Watershed Dynamics and Evolution (WaDE)

ORNL Science Focus Area 2024 Annual Report

Understanding the role of heterogeneous land cover and hydrologic regime on watershed function

Contents

SFA Contact and Sponsor

Contact: Eric Pierce, Oak Ridge National Laboratory, pierceem@ornl.gov

Sponsor: The ORNL WaDE SFA is sponsored by the Environmental System Science (ESS) program within the U.S. Department of Energy's Biological and Environmental Research program. Contact Paul Bayer, ESS Program Manager, paul.bayer@science.doe.gov, Brian Benscoter, brian.benscoter@science.doe.gov, and Beth Drewniak, beth.drewniak@science.doe.gov.

wade.ornl.gov

ESS Environmental System Science

Watersheds are complex systems that provide important ecosystem services, including freshwater resources for energy production, irrigated agriculture, industry, and human consumption. The economic and societal importance of watersheds—and their vulnerability to environmental stresses—is exemplified in the southeastern region of the United States, which includes the Tennessee River Basin. This region comprises large areal-extent coastal and inland low-lying areas, elevated plateaus and highlands, numerous high-growth metropolitan areas, and substantial rural expanses. Furthermore, the southeast region is a North American biodiversity hotspot and home to numerous biologically diverse ecosystems.

Water resources in the southeastern region are vulnerable to changes in land use and land cover (LULC) and a range of climate-induced disturbances. The National Climate Assessment 5 indicates the southeastern United States will experience higher temperatures, more extreme heat events, and an intensifying hydrologic cycle with more frequent and severe storm and drought events. LULC changes can alter water storage and partitioning of rainfall into runoff with a host of cascading consequences for ecosystems and their services while climate change simultaneously changes the frequency and intensity of precipitation events. Existing regional socioeconomic stressors and inequalities exacerbate the impact of these disturbances.

Predicting the interactive consequences of hydrologic intensification and LULC change on watershed function at local to regional scales first requires an improved understanding of the coupled hydro-biogeochemical processes and feedbacks that link uplands, the shallow subsurface, and stream corridors. Predictions also require an improved understanding of how those processes aggregate and exert control on watershed function along a stream network.

To address this challenge, the U.S. Department of Energy's (DOE) Biological and Environmental Research (BER) program supports the Watershed Dynamics and Evolution (WaDE) Science Focus Area (SFA) led by Oak Ridge National Laboratory (ORNL). WaDE will advance predictive understanding of how dominant processes controlling watershed hydro-biogeochemical function operate under a range of hydrologic regimes and vary along stream networks that drain heterogeneous land covers (see Fig. 1, this page).

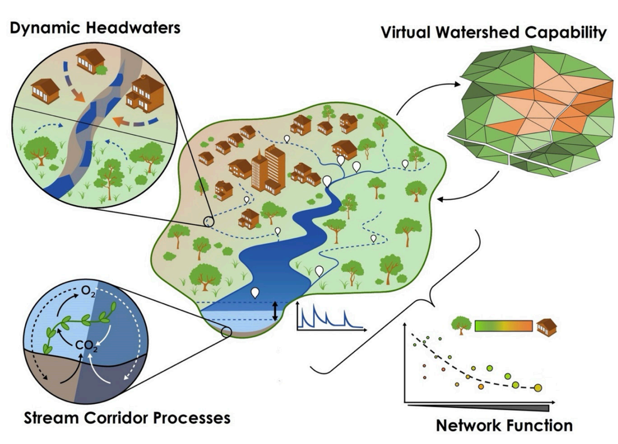


Fig. 1. Research Foci. Conceptualization of 9-year research foci needed to support transferable understanding of watershed hydro-biogeochemical function within and across stream networks that drain heterogeneous land covers: non-perennial dynamics, contributions to stream metabolism, network-scale emergent behaviors, and responses to hydrologic events.

SFA Knowledge Gaps

Land Cover Effects. Researchers lack sufficient understanding of how gradients in land cover affect watershed function.

Hillslope-Catchment Interactions. Researchers have limited understanding of hillslope-catchment interactions and how these interactions vary under different hydrologic regimes and land cover.

Integrated Measures of Watershed Function. Researchers have an incomplete understanding of how measures of stream function, such as stream metabolism, integrate complex watershed properties that vary in space and time.

Observational Networks. Existing observational networks are skewed to high-order streams and end-member systems with either forested, agricultural, or highly urbanized land covers, leading to insufficient observations of low- to mid-order streams with heterogeneous land cover.

Integrated Modeling. Model predictions of watershed function at basin or continental U.S. scales under changing climate scenarios are uncertain because mechanistic understanding of how key processes depend on land cover and hydrologic regimes is incomplete.

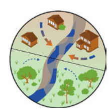
Research Themes

The WaDE SFA is organized around three integrated research themes and a crosscutting modeling activity that together create a multiscale, model-observation-experiment framework to enable hypothesis-driven research addressing the knowledge gaps. Collectively, this framework will advance a deeper predictive understanding of:

- Hydro-biogeochemical processes and feedbacks that control solute mobilization and export from headwater catchments with heterogenous land cover (Theme 1).
- Resultant feedbacks between flow, solute concentrations, and stream function in stream corridors (Theme 2).
- Emergent patterns in stream metabolism at network scales (Theme 3).

This annual report summarizes WaDE accomplishments from July 2023 to June 2024. This period represents the first full year following the SFA's triennial peer review in November 2022 and acceptance in January 2023 by the Environmental System Science program within BER.

Since June 2023, the team has not only published impactful manuscripts, but also held the annual all-hands meeting, performed storm sampling during the first flush after an unprecedented drought, encoded a representation of stream metabolism in the Advanced Terrestrial Simulator (ATS) tool, engaged in STEM (science, technology, engineering, and mathematics) outreach discussions with Oak Ridge High School, placed sensors in 24 mid-order watersheds across the Tennessee River Basin (see Fig. 2A, p. 3) to evaluate assumptions regarding watershed similarity, selected and instrumented all of the intensive sites in watershed 1 [East Fork Poplar Creek (EFPC); see Fig. 2B, p. 3], and initiated observations in watershed 2 (Reddy Creek). The aforementioned highlights as well as others are discussed in greater detail in the following sections.



Theme 1
Dynamic Headwaters

Theme 1 investigates how biogeochemical processes respond to variable saturation in non-perennial channels that connect uplands to the perennial stream network. Non-perennial reaches can make up a significant portion of a stream network and flow seasonally due to variation in the water table (intermittent) and/or periodically in response to rain events (ephemeral). These streams' control on local and downstream biogeochemical processes, such as metabolism, is not well understood. We aim to evaluate the response of non-perennial streams to wetting and drying and assess how these dynamics vary with land cover. Theme 1 combines field-based investigations with laboratory experiments integrated with watershed-scale modeling to advance system-scale understanding of stream metabolism. The overarching research questions in Theme 1 are:

- **Question 1.1:** What are the landscape characteristics that control the frequency and duration of flow in non-perennial streams?

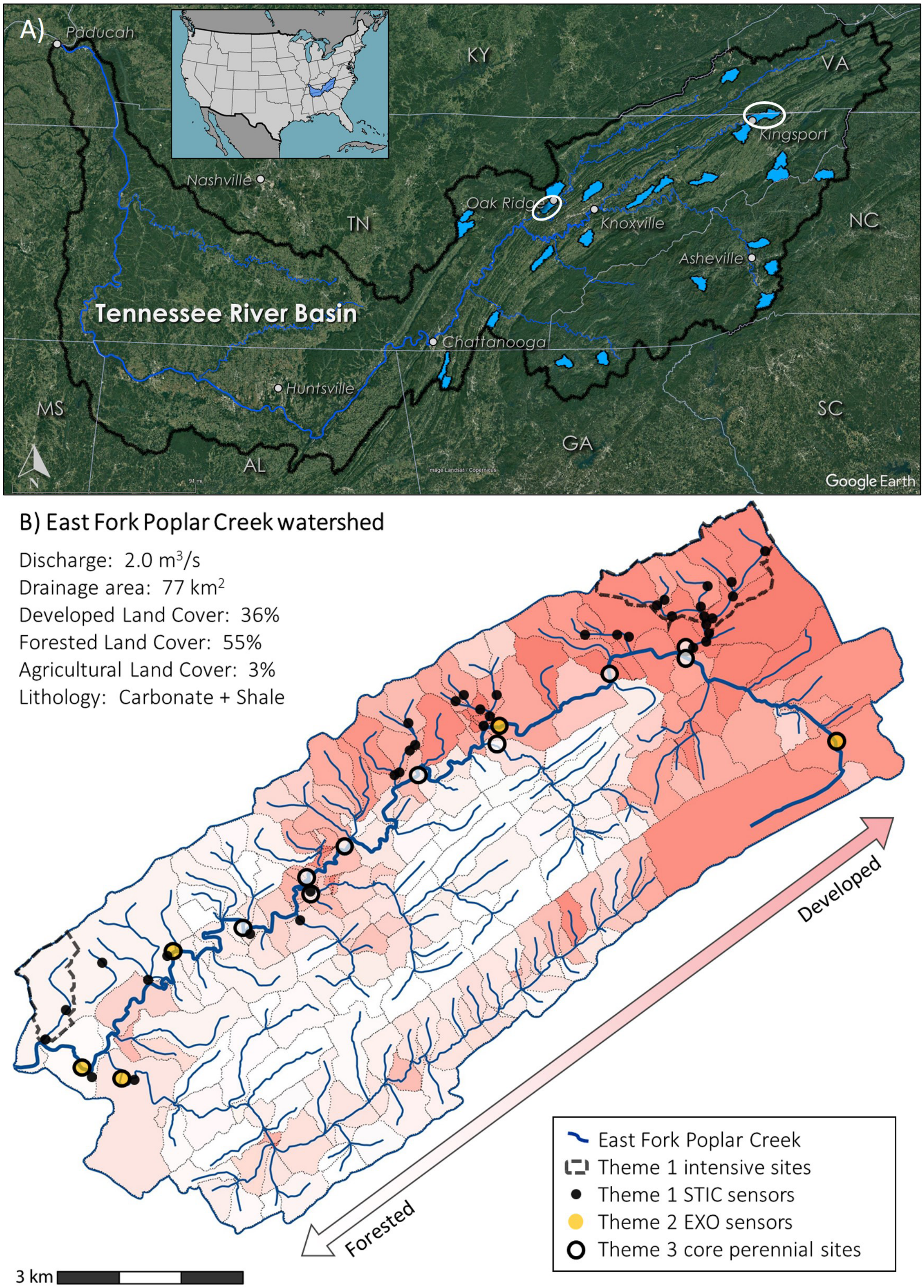


Fig. 2. Mid-Order Study Watersheds Across the Tennessee River Basin. **(A)** Initial two focal watersheds (i.e., East Fork Poplar Creek and Reedy Creek) are marked by white circles. **(B)** Detail of East Fork Poplar Creek watershed showing predominant land cover gradient and established observation sites.

- **Question 1.2:** How do carbon and (micro)nutrient mobilization and chemistry vary in response to changes in sediment saturation across different flow regimes?
- **Question 1.3:** How does variable saturation affect microbiological activity and associated nutrient acquisition and transformation?

FY23–FY24 Accomplishments

In the past year, Theme 1 has focused on assessing stream flow and chemistry across perennial and non-perennial portions of the stream network within the EFPC watershed. As of April 2024, we have completed seven bimonthly synoptic surveys of stream water in conjunction with Themes 2 and 3. Stream water, when present, was analyzed for nutrients (e.g., NO_3^-, NH_4^+, PO_4^{3-}), anions (e.g., Cl^-, SO_4^{2-}), major cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}), dissolved inorganic and organic carbon, and a broad suite of trace elements. Sulfur, oxygen, and carbon isotopes were analyzed on a subset of surface and groundwater samples to identify water sources and contributions from subsurface mineral weathering. Additionally, approximately 40 stream temperature, intermittency, and conductivity (STIC) sensors were co-located with synoptic sampling sites (see Fig. 2B, p. 3) to monitor the occurrence and conductivity of water in the stream channels at high temporal resolution (~15-minute time steps).

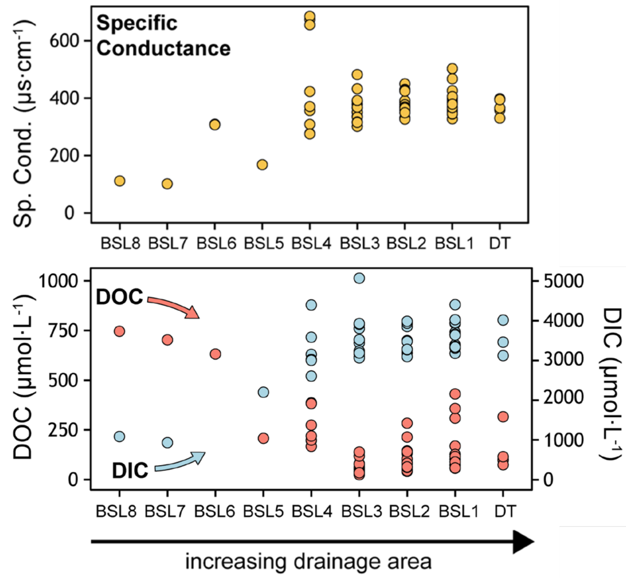


Fig. 3. Conductance and Dissolved Inorganic and Organic Carbon Concentrations. Specific conductance and dissolved inorganic carbon (DIC) concentrations increase while dissolved organic carbon (DOC) concentrations decrease downstream along a stream transect in an urban watershed. The x-axis shows individual sites located along the transect where stream water was collected. Sites BSL8 to BSL5 are non-perennial, while BSL4 to DT are perennial. Multiple points at individual sites represent different sampling dates. Fewer points are shown for the non-perennial sites because water was not always present during sampling campaigns.

Sites within the tributaries have been identified as non-perennial or perennial based on one year of observation and data from STIC sensors. Perennial stream sites have high concentrations of base cations and dissolved inorganic carbon and are chemically distinct from non-perennial stream sites, which are relatively enriched in dissolved organic carbon and select metals (e.g., aluminum and manganese). These results are consistent with a shift from runoff- or interflow-fed non-perennial stream reaches to groundwater-fed perennial reaches (see Fig. 3, this page). Solute concentrations in both non-perennial and perennial streams generally rise with increasing impervious land cover in the contributing catchment and may indicate contributions from urban sources. We are further exploring these patterns using a statistical clustering analysis to examine which solutes are most indicative of different water sources (e.g., interflow, shallow groundwater, deep groundwater) and identify solute sources to the stream at different times of the year.

STIC sensors record distinct flow and conductivity patterns across different synoptic sites (see Fig. 4, p. 5). Ephemeral flow occurs in response to rain events and appears as transient spikes in conductivity. Intermittent flow is observed in streams that remain dry or pooled for a period of the year and then transition to sustained flow, often following a period of ephemeral flow. Perennial flow is recorded as continuously high conductivity under baseflow conditions that dips in response to inputs of dilute water during rain events. Spikes in conductivity above baseline conditions reflect runoff from road salt during snow melt. Modeling crosscut activities use this data to evaluate the expansion and contraction of the stream network and its response to precipitation events across catchments spanning a gradient of land cover (urban to forested).

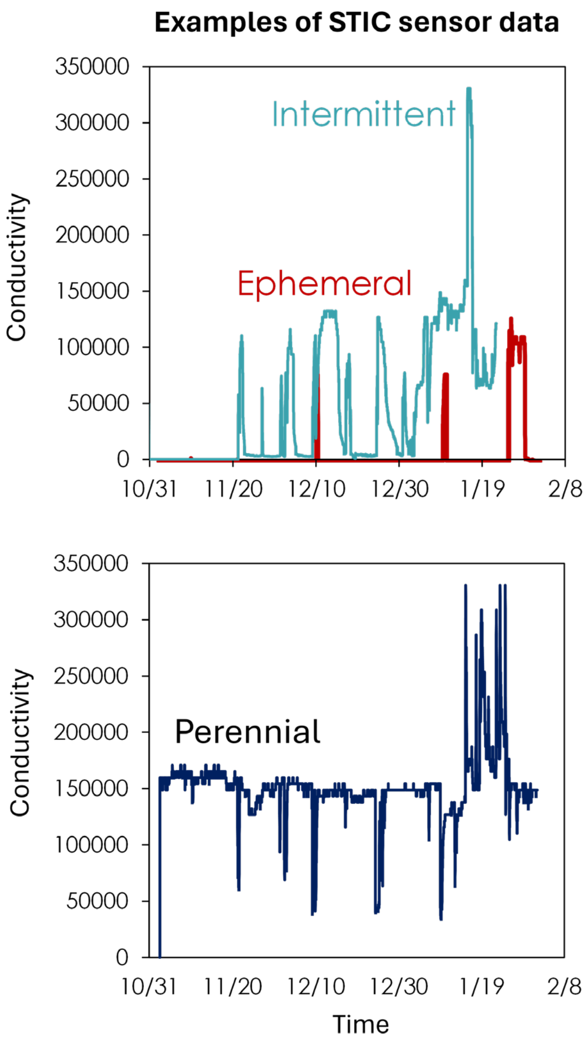


Fig. 4. Observing Conductivity Signals. Ephemeral, intermittent, and perennial flow patterns can be observed using conductivity signals (dimensionless proxy) recorded by stream temperature, intermittency, and conductivity (STIC) sensors, as shown at three different locations in the East Fork Poplar Creek watershed between late October to early February.

We also established two intensive field sites based around non-perennial tributaries selected from our synoptic network. These two contrasting sites, one in a forested catchment and one in an urban catchment, were selected based on land cover, initial evaluations of stream flow and chemistry, and site access. We are using these sites to conduct more intensive measurements targeting understanding of how land cover and underlying geology generate patterns of stream flow and chemistry from the non-perennial headwaters to the perennial portion of the tributary. In March 2024, we installed 22 wells at each site and retained the core material for geochemical analysis. Water level loggers (some with conductivity and temperature) are being installed in each well to evaluate surface-groundwater connections. We also installed a distributed temperature sensor (DTS) and sap flow system at the urban site to monitor surface-groundwater exchange along the stream bed and plant water use, respectively. Self-potential sensors were installed at both sites to examine the direction of water flow at high temporal resolution around trees.

Surface sediments were collected in March 2024 from non-perennial and perennial regions of two intensive field sites to evaluate benthic microbial communities and the composition of water-extractable organic carbon. Fourier-transform ion cyclotron resonance mass spectrometry analyses of water-extractable organic carbon are being performed at the Environmental Molecular Sciences Laboratory through a limited scope proposal. The data will be used to identify potential differences in the complexity and diversity of organic matter in the stream due to differences in streamflow intermittency and land cover.

FY25 Planned Activities

Our objectives for the upcoming year are to (1) develop manuscripts that explore the observed spatiotemporal patterns in stream chemistry; (2) conduct a detailed investigation of surface-groundwater interactions in dynamic headwaters; (3) analyze microbial community composition and functional response to wetting and drying; and (4) evaluate how organic matter and metals are stored in stream sediments and mobilized into surface water using nano- to micron-scale analytical techniques.

We will continue synoptic surveys throughout the stream network to collect at least two complete years of bimonthly data on stream flow and chemistry. These data will support two manuscripts examining (1) the influence of land cover on spatial and temporal patterns in stream chemistry and (2) signatures of rock weathering in EFPC versus the analogous but relatively pristine Walker Branch watershed. Measurements of isotope compositions for dissolved sulfate (^{18}O and ^{34}S) and dissolved inorganic carbon (^{13}C) will be conducted on samples from the stream's main stem, tributaries, and nearby groundwater wells. These analyses aim to differentiate chemical signatures from various sources, including precipitation, and shallow and deep flow paths. Concurrently, researchers will analyze core samples from adjacent boreholes to determine bulk chemistry and mineralogy, enabling the mapping of subsurface reaction fronts. This focus includes the dissolution and precipitation of carbonates and changes in clay mineralogy.

Additional spatially resolved surface-water sampling will be performed at each intensive site (urban and forested) over the summer to investigate time-varying contributions from surface and groundwater sources of dissolved metals and other solutes in perennial and non-perennial stream portions. Groundwater will also be collected periodically from installed wells. During each visit, the team will record *in situ* field parameters (e.g., pH, conductivity, and dissolved oxygen) and collect water that will be analyzed for metals/cations, anions, dissolved organic carbon/dissolved inorganic carbon, and water isotopes (δ^2H and $\delta^{18}O$). The data will be used to conduct an endmember mixing analysis to identify drivers of stream chemistry along a non-perennial to perennial transition and in response to storm events.

We will be using geophysical methods to investigate groundwater–surface water interactions at both intensive sites. Electrical resistivity tomography (ERT), induced polarization (IP), and electromagnetic induction (EMI) surveys will be used to refine subsurface lithology. We may also carry out a seismic refraction survey to improve the subsurface information from ERT, IP, and EMI and map out bedrock topography if possible. Additionally, self-potential datasets supported by nested wells where we measure hydraulic heads will be used to quantify stream-aquifer exchange. DTS datasets will be used to identify zones of anomalous temperature at the urban site (only, given equipment limitations) to find zones of groundwater upwelling. In addition to qualitative information extracted from DTS, vertical temperature probes will be installed along stream channels to quantify upward and downward fluxes in key areas. Hydraulic conductivity will be estimated via slug tests in wells at the site, and stilling wells have been installed to quantify local stream discharge. Combining information on subsurface heterogeneity and hydrologic properties with stream discharge measurements will be used to explore the relationship between subsurface heterogeneity and groundwater–surface water connections, which will be built into local-scale models using ATS to explore flow dynamics in intermittent streams.

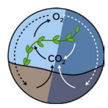
The ecohydrology portion of the project will focus on evaluating plant-water use along the riparian corridor across land-use gradients. Sap flow is currently being monitored in the urban intensive site, and this summer, we will instrument the forested site with sap flow sensors near the already installed groundwater wells. We will also sample stormwater throughout the summer to identify plant-water sources. Vegetation surveys will be conducted across the synoptic sites to facilitate the creation of transpiration water stress variables for future hydrologic models. These data will be used to (1) determine transpiration rates of native woody riparian species and invasive *Pueraria montana* (i.e., kudzu) at both sites, (2) examine the relationship between transpiration, groundwater fluxes, and stream flow across LULC classes, and (3) quantify riparian water stresses as stream channels evolve from non-perennial to perennial systems throughout the water year.

The geophysical and ecohydrological investigations of dynamic wetting and drying of stream channels will provide context for understanding local and downstream biogeochemical processes. Variable saturation gradients generated through intermittent and ephemeral flow influence redox-sensitive processes and the speciation of trace metals. Shifts in oxic-anoxic interfaces due to frequent variations in the underlying water table can affect solubility, mobility, and distribution of micronutrients. We will use synchrotron-based X-ray absorption spectroscopy (XAS) to investigate the partitioning and speciation of iron, manganese, copper (redox-sensitive), and zinc (redox-stable) in sediments, particulates, and periphyton along a land cover gradient. Our goal is to characterize the impact of dynamic redox conditions on metal partitioning between abiotic and biotic phases. We have an active general user proposal to Stanford Synchrotron Radiation Lightsource, through which we will collect initial data during the May through August 2024 run cycle. The XAS data will support a manuscript on the partitioning and speciation of key elements under non-perennial streams' dynamic conditions. We are also exploring the use of single-particle inductively coupled plasma time-of-flight mass spectrometry (SP-ICP-TOF-MS) to quantify metal associations with colloids in surface water. Five stream samples filtered to <0.2 micrometer are being analyzed by SP-ICP-TOF-MS, and the data will be evaluated to quantify the proportion of elements present in ionic versus colloid phases and co-occurrence of elements in single particles.

The microbial ecology team at Kansas State University is preparing a manuscript on the influence of aridity and LULC on the structure and function of the stream microbial community using a previously collected dataset. This work forms the basis for our hypotheses as we transition our efforts to watersheds across the Tennessee River Basin, including EFPC and Reedy Creek. We will present this research at the Ecological Society of America (ESA) 2024 Annual Meeting to introduce the WaDE SFA to the ESA community.

Also, stream sediments collected in March from perennial and non-perennial pools and riffles at intensive sites have been used in a drying and rewetting manipulation experiment measuring sediment respiration and methane flux in saturated, dry, and fluctuating saturated/dry conditions. Within the following year, we will analyze the microbial DNA and enzyme activity from this experiment in support of a manuscript on the impact of drying regimes on stream microbial activity and community. Additionally, stream microbial DNA and enzyme sampling will begin in late June across the EFPC stream network to investigate how differences in flow (perennial versus non-perennial) influence the microbial community structure and function across the urban-forest gradient. Finally, we plan to construct a pipeline to analyze 16S and 18S rRNA gene data (prokaryotes and eukaryotes) as groups of autotrophs and heterotrophs, with the eventual goal of understanding which components of the community are important through dynamics in stream metabolism across the WaDE SFA study region.

In addition to investigations planned for EFPC, Elizabeth Herndon is co-lead on a data synthesis proposal titled "Defining Subsidy-Stress Gradients for Metals and Relevance for U.S. Surface Waters" that was recently accepted by the U.S. Geological Survey Powell Center. This proposal supports a working group comprised of ecologists, physiologists, ecotoxicologists, geochemists, and applied mathematicians who will generate a unified model for how trace metals can be limiting or toxic to stream biota (subsidy-stress thresholds). Furthermore, the working group will synthesize metal concentrations in U.S. streams and evaluate spatiotemporal variability in subsidy-stress gradients. This work is expected to provide information on how watershed properties relate to trace metal concentrations in streams and subsequent implications for stream biotic function.



Theme 2 *Stream Corridor Processes*

Theme 2 studies stream corridor processes at the reach scale using a combination of field experiments, laboratory mesocosm studies, long-term observations, and modeling. Our work is motivated by the knowledge that mid-order streams are reactive conveyors that receive, process, and transport carbon, nutrients, and other solutes from upstream and the surrounding uplands. Further, these mid-order streams are a vital link between low-order headwaters and larger rivers. Nevertheless, they are noticeably under-represented in the research literature, so quantitative understanding of their roles in watershed function is lacking. The overarching research questions in Theme 2 are:

- **Question 2.1:** How are the relative contributions of water-column versus benthic gross primary production (GPP) and ecosystem respiration (ER) to net ecosystem production affected by gradients in sediment pollution and nutrient limitation associated with different land cover?
- **Question 2.2:** How do organic matter inputs and burial alter aerobic and anaerobic metabolism in the stream benthos?

FY23–FY24 Accomplishments

Theme 2 has a specific focus on reach-scale processes along the main stem of EFPC. We expanded our pre-existing network of two long-term observation stations to include a location near the head of the creek and a site on Bear Creek, the largest tributary to EFPC (see Fig. 2B, p. 3). Each station is equipped with (1) a pressure transducer to measure and record water depth and temperature at 15-minute intervals and (2) a multiparameter water quality sonde to measure and record water temperature, pH, specific conductance, dissolved oxygen (DO), and turbidity at 15-minute intervals. Water depth is converted into volumetric discharge using a site-specific rating curve developed by SFA staff. These data are essential for estimation of whole-stream metabolism and material flux, development of concentration-discharge relationships, and assessment of ecosystem resistance and resilience as a function of land cover.

The continuous data records collected at the long-term observation stations are supplemented with grab sampling at regular intervals. Water samples are collected and analyzed for a broad suite of constituents for a complete water analysis—specifically dissolved major and trace metals, dissolved anions (chloride, nitrate, sulfate, phosphate), total and dissolved nutrients (nitrate, phosphate, ammonium), total dissolved carbon, dissolved nonpurgeable organic carbon, and total suspended solids. Data from these sampling efforts support water source attribution and nutrient spiraling analyses, among other things (see Fig. 5, this page). At approximately 2-month intervals, water samples are also collected for microbial community analysis (soon to be supplemented with similar analyses of creek sediments; see Fig. 6, this page).

FY25 Planned Activities

In late summer, the Theme 2 team will complete a network of long-term observation stations with the instrumentation of a site near the mouth of EFPC and below the confluence of Bear Creek with EFPC while maintaining existing stations and associated sampling campaigns. Additionally, we plan to initiate a series of bottle incubation experiments as part of our estimation of whole-stream metabolism after the arrival of new postdoctoral students in July. The essential variable to measure is DO concentration over time. Straightforward in concept, in practice such measurements can be difficult due to the chance of air-water gas exchange overwhelming small

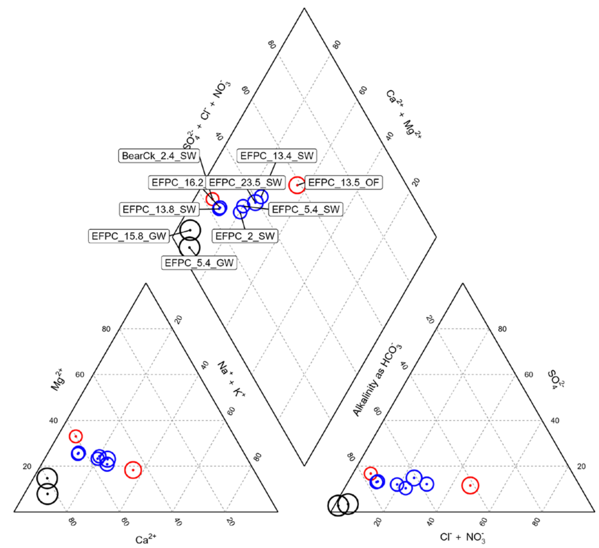


Fig. 5. Water Chemistry Trajectory. The trajectory of water chemistry on a Piper plot indicates increasing groundwater contributions to surface water as the creek flows downstream. Information like this is critical for the watershed-scale hydrological model and has broader implications for the interpretation of ecosystem respiration as inferred from carbon dioxide dynamics in surface water.

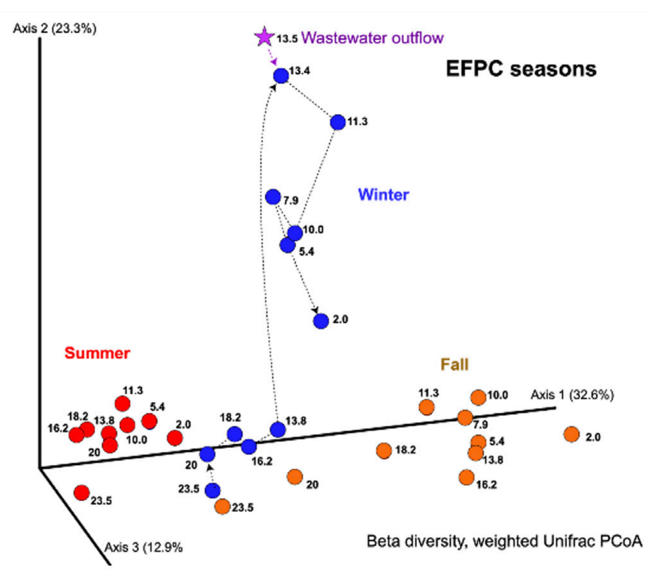
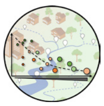


Fig. 6. East Fork Poplar Creek (EFPC) Seasons. Projection of intersite community distances reveals seasonal differentiation of EFPC water microbiomes. The communities are more similar at the head of the creek (EFK23.5). The wastewater effluent has a major effect that dissipates rapidly, suggesting community resilience.

changes in oxygen concentration. To eliminate this source of error, we are evaluating the use of non-invasive fiber-optic measurement technologies. Initial trials have been promising and indicate further testing and implementation are warranted. Lastly, we are coordinating with microbiology team members to assess the effects of light intensity and wavelength on the composition and function of in-stream biofilms.



Theme 3 *Network Function*

Theme 3 investigates the relative drivers and emergent patterns in stream function within and across mid-order stream networks and their response to network position, land cover, and changes in network connectivity resulting from seasonal and event-based flow dynamics. To do so, we integrate measurements from high-frequency sensor networks, high-density synoptic sampling campaigns, intensive network-distributed experiments, and forward and inverse modeling tools.

We utilize whole-stream metabolism, estimated using DO, as an integrated metric of stream function and synchrony/asynchrony as a framework for evaluating spatial-temporal patterns in stream metabolism in relationship to potential drivers. The overarching research questions of Theme 3 are:

- **Question 3.1:** When and where do metabolic regimes synchronize along a stream network, or why do they diverge?
- **Question 3.2:** How do variable inputs of flow and solutes from non-perennial tributaries influence rates of stream metabolism in the downstream mainstem, and how does this effect scale with the length of the flowing network?

FY23–FY24 Accomplishments

Progress this year focused on Question 3.1, evaluating spatiotemporal controls on network-scale synchrony/asynchrony in stream metabolism rates by utilizing high-frequency sensor networks across the middle and upper Tennessee River Basin and within EFPC, complemented by discrete sampling of chemistry, flow, and coupled metabolic functions in EFPC.

Regional Watershed Synoptic Response. To support transferable understanding of watershed hydro-biogeochemical function, the WaDE SFA team focused observations on mid-order watersheds representative of extant variation in the Tennessee River Basin. In FY23, we developed a watershed classification approach to identify representative clusters of watersheds based on key characteristics believed to influence watershed function. We then used this approach to identify our first two focal watersheds (see Fig. 2A, p. 3). We further selected 25 mid-order watersheds representative of extant variation in the Tennessee River Basin and instrumented the outlets with high-frequency DO and conductivity-temperature-depth sensors in March 2023 (see Fig. 2A, p. 3).

A key accomplishment of this year has been maintaining this sensor network and using the resulting data to test the hypothesis that broad patterns in watershed hydro-biogeochemical functions can be predicted by key high-level state and forcing variables. Specifically, we have started to assess the relative responses of flow, temperature, specific conductivity, and DO across the 25 watersheds to event- and seasonal-scale drivers; evaluate the explanatory strength of selected variables and identify additional key variables; evaluate synchrony/asynchrony in response to leaf on/off and basin-wide perturbations; and assess when local conditions and drivers appear to outweigh the effect of high-level variables. Preliminary results indicate that broad patterns in watershed physical (temperature; see Fig. 7, p. 10) and conservative solute (specific conductivity) response can be predicted by key watershed-wide variables, but this is not true in all cases, notably for DO, our reactive solute. Observations and in-depth analysis are ongoing.

Coupled Network-Scale Biogeochemical Patterns. Concurrent with instrumenting the regional watersheds, we also initiated a higher spatial density observation network in watershed 1, EFPC. Here, we aim to characterize and compare spatiotemporal variability in key biogeochemical processes, structural variables, and metabolic biomarkers using a combination of high-frequency sensors, repeat synoptic chemistry sampling, and discrete process

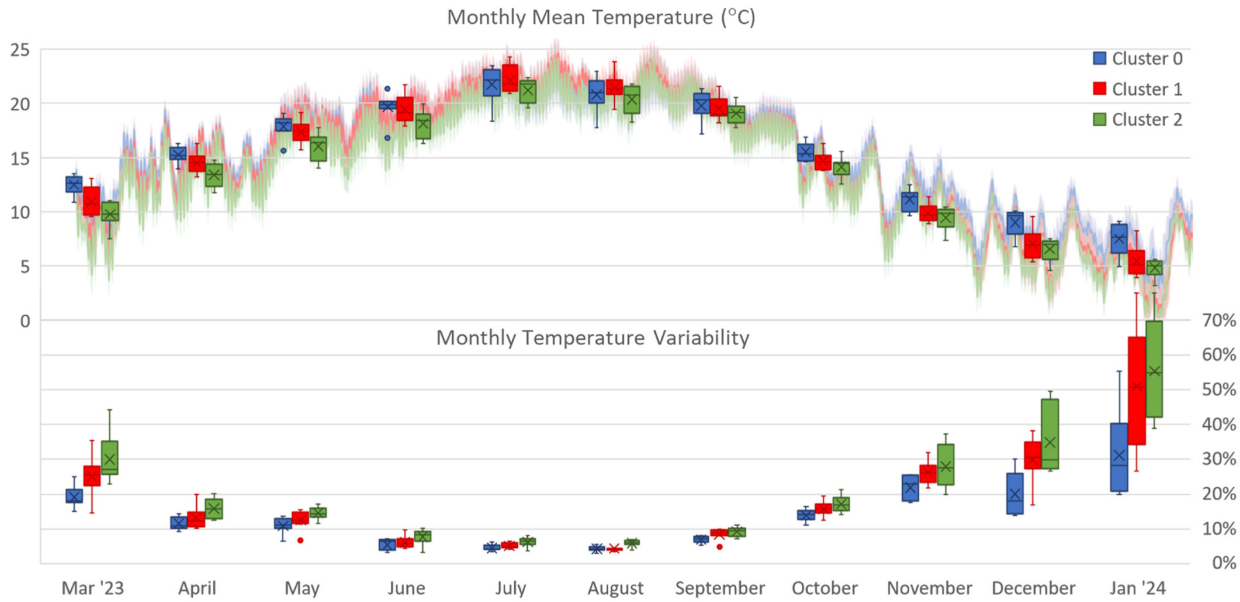


Fig. 7. Monthly Mean Temperature and Temperature Variability Across the Three Clusters. Temperatures are consistently coolest in Cluster 2 (defining characteristics include high elevation), whereas Cluster 0 (defining characteristics include carbonate bedrock) appears thermally buffered, showing the least annual change and lowest temporal variability.

experiments. A key accomplishment in the first year of the WaDE SFA was establishing a high-frequency sensor network in EFPC. A total of 14 sites were selected and instrumented; 10 along the mainstem of EFPC and four in tributaries that enter along the mainstem (see Fig. 2B, p. 3), which are co-located with Theme 2 monitoring sites. At each site, a DO sensor was installed for high-frequency (i.e., daily) estimation of stream metabolism (e.g., GPP, ER). Each site also has a conductivity-temperature-depth sensor and an above-water photosynthetically active radiation sensor. The sensor results to date show a longitudinal gradient in the daily variability of temperature and DO (a proxy for GPP). Stream size, canopy cover, and watershed land cover appear to be significant drivers based on preliminary analysis.

Accompanying the sensor data are monthly measurements of water chemistry (e.g., nutrients, dissolved organic and inorganic carbon, anions, cations, metals) and bimonthly measurements of organic matter decomposition using cotton strips. The cotton-strip technique provides a standardized method for measuring organic matter decomposition as cotton strips are 95% cellulose and allows for robust, cross-site comparisons (Tiegs et al. 2013, 2019). Preliminary results to date show very strong temporal patterns in organic matter decomposition, primarily driven by water temperature. Spatial patterns are muted, although there is a general trend of slower organic matter decomposition rates in tributaries compared to the mainstem (see Fig. 8, p. 11).

FY25 Planned Activities

In the coming year, we plan to conduct additional synoptic sampling at the regional watersheds for discharge, water chemistry, and microbial enzyme activity. We will also continue analyses of the sensor time series, including using power spectra to characterize bulk behavior, and the concepts of spatial stability and synchrony to evaluate the scale, persistence, and coherence of signals relative to the processes driving them. Collectively, these results will allow us to test our original hypothesis and interrogate the spatiotemporal controls on synchrony across stream networks to address Question 3.1.

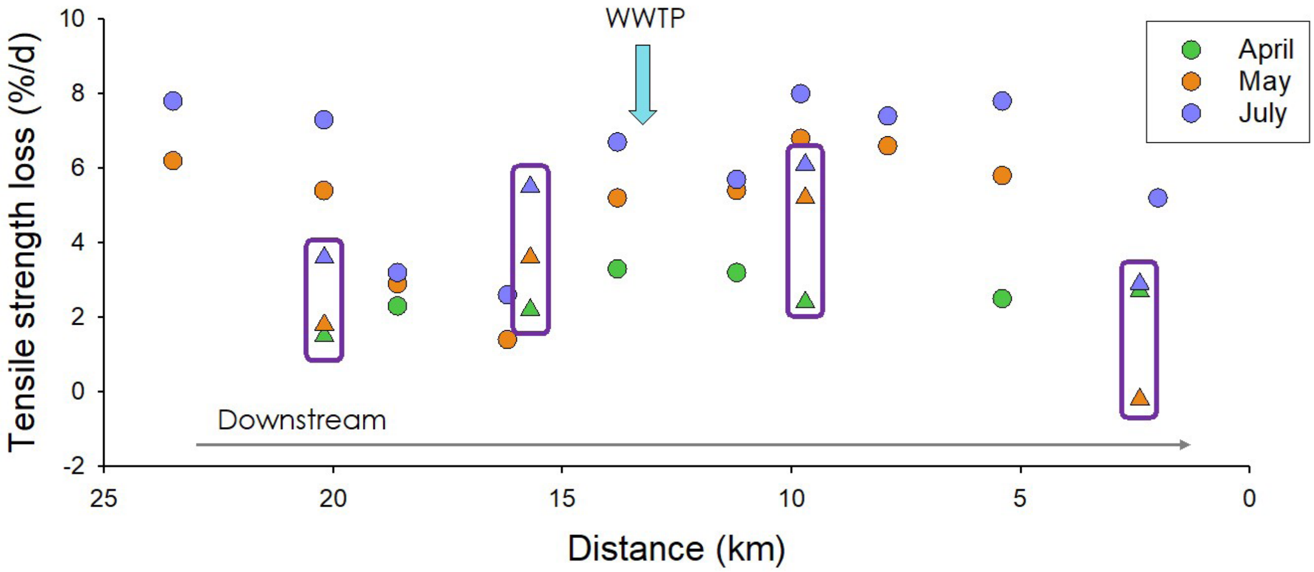


Fig. 8. Organic Matter Decomposition over Time. Tensile strength loss of cotton strips, a measure of organic matter decomposition, in the 10 mainstem sites in East Fork Poplar Creek (circles) and the four main tributaries (triangles) on three dates (i.e., April, May, and July 2023). The location of the wastewater treatment plant effluent is shown with a blue arrow.

In EFPC, we will use the first year of high-frequency sensor data collected at 14 core sites to estimate stream metabolism and address Question 3.1; specifically, what are the spatiotemporal controls on network-scale synchrony/asynchrony in stream metabolism rates? In addition to continuing data collection at these 14 sites (e.g., via sensors, grab samples for water chemistry, and cotton strips for organic matter decomposition), we will initiate measurements of microbial enzyme activity and conduct nutrient/micronutrient limitation assays to provide a more comprehensive assessment of the spatial controls on watershed hydro-biogeochemistry, including impacts of LULC and hydrological variation (e.g., low flows and storms). Lastly, in coordination with Theme 1, we will expand our core sensor network located at sites with perennial flow to include non-perennial sites distributed across the watershed. These sites, in addition to the existing sensor network, nutrient limitation assays, Theme 1 STIC sensors, and flow modeling efforts, will allow us to address Question 3.2.

Modeling Crosscut

The modeling crosscut is developing a virtual watershed modeling capability to support hypothesis-driven modeling subtasks within Themes 1–3. The team will use the watershed modeling simulator ATS (Coon et al. 2019) for integrated surface/subsurface hydrology and solute transport. The Watershed Workflow toolset (Coon and Shuai 2022) will facilitate preparation of the data-intensive model inputs from community data products. ATS is coupled through the Alquimia interface (Molins et al. 2022) to PFLOTRAN (Hammond et al. 2014) for biogeochemical reactions. A novel aspect of this work is the use of ATS's multiscale capability to represent the effects of small-scale hyporheic-zone biogeochemical reactions at the appropriate scale using hyporheic age-based subgrid models. Developed previously (Jan et al. 2021) as a joint effort between the

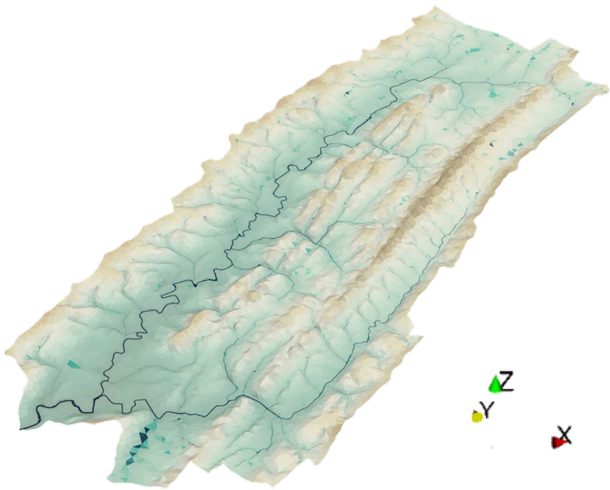


Fig. 9. Advanced Terrestrial Simulator Model of East Fork Poplar Creek. Color scale represents surface elevation except in the streams, which are represented as black.

Critical Interfaces SFA and the IDEAS-Watersheds project and extended and tested in FY23 (Le et al. 2023), the multiscale stream corridor model avoids *ad hoc* upscaling and explicitly accounts for rate-limiting mass transfer between the flowing channel and biogeochemically active transient storage zones. Currently, we are configuring the ATS model to represent EFPC.

FY23–FY24 Accomplishments

Hydrology Model for EFPC. We completed Version 1 of our EFPC hydrology model. The model uses ATS and a recently developed meshing strategy (Rathore et al. 2024) that aligns mesh elements with streams to better represent the stream channel network without excessive computational burden. Using Watershed Workflow, spatially distributed inputs were based on community data products with limited adjustment to subsurface permeability based on Hatcher et al. (1992). Soil properties were not available in the national data products for a subset of the watershed. In that region, random forest regression was used to impute soil properties.

A snapshot from the ATS model of EFPC is shown in Fig. 9, this page. It should be noted that the streams are not imposed in the ATS class of models but emerge from topography and water flow. Importantly, simulated stream discharge at the two stream gauges in EFPC was well reproduced without site-specific calibration (see Fig. 10, this page). We use a modified version of the Kling-Gupta efficiency (KGE) as a performance metric. The original KGE (Kling et al. 2012) combines bias, differences in variability, and timing error quantified through the linear correlation coefficient into a single metric. In our modified KGE (mKGE), we renormalize it so that the value mKGE=0 means the model has the same predictive power as the mean of

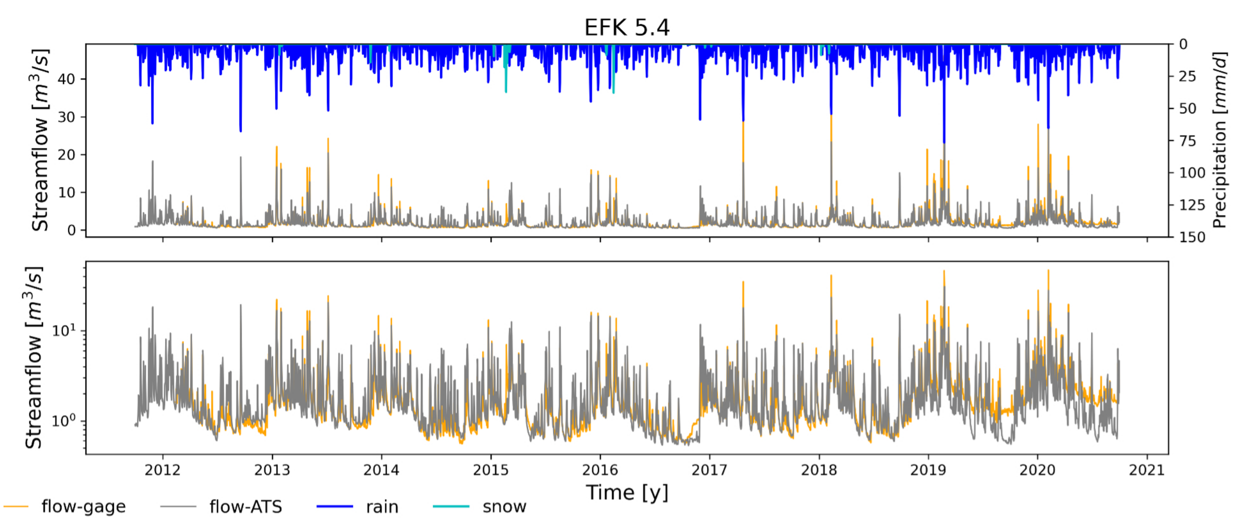


Fig. 10. East Fork Poplar Creek (EFPC) Streamflow. Comparison of Advanced Terrestrial Simulator model results and observed streamflow in EFPC.

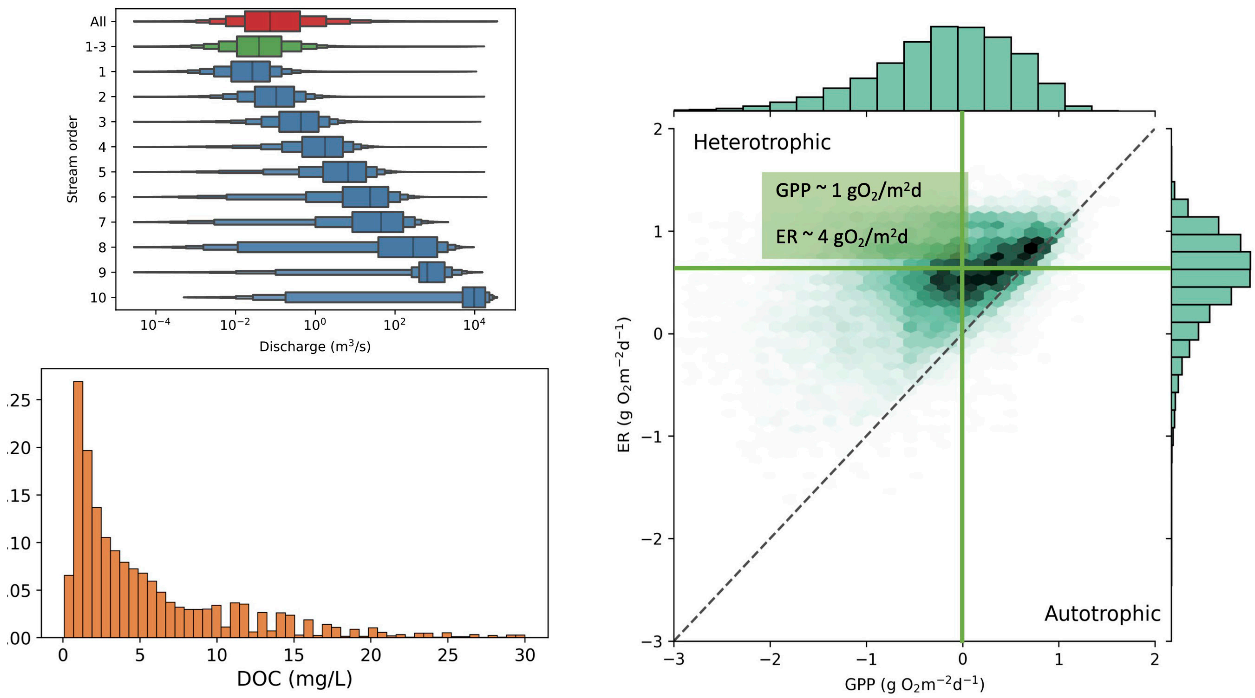


Fig. 11. Meta-Analysis of Input Parameters for WaDE's Stream Metabolism Model. Shown clockwise from upper left are box-whisker plots of stream discharge across stream order, joint distribution of gross primary production (GPP) and ecosystem respiration (ER) rates, and probability density of stream dissolved organic carbon (DOC).

the measured stream discharge time series and mKGE=1 refers to a perfect match between the model and stream gauge. Without calibration, we obtain mKGE=0.84 and 0.71 for two gauge locations, indicating very good model performance. In addition, the model correctly classifies the flow regime as perennial versus non-perennial for 80% of locations monitored by Themes 1–3.

Stream Metabolism Modeling. Using our multiscale stream corridor modeling capability implemented in the ATS-PFLOTRAN system, we extended the widely used single-station metabolism model of Odum (1956) to provide more realistic representations of ecosystem respiration. Specifically, we moved ecosystem respiration into the hyporheic zone with rate-limited mass transfer between the stream channel and hyporheic zone. Separating the mass transfer processes from the reaction model is important for our purposes as the conventional approach conflates the two, which limits transferability. We also used dual-Monod kinetics to represent aerobic respiration in the sediments of the hyporheic zone instead of the first-order reaction in Odum's model. By recasting the model equations into a dimensionless form, we were able to identify several parameter groups that control the model dynamics, the most important being a parameter controlling hyporheic connectivity and a Damkohler number for aerobic respiration in the sediments.

We completed a series of numerical experiments to quantify the differences between Odum's widely used model and our extension. In those experiments, we generated synthetic time series of DO dynamics using our model and then used the time series to estimate parameters in the Odum model. We used the same Markov-Chain Monte Carlo approach as streamMetabolizer (Appling et al. 2018) for the parameter estimation. We repeated the analysis many times for different values of the model input parameters including channel hydraulic parameters, hyporheic exchange, hyporheic residence time, GPP, maximum ER, and Monod parameters. A meta-analysis of community databases and scientific literature was undertaken to identify the relevant ranges for the model parameters. Results of the meta-analysis are shown in Fig. 11, this page.

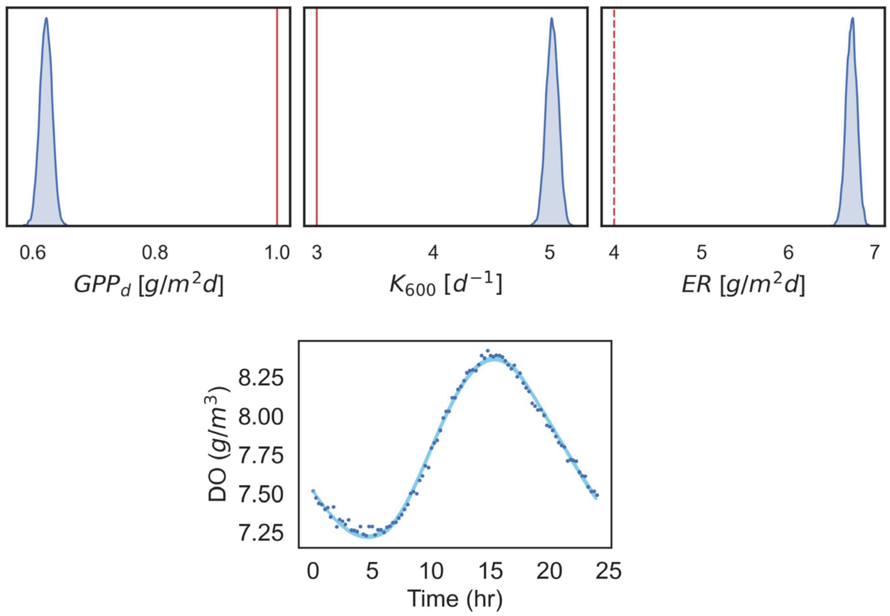


Fig. 12. Results from Numerical Experiments to Quantify Potential Biases in Parameters Estimated Using Odum's Single-Station Model for Stream Metabolism. The top three panels show probability density for estimated parameters versus the true input value (red line). Despite the biased parameters, Odum's model reproduces the observed time series of dissolved oxygen (bottom panel).

Our numerical experiments reveal significant differences between parameters estimated from Odum's model and our more realistic extension for some combinations of hyporheic connectivity, Damkohler number, and daily GPP rate. Importantly, those biases can exist even when both models can reproduce the DO time series (see Fig. 12, this page). These results demonstrate that when key assumptions in Odum's model break down (e.g., when hyporheic connectivity is relatively high), Odum's model can produce a good result (e.g., reproduce O_2 dynamics) for the wrong reason (e.g., unrepresentative parameter values). Our new modeling approach is more general and provides an alternative to Odum's model and streamMetabolizer that is applicable over wider condition ranges.

FY25 Planned Activities

A manuscript on the metabolism modeling work is being prepared and will be submitted for publication. We will continue to develop the EFPC model, which will be used to study the dynamics of expansion and contraction in EFPC.

Selected Research Highlight

In FY24, 26 manuscripts were published or submitted by the SFA team. Of these publications, 18 are published or in press. In this section, we highlight one of these.

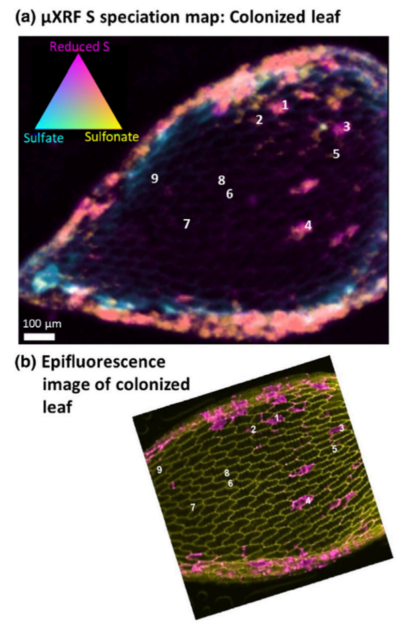
Research Highlight

Sulfur Speciation in Peat Moss Modified by Interactions with Cyanobacteria

Study reveals that Sphagnum *may produce sulfate compounds in response to colonization by mutualistic cyanobacteria for nutrient exchange.*

The Science

Peatland ecosystems are important for terrestrial carbon (C) and nitrogen (N) cycling, occupying 3% of the Earth's land surface yet storing approximately 25% of terrestrial C as recalcitrant organic matter. *Sphagnum* peat moss is responsible for much of the primary production and produces recalcitrant organic matter in these ecosystems, but its growth and productivity depend on symbiotic association with various microbes. *Sphagnum* species are known to exchange C-rich carbohydrates for N-rich molecules produced by symbiotic cyanobacteria, but this conceptual model may overlook a key role for sulfur (S). Using synchrotron-source microprobe techniques, the team determined that *Sphagnum angustifolium* colonization by *Nostoc muscorum* resulted in an enrichment of total S and increases in sulfate compounds relative to reduced S and sulfonate in plant tissues. At the scale of individual hyaline cells, colonized cells exhibited localized enrichment of reduced S surrounded by diffuse sulfonate, similar to observations of isolated *N. muscorum* colonies. Results suggest that colonization stimulates plant S uptake and production of S-containing metabolites that may be converted into reduced S metabolites by cyanobacteria.



Tricolor map of sulfur speciation across a single colonized *Sphagnum angustifolium* leaf **(a)** with the corresponding epifluorescence image showing *Sphagnum* cells in gold and colonizing *Nostoc muscorum* in pink **(b)**.

The Impact

This study indicates that *Sphagnum* may generate oxidized S compounds to exchange for N-rich metabolites produced by cyanobacteria, highlighting an important role for S in peatland biogeochemistry.

Summary

Researchers evaluated how *S. angustifolium* colonization by *N. muscorum* modifies S abundance and speciation at the scales of individual cells and across whole leaves. This mutualistic relationship may result in at least temporary increases in oxidized S compounds within *Sphagnum* tissues that subsequently undergo anaerobic decomposition in saturated peat soils. Additional studies are needed to determine the role of S exchange in driving ecosystem-scale S, N, and C dynamics.

Publication

Herndon, E., J. Richardson, A. Carrell, E. Pierce, and D. Weston. 2023. "Sulfur Speciation in *Sphagnum* Peat Moss Modified by Mutualistic Interactions with Cyanobacteria," *New Phytologist* **241**(5), 1998–2008. DOI:10.1111/nph.19476.

Postgraduate Spotlight

A key goal of the WaDE SFA and ORNL is to develop and train the next generation of scientists and engineers. As part of this year's report, we highlight two of our outstanding postgraduate researchers—Christopher McNabb and Moses Adebayo—who are contributing to WaDE's overall goals and objectives. See WaDE's website for a complete list of the project's postgraduate alumni (wade.ornl.gov/history).

Christopher McNabb

Christopher McNabb graduated from the University of Florida with a bachelor's degree in biotechnology, a minor in plant cellular and molecular biology, and a graduate certificate in wetland and water resource management. During his education at the University of Florida, Christopher worked with Eban Bean studying how preconstruction soil amendments altered water quality in large-scale housing developments.

After completing his undergraduate degree, Christopher earned a master's degree in ecological engineering at The Ohio State University working with Ryan Winston and Vinayak Shedekar. Christopher's thesis project focused on how conservation management practices impacted water quality and soil health in agricultural and natural ecosystems across Ohio. By monitoring soil biogeochemistry, soil microbial communities, and water quality, Christopher was able to identify how certain management practices altered or improved soil health. In addition, Christopher was involved in various stormwater management projects analyzing how best management practices such as rain gardens, wetlands, or cisterns improved water quality.

Between these experiences, Christopher interned at the Ohio Environmental Protection Agency as a wetland and stream mitigation project scientist. Currently, Christopher is a PhD student with Holly Barnard at the University of Colorado–Boulder in the Geography and Hydrological Sciences programs. He joins the ORNL WaDE SFA team to conduct his dissertation work, which will concentrate on how LULC alter non-perennial stream hydrology with a focus on how riparian spaces and species alter the ecohydrological drivers of these systems.

In his spare time, Christopher enjoys competitive swimming, hiking, and foraging.

Moses Adebayo

Moses Adebayo received his bachelor's degree in geology from the University of Ibadan in Nigeria. As an undergraduate, Moses joined the geophysics research group, where he worked on several projects that used electrical resistivity to identify groundwater-bearing zones in fractured rock.

Moses earned his master's degree in geology at the University of Toledo under the mentorship of Kennedy Doro. During his master's program, he worked on the Coastal Observations, Mechanisms, and Predictions Across Systems and Scales–Field, Measurements, and Experiments (COMPASS-FME) project, where he developed a hydrogeophysical framework to monitor infiltration during a simulated ecosystem-scale flooding experiment. His thesis combined the use of time-lapse electrical resistivity tomography and flow modeling using ATS to quantify subsurface hydrologic dynamics at coastal-terrestrial interfaces.

In 2024, Moses began his PhD in the Hydrologic Science and Engineering Program at the Colorado School of Mines under the supervision of Kamini Singha. In his research, he is combining geophysics and hydrogeological techniques (field data and model) to assess the controls of stream intermittency.

Moses' hobbies include playing video games and watching soccer.

National and International Impact

ORNL WaDE SFA team members attend strategic conferences in the United States and abroad to gain insights into the state of the science, share project findings and strategies with the broader watershed and freshwater science research community, and identify collaborative opportunities. From July 2023 to June 2024, SFA scientists delivered or published 23 presentations, abstracts, or posters (see Appendix C, p. 24 for details). In this section, we highlight team members' contributions to the 2023 American Geophysical Union Fall Meeting and the 2024 Environmental System Science Principal Investigators (PI) Meeting.

American Geophysical Union (AGU) Fall Meeting. Several SFA team members attended the AGU Fall Meeting in San Francisco, Calif., on December 11 to 15, 2023. Jesus Gomez-Velez convened a session on groundwater-surface water exchange, while SFA team members Marie Kurz and Scott Painter gave oral presentations and Xin Gu gave a poster presentation during the meeting.

BER's Environmental System Science PI Meeting and Cyberinfrastructure Working Group Meeting. SFA members attended the PI Meeting from April 15 to 17, 2024, at the Hyatt Regency Reston in Reston, Va. SFA team members participated in the working group meeting, plenary, and breakout sessions. Natalie Griffiths gave a plenary presentation entitled "Carbon Biogeochemistry along the Terrestrial-Aquatic Continuum." Matt Cohen served as a panelist on the Mentor Up panel, and Elizabeth Herndon provided a community update on the Environmental System Science coastal workshop and gave a session presentation entitled "Scaling Observations of Carbon Dynamics Across Thawing Tundra."

Organizational Leadership and Collaborative Research Activities

Eric Pierce is the overall SFA program lead and is responsible for ensuring integration and success. He is the point of contact with BER Environmental System Science program managers and speaks to Paul Bayer biweekly on SFA progress and potential issues. Marie Kurz and Elizabeth Herndon serve in programmatic deputy roles to the PI and aid in planning and coordinating the project's overall scientific direction. The theme leaders and modeling activity lead—Elizabeth Herndon and Alex Johs for Theme 1, Scott Brooks for Theme 2, Marie Kurz and Natalie Griffiths for Theme 3, and Scott Painter for Modeling Crosscut—are responsible for integrating activities within and across themes. Theme 1 collaborates with Kamini Singha (Colorado School of Mines) and Holly Barnard (University of Colorado–Boulder). Kamini provides expertise in subsurface geophysics, and Holly provides expertise in how vegetation impacts stream dynamics. Erin Hotchkiss (Virginia Polytechnic Institute and State University) is an aquatic ecologist and biogeochemist with expertise in understanding how environmental change impacts biogeochemical processes in freshwater ecosystems. Erin primarily supports Theme 2 but also engages in research activities in Theme 3. Adam Ward (Oregon State University) and Matt Cohen (University of Florida) collaborate with Theme 3 and provide expertise in network-scale hydrology and ecosystem metabolism, respectively. Lydia Zeglin (Kansas State

ORNL WaDE SFA Partners

Fig. 13. 2024 WaDE All-Hands Meeting Attendees.

University) is a microbial ecologist with expertise in stream microbial diversity; her expertise spans across all three themes in collaboration with ORNL microbial expertise from Melissa Cregger and Mircea Podar. The theme leaders, along with the broader team, meet biweekly to provide updates on current research directions, future plans, and changes in staffing.

Annual All-Hands Meeting

WaDE hosted an all-hands meeting at Dancing Bear Lodge in Townsend, Tenn., on March 19 and 20, 2024 (see Fig. 13, this page). The meeting included members from the SFA Science Advisory Committee and faculty and students from all collaboration institutions. Additionally, WaDE hosted two potential project collaborators, Amy Burgin (Kansas State University) and Jesslyn Brown (U.S. Geological Survey Earth Resources Observation and Science Center), for invited seminars and collaborative discussions.

PIER Plan Accomplishments

WaDE SFA leadership and team members are committed to creating a project culture that is safe, secure, open, and inclusive. WaDE honors the following foundational tenets to achieve the desired project culture. Everyone must act with integrity and build and maintain trust among colleagues, collaborators, and project participants. Four objectives serve as guideposts for the project to achieve the stated goals of the Promoting Inclusive and Equitable Research (PIER) Plan: (1) maintain a project organizational structure, leadership team, culture, and code of conduct that supports diversity, equity, inclusion, and access; (2) identify and participate in enrichment activities that increase social and cultural awareness for the leadership team and project participants; (3) create opportunities for participants from historically marginalized groups in STEM; and (4) implement strategies to develop and retain early and mid-stage researchers. Since June 2023, we have made progress in several elements of the PIER Plan.

Project Culture. As part of a continuous process of developing an inclusive project culture, WaDE SFA team members participated in an AdvanceGEO workshop entitled “Improving Workplace Climate: Empowering Individuals to Become Active Bystanders” on September 22, 2023. The workshop was sponsored by the ORNL Environmental Sciences Division. Additionally, we continue to learn from other successful project cultures, such as the Aquatic Intermittency Effects on Microbiomes in Streams project, through engagement with PI Amy Burgin during the 2024 Science Advisory Committee meeting. Lastly, we conduct informal project socials during field campaigns and project meetings to allow team members to socialize, interact, and build more cohesive relationships.

Creating Opportunities for Participants from Historically Marginalized Groups in STEM. The WaDE SFA team collaborates with researchers from minority-serving institutions (MSIs) and identifies internship opportunities for students attending these institutions. The research collaborations are the result of BER Research Development Partnership Pilot investments with Central Michigan University, Georgia State University, and the University of Minnesota–Duluth.

- Central Michigan University: Natalie Griffiths continues to collaborate with Wendy Robertson and her team at Central Michigan University. This year, we loaned Wendy and her team an aquatic drone, called the AquaBOT, to advance university-supported field research activities. Wendy and her team are using AquaBOT to monitor changes in water quality parameters (e.g., electrical conductivity and nutrient loadings) along the Chippewa River and Muskegon River in central Michigan (see Fig. 14, p. 19). This collaborative effort was featured in the university’s

Fig. 14. Collaboration with Central Michigan University (CMU). WaDE SFA Theme 3 researcher Natalie Griffiths, CMU faculty, and Research Experience for Undergraduates students with the AquaBOT aquatic drone before its Chippewa River maiden voyage. [Courtesy Wendy Robertson, CMU]

Department of Earth and Atmospheric Sciences newsletter.

- Georgia State University: WaDE continues to collaborate with Sarah Ledford and Nadine Kabengi and their students Dre Presswood and Marcus Morris, all of whom attended the Environmental System Science PI Meeting. Marie Kurz hosted Dre in summer 2023 and collaborated on his master's thesis research. WaDE will host Marcus in summer 2024.
- University of Minnesota–Duluth: Cody Sheik, Salli Dymond, and Kathryn Schreiner met for additional discussions. Discussions with Salli Dymond have continued for the WaDE SFA team as we plan to collaboratively deploy soil moisture probes to assess antecedent moisture conditions in WaDE watersheds. We also hosted Kun Zhang for a seminar on March 6, 2024.
- La Salle University: Elizabeth Herndon is hosting Florence Ling, an assistant professor at La Salle University, through the Visiting Faculty Program, which supports faculty from institutions historically underrepresented in the research community.
- Florida A&M University (FAMU): Scott Brooks has been collaborating with two faculty members at FAMU, a historically black university. In the past 12 months, we provided watershed samples for use in graduate student experiments. This summer, a faculty member and several graduate students will visit ORNL for additional discussions about research and future opportunities.

In addition to collaborations, Eric Pierce was able to support the Fostering Great Minds and Great Ideas engagement tour led by Asmeret Asefaw Berhe on February 12 to 15, 2024. As part of the tour, a team of DOE staff and national laboratory researchers visited numerous MSIs in Texas, New Mexico, and Arizona, including Northern Arizona University, Arizona State University, University of Texas–El Paso, New Mexico State University, South Mountain Community College, Estrella Mountain Community College, and Coconino Community College. The tour aimed to introduce faculty and students to the broad array of collaborative and internship opportunities at DOE and the national laboratories, which is expected to result in future collaborations.

WaDE team members, Eric Pierce and Kamini Singha, contacted John Alexander, an environmental science teacher at Oak Ridge High School, to discuss how the urban intensive site might interest his students. Kamini has developed a stream-temperature focused lab for high schoolers that they will pilot over the next few years. Additionally, Elizabeth Herndon hosted a high school intern, Joshua Martinez, through ORNL's Next Generation STEM Internship Program in summer 2023. Matthew Berens developed a hands-on field exercise for high school students participating in the ORNL Science Accelerating Girls' Engagement program in summer 2023. These activities were performed with the goal of building a future STEM pipeline by increasing exposure to high school students.

Lastly, numerous team members supported undergraduate and post-graduate student internships and extended research opportunities for students from underrepresented groups in STEM.

- WaDE hosted postgraduate Ethan White from Prairie View A&M University and Kayla Summerlot from the University of Tennessee–Knoxville.
- Estefania Garcia will join the team at ORNL in August 2024 as an awardee of the Office of Science Graduate Student Research program's 2023 Solicitation 2. Her proposal on "The Role of Redox Fluctuations and Iron Oxide Colloids on Arsenic and Phosphorus Transport"

complements the BER Environmental System Science priority research area with a focus on watershed hydro-biogeochemistry and nutrient and elemental cycling. The proposal is aligned with her graduate research on the speciation and transport of heavy metals in coal fly ash under disposal settings at the Georgia Institute of Technology with supervisor Yuanzhi Tang. Estefania will collaborate with Alexander Johs in the Environmental Sciences Division at ORNL.

- Scott Brooks hosted five graduate students from New Mexico State University (NMSU), an MSI, between March and December 2023. The students were part of a collaborative effort between ORNL, NMSU, and the U.S. Geological Survey to quantify surface water–groundwater exchange in the main stem of EFPC. The students have been conducting different geophysical surveys to identify preferential flow paths and subsurface water movement.

National Laboratory Investments

ORNL is committed institutionally to the success of the WaDE SFA program. In FY24, ORNL supported one Laboratory-Directed Research and Development project and invested over $250k in equipment in support of the WaDE SFA.

Appendix A. References Cited

Appling, A.P., R.O. Hall, C.B. Yackulic, and M. Arroita. 2018. “Overcoming Equifinality: Leveraging Long Time Series for Stream Metabolism Estimation,” *Journal of Geophysical Research-Biogeosciences* **123**, 624–45. DOI:10.1002/2017jg004140.

Coon, E.T., and P. Shuai. 2022. “Watershed Workflow: A Toolset for Parameterizing Data-Intensive, Integrated Hydrologic Models,” *Environmental Modelling & Software* **157**, 105502. DOI:10.1016/j.envsoft.2022.105502.

Coon, E.T., et al., 2019. Advanced Terrestrial Simulator. DOI:10.11578/dc.20190911.1.

Hammond, G.E., P.C. Lichtner, and R.T. Mills. 2014. “Evaluating the Performance of Parallel Subsurface Simulators: An Illustrative Example with PFLOTRAN,” *Water Resources Research* **50**, 208–28. DOI:10.1002/2012wr013483.

Hatcher, Jr., R.D., P.J. Lemiszki, J.L. Foreman, R.B. Dreier, R.H. Ketelle, R.R. Lee, S.Y. Lee, D.A. Lietzke, and W.M. McMaster. 1992. “Status Report on the Geology of the Oak Ridge Reservation.” Office of Environmental Restoration and Waste Management. DOI:10.2172/6575260.

Jan, A., E.T. Coon, and S.L. Painter. 2021. “Toward More Mechanistic Representations of Biogeochemical Processes in River Networks: Implementation and Demonstration of a Multiscale Model,” *Environmental Modelling & Software* **145**, 105166. DOI:10.1016/j.envsoft.2021.105166.

Kling, H., M. Fuchs, and M. Paulin. 2012. “Runoff Conditions in the Upper Danube Basin Under an Ensemble of Climate Change Scenarios,” *Journal of Hydrology* **424–25**, 264–77. DOI:10.1016/j.jhydrol.2012.01.011.

Le, P.V.V., S.S. Rathore, and S.L. Painter. 2023. “A Multiscale Model for Solute Transport in Stream Corridors with Unsteady Flow,” *Journal of Hydrology* **622**, 129670. DOI:10.1016/j.jhydrol.2023.12967.

Molins, S., D. Svyatsky, Z. Xu, E.T. Coon, and J.D. Moulton. 2022. “A Multicomponent Reactive Transport Model for Integrated Surface-Subsurface Hydrology Problems,” *Water Resources Research* **58**, e2022WR032074. DOI:10.1029/2022WR032074.

Odum, H.T. 1956. “Primary Production in Flowing Waters,” *Limnology and Oceanography* **1**, 102–17. DOI:10.4319/ lo.1956.1.2.0102.

Rathore, S.S., E.T. Coon, and S.L. Painter. 2024. “A Stream-Aligned Mixed Polyhedral Meshing Strategy for Integrated Surface-Subsurface Hydrological Models,” *Computers & Geosciences* **188**, 105617. DOI:10.1016/j.cageo.2024.105617.

Tiegs, S.D., D.M. Costello, M.W. Isken, G. Woodward, P.B. McIntyre, M.O. Gessner, E. Chauvett, A.S. Flecker, et al. 2019. “Global Patterns and Drivers of Ecosystem Functioning in Rivers and Riparian Zones,” *Science Advances* **5**(1), eaav0486. DOI:10.1126/sciadv.aav0486.

Tiegs, S.D., J.E. Clapcott, N.A. Griffiths, and A.J. Boulton. 2013. “A Standardized Cotton-Strip Assay for Measuring Organic-Matter Decomposition in Streams,” *Ecological Indicators* **32**, 131–39. DOI:10.1016/j.ecolind.2013.03.013.

Appendix B. SFA Publications

Manuscripts Published or In Press

Buser-Young, J.Z., P.E. Garcia, M. Schrenk, P. Regier, N.D. Ward, K. Biçe, S. Brooks, E. Freeman, and C. Lønborg. 2023. "Determining the Biogeochemical Transformation of Global River Organic Matter Composition Using Molecular Signatures," *Frontiers in Water* **5**. DOI:10.3389/frwa.2023.1005792.

Du, H., X. Yin, X. Gu, D. Wang, E.M. Pierce, and B. Gu. 2023. "Dissolved Elemental Mercury [Hg (0) aq] Reactions and Purgeability in the Presence of Organic and Inorganic Particulates," *Environmental Science & Technology Letters* **10**(8), 691–97. DOI:10.1021/acs.estlett.3c00275.

Gonzalez-Duque, D., J.D. Gomez-Velez, J.P. Zarnetske, X. Chen, and T.D. Scheibe. 2024. "Sinuosity-Driven Hyporheic Exchange: Hydrodynamics and Biogeochemical Potential," *Water Resources Research* **60**, e2023WR036023. DOI:10.1029/2023WR036023.

Gonzalez-Duque, D., J.D. Gomez-Velez, M.A. Person, S. Kelley, K. Key, and D. Lucero. 2024. "Groundwater Circulation Within the Mountain Block: Combining Flow and Transport Models with Magnetotelluric Observations to Untangle Its Nested Nature," *Water Resources Research* **60**, e2023WR035906. DOI:10.1029/2023WR035906.

Herndon, E., J. Richardson, A. Carrell, E.M. Pierce, and D. Weston. 2024. "Sulfur Speciation in *Sphagnum* Peat Moss Modified by Mutualistic Interactions with Cyanobacteria," *New Phytologist* **241**(5). DOI:10.1111/nph.19476.

Herndon, E., M. Newcomer, L. Ma, and A. Shiller. 2024. In press. "Trace Elements and Their Isotopes in Streams and Rivers," In *Treatise on Geochemistry Volume 3*. Invited and peer-reviewed.

Ikard, S.J., K.C. Carroll, D.F. Rucker, R.F. Adams, and S.C. Brooks. 2023. "Geoelectric Survey of Surface-Water and Groundwater Exchange in East Fork Poplar Creek, Oak Ridge, Tennessee," *Geophysical Research Letters* **50**(8), e022GL102616. DOI:10.1029/2022GL102616.

Johs, A., S. Qian, L. Coates, B.H. Davison, J. Elkins, X. Gu, J. Morrell-Falvey, H. O'Neill, J.M. Warren, E.M. Pierce, and K. Herwig. 2024. "New Opportunities for Neutrons in Environmental and Biological Sciences," *Frontiers of Environmental Science & Engineering* **18**(7), 92. DOI:10.1007/s11783-024-1852-z.

Kim, Y.G., S.Y. Kwon, S.J. Washburn, S.C. Brooks, J.W. Yoon, and L. Besnard. 2024. "Reconsidering Mercury Sources and Exposure Pathways to Bivalves: Insights from Mercury Stable Isotopes," *Water Research* **248**, 120843. DOI:10.1016/j.watres.2023.120843.

Kurz, M.J., and J.L.A. Knapp. 2023. "Using Diel Solute Signals to Assess Ecohydrological Processing in Lotic Systems." In *Ecohydrological Interfaces*. Eds. Krause, S., D.M. Hannah, and N.B. Grimm. John Wiley & Sons Ltd.

Liang, X., H. Zhong, A. Johs, P. Lei, J. Zhang, N. Tas, L. Zhang, L. Zhao, N. Zhu, X. Yin, L. Wang, E.Y. Zeng, Y. Gao, J. Zhao, D.A. Pelletier, E.M. Pierce, and B. Gu. 2023. "Light-Independent Phytoplankton Degradation and Detoxification of Methylmercury in Water," *Nature Water* **1**, 705–15. DOI:10.1038/s44221-023-00117-1.

Montgomery, A., E. Herndon, C. Sims, and S. Jagadamma. 2023. "Manganese Sources and Rates Impact Plant Mn Concentrations and Soil Mn Fractions," *Soil Science Society of America Journal* **87**(5), 1120–35. DOI:10.1002/saj2.20570.

Perez, G., J.D. Gomez-Velez, and S.B. Grant. 2024. "The Sanitary Sewer Unit Hydrograph Model: A Comprehensive Tool for Wastewater Flow Modeling and Inflow-Infiltration Simulations," *Water Research* **249**, 120997. DOI:10.1016/j.watres.2023.120997.

Perez, G., J.D. Gomez-Velez, X. Chen, and T. Scheibe. 2023. "The Directional Unit Hydrograph Model: Connecting Streamflow Response to Storm Dynamics," *Journal of Hydrology* **627**, 130422. DOI:10.1016/j.jhydrol.2023.130422.

Rathore, S.S., A.S. Ward, and S.L. Painter. 2023. "Numerical Evaluation of Photosensitive Tracers as a Strategy for Separating Surface and Subsurface Transient Storage in Streams," *Journal of Hydrology* **624**, 129931. DOI:10.1016/j.jhydrol.2023.129931.

Salazar, J.F., R.D. Molina, J.I. Zuluaga, and J.D. Gomez-Velez. 2024. In press. "Wetting and Drying Trends in the Land-Atmosphere Reservoir of Large Basins Around the World," *Hydrology and Earth System Sciences*. DOI:10.5194/hess-2023-172.

Tang, W., X. Bai, Y. Zhou, C. Sonne, M. Wu, S.S. Lam, H. Hintelmann, C.P.J. Mitchell, A. Johs, B. Gu, L. Nunes, C. Liu, N. Feng, S. Yang, J. Rinklebe, Y. Lin, L. Chen, Y. Zhang, Y. Yang, J. Wang, S. Li, Q. Wu, Y.S. Ok, D. Xu, H. Li, X.X. Zhang, H. Ren, G. Jiang, Z. Chai, J. Zhao, and Y. Gao. 2024. "A Hidden Demethylation Pathway Removes Mercury from Rice Plants and Mitigates Mercury Flux to Food Chains," *Nature Food* **5**, 72–82. DOI:10.1038/s43016-023-00910-x.

Wang, Y.L., K. Ikuma, S.C. Brooks, M.S. Varonka, and A. Deonarine. 2024. "Microbial and Geochemical Drivers for Mercury Methylation in Aquatic Sediments: Importance of Non-Hg Methylators," *Environmental Pollution* **346**(4), 123573. DOI:10.1016/j.envpol.2024.123573.

Manuscripts Submitted or In Review

Bhide, S.V., S.B. Grant, S.S. Kaushal, K. McGuire, J.D. Gomez-Velez, E.R. Hotchkiss, M.A. Rippy, P. Vikesland, S. Saksena, T. Schenk, S. Curtis, J. Webber, J. Jastram, and A. Sekellick. In review. "Stream Water Age Drives Patterns of Inland Freshwater Salinization," *Science Advances*.

Danczak, R.E., A.E. Goldman, M. Borton, R.K. Chu, J.G. Toyoda, V.A. Garayburu-Caruso, E.B. Graham, J.W. Morad, L. Renteria, J.R. Wells, S. Arnon, S. Brooks, E. Bar-Zeev, M. Jones, N. Jones, J. Lewandowski, C. Meile, B.M. Muller, J. Schalles, H. Schulz, A. Ward, and J.C. Stegen. Submitted. "Meta-Metabolome Ecology Reveals That Geochemical Conditions and Microbial Functional Potential Are Linked to DOM Development Across Seven Rivers," *Science of the Total Environment*.

Jamil, A., D.F. Rucker, D. Lu, H. Cao, S. Brooks, and K.C. Carroll. In revision. "Comparison of Machine Learning and Electrical Resistivity Arrays to Inverse Modeling for Locating and Characterizing Subsurface Targets," *Journal of Applied Geophysics*.

Le, P.V.V., S.S. Rathore, E.T. Coon, A. Ward, R. Haggerty, and S.L. Painter. In review. "Hydrologic Connectivity and Solute Transport in a Mountain Stream: Insights from a Long-Term Tracer Test and Multiscale Transport Modeling Informed by Machine Learning," *Journal of Hydrology*.

Li, H., B. Atkins, S. Williams, H. Yin, B. Reinhart, and E. Herndon. In review. "Sorption and Oxidative Degradation of Small Organic Molecules on Mn-Oxides—Effects of pH and Mineral Structures," *Environmental Science & Technology.*

Stegen, J., et al. In review. "Reviews and Syntheses: Variable Inundation Across Earth's Terrestrial Ecosystems," *EGUsphere.*

Wu, L., J.D. Gomez-Velez, L. Li, and K.C. Carroll. Submitted. "The Fragility of Bedform-Induced Hyporheic Zones," *Water Resources Research*.

Zheng, K., K.W. Rush, S.S. Date, A. Johs, J.M. Parks, A.S. Fleischhacker, M.J. Abernathy, R. Sarangi, and S.W. Ragsdale. In review. "*S*-Adenosyl-*L*-Methionine Is the Unexpected Methyl Donor for the Methylation of Mercury by the Membrane-Associated HgcAB Complex," *Proceedings of the National Academy of Sciences USA*.

Data Product Releases

Brooks, S.C., and K.A. Lowe. 2023. [Data Set] East Fork Poplar Creek Discharge at Kilometer 5.4 Water Year 2022. ORNL Mercury Science Focus Area (SFA) Data Collection, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, USA. DOI:10.12769/2203245. https://msfa.ornl.gov/data/pages/MCI556.html

Brooks, S.C., and K.A. Lowe. 2023. [Data Set] East Fork Poplar Creek Sonde Data at Kilometer 5.4 Water Year 2022. ORNL Mercury Science Focus Area (SFA) Data Collection, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, USA. DOI:10.12769/2203246. https://msfa.ornl.gov/data/pages/MCI557.html

Brooks, S.C. and K.A. Lowe. 2023. [Data Set] East Fork Poplar Creek Discharge at Kilometer 16.2 Water Year 2022. ORNL Mercury Science Focus Area (SFA) Data Collection, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, USA. DOI:10.12769/2203247. https://msfa.ornl.gov/data/pages/MCI558.html

Brooks, S.C. and K.A. Lowe. 2023. [Data Set] East Fork Poplar Creek Sonde Data at Kilometer 16.2 Water Year 2022. ORNL Mercury Science Focus Area (SFA) Data Collection, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, USA. DOI:10.12769/2203248. https://msfa.ornl.gov/data/pages/MCI559.html

Appendix C. Presentations and Conferences

Abernathy, M.J., A. Johs, A.A. DiSpirito, J.D. Semrau, E.M. Pierce, and R. Sarangi. 2023. "Methanobactin SB2: A Multipurpose Chalkophore for Hazardous Metal Binding," *ACS Fall Meeting*. San Francisco, Calif., August 13–17, 2023.

Abernathy, M.J., A. Johs, A.A. DiSpirito, J.D. Semrau, E.M. Pierce, G.N. George, and R. Sarangi. 2024. "Metal Sequestration by Extracellular Peptides," *V.M. Goldschmidt Conference*. Chicago, Ill., August 18–23, 2024.

Adebayo, M.B., and K. Singha. 2024. "A Hydrogeophysical Framework to Access the Controls of Stream Intermittency in a Mid-Order Watershed," *International Meeting for Applied Geoscience & Energy*, Society of Exploration Geophysicists.

Berens, M.J., A. Johs, X. Gu, M. Kurz, N.A. Griffiths, S.C. Brooks, K. Lowe, E.M. Pierce, and E. Herndon. 2024. "Landscape Controls on Flow Patterns and Solute Dynamics in Non-Perennial Headwater Tributaries," *WaDE SFA Annual All-Hands Meeting*. Oak Ridge, Tenn. Poster.

Brooks, S.C., E.R. Hotchkiss, K. Lowe, X. Yin, and M. Podar. 2024. "Watershed Dynamics and Evolution Science Focus Area Theme 2: Stream Corridor Processes," *Environmental System Science Principal Investigator (PI) Meeting*. Reston, Va., April 16–17 2024.

Dwivedi, D., C.I. Steefel, B. Arora, J.F. Banfield, J. Bargar, M. Boyanov, S.C. Brooks, X. Chen, S. Hubbard, D.I. Kaplan, K.M. Kemner, P.S. Nico, E.J. O'Loughlin, E.M. Pierce, S.L. Painter, T.D. Scheibe, H.M. Wainwright, K. Hurst Williams, and M. Zavarin. 2023. "From Legacy Contamination to Watershed Systems Science: A Review of Scientific Insights and Technologies Developed Through DOE-Supported Research in Water and Energy Security," *American Geophysical Union Fall Meeting*. San Francisco, Calif., December 11–15, 2023.

Griffiths, N.A., E. Pierce, M. Kurz, E. Herndon, S. Brooks, A. Johs, S. Painter, J. Gomez-Velez, S. Rathore, M. Podar, M. Cregger, and WaDE SFA collaborators. "Understanding the Role of Heterogeneous Land Cover and Hydrologic Regimes on Stream and Watershed Hydrobiogeochemical Function: A Research Overview," *Society for Freshwater Science, Southeast USA Chapter Conference*. Columbus, Ga., November 2023. Poster presentation.

Griffiths, N.A., E. Pierce, M. Kurz, E. Herndon, S. Brooks, A. Johs, S. Painter, J. Gomez-Velez, S. Rathore, M. Podar, M. Cregger, and WaDE SFA collaborators. "Understanding the Role of Heterogeneous Land Cover and Hydrologic Regimes on Stream and Watershed Hydrobiogeochemical Function: A Research Overview," *Symposium on Urban Stream Ecology*. Brisbane, Australia, May 2023. Poster presentation.

Gu, X., H. Kim, and S. Brantley. 2023. "Fracturing, Weathering and Subsurface Particle Transport at Two Critical Zone Observatories," *American Geophysical Union Fall Meeting*. San Francisco, Calif., December 11–15, 2023.

Gu, X., M.J. Berens, A. Johs, E. Herndon, S.C. Brooks, N. Griffiths, M. Kurz, K. Lowe, X. Yin, D. Lu, and E. Pierce. 2023. "Differential Effects of Chemical Weathering, Industrialization, and Urbanization on Stream Water Chemistry in Contrasting Watersheds at Oak Ridge, Tennessee, USA," *American Geophysical Union Fall Meeting*. San Francisco, Calif., December 11–15, 2023.

Herndon, E., K. Bidas, H. Li, F. Santos, and B. Sulman. 2023. "The Roles of Manganese in Stabilizing and Destabilizing Soil Organic Matter," *V.M. Goldschmidt Conference*. Lyon, France. Invited keynote.

Jamil, A., D. Lu, D.F. Rucker, S.C. Brooks, and K.C. Carroll. 2024. "Integrating Machine Learning in Electrical Resistivity Inversion for Subsurface Characterization and Bedrock Mapping," *36th Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP).* Tucson, Ariz., March 24–28, 2024.

Jamil, A., D. Rucker, K. Carroll, D. Lu, and S. Brooks. 2024. "Machine Learning Surrogate Model Development for Electrical Resistivity Inversion and Bedrock Mapping," *Waste Management Symposia*. Phoenix, Ariz., March 10–14, 2024.

Kurz, M.J., E. Herndon, A. Johs, S.C. Brooks, N.A. Griffiths, S. Painter, E.M. Pierce, and WaDE SFA Team. 2023. "Understanding the Role of Heterogeneous Land Cover and Hydrologic Regimes on Stream and Watershed Hydro-Biogeochemical Function," *Gordon Research Conference on Catchment Science: Interactions of Hydrology, Biology and Geochemistry*. Andover, N.H.

Kurz, M.J., J.D. Gomez-Velez, D. Lu, N. Griffiths, S.C. Brooks, A.S. Ward, M.J. Cohen, K.A. Lowe, X. Gu, and E.M. Pierce. 2023. "Developing and Evaluating a Watershed Classification Approach to Support Transferability of Watershed Process Understanding," *American Geophysical Union Fall Meeting*. San Francisco, Calif., December 11–15, 2023.

Kurz, M.J., N. Griffiths, D. Lu, M.J. Cohen, L. Zeglin, A.S. Ward, and J.D. Gomez-Velez. 2024. "Watershed Dynamics and Evolution SFA Theme 3: Organizational Controls on Stream Function Within and Across Mid-Order Watersheds with Heterogeneous Land Cover," *Environmental System Science Principal Investigator (PI) Meeting*. Reston, Va., April 16–17, 2024.

Surendran, S., S. Brooks, T. Mathews, C. DeRolph, and A. Nandialath. 2023. "Empirical Investigation of Methylmercury Formation in the Aquatic Ecosystem: Why Do Physical and Chemical Factors Matter?" *American Geophysical Union Fall Meeting*. San Francisco, Calif., December 11–15, 2023.

Ogbughalu, O.T., A.A. Carrell, S.C. Brooks, B. Kristy, D.M. Klingeman, and M.A. Cregger. 2023. "Watershed Urbanization Stimulates Unique Variations in Structural Responses Across Kingdoms and Alters Cross-Kingdom Association Networks," *ASM Microbe 2023*. Houston, Texas, June 15–19, 2023

Painter, S.L., E.T. Coon, A. Jan Khattak, S. Rathore, P. Le, R. Garimella, and D. Svyatsky. 2024. "Challenges and Progress in Multiscale Modeling of Watershed Systems," *Scale Bridging Meeting and Workshop*. Los Alamos, N.M., April 22–26, 2024. (Invited).

Painter, S.L., E.T. Coon, S. Bhanja, J. Gomez-Velez, P.V.V. Le, and S. Rathore. 2023. "High-Resolution and Multiscale Process-Based Modeling of Watershed Hydrology and Reactive Transport with Amanzi-ATS," *Gordon Research Conference on Catchment Science*. Andover, N.H., June 18-23, 2023.

Painter, S.L., J. Gomez-Velez, and S. Rathore. 2023. "High-Resolution and Multiscale Process-Based Modeling of Watershed Hydrology and Reactive Transport with Amanzi-ATS," *American Geophysical Union Fall Meeting*. San Francisco, Calif., December 11–15, 2023.

Pierce, E.M., M. Kurz, E. Herndon, A. Johs, S. Brooks, N.A. Griffiths, S. Painter, S. Rathore, J. Gomez-Velez, X. Gu, D. Lu, K. Singha, H. Barnard, E.R. Hotchkiss, M. Cohen, L. Zeglin, and A. Ward. 2024. "Watershed Dynamics and Evolution Science Focus Area: Overview," *Environmental System Science Principal Investigator (PI) Meeting*. Reston, Va, April 16–17, 2024.

Roberts, D., J. Brisendine, K. Freeman, A. Wolher, S.G. Thomas, C. Utzman, and L. Zeglin. 2024. "Aridity Predicts Stream Microbial Community Composition and Function Better than Land Use Across a Broad Spatial Gradient," *WaDE SFA Annual All-Hands Meeting*. Oak Ridge, Tenn.

Appendix D. Acronyms and Abbreviations

AGU	American Geophysical Union
ATS	Advanced Terrestrial Simulator
BER	Biological and Environmental Research program
C	carbon
CMU	Central Michigan University
COMPASS-FME	Coastal Observations, Mechanisms, and Predictions Across Systems and Scales–Field, Measurements, and Experiments
DIC	dissolved inorganic carbon
DO	dissolved oxygen
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
DTS	distributed temperature sensor
EFPC	East Fork Poplar Creek
EMI	electromagnetic induction
ER	ecosystem respiration
ERT	electrical resistivity tomography
ESA	Ecological Society of America
FAMU	Florida A&M University
FY	fiscal year
GPP	gross primary production
IP	induced polarization
KGE	Kling-Gupta efficiency
LULC	land use and land cover
mKGE	modified Kling-Gupta efficiency
MSI	minority-serving institution
N	nitrogen
NMSU	New Mexico State University
ORNL	Oak Ridge National Laboratory
PI	principal investigator
S	sulfur
SFA	science focus area
SP-ICP-TOF-MS	single-particle inductively coupled plasma time-of-flight mass spectrometry
STEM	science, technology, engineering, mathematics
STIC	stream temperature, intermittency, and conductivity
WaDE	Watershed Dynamics and Evolution
XAS	X-ray absorption spectroscopy