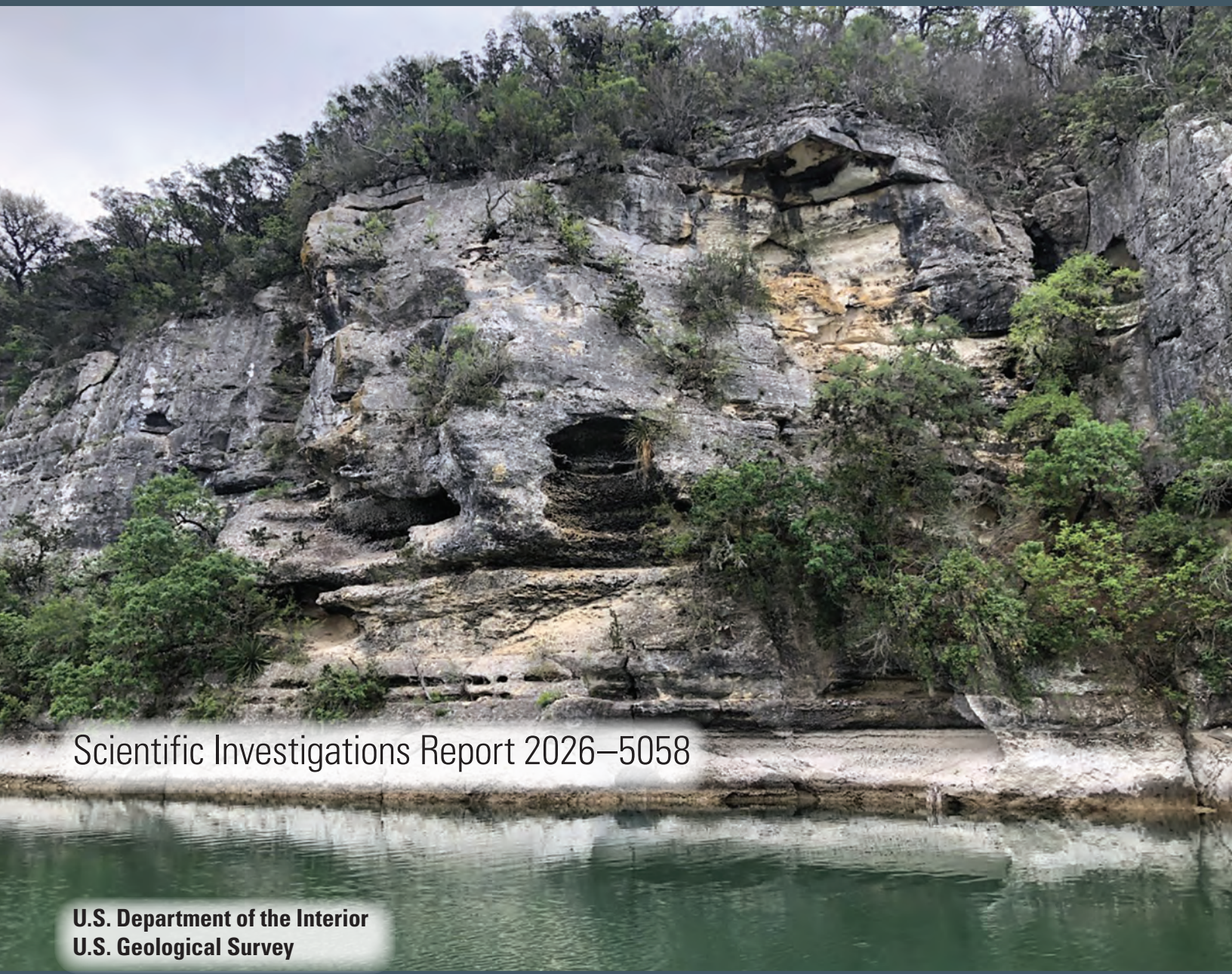
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Continuous Monitoring and Temporal Variability of Fluorescence of Dissolved Organic Matter in Karst Groundwater of the Edwards Aquifer, South-Central Texas, 2019–24



Scientific Investigations Report 2026–5058

U.S. Department of the Interior
U.S. Geological Survey

Front cover. Exposed porous Edwards aquifer limestone and underlying Trinity aquifer limestone at Medina Lake near San Antonio, Texas. Photograph by Allan Clark, U.S. Geological Survey.

Back cover. The Frio River at Concan, Tex.: a major source of water to the Edwards aquifer. Photograph by Lisa Ashmore, U.S. Geological Survey.

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Area	
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
liter (L)	0.2642	gallon (gal)
	Flow rate	
meter per day (m/d)	3.281	foot per day (ft/d)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$°F = (1.8 \times °C) + 32$.

Datums

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29) or the North American Vertical Datum of 1988 (NAVD 88).

Altitude, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Specific conductance is in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

DO	dissolved oxygen
DOC	dissolved organic carbon
DOM	dissolved organic matter
fDOM	fluorescence of dissolved organic matter
FNU	formazin nephelometric units
GOES	Geostationary Operational Environmental Satellite
µg/L as QSE	micrograms per liter as quinine sulfate equivalents
µm	micrometer
mL	milliliter
IFE	inner-filter effect
N	normal
NWQL	National Water Quality Laboratory
NWIS	National Water Information System
OMRL	Organic Matter Research Laboratory
SC	specific conductance
USGS	U.S. Geological Survey
WLA	water-level altitude

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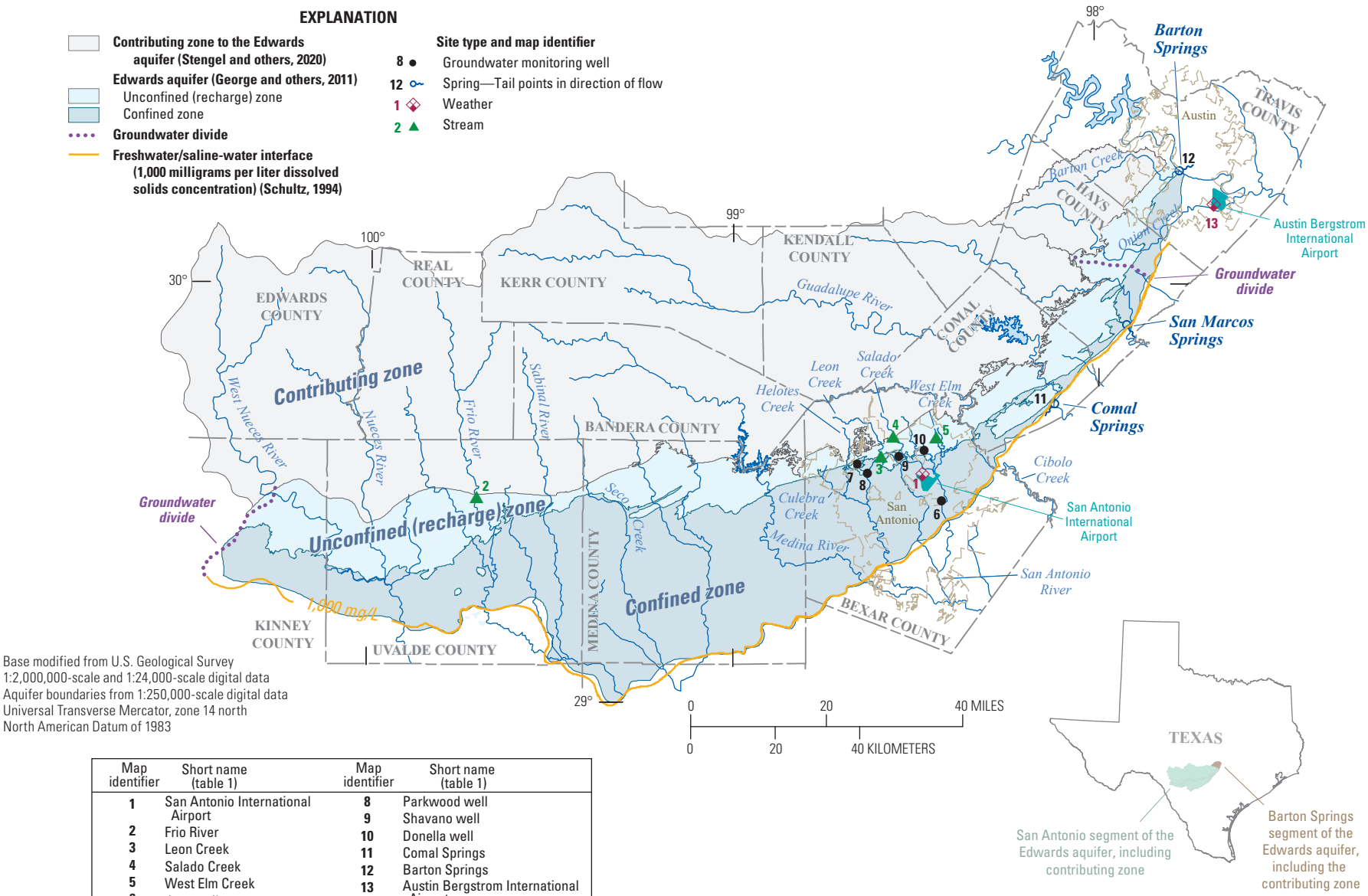
Abstract

Widespread urbanization on the Edwards aquifer recharge zone in south-central Texas has prompted the development of new approaches and tools for evaluating the current and future status of water quality in the San Antonio and Barton Springs segments of the Edwards aquifer. The U.S. Geological Survey, in cooperation with the San Antonio Water System and the City of Austin, applied continuous monitoring of fluorescence of dissolved organic matter (fDOM) to characterize the sources and transport of dissolved organic matter and associated constituents in the Edwards aquifer. Continuous fDOM time-series data were adjusted using empirically derived temperature, turbidity, and inner-filter-effect correction factors prior to analysis and interpretation. Fully corrected fDOM time-series data from the study sites were evaluated for short- and long-term temporal variability in fDOM in the context of the hydrologic and climatic conditions that occurred during the 5-year study period to understand vulnerability of the aquifer to potential contaminants in recharge. Study results indicate that fDOM is an effective proxy for dissolved organic carbon that, in turn, is indicative of the influx of recent surface water and associated contaminants, and thus, aquifer vulnerability to those contaminants. Although other continuously monitored water-quality parameters provide insights into changes in water quality in response to varying hydrologic conditions, the quantitative relation between fDOM and dissolved organic carbon directly indicates the timing and magnitude of pulses of organic constituents derived from the land surface, whereas other water-quality parameters do not.

Introduction

The San Antonio segment of the Edwards aquifer (fig. 1) is a designated sole-source aquifer that is the principal water supply for approximately 1.7 million people in and around San Antonio in south-central Texas (Tremallo and others, 2015; Greater Edwards Aquifer Alliance, 2025; U.S. Environmental Protection Agency, 2026). The Barton Springs segment of the Edwards aquifer supplies water to approximately 50,000 residents in Austin, Tex. (Greater Edwards Aquifer Alliance, 2025). Widespread urbanization on the Edwards aquifer, especially in the unconfined (recharge) zone (Musgrove and others, 2016) may affect the current and future status of groundwater quality in both segments of the Edwards aquifer (fig. 1). These segments are separated by a groundwater divide that bisects Hays County. The recharge zone of the San Antonio segment covers about 3,160 square kilometers, and the recharge zone of the Barton Springs segment covers about 400 square kilometers. In both aquifer segments, most recharge to the aquifer is from losing streams that drain the contributing zone and cross the unconfined (recharge) zone (Slade and others, 1986; Maclay and Land, 1988; Thorkildsen and McElhaney, 1992). Both aquifer segments are culturally important and drive local economies by providing recreational opportunities at springs and spring-fed rivers (Edwards Aquifer Authority, 2017). Furthermore, springs and groundwater ecosystems provide habitat for threatened and endangered endemic species (Edwards Aquifer Authority, 2017).

The rocks that host the San Antonio and Barton Springs segments of the Edwards aquifer (hereinafter referred to collectively as the “Edwards aquifer”) are primarily composed of faulted limestone and are therefore subject to dissolution and the formation of karst features that can rapidly transmit large amounts of water (Rose, 1972; White, 1988). Flow paths within karst aquifers can be further characterized along a spectrum of diffuse- versus conduit-dominated flow, where diffuse flow refers to flow within the matrix pore space and micro-joints or fractures of the aquifer bedrock, and conduit flow refers to flow through solution-widened joints, fractures, and conduits (Wong and others, 2012). Groundwater recharge occurs primarily in the unconfined (recharge) zone (fig. 1), where intermittent flows in losing streams and recharge features provide rapid transport of surface water into the aquifer (Puente, 1978; Maclay and Land, 1988; Barker and Ardis, 1996; Wong and others, 2012). The karst setting makes



Map identifier	Short name (table 1)	Map identifier	Short name (table 1)
1	San Antonio International Airport	8	Parkwood well
2	Frio River	9	Shavano well
3	Leon Creek	10	Donella well
4	Salado Creek	11	Comal Springs
5	West Elm Creek	12	Barton Springs
6	J–17 well	13	Austin Bergstrom International Airport
7	Western Oak well		

Figure 1. Hydrogeologic setting and study site locations in the San Antonio and Barton Springs segments of the Edwards aquifer, south-central Texas.

the Edwards aquifer particularly vulnerable to contamination from the land surface, and factors such as land cover, aquifer hydrogeology, and changes in hydrologic conditions affect aquifer recharge and vulnerability (Opsahl and others, 2018). Land-cover changes are of particular interest, given ongoing development on the unconfined (recharge) zone (Sharp, 2019). Previous studies of groundwater in the Edwards aquifer have documented the presence of numerous contaminants, including volatile organic compounds, nutrients, bacteria, pesticides, a variety of wastewater-derived compounds, and pharmaceuticals, which are commonly associated with land-surface processes and urban stormwater runoff (Mahler and others, 2006, 2011a, b; Mahler and Massei, 2007; Musgrove and others, 2010, 2011, 2016; Opsahl and others, 2018, 2020; Mahler and Musgrove, 2019; Opsahl and Musgrove, 2023). These studies are traditionally based on intensive synoptic groundwater and surface-water sampling efforts and thus do not capture the full temporal variability of groundwater quality in the Edwards aquifer.

Continuous monitoring technologies show promise for improved understanding of the timing and variability of water-quality responses, especially during and after periods of groundwater recharge, when rapid changes in water quality are most likely to occur (Mahler and others, 2006; Opsahl and others, 2018, 2020). Continuous monitoring of water-quality parameters at 15-minute or hourly intervals has been implemented at selected groundwater wells and springs in the Edwards aquifer (U.S. Geological Survey, 2025). Continuous specific conductance (SC) in particular can act as a tracer of recently infiltrated surface water, which typically has relatively low SC compared to groundwater in the Edwards aquifer (Opsahl and others, 2018). Continuous nitrate plus nitrite (hereinafter referred to as "nitrate" because nitrite is typically at trace levels in groundwater and surface water [Pellerin and others, 2013; Opsahl and others, 2018]) has proven to be a tracer of nitrate and total nitrogen in oxic groundwater of the Edwards aquifer (Opsahl and others, 2018), where nitrate is typically the dominant form of nitrogen. Most recently, sensors to continuously monitor fluorescence of dissolved organic matter (fDOM) have been developed to trace the movement of dissolved organic matter (DOM) (Downing and others, 2012; Booth and others, 2023; Akie and others, 2024). DOM represents all dissolved organic compounds (containing carbon, oxygen, nitrogen, and other elements) in water, whereas dissolved organic carbon (DOC) represents only the carbon component of dissolved organic compounds, which can be measured (Wood and others, 2011). Only a small portion of the DOM in groundwater fluoresces; however, where a strong correlation between fDOM values and DOC concentrations exists, continuous fDOM can be applied as a proxy for DOC concentration and transport. Understanding continuous fDOM in groundwater provides insights into organic contaminant transport and microbial and geochemical processes (Shen and others, 2015). In 2019, the U.S. Geological Survey (USGS), in cooperation with the San Antonio Water System and the City of Austin, began continuous monitoring of fDOM and related water-quality parameters at selected sites in or near the Edwards aquifer to provide the data needed to better understand temporal changes in water quality that occur within the aquifer over short- and long-term time scales.

Purpose and Scope

This report describes results of a study of fDOM in groundwater of the Edwards aquifer in south-central Texas during a 5-year study period from October 2019 to September 2024. The objectives were (1) to present methods for developing fully corrected time series of fDOM continuous monitoring data in karst groundwater characteristic of the Edwards aquifer, and (2) to assess fDOM temporal variability in unconfined groundwater monitoring wells and USGS 08155500 Barton Springs at Austin, Tex. (hereinafter referred to as "Barton Springs" [fig. 1; table 1]). fDOM was used as a proxy for DOC to better understand surface-water/groundwater interactions and their associated implications for karst aquifer vulnerability to surface-derived, anthropogenic contaminants. Fully corrected fDOM time-series data from the study sites were evaluated for short- and long-term temporal variability in fDOM in the context of the hydrologic and climatic conditions that occurred during the 5-year study period.

Table 1. Description of sites at which hydrologic or water-quality data were collected, south-central Texas, 2019–24.

[fig., figure; ft, foot; dd, degrees; mm, minutes; ss, seconds; GHCND, Global Historical Climatology Network Daily; TX., Texas; US, United States; NA, not applicable; USGS, U.S. Geological Survey; Rv, River; Ck, Creek; IH, Interstate Highway; nr, near; Rd, road; W, West; EAA, Edwards Aquifer Authority; NGVD 29, National Geodetic Vertical Datum of 1929; NAVD 88, North American Vertical Datum of 1988; Spgs, springs]

Map identifier (fig. 1)	Site number	Site name	Short name	Site type
1	GHCND USW00012921[1]	San Antonio International Airport, TX US	San Antonio International Airport	Weather
2	USGS 08195000[2]	Frio Rv at Concan, TX	Frio River	Stream
3	USGS 08180990[2]	Leon Ck at IH 10 and Loop 1604 nr San Antonio, TX	Leon Creek	Stream
4	USGS 08178585[2]	Salado Ck at Wilderness Rd, San Antonio, TX	Salado Creek	Stream
5	USGS 08178638[2]	W Elm Ck at Encino Rio at San Antonio, TX	West Elm Creek	Stream
6	EAA 36837203[3]	Bexar County index well (J-17)	J-17 well	Groundwater monitoring well[4]
7	USGS 293405098394201[2]	AY-68-27-609 (Western Oak)	Western Oak well	Groundwater monitoring well[5]
8	USGS 293252098380801[2]	AY-68-27-610 (Parkwood Park)	Parkwood well	Groundwater monitoring well[5]
9	USGS 293516098325501[2]	AY-68-28-211 (Shavano Park at Fawn Drive)	Shavano well	Groundwater monitoring well[5]
10	USGS 293559098284801[2]	AY-68-29-112 (Donella)	Donella well	Groundwater monitoring well[5]
11	USGS 08168710[2]	Comal Springs at New Braunfels, TX	Comal Springs	Spring
12	USGS 08155500[2]	Barton Spgs at Austin, TX	Barton Springs	Spring
13	GHCND USW00013904[6]	Austin Bergstrom International Airport, TX US	Austin Bergstrom International Airport	Weather

[1]National Oceanic and Atmospheric Administration (2025a).

[2]U.S. Geological Survey (2025).

[3]Edwards Aquifer Authority (2025).

[4]Groundwater well is completed in the confined zone of the Edwards aquifer (fig. 1).

[5]Groundwater well is completed in the unconfined (recharge) zone of the Edwards aquifer (fig. 1).

[6]National Oceanic and Atmospheric Administration (2025b).

Continuous Monitoring of fDOM

Monitoring fDOM in groundwater poses numerous challenges, including requisite corrections for instrument drift and fouling, as is the case with monitoring other continuous water-quality parameters. However, additional corrections for fDOM, including temperature, turbidity, and inner-filter effects (IFEs) are required to develop fully corrected fDOM time-series data. Temperature corrections can be derived in the laboratory using representative ambient water. Turbidity values in the Edwards aquifer are typically less than 10 formazin nephelometric units (FNU); however, relatively high turbidity values are observed occasionally, in response to recharge events, and must be accounted for by either developing correction factors, described in more detail in Booth and others (2023), or by setting thresholds for data. IFEs, defined as interferences associated with ambient DOM that cause quenching and reductions in the excitation and emission light bands, can be evaluated in the laboratory using dilution experiments (Booth and others, 2023) or by setting thresholds.

Sensor Calibration

For this study, fDOM values were measured in units of micrograms per liter as quinine sulfate equivalents (µg/L QSE) using calibrated EXO1 and EXO2 fDOM sensors (Xylem Incorporated, 2025a, b) following previously published

Table 1. Description of sites at which hydrologic or water-quality data were collected, south-central Texas, 2019–24.—Continued

[ft, foot; dd, degrees; mm, minutes; ss, seconds; GHCND, Global Historical Climatology Network Daily; TX., Texas; US, United States; NA, not applicable; USGS, U.S. Geological Survey; Rv, River; Ck, Creek; IH, Interstate Highway; nr, near; Rd, road; W, West; EAA, Edwards Aquifer Authority; NGVD 29, National Geodetic Vertical Datum of 1929; NAVD 88, North American Vertical Datum of 1988; Spgs, springs]

Map identifier (fig. 1)	Well depth (ft below land surface)	Land surface altitude (ft above vertical datum)	Vertical datum	Latitude (north, dd mm ss)	Longitude (west, dd mm ss)
1	NA	NA	NA	29°32′40″	98°29′02″
2	NA	NA	NA	29°29′18″	99°42′16″
3	NA	NA	NA	29°35′35″	98°35′57″
4	NA	NA	NA	29°37′50″	98°33′55″
5	NA	NA	NA	29°37′46″	98°26′56″
6	874	731	NGVD 29	29°28′45″	98°25′57″
7	261	960	NAVD 88	29°34′05″	98°39′42″
8	229	896	NAVD 88	29°32′52″	98°38′08″
9	300	975	NAVD 88	29°35′16″	98°32′55″
10	260	889	NAVD 88	29°35′59″	98°28′48″
11	NA	NA	NA	29°42′21″	98°07′20″
12	NA	NA	NA	30°15′48″	97°46′16″
13	NA	NA	NA	30°10′59″	97°40′47″

techniques (Booth and others, 2023). A value of 1 µg/L as QSE is equal to the amount of fluorescence produced by a 1-µg/L solution of a quinine sulfate solution prepared in a 0.1-normal (N) sulfuric acid solution. Groundwater from the Edwards aquifer is characterized by DOC concentrations of 0.25–3.0 milligrams per liter (mg/L), which produce fDOM values less than 100 µg/L as QSE (this study). On the basis of this range of fDOM values, a two-point calibration using deionized water (0.0 µg/L as QSE) and a 100-µg/L as QSE standard was used to calibrate the fDOM sensors.

This study followed the procedures for preparation of quinine sulfate standard solutions and calibration detailed in Booth and others (2023) and Xylem Incorporated (2025c). A 1,000-mg/L stock solution was prepared by measuring 100 milligrams of quinine sulfate into a 100-milliliter (mL) volumetric flask and bringing it to volume in 0.1-N sulfuric acid. The stock solution was then stored in a 125-mL amber glass bottle at room temperature. A 100-microliter aliquot of the stock solution was pipetted into a 1,000-mL volumetric flask and brought to volume using 0.1-N sulfuric acid to make the 100-µg/L as QSE standard solution. The stock solution was checked monthly to ensure stability. Results indicate that the stock solution remained stable for at least 6 months at room temperature.

fDOM measurements are affected by water temperature, but the fDOM sensors are not temperature compensated; therefore, temperature corrections were needed during the calibration procedure. Corrections for temperature used the following equation from Watras and others (2011) as described by Booth and others (2023, p. 37):

$$fDOM_T = fDOM_m/[1+\rho\ (T_m - T_r)], \quad (1)$$

where

$fDOM_T$ is the temperature-corrected sensor signal;
$fDOM_m$ is the original measured sensor signal not corrected for temperature effects;
ρ is a sensor-specific temperature coefficient;
T_m is the measured water temperature, in degrees Celsius (°C); and
T_r is the reference temperature, 25 °C.

The values for $fDOM_m$ and T_m are measured, whereas ρ and T_r are constants. The temperature coefficient, ρ, is determined as

$$\rho = \text{slope of the linear regression of } T_m \text{ versus } fDOM_m/fDOM_m \text{ at } T_r. \quad (2)$$

The relation between fDOM values and temperature for the sensors is provided by the manufacturer (Xylem Incorporated, 2025c) using a reference temperature of 22 °C. The shifts reported by the manufacturer are 0.450 µg/L as QSE per 1 °C for a 100-µg/L as QSE standard solution. However, Booth and others (2023) recommend using a reference temperature of 25 °C, and the temperature shifts provided by the manufacturer were adjusted accordingly (table 2). During calibration with the 100-µg/L as QSE standard solution, the temperature of the standard solution was noted, and the actual standard value corresponding to that temperature (table 2) was considered the calibration standard value. Alternatively, the regression equation derived from the data in table 2

$$fDOM_T = (-0.450*T_m)+111.25, \quad (3)$$

can be used to compute the temperature-corrected standard value.

Reference sensors are fDOM sensors that are calibrated once and then used only in the laboratory to test the accuracy of freshly prepared 100-µg/L as QSE calibration solutions. The use of reference sensors is described in detail in Booth and others (2023). Briefly, during calibration checks in the laboratory or when sensors were recalibrated, the reference sensor was checked using the 100-µg/L as QSE standard solution. If temperature-corrected reference sensor values were within the calibration criterion of ±5 percent (between 95 and 105 µg/L as QSE at 25 °C using a 100-µg/L as QSE standard solution), the standard solution was used. If values were outside the calibration criterion, then the standard solution was remade and rechecked using the reference sensor. A long-term record of reference sensor checks was maintained to provide a practical measure of variability of factors that influence laboratory calibration procedures.

Correcting and Thresholding fDOM Time-Series Data

Raw fDOM time-series data collected at monitoring sites must be corrected to accurately represent fDOM values and to use fDOM as a proxy for DOC in groundwater. Data processing procedures used in this study generally followed USGS guidelines for continuous monitors (Wagner and others, 2006) and fDOM sensors (Booth and others, 2023). Spikes and other values outside of instrument specifications were removed during the initial screening of new data. Data were

Table 2. Temperature and fluorescence data for 100 micrograms per liter as quinine sulfate equivalents (µg/L as QSE) standard solution using the EXO2 fluorescence of dissolved organic matter (fDOM) sensor.

[Modified from Xylem Incorporated (2025c)]

Standard temperature (degrees Celsius)	Temperature-corrected standard fDOM value (µg/L as QSE)
8.0	107.65
9.0	107.20
10.0	106.75
11.0	106.30
12.0	105.85
13.0	105.40
14.0	104.95
15.0	104.50
16.0	104.05
17.0	103.60
18.0	103.15
19.0	102.70
20.0	102.25
21.0	101.80
22.0	101.35
23.0	100.90
24.0	100.45
25.0	100.00
26.0	99.55
27.0	99.10
28.0	98.65
29.0	98.20
30.0	97.75

then checked to determine if corrections or thresholds for (1) sensor fouling and (or) calibration drift, (2) temperature, (3) turbidity, or (4) IFEs were needed.

Fouling and Drift Correction

Fouling and drift corrections were applied by using the methods of Booth and others (2023) when the fDOM values exceeded the calibration criterion of ±1 µg/L as QSE or ±5 percent of the measured value of the 100-µg/L as QSE standard solution, whichever was greater. Additional corrections or thresholds for in situ temperature, turbidity, and IFEs were then applied, in that order.

Temperature Corrections

An equation for temperature corrections to the fDOM time-series data was empirically derived through a series of experiments using filtered groundwater samples collected from USGS 293516098325501, hereinafter referred to as the "Shavano well" (fig. 1; table 1). Groundwater from the Shavano well was assumed to be representative of groundwater and spring water from all sites in this study. Water samples were collected using a groundwater pump as part of routine sampling events at this site. Water was filtered in the field, brought back to the laboratory, and stored in the refrigerator until analysis a few days later. Samples were brought to room temperature prior to running the experiments. Each of two experiments used an EXO2 monitor equipped with a combined temperature and specific-conductance sensor and two fDOM sensors, yielding four separate time series referred to as "trials." A magnetic stir bar was placed in the calibration cup to facilitate mixing. The calibration cup (with stir bar) was rinsed three times with the Shavano well groundwater sample and then filled to the recommended level for measurements. The monitor was placed upright in a large glass beaker containing enough water to surround the outside of the calibration cup. The beaker was placed on a heating stir plate, and the heater and magnetic stir plate were turned on. fDOM values were recorded at 1.0 °C intervals between 18.0 and 26.0 °C. This temperature range bracketed typical groundwater temperatures in the monitoring wells, which are fairly constant at about 21.0–22.0 °C, and spring-water temperatures at Barton Springs, which are about 18.0–23.0 °C (U.S. Geological Survey, 2025). Initial fDOM values for the groundwater at 18 °C were about 4.7–6.9 µg/L as QSE in each of the four trials (fig. 2*A–D*). The inverse relation between temperature and fDOM was evident in each of the four trials, although the magnitude of change was small (less than 1.5 µg/L as QSE across the temperature gradient). Trials 1 and 3 had similar initial fDOM values because measurements were made with the same probe, and the same is true for trials 2 and 4. These differences may have resulted from slight differences in calibration, although they were within 2 times the calibration criterion. The purpose of these experiments was to examine changes in fDOM versus temperature and not differences between probes. Sensor-specific ρ values from the four trials were computed using equation 2 and then averaged to obtain the ρ value (−0.01922) used for the temperature correction (eq. 1) applied to the fDOM time-series data.

Turbidity Threshold

Using a turbidity threshold, rather than laboratory-derived equations, is a more practical approach for groundwater systems, where turbidity is relatively low and samples with elevated turbidity are difficult to collect because turbidity peaks are short-lived and rarely coincide with the timing of sample collection. Unfiltered and filtered groundwater samples were compared to derive a screening tool for censoring fDOM data when turbidity exceeded a predetermined threshold. Discrete groundwater samples were collected during intervals when turbidity pulses occurred in the in situ fDOM time-series data, then filtered (0.2-micrometer [µm] pore size) to remove particulate material. Filtered samples were shipped to the USGS Organic Matter Research Laboratory (OMRL) in Sacramento, California, for analysis of fluorescence and related water-quality parameters. The OMRL provided independent temperature-, turbidity-, and IFE-corrected fDOM values; these filtered (laboratory) fDOM values were compared with temperature-corrected, unfiltered (in situ) fDOM values to select an appropriate turbidity threshold for the Edwards aquifer.

The selected turbidity threshold was based on a comparison of 14 temperature-corrected unfiltered (in situ) measurements and filtered (laboratory) samples collected from the five study sites (table 3). Turbidity values ranged from 0.3 to 9.8 FNU, temperature-corrected unfiltered (in situ) fDOM values ranged from 1.9 to 47.0 µg/L as QSE, and filtered (laboratory) fDOM values ranged from 2.5 to 44.2 µg/L as QSE. A strong correlation was evident between the temperature-corrected unfiltered (in situ) and filtered (laboratory) fDOM values (fig. 3). However, most of the temperature-corrected unfiltered (laboratory) fDOM values, including those associated with the two highest turbidity values (8.3 and 9.8 FNU), were lower than the unfiltered (in situ) fDOM values (table 3). A comparison of these results indicates that there is minimal turbidity interference associated with fDOM measurements below 10.0 FNU, which is a relatively low turbidity value in comparison to values found in most streams (Anderson, 2005). A threshold of 10 FNU was selected, and corresponding fDOM data were censored from the dataset if turbidity values exceeded 10 FNU. Periods when turbidity exceeded 10 FNU were short and infrequent, and thus data losses were minimal throughout the study.

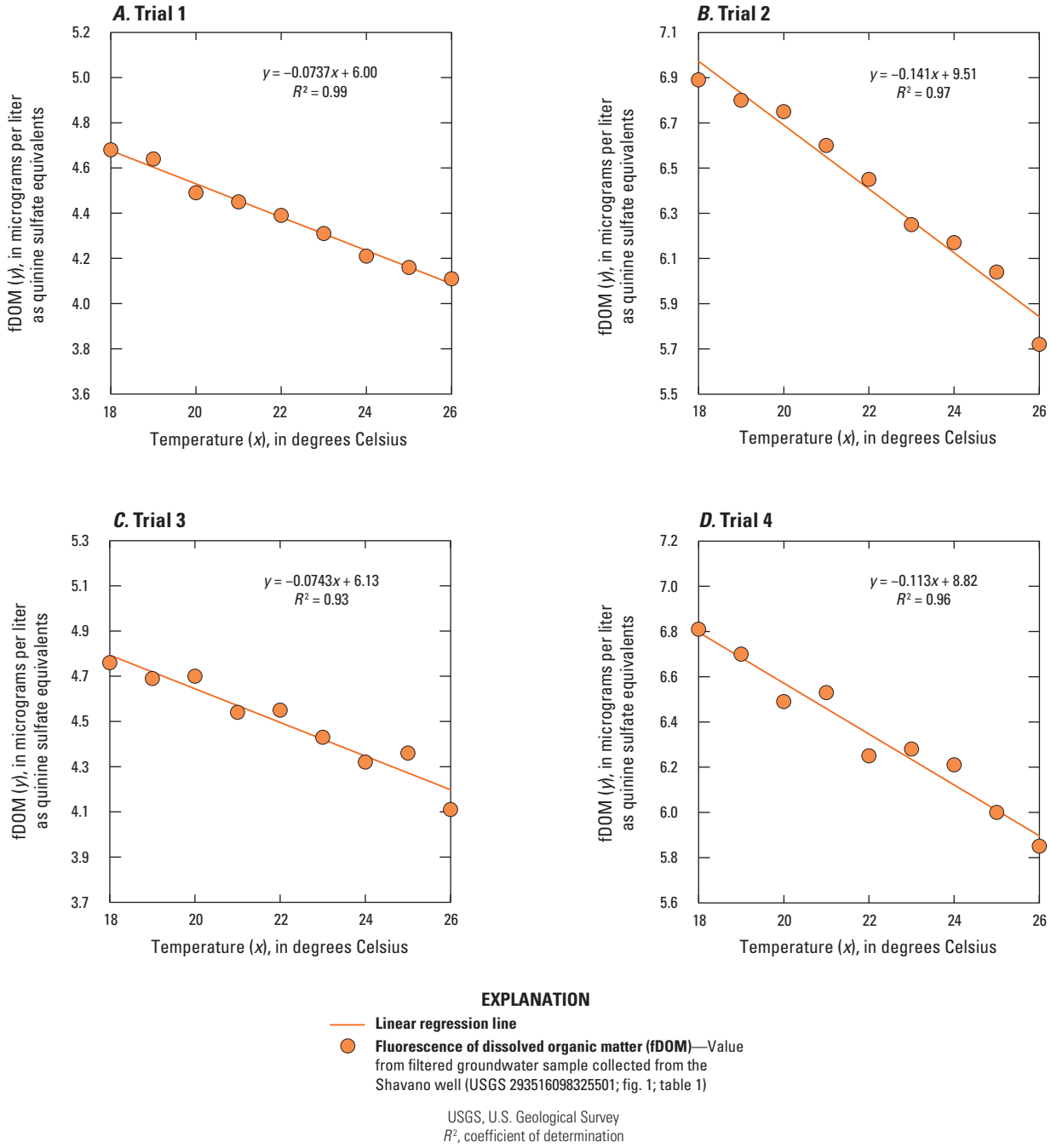


Figure 2. Fluorescence of dissolved organic matter values from filtered groundwater samples collected from the Shavano well (USGS 293516098325501) across a temperature gradient for (*A*) trial 1, (*B*) trial 2, (*C*) trial 3, and (*D*) trial 4.

Inner-Filter Effect Threshold

IFEs were evaluated in laboratory dilution experiments by sequentially diluting a sample to the point where optical interference no longer occurred during the measurements (Booth and others, 2023). Water samples were collected from recharge streams, groundwater monitoring wells, and a spring (table 4) to represent the broad range of fDOM values that could occur in the recharge zone. The fDOM values (13.1–59.8 µg/L as QSE) for groundwater samples used to evaluate IFEs were high in comparison to baseline fDOM values (0–6 µg/L as QSE; this study) typical of Edwards aquifer groundwater. Groundwater samples with higher fDOM values represent conditions when ambient DOM is higher and IFEs are more likely to occur.

For each experiment, a 1.0-liter sample was collected and filtered (0.2-µm pore size) to prevent turbidity effects that would confound the results. A calibrated EXO1 monitor was equipped with a combined temperature-conductance sensor and an fDOM sensor. An EXO1 monitor was used instead of

Table 3. Comparison of temperature-corrected unfiltered (in situ) fluorescence of dissolved organic matter (fDOM) values and filtered (laboratory) fDOM values of discrete water samples from selected groundwater monitoring wells and springs.

[Sample times shown in 24-hour format. FNU, formazin nephelometric units; OMRL, Organic Matter Research Laboratory; µg/L as QSE, micrograms per liter as quinine sulfate equivalents]

Short name	Sample date	Sample time	Turbidity, in situ (FNU)	Temperature-corrected unfiltered (in situ) fDOM values (µg/L as QSE)	Filtered (OMRL) fDOM values (µg/L as QSE)
Western Oak well	10/18/2021	1400	0.3	4.0	4.1
Western Oak well	1/12/2022	1000	0.3	2.9	4.5
Parkwood well	7/7/2021	1000	0.8	11.5	11.1
Parkwood well	10/19/2021	1100	0.3	2.2	3.3
Parkwood well	1/10/2022	1100	0.3	1.9	2.6
Shavano well	5/3/2021	1615	2.6	37.9	32.9
Shavano well	10/21/2021	1000	0.3	19.1	15.1
Shavano well	1/13/2022	1130	1.5	6.5	5.9
Donella well	9/30/2021	1000	1.3	20.1	16.3
Donella well	10/25/2021	1030	2.0	8.5	6.8
Donella well	1/11/2022	1000	0.8	3.0	2.5
Barton Springs	5/1/2021	1310	3.8	6.4	5.4
Barton Springs	5/2/2021	0915	8.3	15.1	12.6
Barton Springs	5/25/2021	1400	9.8	47.0	44.2

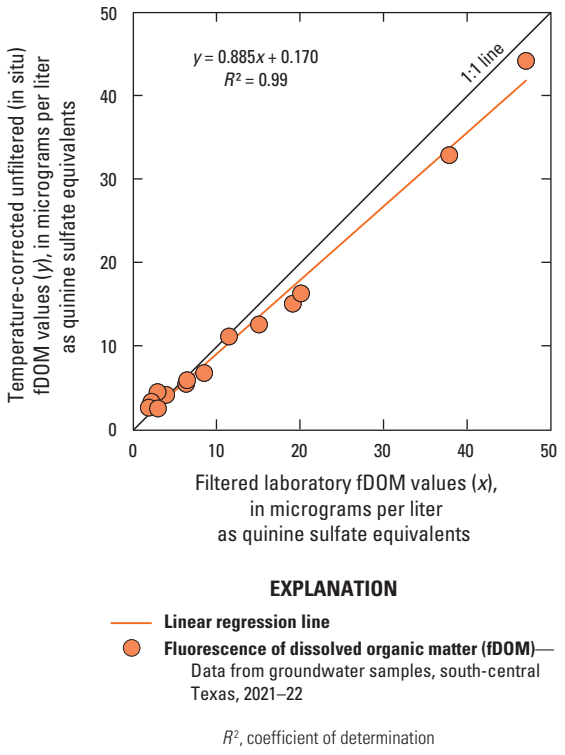


Figure 3. Comparison of unfiltered temperature-corrected (in situ) fluorescence of dissolved organic matter (fDOM) values and filtered (laboratory) fDOM values from discrete water samples collected from groundwater monitoring sites, south-central Texas, 2021–22.

the EXO2 monitor, because the EXO1 monitor requires less water in the calibration cup for measurements. Each sample was brought to room temperature; the monitor's calibration cup was rinsed three times with the sample water and then filled to the proper level for measurement. Water temperature and temperature-corrected filtered fDOM measurements were recorded, then the process was repeated for 75.0-, 50.0-, 25.0-, and 12.5-percent diluted sample aliquots. Calculated fDOM values across the dilution series were computed by using the measured 12.5-percent value (with presumably no IFEs) and then back-calculating fDOM values for the other dilutions and the undiluted sample. Calculated fDOM values should represent the actual fDOM values because there are presumably no IFEs in the 12.5-percent diluted sample on which the calculated fDOM values were based. For example, the measured temperature-corrected filtered fDOM value was 18.8 µg/L as QSE for the 12.5-percent dilution of the Frio River sample collected on June 23, 2021 (table 4), and the calculated fDOM values were 37.6, 75.2, 112.8, and 150.4 µg/L as QSE for the 25-, 50-, and 75-percent diluted samples and the undiluted sample, respectively.

Two examples of how IFE corrections were derived are shown in figure 4: a surface-water sample where an IFE correction was needed (fig. 4*A*), and a groundwater sample where an IFE correction was not needed (fig. 4*B*). In each dilution series, the calculated fDOM values were plotted against the temperature-corrected filtered fDOM values, and a second-order polynomial was fit to the data (fig. 4). A 1:1 line shows deviations in fDOM values across the dilution gradient.

Table 4. Comparison of temperature-corrected filtered fluorescence of dissolved organic matter (fDOM) values and fully corrected fDOM values based on manual dilution experiments using discrete water samples collected from streams, groundwater monitoring wells, and a spring, south-central Texas, 2021–23.

[Sample times shown in 24-hour format. µg/L as QSE, micrograms per liter as quinine sulfate equivalents]

Short name (table 1; fig. 1)	Sample date	Sample time	Temperature- corrected filtered fDOM values (µg/L as QSE)	Fully corrected fDOM values (µg/L as QSE)	Relative percent difference[1]	Calibration criterion multiplied by 2 (µg/L as QSE)[2]
			Streams			
West Elm Creek	4/30/2021	1830	93.8	98.2	5	9.8
Leon Creek	5/1/2021	0101	60.6	62.9	4	6.3
Salado Creek	5/24/2021	1912	78.8	77.2	1	7.7
Frio River	6/23/2021	0830	126.4	150.9	18	15.1
Leon Creek	7/5/2021	2130	54.9	57.6	5	5.8
			Groundwater monitoring wells			
Shavano well	5/3/2021	1615	38.9	37.9	3	3.8
Donella well	9/30/2021	1000	17.8	18.8	6	1.9
Shavano well	10/21/2021	1000	17.7	19.1	8	1.9
Shavano well	4/7/2023	1015	21.6	21.8	1	2.2
Shavano well	4/21/2023	1130	59.8	64.1	7	6.4
			Spring			
Barton Springs	5/2/2021	0915	13.1	12.8	2	1.3

[1]Relative percent difference was calculated as the absolute difference between temperature-corrected fDOM and fully corrected fDOM, divided by the average of these two values.

[2]Calibration criterion multiplied by 2 was computed as 5 percent of the fully corrected fDOM value multiplied by 2 (Booth and others, 2023).

The second-order polynomial equation was used to calculate fully corrected values using the temperature-corrected filtered fDOM values. (There should be no turbidity effects in filtered water.) The relative percent difference for the temperature-corrected filtered fDOM value of 126 µg/L as QSE and the fully corrected value of 150.9 µg/L as QSE for the stream sample from the Frio River (fig. 4*A*) was 18 percent. The difference in values (table 4) fell outside the calibration criterion times 2, the criterion recommended for applying IFE corrections (Booth and others, 2023). The relative percent difference for the temperature-corrected filtered fDOM value of 21.6 µg/L as QSE for the groundwater sample from the Shavano well (fig. 4*B*) was not substantially different from the fully corrected value of 21.8 µg/L as QSE because values were within the calibration criterion times 2. The notably larger relative percent difference for the surface-water sample in comparison to the groundwater sample is caused by the quenching of fluorescence, resulting in a large IFE for the surface-water sample.

The relative percent differences between temperature-corrected filtered fDOM and fully corrected fDOM (corrected for temperature and IFE) were 1–18 percent among all dilution experiments, with a somewhat positive bias in most instances (table 4). The small negative bias observed in some comparisons is attributed to analytical variability because fully corrected fDOM values should never be lower than temperature-corrected filtered fDOM values. To determine if fully corrected fDOM values were within an acceptable range without correction, the following calibration criterion was used: 5 percent of the temperature-corrected filtered fDOM value determined from the dilution experiments multiplied by 2 (Booth and others, 2023). In all samples except the Frio River sample, the IFE-corrected fDOM values fell within this criterion and corrections for IFE were not necessary, although they still could be applied (fig. 5, table 4). The Frio River sample had the greatest fDOM value, and an IFE correction was needed to fully correct the fDOM data.

A systematic method based on dilution experiments was used to ensure that IFEs were accounted for in the fDOM time-series data from groundwater sites. A summary of the dilution experiment fDOM comparison (fig. 5) shows a strong correlation overall but a deviation from the 1:1 mixing line for samples with greater fDOM values, about 98 µg/L as QSE and above, from two of the stream sites. Given the linearity in the fDOM comparison up to 98 µg/L as QSE and the differences between fully corrected data within the calibration criterion, the selected approach was to censor temperature-corrected time-series data from continuous fDOM monitors above 100 µg/L as QSE rather than derive an equation to correct the fDOM data. This threshold approach is practical because

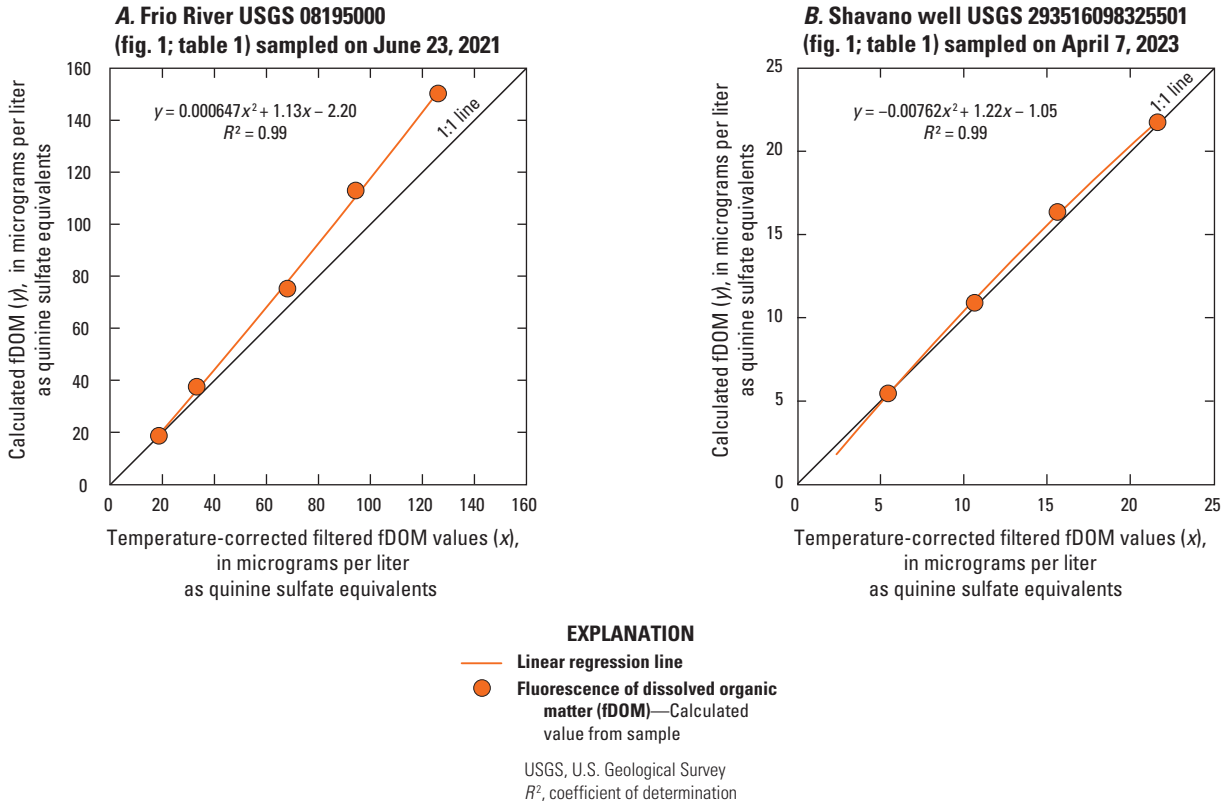


Figure 4. Comparison of temperature-corrected filtered and calculated fluorescence of dissolved organic matter values from dilution experiments using water samples collected from (*A*) the Frio River on June 23, 2021, and (*B*) the Shavano well on April 7, 2023, south-central Texas.

to date (2026), no fDOM values above 70 µg/L as QSE have been measured in groundwater from any of the groundwater monitoring wells or springs used in this study; thus, no data collected during the 5-year study period required censoring.

Field Study Design

The long-term monitoring program initiated between the San Antonio Water System and the USGS in 2012 (Opsahl and others, 2026b) includes fDOM sensors installed in October 2019 at four monitoring well locations in the unconfined recharge zone of the San Antonio segment of the Edwards aquifer (fig. 1; table 1). These wells were part of a 30-well network constructed in 1998 in cooperation with the Edwards Aquifer Authority as part of the USGS National Water-Quality Assessment (NAWQA) Program (Bush and others, 2000; Musgrove and others, 2010). The San Antonio segment monitoring program also includes stream sites (fig. 1; table 1) to characterize stormwater recharge. The City of Austin and USGS added an fDOM sensor in January 2020 to the long-term monitoring array at Barton Springs, which is the primary discharge point for the Barton Springs segment of the Edwards aquifer (fig. 1; table 1). The data-collection sites have been described in detail by Mahler and others (2006, 2011b), Opsahl and others (2018, 2020), and Musgrove and others (2019, 2023), who also documented similarities in water-quality parameters, major- and trace-element chemistry, nutrient and pesticide chemistry, and DOC concentrations among the study sites. The data-collection sites were chosen to include both urbanized and rural portions of the recharge zone and to represent a range of hydrologic responses following rainfall/recharge events.

Continuous hydrologic and water-quality data collected over the 5-year study period (October 1, 2019–September 30, 2024) included water-level altitude (WLA), spring discharge, water temperature, SC, turbidity, fDOM, and nitrate. Discrete water-quality samples were collected periodically throughout the study period and analyzed for DOC. Ancillary data included rainfall data from weather sites, WLA data from EAA 36837203 (hereinafter referred to as the "J-17 well" [fig. 1; table 1]), and spring discharge data from Comal and Barton Springs to better characterize regional hydrologic conditions that influenced the aquifer during the 5-year study period.

Continuous Water-Level Altitude Measurements

Continuous water-level data were collected from the groundwater monitoring wells (fig. 1; table 1) using methods described by Cunningham and Schalk (2011). Each well was equipped with a pressure transducer, data recorder, and

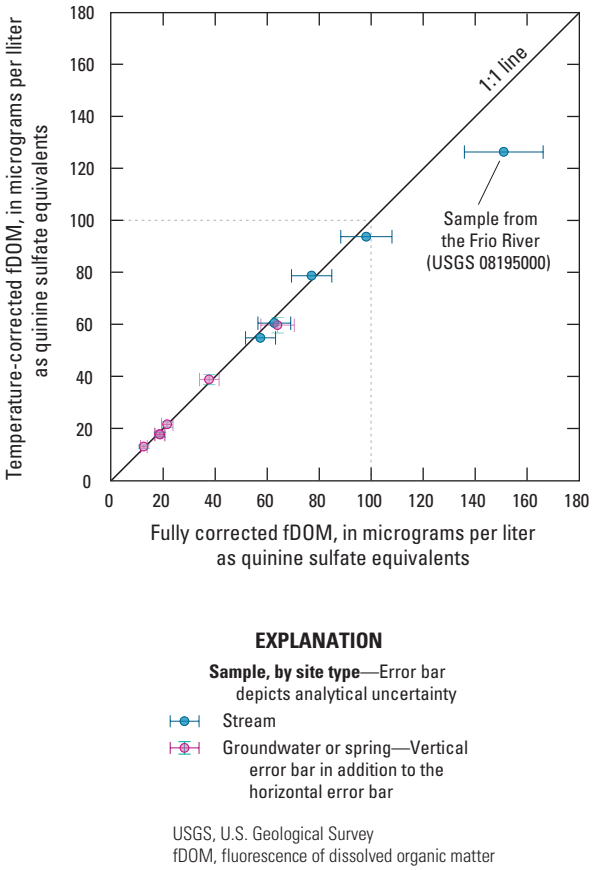


Figure 5. Comparison of temperature-corrected filtered fluorescence of dissolved organic matter (fDOM) values and fully corrected fDOM values based on manual dilution experiments using water samples collected from stormwater runoff and groundwater sites, south-central Texas, 2021–23.

Geostationary Operational Environmental Satellite (GOES) transmitter. Water-level data were recorded in feet (ft) below a known land-surface datum (table 1) at 15-minute intervals, periodically verified against a calibrated water-level tape, and corrected as described by Cunningham and Schalk (2011). The 15-minute water-level data were transmitted hourly via GOES to the USGS National Water Information System (NWIS) database (U.S. Geological Survey, 2025). The water-level data were then converted to WLA data by subtracting the water level (below land surface) from the altitude of the land-surface datum (table 1).

Continuous Water-Quality Monitoring

The groundwater monitoring wells and Barton Springs were instrumented with multiparameter EXO2 water-quality sensors (Xylem Incorporated, 2025b) to continuously measure temperature, SC, turbidity, nitrate, and fDOM data. The water-quality sensors were periodically cleaned and calibrated using methods described by Wagner and others (2006) and Booth and others (2023). The water-quality data were recorded at 15-minute intervals and transmitted hourly via GOES to the NWIS database (U.S. Geological Survey, 2025). At Barton Springs, the water-quality sensor was installed in the main orifice. For the groundwater monitoring wells, sensors were positioned within the screened interval and moved upwards or downwards as necessary if substantial changes in WLAs occurred over the study period. Water-quality data from these wells were assumed to be representative of the entire saturated zone for each site; previous studies have indicated that the Edwards aquifer is vertically well mixed (Lindgren, 2006; Musgrove and others, 2010, 2011), which is consistent with the generally high porosity and transmissivity of the aquifer.

Discrete Water-Quality Sample Collection

Discrete DOC samples were collected from monitoring wells, stormwater-runoff sites, and springs during periods of baseline conditions and during periods of recharge corresponding to increases in WLAs and spring discharge. Samples were collected following procedures outlined in the "USGS National Field Manual for the Collection of Water-Quality Data" (U.S. Geological Survey, variously dated). Grab samples were collected from the main orifice at Barton Springs. A Grundfos Redi-Flo2 pump (Geotech, 2019) equipped with polytetrafluoroethylene (PTFE) tubing was used to sample groundwater monitoring wells. Prior to sample collection, at least three well-casing volumes were purged, and selected field water-quality parameters (water temperature, DO, pH, turbidity, and SC) were monitored until stable to ensure that the sampled groundwater was representative of the surrounding formation; the values of field water-quality parameters were recorded just prior to sample collection (Wilde, variously dated). PTFE bailers were used to collect DOC samples when the depth to groundwater in a well was greater than 250 ft below land surface, exceeding the pump's capability to collect water, or when there was insufficient water in the well to pump and the well was nearly dry. Given the generally high porosity and transmissivity of the unconfined zone of the Edwards aquifer, the bailed samples were considered representative of the groundwater in the aquifer. All water-quality samples were filtered (0.2-µm pore size) and analyzed for DOC concentrations by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, or the OMRL in Sacramento, California. Data from the NWQL are stored in the NWIS database (U.S. Geological Survey, 2025); data from the OMRL are provided in Opsahl and others (2026a). Instantaneous fDOM values from the continuous monitors in the groundwater monitoring wells were recorded at the time of sample collection. For samples collected at sites without continuous monitors, additional water samples were collected, filtered, and either analyzed for fDOM in the laboratory using calibrated fDOM probes or sent to the OMRL for fDOM analysis.

Quality-Assurance Sample Collection

Quality-assurance samples were used to examine the potential for DOC contamination during sample collection and processing (Mueller and others, 2015). Six equipment-blank samples were collected by running organic-free blank water through the groundwater pump and sample processing equipment. Equipment-blank samples were collected in the field prior to collecting environmental samples using the groundwater pump. In addition, two equipment-blank samples were collected by running organic-free blank water through the bailer and sample processing equipment. All equipment-blank samples were analyzed at the NWQL for DOC using the same analytical methods used for environmental samples. DOC concentrations in seven of the eight equipment-blank samples were either (1) below the detection level or (2) above the detection level but below the reporting level for this method, indicating little or no DOC contamination in comparison to environmental samples. One equipment-blank sample collected from the groundwater pump before collecting an environmental sample showed an unacceptable level of DOC contamination, with a concentration exceeding that in the corresponding environmental sample. In this instance, the corresponding environmental sample DOC value was rejected and removed from the dataset.

Temporal Variability of fDOM in the Edwards Aquifer

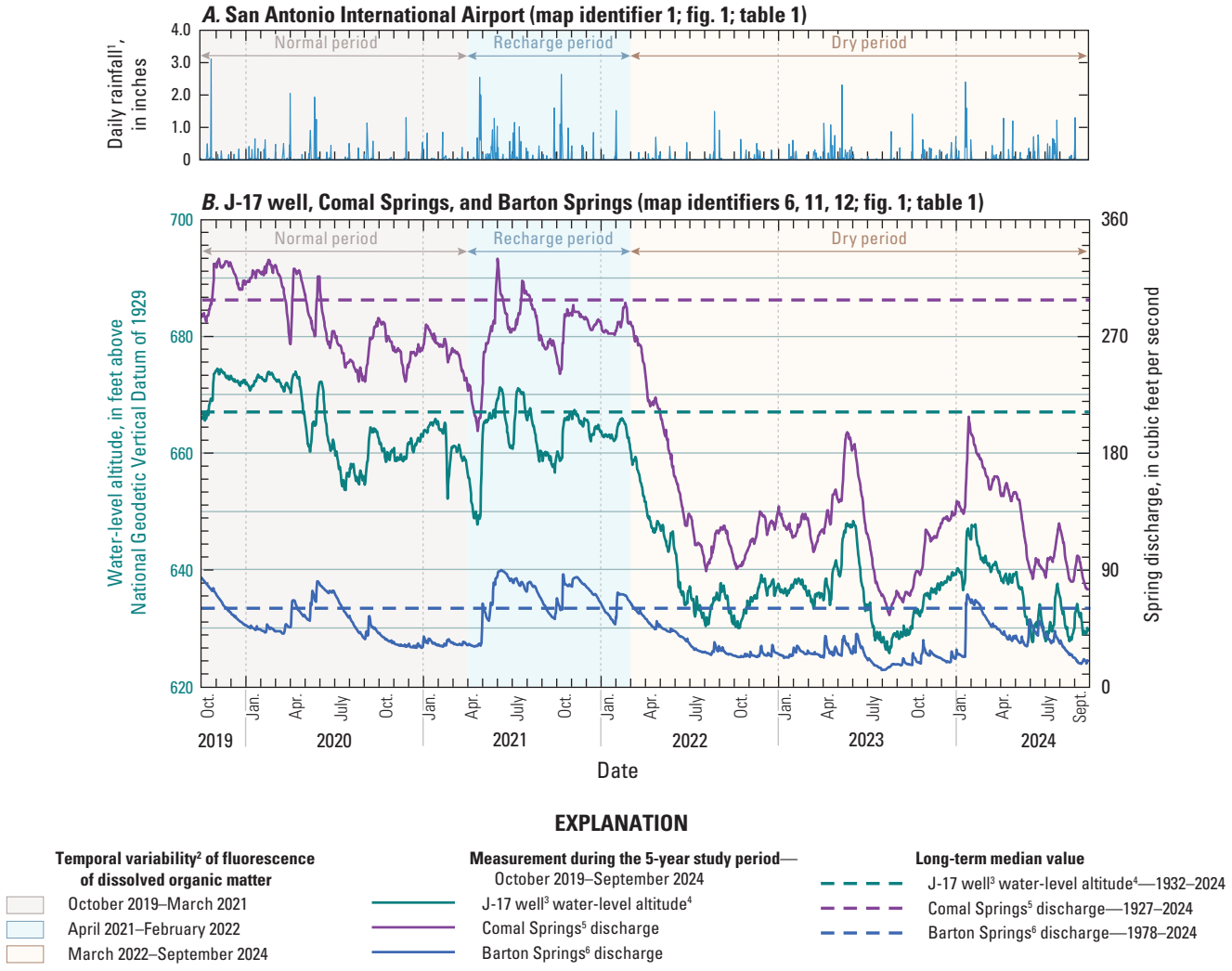
South-central Texas is characterized by hydrologic and climatic extremes (Griffiths and Strauss, 1985; Jones, 1991). Hydrologic and climatic data from GHCN USW00012921 (hereinafter referred to as "San Antonio International Airport" [fig. 1; table 1]), the J-17 well, Barton Springs, and USGS 08168710 Comal Springs at New Braunfels, Tex. (hereinafter referred to as "Comal Springs" [fig. 1; table 1]) (fig. 6*A, B*), were considered to be representative of hydrologic conditions in the study area. Data from these sites were therefore used to establish context for analysis of temporal variability of fDOM in groundwater of the Edwards aquifer during the study period. WLAs in the J-17 well and spring flows at Barton and Comal Springs during October 2019–February 2022 were generally near or slightly below long-term median values (fig. 6), sustained by frequent rainfall and corresponding groundwater recharge. A period of increased rainfall and groundwater recharge during April–October 2021 caused WLAs in the J-17 well to rise more than 20 ft and discharges at Comal Springs to increase by more than 125 ft^3/s, which maintained aquifer levels close to long-term median values through February 2022. During March–July 2022, rainfall events were relatively small and infrequent, causing precipitous declines in WLA and spring discharge. For the purposes of this report, October 2019–March 2021 is referred to herein as the "normal period," April 2021–February 2022 is referred to as the "recharge period," and March 2022–September 2024 is referred to as the "dry period." Although episodes of rainfall/recharge occurred periodically during the dry period, WLAs in the J-17 well and spring discharges at Comal and Barton Springs generally remained below long-term median values and were consistent with drought conditions.

Groundwater Monitoring Wells (San Antonio Segment of the Edwards Aquifer)

WLAs in the groundwater monitoring wells provide context for understanding temporal variability in fDOM during the study period (fig. 7*A–D*). Baseline fDOM values (that is, fDOM values not associated with increases caused by rainfall/recharge events) ranged from about 0 to 6 µg/L as QSE across all wells (fig. 7*A–D*). Small stepwise shifts in the time-series data likely occurred when fDOM sensors were replaced or if there were slight differences in the standard solutions used prior to redeployment of sondes after monitoring equipment was serviced. Wells are discussed next in order of increasing complexity and variability of fDOM monitoring data.

USGS 293405098394201, hereinafter referred to as the "Western Oak well" (fig. 1; table 1), showed a steady decline in WLA during the normal period, an increase in WLA of about 30 ft at the onset of the recharge period, and a steady decline in WLA during the dry period through 2022, after which WLA approached the bottom of the well (fig. 7*A*). fDOM remained at baseline values until December 2022, when the well (261 ft deep) was nearly dry; continuous monitoring of WLA was only periodically available, and fDOM monitoring was not possible at this time. No increases in fDOM relative to baseline occurred during the recharge period, indicating that recharge water with a recent surface-water signature likely did not contribute to the WLA increase observed during this time. Therefore, flow paths associated with recharge near the Western Oak well are likely dominated by diffuse flow rather than conduit flow. This conclusion is further supported by a lack of rapid and short-term increases in WLAs following rainfall events during the recharge period as observed for the regional indicators (fig. 6*A, B*). The Western Oak well thus appears to have relatively low vulnerability to changes in water quality during periods of rapid groundwater recharge.

The pattern of WLAs in USGS 293252098380801, hereinafter referred to as the "Parkwood well" (figs. 1, 7*B*; table 1), was similar to that of the Western Oak well (fig. 7*A*) with a gradual WLA decrease during the normal period, followed by a WLA increase during the recharge period, and the predominance of baseline fDOM values throughout the entire study period. However, rapid increases in fDOM occurred twice in 2021 during the recharge period, reaching peaks greater than 10 µg/L as QSE. These fDOM increases were accompanied by small but rapid increases in WLA, indicating that conduit flow in the aquifer is more likely at this well than at the Western Oak well (fig. 7*A*). The influence of

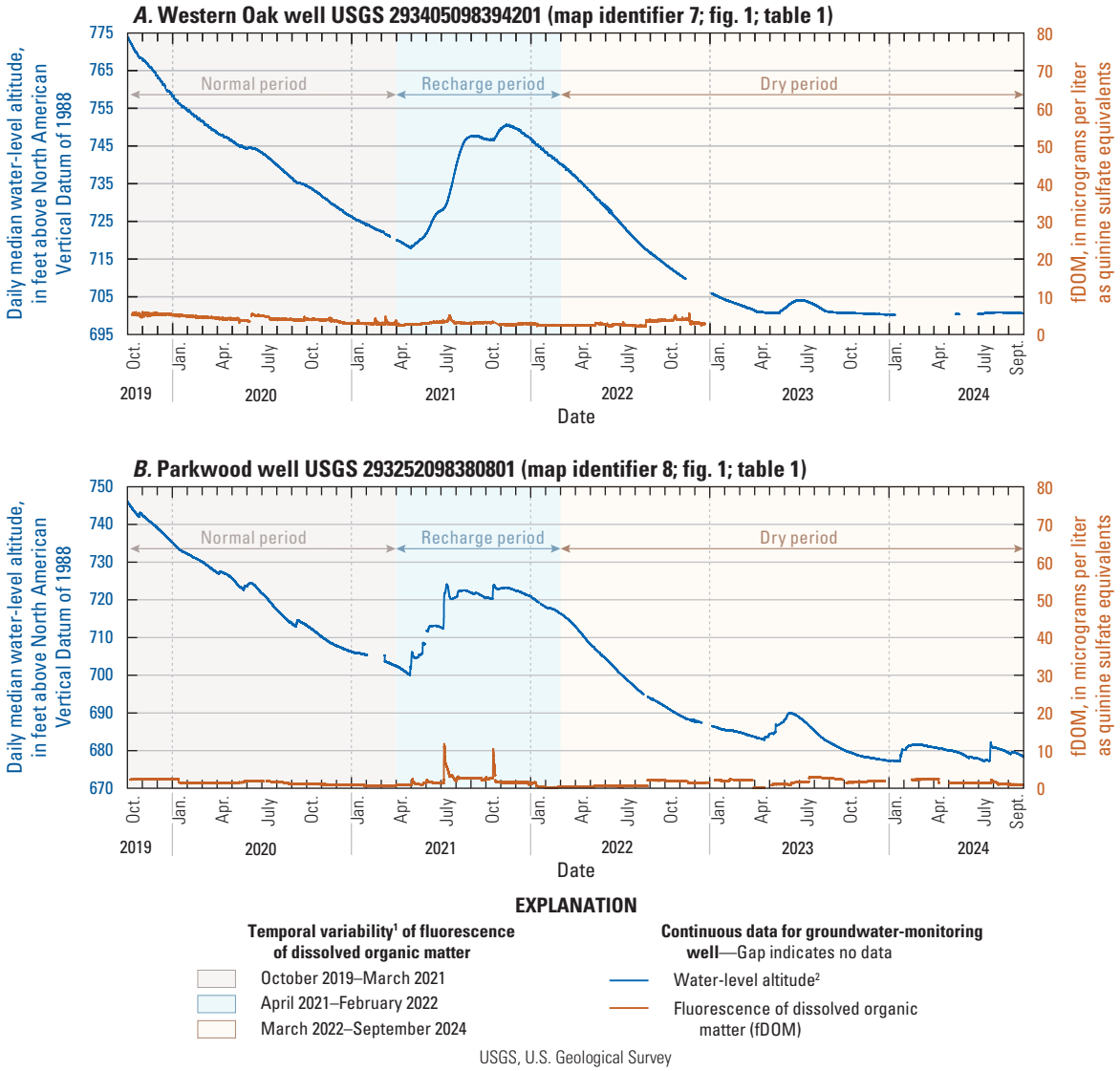


[1]Data for San Antonio International Airport, Texas weather station GHCN USW00012921 from National Oceanic and Atmospheric Administration (2025).
[2]For the purposes of this report, October 2019–March 2021 is referred to as the "normal period," April 2021–February 2022 is referred to as the "recharge period," and March 2022–September 2024 is referred to as the "dry period."
[3]Groundwater monitoring well J-17 (EAA 36837203 [TWDB 36837203]; map identifier 6; fig. 1; table 1). Data from EAA (2025).
[4]Water-level altitudes in the groundwater monitoring wells provide context for understanding temporal variability in fluorescence of dissolved organic matter during the study period.
[5]Comal Springs (USGS 08168710; map identifier 11; fig. 1; table 1). Data from USGS (2025).
[6]Barton Springs (USGS 08155500; map identifier 12; fig. 1; table 1). Data from USGS (2025).

GHCN, Global Historical Climatology Network; EAA, Edwards Aquifer Authority; TWDB, Texas Water Development Board; USGS, U.S. Geological Survey

Figure 6. Time series of (*A*) daily rainfall for San Antonio International Airport (Global Historical Climatology Network [GHCN] USW00012921), (*B*) water-level altitudes at the J-17 well (Edwards Aquifer Authority [EAA] 36837203), and discharges at Comal Springs (USGS 08168710) and Barton Springs (USGS 08155500), south-central Texas, October 2019–September 2024.

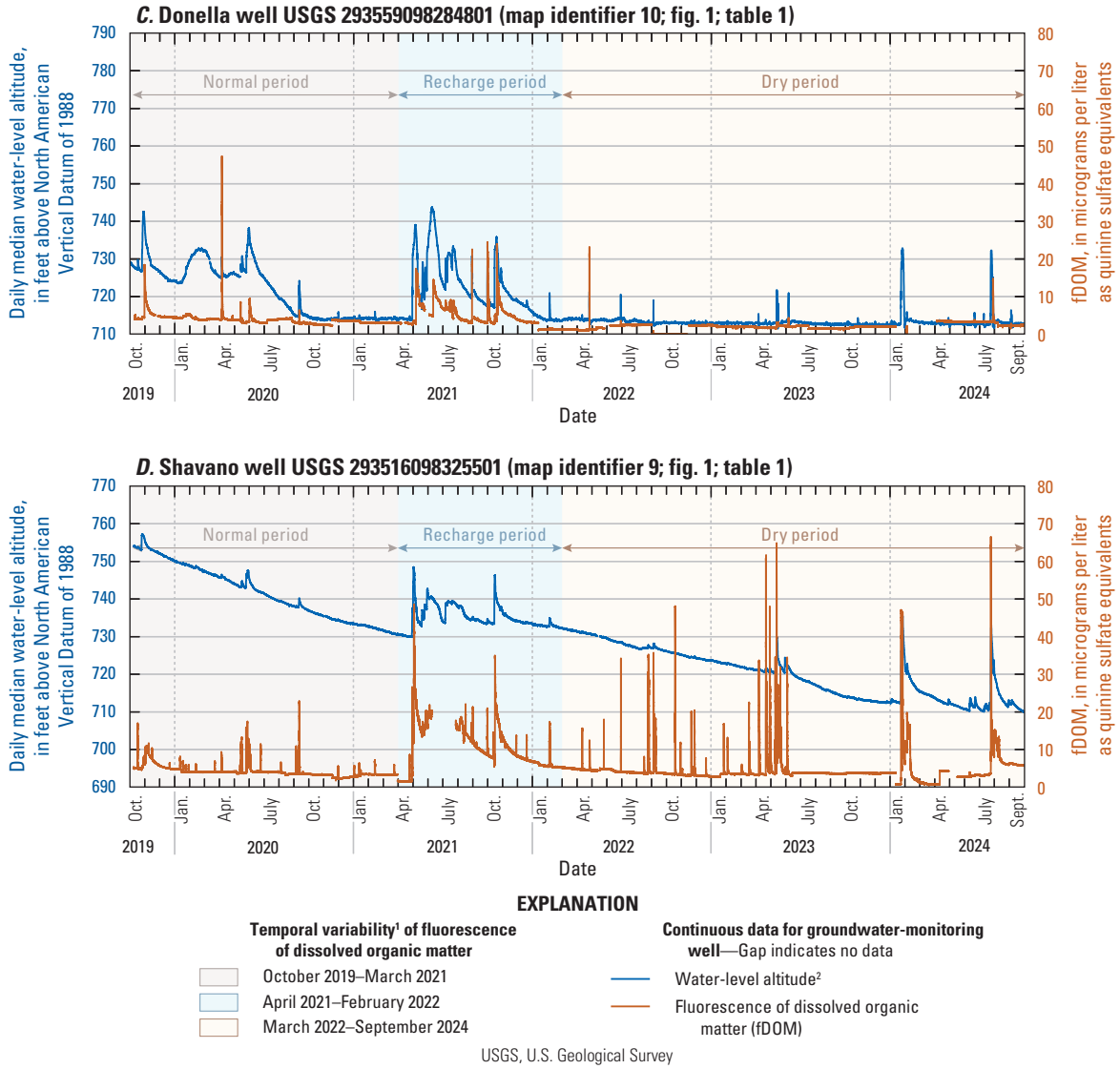
recent surface-water recharge at the Parkwood well (fig. 7*B*) was documented by Opsahl and others (2018) during a prolonged recharge period in 2015–17. During that period, continuous WLA and SC measurements indicated frequent influxes of surface-water recharge with lower SC values. Concurrent groundwater samples were compositionally similar to surface-water runoff from the adjacent recharge stream, Leon Creek (fig. 1), on the basis of major ion, nutrient, and pesticide geochemistry. In the present study, prolonged drought conditions resulted in minimal surface-water flow events in nearby ephemeral streams that, in turn, limited recharge from surface water that might influence flow paths to this well. Historical data indicate that the Parkwood well can be influenced by recent recharge from surface water through conduit flow paths during wetter hydrologic conditions and, thus, is occasionally vulnerable to contaminants in recharge from surface water.



[1]For the purposes of this report, October 2019–March 2021 is referred to as the "normal period," April 2021–February 2022 is referred to as the "recharge period," and March 2022–September 2024 is referred to as the "dry period."

[2]Water-level altitudes in the groundwater monitoring wells provide context for understanding temporal variability in fluorescence of dissolved organic matter during the study period.

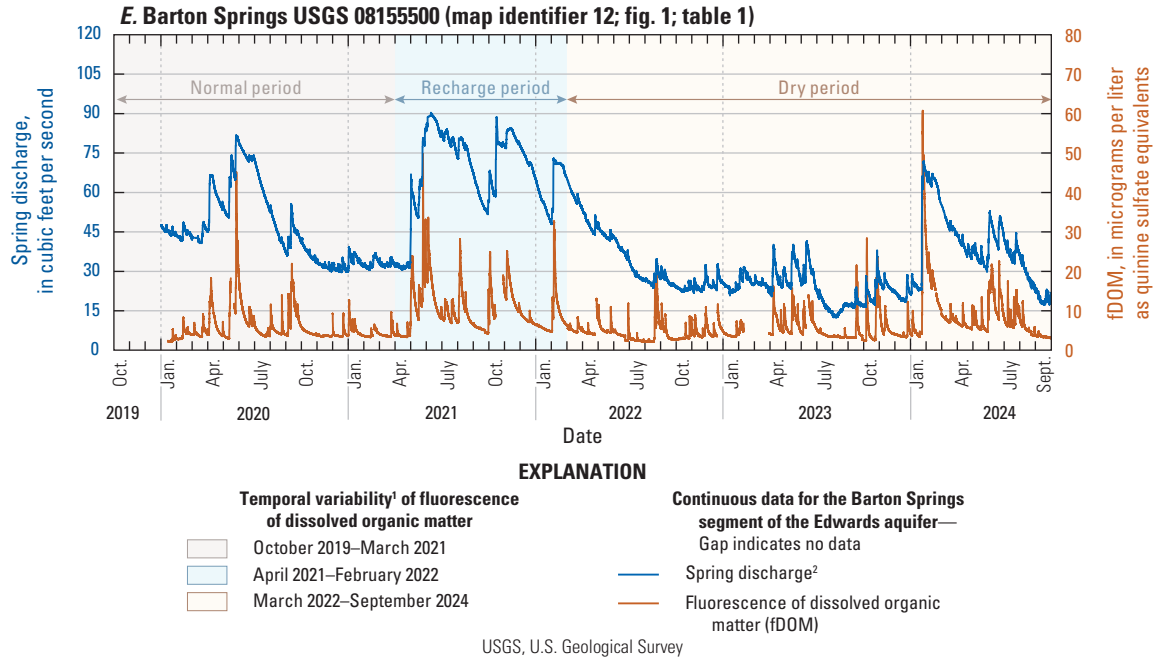
Figure 7. Continuous water-level altitude (WLA) and fluorescence of dissolved organic matter (fDOM) data for the (*A*) Western Oak well, (*B*) Parkwood well, (*C*) Donella well, (*D*) Shavano well, and (*E*) discharge and fDOM data for Barton Springs, October 2019–September 2024. Y-axis results for WLA and fDOM are shown on the same scale (ranges of 80 feet and 80 micrograms per liter as quinine sulfate equivalents, respectively) for comparability.



[1]For the purposes of this report, October 2019–March 2021 is referred to as the "normal period," April 2021–February 2022 is referred to as the "recharge period," and March 2022–September 2024 is referred to as the "dry period."

[2]Water-level altitudes in the groundwater monitoring wells provide context for understanding temporal variability in fluorescence of dissolved organic matter during the study period.

Figure 7.—Continued



[1]For the purposes of this report, October 2019–March 2021 is referred to as the "normal period," April 2021–February 2022 is referred to as the "recharge period," and March 2022–September 2024 is referred to as the "dry period."

[2]Water-level altitudes in the groundwater monitoring wells provide context for understanding temporal variability in fluorescence of dissolved organic matter during the study period.

Figure 7.—Continued

WLAs in USGS 293559098284801, hereinafter referred to as the "Donella well" (figs. 1, 7*C*; table 1), generally declined during the normal period and increased during the recharge period. Unlike the other monitoring wells, WLAs at the Donella well plateaued at about 712 ft above the North American Vertical Datum of 1988 (NAVD 88) and did not show appreciable declines beyond that threshold, even during the dry period. One possible explanation for these observations is that the aquifer at this location may be more highly connected to the regional aquifer system at altitudes above 712 ft above NAVD 88 and thus can more readily receive and lose water to the regional aquifer system. At altitudes below 712 ft above NAVD 88, the limestone matrix of the saturated zone may be hydrologically isolated from regional groundwater withdrawals, and small groundwater losses are roughly balanced by new, upgradient groundwater inputs. WLAs in the Donella well showed more frequent short-term and rapid hydrologic responses to rainfall events in comparison to those in the Western Oak and Parkwood wells, and these responses appeared to correspond more to individual rainfall events than to regional hydrologic conditions (fig. 6*A, B*). The short-term peaks in WLAs were typically accompanied by peaks in fDOM of varying magnitude; the greatest fDOM value, 47 µg/L as QSE, occurred in April 2020 (fig. 7*C*). The fDOM peaks were brief, and values typically returned to baseline levels quickly, often in less than 24 hours. There appears to be considerable conduit flow in the aquifer at this location, at least when water levels exceed 712 ft above NAVD 88, as evidenced by frequent intrusions of more recent surface-derived recharge with greater fDOM values. These short-term changes in groundwater quality occurred throughout the study period, although less frequently during the dry period. On the basis of the combination of hydrologic responses and frequent inputs of fDOM, the Donella well shows high vulnerability to contaminants in recharge surface-water in comparison to the Western Oak and Parkwood wells.

WLAs in the Shavano well generally declined during the study period, with the exception of the recharge period when several prolonged recharge pulses occurred (fig. 7*D*). Also, WLAs increased in January and July 2024 as a result of short-term recharge events following storms. In contrast to the WLA time series, the fDOM time series at the Shavano well showed multiple peaks of varying magnitude throughout the study period (fig. 7*D*); the greatest fDOM value (67 µg/L as QSE) was measured during a recharge event in July 2024. fDOM values remained greater than 10 µg/L as QSE for most of the April 2021–February 2022 recharge period, although an equipment failure resulted in a data gap during June–July 2021. This pattern of prolonged influx of surface-water recharge, indicated by fDOM values greater than 10 µg/L as QSE, was not observed in the other groundwater monitoring wells.

Pulses in fDOM at the Shavano well occurred frequently during the study period, often when no visual change in WLA was apparent (fig. 7*D*). For example, during the dry period between March 2022 and September 2024, more

than 20 fDOM pulses exceeded 10 µg/L as QSE, yet only a few measurable increases in WLAs were observed during this same period. These fDOM pulses typically followed rainfall events (fig. 6) small enough to allow downward movement of fDOM without causing a rise in the regional water table. These frequent intrusions of fDOM indicate strong connectivity with the land surface and more direct pathways for water movement from recharge streams into the unconfined aquifer at this location. Relatively few instances of elevated fDOM (greater than 20 µg/L as QSE) occurred during the normal period in comparison to the dry period (fig. 7*D*), even with larger rainfall events that were expected to cause larger increases in fDOM. One possible explanation is that intrusion of recharge surface water through conduits was more restricted at higher WLAs because of greater head pressures. There also could be mixing and dilution with ambient aquifer water in the groundwater flow paths resulting in a lower proportion of fDOM being recorded at higher WLAs. When WLAs are lower, head pressures are reduced, allowing conduit flow downgradient to proceed more rapidly, increasing the proportion of surface-water recharge and increasing fDOM values. Among the four groundwater monitoring wells, the Shavano well had the most frequent intrusion of fDOM as well as the greatest fDOM values, indicating relatively high vulnerability to contaminants in recharge surface-water in comparison to the other groundwater monitoring wells.

Barton Springs (Barton Springs Segment of the Edwards Aquifer)

Discharges at Barton Springs (fig. 7*E*) generally followed a pattern similar to WLAs in groundwater monitoring wells in the San Antonio segment of the Edwards aquifer (fig. 7*B–D*) and the regional hydrologic indicators (fig. 6). However, during the normal period, notable increases in discharge occurred at Barton Springs (in mid-2020) that were less evident than increases in WLAs for the groundwater monitoring wells in the San Antonio segment. Nevertheless, given the overall similarity in regional hydrologic conditions, the same intervals and conditions (normal, recharge, and dry periods) are used to discuss Barton Springs.

In the Barton Springs segment of the Edwards aquifer, Garner and Mahler (2007) and Wong and others (2012) (among others) used temporal correlations between stream-loss estimates, spring discharges, groundwater SC, and dye traces to identify losing streams along conduit flow routes as dominant sources of recharge to the aquifer. Dye traces have documented surface-water transport as rapid as 12 kilometers per day through major conduit flow routes to Barton Springs (Hauwert, 2009). Along the continuum from diffuse- to conduit-dominated flow, Barton Springs likely represents a conduit-dominated-flow endmember. This hypothesis is supported by the fDOM time-series data for Barton Springs, which indicate more frequent and longer duration fDOM pulses (fig. 7*E*) in comparison to those at the four monitoring wells (fig. 7*A–D*). The largest pulses in fDOM occurred at the leading edge of sharp increases in discharge during the study period, indicating a pattern of surface-water recharge and subsequent rapid discharge at Barton Springs following rainfall/recharge events. Recharge pulses are common, with only limited and brief occurrences of baseline fDOM conditions. On the basis of mass-balance modeling, Wong and others (2012) hypothesized that the majority of Barton Springs discharge is sourced from recent (days to months) surface-water recharge. Work by Mahler and Massei (2007) indicated that complex recharge pulses can result from multiple storm events because of varying transit times through the aquifer from different recharge sources. The predominance of fDOM values above the baseline may also result from a relatively short residence time of recent surface-water recharge prior to discharge at Barton Springs, in contrast to the relatively long residence times of recharge water for some of the unconfined monitoring wells and for the San Antonio segment in general (Musgrove and others, 2023). These results collectively indicate that, of the sites considered in this study, Barton Springs is likely the most vulnerable to surface-water contaminants.

Insights from Multiple Water-Quality Parameters

Multiparameter continuous monitoring at the unconfined groundwater monitoring wells and Barton Springs provides additional information about the variability in source waters contributing to groundwater recharge and the factors influencing the variability of fDOM values specifically. The groundwater monitoring wells and Barton Springs are characterized by relatively high baseline (non-recharge condition) SC and nitrate values, and relatively low turbidity and fDOM values relative to those for surface-water in recharge streams (Musgrove and others, 2011; Opsahl, 2012; Opsahl and others, 2018, 2020; this study). Given that the Shavano well and Barton Springs are among the most vulnerable study sites, they were selected to provide examples of how multiple water-quality parameters vary during periods of groundwater recharge.

At the Shavano well, multiple water-quality parameters showed short-term enhanced variability in response to episodes of rainfall/runoff and associated groundwater recharge. During October 13–15, 2021, approximately 4.2 inches (in.) of rainfall was measured at San Antonio International Airport (figs. 1, 6; table 1), more than half of which fell on October 13 (National Oceanic and Atmospheric Administration, 2025a). In response, WLA rose rapidly in the well by about 13 ft over a 24-hour period, from late on October 13 through late October 14, with small concurrent changes in fDOM, nitrate, or SC (fig. 8*A, B*). On October 15, rapid changes in water quality occurred, with fDOM increasing to about 35 µg/L as QSE, nitrate decreasing to 1.4 mg/L (as nitrogen), and SC decreasing to

about 497 microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C) (fig. 8*A, B*). These peak or trough values were consistent with the greater fDOM, lower nitrate, and lower SC values characteristic of surface-water in recharge streams (Musgrove and others, 2011; Opsahl, 2012; Opsahl and others, 2018, 2020; this study). Notably, the water-quality response lagged behind the WLA response, reflecting an initial pressure pulse before ambient groundwater was displaced by more recent recharge from surface-water. Following this recharge event, WLA declined to a new, higher baseline and water-quality parameters shifted over several days toward baseline values as the pulse of surface-water recharge moved through the aquifer. Similar variability—with water-quality shifts toward the composition of surface-water recharge with elevated fDOM, then a return to baseline values—is common among the monitoring wells in this study, with the exception of the Western Oak well where no notable changes in fDOM occurred during the study period (fig. 7*A*).

In contrast to the October 2021 recharge event, a notably different response occurred at the Shavano well in response to a smaller rainfall/recharge event in September 2022 (fig. 9*A, B*). On September 3, 2022, 0.92 in. of rainfall was measured at San Antonio International Airport (National Oceanic and Atmospheric Administration, 2025a) (fig. 6); in response, the WLA rose by about 1 ft, and changes in water quality occurred about 4 hours later (fig. 9*A, B*). Similar to most recharge responses at this site, SC decreased rapidly from a baseline value of about 610 µS/cm at 25 °C to about 530 µS/cm at 25 °C in less than 6 hours. fDOM increased and peaked at about 36 µg/L as QSE. Nitrate, however, increased

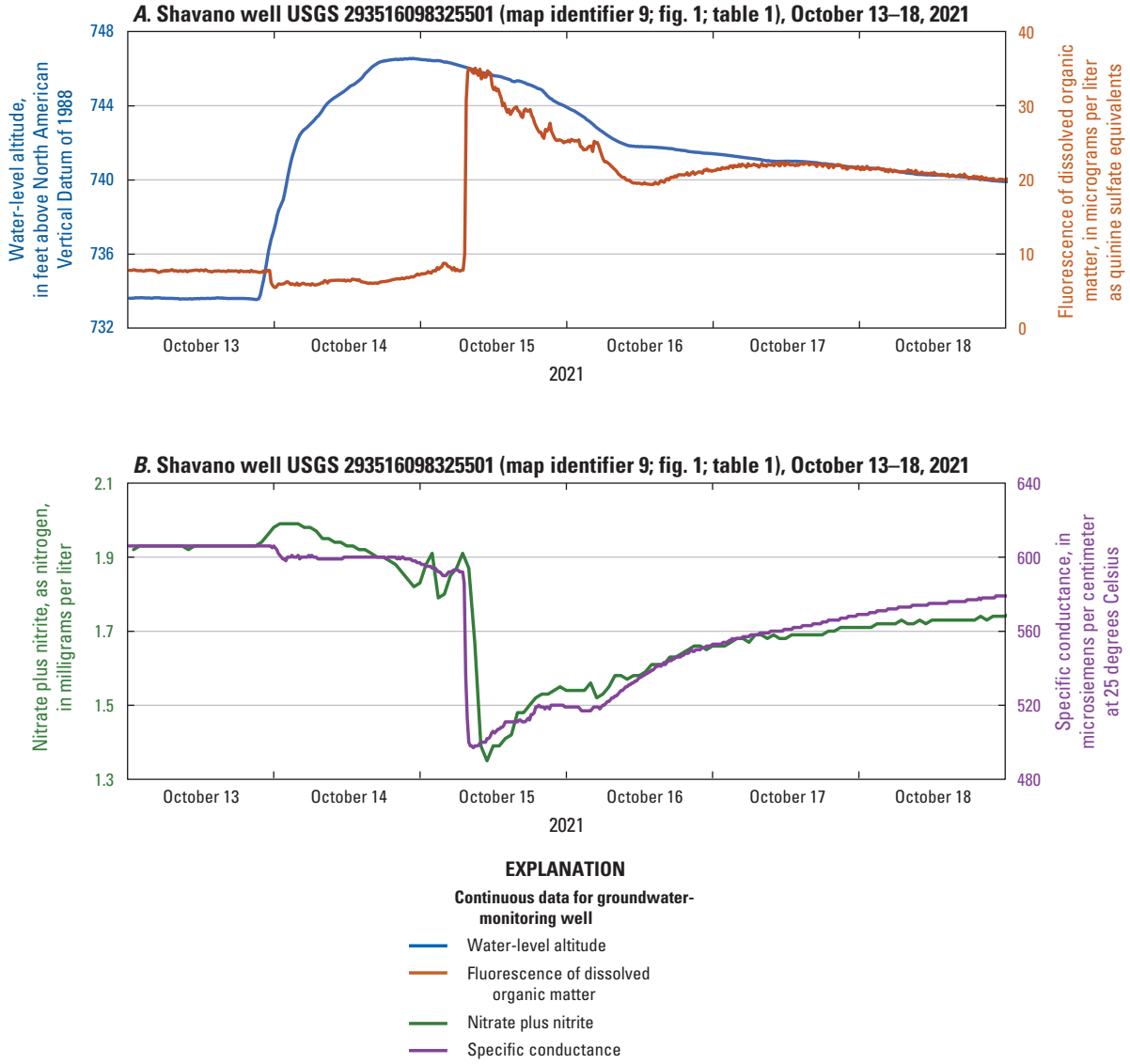


Figure 8. Continuous (*A*) water-level altitudes (WLAs) and fluorescence of dissolved organic matter (fDOM) values, and (*B*) nitrate concentrations and specific conductance values for the Shavano well (fig. 1; table 1), October 13–18, 2021.

substantially, peaking at about 4.6 mg/L, much greater than baseline concentrations in groundwater throughout most of the aquifer (Opsahl and others, 2018). Although uncommon, an increase in nitrate concentration concurrent with an fDOM increase in response to rainfall/recharge has been previously observed at this site (U.S. Geological Survey, 2025). Measured concentrations of total nitrogen in stormwater runoff from recharging creeks in the San Antonio area have not, to date, exceeded 3 mg/L (Opsahl and others, 2018), and conversion of all total nitrogen to nitrate would still not account for the observed elevated concentrations of nitrate. Therefore, an additional water source, likely with a wastewater component, might account for both elevated nitrate and elevated fDOM.

Variability in continuous hydrologic and water-quality parameters at Barton Springs during periods of groundwater recharge was similar to the variability observed at most of the monitoring wells. For example, over an approximately 6-week period between April 28 and June 12, 2021, discharge at Barton Springs nearly tripled, increasing by about 58 ft^3/s (fig. 10*A*) in response to multiple rainfall/recharge events. Within this relatively wet period, 0.5 in. or more of rainfall was measured on 10 days at GHCND USW00013904, hereinafter referred to as "Austin Bergstrom International Airport" (fig. 1; table 1; National Oceanic and Atmospheric Administration, 2025b). Discharge increased rapidly beginning on May 1, 2021, and then in a subsequent series of stepwise increases, between May 16 and June 4, 2021.

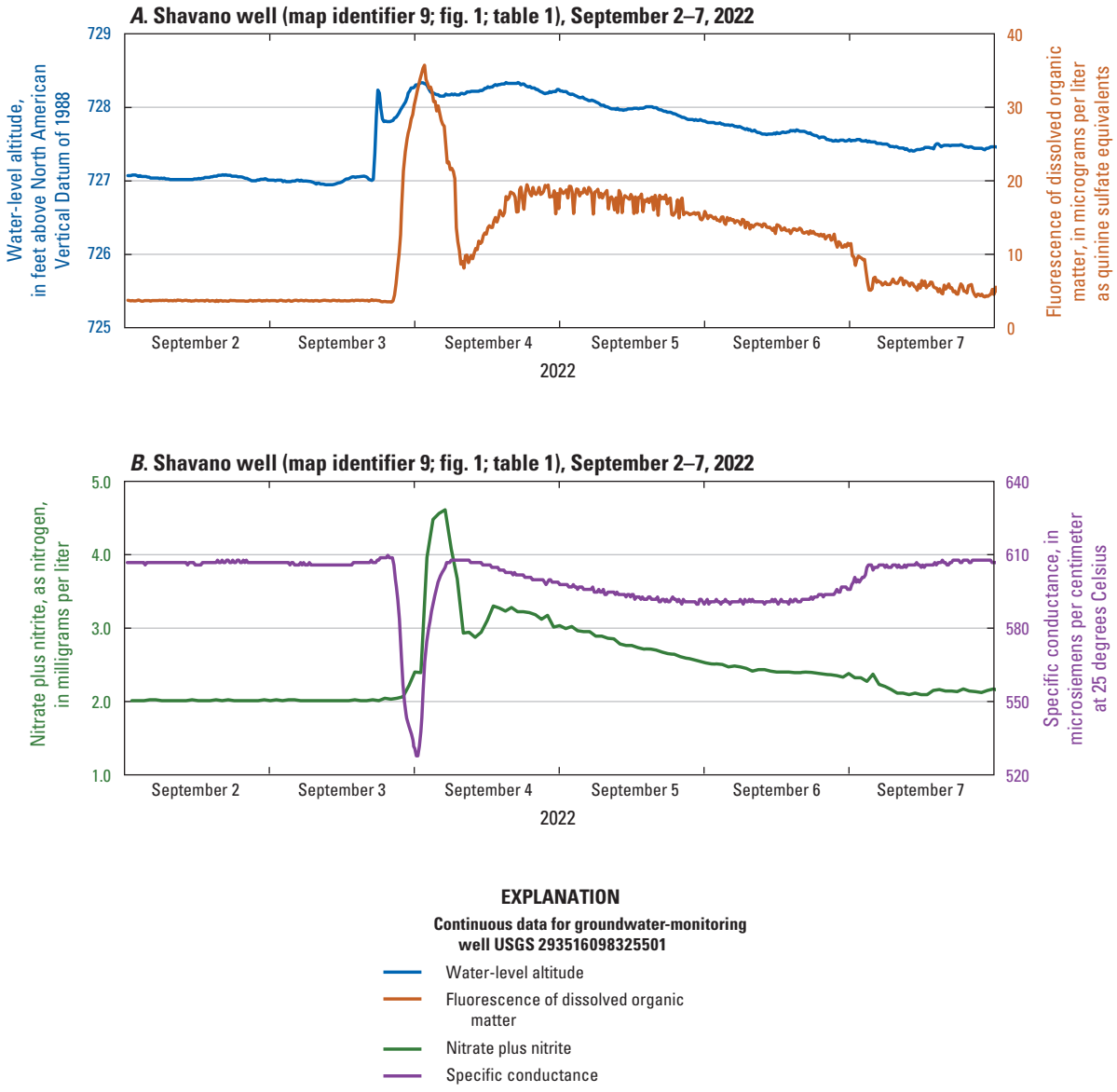


Figure 9. Continuous (*A*) water-level altitudes (WLAs) and fluorescence of dissolved organic matter (fDOM) values, and (*B*) nitrate concentrations and specific conductance values for the Shavano well (fig. 1; table 1), September 2–7, 2022.

During the earlier part of this interval (May 1–3), in response to the initial rainfall/recharge event and discharge increase, SC decreased by about 100 µS/cm at 25 °C, fDOM peaked at about 24 µg/L as QSE, and nitrate fluctuated but showed a net decrease from about 1.7 to 1.1 mg/L (fig. 10*A, B*). Beginning on May 16, 2021, the stepwise increases in discharge were accompanied by similar changes in water-quality parameters that lagged only a few hours behind the discharge increases. Changes included concurrent steep declines in SC and nitrate and steep increases in fDOM, with a maximum value of 50 µg/L as QSE. These observed water-quality changes were nearly synchronous and consistent with rapid influxes of surface-water recharge.

During a different rainfall/recharge event that occurred in January 2024, 3.54 in. of rainfall was measured at Austin Bergstrom International Airport during January 21–25 (National Oceanic and Atmospheric Administration, 2025b), and discharge at Barton Springs increased by about 43 ft^3/s over several days (fig. 11*A*). Small changes in fDOM, nitrate, and SC were apparent shortly after discharge began to increase; however, much larger and rapid changes occurred as the initial discharge increase was near its peak: SC initially dropped from about 710 µS/cm at 25 °C to about 580 µS/cm at 25 °C, with concurrent small changes in fDOM and nitrate. SC then increased to about 660 µS/cm at 25 °C, accompanied by an increase in nitrate concentration from about 1.5 to 2.0 mg/L (fig. 11*A, B*). As SC and nitrate concentration declined from their peaks, fDOM values rose rapidly to just

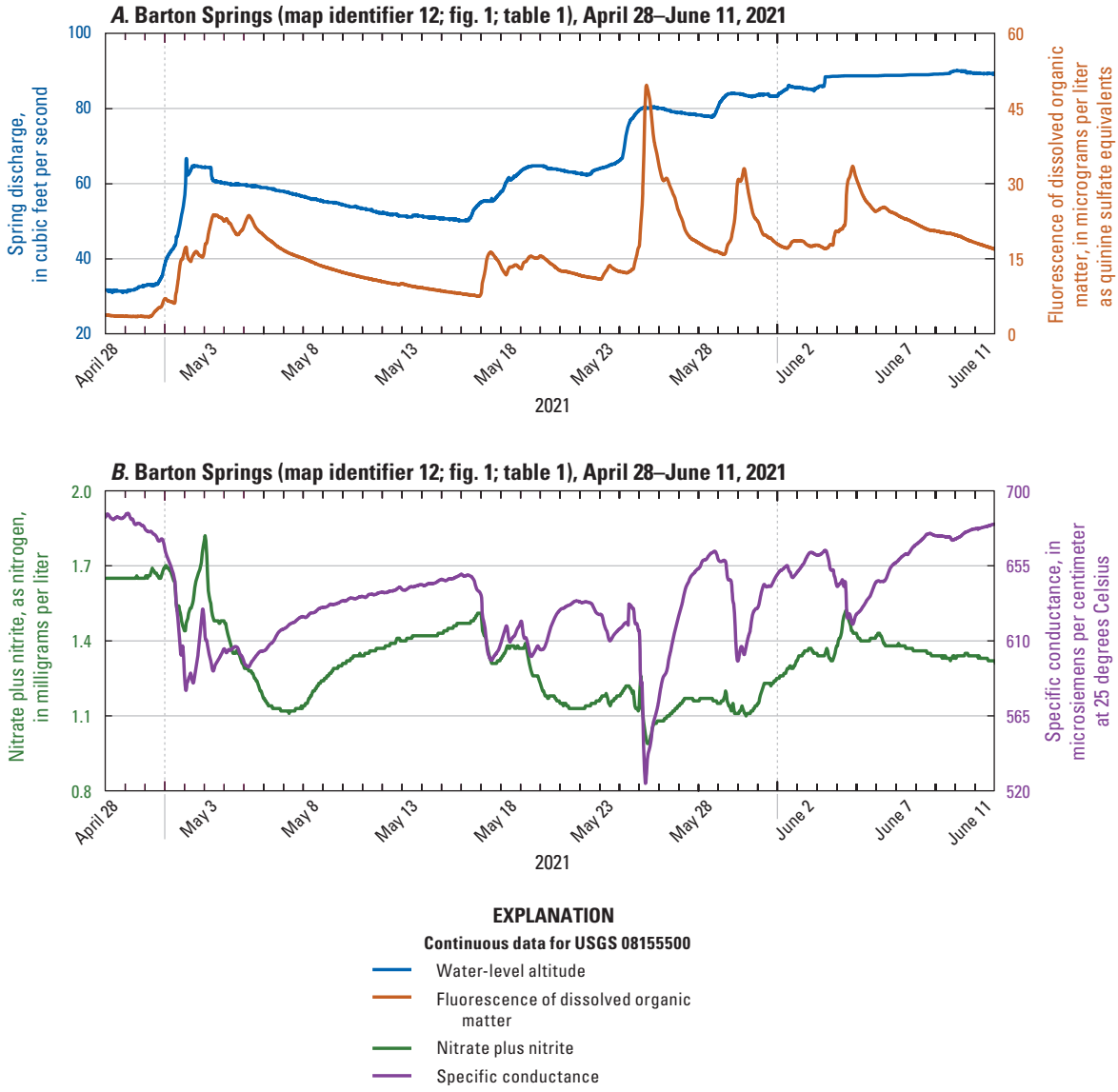


Figure 10. Continuous (*A*) discharge values and fluorescence of dissolved organic matter (fDOM) values, and (*B*) nitrate concentrations and specific conductance values for Barton Springs (fig. 1; table 1), April 28–June 11, 2021.

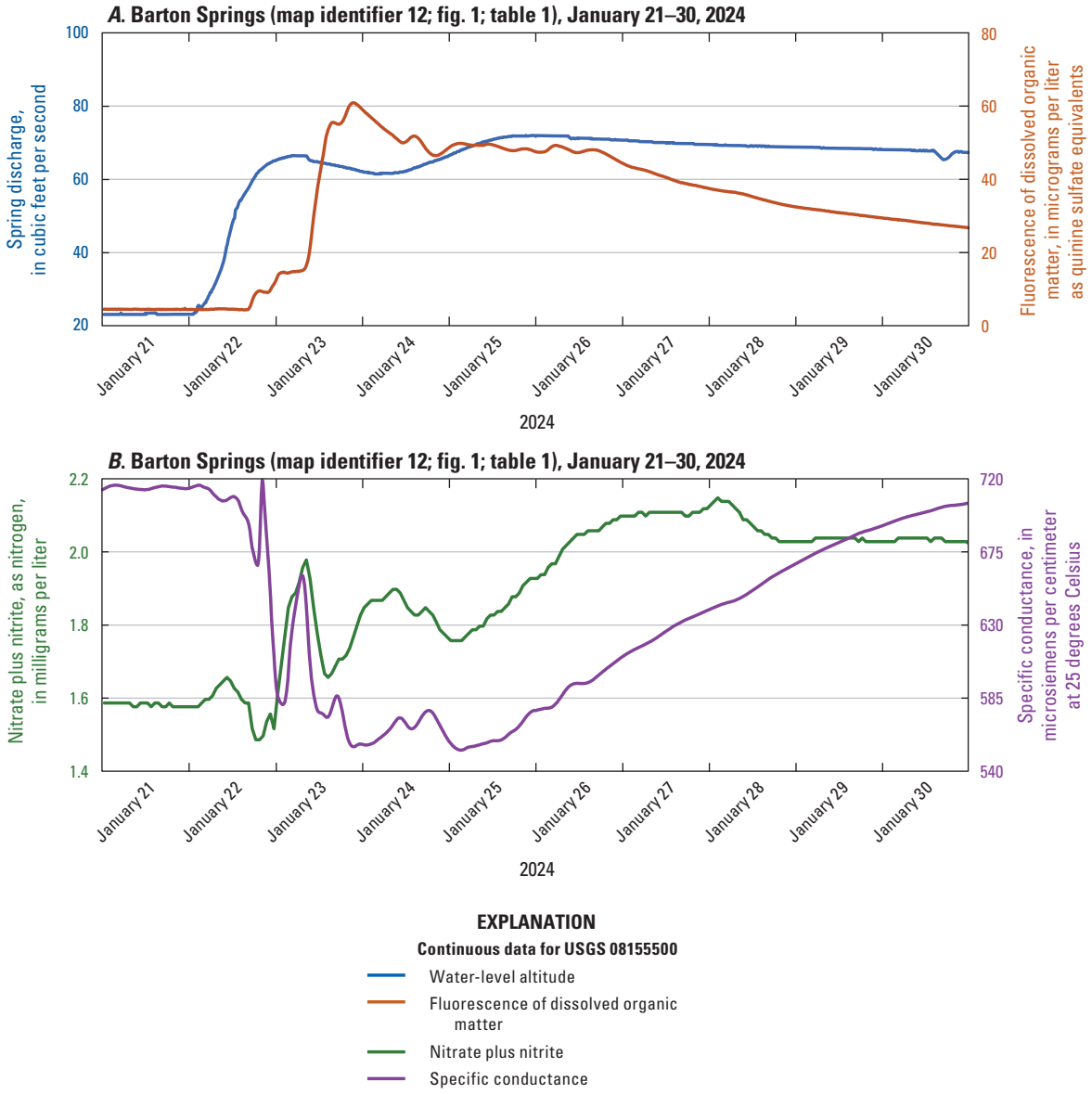


Figure 11. Continuous (*A*) discharge values and fluorescence of dissolved organic matter (fDOM) values, and (*B*) nitrate concentrations and specific conductance values for Barton Springs (fig. 1; table 1), January 21–30, 2024.

over 60 µg/L as QSE. When discharge stabilized, SC and fDOM values trended toward their initial baseline values, but nitrate continued to increase and stabilized at a concentration greater than the initial baseline concentration. The timing and direction of water-quality responses are indicative of variability in the composition of recharge water during this event, which might result from varying proportions and timing of surface-water recharge from different recharging streams. Although nitrate concentration increased over the course of this recharge event, values are within the known range for surface-water and not indicative of any high-nitrate source. The parallels in water-quality variability for the unconfined monitoring wells and Barton Springs are indicative of the consistent influence of conduit flow in response to rainfall/recharge events. At each site, differences in hydrologic conditions and antecedent conditions can affect the specific response to rainfall/recharge events (Mahler and Massei, 2007).

fDOM as a Proxy for DOC Concentration

A total of 106 DOC samples were collected from four groundwater monitoring wells and Barton Springs during baseline conditions and in response to rainfall/recharge events. Baseline fDOM values typically were about 1–5 µg/L as QSE, and baseline DOC concentrations were about 0.25–0.70 mg/L (fig. 12). Musgrove and others (2010) reported a median DOC concentration of 0.40 mg/L for 65 groundwater samples from the Edwards aquifer, which is consistent with baseline values measured in this study. Samples with DOC concentrations above baseline values were usually, but not always, associated with samples collected following rainfall/recharge events. At other times, DOC concentrations above baseline values were evident without a corresponding rise in WLA. Although resolving baseline and surface-water sources of fDOM remains challenging, the occurrence of elevated fDOM values well above baseline (typically greater than 10 µg/L as QSE) and correspondingly greater DOC concentrations (greater than 1.0 mg/L and as high as about 3.0 mg/L) provides insight into the relation between these water-quality parameters.

Data collected in this study support the use of fDOM as a proxy for DOC in Edwards aquifer groundwater, at least for DOC concentrations less than 3.0 mg/L and fDOM values less than 51 µg/L as QSE. fDOM and DOC data collected from all sites are correlated (coefficient of determination of 0.86) across the range of measured values (fig. 12). Although groundwater DOC concentrations in this study did not exceed 3.0 mg/L, DOC concentrations greater than 11 mg/L have been reported in streams in the study area (Opsahl and others, 2020). Surface-water recharge having higher DOC concentrations likely mixes to varying degrees with ambient groundwater having lower DOC concentrations, resulting in dilution of DOC concentrations in rainfall/recharge samples from groundwater. At Barton Springs, for example, inverse geochemical modeling has constrained surface-water/groundwater mixing, indicating that mixing

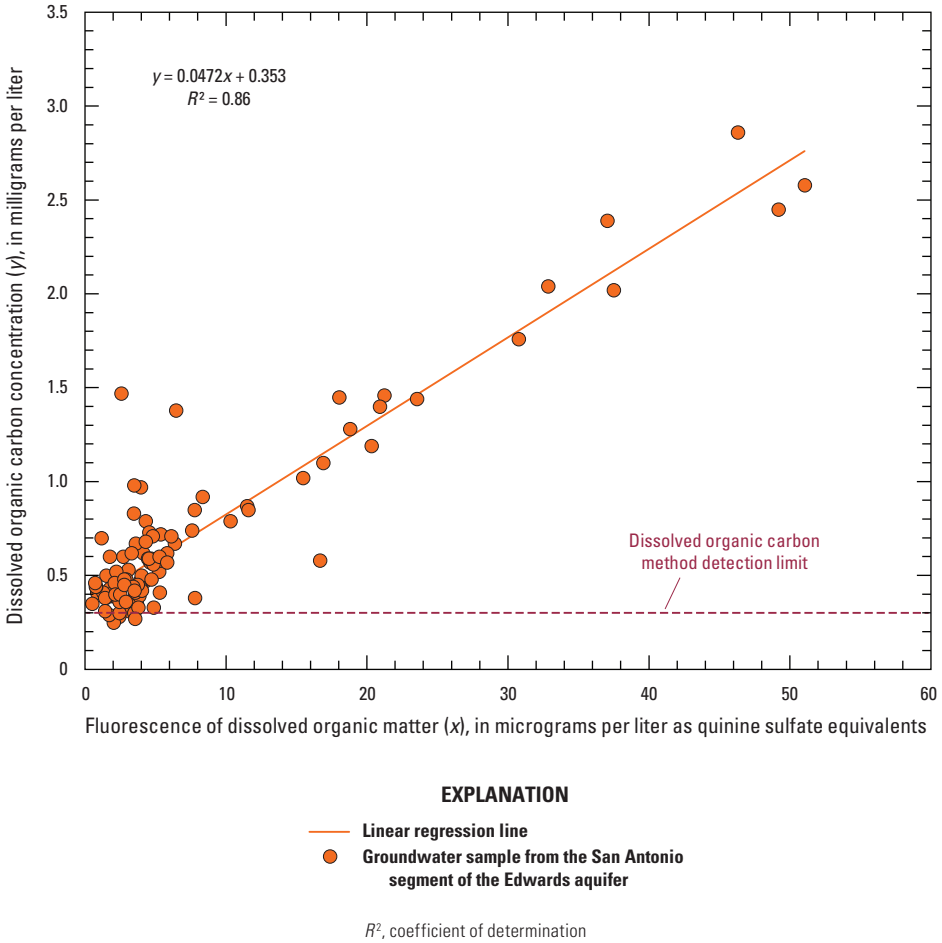


Figure 12. Relation between dissolved organic carbon and fluorescence of dissolved organic matter (fDOM) for groundwater samples from the San Antonio segment of the Edwards aquifer, south-central Texas, 2019–24.

proportions may vary considerably with hydrologic conditions (Wong and others, 2012). Microbial degradation of DOC likely also plays an important role in the transformation of DOC in groundwater of the Edwards aquifer (Cooper and others, 2016), although degradation was not specifically addressed in this study.

fDOM as a Tracer of Surface-Water Recharge and Aquifer Vulnerability

fDOM monitoring, when used as a proxy for DOM in surface-water recharge, can provide a tool for understanding recharge processes and the transport of stormwater-runoff-derived contaminants into the Edwards aquifer. Prior studies of the Edwards aquifer have documented the transport of a variety of anthropogenic contaminants into the aquifer during episodes of rainfall/recharge (Mahler and Massei, 2007; Mahler and others, 2011a, b; Musgrove and others, 2011; Opsahl and others, 2018, 2020). Furthermore, influxes of recharge and associated contaminants were shown to vary on the basis of hydrologic conditions (Mahler and Massei, 2007; Wong and others, 2012). The abundance and frequency of pesticide detections is likely greater in urban settings (Opsahl and others, 2020). These observations are consistent with results from this study in which influxes of fDOM into the aquifer vary on the basis of antecedent hydrologic conditions. For example, differences in the timing and magnitude of fDOM pulses were evident at the Shavano well, with larger more frequent pulses occurring during relatively dry conditions when WLAs were low. These results are consistent with previous studies indicating that the speed and efficiency of transport through karst conduits and the balance of recharge going into matrix storage varies with hydrologic conditions; under relatively dry hydrologic conditions, when spring discharge and WLAs are low, focused recharge travels unimpeded through aquifer conduits (Mahler and Massei, 2007). These results suggest that the aquifer is more directly vulnerable to recharge-associated contaminants during dry conditions. Under wet hydrologic conditions, when spring discharge and WLAs are higher, aquifer conduits may be saturated, recharge is more likely to initially go into matrix storage, and the spring/well response is dampened (Mahler and Massei, 2007).

The spatial variability in fDOM and corresponding water-quality parameters in response to rainfall/recharge events covers a large range, from sites with little temporal response (for example, the Western Oak well) to sites with rapid responses reflecting discrete recharge pulses (for example, the Shavano well and Barton Springs). These differences reflect the complex nature of karst, with low-storage, high-transmissivity conduits embedded in a high-storage, low-transmissivity matrix (Atkinson and others, 1973; Martin and others, 2006; White 2012). The response of different study sites indicates they extend across a continuum from diffuse- to conduit-dominated flow. For the groundwater monitoring wells, this likely reflects the intersection of the well bore with conduits linked to surface recharge features and losing streams. At Barton Springs, discharge integrates all processes occurring along the aquifer flow paths, including multiple, highly transmissive, conduit-dominated source inputs (Quinlan, 1989). Higher baseline fDOM values and more frequent fDOM peaks in comparison to the monitoring wells demonstrate that Barton Springs is the study site most vulnerable to surface-water contamination during periods of groundwater recharge.

Summary

Widespread urbanization on the Edwards aquifer, especially in the unconfined (recharge) zone may affect the current and future status of groundwater quality in the San Antonio and Barton Springs segments of the Edwards aquifer (hereinafter referred to collectively as the “Edwards aquifer”). The karst setting makes the Edwards aquifer particularly vulnerable to contamination from the land surface, and factors such as land cover, aquifer hydrogeology, and changes in hydrologic conditions affect aquifer recharge and vulnerability. Understanding the behavior of continuous fluorescence of dissolved organic matter (fDOM) in groundwater provides insights into organic contaminant transport and microbial and geochemical processes. The U.S. Geological Survey, in cooperation with the San Antonio Water System and the City of Austin, Texas, began continuous monitoring of fDOM and related water-quality parameters at selected sites in or near the Edwards aquifer to provide the data needed to better understand temporal changes in water quality that occur within the aquifer over short- and long-term time scales.

Corrections for fDOM, including temperature, turbidity, and inner-filter effects, are required to develop fully corrected fDOM time-series data. A sensor-specific temperature coefficient of −0.01922 was computed from laboratory experiments and applied to fDOM time-series data. A screening threshold for turbidity of 10 formazin nephelometric units was selected, and corresponding fDOM data were censored from the dataset if turbidity values exceeded this threshold. A screening threshold for inner-filter effects of 100 micrograms per liter as quinine sulfate equivalents (µg/L as QSE) was derived, and fDOM data were censored from the dataset if fDOM values exceeded this threshold.

Continuous hydrologic and water-quality data collected over the 5-year study period (October 1, 2019–September 30, 2024) included water-level altitudes (WLAs), spring discharges, water temperatures, specific conductance values, turbidity values, fDOM values, and nitrate (plus nitrite) concentrations. Baseline fDOM values (that is, fDOM values not associated with increases caused by rainfall/recharge events) ranged from about 0 to 6 µg/L as QSE across all sites. fDOM values above 10 µg/L as QSE were typically associated

with rainfall events, and fDOM values during periods of groundwater recharge regularly exceeded 30 µg/L as QSE and occasionally exceeded 60 µg/L as QSE at sites with greater connectivity to the land surface. The Western Oak well thus appears to have relatively low vulnerability to changes in water quality during periods of rapid groundwater recharge. The Parkwood well can be influenced by recent recharge from surface water through conduit flow paths during wetter hydrologic conditions and, thus, is occasionally vulnerable to contaminants in recharge from surface water. On the basis of the combination of hydrologic responses and frequent inputs of fDOM, the Donella well shows high vulnerability to contaminants in recharge surface-water in comparison to the Western Oak and Parkwood wells. Among the four groundwater monitoring wells, the Shavano well had the most frequent intrusion of fDOM, as well as the greatest fDOM values, indicating relatively high vulnerability to contaminants in recharge surface water in comparison to the other groundwater monitoring wells. The predominance of fDOM values above baseline values may also result from a relatively short residence time of recent surface-water recharge prior to discharge at Barton Springs in comparison to relatively long residence times of recharge water for some of the unconfined monitoring wells and for the San Antonio segment of the Edwards aquifer in general. These results collectively indicate that Barton Springs is likely the most vulnerable site to surface-water contaminants of those considered in this study.

A total of 106 dissolved organic carbon (DOC) samples were collected from four groundwater monitoring wells and Barton Springs to evaluate fDOM as a proxy for DOC. Baseline fDOM values typically were about 1–5 µg/L as QSE, and baseline DOC concentrations were about 0.25–0.70 milligram per liter. Samples with DOC concentrations above baseline values were usually, but not always, associated with samples collected following rainfall/recharge events. Data collected in this study support the use of fDOM as a proxy for DOC in Edwards aquifer groundwater, at least for DOC concentrations less than 3.0 milligrams per liter and fDOM values less than 51 µg/L as QSE.

fDOM monitoring, when used as a proxy for DOC in surface-water recharge, is a tool for understanding recharge processes and the transport of stormwater-runoff-derived contaminants into the Edwards aquifer. Influxes of recharge and associated contaminants were shown to vary on the basis of hydrologic conditions. Under relatively dry hydrologic conditions, when spring discharge and WLAs are low, focused recharge may travel unimpeded through aquifer conduits, suggesting that the aquifer is more directly vulnerable to recharge-associated contaminants during dry hydrologic conditions. Under relatively wet conditions, when spring discharge and WLAs are high, aquifer conduits may be saturated, recharge may be more likely to initially go into matrix storage, and the spring/well response is dampened. The spatial variability in fDOM and corresponding water-quality parameters in response to rainfall/recharge events covers a large range, from sites with little temporal response (for example, the Western Oak well) to sites with rapid responses reflecting discrete recharge pulses (for example, the Shavano well and Barton Springs). The wide range in site responses to rainfall/recharge events is consistent with a correspondingly wide range in immediate vulnerability to surface-derived contaminants across the recharge zone of the Edwards aquifer. Although other continuously monitored water-quality parameters provide insights into changes in water quality in response to varying hydrologic conditions, the quantitative relation between fDOM and dissolved organic carbon directly indicates the timing and magnitude of pulses of organic constituents derived from the land surface, whereas other water-quality parameters do not.

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