EPA United States Environmental Protection Agency

QUALITY ASSURANCE PROJECT PLAN

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

Nature based infrastructure for water reuse in floodplain river systems

EPA Project Lead:

EPA Project Lead: Ken Forshay

Project Type: Measurement

QA Category B

Intramural

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Prepared By:

Ken Forshay

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Approval Page

QA Project Plan Title:	Nature based infrastructure for water reuse in floodplain river systems
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If Intramural or Extramural, EPA Project Approvals	
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If Extramural, Contractor Approvals	
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A.2 Table of Contents

Table of Contents

Tables

Figures

Table 1. Acronyms

EPA	Environmental Protection Agency
ORD	Office of Research Development
CESER	Center for Environmental Solutions and Emergency Response
GCRD	Groundwater Characterization and Remediation Division
TSERB	Technical Support and Environmental Restoration Branch
OK	Oklahoma
UC Davis	University of California, Davis
SOP	Standard Operating Procedure
QAPP	Quality Assurance Project Plan
QAM	Quality Assurance Manager
QA	Quality Assurance
QL	Quantitative Limit
RPD	Relative Percent Difference
GC	Gas Chromatography
IRMS	Isotope Ratio Mass Spec
DEA	Denitrification Enzyme Activity
PDB	PeeDee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
NIST	National Institute of Standards and Technology
IAEA	International Atomic Energy Agency
STICS	Scientific and Technical Information Clearance System
ANOVA	Analysis of Variance
GLM ANOVA	General Linear Model Analysis of Variance
GF/F	Glass Fiber Filter
HDPE	High-Density Polyethylene
ORP	Oxidation-Reduction Potential
LDO	Luminescent Dissolved Oxygen
FS	Field Sheet

SECTION A – PROJECT MANAGEMENT

(A.1 and A.2 are previously provided as Approvals page and Table of Contents)

A.3 Distribution List

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.4. 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 will also be responsible for timely communications with all involved participants and will retain copies of all management reports, memoranda, and facilitate correspondence between research task personnel. Table 2 serves as the distribution list and summary of project participants. Table 2 also lists responsibilities of the participants.

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A.4 Project/Task Organization

Table 2. Project Participants and Responsibilities

Name	Organization	Role	Responsibility	Distribution List
Ken Forshay	EPA/ORD/CESER/ GCRD/TSERB	Project Lead	• Principal Investigator • Project Management • QAPP preparation • Sample collection and analysis • Data reduction/validation/ analysis • Report preparation • Ensuring the project adheres to the project QA requirements as described in this QAPP	Yes
Mustafa Bob	EPA/ORD/CESER/ GCRD/IO	QA Manager	• Oversight of QA program implementation	Yes
Cherri Adair	EPA/ORD/CESER/ GCRD/IO	Health and Safety Manager	• Oversight of health and safety implementation	Yes
David Burden	EPA/ORD/CESER/ GCRD/TSERB	Branch Chief	• Project administration • Budget oversight	Yes
Russell Neill	EPA/ORD/CESER/ GCRD/TSERB	Field Director	• Field sampling • Equipment maintenance • Data collection	Yes
Katherine Buckler	ORAU	NSSC	• Field Preparation • Field sampling • Equipment maintenance • Data collection	Yes

Experimental and analytical support for this project is provided by US Environmental Protection Agency, Office of Research and Development, Groundwater Characterization and Remediation Devision (GCRD). Analytical support for general parameter measures will be performed by GCRD General Parameters lab, gas analyses will be performed by the GCRD General Parameters, and isotope measures will be performed by GCRD (stable isotopes of H and O in water) and the UC Davis stable isotope facility (stable isotopes of N, O, and C). We will coordinate with other institutions and amend the QAPP as needed.

A.5 Problem Definition and Background

The use of nature-based infrastructure including naturally occurring, restored, or constructed wetlands in and around river floodplains are thought to provide beneficial ecosystem services that can improve water quality (e.g. Forshay and Stanley 2005, Narr et al. 2019, Forshay et al. 2022). Municipalities across the U.S. are challenged with the ongoing demand for safe and sustainable potable water as well as ever increasing requirements to improve wastewater quality to near potable levels. This has stimulated the consideration of reuse of treated wastewater effluent for credit toward potable reuse. By moving highly treated effluent through nature-based infrastructure the potential for indirect potable reuse is possible with nature-based infrastructure that can facilitate the reuse of discharged water. The City of Norman is working to improve the quality of their wastewater discharge and desire to increase water availability and quantity by moving discharge from one receiving system, the Canadian River to an existing multi use reservoir. Lake Thunderbird provides municipal and industrial water to approximately 250,000 customers in Norman, Midwest City, and Del City, Oklahoma. During times of drought, water reserves in Lake Thunderbird become depleted, potentially leaving the reservoir too low to provide for the designated use. One proposed method to combat deficiency is an Indirect Potable Reuse (IPR) project where treated municipal wastewater is diverted into Lake Thunderbird from the City of Norman Water Reclamation Facility via Dave Blue Creek, then blended with existing reserves before redistribution to the Water District. A constructed floodplain wetland may be constructed to connect treated effluent with biogeochemically active wetland system before entering Lake Thunderbird. (Figure 1)

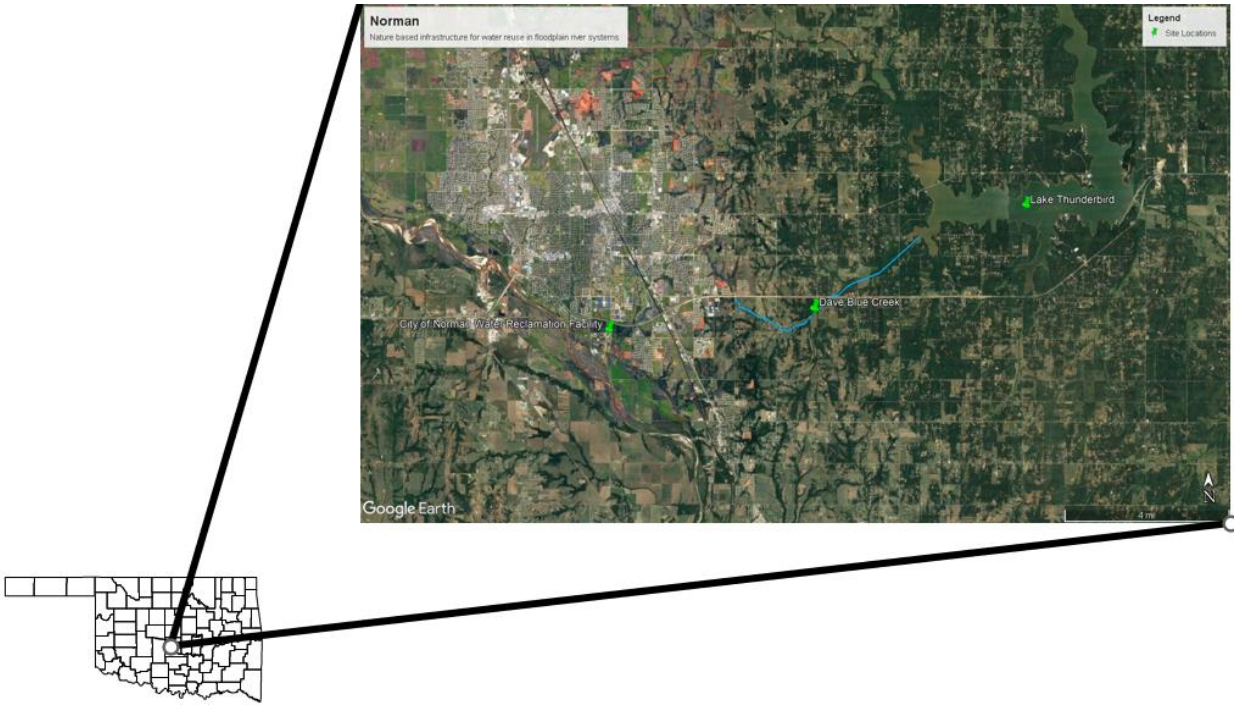

Figure 1. Approximate area of research. Green markers indicate the treatment facility, Dave Blue Creek, and Lake Thunderbird.

The concern is that excess nutrients including nitrate-nitrogen (NO_3^--N) and phosphate (PO_4^-) threaten ecosystem and human health. River ecosystems and lakes, like Dave Blue Creek and Lake Thunderbird, are subject to elevated nitrogen (N) and phosphorus (P) inputs and possess limited capacity to remove nutrients within the main channel or within inland groundwater systems due to hydrologic flow paths that allow limited contact with reactive substrates (benthic sediments or plant root zones). Floodplain wetlands are critical habitats that may support elevated nutrient retention of enriched watersheds by effectively increasing contact of NO_3^--N and nutrients with areas of biogeochemically active sediments or plant root zones. Both surface sediments and subsurface hyporheic sediments within floodplain wetlands can increase surface area for N removal by connecting hydrologic flow paths carrying NO_3^--N rich waters with active denitrification zones. Floodplain wetlands can also be zones of P uptake due to plant growth and abiotic retention. Restoration of large river floodplains and installation of wetlands is a potential means for increasing this interaction between NO_3^--N, P, and nutrient rich water with biogeochemically active substrates.

The expansion of floodplain wetland areas during restoration increases interaction between water inputs from both upland and river sources, but also provides opportunities for municipal discharge to floodplain areas. For example, when wastewater treatment plants are located near restored floodplains, they may choose to discharge onto the floodplain rather than directly into the river. This can add diverse ecosystem services and water purifying benefits. However, the result of these restoration practices and discharge on nutrient pollution is still uncertain. Understanding the biogeochemical repercussions of redirecting wastewater treatment effluent onto floodplains is a primary goal in assessing the consequences of floodplain restoration. These

restoration activities (including the discharge of treated effluent onto the floodplain), provide a valuable opportunity to assess restoration consequences for N and P removal in floodplain ecosystems. The goal of this research is to provide information about how floodplain restoration and modifications of hydrologic connectivity may enhance ecosystem services related to nutrients and the overall ecological condition of stream and river ecosystems. We will identify biogeochemical N removing hotspots in a floodplain-river system based on denitrification potential and hydrologic connectivity that may create large N or P sinks that could be implemented along large river floodplain complexes to enhance ecosystem services when restoration is desired with the goal of evaluating the benefits of nature-based infrastructure to support indirect potable reuse.

There is a critical need to determine how N and other nutrient removal ecosystem services occur in response to floodplain wetland construction, as the results of these nature-based practices on nutrient processing are not well established. This study will be conducted along Dave Blue Creek and the Canadian River in Norman, Oklahoma. Dave Blue Creek is a tributary of Lake Thunderbird in Oklahoma. Land use around Dave Blue Creek consists of primarily agricultural and urban land uses. The restoration is managed primarily by the City of Norman. We will evaluate nutrient composition in the surface water and shallow groundwater and measure the denitrification potential of several of these key habitats before and after restoration.

A.6 Project Description and Objectives

The objective of this work is to use quantitative and qualitative methods to determine N and P nutrient dynamics in the surface and subsurface, perform denitrification and other biogeochemical measurements, soil respiration measurements, nutrient monitoring, hydrologic monitoring, estimates of N and P removal rates at the surface and subsurface will be developed, and determine what controls denitrification and P retention in river floodplains undergoing restoration and treated effluent discharge. We will 1) identify critical floodplain wetland characteristics that support N and P retention in the surface and subsurface sediments that can be promoted in these novel nature-based solutions with treated effluent discharge, 2) develop denitrification and respiration estimates within select habitats of the Dave Blue Creek floodplain, and 3) determine limiting factors such as nitrate, carbon, and/or hydrological factors that dictate the capacity of these habitats to support N and P retention. These results are intended to contribute to the development of approaches to quantify, protect, and manage ecosystem services (the outputs of ecosystem processes that contribute to human well-being) derived from nature-based infrastructure.

Specific questions

- Does a nature-based wetland system enhance nutrient removal?
- Do wetland areas of a floodplain act as sources of organic carbon and thus hotspots of nutrient retention or sources of greenhouse gasses like nitrous oxide and methane in floodplain ecosystems?
- Does surface and groundwater hydrology control nutrient processing in these systems?
- Does discharge of treated effluent to floodplains alter water quality?

Hypotheses

- Organic carbon availability will correlate with bioavailable N negatively and P positively in shallow groundwater due to biogeochemically mediated redox relationships.
- The less frequently wetted areas will have lower carbon content, which will cause incomplete denitrification and decrease available ortho phosphorus.
- Variability in annual hydrologic regime alters hyporheic flowpath both in and out of the floodplain hyporheic zone, which controls nutrient concentration in the subsurface.
- Geomorphic structures that retain carbon and receive nitrate are capable of elevated denitrification rates but may release ortho phosphorus.
- Denitrification in newly constructed floodplain wetlands will develop quickly and provide enhanced N retention as organic carbon accumulates, where retention is defined as the difference between inflow and outflow of N moving through the aquatic system.
- Hotspots of denitrification and other biogeochemical activity will occur in the subsurface because they concentrate organic matter and substrate for retention of N.
- Nature-based wetland construction activities that enhance organic carbon accumulation and improve denitrifying substrates may enhance denitrification but increase dissolved P therefore attention to P retaining processes like plant uptake will be critical for success.

TABLE 3. Gantt chart of expected timeline.

Activity	2023	2023-2024 (Following QAPP Approval)	2025-2029
QAPP Preparation and Approval			
Site Selection/ Method Development			
Sample Collection			
Data Analysis			
Writing			

QAPP Preparation and Approval will be completed March 2023. Sample collection at the Norman Water Reclamation Facility and Dave Blue Creek constructed wetland sites will begin in ~the summer of 2023 and will continue for approximately 20 quarterly sample periods (~5 years), followed by data analysis and writing. (Table 3)

A.7 Special Training/Certification

No special training or certifications will be required for completion of this project. Sampling methodologies will be found in subsequent sections of this QAPP. Additional guidance can be found in Standard Operating Procedures (SOPs), listed in this QAPP.

A.8 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.

Electronic project records will be maintained by the project lead on the ORD network drive:

https://usepa.sharepoint.com/:f:/r/sites/ForshayResearchGroupEnhancementTeam/Shared%20Documents/General/NormanWetland?csf=1&web=1&e=Dax7Er
Environmental Protection Agency (EPA)/Forshay Research Group Enhancement Team – Documents/General/NormanWetland

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.

Paper records will be generated using data sheets found in Appendix 2 and will be stored in a records binder, currently located in RSKERC 356.

SECTION B – DATA GENERATION & AQCUISITION

B.1 Experimental Design

The research at the City of Norman Water Reclamation Facility at the Canadian river and along Dave Blue Creek will provide a unique opportunity to study river floodplain wetland infrastructure and provide insight to the nutrient and biogeochemical composition of sediment and water in nature-based systems. This site can be used to inform decision making with respect to ecosystem services, particularly water quality management. The Dave Blue Creek site is near the City of Norman Water Reclamation Facility and actively being developed for research and teaching by the University of Oklahoma. Floodplain wetland construction to first include pilot scale installations will occur at the site as well as the movement of effluent discharge as part of

the construction activities. This discharge will travel across the floodplain to a pond wetland near the river instead of being released in the center of the channel.

During each of the water / sediment sampling events at the Norman floodplain on the Canadian River and Dave Blue Creek site, the sampling strategy will include up to 50 sediment samples to estimate denitrification rates within the floodplain (n = 50), up to 20 quarterly events. Surface and well water from up to 30 locations and sediment from cores will be collected with an additional 10% (~every 10^{th} sample) collected as duplicates for QC of each sample. Surface water sites are to be determined in the field as available, up to 10 locations, but will be preferentially collected near ground water monitoring well locations.

In order to evaluate the influence of habitat type on denitrification and nutrient composition in sediments and soils as well as deeper samples, the sampling strategy will include collecting samples from the top 10 cm and deeper core samples at up to 50 sites, stratified across dry and wet habitats. The sediment sample locations will be determined in the field to collect representative samples based on field observed factors. Sediment will be sampled at the site near Dave Blue Creek as shallow cores to compose an elevation gradient that includes diverse geomorphic structures. Actual sample collection location will be based on professional judgment in the field to include: 1) surface, shallow aquifer, and wet habitats inside/outside the construction or discharge areas.

The number of groundwater-monitoring wells and surface water sites at the Norman location has yet to be determined, but we will likely sample up to 20 wells and 10 surface water sites after and prior to construction. The location of the wells will include areas inside and outside the constructed wetland, both upstream and downstream along anticipated flowpath based on topographical observation. Wells in Norman will have 2” pvc well casings with 6” boreholes that are sand packed and sealed with bentonite. Samples will be collected once each season after installation (~ summer 2023) for 5 years (n = 20 collection periods) in Norman.

See Appendix 2 for description of numbers of bottles, bottle types, and QC samples to be taken for water samples.

Sediments, soils, ground water, and surface water in and around the floodplain represent the possible nutrient pools for excess nutrients and provide insight into the dynamics of nutrient processing that occurs within the floodplain. Although direct process measures in the field are developing, episodic sample collection and laboratory-based assays can provide broad insight into the nutrient and biogeochemical dynamics occurring in the floodplain.

B.2 Process Measurements

Process measurements will follow those described in QAPP_K-GCRD-0018423. Methods are as follows:

Denitrification estimates
Denitrifying Enzyme Activity in Sediments: Sediment denitrification assays will be performed using the denitrification enzyme activity method, acetylene block technique (Tiedje et al. 1989,

Holmes et al. 1996, Groffman et al. 1999). This approach has been used successfully in previous floodplain studies (e.g. Forshay and Stanley 2005). The procedure is described in K-GCRD-SOP-1398-0. We will use 4.7 cm diameter cores to transfer the top 5 cm for surface sediments and 5 cm at known depth for hyporheic zone measurements into 250ml microcosms fitted with a gas-tight lid and gas sampling septum. To estimate denitrification rates, ambient river water or deionized water will be used during sediment incubations. Amendments of organic carbon (dextrose), and NO_3^--N (KNO_3) will be added in a factorial design to determine potential denitrification and limiting nutrient. We will use chloramphanicol to inhibit de-novo enzyme production, which provides a reasonable estimate of in-situ denitrification rates in NO_3^--N rich systems (Bernot et al. 2003, Groffman et al. 2006). Nitrous oxide gas will be sampled at approximately 10 minutes and one hour to determine denitrification rates during the linear phase of nitrous oxide evolution. Sediment will be dried and weighed to determine denitrification rates on a per unit sediment mass basis.

Sediment from each site will also be KCl extracted to determine bound nitrate and ammonium and dissolved organic carbon content using aqueous extracts from the sediment. To determine organic matter fraction of sediments the dried sediments will be combusted at 500^{o}C and weighed. The loss of mass is the organic matter fraction and will be correlated with organic carbon samples from those sediments. For up to four seasonal sampling dates we will collect cores from habitat types that incorporate elevation gradient. Incubations will be carried out at temperatures within 2 ° C of field temperatures.

Respiration estimates in Sediments

Sediment respiration rates will be measured using a modified version of the Denitrification Enzyme Activity (DEA) assay K-GCRD-SOP-1398-0. An SOP will be developed specifically for this measurement or the DEA method will be modified to include this approach. In brief, sediment samples will be used to perform slurry incubations with deionized water in sealed jars with septa lids. CO_2 accumulation over time will provide the indicator of respiration rate. CO_2 samples will be collected and handled much like the N_2O samples in the DEA assays without additional chemicals other than water added to the slurry and without evacuation* (* TBD depending on sensitivity of the assay). Those CO_2 samples will be collected in gas tight vials and analyzed as bulk CO_2 to provide an indicator of aerobic respiration. The calculations for total respiration will be developed as part of the SOP. Rates will likely be reported as mass per unit dry weight or unit area.

Isotopes of Nitrate and Water

Denitrification can cause enrichment of ^{15}N in nitrate. Oxygen and hydrogen isotopes in water can be used to indicate the source (river or groundwater) of the shallow groundwater. Therefore, comparisons of ^{15}N in nitrate and both hydrogen and oxygen isotopic ratios of hyporheic water, groundwater, and the river channel produce an indicator of where the water in shallow groundwater wells is coming from and how much denitrification is occurring. These measures are mostly qualitative with respect to actual denitrification rates, but relative comparisons between hyporheic water sites or along hyporheic flowpaths can provide evidence for the occurrence of denitrification. This information will supplement our understanding of denitrification rates based on the more quantitative, but also more labor-intensive acetylene

block measures of denitrification. We will collect samples from each well, the main channel of the river, and if available, surface water from the habitat types to be analyzed for ^{15}N of nitrate and both O and H isotopes of water. See table 5.

Push-pull (in-situ) Method
Denitrification rates will be measured in groundwater by quantifying *in situ* the conversion of isotopically enriched nitrate to gaseous forms (Addy, 2002, J-WECD-ECB-SOP-990-1). Mini-peizometers will be installed using a Bosch Hammer Drill in 12 locations at each site in Norman that encompass an elevation gradient in addition to other relevant site-specific gradients. 10.5 L of groundwater will be pumped from each well on day 1. On day 2, ambient ^{15}N will be sampled and dissolved oxygen concentrations will be measured in each well. 160 ml of a 'master solution' (128 ml of 28.873 g KNO_3 in 2 L of deionized water + 32 ml of 13.48g ^{15}N-KNO_3 in 1 L of deionized water) will be added to 9.84 L of the previously collected ground water sample to create a 'dosing solution'. This solution will be bubbled with sulfur hexafluoride for approximately 20 minutes to reduce the dissolved oxygen concentrations to those of the ambient ground water and then slowly pumped into the mini-piezometer. The dosing solution will be sampled 1/3 and 2/3 of the way through the 'push' process to ensure ambient DO is maintained. After 4 hours, 3 L of groundwater will be slowly pumped back out of the well and sampled at 0.5 L intervals. Helium will be added to the headspace of all samples directly after the 'push' and 'pull'. Nitrogen may be substituted for He in headspace in the field when denitrification rates are expected to be low because the enrichment of gas is compared by difference and very low concentrations of N_2 may limit isotopic analysis. After allowing the headspace to equilibrate for 24 hours at 4 ˚C, the headspace will be sampled, placed into a pre-evacuated, 6 ml exetainer, and sent to Kerr Lab for GC/μECD analysis of nitrous oxide and sulfur hexafluoride in gaseous samples (K-GCRD-SOP-3458-0) and to UC Davis for isotopic analysis of $^{15}N_2O$ and $^{15}N_2$. Either two 6ml aliquots (2 vials) or one 12ml vial are over pressurized to 14ml to facilitate the 1-2ml sample collected for GC. The sample is then brought back to $4^{O}C$ and vented prior to analysis at UC Davis. The venting would approximate one atm of pressure remaining in the vial and allow the complete vial purge used by the stable isotope analysis to represent the mass and volume of the headspace subsample of push-pull solution equilibration. Nine to 12 additional liters of groundwater will be removed from each well after the 'pull' and stored in a carboy to ensure that all the tracer is removed from the well. Estimates of *in situ* denitrification rates will be calculated based on the production of enriched $^{15}N_2O$ and $^{15}N_2$ gases relative to sulfur hexafluoride retrieval.

B.3 Sampling Methods

Sampling methods will follow those described in QAPP_K-GCRD-0018423. Methods are as follows:

Ground Water
See Appendix 1, 'Ground Water Monitoring Sampling' for a detailed description of the sampling procedure. Groundwater samples will be collected via peristaltic pump from wells directly into HCl acid washed and DI rinsed polyethylene bottles and are filtered or not, depending on the sample, and preserved as described in Appendix 2.

Water samples for dissolved gas samples will be collected directly into sealed septa vials (e.g. exetainers or serum bottles) in the field without headspace and without filtering.

Samples with 48 hour holding times (i.e. ortho phosphorus and nitrate) may be frozen for preservation if analyses cannot be completed in 48 hours which has been shown to be effective in low calcium carbonate and low DOC waters (Avanzino and Kennedy 1993, Fellman et al. 2008) and we will document a frozen vs. unfrozen comparison of several representative samples if needed.

Surface Water
Surface water samples will be collected by submerging bottles in water avoiding sediment plumes. Three rinses of source water will be done in the field for each sample collection. Sample bottles and preservation as well as filtration will be identical to ground water samples.

Sediment
Sediment samples for denitrification assays will be collected as 4.7 cm diameter x 5-10 cm deep cores or surface shoveled from the top 10 cm and subsamples for sediment analyses will be taken from those cores or bags. Deeper cores will be collected by geoprobe drill rig and sectioned for analyses. Samples will either be placed in plastic bags on ice or left intact depending on the need for discrete depth identification.

Sample containers
See Appendix 2 (water only)

Sample preservation requirements
See table 2 (includes sediment) and Appendix 2.

Sample identification
Samples will be noted with a unique site ID, date, replicate number, and initialed in the field upon collection or in the lab when appropriate.

B.4 Measurement Procedures

Measurement Procedures will follow those described in QAPP_K-GCRD-0018423. Procedures are as follows:

See Table 5 for SOPs and methods to be used.

See B.2 for discussion of procedures for Denitrifying Enzyme Activity, Respiration Estimates, and Push-Pull.

Hydrologic water level

Water level in monitoring wells will be monitored manually via electric tape to the nearest 3 millimeters prior to sampling. Water level loggers will also be used for continuous monitoring

between sampling events, models to be determined based on availability (K-GCRD-SOP-1132-0 and K-GCRD-SOP-1134-0 will be used). See Appendix 1.

Water and dissolved gas sample protocols and analysis

Measures of pH, ORP, Temp, Specific Conductance, DO, and turbidity will be performed in the field using handheld meters calibrated daily. In-house analyses by the RSKERC General Parameters lab will be performed on aqueous samples for general parameters (Br^-, Cl^-, I^-, o-P, SO_4, NO_3, NO_2, NH_4, TKN, TDN, TP, TDP, TOC, DOC, DIC, TIC, alkalinity) (See Table 5). Dissolved metals will be collected and analyzed using K-GCRD-SOP-1154-1. Dissolved gas samples (N_2O, CH_4, CO_2, and H_2) will be collected from wells and surface water brought to the lab in gas-tight septa vials (12 mL exetainers or 60 mL serum bottles) and analyzed under K-GCRD-SOP-1160-0 and K-GCRD-SOP-1088-5. Total organic carbon (TOC), Total inorganic carbon (TIC), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) will be analyzed using K-GCRD-SOP-1165-0. TOC and TIC water samples will be placed in a 40 mL VOA vial, while DOC and DIC samples will be passed through a pre-combusted nominal 0.7 µm GF/F filter before being poured into a VOA vial. As a note, glass fiber filters are used because other membrane filters may contaminate due to the intrinsic carbon content of the filter. See Table 5.

Carbon, Nitrogen, and Stable Isotope Analyses

Stable isotopes of water (H and O) will be determined using K-GCRD-SOP-1137-1 with a Picarro cavity ring-down spectrometer. Stable isotopes of ^{15}N from nitrate will be analyzed using biotic conversion of nitrate to nitrous oxide. This will provide ^{18}O and ^{15}N from nitrate. Currently, there is no internationally accepted N_2O standard for isotope ratios, thus the ratios of ^{15}N and ^{18}O from a reaction N_2 with CO_2 based on PDB (PeeDee Belemnite) and Air standards at the UC Davis stable isotope lab will be used. Two working standards are analyzed every 10 samples. The working standards are mixtures of N_2 and N_2O (e.g., 3% N_2 + 1 ppm N_2O with the balance He or 1 ppm N_2O with balance N_2). The N_2 is calibrated against an Oztech N_2 standard (delta ^{15}N vs air = -0.74). UC Davis calibrated ^{15}N and ^{18}O by reacting the N_2O with glassy carbon at 1400°C to convert N_2O to N_2 + CO. The resulting N_2 was calibrated against the Oztech N_2 standard and the CO was calibrated against an Oztech CO_2 standard (after converting CO_2 to CO in a similar manner).

Sediment samples are dried and then analyzed for POC (particulate organic carbon), PN (particulate nitrogen), ^{13}C, and ^{15}N content. Bulk PC, POC (with acidification thereby converting inorganic carbon to CO_2), and PN samples are analyzed on a Europa Hydra 20-20 continuous flow isotope ratio mass spectrometer at the University of California Davis Stable Isotope Facility. Before analysis, the sediment samples will be dried at 50 °C for 48 hours and stored in desiccators prior to shipping. Prior to sample processing Leco brand soil standard samples for %C and %N are included every 10-15 samples. During analysis, samples are interspersed with several replicates of at least two different laboratory standards by UC Davis. These laboratory standards, which are selected to be compositionally similar to the samples being analyzed, have been previously calibrated against NIST Standard Reference Materials (IAEA-N1, IAEA-N2, IAEA-N3, USGS-40, and USGS-41). UC Davis uses laboratory standards suitable for the types

of samples and their C and N content, including NIST 1547 peach leaves, NIST 1577b bovine liver, acetanilide, cellulose, glycine, sucrose, and ammonium sulfate. It is possible to measure each sample package only once so replicate measurements require replicate samples.

All isotope ratios ^{13}C:^{12}C, ^{2}H:^{1}H,^{18}O:^{16}O,and ^{15}N:^{14}N will reported as a per-mil difference between the ratio of the sample to the standard (PDB, VSMOW, and AIR depending on the media):
$\delta‰ = [R_{sample}/R_{std} - 1] \times 1000$.

Calibration Procedures

Calibration procedures as well as quality control measures for lab-based measurements are discussed in their respective SOPs, see Table 5.

Field measures of dissolved oxygen, ORP, specific conductance, temperature, and pH, will be performed using a handheld meter using the protocol specified in the meter manufacturer's documentation and K-IO-SOP-1260-2. Meters are calibrated daily before use and calibration is checked at the end of the day. See attached 'Calibration Data Sheet' for these checks and associated acceptance criteria. Also see attachment, 'Calibration Solutions Used' to document lot numbers, expiration dates, etc.

B.5 Quality Control

Table 4. Field QC

QC Sample	Purpose	Method	Frequency	Acceptance Criteria/ Corrective Actions
Equipment Blanks	Assess contamination from field equipment, sampling procedures, decon procedures, sample container, preservative, and shipping.	Apply only to samples collected via equipment, such as those pumped from wells or filtered samples: Reagent water is pumped through sampling equipment, filtered, if required, and collected into bottles and preserved same as samples.	One per sample event	< 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 collect one duplicate sample.	Report duplicate data: RPD $\leq$ 30 for results greater than 5xQL. The affected data will be flagged as needed.

QC Sample	Purpose	Method	Frequency	Acceptance Criteria/ Corrective Actions
Temperature Blanks	Measure temperature of samples in the ice chest.	Water sample that is transported in ice chest to lab.	Not required, but if used place one per ice chest.	Record temperature; condition noted on Sample Log-In form
Field Blanks	Assess contamination introduced from sample container with applicable preservative.	In the field, RO water is collected into sample containers with preservatives.	One per sample event	< QL: Sample will be flagged if >QL and analyte concentration < 10x concentration in blank.
Trip Blanks (dissolved gas only)	Assess contamination during transportation.	Fill bottles with reagent water, take to field and returned without opening.	One in each ice chest with dissolved gas samples.	< QL: Sample will be flagged if >QL and analyte concentration < 10x concentration in blank.

Table 5. SOPs and Methods for All Measurements and Matrices

Matrix	Target analyte/ measure/ parameter	Units	Size (mass or Volume)	Preservation Method	Collection Frequency	Total number of samples	Holding time	SOP or Method	Comments
Surface and Ground Water	Alkalinity	mg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1151-1	
Surface and Ground Water	Br, Cl, I, o-P, SO_4, NO_3, NO_2	mg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	Br, Cl, I, SO_4, NO_3, NO_2 by IC K-GCRD-SOP-3329-2 o-P by Lachat K-GCRD-SOP-1151-1	
Surface and Ground Water	CO_2, N_2O, CH_4	µg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1160-0 & K-GCRD-SOP-1088-5	
Surface and Ground Water	Dissolved Metals	mg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1154-1	
Surface and Ground Water	NH_4, NO_2+NO_3	mg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1151-1	
Surface and Ground Water	TKN, TP	mg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1151-1	
Surface and Ground Water	TDN, TDP	mg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1151-1	
Surface and Ground Water	TOC/DOC	mg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1165-0	
Surface and Ground Water	TIC/DIC	mg/L	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1165-0	
Surface and Ground Water	^{15}N and ^{18}O from nitrate	per mil	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	IRMS (Isotope Ratio Mass Spec)	
Sediment	Carbon and Nitrogen	g/g	5 grams	Dried at 50 C and stored dry	4 per year	up to 30 per event	28 day for sediments stored at <6 deg C, indefinitely for dried samples	See Sec. B4 on Carbon, Nitrogen, and Stable Isotope Analysis	Capsule blanks, organic carbon standard
Sediment	^{15}N and ^{13}C	Per mil	5 grams	Dried at 50 C and stored dry	4 per year	up to 30 per event	28 day for sediments stored at <6 deg C, indefinitely for dried samples	IRMS	Capsule blanks, organic carbon standard

Surface and Ground Water	H and O isotopes	per mil	See Appendix 2	See Appendix 2	4 per year	up to 30 per event	See Appendix 2	K-GCRD-SOP-1137-0	
Sediment Slurries	Denitrification Rate (N_2O)	N/g/day based on N_2O	100 grams	1-6 °C on ice or refrigeration prior to processing Do Not Freeze	4 per year	up to 200 per event	Assays begin within 14 days of collection	K-GCRD-SOP-1398-0 K-GCRD-SOP-1098-3	Gas samples stored at room temp in 5.9ml exetainer vials
Sediment slurries	Respiration rate (CO_2)	N/g/day based on CO2	100 grams	1-6 °C on ice or refrigeration prior to processing Do Not Freeze	4 per year	up to 200 per event	Assays begin within 14 days of collection	SOP TBD modified from K-GCRD-SOP-1398-0 and K-GCRD-SOP-1098-3	Gas samples stored at room temp in 5.9ml exetainer vials
Ground water	Denitrification rate (N_2O and SF_6)	N/ml/day based on N_2O	125 ml	1-6°C for 24 hours prior to processing	1 per year	Up to 12 per event	24 hours	J-WECD-ECB-SOP-990-1 & K-GCRD-SOP-3458-0	Gas samples stored at room temp in 5.9ml or 12ml exetainer vials
Sediment	OM fraction	g/g	100 grams	1-6 °C on ice or refrigeration prior to processing	4per year	up to 50 per event	Sediments should be dried within 21 days of assay	K-GCRD-SOP-1111-0	part of DeN measurements gathered as 4 reps per sample
Sediment extracts	Aqueous extractions of DOC	mg/Kg	10 grams	1-6 °C on ice or colder prior to processing	4 per year	up to 50 per event	14 days	K-GCRD-SOP- 1130-0 & K-GCRD-SOP-1165-0	Sediment may be frozen for storage
Sediment extracts	KCl extractions for NH4, NO3+NO2	mg/Kg	10 grams	1-6 °C on ice or colder prior to processing	4 per year	up to 50 per event	14 days	K-GCRD-SOP-1130-0 & K-GCRD-SOP-1151-1	Sediments may be frozen for storage
Surface and Ground Water	Dissolved Oxygen	mg/L	NA	NA	4 per year	up to 30 per event	NA**	Measured in the field K-IO-SOP-1260-2	Based on EPA Method 360.1
Surface and Ground Water	pH	pH	NA	NA	4 per year	up to 30 per event	NA**	Measured in the field K-IO-SOP-1260-2	Based on EPA Method 150.2
Surface and Ground Water	Temperature	°C	NA	NA	4 per year	up to 30 per event	NA**	Measured in the field K-IO-SOP-1260-2	Based on EPA Method 170.1

Surface and Ground Water	ORP	mV	NA	NA	4 per year	up to 30 per event	NA**	Measured in the field K-IO-SOP-1260-2	No EPA Method
Surface and Ground Water	Sp. Cond	µS/cm	NA	NA	4 per year	up to 30 per event	NA**	Measured in the field K-IO-SOP-1260-2	Based on EPA Method 120.1

**Analyze immediately during sample collection.

B.6 Sample Shipment

Samples will be driven to RSKERC via field crew. If shipment is required, ship overnight to:

Kenneth J. Forshay
U.S. Environmental Protection Agency
Robert S. Kerr Environmental Research Center
919 Kerr Research Drive
Ada, Oklahoma 74820
(580) 436-8912 (phone)
forshay.ken@epa.gov

Shipping and handling procedures
Samples will be packed in ice chests and driven back to Kerr Lab on ice. Samples to be sent to other labs, such as UC Davis, will be shipped from Kerr Lab.
Samples collected that have finite holding times will not be archived beyond one year.
Filtered N and O isotopes of nitrate in water and soil samples following denitrification assay sample removal will be stored frozen at -10 to -20ºC at Kerr Lab.
Upon collection, samples will be documented, and all transfers of custody will be noted to include sample login (Analytical Sample Record) form in each ice chest.

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.

Publications resulting from this project will undergo ORD clearance in STICS and external peer-review of the journal article(s)..

SECTION D – DATA VALIDATION AND USABILITY

D.1 Data Review, Verification and Verification Methods

Data sets will be verified for completeness, correctness, and conformance with the methods. Data verification 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 Lab process will evaluate the data at the analyte and sample level by comparing results of the QC checks against the SOP performance criteria.
For field measurements, the Project Lead will verify the field data collected to ensure they meet requirements as defined in the QAPP.
Any data that does not conform will be flagged to alert the PI. The PI will further examine flagged data to determine if it is acceptable. While [K-GCRD-SOP-1130-0 RSKSOP-322] (for KCl extraction of sediments) has acceptance limits at 80-120% recovery for matrix spikes, for the purposes of this project, 70-130% recovery is acceptable. The PI will evaluate or validate project data to ensure they meet project requirements. This may include range checking for outliers, reviewing project notebooks, etc.

The highest probability for data integrity problems is likely to arise from data transcription errors. Data integrity will be controlled via a 10% check conducted after all data transcriptions. This will follow transcription from both paper records (Appendix) and electronic data reports. All checks will be documented by the reviewer.

Statistical Analyses

Statistical analyses will be performed on the data sets to compare means and make inferences. For example, denitrification rate data structured by season, treatments, and habitat types will be compared using general linear model analysis of variance (GLM ANOVA) based on a factorial design and Tukey's pairwise post-hoc test in SPSS for within factor comparisons. Comparisons of water chemistry parameters will be done using analysis of variance (ANOVA) with appropriate post-hoc tests (probably Tukey's HSD, but it depends on variance in the data) to compare geomorphic structures, and season, regression analyses will be performed on denitrification rates, physical, and chemical parameters to determine other potential drivers of denitrification. These parameters may be added to the GLM ANOVA as covariates as needed depending on colinearity. Descriptive statistics including mean and standard deviation will also be calculated for all appropriate measures. There is possibility that the analytical software will change to R or something else. We will report this in publication documents.

A variety of statistical analyses and methods to be determined will be used to describe the diverse data, the previous description is just one example.

D.2 Reconciliation with User Requirements

Data will be presented in tabular format or in figures. The data will be evaluated by the project lead to ensure they conform to the QA objectives of the project. Results from all analyses will be required to meet data quality objectives or marked with appropriate data qualifiers.

The project lead shall use the results of the data review, verification, and validation process to assess whether the data quality meets the project requirements and thereby the user requirements. If there are data quality issues that may impact their use, the impact will be evaluated by the project lead. The project lead may seek assistance from QA staff as needed.

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REVISION HISTORY

Revision #	Description	Effective Date
0	Initial Version	Date of Management Approval

Appendix 1: Groundwater Monitoring Sampling

Groundwater monitoring wells are sensitive to contamination and water removal. Excessive pumping rates or disturbance may alter water levels, degrade the integrity and quality of samples for other users, and/or require re-development of the well. Therefore, it is critical to follow the protocol and sampling schedule described below. Only those individuals familiar with this protocol shall collect samples.

The sampling team includes the following individuals:
Ken Forshay, EPA, GCRD, Ada, OK
Katie Buckler, EPA, GCRD, Ada, OK
Russell Neill, EPA, GCRD, Ada, OK

Sampling Schedule:
The wells shall be installed in 2023 then developed and sampled on a quarterly basis.

Equipment and supplies needed for well sample collection:
All equipment shall be clean and de-contaminated using DI water prior to arrival in the field or in the field between well sites.

1. Cole Parmer peristaltic pump with clean silicone, and polyethylene tubing for each well sampled.
2. Multimeter (Hydrolab or YSI as available) with appropriate flow cell
3. Electric tape for measuring water level (Solinst, model 101 mini with mm increments)
4. DI squirt bottle
5. Nitrile gloves for handling samples and sample equipment
6. Field Notebook and pen
7. Sample bottles and filters (Appendix 2).
8. Large carboy for purge water
9. Copy of this QAPP and SOPs listed in this QAPP.

Well Sampling Order of Data Collection:

1. Inspect the exterior and interior of the well for damage. Note any irregularities.
2. Open the well and measure water table depth with electric tape if sondes or loggers are not present, otherwise remove sondes or loggers and allow water level to equilibrate (2 minutes) then measure water level.
3. Determine purge volume
4. Purge then measure field parameters
5. Collect samples
6. Measure total volume extracted
7. Deploy new sondes and loggers
8. Lock well and pick up any debris
9. Notes on sample handling
10. Decontamination

1. **Inspection:** Inspect wells to assure that they have not been tampered with, the locks are secure, and the seal at the well pipe-ground contact is intact. Note any irregularities.

2. **Water Level Measurement:** Prior to sampling, obtain water level with a water tape [K-GCRD-SOP-1132-0 as depth below top of PVC well casing. Record the date, time to the minute, well identification number, depth below top of PVC well casing. At certain specified sampling times (up to 4 per year), deploy self-contained water level/temperature loggers [K-GCRD-SOP-1134-0)] to 5 cm above bottom of each well. At certain specified sampling times (up to 4 per year), retrieve water level/temperature data loggers note logger id on data sheet, stop the logger(s) using either the Solinst Levelogger (v. 3.1.1 or later) or the Diver-Office Software (v. 2012.1 or later), and store the data files to OneDrive https://usepa.sharepoint.com/:f:/r/sites/ForshayResearchGroupEnhancementTeam/Shared%20Documents/General/NormanWetland?csf=1&web=1&e=Dax7Er
    a. If no sondes are present, measure depth to water with pre-cleaned, two-wire depth gauge by two consecutive readings that agree to the nearest 1 mm.
    b. If sondes or loggers are present, remove the devices and allow the well to equilibrate (~ 2 minutes), then measure as described in 2a.

3. **Well Extraction Volume Calculation: Use the following equation to determine purge volume.**
   $Purge\ Volume\ in\ mL = 3 \times \pi r^2 \mathrm{H}$ Equation 1

   Where: H = height of water in cm
   r = ½ diameter of well casing in cm

4. **Well Purging and field-parameter measurement:** Monitoring wells will be purged using a peristaltic pump. Purging shall proceed until three (3) well volumes are removed (see Eqn. 1). Do not pump at flow rates above 500 ml min^{-1}
    a. Calibrate Hydrolab or YSI probes following user's manual
    b. Rinse probes and flow cell, including threads with DI or distilled water
    c. Attach peristaltic pump head to clean polyethylene tubing and insert into the well. Set the tubing inlet approximately 6 inches from the bottom.
    d. Begin pumping / purging, set pump to flow rate of <500 ml min^{-1}, collect effluent in carboy or bucket.
    e. There will often be sediment on the bottom of the well. Allow sediment to clear out of well and tubing. If sediment does not clear, lower the tube into the sediment to remove sediment source and purge until the water runs clear.
    f. Rinse tubing with sample water
    g. Begin filling flow cell
    h. Turn on stir bar if present when cell is full
    i. Allow probe values to equilibrate, i.e. temp, pH, DO (≥ 1 minute)
    j. Measure pH, temperature, dissolved oxygen, Oxidation Reduction Potential (ORP) and specific conductivity continuously. After at least three (3) well volumes are removed, record probe parameters when readings of all three

parameters have stabilized to within 0.5 degrees C, 0.1 pH unit, and 5% for other parameters.

5. Fill sample bottle at flow rate < 500 ml/min
    a. See appendix 2 for details on samples that need to be collected
    b. Rinse sample bottles with sample water
    c. Collect samples
    d. Filter and acidify as needed
    e. Place water samples on ice and refrigerate at 1-6ºC as soon as possible.
    f. Notes should be taken on the visible condition of the water extracted- cloudy, rusty, muddy, presence of an odor, etc.
6. **Extraction volume measurement:** The total volume of water extracted shall be measured by filling and emptying a large container such as a 20 liter carboy or other suitable measuring device. After each fill, the water should be disposed at least 3 meters from the pumping well. The total volume extracted should be entered in the field notes as the sum of all sample and purge water.
7. **Deploy new sondes and loggers:** Be sure to record time of deployment and place the removed sondes or loggers in a labeled bag.
8. **Lock the well cap and clean up. Make any additional notes.**
9. **Details on sample and data handling and shipping:** Sample-holding times should be limited to those required by the Ada EPA lab for particular sample types. Sample collection date and shipping should be coordinated with the Ada lab to assure that these times are met. Samples for dissolved analyses should be filtered through a pre-combusted GF/F filter. Approximately 5 milliliters of filtered sample should be discharged through the filter before filling the sample bottle. Samples should be packed in ice in a cooler immediately after collection. Samples should be shipped the day of or day after collection and shipped to the lab to arrive within 24 hours because some holding times are as short as 48 hours. See the attached sample collection protocol (appendix 2) and data sheet (appendix A2). Note the following on the data sheet for each well (appendix A2).
    a. Date
    b. Well identification number
    c. Time the well is opened
    d. Personnel
    e. Data recorded as described above: Start and end time for purging
    f. Purge method and total volume removed
    g. All measurements as described in the protocol

The remaining water samples shall be shipped or delivered overnight to:

Kenneth J. Forshay
U.S. Environmental Protection Agency
Robert S. Kerr Environmental Research Center
919 Kerr Research Drive
Ada, Oklahoma 74820
(580) 436-8912 (phone)
(580) 436-8703 (fax)

forshay.ken@epa.gov

10. **Equipment decontamination:** The equipment should be cleaned and rinsed with DI water.

Appendix 2: Requirements and protocol for water sample collection

Several sample types will be collected during this effort. Some samples will require direct collection into sample vials, others will require filtering and some type of preservation prior to leaving the field, and others only require that the sample be placed on ice prior to shipping to the lab.

Sample	Bottle type	Bottle Volume	Prep and Preservation	Analytes	Holding Time	Destination	Comments
Alkalinity	HPDE	125 ml	Not filtered Store cold 1-6 deg C	Alkalinity	up to 14 days	EPA General Parameters Lab Ada, OK	
Total Nutrients (not filtered, acidified)	HPDE	125 ml	Not filtered, Acidified to pH <2 with sulphuric acid. Store cold 1-6 deg C	Total P, Total N	up to 28 days	EPA General Parameters Lab Ada, OK	
Dissolved Nutrients(Filtered & Acidified)	HPDE	125 ml	Filtered and Acidified to pH <2 with sulphuric acid. Store cold 1-6 deg C	TDN, TDP, NH_4+, (NO_2+NO_3-)	up to 28 days	EPA General Parameters Lab Ada, OK	
Nutrients and Anions (Filtered Only)	HPDE	125 ml	Filtered not Acidified. Store cold 1-6 deg C	Br-, NO_2-(N), NO3-(N), Cl^-, I^-, SO_4^{2-} and PO_4^{3-}	48 Hrs for N and P, 28 days for others	EPA General Parameters Lab Ada, OK	
Dissolved Organic Carbon	Glass VOA vials	Two x's 40 ml	Filtered not Acidified. Store cold –1-6 deg C	Dissolved Organic Carbon	up to 7 days	EPA General Parameters Lab Ada, OK	
Total Organic Carbon	Glass VOA vials	Two x's 40 ml	Not filtered not Acidified. Store cold –1-6 deg C	Total Organic Carbon	up to 7 days	EPA General Parameters Lab Ada, OK	
Dissolved Metals	HPDE	60 ml	Filtered and Acidified to pH <2 with nitric acid. Store room temp	"Full Suite" to include Fe, Na, Ca, Mg, Mn,	6 mos	GCRD metals lab	
Dissolved Gas	Glass Serum vials with crimp caps	Three x's 60 ml	Not filtered Capped with teflon-lined butyl rubber septa without bubbles. Store cold 1-6 deg C	CO_2, N_2O, $CH_4$and H_2	7 days	Current – EPA General parameters lab Ada, OK	Crimp vials until the cap cannot be turned by hand
Nitrate Isotopes	HPDE	125 ml	Filtered Freeze to -20 deg C	del^{15}N and del ^{18}O	Stable Holding time not known	Ken Forshay, EPA Lab Ada, OK	
Water Isotopes	Glass VOA vials Or conical cap scintillation vials	40 ml	Not filtered Room temp or 1-6 deg C	Isotopes of water, H & O	Stable	EPA GP lab Lab Ada, OK	
Total Inorganic Carbon	Glass VOA vials Same vials as TOC	Two x's 40 ml	Not filtered not Acidified. Store cold 1-6 deg C	Total Inorganic Carbon	14days	EPA General Parameters Lab Ada, OK	
Dissolved Inorganic Carbon	Glass VOA vials Same vials as DOC	Two x's 40 ml	Filtered not Acidified. Store cold 1-6 deg C	Dissolved Inorganic Carbon	14days	EPA General Parameters Lab Ada, OK	

Once readings from the multi-parameter probe are stable and have been recorded, continue pumping at the same rate, but remove the inflow to the meter and use this line to fill sample bottles below in the following sequence.

1. Directly filled bottles:
    a. Dissolved gas: collect water directly into 60ml serum bottle to the very top. Allow water to overflow, then seal with the teflon-lined/butyl rubber cap and crimp cap, avoiding any air bubbles and delay in sealing. Test seal by twisting crimp cap. If it moves re-crimp, if it continues to move a new capper is needed. If necessary, the small vials can be filled and sealed under water in a larger container to avoid gas bubbles. These samples will be shipped to GCRD for N_2O, CH_4, and CO_2 analysis.

    b. Total Nutrients (Total N, Total P): collect total nutrient samples in the field in 125 ml certified clean nutrient bottles (HDPE) or HCl washed and DI rinsed HDPE bottles. These samples will be preserved with H_2SO_4 at pH < 2 and kept on ice or refrigerated. Bottles should only be filled to the shoulder in case they are frozen.

    c. Total Organic Carbon & Total Inorganic Carbon (TOC&TIC): collect water directly into two 40 ml VOA vials (certified clean glass vials with Teflon septa).

    d. A 125 ml polyethylene bottle should be filled and sent for analyses at GCRD including alkalinity.

    e. Water Isotopes: fill a 40 ml glass isotope vial with cap with unfiltered water until overflowing before capping. Try to eliminate any headspace in the vial. This sample does not need to be held on ice.

2. Filtered samples:
    a. Dissolved nutrients and anions (TDN, TDP, SRP (o-PO_4), NH_4, NO_3, NO_2, Br, Cl, I, and SO_4), collect in the field directly in a large (1-4 liter) certified clean or HCl washed and DI rinsed polyethylene bottle in the field or filter all samples directly. From the container, water for filtering can be gathered, except for Carbon and metals (which should be filtered immediately). Filter using pre-combusted Whatman GF/F filters in acid washed syringe holders (typically 25mm diameter) or Inject filtered sample directly into two 125 ml clean HDPE bottles. Fill to the shoulder. One of these bottles should be acidified with H_2SO_4 pH< 2. The other should be left without acid. The samples should be shipped immediately, but can be frozen and stored for later shipment if necessary. Holding times for Nitrate and SRP are 48 hours unless frozen.

    b. Stable isotopes of Nitrate: Collect one 125 ml clean HDPE (polyethylene) bottle filled to the shoulder with syringe-filtered water as described above. Freeze this sample as soon as possible. Holding time is not documented, but Nitrate is quite stable in frozen solution (Avanzino and Kennedy 1993) particularly in low calcium waters (Gardolinski et al. 2001).

    c. Dissolved Metals: Using a syringe and filter, filter water directly into a 125 ml HDPE bottle up to the shoulder. Add HNO_3 to bring pH < 2. Filter immediately because oxidation may cause precipitation of metals that will be filtered out.

Holding time is 28 days after preservation for mercury and six months for other metals, but should be sent to GCRD immediately. This sample does not need to be held on ice.

d. Dissolved Organic Carbon and Dissolved Inorganic Carbon (DOC & DIC): Filter 40 ml directly into two 40 ml VOA vials using a syringe filter. Holding time is 7 days, should be sent to GCRD immediately on ice.

3. QA/QC: Collect field duplicates every 10^{th} point (well or surface water) sample and an additional duplicate every 20^{th} sample for lab spikes and recovery for carbon samples only. The sample volumes are sufficient for spikes for other parameters. Create Equipment Blanks using DI or ultrapure water, processed through sampling apparatus, filtered, acidified and collected into sample bottles on each day of sampling as done for the constituents of interest. Provide samples of the original blank water without running through equipment for each week of equipment blanks to total three samples. These samples should be bottled and preserved like field samples and designated as Blank Source Water or Field Blanks and identify the source. A Trip Blank will be included in each ice chest with samples for dissolved gases (bottles are filled with blank water in lab prior to shipment to field).
4. Storage: All samples should be collected, transported on ice (ice is not required for metals and water isotope samples), and shipped to GCRD. The samples with short holding times (i.e. un acidified samples of nitrate, nitrite, and phosphate) must be sent as soon as possible.

FS.1 NORMAN FLOODPLAIN FIELD SHEET

Field ID_____ GPS_____ Page _____ of _____

Sampling Date	Sample Type	Comments	Samples Collected	Field Measurements
	Surface Water or Ground Water or Blank Water		**Water (F-filtered or NF-nonfiltered):** ____ Nutrients Dissolved; 125ml HDPE; Acidified (H_2SO_4); F ____ Nutrients Dissolved; 125ml HDPE; Not Acidified; F ____ Nutrients Total; 125ml HDPE; Acidified (H_2SO_4); NF ____ Alkalinity; 125ml HDPE; NF ____ Dissolved gas; 2-60 ml glass bottles; NF ____ Metals; 60 ml round HDPE; Acidified (HNO_3); F ____ Water isotopes; 40 ml glass vial; NF ____ TOC/TIC; 2-40 ml glass vial; NF ____ DOC/DIC; 2-40 ml glass vial; F ____ N and O isotopes; 60 ml round HDPE; F	Temp (°C): BP (mmHg): Sp.Cond. (µS/cm): DO (%sat): DO (mg/L): pH: ORP (mV): Turbidity (NTU):

Inspection Notes:		
Note of sondes/data loggers present: Time removed:_____ Time redeployed: _____		
Time Well Opened_____ & Closed _____	Depth to well bottom (m): _____ Depth to water (m): _____ Height of water (m): _____	Total Volume of water removed from well (est. L):
Purge Time Start _____ & End _____		
Personnel:	Purge Volume (L):	

FS.2 Calibration Data Sheet

Date: _____

Project: _____

Sonde Description:_____(Serial #)

Barometric pressure from Airport:_____inches of Hg = _____X 25.4 mm of Hg = _____mm of Hg

Temperature: _____ (no calibration needed)

	Calibration Standard Value	AM reading after calibration	QA Requirement (differences are AM vs. PM)	PM reading after last sample	QA Check AM vs.PM
Sp. Con (DI Water)	**0 (blank)**		**<5 µS/cm**		
Sp. Cond (~1000 microseimens)			**+/- 10% difference**		
LDO %	**@_____mmHg**		**+/- 10% difference**		
LDO (with DI water)			**+/- 10% difference**		
pH 4	**4.00**		**+/- 0.5**		
pH 7	**7.00**		**+/- 0.5**		
pH 10	**10.00**		**+/- 0.5**		
ORP			**+/- 10% difference**		
Turbidity (DI Water)	**0 (blank)**		**<5 NTU**		
Turbidity (~1000 NTU)			**+/- 10% difference**		

FS.3 Calibration Solution Data Sheet

Personnel: _____

Calibration Solutions Used

Project: _____ Date:_____

Personnel: _____

1. **Conductivity Solutions**

Lot #_____Part#_____for _____microsiemens

Expiration Date: _____

Lot #_____Part#_____for _____microsiemens

Expiration Date: _____

Lot #_____Part#_____for _____microsiemens

Expiration Date: _____

Vendor/Company Name: _____

2. **ORP Solutions**

Lot #_____Part# _____ Expiration Date:_____

Vendor/Company Name: _____

3. **pH Buffer Solutions**

Lot #_____Part# _____for _____pH
Expiration Date_____

Lot #_____Part# _____for _____pH
Expiration Date_____

Lot #_____Part# _____for _____pH
Expiration Date_____

Vendor/Company Name: _____

4. **Turbidity Solutions**

Lot#_____Part# _____for_____NTU
Expiration Date_____

Lot#_____Part# _____for_____NTU
Expiration Date_____

Vendor/Company Name: _____