contact AGI for this service.

5.10.5 Other QA/QC

When feasible, orient survey transects perpendicular to linear sources of interference (e.g. power lines, metal fences) to minimize their effect.

ERI survey layout is typically performed using a tape measure. Standard survey methods may be used to determine relative elevation electrodes. Position accuracy requirements shall be addressed in the quality assurance project plan (QAPP).

Troubleshooting tips may be found in Appendix F.

6 RECORDS GENERATED

File Type	**Records Schedule Title & Agency File Code**	**Closure**	**Retention**	**Custodian/location of records**
Project-specific field notebooks in which run data is recorded.	**Environmental Programs and Projects** – Long-term environmental program and project records 108_1035b	Close when activity, project, or topic completed.	Destroy 20 years after file closure.	Custodian – Principal Investigator Location – Principal Investigator's office until project closed, then transfer to long-term storage.
Site-specific (Superfund) related project-specific field notebooks in which run data is recorded.	**Environmental Programs and Projects** – Long-term environmental program and project records – Site-Specific 108_1036c	Close when activity, project, or topic completed.	Destroy 30 years after file closure.	Custodian – Principal Investigator Location – Principal Investigator's office until project closed, then transfer to long-term storage.
Instrument Use, Maintenance, Calibration Logs	**Environmental Programs and Projects** – Short-term environmental program and project records 108_1035d	Close when activity, project, or topic completed.	Destroy 5 years after file closure.	Custodian - PI Instrument Use, Maintenance, Calibration Logs maintained with instrument.
Data files	**Environmental Programs and Projects** – Short-term environmental program and project records 108_1035d	Close when activity, project, or topic completed.	Destroy 5 years after file closure unless Site-specific (Superfund) related project- then Destroy 30 years after file closure.	Custodian – Principal Investigator Location – Principal Investigator's OneDrive

7 REFERENCES

Advanced Geosciences, Inc., 2011, "Instruction Manual for SuperSting™ Earth Resistivity, IP and SP System & PowerSting™ External High Power Transmitters," Austin, Texas.

ASTM, Standard D6429-99, 2006, "Standard Guide for Selecting Surface Geophysical Methods," ASTM International, West Conshohocken, PA.

ASTM, Standard D6431-99, 2010, "Standard Guide for Using the Direct Current Resistivity Method for Subsurface Investigation," ASTM International, West Conshohocken, PA.

ASTM, Standard G57-06, 2006, "Standard Test Method for Field Measurement of Soil Resistivity Using the Wenner Four-Electrode Method," ASTM International, West Conshohocken, PA.

Lane, John W. Jr., Haeni, F. P., & Watson, W. M. 1995. Use of a square-array direct-current resistivity method to detect fractures in crystalline bedrock in New Hampshire. Ground Water, 33(3), 476–485.

Loke, M. H., 2011, Tutorial : 2-D and 3-D electrical imaging surveys, available for free download (http://www.geoelectrical.com/coursenotes.zip).

Miller, C.R., Routh, P.S., Brosten, T.R., and McNamara, J.P. (2008). Application of time-lapse ERT imaging to watershed characterization. Geophysics, 73, G7-G17.

Ramirez, A. L., Daily, W. D., & Newmark, R. L. 1995. Electrical resistance tomography for steam injection monitoring and process control. Journal of Environmental and Engineering Geophysics, 0, 39–527.

Zonge, Ken, Wynn, Jeff, & Urquhart, Scott. 2005. Resistivity, induced polarization, and complex resistivity. Pages 265–300 of: Butler, Dwain K. (Ed.), Near Surface Geophysics, Society of Exploration Geophysics Investigations, no.13.

Zhou, Qi You, Shimada, Jun, & Sato, Akira. 2001. Three-dimensional spatial and temporal monitoring of soil water content using electrical resistivity tomography. Water Resources Research, 37(2), 273–286.

8 REVISION HISTORY

Revision #	Description	Effective Date
0	Initial Version	06/25/2019
1	Revised to reflect reorganization and the new CESER SOP template. A PDF document of SuperSting instrument manual as well as other documents showing different instrument tests and troubleshooting were added to this version of the SOP.	Date of Management Approval

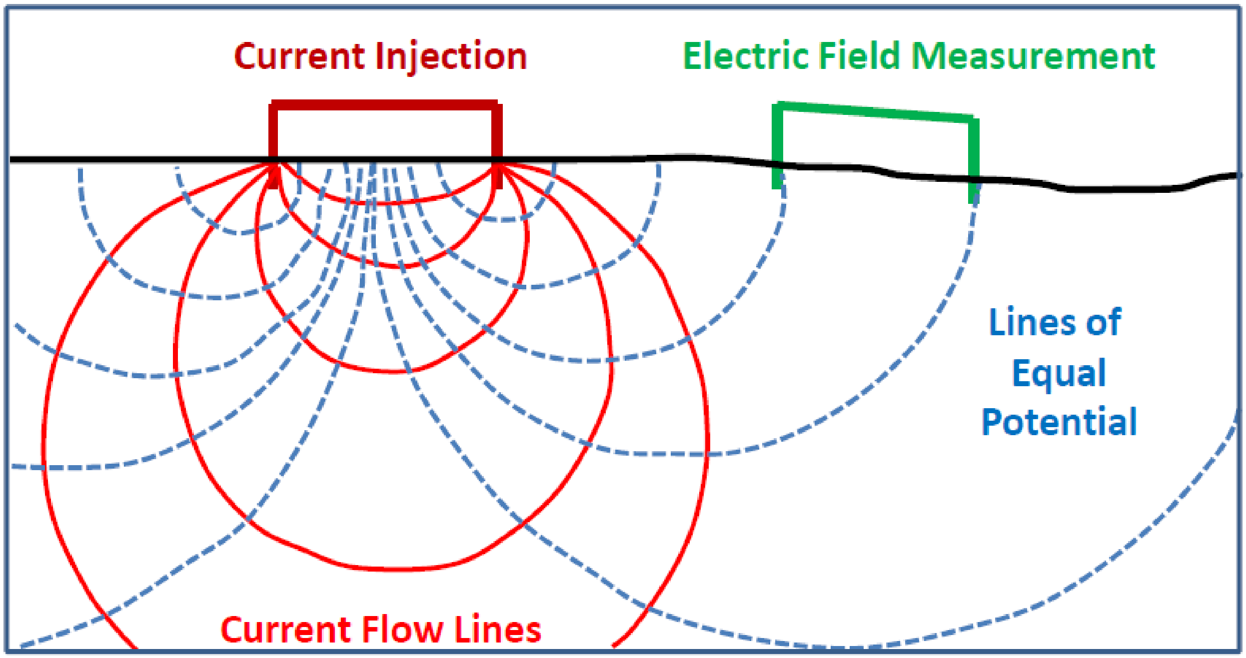


Figure 1: Sketch showing the source dipole (current injection) and the measurement dipole (electric field measurement) required to perform an electrical resistivity measurement (dipole-dipole array).

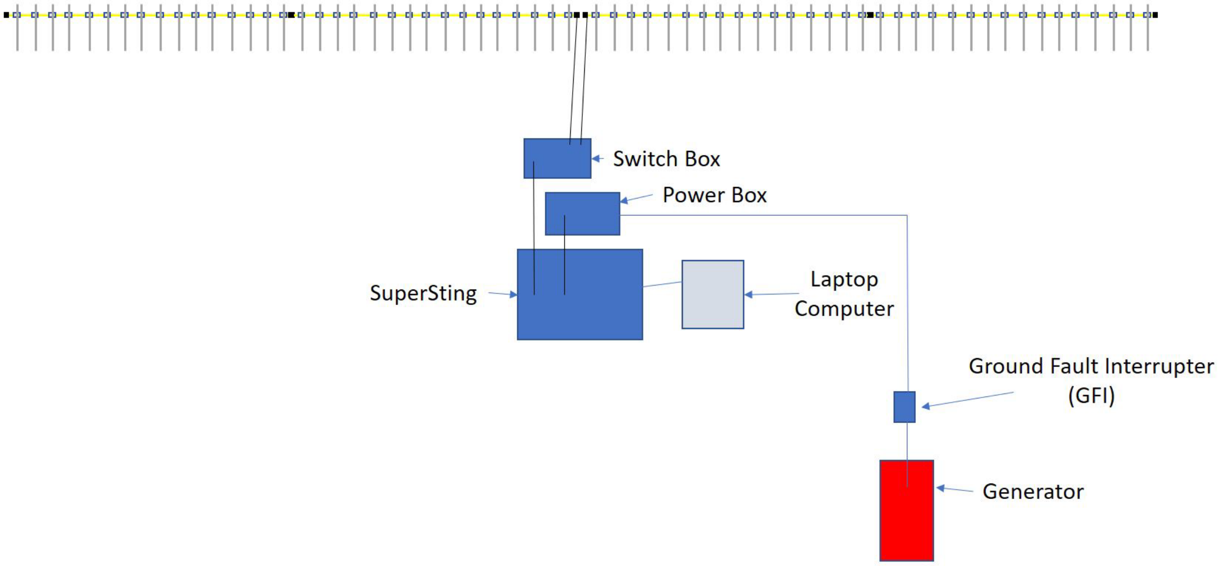


Figure 2: Schematic diagram showing typical equipment required for performing electrical resistivity measurements.

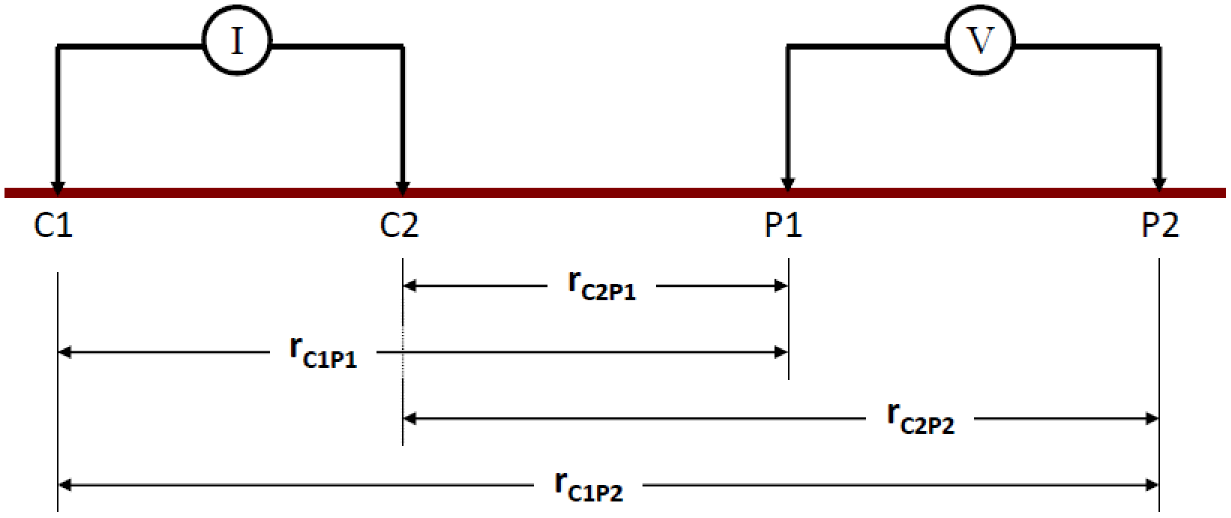


Figure 3: Distances used to calculate the geometric factor for an electrical resistivity measurement.

APPENDIX A

Recommended Operational Settings (for a 64-electrode set up)

Select :

- Automatic Mode
- Create Data File: Type unique data file name with no more than 8 alphanumeric characters, then press ENTER key
- Select command file to be used
- Select units used. + or – to scroll up or down
- Enter Electrode spacing (Scaling factor – default = 1)
- Edit survey information
  - Start X=0.0 m
  - Start Y=0.0 m
  - Start Z=0.0 m
  - Start command line #: 1
  - Roll-along: No
  - End Address: Off (Set to electrode number if obstacle encountered; electrodes beyond that number will not be included in survey).

Enter to continue, or Men: Up Level (go up level for second test if electrode array is same as used for first test).

Select 1. Switch box

Select 8 for Eight channel (R8)

Select 4. Dipole-Dipole

Test mode – 1. Press F1 to initiate Contact resistance test (measures contact resistance along the complete electrode cable layout. Values <2000 ohm-m are considered good. If values >2000 ohm-m check electrode pair to make sure there is good contact to the ground and that the electrode is in good contact with stake. It may be helpful to push stake deeper and/or pour salt water on ground where electrode makes contact. F2 will skip the problem pair of electrodes and continue testing contact resistance along the cable.

Measurement Settings M61

- Cycles: 2
- Max Error: 2.0
- Max Repeat: 1
- Max Current: 2000 mA

- Measurement Time: 1.2 Seconds
- Separate Potential: Off
- Measure mode: RES
- Use Command File Addresses
- Defaults: USER

Cable Address Setup M62

1.New cable sections

Addr	Low:	High:
Section	AddrL	AddrH
1	1	16
2	17	32
3	33	48
4	49	64

Men: Up level

M64 General Settings

- Automatic shutoff: ON
- Start firmware update
- Switch COM Delay: 60 ms
- Set defaults
- Commutate Delay: 100 ms
- Sting/Swift Cable: Off
- HIVOLT: 384
- Baud Rate:38400
- Show Apparent Res: OFF

Men: Up level

Press MEA to start measurement

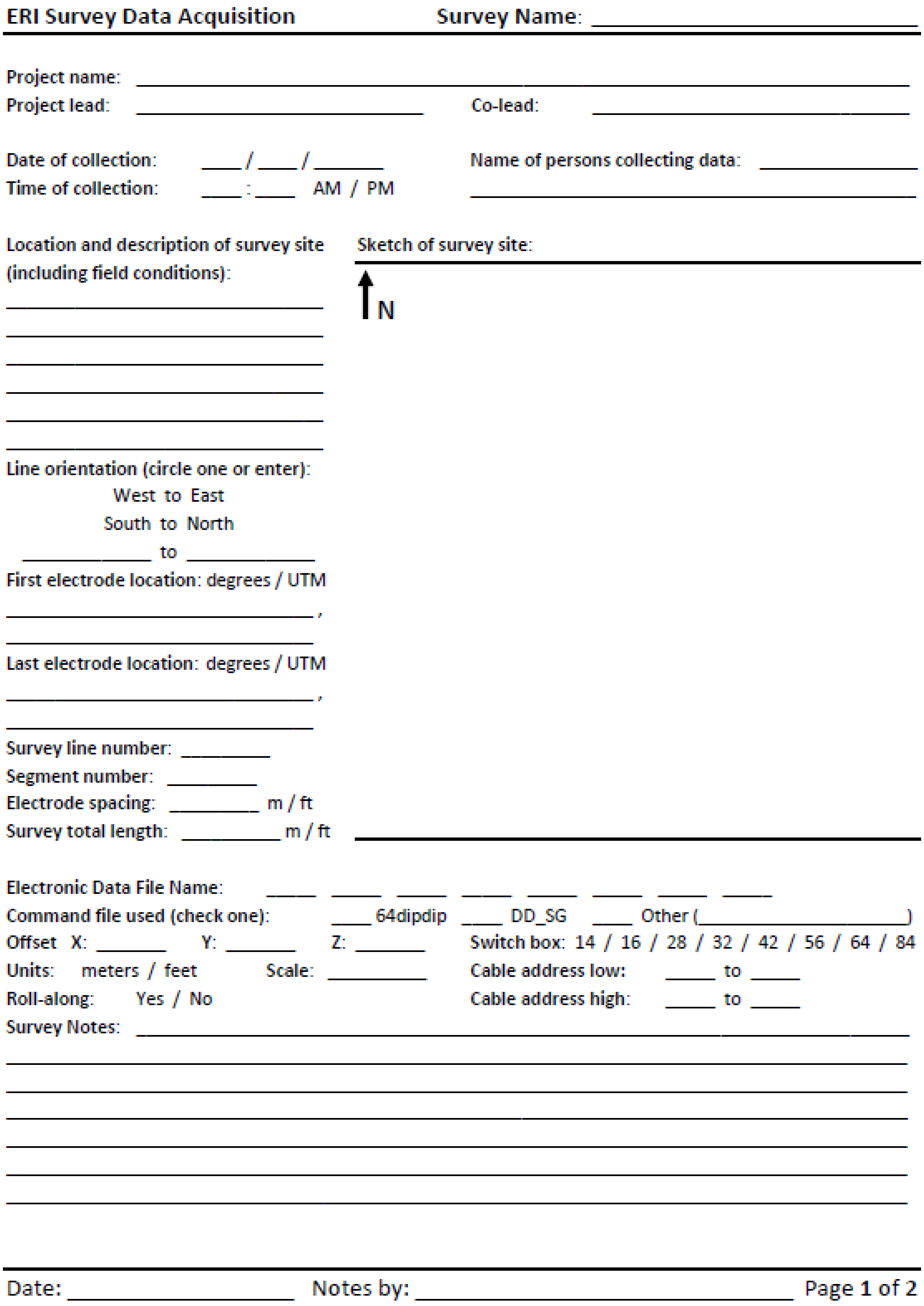
APPENDIX B

Recommended Data Download Steps

1. Connect the SuperSting to the field computer using the “Cable for communication SuperSting/PC MS Windows type computer.” Connect the cable to the 9-pin serial port on the field computer and to the SuperSting front panel connector marked “PC SERIAL COM.”
2. Turn the instrument on. Press any key to get to the main menu. Note that you must be in the main menu or the first level submenu when connecting to the computer.
3. Start the AGI SuperSting Administrator software.
4. Click on the SuperSting control center module button.
5. Select the appropriate com port, found under the Config option on the menu bar.
6. Click on the “Connect” button. Green light between the connect and disconnect buttons will now indicate that the connection is established. Available command files and data files in the SuperSting will also be listed in the respective windows on the computer screen.
7. In the “Data files” window select the data file to download by right clicking on the file name. Click on “Read File” and select where to save the file.
8. When the transfer is finished a sign with the text “Selected measure file read from instrument. File set saved as: ......”. Click OK.
9. Click on the “Disconnect” button. Red light between the connect and disconnect buttons will indicate there is no longer a connection. Close the software and disconnect the field computer and power down the SuperSting.
10. Note that a red cross will mark each data file in the Administrator window, which has not been downloaded to a computer. To erase a data file, right click on the data file in the Administrator window and then click on “Erase File”. If the selected data file is marked by a red cross, a warning will be issued before the data file can be erased.

APPENDIX C

Example: ERI Data Acquisition Form



ERI Survey Data Acquisition **Survey Name:** ____________________________

Project name: ____
Project lead: __________________________ Co-lead: _____________________________

Date of collection: ____ / ____ / _______ Name of persons collecting data: ______________
Time of collection: ____ : ____ AM / PM ____

Location and description of survey site (including field conditions):
____
____
____
____
____
____

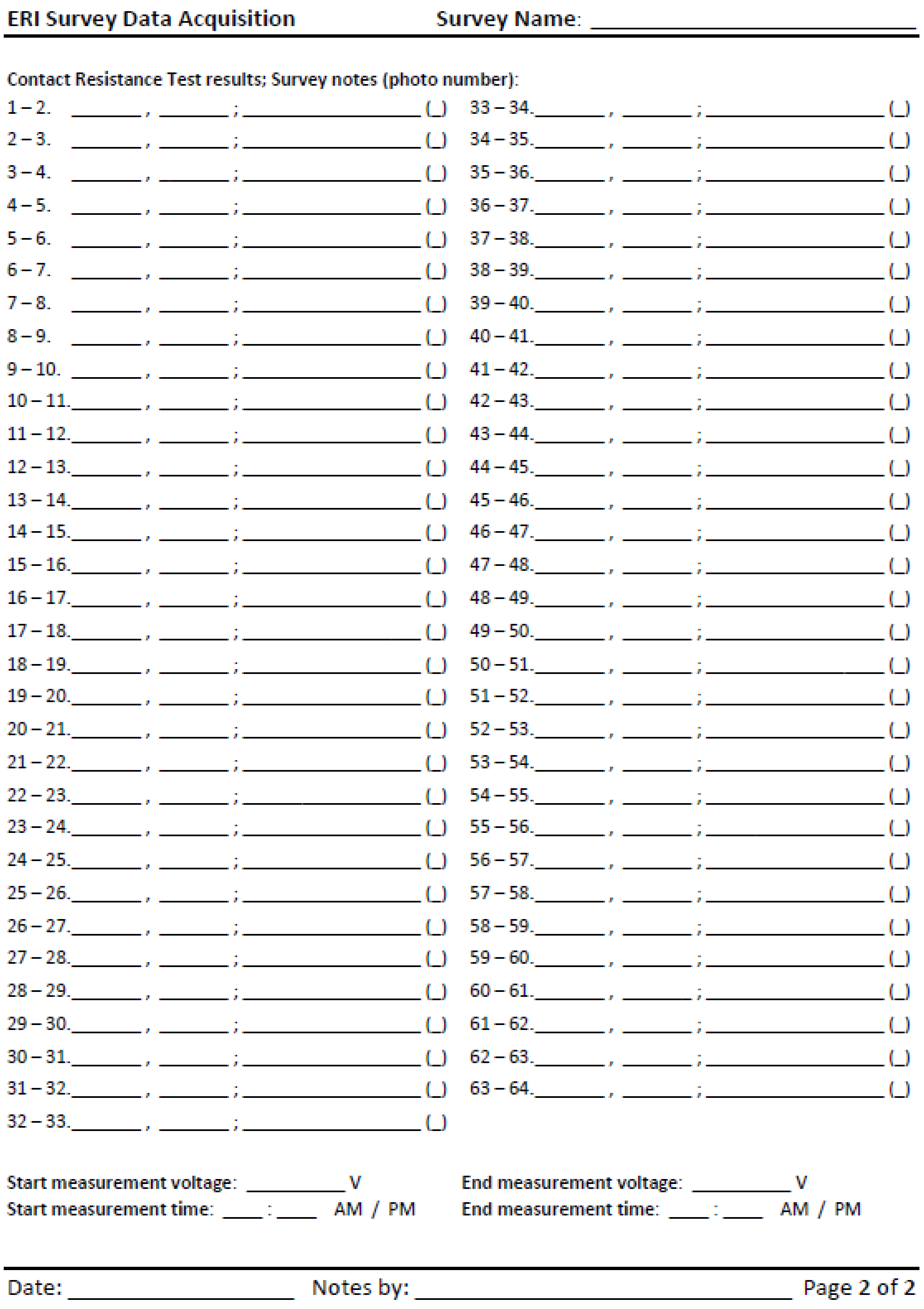
Sketch of survey site:

N

Line orientation (circle one or enter):
West to East
South to North
____________ to ____________
First electrode location: degrees / UTM
______________________________ ,
____
Last electrode location: degrees / UTM
______________________________ ,
____
Survey line number: _________
Segment number: _________
Electrode spacing: _________ m / ft
Survey total length: __________ m / ft

Electronic Data File Name: _____ _____ _____ _____ _____ _____ _____ _____
Command file used (check one): ____64dipdip ____ DD_SG ____ Other (____________________)
Offset X: _______ Y: _______ Z: _______ Switch box: 14 / 16 / 28 / 32 / 42 / 56 / 64 / 84
Units: meters / feet Scale: __________ Cable address low: _____ to _____
Roll-along: Yes / No Cable address high: _____ to _____
Survey Notes: ____
____
____
____
____
____
____

Date: __________________ Notes by: ______________________________ Page **1** of **2**



ERI Survey Data Acquisition **Survey Name:** ______________________________

Contact Resistance Test results; Survey notes (photo number):

1 – 2. _______ , _______ ; _________________ (_)
2 – 3. _______ , _______ ; _________________ (_)
3 – 4. _______ , _______ ; _________________ (_)
4 – 5. _______ , _______ ; _________________ (_)
5 – 6. _______ , _______ ; _________________ (_)
6 – 7. _______ , _______ ; _________________ (_)
7 – 8. _______ , _______ ; _________________ (_)
8 – 9. _______ , _______ ; _________________ (_)
9 – 10. _______ , _______ ; _________________ (_)
10 – 11._______ , _______ ; _________________ (_)
11 – 12._______ , _______ ; _________________ (_)
12 – 13._______ , _______ ; _________________ (_)
13 – 14._______ , _______ ; _________________ (_)
14 – 15._______ , _______ ; _________________ (_)
15 – 16._______ , _______ ; _________________ (_)
16 – 17._______ , _______ ; _________________ (_)
17 – 18._______ , _______ ; _________________ (_)
18 – 19._______ , _______ ; _________________ (_)
19 – 20._______ , _______ ; _________________ (_)
20 – 21._______ , _______ ; _________________ (_)
21 – 22._______ , _______ ; _________________ (_)
22 – 23._______ , _______ ; _________________ (_)
23 – 24._______ , _______ ; _________________ (_)
24 – 25._______ , _______ ; _________________ (_)
25 – 26._______ , _______ ; _________________ (_)
26 – 27._______ , _______ ; _________________ (_)
27 – 28._______ , _______ ; _________________ (_)
28 – 29._______ , _______ ; _________________ (_)
29 – 30._______ , _______ ; _________________ (_)
30 – 31._______ , _______ ; _________________ (_)
31 – 32._______ , _______ ; _________________ (_)
32 – 33._______ , _______ ; _________________ (_)
33 – 34._______ , _______ ; _________________ (_)
34 – 35._______ , _______ ; _________________ (_)
35 – 36._______ , _______ ; _________________ (_)
36 – 37._______ , _______ ; _________________ (_)
37 – 38._______ , _______ ; _________________ (_)
38 – 39._______ , _______ ; _________________ (_)
39 – 40._______ , _______ ; _________________ (_)
40 – 41._______ , _______ ; _________________ (_)
41 – 42._______ , _______ ; _________________ (_)
42 – 43._______ , _______ ; _________________ (_)
43 – 44._______ , _______ ; _________________ (_)
44 – 45._______ , _______ ; _________________ (_)
45 – 46._______ , _______ ; _________________ (_)
46 – 47._______ , _______ ; _________________ (_)
47 – 48._______ , _______ ; _________________ (_)
48 – 49._______ , _______ ; _________________ (_)
49 – 50._______ , _______ ; _________________ (_)
50 – 51._______ , _______ ; _________________ (_)
51 – 52._______ , _______ ; _________________ (_)
52 – 53._______ , _______ ; _________________ (_)
53 – 54._______ , _______ ; _________________ (_)
54 – 55._______ , _______ ; _________________ (_)
55 – 56._______ , _______ ; _________________ (_)
56 – 57._______ , _______ ; _________________ (_)
57 – 58._______ , _______ ; _________________ (_)
58 – 59._______ , _______ ; _________________ (_)
59 – 60._______ , _______ ; _________________ (_)
60 – 61._______ , _______ ; _________________ (_)
61 – 62._______ , _______ ; _________________ (_)
62 – 63._______ , _______ ; _________________ (_)
63 – 64._______ , _______ ; _________________ (_)

Start measurement voltage: __________ V
Start measurement time: ____ : ____ AM / PM
End measurement voltage: __________ V
End measurement time: ____ : ____ AM / PM

Date: ____________________ Notes by: ________________________________ Page 2 of 2

Click on the embedded file to open:

ERI Survey Data
Acquisition Form.pdf

APPENDIX D

Receiver Test

Click on the embedded file to open:

AGI_Perform the
SuperSting R8 Receive

APPENDIX E

Relay Test

Click on the embedded file to open:

AGI_Perform the
SwitchBox Relay Test.

APPENDIX F

Troubleshooting Tips

Click on the embedded file to open:

AGI_SuperSting
Troubleshooting FAQ.

APPENDIX G

SuperSting Manual

Click on the embedded file to open:

SuperStingManual.pd
f

Document C-3: EPA Method 170.1 from "EPA 600/4-79-020 Methods for Chemical Analysis of Water and Wastes"

TEMPERATURE

Method 170.1 (Thermometric)

STORET NO. 00010

1 Scope and Application
  - 1 1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes

2 Summary of Method
  - 2 1 Temperature measurements may be made with any good grade of mercury-filled or dial type centigrade thermometer, or a thermistor

3 Comments
  - 3 1 Measurement device should be routinely checked against a precision thermometer certified by the National Bureau of Standards

4 Precision and Accuracy
  - 4 1 Precision and accuracy for this method have not been determined

5 Reference
  - 5 1 The procedure to be used for this determination is found in
    Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 125, Method 212 (1975)

Approved for NPDES
Issued 1971

Document C-4: EPA Method 120.1 from “EPA 600/4-79-020 Methods for Chemical Analysis of Water and Wastes”

CONDUCTANCE

Method 120.1 (Specific Conductance, *u*mhos at 25°C)

STORET NO. 00095

1 Scope and Application
  - 1 1 This method is applicable to drinking, surface, and saline wates, domestic and industrial wastes and acid rain (atmospheric deposition)

2 Summary of Method
  - 2 1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent
  - 2 2 Samples are preferable analyzed at 25°C If not, temprature corrections aremade and results reported at 25°C

3 Comments
  - 3 1 Instrument must be standardized with KCl solution before daily use
  - 3 2 Conductivity cell must be kept clean
  - 3 3 Field measurements with comparable instruments are reliable
  - 3 4 Temperature variations and corrections represent the largest source of potential error

4 Sample Handling and Preservation
  - 4 1 Analyses can be performed either in the field or laboratory
  - 4 2 If analysis is not completed within 24 hours of sample collection, sample should be filtered through a 0 45 micron filter and stored at 4°C Filter and apparatus must be washed with high quality distilled water and pre-rinsed with sample before use

5 Apparatus
  - 5 1 Conductivity bridge, range 1 to 1000 μmho per centimeter
  - 5 2 Conductivity cell, cell constant 1 0 or micro dipping type cell with 1 0 constant YSI #3403 or equivalent
  - 5 4 Thermometer

6 Reagents
  - 6 1 Standard potassium chloride solutions, 0 01 M Dissolve 0 7456 gm of pre-dried (2 hour at 105°C) KCl in distilled water and dilute to 1 liter at 25°C

7 Cell Calibration
  - 7 1 The analyst should use the standard potassium chloride solution (6 1) and the table below to check the accuracy of the cell constant and conductivity bridge

Approved for NPDES
Issued 1971
Editorial revision, 1982

Conductivity 0 01 m KCl

°C	Micromhos/cm
21	1305
22	1332
23	1359
24	1386
25	1413
26	1441
27	1468
28	1496

8. Procedure

8.1 Follow the direction of the manufacturer for the operation of the instrument

8 2 Allow samples to come to room temperature (23 to 27°C), if possible

8.3 Determine the temperature of samples within 0 5°C If the temperature of the samples is not 25°C, make temperature correction in accordance with the instruction in Section 9 to convert reading to 25°

9 Calculation

9 1 These temperature corrections are based on the standard KCl solution

9.1 1 If the temperature of the sample is below 25°C, add 2% of the reading per degree

9 1 2 If the temperature is above 25°C, subtract 2% of the reading per degree

9.2 Report results as Specific Conductance, µmhos/cm at 25°

10. Precision and Accuracy

10.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results

Increment as Specific Conductance	Precision as Standard Deviation	Accuracy as Bias, %	Bias, umhos/cm
100	7 55	–2 02	–2 0
106	8 14	–0 76	–0 8
808	66 1	–3 63	–29 3
848	79 6	–4 54	–38 5
1640	106	–5 36	–87 9
1710	119	–5 08	–86 9

(FWPCA Method Study 1, Mineral and Physical Analyses)

10 2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 µmhos/cm at 25°C, the standard deviation was ±6

Bibliography

1 The procedure to be used for this determination is found in Annual Book of ASTM Standards Part 31, "Water," Standard D1125-64, p 120 (1976)

2 Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 71, Method 205 (1975)

3 Instruction Manual for YSI Model 31 Conductivity Bridge

4 Peden, M E , and Skowron "Ionic Stability of Precipitation Samples," Atmospheric Environment, Vol 12, p 2343-2344, 1978

Document C-5: K-GCRD-SOP-1134-0: SOP for Water Level Monitoring Using Automated Pressure Transducer/Data Loggers

Standard Operating Procedure for
Water Level Monitoring Using Automated Pressure Transducer/Data Loggers

I. Disclaimer

This standard operating procedure has been prepared for the use of the Ground Water and Ecosystems Restoration Division of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations. **THIS IS NOT AN OFFICIAL EPA APPROVED METHOD.** This document has not been through the Agency's peer review process or ORD clearance process.

II. Purpose (Scope and Application)

This procedure is intended for the acquisition of water level data, measured as pressure, using an automated pressure transducer/data logger in a monitoring well or surface water body. The procedure may be used with either vented or unvented pressure transducers. The data are used to assess site hydrology, including hydraulic gradients and temporal changes due to changes in recharge and discharge.

III. Method Summary

Automated pressure transducers with associated data loggers are used to measure changes in water levels in wells and surface water bodies. This SOP documents procedures for deployment of these devices and calculation of associated water elevations using the data obtained from the device. The procedure involves installation of the device within the water column of a well or surface water body, independent measurements of water level with respect to an established reference point, retrieval of the data from the logger, and calculation of water elevations with respect to the reference point.

IV. Reagents/Chemicals/Gases

Not applicable.

V. Equipment/Apparatus

The following equipment is needed using this procedure:

- Water-level indicator (two-wire electrical sounder), equipped with a sufficient length of cable to reach the deepest anticipated water level. The cable should be graduated into 0.01ft or 1 mm intervals
- Extra batteries for the water level indicator
- Extra batteries for pressure transducer/data logger, if batteries are user replaceable
- Decontamination supplies (*e.g.*, deionized or distilled water, Liquinox, brush, plastic bucket, clean spray bottles, paper towels) used for decontamination of the water level indicator probe
- Keys for locked protective casings
- Tools (*e.g.*, wrenches), as needed, to enter well vault boxes
- LevelTroll, Levelogger, or equivalent submerged pressure transducer/data logger
- BaroTroll, Barologger, or equivalent barometric pressure logger, if absolute (unvented) pressure transducers are used
- Vented well cap
- Vented cables if vented pressure transducers are used
- Stainless steel cable if absolute (unvented) transducers are used
- Computer with software for communicating with data logger
- Communications cable for communicating with data logger
- Waterproof field notebook and pen
- User guide for specific pressure transducer/data logger to be deployed

VI. Health & Safety Precautions

Appropriate personal protective equipment and procedures, as defined in the site-specific Health & Safety Plan, should be used at all contaminated sites.

VII. Interferences

1. Water levels in unvented wells may not be representative of aquifer conditions. Pressure transducers/data loggers used under this SOP should only be deployed in vented wells or in surface water bodies.

VIII. Procedure

The following procedure describes data acquisition using automated pressure transducer/data loggers in its simplest form. Additional details regarding logger usage can be found in the product-specific user guides.

Deployment of Pressure Transducer/Data Logger in a Well

1. Remove the well cover and wait at least five minutes prior to conducting measurements and installing equipment, if the well casing is not vented to the atmosphere. Indications of air movement in or out of the well should be recorded in the notebook.

2. Turn the electric water level indicator on and check its operation by depressing the “Test” button and listening for the tone.

3. Lower the probe of the electric water level indicator into the riser casing until water is encountered, as indicated by the instrument signal. The water level is then measured to the nearest 0.01 ft or 1 mm with respect to the established reference point. This reference point is usually a mark on the top of the well casing.

WARNING: Do not use the water level indicator to measure the total depth of the well unless it is equipped with a submersible probe. Doing so may damage the probe.

4. In the field notebook, record the well name, the make/model of the water level indicator, the measured depth to water, the date/time of measurement, and a description of the measurement reference point (*e.g.*, north side of well casing), if an established point is not found.

5. Wait one minute and repeat Step 3. If the measured water level is not within 0.02 ft or 2 mm of the value obtained in Step 3, record the value and time, wait 5 min, and repeat. Continue this procedure until water level stabilizes.

6. Remove the probe from the well and decontaminate the probe using procedures outlined in site-specific documents such as the QAPP. If no site-specific procedures are established, rinse the probe with distilled water and wipe dry.

7. Using the computer and communications cable, check the data logger battery capacity and replace batteries, if necessary, synchronize the data logger clock with the computer clock, and program the data logger for data acquisition. Typical information to be provided includes the names of the site and well, time to start data acquisition, and frequency of data acquisition. In general, the acquisition frequency should be sufficiently high as to capture any changes of interest. For example, if rapid changes within a day are not anticipated based on the hydrogeologic setting or are not of interest based on the data quality objectives for the investigation, a measurement frequency of once per day may be appropriate. If rapid changes are anticipated and of interest, such as the maximum response due to rapid changes in nearby surface water elevations, a higher data acquisition frequency (*e.g.*, every hour or even every half hour) may be appropriate.

8. If the pressure transducer/data logger is of vented construction, attach a vented cable to the logger and secure it to the well head or to a vented cap. If the pressure transducer/data logger is of non-vented construction, attach a stainless steel cable to the logger and to the well head or to a vented cap. The cable length should be sufficient to suspend the logger within the water column throughout the duration of the planned logging period but not so deep as to place the logger deeper than its rated pressure range during the logging period.

9. Place the pressure transducer/data logger in the well and attach the well cap.

10. Repeat Step 7 using a BaroTroll, Barologger, or equivalent barometric pressure logger, if pressure transducers/data loggers of unvented construction are used. Set the times of data acquisition to be identical to those specified in Step 7. A minimum of one BaroTroll or Barologger is needed for each site. A barometric pressure logger is not needed if loggers of vented construction are used.

11. Attach a stainless steel cable to the BaroTroll or Barologger and to the well head or to a vented cap. The cable length should be sufficient to suspend the logger within the air column throughout the duration of the planned logging period. Place the BaroTroll or Barologger in the well and attach the well cap. Alternatively, the BaroTroll or Barologger may be placed outside of a well at any dry, secure location open to the atmosphere.

12. Allow the data logger installed in Step 9 to equilibrate to the water conditions for at least one hour.

13. At a time within approximately two hours of a measurement made by the pressure transducer/data logger, repeat Steps 2 through 4 to obtain a manual water level measurement to allow calculation of groundwater elevations from the transducer data.

Deployment of Pressure Transducer/Data Logger in a Surface Water Body

14. Using the computer and communications cable, check the data logger battery capacity and replace batteries, if necessary, synchronize the data logger clock with the computer clock, and program the data logger for data acquisition. Typical information to be provided includes the names of the site and surface water monitoring location, time to start data acquisition, and frequency of data acquisition. In general, the acquisition frequency should be sufficiently high as to capture any changes of interest. For example, if rapid changes within a day are not anticipated or are not of interest based on the data quality objectives for the investigation, a measurement frequency of once per day may be appropriate. If rapid changes are anticipated and of interest, a higher data acquisition frequency (*e.g.*, every hour or even every few minutes) may be appropriate.

15. If the pressure transducer/data logger is of vented construction, attach a vented cable to the logger and secure it to a fixed point in or adjacent to the surface water body. If the pressure transducer/data logger is of non-vented construction, attach a stainless steel cable to the logger and secure it to a fixed point in or adjacent to the surface water body. Suspend the pressure transducer/data logger in the surface water body such that the logger will not be covered with sediment during the period of logger operation.

16. Repeat Step 14 using a BaroTroll, Barologger, or equivalent barometric pressure logger, if pressure transducers/data loggers of unvented construction are used. A minimum of one BaroTroll or Barologger is needed for each site. A barometric pressure logger is not needed if loggers of vented construction are used.

17. Place the BaroTroll, Barologger, or equivalent tool in a dry, secure location open to the atmosphere.

18. Allow the data logger installed in Step 15 to equilibrate to the water conditions for at least one hour.

19. At a time within approximately two hours of a measurement made by the pressure transducer/data logger, obtain and record a measurement of the surface water elevation relative to an established datum to allow calculation of surface water elevations from the transducer data. Such a measurement may be obtained by reading the water level from a previously established staff gauge, measuring the depth to water from a surveyed point, or equivalent means.

Downloading Data from Pressure Transducer/Data Logger

20. Repeat Step 13 or Step 19 for data loggers installed in wells and surface water bodies, respectively.

21. Remove the data logger from the well or surface water body. Download the data to the computer using the appropriate software and communications cable. Replace the logger in the well if data logging is to be continued. Otherwise, decontaminate the data logger as required by site-specific plans.

22. Download data from the BaroTroll, Barologger, or equivalent barometric pressure logger using the appropriate software and communications device. Replace the barometric pressure logger if data logging is to be continued.

23. Backup all electronic files to suitable media (*e.g.*, flash drive, portable hard drive, compact disk).

Calculating Water Elevations from Pressure Transducer Data

24. Since absolute (unvented) pressure transducers measure total (water plus atmospheric) pressure, barometric pressure changes must be removed from data obtained using such tools before water elevations are calculated. This process is termed barometric pressure compensation. Compensation is performed by subtracting the barometric pressure measured by the barometric pressure logger from the total pressure measured by the absolute data logger as outlined in Section X, Step 1. Since barometric pressure and water levels vary with time, measurements of barometric pressure and water pressure obtained at the same time should be used during compensation. If vented pressure transducers are used, the data downloaded from the logger are already compensated for barometric pressure.

25. Calculate water elevations from the data obtained in Steps 13, 19, and 20 relative to mean sea level or another established datum using the equation in Section X, Step 2.

26. Calculate the water elevations from the data obtained in Step 24 using the equation in Section X, Step 3.

27. When data loggers are used over extended periods of time (*e.g.*, weeks to months) linear

instrument drift is commonly observed. If the difference between the water elevation calculated in Step 25 using the data obtained in Step 13 or 19 and that calculated for the same measurement time in Step 26 is greater than 0.02 then compensate the water elevations calculated in Step 26 for instrument drift using the equation in Section X, Step 4.

IX. QA/QC

1. All field data should be recorded in a bound, waterproof notebook. The recorded data should include:

a. Date, time, and location of measurements
b. Name of person performing the measurements
c. Well identification numbers
d. Make/model of water level indicator
e. Make/model of pressure transducer/data loggers
f. Make/model of barometric pressure logger, if used
g. Measurements and measurement times as dictated in Section VIII
h. Notes concerning any conditions that may significantly affect measurement results
i. Names of downloaded data files

2. This procedure uses repeated measurements to determine stable water levels that are representative of aquifer conditions rather than transient phenomena resulting from pressure changes that can occur when a sealed well is uncapped.

3. The primary measurement device (*i.e.*, the pressure transducer) is calibrated by the manufacturer. The instrument should be re-calibrated on the schedule stated in the equipment manual.

4. Backup all electronic files using suitable media (*e.g.*, flash drive, portable hard drive, compact disk) prior to returning to the laboratory.

5. Appropriate corrective actions involving pressure transducer/data loggers and associated equipment should be determined from diagnostic guides in operation manuals.

X. Calculations

1. Water pressure data from absolute pressure transducers are compensated for barometric pressure effects using the following equation:

$WP_{t=i}$ (ft of water) = $P_{t=i}$ (ft of water) – $B_{t=i}$ (ft of water)

where:

$WP_{t=i}$ = water pressure measured at time i
$P_{t=i}$ = water + atmospheric pressure measured at time i
$B_{t=i}$ = atmospheric pressure measured by BaroTroll, Barologer or similar device at time i

2. The following equation is used to calculate water elevation:

E_{water} (ft MSL) = $E_{Reference\ Point}$ (ft MSL) – DTW (ft)

where:

E_{water} = Elevation of water surface above mean sea level
$E_{Reference\ Point}$ = Elevation of reference point above sea level
DTW = Depth to water measured relative to the reference point

3. Water elevations are calculated from water pressure data that have been obtained from a vented pressure transducer or compensated for barometric pressure in Step 1 of this section if an absolute pressure transducer was used using the following equation,:

E_{XDi} (ft MSL) = (E_1 (ft MSL) – WP_1 (ft of water)) + WP_i (ft of water)

where:

E_{XDi} = Elevation of water surface from pressure data point i
E_1 = Water elevation calculated using equation in Step 2 of this section with water surface measurement made in Section VIII, Step 13 or Step 19 for wells or surface water, respectively
WP_1 = Water pressure obtained using equation in Step 1 of this section for data point measured at time equivalent to that of E_1

WP_i = Water pressure obtained using equation in Step 1 of this section for data point i

4. Water elevations calculated in Step 3 of this section can be compensated for instrument drift over time using the following equation:

$$E_{XDCi} \text{ (ft MSL)} = (ET_i \text{ (hr)} / ET_{TOTAL} \text{ (hr)}) * (E_2 \text{ (ft MSL)} - E_{XD2} \text{ (ft MSL)}) + E_{XDi} \text{ (ft MSL)}$$

where:

E_{XDCi} = Elevation of water surface from pressure data point i compensated for instrument drift
ET_i = Elapsed time between measurement times of data point i and water elevation measured in Section VIII, Step 13 or 19
ET_{TOTAL} = Elapsed time between measurement times of manual water level measurements obtained in Section VIII, Steps 13 or 19 and Step 20
E_2 = Water elevation measured in Section VIII, Step 20
E_{XD2} = Elevation of water surface from pressure data point i obtained at time equivalent to time of E2 calculated using equation in Step 3 of this section
E_{XDi} = Elevation of water surface from pressure data point i calculated using equation in Step 3 of this section

XI. Miscellaneous Notes

None.

XII. References

See manufacturer’s documentation for specific pressure transducer/data logger used.

Document C-6: EPA Method 9056A from “EPA SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods”

METHOD 9056A

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method addresses the sequential determination of chloride (Cl^-), fluoride (F^-), bromide (Br^-), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}) anions in aqueous samples, such as drinking water, wastewater, aqueous extracts of solids, and the collection solutions from the bomb combustion of solid waste samples (Method 5050).

1.2 The lower limit of quantitation (LLOQ), the lowest concentration level that can be measured within stated accuracy limits, varies for each individual analyte anion and as a function of sample size.

1.3 Maximum column loading should not exceed approximately 500 ppm total anions when using a 50-µL sample loop and the columns listed in Sec. 6.1. Dilution of samples may allow higher concentration samples to be analyzed.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A small volume of aqueous sample is injected into an ion chromatograph to flush and fill a constant-volume sample loop. The sample is then injected into a flowing stream of carbonate-bicarbonate eluent.

2.2 The sample is pumped through two different ion exchange columns, then a conductivity suppressor device, and into a conductivity detector. The two ion exchange columns, a precolumn or guard column and a separator column, are packed with an anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The conductivity suppressor is an ion exchange-based device that reduces the background conductivity of the eluent to a low or negligible level and simultaneously converts the anions in the sample to their more conductive acid forms. The separated anions in their acid forms are measured using an electrical conductivity cell. Anion identification is based on the comparison of analyte signal peak retention times relative to those of known standards. Quantitation is accomplished by measuring the peak area and comparing it to a calibration curve generated from known standards.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Any species with a retention time similar to that of the desired anion will interfere. Large quantities of ions eluting close to the anion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the method of standard additions can also be used. For example, high levels of organic acids that may interfere with inorganic anion analysis may be present in industrial wastes. Two common species, formate and acetate, elute between fluoride and chloride.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (100 times more concentrated than the solution described in Sec. 7.3) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in ion chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks (Sec. 9.3.1). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to Chapter Three for general guidance on the cleaning of glassware.

4.4 Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems. The associated method blanks must also be filtered if any samples or reagents have undergone filtration.

4.5 The acetate, formate, and other monovalent organic acid anion elute early in the chromatographic run and can interfere with fluoride. The retention times of anions may differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples where acetate is used for pH adjustment.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Ion chromatograph -- Capable of delivering 1 to 5 mL of eluent per min at a pressure of 1000 to 4000 psi (6.5 to 27.5 MPa). The chromatograph must be equipped with an injection valve, a 25- to 100-µL sample loop, and set up with the following components, as schematically illustrated in Figure 1.

6.1.1 Precolumn -- A guard column placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents. An example of a suitable column is the Dionex IonPac® AG4A-SC, or equivalent.

6.1.2 Separator (or analytical) column -- A column packed with an anion exchange resin, suitable for resolving F^-, Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}. An example of a suitable column is the Dionex IonPac® AS4A-SC, or equivalent.

6.1.3 Conductivity suppressor -- An ion exchange-based device that is capable of converting the eluent and separated anions to their respective acid forms. Examples of suitable suppressors include the Dionex AMMS-II or ASRS Ultra, or equivalent.

6.1.4 Conductivity detector -- A low-volume, flow-through, temperature-compensated, electrical conductivity cell (approximately 1.25-µL volume), equipped with a meter capable of reading from 0 to 1,000 Siemens/cm on a linear scale. An example of a suitable conductivity detector is the Dionex CD20 or equivalent.

6.1.5 Pump -- Capable of delivering a constant flow of approximately 1 to 5 mL/min throughout the test and tolerating a pressure of 1000 to 4000 psi (6.5 to 27.5 MPa).

6.2 Syringe -- Minimum capacity of 1 mL, equipped with a male pressure fitting.

6.3 Appropriate chromatographic data and control software to acquire data. Dionex PeakNet was used to record and process the chromatogram shown in Figure 2. Alternatively, an integrator or recorder can be used to integrate the area under the chromatographic peaks. If an integrator is used, the maximum area measurement must be within the linear range of the integrator. The recorder should be compatible with the detector output with a full-scale response time of 2 seconds or less.

6.4 Analytical balance -- Capable of weighing to the nearest 0.0001 g.

6.5 Pipets, Class A volumetric flasks, beakers -- Assorted sizes.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water -- All references to water in this method refer to reagent water, as defined in Chapter One.

7.3 Eluent, 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3 -- Dissolve 0.2856 g of sodium bicarbonate (1.7 mM $NaHCO_3$) and 0.3816 g of sodium carbonate (1.8 mM Na_2CO_3) in reagent water and dilute to 2 L with reagent water or follow manufacturer's guidance for the proper eluent for each specific column.

7.4 Conductivity suppressor regenerant solution (25 mM H_2SO_4), if required -- Add 2.8 mL of concentrated sulfuric acid (H_2SO_4) to 4 L of reagent water.

7.5 Stock solutions (1,000 mg/L) -- Certified standards may also be purchased and used as stock solutions. Stock solutions are stable for at least 1 month when stored at #6 EC.

7.5.1 Bromide stock solution (1.00 mL = 1.00 mg of BrG) -- Dry approximately 2 g of sodium bromide (NaBr) for 6 hr at 150 °C, and cool in a desiccator. Dissolve 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.2 Chloride stock solution (1.00 mL = 1.00 mg of ClG) -- Dry sodium chloride (NaCl) for 1 hr at 600 °C, and cool in a desiccator. Dissolve 1.6484 g of the dry salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.3 Fluoride stock solution (1.00 mL = 1.00 mg of FG) -- Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Store in a chemical-resistant glass or polyethylene container.

7.5.4 Nitrate stock solution (1.00 mL = 1.00 mg of NO_3^-) -- Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105 °C for 24 hr. Dissolve exactly 1.3707 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.5 Nitrite stock solution (1.00 mL = 1.00 mg of NO_2^-) -- Place approximately 2 g of sodium nitrate ($NaNO_2$) in a 125 mL beaker and dry to constant weight (about 24 hr) in a desiccator containing concentrated H_2SO_4. Dissolve 1.4998 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE: Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE: Prepare sterile bottles for storing nitrite solutions by heating them for 1 hr at 170 °C in an air oven.

7.5.6 Phosphate stock solution (1.00 mL = 1.00 mg of PO_4^{3-}) -- Dissolve 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4) in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.7 Sulfate stock solution (1.00 mL = 1.00 mg of SO_4^{2-}) -- Dissolve 1.4790 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.6 Anion calibration standards

Prepare a blank and at least three combination anion calibration standards containing the anions of interest. The combination anion solutions must be prepared in Class A volumetric flasks (see Table 2). Calibration standards should be prepared weekly, except for those that contain nitrite and phosphate, which should be prepared fresh daily. The validity of standards can be confirmed through the analysis of a freshly prepared ICV (Sec. 10.6).

7.6.1 Prepare the high-range calibration standard solution by combining the volumes of each anion stock solution specified in Sec. 7.5 in a Class A volumetric flask and diluting the mixture to 1 L with reagent water.

7.6.2 Prepare the intermediate-range calibration standard solution by diluting 10.0 mL of the high-range calibration standard solution (Sec. 7.6.1) to 100 mL with reagent water.

7.6.3 Prepare the low-range calibration standard solution by diluting 20.0 mL of the intermediate-range calibration standard solution (Sec. 7.6.2) to 100 mL with reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three, "Inorganic Analytes."

8.2 Preserve samples at ≤6 °C. If nitrite, nitrate and phosphate are analytes of interest, samples should be analyzed within 48 hr of collection. A longer holding time may be appropriate for chloride, fluoride, sulfate and bromide.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with the sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for the target analyte in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish an initial demonstration of proficiency.

9.3 Sample quality control for preparation and analysis.

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, the laboratory should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch. Any method blanks, matrix spike samples, replicate samples and LCSs should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

The following should be included within each analytical batch.

9.3.1 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank. Refer to Chapter One for the proper protocol when analyzing blanks.

9.3.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses, or set by the method quality objectives (MQOs)/data quality objectives (DQOs) of the project. In the absence of historical data or well-defined MQOs/DQOs, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data must be no wider that ± 20%. Consult Method 8000 for further information on developing acceptance criteria for the LCS. When the result of a matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS result is used to verify that the laboratory can perform the analysis in a clean matrix. If the LCS result is not acceptable, then the LCS must be reanalyzed once. If the results are still unacceptable, then all samples analyzed after the last acceptable LCS must be reprepared and reanalyzed.

9.3.3 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

9.3.3.1 At least one matrix spike (MS) sample should be analyzed within each analysis batch for determining method bias and/or sample matrix effects. The MS percent recovery (%R) is calculated as follows:

$$\%R = \frac{\left(MSSR - SR \right)}{SA} \times 100$$

Where:
MSSR = MS Sample Result
SR = Sample Result
SA = Spike Added

When the sample concentration is less than the LLOQ, use SR = 0 for purposes of calculating %R.

9.3.3.2 The method control limits for %R are 80 - 120. Alternate limits may be used provided that they meet the data quality objectives of the specific project. Failure to meet the MS %R criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem. If %R is outside the control limits and all other QC data is within limits, a matrix effect is suspected. The associated data should be flagged according to project specifications or noted in the comments section of the report.

9.3.3.3 A duplicate or matrix spike duplicate (MSD) should be analyzed within every analytical batch in order to establish the precision of the method. Calculate the relative percent difference (RPD) between the sample and duplicate result as follows.

$$\mathrm{RPD} = \frac{\left|\mathrm{S} - \mathrm{D}\right|}{\left(\mathrm{S} - \mathrm{D}\right)/2} \times 100$$

Where:
RPD = Relative Percent Difference
S = Sample or MS Sample Result
D = Duplicate or MSD Result

9.3.3.4 The method control limit for RPD is 15% for all sample concentrations that are near or above the mid-range of the calibration curve. The method control limit for RPD is 50% for sample concentrations that are near the low-range of the calibration curve. Alternate limits may be used provided that they meet the data quality objectives of the specific project. Failure to meet the duplicate RPD criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1, or as recommended by the manufacturer.

10.2 For each analyte of interest, prepare a blank and calibration standards at a minimum of three concentrations by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. A sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration at or below the laboratory's lower limit of quantitation (LLOQ). The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector.

10.3 The laboratory should establish the LLOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration levels or use of the LLOQs as the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LLOQ recoveries must be within 50% of the true values to verify the data reporting limit.

10.4 After a stable baseline is obtained (approximately 30 min), begin to inject standards starting with the lowest concentration standard and increasing in concentration to the highest standard. Use a fixed injection volume between 25 and 100 µL (determined by injection loop volume) for each calibration standard. Record the peak area responses and retention times for each analyte.

10.5 Establish the individual analyte calibration curves by plotting the peak area responses for each standard against the corresponding concentrations. Use a least squares linear regression to calculate the calibration curve formula. The linear correlation coefficient should be equal to or greater than 0.995. A weighted least squares regression may also be performed using 1/concentration or $1/(\text{concentration})^2$ as the weighting factor. The acceptance criterion for the calibration curve should be a correlation coefficient of 0.995 or higher. Refer to Method 8000 for additional guidance on calibration procedures.

10.6 Verify the accuracy of the initial calibration curve by analyzing an initial calibration verification (ICV) standard. The ICV standard must be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for the ICV standard must be no greater than ± 10% of its true value. If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed. The analysis data for the ICV must be kept on file with the sample analysis data.

10.7 Verify the accuracy of the working calibration curve on each working day, or whenever the anion eluent composition or strength is changed, and for every batch of 10 or less samples, through the analysis of a continuing calibration verification (CCV) standard. The CCV should be made from the same material as the initial calibration standards at or near mid-range. The acceptance criteria for the CCV standard should be ± 10% of its true value for the calibration to be considered valid. If the CCV standard result does not meet the acceptance criterion, sample analysis must be discontinued, the cause determined, and the instrument recalibrated. All samples analyzed after the last acceptable CCV should be reanalyzed. The analysis data for the CCV should be kept on file with the sample analysis data.

10.8 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading should not exceed approximately 500 ppm total anions when using a 50-µL sample loop and the columns listed in Sec. 6.1.

11.0 PROCEDURE

11.1 Sample preparation

When aqueous samples are injected, the water passes rapidly through the columns, and a negative "water dip" is observed that may interfere with the early-eluting fluoride and/or chloride ions. In combustate samples generated by bomb combustion (Method 5050), the water dip should not be observed, since the collecting solution is a concentrated eluent solution that will be equivalent to the eluent strength when diluted to 100-mL with reagent water according to the bomb combustion procedure. Any dilutions required in analyzing other water samples should be made with the eluent solution. The water dip, if present, may be removed by adding concentrated eluent to all samples and standards such that the final sample/standard solution is equivalent to the eluent concentration. When a manual system is used, it is necessary to micropipet concentrated buffer into each sample. The recommended procedure follows:

11.1.1 Prepare a 100-mL stock of eluent 100 times a normal concentration by dissolving 1.428 g of $NaHCO_3$ and 1.908 g of Na_2CO_3 in 100 mL of reagent water or use the manufacturer’s specified eluent. Cover or seal the volumetric flask.

11.1.2 Pipet 5 mL of each sample into a clean polystyrene micro-beaker. Micropipet 50 mL of the concentrated buffer into the beaker and stir well.

11.1.3 Dilute the samples with eluent, if necessary, to concentrations within the linear range of the calibration.

11.2 Sample analysis

11.2.1 Establish ion chromatographic operating parameters exactly equivalent to those used for calibration (Sec. 10.0). Establish a stable baseline. This should take approximately 30 min.

11.2.2 Establish a valid initial calibration or otherwise verify the working calibration curve as outlined in Sec.10.0.

11.2.3 Inject a suitable volume of sample or QC standard into the IC instrument. Use an injection volume that is optimal for the specific analytical column and instrument system. The volume of sample injected must be consistent with that used for calibration (Sec. 10.0). Record the resulting analyte peak sizes in area units as well as the peak retention times.

11.2.4 For each sample or QC standard, identify each analyte by comparing the peak retention time to the established retention time window. The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day, and may include concentrations from both ends of the calibration range. Three times the standard deviation of a retention time may be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.2.5 If the peak area response exceeds the working calibration range, then dilute the sample with an appropriate amount of reagent water or eluent and reanalyze.

11.2.6 If the resulting chromatogram for a particular sample fails to produce adequate resolution such that the identification of the anion of interest is questionable, prepare a new sample spiked with a known amount of the anion under question and reanalyze in order to confirm the presence or absence of analyte.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Using the established calibration curve, compute the concentration of each analyte in each analysis sample or QC standard based on the peak area response. Most chromatography data analysis software systems perform such calculations automatically.

12.2 Calculate the concentration of analyte in the original sample as follows:

$$\text{Final result (mg/L)} = (C)(D)$$

Where:
C = Concentration from calibration curve (mg/L)
D = Dilution factor (if needed)

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Examples of single-operator accuracy and precision values for reagent, drinking, and surface water, and mixed domestic and industrial waste water are listed in Table 3. See EPA Method 300.0 for examples of multiple laboratory determinations of bias for the analytes using an IonPac AS4A column, bicarbonate/carbonate eluent, AMMS suppressor and conductivity detection (see Ref. 1). These data are provided for guidance purposes only.

13.3 Combustate samples

Tables 4 and 5 are based on 41 data points obtained by six laboratories, in which each laboratory analyzed four used crankcase oils and three blends of fuel oil with crankcase oil. Each analysis was performed in duplicate. The oil samples were combusted using Method 5050. Each point represents the duplicate analyses of a sample. One point was judged to be an outlier and was not included in the results. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, USEPA Method 300.0, "Determination of Inorganic Anions by Ion Chromatography," EPA-600/R-93-100, August 1993.

2. Annual Book of ASTM Standards, Volume 11.01 Water, "Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography," D 4327-97, 1998.

3. Standard Methods for the Examination of Water and Wastewater, Method 4110, "Determination of Anions by Ion Chromatography," 18th Edition of Standard Methods, 1992.

4. Dionex, DX-500 System Operation and Maintenance Manual, Dionex Corp., Sunnyvale, CA 94086, 1996.

5. A. Gaskill, E. D. Estes, D. L. Hardison, and L. E. Myers, "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels," prepared for U.S. Environmental Protection Agency Office of Solid Waste, EPA Contract No. 68-01-7075, WA 80, July 1988.

17.0 TABLES, DIAGRAMS, FLOW CHARTS AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE CHROMATOGRAPHIC CONDITIONS AND RETENTION TIMES IN REAGENT WATER

Chromatographic Conditions	
Columns	See Secs. 6.1.1-6.1.2
Conductivity suppressor	See Sec. 6.1.3
Conductivity detector	See Sec. 6.1.4
Eluent	See Sec. 7.3
Sample loop	50 µL
Pump flow rate	2.0 mL/min

Analyte	Concentration of Mixed Standard (mg/L)	Retention Time (min)[a]
Fluoride	2.0	1.2
Chloride	3.0	1.7
Nitrite-N	2.0	2.0
Nitrate-N	5.0	3.2
o-Phosphate-P	2.0	5.4
Sulfate	15.0	6.9

[a] The retention time given for each anion is based on the equipment and analytical conditions described in the method. Use of other analytical columns or different eluent concentrations will affect retention times accordingly.

Data are taken from Ref. 1 and are provided for guidance purposes only.

TABLE 2

EXAMPLE STANDARD SOLUTIONS FOR INSTRUMENT CALIBRATION

		Concentration in mg/L		
Analyte	Volume of Stock Solution (in mL) used to prepare High-Range Standard[1]	High-Range Standard	Intermediate-Range Standard	Low-Range Standard
Fluoride (F^-)	10	10	1.0	0.2
Chloride (Cl^-)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (PO_4^{3-})	50	50	5.0	1.0
Bromide (Br^-)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{2-})	100	100	10.0	2.0

[1] Volumes of each stock solution (1.00 mL = 1.00 mg) that are combined in a Class A volumetric flask and diluted to 1 L to prepare the high-range calibration standard (refer to Sec. 7.5). These data are provided for guidance purposes only.

TABLE 3

EXAMPLE SINGLE-OPERATOR ACCURACY AND PRECISION

Analyte	Sample Type	Spike (mg/L)	Mean Recovery (%)	Std. Dev. (mg/L)
Chloride	RW	0.050	97.7	0.0047
	DW	10.0	98.2	0.289
	SW	1.0	105.0	0.139
	WW	7.5	82.7	0.445
Fluoride	RW	0.24	103.1	0.0009
	DW	9.3	87.7	0.075
	SW	0.50	74.0	0.0038
	WW	1.0	92.0	0.011
Nitrate-N	RW	0.10	100.9	0.0041
	DW	31.0	100.7	0.356
	SW	0.50	100.0	0.0058
	WW	4.0	94.3	0.058
Nitrite-N	RW	0.10	97.7	0.0014
	DW	19.6	103.3	0.150
	SW	0.51	88.2	0.0053
	WW	0.52	100.0	0.018
o-Phosphate-P	RW	0.50	100.4	0.019
	DE	45.7	102.5	0.386
	SW	0.51	94.1	0.020
	WW	4.0	97.3	0.04
Sulfate	RW	1.02	102.1	0.066
	DW	98.5	104.3	1.475
	SW	10.0	111.6	0.709
	WW	12.5	134.9	0.466

All data are taken from Ref. 1 and are based on the analyses of seven replicates. These data are provided for guidance purposes only.

RW = Reagent water
DW = Drinking water
SW = Surface water
WW = Waste water

TABLE 4

EXAMPLE REPEATABILITY AND REPRODUCIBILITY DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY ANALYSIS

Average Value (µg/g)	Repeatability (µg/g)	Reproducibility (µg/g)
500	467	941
1,000	661	1,331
1,500	809	1,631
2,000	935	1,883
2,500	1,045	2,105
3,000	1,145	2,306

Data are taken from Ref. 5 and are provided for guidance purposes only.

TABLE 5

EXAMPLE RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY ANALYSIS

Amount Expected (µg/g)	Amount Found (µg/g)	Bias (µg/g)	Bias (%)
320	567	247	+77
480	773	293	+61
920	1,050	130	+14
1,498	1,694	196	+13
1,527	1,772	245	+16
3,029	3,026	-3	0
3,045	2,745	-300	-10

Data are taken from Ref. 5 and are provided for guidance purposes only.

FIGURE 1

SCHEMATIC OF ION CHROMATOGRAPHY INSTRUMENTATION

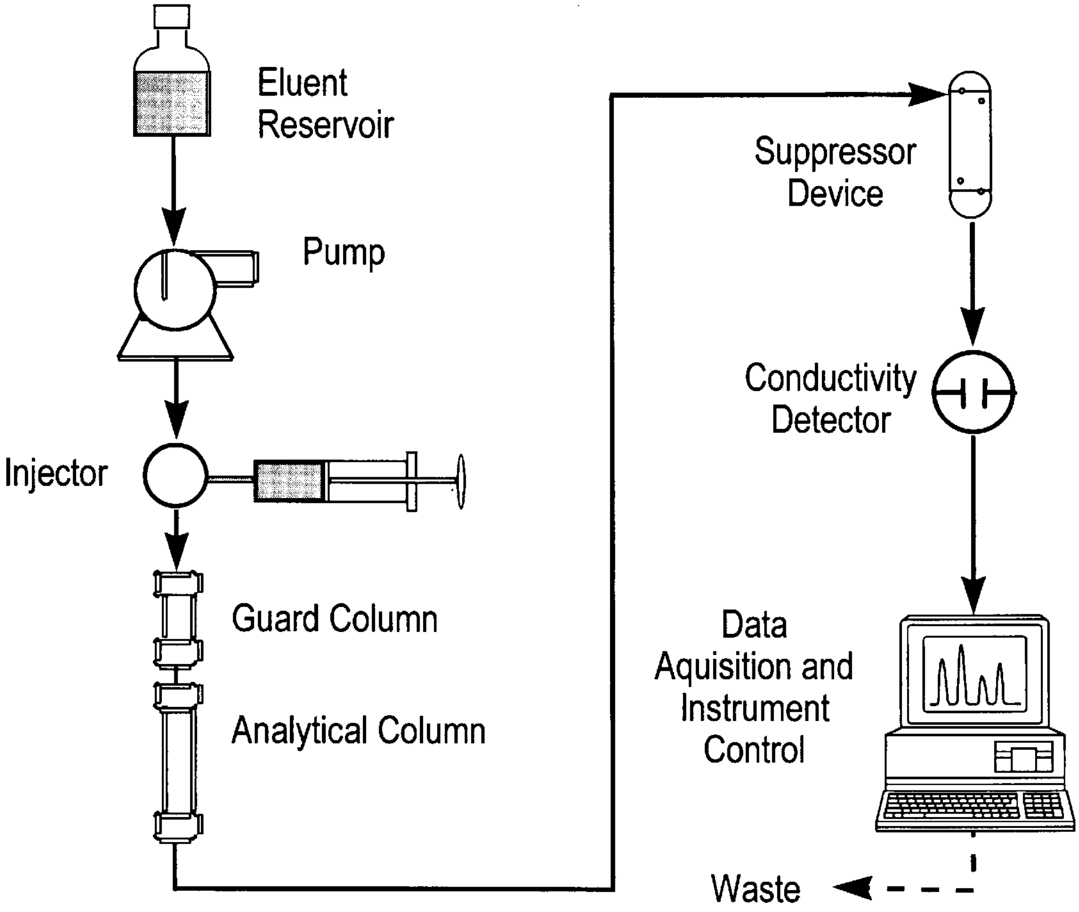
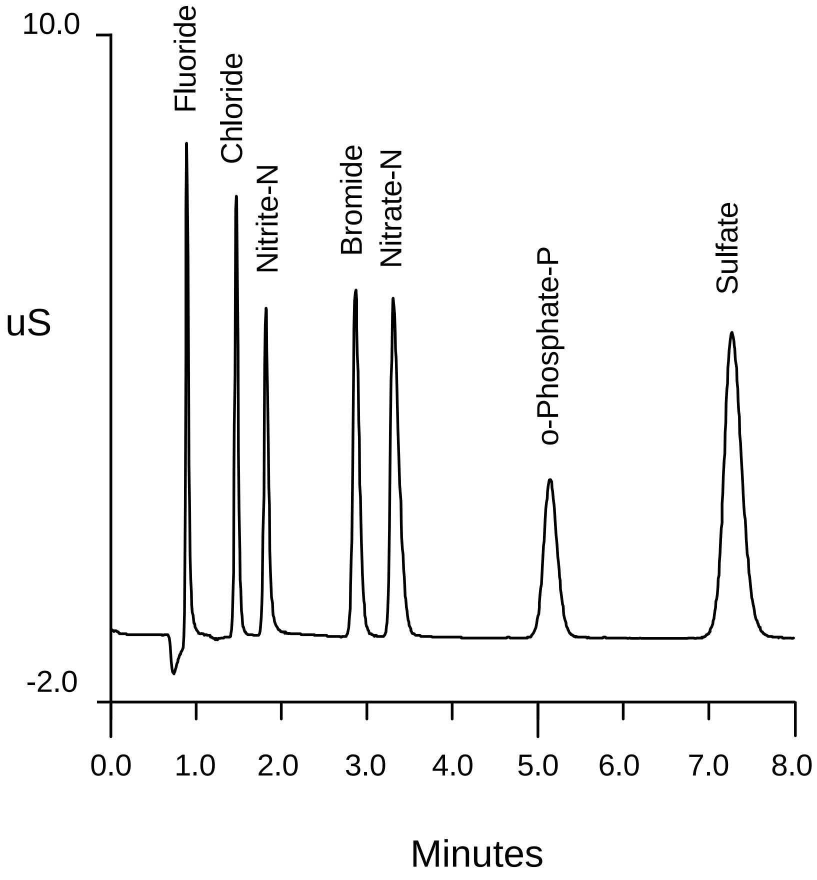


FIGURE 2

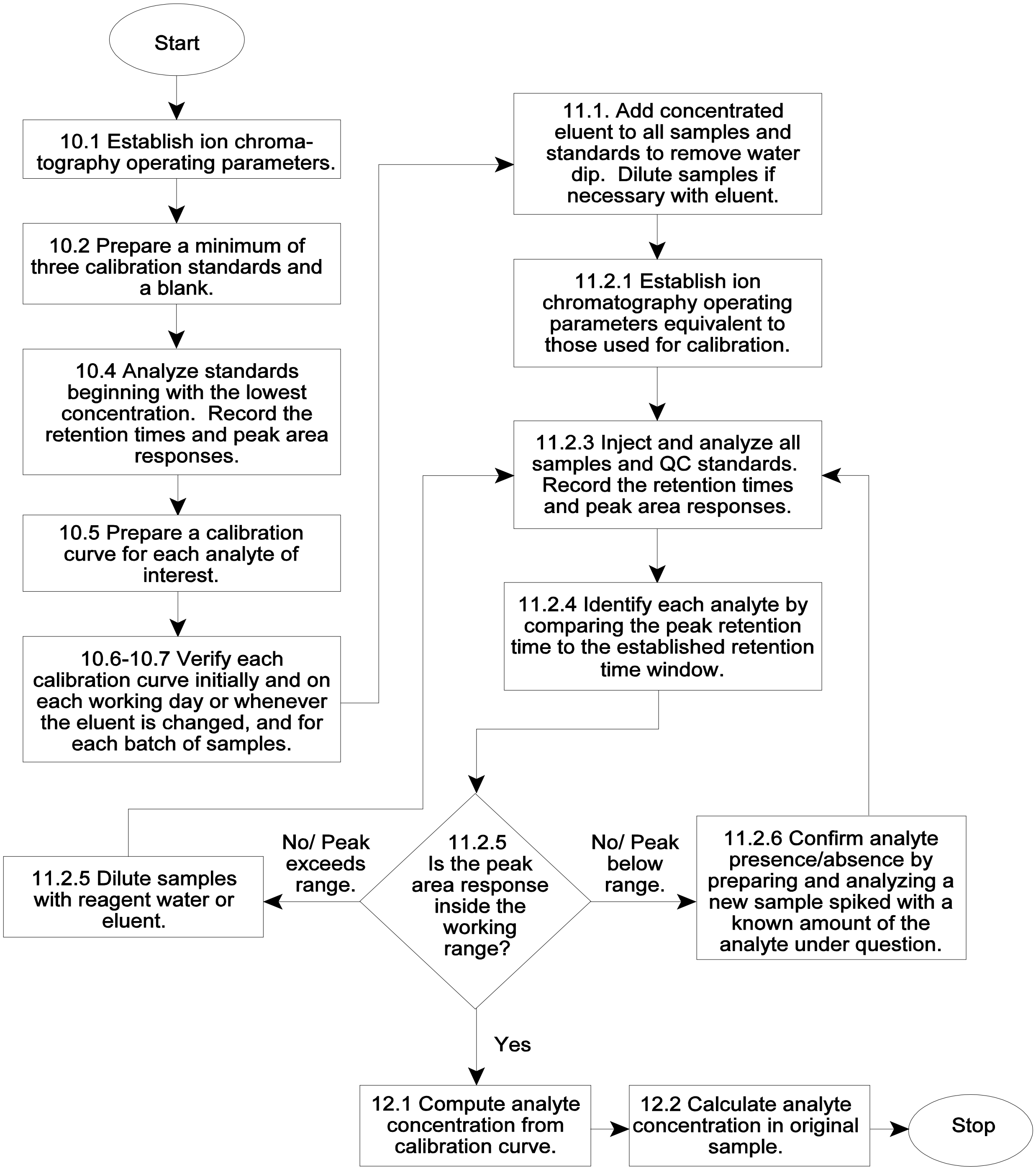
EXAMPLE ANION PROFILE



This figure is provided for guidance purposes only.

METHOD 9056A

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY



Document C-7: Groundwater Tracing Particle Sampling Protocol

Groundwater Tracing Particle Sampling Protocol

The project team will perform passive and active sampling to detect groundwater tracing particles (GTP) in wells and springs. The particles are designed such that they may be captured in well and spring samples and subsequently identified in the laboratory, or detected in situ in the field. They are designed to be (i) neutrally buoyant, which allows them to move freely in water, (ii) fluorescent, which will allow for their detection with a black light source, and (iii) magnetic, which will allow the particles to be captured and retained with rare earth magnets.

Passive Sampling

Passive sampling will use three approaches for particle detection, each of which have not yet been installed and are contingent upon approval form ODEQ:

1. Rare earth magnets will be installed at Byrds Mill Spring and other springs to capture any particles that migrate all the way from the EAR sinkhole to the spring and flow out of the aquifer in the water column.
2. Sediment traps will be deployed in wells EAR 1 - EAR 5 to passively capture particles that migrate into boreholes. Material collected in sediment traps will periodically be removed and laboratory analysis will be performed to identify the presence of any fluorescent or magnetic particles. The interval at which material in sediment traps needs to be collected at each location will be evaluated and adjusted on an ongoing basis as long-term monitoring proceeds.
3. The project team will perform periodic black light surveys of the spring enclosure situated over the Byrds Mill Spring pool to identify fluorescence and, subsequently, detect the presence of any GTPs discharging from the spring orifices. The interval at which black light surveys need to be performed at Byrds Mill Spring will be evaluated and adjusted on an ongoing basis as long-term monitoring proceeds.

These passive detection approaches will be utilized for a period of one year after the completion of the sub-tests.

Active Sampling

During well sampling associated with long-term monitoring after tracer releases, in-line sediment trapper filters (shown in Figure 1) will be used during well purging and sampling to filter out and retain any particles that migrate to monitoring wells. The material that collects in each filter will be examined for magnetic or fluorescent characteristics to detect the presence of GTPs. A rare earth magnet will be inserted in the filter setup to provide an additional mechanism to capture the GTPs. Active sampling for GTPs as part of long-term monitoring activities will allow for a larger capture zone for the particles than passive sampling alone.

Figure 1: In-line sediment trapper filter example

Capture Analysis

The expectation of the experiment is that particles will make it to one to three EAR wells during a one-year monitoring period. The particles are only expected to make the full distance to one of the local springs during high flow storm events, if at all. The number of particles detected and the associated time of travel for any detected particles will provide information on conduit size and transport properties in the groundwater system underlying the EAR site. If significant quantities of particles are captured, their mass will be used to estimate the number of particles which migrated through the system. If a small number of particles are captured, they will be counted visually as individual particles.

Document C-8: USGS Tracer Test Documentation Memo

USGS Tracer Test Documentation and Methods Memo for the EARs Site Arbuckle-Simpson Aquifer

October 19, 2021

Shana Mashburn, Kayla Lockmiller

This memo was developed for the Enhanced Aquifer Recharge site, using a hydrogeologic, geophysical, and geochemical methods team, to understand the information and data documentation required for using the interpreted results of a planned tracer test in the Arbuckle-Simpson Aquifer (ASA) Phase 2 study and associated U.S. Geological Survey (USGS) publications. Methods used for this project will be similar to Chapter 3 in Rosenberry and LaBaugh (2008).

Tracer tests, which can define the estimates of localized recharge, residence times, flow paths, and/or hydraulic characteristics of a specific aquifer or aquifer system, are an integral part of USGS interpretive ground-water investigations. The results of these tracer tests are critical components of flow-system analysis and are important to conclusions published in USGS reports. Consequently, reported aquifer characteristics including hydraulic conductivity, transmissivity, storativity, and other hydraulic characteristics derived from this test or additional aquifer test analyses must be clearly documented and technically defensible.

Documentation of Tests: The following elements should be documented for this specific tracer test and associated slug tests. These elements assume that this test is comprised of an injection site at the EARs sinkhole, one or more observation wells, and downstream observation at Byrd’s Mill Spring. The ten elements of proper documentation are as follows:

1. A brief description of the test which includes the purpose, date, test procedures, and methods of analysis for the results. Any unique or unusual features or problems related to the test or to the collection and analysis of test data should be described. A brief description of the assumptions used in analyzing the test results also should be included as needed to clarify the test.
2. A sketch of the test site showing the distances from the injection site to all observation wells and the location of any boundaries, streams, springs, ditches, pumping or flowing wells, or other features that possibly could influence test results. Where the test includes multiple wells, the sketch of the test site should be drawn to scale.
3. Description of test and observation wells construction, including screened and open interval(s), casing and screen diameters, and location of filter pack and grouted intervals.
4. A description of the site hydrogeologic characteristics, including sections that show the major water-bearing and confining units. The intervals of the observation wells that are screened or open should be depicted on the logs or sections. Borehole geophysical logs and surface geophysics can be useful in helping determine site hydrogeologic characteristics, but not required for tracer test documentation.
5. Complete time-discharge records of any influencing wells, springs or streams nearby.
6. Complete water-level records and hydrographs (including from weir measurements) showing pre-test trends and water levels during the testing phase.
7. Description of methods and computations showing any adjustments for pre-test trends, or adjustments to account for extraneous effects not related to the tracer test.
8. All plots of observed or adjusted data used to determine hydraulic characteristics and computations.
9. Concentration or mass of tracer released, location, and time released.
10. Downstream tracer-detection measurements, whether from a data logger, field meter, or samples collected to identify the breakthrough curve characteristics and calculation of total mass resurged at expected outflow sites.

All outputs from the data-collection equipment should be included in an electronic archive (for example, data logger output files, output files from data-analysis programs, and summary data files created in other software packages such as Excel). If possible, all files should be saved as text files (ASCII), in addition to any proprietary formats, to ensure that they remain available even if proprietary software changes. The theoretical basis of any software should be documented and it should be demonstrated that a test-data set can be correctly analyzed using the software. Submittal of a computer-software analysis does not eliminate the need for the information described in element 8, above.

Methods: The tracer test(s) performed for use in the Phase 2 Eastern Arbuckle-Simpson Aquifer study will be interpreted both qualitatively and, more importantly, quantitatively using the methods described in this section.

Fully quantitative dye-tracer tests require accurate measurement of the amount (mass) of tracer dye (in this case, fluorescent-magnetic nanoparticles) injected, the discharge from the spring or aquifer during the test, and the concentration or total mass of tracer dye resurging from the aquifer. Quantitative dye-tracer tests are primarily used to obtain information about the time-of-travel and breakthrough characteristics of the tracer dye—which are important to contaminant-related studies—and to investigate karst conduit structure and flow properties (Field and Nash, 1997). Provided that discharge is measured simultaneously with tracer concentration at all dye-resurgence points, tracer mass recovery can be determined and used to make reliable estimates of conduit hydraulic properties including mean residence time, mean flow velocities, longitudinal dispersion, and storage (Field, 2002).

Historically, a variety of equations have been devised to estimate the quantity of dye needed for tracer test injections, based largely on distance to the anticipated resurgence point and/or estimated ground-water flow velocities. Most of these are difficult to apply in practice and do not provide a means for the investigator to predict and manage the resurgent concentration of tracer dye. These shortcomings are addressed in methods devised by Field (2003) and by Worthington and Smart (2003).

The method proposed by Worthington and Smart (2003) relies upon the empirically derived equations:

$$M = 19\ (LQC)\ 0.95$$

$$\text{and } M = 0.73\ (TQC)\ 0.97$$

where M is mass of tracer dye injected (grams/meter^3), L is anticipated distance between the injection site and the anticipated primary resurgence site (meters), Q is discharge at the anticipated resurgence (meters^3/second), C is peak tracer concentration at the anticipated resurgence (grams/meter^3), and T is travel time as determined from prior tracing test results (seconds). Using either equation, the investigator can select a target concentration desired for resurging tracer dye and solve to determine the required amount (mass) of dye needed for injection.

For quantitative analysis, all fluorometers must be calibrated so that the concentration of dye is determined by the fluorescent intensity of the sample measured relative to that of dye-concentration standards. Standards are prepared from the tracer-dye stock solution by using gravimetric and serial dilution techniques in the manner described by Wilson and others (1986) or Mull and others (1988).

Analysis of dye-breakthrough curves (measured dye concentration over time) obtained via quantitative dye-tracer tests is an effective means of determining conduit-flow characteristics in karst aquifers (Smoot and others, 1987). Advantages provided by using this method, listed by Kincaid and others (2005), include:

- Plotting of the increase and decrease in fluorescence increases the confidence that tracer-test results are accurate and reflect the actual passage of the injected tracer dye through the aquifer.
- More accurate estimates of flow velocity can be calculated using time-to-peak concentrations.
- Integrating the area under the dye-breakthrough curve allows for estimation of the mass of tracer recovered at a sampling site and, therefore, the relative contribution of flow from the injection site to the tracer resurgence site.
- If it can be assumed that 100 percent of the tracer dye was recovered, evaluation of the shape of the dye-breakthrough curve provides data needed for estimation of hydraulic properties such as longitudinal dispersion, Reynolds and Peclet numbers, and discharge.

Important characteristics of the dye-breakthrough curve (fig. 1) include the first arrival or time to the leading edge of the dye pulse, time to peak concentration, elapsed time of passage of the dye pulse, and time to trailing edge or passage of the dye pulse. As Field (1999) notes, these characteristics are not entirely objectively defined because they are dependent on sampling frequency and instrument sensitivity. Apart from sampling frequency bias, the shape and magnitude of the dye-breakthrough curve are most influenced by: (1) the amount of dye injected, (2) the velocity and magnitude of the flow, (3) internal structure and hydraulic properties of the conduit flow path taken by the tracer dye, and (4) other factors that affect mixing and dispersion of the tracer dye in the aquifer (Smart, 1998; Field, 1999). Thus, the dye-breakthrough results obtained represent the transport characteristics of the tracer dye under the hydrologic conditions occurring during a particular test. Repeated quantitative tracer tests may be needed to characterize tracer dye characteristics under different flow conditions.

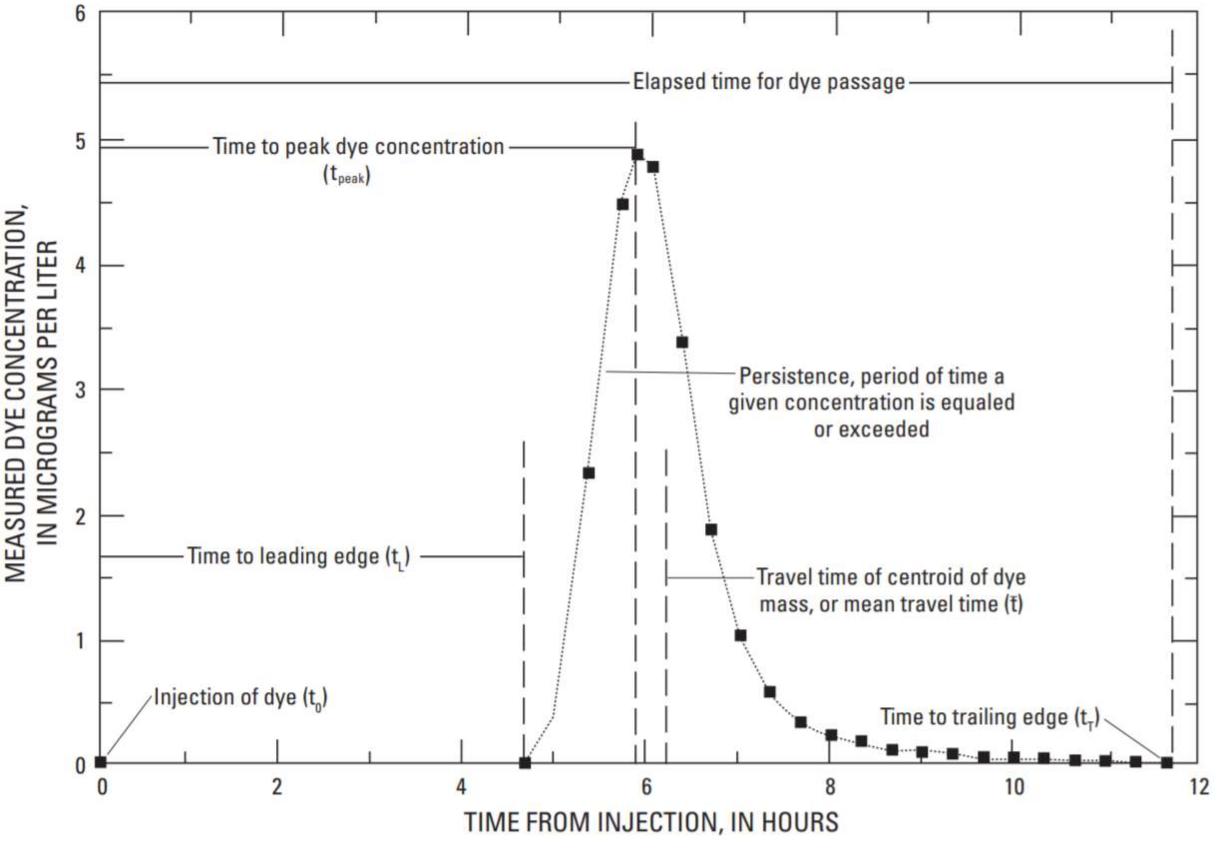


Figure 1. Some important physical characteristics of a dye-breakthrough curve (from Mull and others, 1988).

The physical properties of the dye-breakthrough curve provide information about conduit structure and organization (Smart, 1998). The dispersion of a dye plume increases with time and distance, and the pattern of dye recovery obtained reflects the effects of processes such as dilution, longitudinal dispersion, divergence, convergence, and storage, which are related to discharge and conduit geometry. The effects of longitudinal dispersion of the dye pulse usually are seen as a lengthening of the breakthrough curve ("tailing"), and the effects of tracer retardation usually are seen as multiple secondary peaks in dye concentration along the profile of the breakthrough curve. Interpretation of complex or multipeaked dye-breakthrough curves may be difficult because the factors contributing to tracer dispersion or retardation may include anastomosing (bifurcation or braiding) conduit-flow paths; flow reversal in eddies and variability in conduit cross-sectional areas (Hauns and others, 2001); intermittent storage and flushing of hydraulically stagnant zones (Smart, 1998); and interconnected zones of higher and lower fracture permeabilities (Shapiro, 2001). The potential effects of such factors on the shapes of dye-breakthrough curves under high-flow and low-flow conditions are illustrated in figure 2. Interpretation of the physical characteristics of the breakthrough curves usually cannot be based solely on the pattern of recovery of dye, but also on knowledge of the physical hydrogeology and conduit structure in the karst aquifer under study (fig. 2; Jones, 1984). A variety of hydraulic properties, including the hydraulic radius or (assuming open-channel flow conditions) hydraulic depth, Peclet number, Reynolds number, Froude number, and hydraulic head loss can be estimated using dye-breakthrough curve data if it can be assumed that nearly 100 percent of the tracer dye was recovered (Field, 1999; Mull and others, 1988; Field, 2002). The computer program QTRACER2 (Field, 2002), automates curve plotting and facilitates many of the calculations involved in the dye-breakthrough curve analysis obtained by analysis of dye-breakthrough curve data.

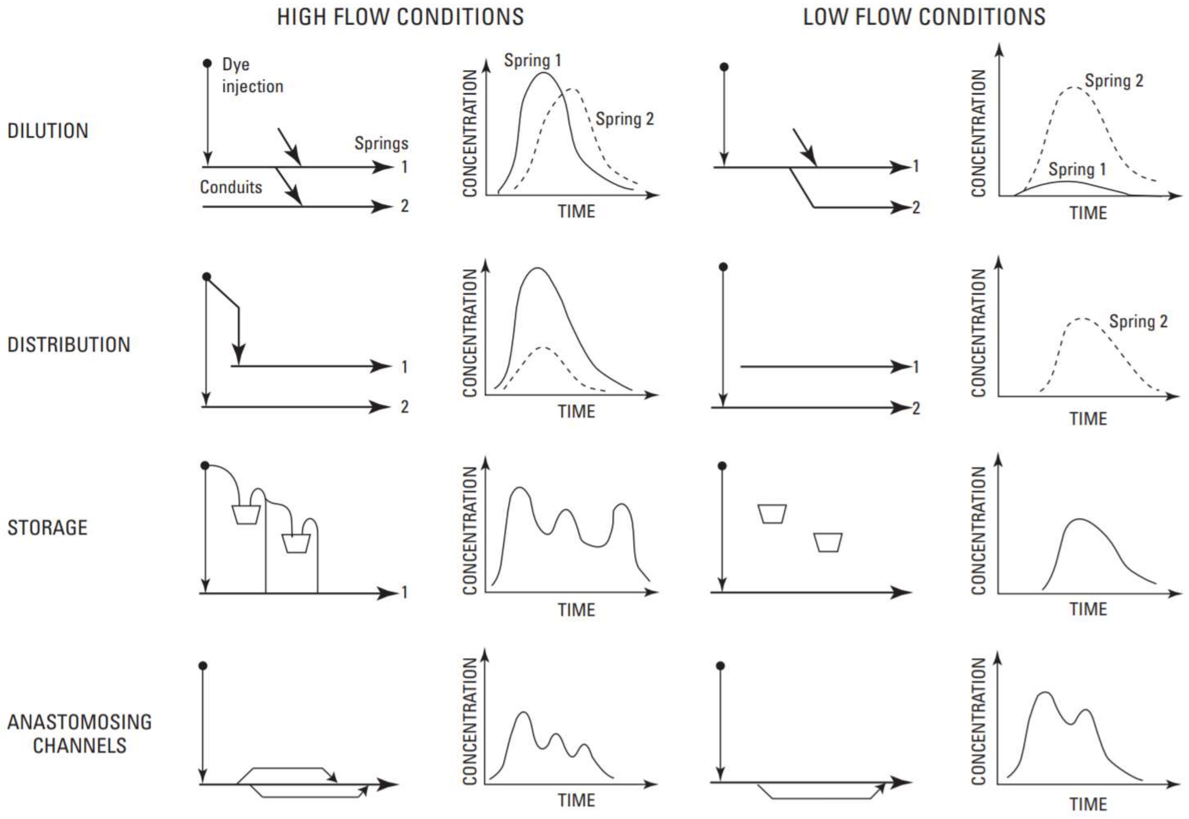


Figure 2. Shapes of hypothetical dye-breakthrough curves affected by changes in hydrologic conditions (high flow, low flow) and conduit geometry (modified from Jones, 1984, after Smart and Ford, 1982). Used with permission from the National Speleological Society (www.caves.org).

Mean tracer-dye residence time is estimated by the equation:

$$t_m = \int_0^\infty t C(t) Q(t)\, dt \,/ \int_0^\infty C(t) Q(t)\, dt$$

where t is time of sample collection, C(t) is measured dye concentration of the sample, and Q(t) is the discharge measured at the sampling location.

Mean tracer velocity (of the dye mass centroid) represents the average rate of travel of dye through the karst basin and is estimated by:

$$V_{(M)} = \int_0^\infty (1.5x/t) C(t) Q(t)\, dt \,/ \int_0^\infty C(t) Q(t)\, dt$$

where x is straight-line distance between the dye injection and resurgence site, and 1.5 is a constant representing the conduit sinuosity factor (Field, 1999).

It is important to assess tracer mass recovery as a starting point in the analysis of quantitative dye-tracing tests. The quality of the tracer experiment may be quantified in terms of the relation between the mass of dye tracer injected (M_{in}) during the experiment and the total mass of dye tracer recovered (M_r). A test accuracy index (AI) proposed by Sukhodolov and others (1997) is calculated by:

$$AI = M_{in} - M_r / M_{in}$$

This index provides a semiquantitative assessment of the quality of the test. A value AI = 0 indicates a perfect tracing experiment with no loss of tracer dye mass. A positive AI value indicates that more tracer dye mass was injected than was recovered—a common result, whereas a negative value indicates more dye mass was recovered than was injected—an impossibility unless residual tracer dye is present in the aquifer, errors are made in determining the dye concentration in test samples, or initial calculations of the injected dye mass are in error.

In the previous equation, the value for M_r, the total mass of tracer dye recovered is given by the equation:

$$M_r = \int_0^\infty C(t)\,Q(t)\,dt.$$

A simple summation algorithm can be used to facilitate the calculations needed to obtain the value for M_r as described by Field (2002):

$$M_r = \int_0^\infty C(t)Q(t)\,dt \approx,$$

$$\sum_{i=1}^{n} C(i)Q(i)\,\Delta t_i \approx,$$

$$t_c \sum_{i=1}^{n} (C_i Q_i),$$

where t_c is a time conversion needed to obtain units of mass only. The previous equations assume that the total dye mass is recovered at a single spring site. If dye has resurged at multiple spring outlets, these calculations are repeated for each site and the results are summed to obtain M_r.

In summary, reported aquifer characteristics that are calculated from tracer-tests must be clearly documented and technically defensible. As such, the USGS technical lead, Shana Mashburn, or her designee, will prepare a formal tracer-test packet that includes the ten documentation elements outlined in this memo, the methods for conducting successful tracer tests (as described above), and requirements for interpretation of results by USGS standards. Tracer-test results and all information provided in the completed tracer-test packet will be reviewed and approved within the USGS review process. This review includes checking of the field data and a verification that the test results are appropriate, given the site hydrogeology, well construction, and test conditions, and assurance that the test results have been reviewed independently. Once approved, test results, hydraulic characteristics, and related site and well data will be archived and entered into USGS NWIS database, and results will be readily available to publish as part of the Arbuckle-Simpson Aquifer Phase 2 study results.

References

Field, M.S., 1999, Quantitative analysis of tracer breakthrough curves from tracing tests in karst aquifers, in Palmer, A.N., Palmer, M.V., and Sasowsky, I.D., eds., Karst modeling: Leesburg, Va., Karst Waters Institute Special Publication 5, p. 163–171.

Field, M.S., 2002, The QTRACER2 program for tracer-breakthrough curve analysis for tracer tests in karstic aquifers and other hydrologic systems: U.S. Environmental Protection Agency Publication EPA/600/R–02/001, 179 p.

Field, M.S., 2003, Tracer-test planning using the Efficient Hydrologic Tracer-Test Design (EHTD) Program: Washington, D.C., U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, EPA/600/R–03/034, 103 p.

Field, M.S., and Nash, S.G., 1997, Risk assessment methodology for karst aquifers—(1) Estimating karst conduit-flow parameters: Environmental Monitoring and Assessment, v. 47, no. 1, p. 1–27.

Hauns, M., Jeannin, P.-Y., and Atteia, O., 2001, Dispersion, retardation and scale effect in tracer breakthrough curves in karst conduits: Journal of Hydrology, v. 241, p. 177–193.

Jones, W.K., 1984, Analysis and interpretation of data from tracer tests in karst areas: National Speleological Society Bulletin, v. 46, p. 41–47.

Kincaid, T.R., Hazlett, T.J., and Davies, G.J., 2005, Quantitative groundwater tracing and effective numerical modeling in karst—An example from the Woodville Karst Plain of North Florida, in Beck, B.F., ed., Sinkholes and the engineering and environmental impacts of karst, Proceedings of the 10th Multidisciplinary Conference, San Antonio, Texas, September 24–28, 2005: Geological Institute of the American Society of Civil Engineers, Geotechnical Special Publication no. 144, p. 114–121.

Mull, D.S., Liebermann, T.D., Smoot, J.L., and Woosley, Jr., L.H., 1988, Application of dye-tracing techniques for determining solute-transport characteristics of ground water in karst terranes: Atlanta, Ga., U.S. Environmental Protection Agency, EPA Report 904/6–88–001, 103 p.

Rosenberry, D.O., and LaBaugh, J.W., 2008, Field techniques for estimating water fluxes between surface water and ground water: U.S. Geological Survey Techniques and Methods 4–D2, 128 p.

Shapiro, A.M., 2001, Effective matrix diffusion in kilometer-scale transport in fractured crystalline rock: Water Resources Research, v. 37, p. 507–522.

Smart, C.C., and Ford, D.C., 1982, Quantitative dye tracing in a glacierized alpine karst: Beitraege Zur Geologie der Schweiz—Hydrologie, v. 28, no. 1, p. 191–200.

Smart, C.C., 1998, Artificial tracer techniques for the determination of the structure of conduit aquifers: Ground Water, v. 26, p. 445–453.

Smoot, J.L., Mull, D.S., and Liebermann, T.D., 1987, Quantitative dye tracing techniques for describing the solute transport characteristics of ground-water flow in karst terrane, in Proceedings of the Second Multidisciplinary Conference on Sinkholes and the Environmental Impacts of Karst, Orlando, Florida, February 9–11, 1987: National Water Well Association, p. 269–275.

Sukhodolov, A.N., Nikora, V.I., Rowin´ski, P.M., and Czernuszenko, W., 1997, A case study of longitudinal dispersion in small lowland rivers: Water Environmental Resources, v. 97, p. 1246–1253

Wilson, J.F., Jr., Cobb, E.D., and Kilpatrick, F.A., 1986, Fluorometeric procedures for dye tracing: U.S. Geological Survey Techniques for Water Resources Investigations, book 3, chap. A12, 34 p.

Worthington, S.R.H., and Smart, C.C., 2003, Empirical determination of tracer mass for sink to spring tests in karst, in Beck, B., ed., Sinkholes and the engineering and environmental impacts of karst: Huntsville, Ala., Proceedings of the Ninth Multidisciplinary Conference, September 6–10, 2003, p. 287–295.

Document C-9: Well Construction Variance Submission to City of Ada

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
GROUND WATER AND ECOSYSTEMS RESTORATION DIVISION
PO BOX 1198 • ADA, OK 74821

April 1, 2021

OFFICE OF
RESEARCH AND DEVELOPMENT

MEMORANDUM

SUBJECT: Well construction variance request.

FROM: Randall Ross, Ph.D., Hydrologist
Applied Research and Technical Support Branch

TO: Cody Holcomb, City Manager
Ada, Oklahoma

Per our previous discussions, please find below the necessary information for the city of Ada to submit well construction variance to the OWRB. If you have any questions, please do not hesitate to contact me at your convenience (580-421-5205).

The locations of the proposed wells is approximately 3 miles southwest of Fittstown, OK (Sec. 4, T1N, R6E) (Figure 1, Table 1). The wells will be constructed to prevent the downward migration of surface runoff via the well annulus and allow continued study of the aquifer after well completion. The West Spring Creek formation underlies the study area. The upper 250 feet of borehole will be sealed with bentonite and cement, leaving the lower portion of the borehole open for further study (Figures 2 and 3). Open-hole completion is required to allow testing (hydrogeologic, geophysical and geochemical) of discreet fracture zones that may contribute to groundwater flow. All wells will be drilled with to depths of approximately specified in Table 1 using air rotary drilling methods. Formation material will be obtained for further characterization at approximately 20-40 ft intervals. Ten-inch PVC surface casing will be installed to a depth of approximately 250 ft bls. A surface seal will be installed from 10 ft bls to land surface using cement grout. A 3 ft x 3 ft concrete surface pad will be installed around a steel protective case with locking cap.

Well Name	Latitude	Longitude
EAR-102D	34.588617°	-96.673729°
EAR-102I	34.588086°	-96.674968°
EAR-103D	34.591353°	-96.679280°
EAR-103I	34.591154°	-96.679353°
EAR-106D	34.585878°	-96.680424°
EAR-106I	34.585846°	-96.680536°

Table 1. Approximate locations of proposed wells.

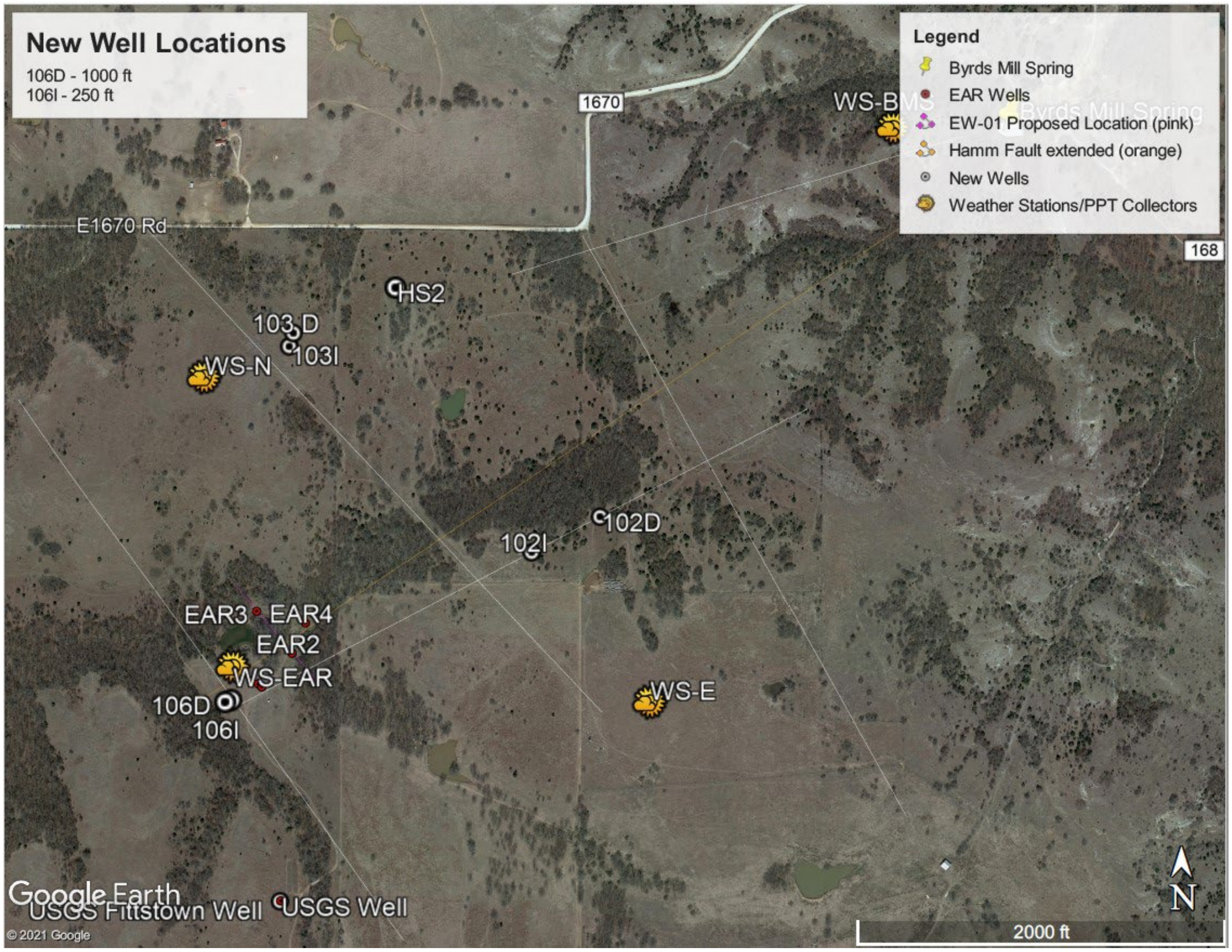
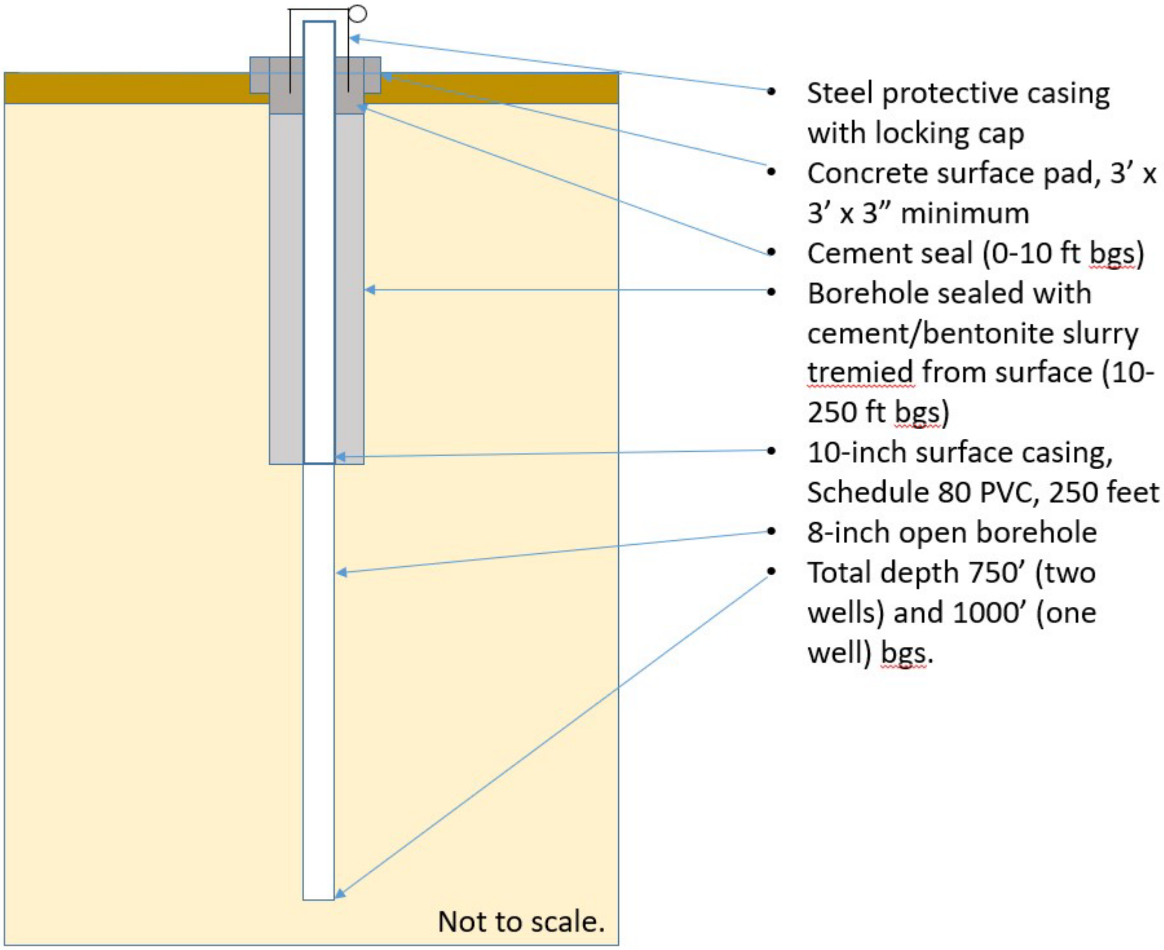


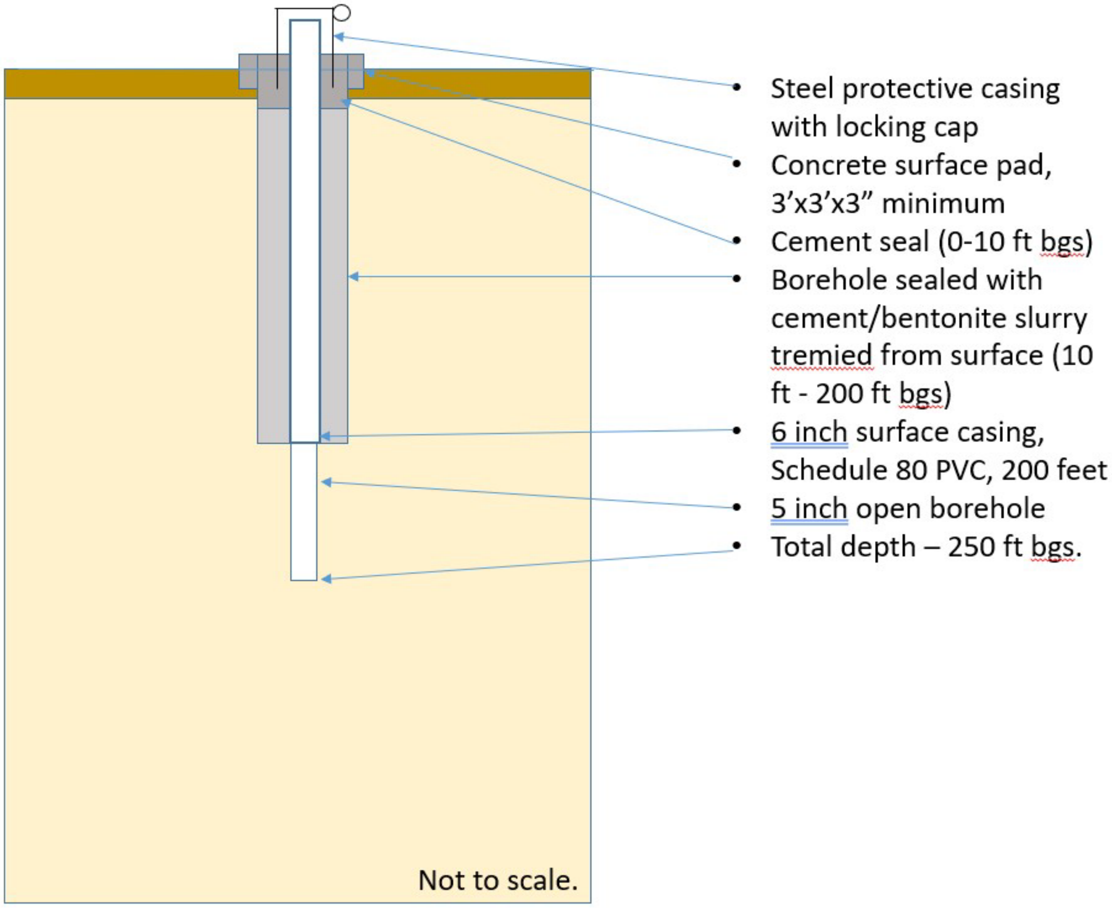
Figure 1. Approximate location of proposed wells Sec. 4, T1N, R6E.



- Steel protective casing with locking cap
- Concrete surface pad, 3’ x 3’ x 3” minimum
- Cement seal (0-10 ft bgs)
- Borehole sealed with cement/bentonite slurry tremied from surface (10-250 ft bgs)
- 10-inch surface casing, Schedule 80 PVC, 250 feet
- 8-inch open borehole
- Total depth 750’ (two wells) and 1000’ (one well) bgs.

Not to scale.

Figure 2. Proposed deep well construction details.



- Steel protective casing with locking cap
- Concrete surface pad, 3’x3’x3” minimum
- Cement seal (0-10 ft bgs)
- Borehole sealed with cement/bentonite slurry tremied from surface (10 ft - 200 ft bgs)
- 6 inch surface casing, Schedule 80 PVC, 200 feet
- 5 inch open borehole
- Total depth – 250 ft bgs.

Not to scale.

Figure 3. Proposed intermediate well construction details.

Appendix D: City of Ada/ODEQ Correspondence Permitting Sub-test 1

Work Plan: Stage 1 System Test

I. Objectives:

   a. Test water delivery system components (ie: tanks, pumps, valves, suction hose, discharge hose). Field personnel will monitor to make sure system integrity is maintained and evaluate both the set-up time and break-down time needed for the test.
   b. Determine discharge rate (gal/min). Time will be determined from start of pumps to flow interruption when tank is empty. Average flow rate = 2500 gal/pump time.
   c. Determine temperature differential. A handheld infrared thermometer will be used to continuously monitor record discharge water temperature.
   d. Evaluate Potential Temperature and Water Table Elevation Changes in monitoring well network. Currently deployed HOBO data logger will be recovered and down-loaded after test to evaluate collected temperature and pressure data.

II. Narrative:

The duplicate (2) 2500 gallons storage tanks will be filled with freshly collected native Arbuckle-Simpson Aquifer ground water, discharging spring from Byrds Mill Spring utilizing a City of Ada (potable) water truck. Each filled storage tanks will be connected to a new, dedicated general purpose 2-Inch centrifugal water pump with maximum rate capacity of 164 GPM, through a 20' quick-connect 2" vacuum hose. The discharge side of the pump will be connected to 300' of 2" quick-connect discharge hose, which will deliver water to the EAR site sinkhole. Data loggers (HOBO: temperature, pressure) will be deployed in nearby monitoring wells and will be utilized to detect any possible changes in aquifer conditions.

III. Site and Test Conditions:

   a. Injection Water. The injection water will essentially native ground water reintroduced through the test site sink hole. No amendments are planned for the Stage 1 System Test. We expect, approximately, a 20°F temperature differential between the injected water (expected discharge temperature 80°F) and the *in-situ* conditions found in the Arbuckle Simpson Aquifer (approximately 60°F year-round). We expect to see, at most, transient temperature impacts of a few degrees in the nearby monitoring well, as mixing equilibrates the introduced and native aquifer water. A transient 20°F or less degree temperature differential will have little impact on native microorganisms. Recent water quality analysis is included in Appendix A Chemical Analysis, and Appendix B bacterial analysis.

   b. Aquifer Water. The Arbuckle Simpson ground water at the EAR test site (and Byrds Mill Spring) is consistent with the calcium magnesium bicarbonate water found in the eastern part of the Arbuckle-Simpson aquifer (1).

IV. References

1. Christenson, S., A.G. Hunt, and D.L. Parkhurst. 2009. Geochemical Investigation of the Arbuckle-Simpson Aquifer, South-Central Oklahoma, 2004–06. Scientific Investigations Report2009–5036. U.S. Department of the Interior U.S. Geological Survey.

Appendix A: Byrds Mill Spring Chemical Analysis Data

Parameter	Units	Sample Date		
		2/3/21	**4/30/21**	**6/16/21**
Temp	°C	17.2	17.4	17.6
SPC	mS/cm	0.624	0.628	0.616
TDS	mg/L	403	410	403
DO	mg/L	6.77	6.31	5.90
pH		7.08	7.04	7.16
ORP	mV	258.4	64.2	127.3
Eh	mV	207.1	207.0	207.2
Turbidity	NTU	0.84	1.33	2.41
Alkalinity	mg $CaCO_3$/L	288	290	260
Hardness	mg $CaCO_3$/L	548	330	270
Fe^{2+}	mg Fe^{2+}/L	0.18	<0.10	<0.10
H_2S	mg S/L	<0.10	<0.10	<0.10
Br	mg/L	0.03	<0.20	0.03
Cl	mg/L	3.33	3.39	3.32
SO_4	mg/L	9.06	8.56	8.81
F	mg/L	0.07	0.08	0.08
I	µg/L	2.8	2.13	4.31
DOC	mg/L	0.22	0.40	0.23
TIC	mg/L	84.8	83.2	81.5
NO_3 + NO_2	mg N/L	0.89	0.93	0.89
NH_3	mg N/L	<0.02	<0.10	<0.05
TKN	mg N/L	0.09	0.83	0.93
PO_4	mg P/L	<0.050	0.025	0.025
Total P	mg P/L	<0.100	0.020	0.016

*Prelininary Results: Approved EPA methods if available

ERT
ENVIRONMENTAL RESOURCE TECHNOLOGIES
Analytical Laboratory and Environmental Consulting
DEQ State ID 8304, D9935

Appendix B: Bacterial Anaysis

CITY OF ADA
231 S TOWNSEND
ADA OK 74820

ERT Login No. 106836
Date Received: 06/16/21
Date Reported: 06/23/21

Project: EAR

- Certificate of Analysis -

Parameter	Results	Units	Analysis Date/Time	Analyst	RL	Method
106836-01	**Sample: P061621A**					**Date Sampled: 06/16/2021**
E.coli	21.3	MPN/100ml	06/16/21 13:40	SH	1	SM 9223B
106836-02	**Sample: P061621B**					**Date Sampled: 06/16/2021**
E.coli	17.3	MPN/100ml	06/16/21 13:40	SH	1	SM 9223B
106836-03	**Sample: S061621A**					**Date Sampled: 06/16/2021**
E.coli	<1.0	MPN/100ml	06/16/21 13:40	SH	1	SM 9223B
106836-04	**Sample: S061621B**					**Date Sampled: 06/16/2021**
E.coli	<1.0	MPN/100ml	06/16/21 13:40	SH	1	SM 9223B

Approved By Tim Hensley
Tim Hensley (Laboratory Director)

P samples are EAR Test Site Pond
S Samples are Bryds Mill Spring

Document D-2: ODEQ Letter Permitting Sub-test 1

Document D-2: ODEQ Letter Permitting Sub-test 1

OKLAHOMA
DEPARTMENT OF ENVIRONMENTAL QUALITY

SCOTT A. THOMPSON
Executive Director

OKLAHOMA DEPARTMENT OF ENVIRONMENTAL QUALITY

KEVIN STITT
Governor

July 29, 2021

Mr. Cody Holcomb
City Manager
City of Ada
231 S. Townsend
Ada, OK 74820

Re: Systems Test – Limited-Scale Aquifer Storage and Recovery (LSASR) Pilot Project

Dear Mr Holcomb:

In an email dated July 26, 2021, the Department of Environmental Quality (DEQ) received the City of Ada's request to conduct a systems test for the purpose of gathering information for its future LSASR pilot project. The systems test will consist of testing water delivery system components, determining discharge rate and temperature of the injected water; as well as evaluating potential temperature and water table elevation changes in the monitoring well network. The injected water will be Arbuckle-Simpson Aquifer groundwater, collected from Byrds Mill Spring, with the expected injected temperature of the water not to exceed 90 degrees Fahrenheit.

DEQ approves the city to proceed with the systems test. Please measure the temperature of the water prior to injection. If it exceeds 90 degrees Fahrenheit, you must contact DEQ before moving forward with the test.

Please include the results obtained from the systems test as part of the forthcoming LSASR pilot project permit application. If you have any questions, please contact me at 405-702-5188 or Hillary.Young@deq.ok.gov.

Sincerely,

Hillary Young

Hillary Young, P.E.
Chief Engineer
Land Protection Division
Oklahoma Department of Environmental Quality

Appendix E: Preliminary Electrical Hydrogeology of the City of Ada MAR Research Site

Appendix E

Preliminary Electrical Hydrogeology of the City of Ada MAR Research Site

1. Executive Summary

Electrical Hydrogeology has developed over the last 30 years to allow for collection of subsurface electrical data that can be used to develop conceptual site models for aquifers. Electrical resistivity is one of the oldest methods utilized by geophysicists. Electrical Resistivity Imaging (ERI) surveys rapidly collect thousands of measurements to allow for use as a subsurface imaging tool. This tool is similar to seismic surveys for the oil industry in that it creates an “electrical picture” of the subsurface.

This appendix presents the methods and equipment used to conduct ERI experiments at the City of Ada MAR Research Site. The preliminary results of the imaging for the site are presented. This is followed by a discussion of the implications of these results and plans for research on the site using the technique.

During previous work, researchers evaluated the thickness, conductivity, and storage properties of the mantled epikarst (Klimchouk, 2004) of the Arbuckle-Simpson aquifer at three sites (Halihan et al., 2004; Halihan et al., 2009; Sample, 2008). Soil database thicknesses correlated with the thicknesses derived from direct push depth of refusal. The results showed the epikarst zone is approximately nine times larger than the soil zone. The storage potential of the mantled epikarst region of the aquifer is the same order of magnitude as storage in the rest of the aquifer. This will influence recharge and contaminant transport at the MAR Site.

Previous work also illustrated that faults are easily detected in ERI images across the aquifer (Halihan et al., 2009; Riley, 2006). The faults tend to be near vertical with a fault zone width that extends 5-10 meters. Overall, ERI was shown to be a suitable technique to assist with characterizing the Arbuckle-Simpson aquifer (ASA). The aquifer has a range of electrical conductivities that are suitable for imaging, and the images have illustrated features that would be difficult to characterize using other available techniques.

Electrical characterization of the City of Ada MAR Research Site indicates that the epikarst structure and fault detection are similar to previous studies (Halihan et al., 2009). The City of Ada worked with the EPA to collect large scale ERI lines at the kilometer scale. The results indicate that a mapped fault likely connects the MAR sinkhole with Byrds Mill Spring through the vadose zone with a karst area and in the phreatic zone with a fault. This set of deep imaging illustrates some electrical boundaries in the stratigraphy that will be investigated with future drilling and logging. This report is still under review for QAQC with the EPA and is not available at this time.

A Temporal Electrical Resistivity Imaging (TERI) cable was installed at the site and has been used to collect some preliminary images for the site. During the preliminary data collection, the aquifer underwent a drying phase due to a lack of precipitation during the fall of 2021. The results indicate that the epikarst zone undergoes drainage in a pattern consistent with the weathering expected at the site. The results are also consistent with water table measurements in the nearby wells.

2. Introduction (adapted from Halihan et al., 2009)

The characterization of fractured and karstic aquifers has been attempted for many years, but our capabilities to adequately characterize these complex aquifers have not increased significantly. Much of our understanding of the flow in these aquifers has been generated from field experiments using well data or exposed rock, either in the surface or subsurface. The lack of characterization data generally stems from the cost involved in drilling, completing, maintaining and sampling wells. This cost is higher in fractured and karstic aquifers because of higher drilling costs and because heterogeneous flow fields typically require more data than are available from discrete sampling techniques that provide only limited 2- or 3-dimensional data.

Resolving these issues requires data that allow areas or volumes of the subsurface to be examined, instead of discrete sampling data alone. Most importantly, methods employed need to be economical when compared to alternative techniques.

2.1 Existing techniques

Existing methods for characterizing the ASA have relied on two detection and monitoring strategies. The first strategy involves discrete point sampling of fluids using wells, springs or multilevel piezometers whose data are integrated and interpreted. The second strategy uses indirect measurements through surface or borehole geophysical techniques.

The difficulty with point sampling techniques is that sufficient sampling can be expensive because of drilling costs, sampling time, sample analysis and data integration and interpretation time. Additionally, determining whether fractures or karst features exist between sampling locations using piezometers can be difficult or impossible to determine. Point sampling methods can miss conduits not sampled by wells, or barriers to flow like vertical faults that are not sampled with a traditional piezometer monitoring grid.

2.2 Electrical Resistivity Imaging

A solution to some of these sampling problems in the vadose and phreatic zones is the utilization of ERI to provide more complete site data coverage. A temporary surface system can be used to evaluate a 2-D or 3-D portion of subsurface, or cable can be installed in boreholes to image to deeper depths with higher resolution. Cables can also be permanently installed in shallow trenches or in boreholes for long-term monitoring applications or TERI.

Electrical resistivity measurements have been used since the 1830's to interpret the geology of the earth (Van Nostrand and Cook, 1966). The technique introduces current into the ground and the potential field is measured. Electrical Resistance Tomography (ERT) is a method of obtaining resistivity measurements that determines the electrical conductivity of the ground using subsurface electrodes (Daily et al., 2004). In contrast, a multielectrode array uses electrodes only on the surface. ERI is a general term used to indicate that a high-resolution electrical resistivity technique is being used without naming each electrode configuration differently. When multiple images are collected at the same location over time, it is referred to as TERI. TERI datasets allow processes that change the electrical properties of the subsurface to be monitored.

An electrical resistivity image is an inverted model of hundreds to thousands of measurements using a four electrode setup for each measurement. A single electrical measurement does not yield significant information, similar to a single pixel on a digital photo. However, hundreds of measurements of a site can produce a 2-D or 3-D electrical image of the subsurface. In general, in an electrical resistivity image, flow features (such as faults that conduct fluids) and higher porosity lithologies are indicated by low resistivity anomalies. Additionally, the hydraulic parameters of the formation may be estimated using electrical methods (Purvance and Andricevic, 2000a, b). The electrical data produced from this type of study may help characterize heterogeneity, fractures, and aquifer parameters (Herwanger et al., 2004; Niwas and de Lima, 2003).

2.3 ERI for the Arbuckle-Simpson Aquifer

As ERI capabilities progress due to increases in field data acquisition capabilities and computing speed, the question arises as to whether ERI techniques can be employed effectively as a method to assist with the development of conceptual models for fractured rock or karstic aquifers. Can ERI provide data that would not otherwise be available using standard techniques? Can ERI be utilized in a deep borehole configuration to provide high resolution data at depth? And finally, does the ASA have sufficient conductivity to allow ERI to be performed?

The research previously performed in the aquifer addressed the above questions and was part of the larger Arbuckle-Simpson Hydrology Project (Halihan et al., 2009). During the ERI work, three features of the resulting images generated interest among the scientists evaluating the aquifer. First, the technique indicated that a consistent 30 foot (10 m) zone of conductive media exists near the surface. This is likely a zone of epikarst that would be able to store significant amounts of water. Secondly, the images showed significant vertical conductivity zones. The zones are not highly linear in most cases. These features are interpreted as fracture zones which can transmit water to depth in the aquifer. These features extend more than 100 ft (30 m) into the subsurface in some of the images. Finally, images showed several faults, indicating that the method is effective for imaging faults in this area.

Subsequent ERI research has been used to investigate four other major research objectives in the ASA. First, the background properties of the major lithologies were assessed using quarries and outcrops (Halihan et al., 2004; Halihan et al., 2009). Second, the properties of the epikarst zone of the aquifer were evaluated (Sample, 2008). Third, the fault orientations in the aquifer were measured for several major faults (Riley, 2007). Finally, a borehole technique was evaluated for use in the ASA (Halihan et al., 2009).

Preliminary experiments in electrical hydrogeology have been conducted at the City of Ada MAR Research Site. This appendix presents the methods and equipment used to conduct these experiments as well as conditions at the MAR site. This is followed by a discussion of the implications of these results and conclusions for the aquifer.

3. General Methods and Equipment for City of ADA MAR Research Site ERI Surveys (adapted from Halihan et al., 2009)

ERI is based on the measurement of electrical resistivity. The method requires that precision electrical measurements be made repeatedly. Once a sufficient number of high-quality measurements have been obtained, a solution to the electrical properties of the subsurface can be obtained through inversion. Obtaining a repeated set of data at a single location produces a TERI dataset and can be used to evaluate temporal changes.

3.1 Resistivity

Resistance [ohms] is a fundamental property of a volume of material and is defined as the material's opposition to the flow of electrical current (Reynolds, 1997). Given a uniform cubic volume with length (L) and cross-sectional area (A), the resistance of the material will be proportional to the potential drop of an applied current (V/I). Resistivity [ohm-m] is related to this property and is expressed as a resistance through a distance, which makes it independent of material geometry. Resistance (R) and resistivity (ρ) can be expressed by the following equations (Reynolds, 1997):

$$R = V/I \text{ (ohms – } \Omega\text{) (Ohm's Law)}$$

$$\rho = V/I * A/L \text{ (ohm-meters – } \Omega\text{-m).}$$

Electrical resistivity is most commonly measured by applying a known direct or low frequency alternating current through two electrodes and measuring the potential field with another pair of electrodes. Modern technology allows this process to be controlled by automated systems with command files directing which combinations of source and potential electrodes are used and when (Ramirez et al., 1993). Automated systems are often capable of collecting hundreds to thousands of data points within an hour. Previously, hand collection systems would only acquire approximately 80 measurements per day. Additionally, advancements in inversion software allow field data to be quickly inverted and interpreted (Loke and Barker, 1996).

Resistivity can be considered to be a function of the rock porosity, volumetric fraction of saturated pores, and the resistivity of the pore water (Archie, 1942). In many cases, it is the pore fluids that contribute more to the overall resistivity signature than the host rock. Thus, for this study, one would expect that conductive anomalies are associated with larger water contents or more damaged lithologies. The signal strength in resistivity is the collected data value of voltage/current (V/I). Commonly measurements are taken twice to observe a repeatability error for each measurement.

3.2 Data Collection

Data were collected for this study using an Advanced Geosciences, Inc. SuperSting 8-channel resistivity instrument (Figure 1).

Figure E1. (Left) SuperSting 8-channel resistivity instrument and switchbox.(Right) Field data collection at MAR site.

A 56-electrode surface array was used to collect surface data. The 56-electrode system performed switching with a switchbox (Figure E1). A 20-meter spacing ERI line was collected using a GeoTrax Survey™ method with electrodes placed temporarily in the ground during data collection. A 4-meter TERI dataset was collected by collecting two datasets on a permanently installed cable downgradient of the MAR sinkhole.

4. Site Description

The City of Ada MAR Research Site is located approximately a mile SW of Byrds Mill Spring, near Fittstown, Pontotoc County, Oklahoma (Figure E2). The site is underlain by the rocks of the West Spring Creek formation. The topography at the site is gently rolling to essentially flat near the sinkhole. Soil cover is thicker in the lowlands near the sinkhole and thin on the surrounding topography. The site has a history of use as rangeland for cattle. An inferred fault is identified in the literature as crossing the site from the southwest to the northeast (Ham, 1969; Fairchild et al., 1990). Two ERI lines were collected on the site to investigate epikarst development and recharge processes (Figures 2 and 3).

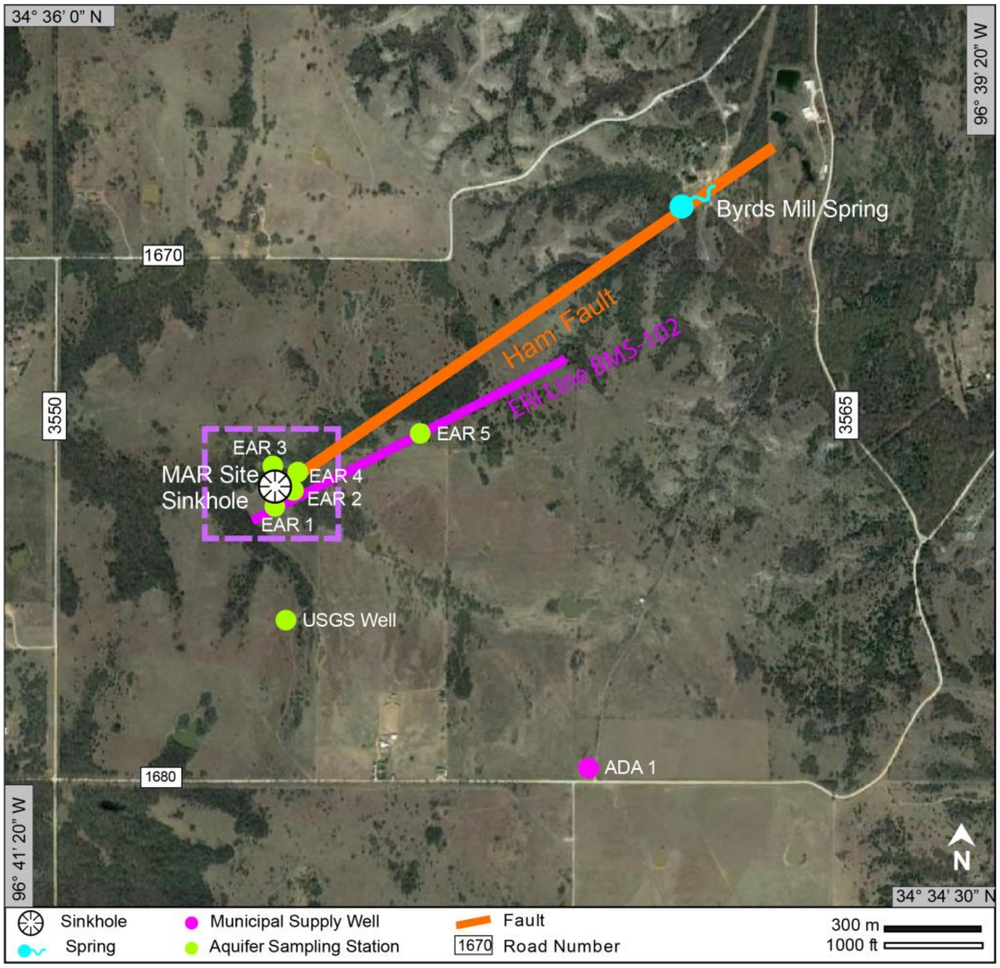


Figure E2. Map showing City of Ada MAR Research Site and Byrds Mill Spring showing location of ERI line BMS-102 in purple. Aerial photo courtesy of Google Earth.

ERI Line BMS-102 was collected parallel to the Ham Fault to evaluate stratigraphy and flow features perpendicular to the Ham Fault (Figure E2). The line length was 1100 m (3600 ft) with a depth of investigation of 220 m (720 ft). The image resolution was 10 m (33 ft). This line allowed a deeper evaluation of the electrical structure of the stratigraphy on site.

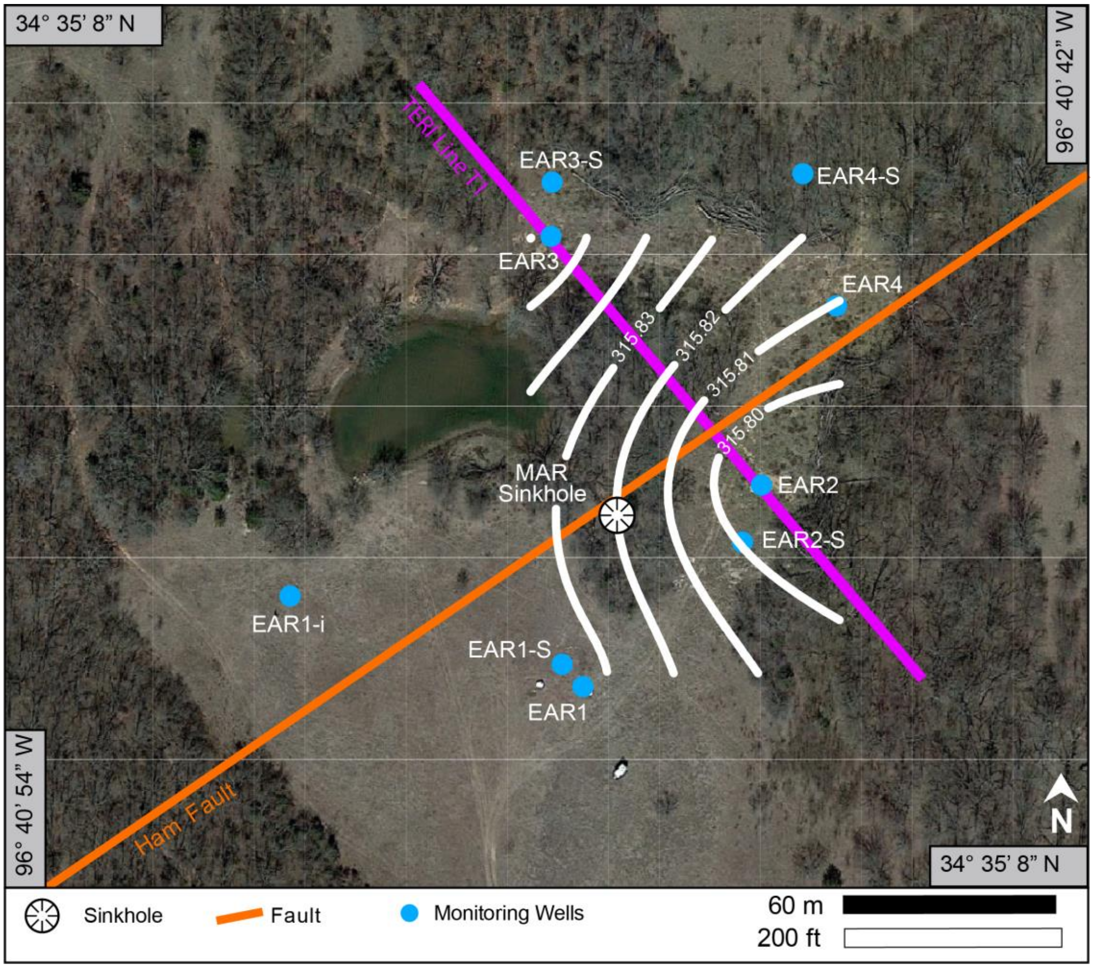


Figure E3. City of Ada MAR Research Site map with location of TERI monitoring cable in purple. Aerial photo courtesy of Google Earth.

The installed TERI line T1 was collected across the Ham Fault downgradient of the MAR site sinkhole (Figure E3). The line was established along wells EAR2 and EAR3 to evaluate electrical changes that correlate to well data and can observe potential tracer movement. The electrodes were trenched into the site and coupled to the soil using grounding grout. A PVC riser was inserted at the center of the line to protect the cables where they surface. The setup allows repeated data collections to monitor seasonal changes, tracer tests, and storm events. The line length is 220 m (720 ft) with a depth of investigation of 44 m (144 ft). The image resolution is 2.0 m (6.6 ft).

5. Preliminary Results

Electrical resistivity values at the City of Ada MAR Research Site generally increase with depth (Figures D4 and D5). In general, the upper 10-25 m (30-80 ft) of the ERI images shows a relatively high degree of electrical variability (25 to over 100 ohm-m) as compared to the observed electrical variability below that depth which is consistently higher resistivity away from vertical fault zones. The observed electrical variability appears to be highest near the surface and the degree of electrical variability appears to decrease and become more homogeneous with depth. The zone of relatively high electrical variability appears to vary considerably in thickness across the ERI image. The ERI data from each of the field site show similar electrical features in the shallow subsurface that are consistent with the electrical variability associated with epikarst zones in karst.

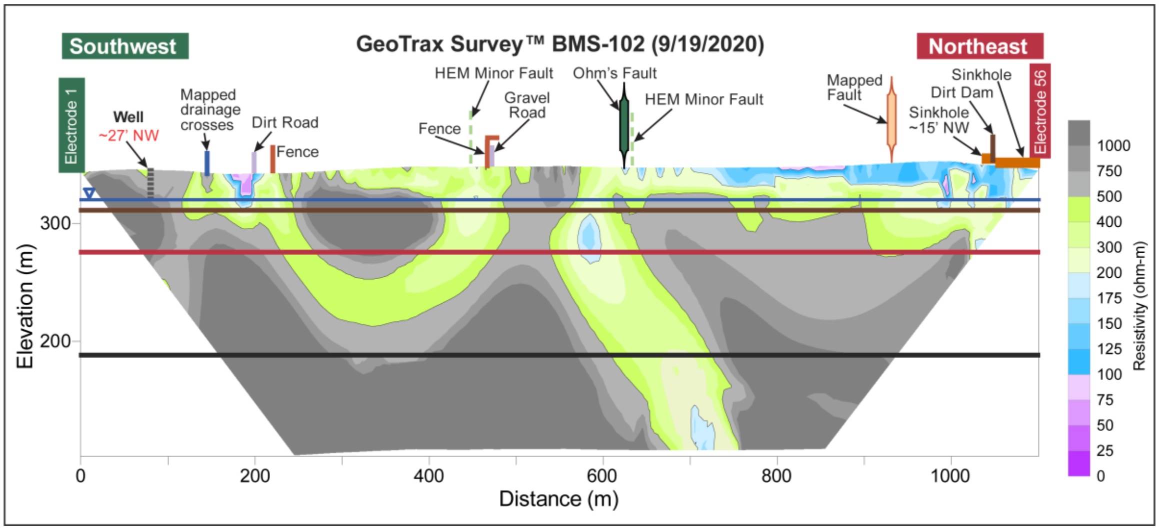


Figure E4. ERI line BMS-102 collected over MAR Site parallel to Ham Fault. Depth of investigation is 220 m (720 ft). Vertically conductive feature (green/blue) at 600-800 lateral distance will be drilled as station EAR5 to install wells in the electrically conductive features that are expected to be hydraulically conductive as well.

The observed variability in the electrical properties of the subsurface materials is greatly decreased at depth but continues to extend to depths below the indicated static water level (Figures E4 and E5). The electrical variability observed extending vertically to the bottom of the ERI image may indicate that weathering processes associated with the epikarst zone extend into the phreatic zone along fractures or faults. A clear relation appears to exist between the observed electrical resistivity features and the measured static water level at the site during the dry period when the data were obtained.

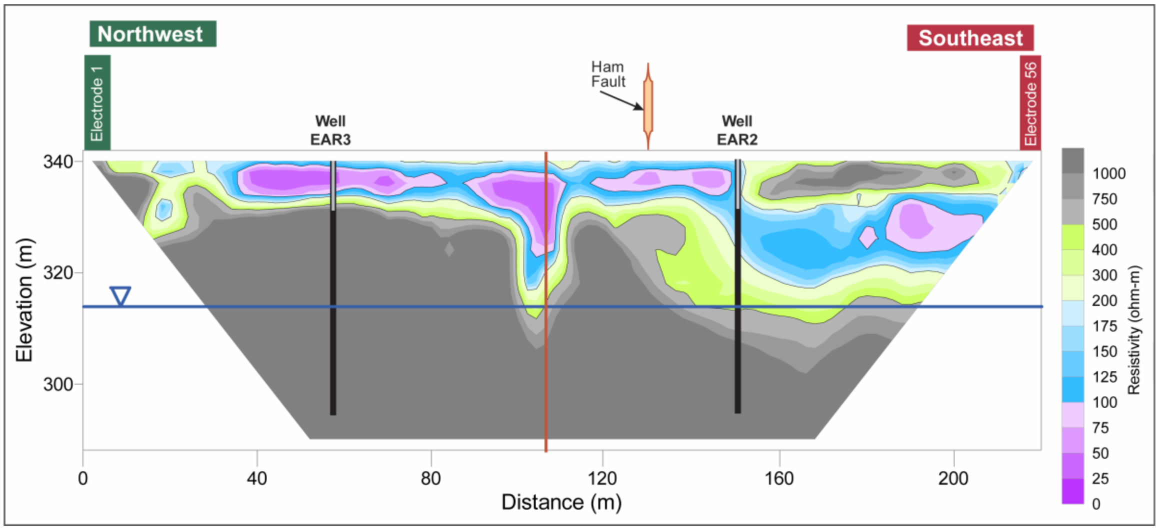


Figure E5. ERI line T1 collected during February 2022 over MAR site perpendicular to the Ham Fault immediately downgradient of the MAR sinkhole. Depth of investigation is 44 m (144 ft). The dark orange line is provided as a feature comparison to the same feature in the differenced TERI dataset shown in Figure E6. The Ham Fault feature listed at the top of the figure corresponds to the straight line fault delineation between the MAR site and Byrds Mill Spring, shown in Figure E2 and E3.

A TERI image was obtained by differencing a dataset from August 2021 with a dataset from February 2022. This time period had little precipitation and a steady decline in water level in the on-site monitoring wells. Well EAR2 declined by approximately 3.4 m (11 ft) during this period. The negative change in conductivity (increase in resistivity) during this time period indicates areas where drainage occurred in the vadose and phreatic zones during the time period. The higher changes are expected to correlate with fluid losses in areas of higher porosity in these datasets (Halihan et al., 2009; Sample, 2008). The results indicate, in general, that the larger volumes of drainage (dark brown) occurred in the shallow epikarst. The dark brown feature in Figure E6 adjacent to well EAR2 indicates a zone where a bedrock conduit exists that is draining the rock body at that location.

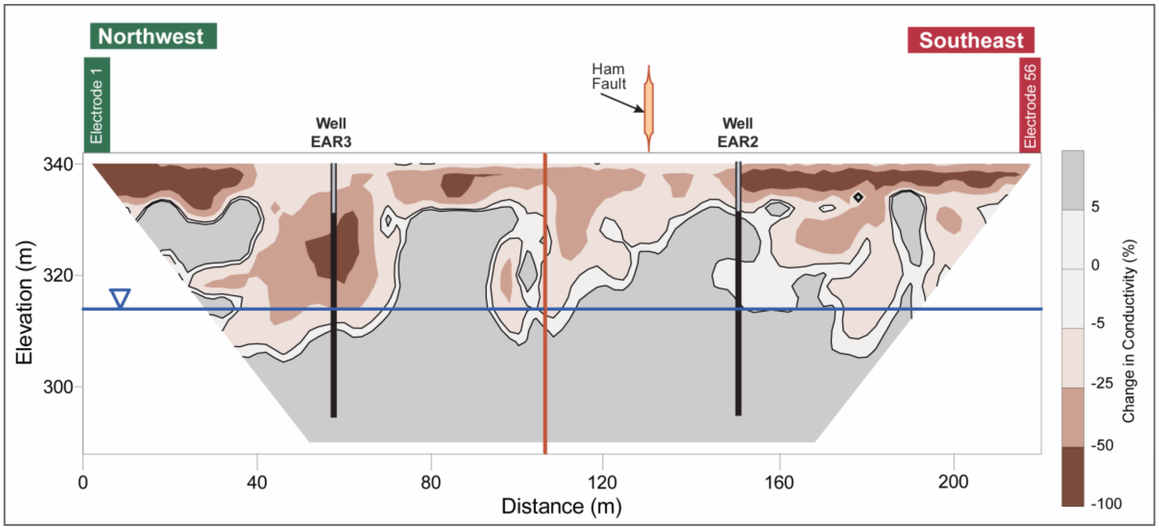


Figure E6. TERI line T1 evaluating drying at the MAR site from August 2021 to February 2022. Depth of investigation is 44 m (144 ft). Negative changes in conductivity (decreases in resistivity) are plotted to evaluate locations where fluids have drained from the aquifer during this period. The vertical dark orange line in the Ham fault zone corresponds to an identical line in Figure E5 for comparison. The Ham Fault feature listed at the top of the figure corresponds to the straight line fault delineation between the MAR site and Byrds Mill Spring.

6. Discussion

The ERI images from the Arbuckle-Simpson aquifer indicate that ERI can be a useful tool for improving conceptual models of the MAR site. The data that has been collected in this aquifer over many years and at many locations is of high quality and provides useful information about the variability of the aquifer. In some bedrock settings with a high resistivity lithology, it can be difficult to employ ERI techniques. The resistivity of the Arbuckle-Simpson, however, is highly variable and provides a range of electrical properties which can be easily imaged with ERI techniques.

Surface imaging can provide information on fault location along with data about the thickness of the soil zone and the soil/bedrock interface or epikarst zone. This will be important for identifying the storage properties of the aquifer in shallow areas for ground water models. The ERI data suggest that the faults can be hydraulically conductive, and drilling will evaluate the changes and connections in these pathways.

Temporal imaging of the aquifer indicates that fluid draining can be observed during times of low precipitation. The decrease in resistivity in the TERI image is a clear indicator of fluid drainage that can be monitored to evaluate seasonal and storm changes in the aquifer. Monitoring will occur during tracer tests to evaluate the migration of tracer into the aquifer.

7. Conclusions

ERI data was used to address four preliminary objectives for the MAR site. First, the background properties of the stratigraphy were assessed to evaluate the vertical locations of electrical variability. Second, the properties of the epikarst zone of the aquifer were evaluated. Third, the fault structure in the aquifer was measured for a couple of major faults. Finally, a TERI technique was used to evaluate aquifer drainage during a dry period.

For the MAR site and for previous studies, the lithologies of the ASA have good electrical properties to evaluate epikarst and rapid flowpaths and a wide range of resistivities that make the technique useful for electrical stratigraphic mapping in the aquifer.

The epikarst zone is readily apparent in the ERI datasets. The hydraulic conductivity and porosity of these areas is anticipated to be high based on previous research (Halihan et al., 2009). This should influence tracer migration at the site: tracer will likely move laterally through the vadose zone prior to reaching the water table. At the MAR site, faults are readily apparent in ERI images above and below the water table. The faults tend to be near vertical with a fault zone that has significant width.

The TERI dataset provided a good indication that the installed TERI cable line T1 can provide good data for tracer migration through the T1 data plane as electrically conductive tracer is added at the sinkhole. Whether the tracer migrates laterally through the vadose zone or drops to the water table, the migration through the T1 plane is expected to be detectable using this approach. Further monitoring of the T1 cable will continue as part of the tracer testing and further research for the MAR site.

8. References

Archie, G. E., 1942, The electrical resistivity log as an aid to determining some reservoir characteristics.: Transactions of the American Institute of Mechanical Engineers, v. 146, p. 389-409.

Daily, W., A. Ramirez, A. Binley, and D. LaBrecque, 2004, Electrical resistance tomography: The Leading Edge, p. 438-442.

Fairchild, R. W., R. L. Hanson, and R. E. Davis, 1990, Hydrology of the Arbuckle Mountains area, south-central Oklahoma, *in* Oklahoma Geological Survey (OGS), ed., Circular 91, Norman, OK, p. 112.

Halihan, T., S. Paxton, J. Puckette, and M. Sample, 2004, Preliminary Electrical Resistivity Imaging Report for: The Arbuckle-Simpson Hydrology Study, p. 27.

Halihan, T., J. Puckette, M. Sample, and M. Riley, 2009, Electrical resistivity imaging of the Arbuckle-Simpson aquifer: Final report submitted to the Oklahoma Water Resources Board, Oklahoma State University School of Geology, 92 p.

Ham, W. E., 1969, Regional geology of the Arbuckle Mountains, Oklahoma: Guidebook 17: Norman, OK, 52 p.

Herwanger, J. V., M. H. Worthington, R. Lubbe, and A. Binley, 2004, A comparison of cross-hole electrical and seismic data in fractured rock: Geophysical Prospecting, v. 52, p. 109-121.

Klimchouk, A., 2004, Towards defining, delimiting and classifying epikarst: Its origin, processes and variants of geomorphic evolution: Speleogenesis and Evolution of Karst Aquifers, v. 2, p. 1-13.

Loke, M. H., and R. D. Barker, 1996, Rapid least-square inversion of apparent resistivity pseudosections using a quasi-Newton method: Geophysical Prospecting, v. 44, p. 131-152.

Niwas, S., and O. A. L. de Lima, 2003, Aquifer parameter estimation from surface resistivity data: Ground Water, v. 41, p. 94-99.

Purvance, D. T., and R. Andricevic, 2000a, Geoelectric characterization of the hydraulic conductivity field and its spatial structure at variable scales: Water Resources Research, v. 36, p. 2915-2924.

Purvance, D. T., and R. Andricevic, 2000b, On the electrical-hydraulic conductivity correlation in aquifers: Water Resources Research, v. 36, p. 2905-2913.

Ramirez, A., W. Daily, D. LaBrecque, E. Owen, and D. Chesnut, 1993, Monitoring an underground steam injection process using electrical resistance tomography, Water Resources Research, United States, American Geophysical Union: Washington, DC, United States, p. 73.

Reynolds, J. M., 1997, An introduction to applied and environmental geophysics: Chichester; New York, John Wiley, ix, 796 p.

Riley, M., 2007, Investigation of Fault Properties Using Electrical Resistivity Imaging, Oklahoma State University, Stillwater, 56 p.

Sample, M. A., 2008, Characterization of the Epikarst over the Hunton Anticline, Arbuckle-Simpson Aquifer, Oklahoma, Oklahoma State University, Stillwater, 207 p.

Stollar, R. L., and P. Roux, 1975, Earth resistivity surveys; a method for defining ground-water contamination, Ground Water, United States, National Water Well Association, Ground-Water Technology Division : Urbana, IL, United States, p. 145.

Van Nostrand, R. G., and K. L. Cook, 1966, Interpretation of Resistivity Data, Geological Survey Professional Paper, United States Government Printing Office, Washington, United States Geological Survey.

End of Appendix E
