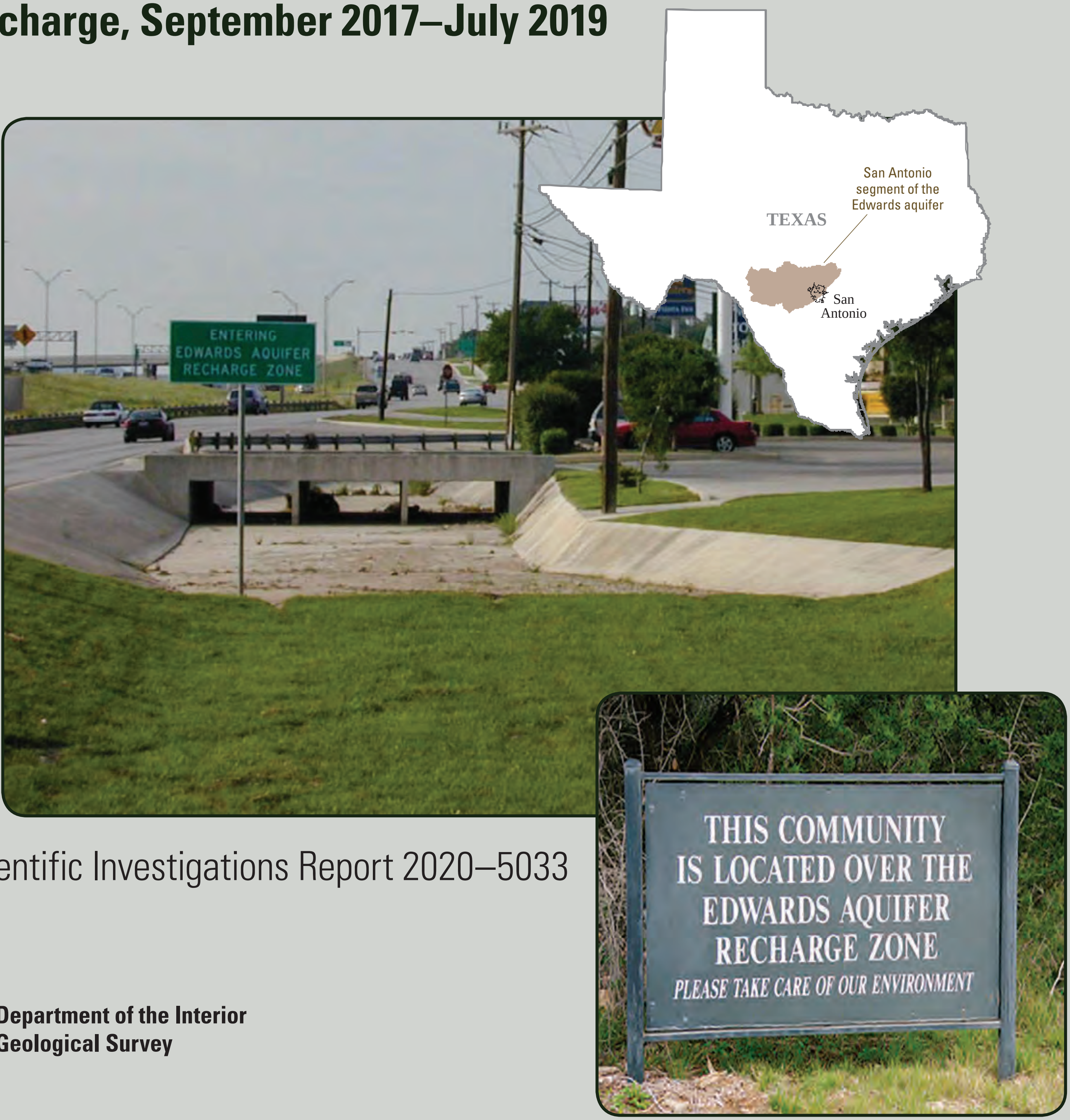
Prepared in cooperation with the City of San Antonio

Temporal and Spatial Variability of Water Quality in the San Antonio Segment of the Edwards Aquifer Recharge Zone, Texas, With an Emphasis on Periods of Groundwater Recharge, September 2017–July 2019



Scientific Investigations Report 2020–5033

U.S. Department of the Interior
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Front cover.

Top, Urbanization on the Edwards aquifer recharge zone in San Antonio, Texas.

Bottom, Edwards aquifer recharge zone community-awareness sign.

Back cover.

Top left, U.S. Geological Survey hydrographers collecting a groundwater sample at the Encino Rio site.

Top right, Pump hoist truck at the Shavano Park at Fawn Drive site.

Bottom, Flood event at the West Elm Creek at Encino Rio site.

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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)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
ounce, fluid (fl. oz)	0.02957	liter (L)
pint (pt)	0.4732	liter (L)
quart (qt)	0.9464	liter (L)
gallon (gal)	3.785	liter (L)
cubic inch (in^3)	0.01639	liter (L)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	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
	Volume	
liter (L)	33.81402	ounce, fluid (fl. oz)
milliliter (mL)	0.03381	ounce, fluid (fl. oz)

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

°F = (1.8 × °C) + 32.

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

°C = (°F – 32) / 1.8.

Datum

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

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

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

Supplemental Information

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

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L), micrograms per liter (µg/L), or nanograms per liter (ng/L). Milligrams per liter and micrograms per liter are units expressing the concentration of chemical constituents in solution as weight of solute (milligrams, micrograms, or nanograms) per unit volume (liter) of water.

Isotope Unit Explanations

Per mil (‰): A unit expressing the ratio of stable-isotope abundances of an element in a sample to those of a standard material. Per mil units are equivalent to parts per thousand. Stable-isotope ratios are computed as follows (Kendall and McDonnell, 1998):

$$\delta X = \{(R\text{sample} - R\text{standard})/R\text{standard}\} \text{ x } 1{,}000$$

where

δ is the “delta” notation,
X is the heavier stable isotope, and
R is ratio of the heavier stable isotope to the lighter stable isotope in a sample or standard.

The δ values for stable-isotope ratios discussed in this report are referenced to the following standard materials.

Element	*R*	Standard identity and reference
Hydrogen	Hydrogen-2/hydrogen-1 (δD)	Vienna Standard Mean Ocean Water (VSMOW) (Fritz and Fontes, 1980)
Oxygen	Oxygen-18/oxygen-16 (δ^{18}O)	Vienna Standard Mean Ocean Water (VSMOW) (Fritz and Fontes, 1980)
Nitrogen-nitrate	Nitrogen-15/nitrogen-14 (δ^{15}N- NO_3)	USGS34 potassium nitrate (KNO_3) and USGS32 KNO_3 (Böhlke and others, 2003)
Oxygen-nitrate	Oxygen-18/oxygen-16 of nitrate (δ^{18}O-NO_3)	USGS34 KNO_3 and USGS35 sodium nitrate ($NaNO_3$) (Böhlke and others, 2003)

Abbreviations

<	less than
$\delta^{18}O$	delta oxygen-18
$\delta^{18}O\text{-}NO_3$	delta oxygen-18 of nitrate
δD	delta deuterium
Ca	calcium
CAAT	chlorodiamino-s-triazine
CEAT	2-chloro-6-ethylamino-4-amino-s-triazine
CIAT	2-chloro-4-isopropylamino-6-amino-s-triazine
Cl	chloride
DON	dissolved organic nitrogen
E	estimated
GOES	Geostationary Operational Environmental Satellite
HCO_3	bicarbonate
K	potassium
LRL	laboratory reporting level
MCL	maximum contaminant level
MDL	method detection level
Mg	magnesium
N	nitrogen
n	number
Na	sodium
NH_4	ammonia
NO_2	nitrite
NO_3	nitrate
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OIAT	2-hydroxy-4-isopropylamino-6-amino-s-triazine
OIET	2-hydroxy-4-isopropylamino-6-ethylamino-s-triazine
ortho-P	orthophosphate
P	phosphorus
QA	quality assurance
RPD	relative percent difference
RRL	raised reporting level
SC	specific conductance
SiO_2	silica
SO_4	sulfate
Sr	strontium
$^{87}Sr/^{86}Sr$	strontium-87/strontium-86
SUNA	Submersible Ultraviolet Nitrate Analyzer
TDN	total dissolved nitrogen
TN	total nitrogen
TON	total organic nitrogen
USGS	U.S. Geological Survey
WLA	water-level altitude

U.S. Geological Survey hydrographers preparing the Shavano Park at Fawn Drive site for hydrologic and water-quality monitoring.

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By Stephen P. Opsahl, MaryLynn Musgrove, and Keith E. Mecum

Abstract

Ongoing urbanization on the Edwards aquifer recharge zone in the greater San Antonio area raises concern about the potential adverse effects on the public water supply from development. To address this concern, the U.S. Geological Survey, in cooperation with the City of San Antonio, studied patterns of temporal and spatial changes in water quality at selected surface-water and groundwater sites in the Edwards aquifer recharge zone, with an emphasis on changes during periods of groundwater recharge. Water-quality characteristics were continuously monitored and discrete water samples were collected at two sets of paired surface-water (stream) and groundwater (well) sites during a 2-year period (2017–19) that included relatively dry conditions and a large recharge event in September 2018 when as much as 16 inches of rain fell in parts of the study area.

Continuous monitoring of water-level altitude, specific conductance, and concentrations of nitrate in two wells completed in the Edwards aquifer provided high-resolution data showing detailed changes in water quality across a broad range of hydrologic conditions. Water levels in the wells responded rapidly (within hours to days) to recharge from both small and large rainfall and runoff events; changes in groundwater quality as a consequence of the influx of surface-derived recharge were indicated by changes in values of the monitored characteristics. A broad range in measured values of the stable isotopes of water expressed as delta deuterium and delta oxygen-18 in the water samples collected from two streams (Salado and West Elm Creeks), in comparison to the tight clustering of the values of these isotopes in groundwater samples, indicates that source waters (surface waters) of widely varying chemical characteristics become homogenized within the aquifer system.

Concentrations of major ions, trace ions, and nutrient concentrations in stormwater runoff indicate a combination of land-derived and rainfall-derived constituents. The distribution of concentrations of nitrogen species (nitrite, nitrate, and nitrogen in ammonia) among sampling sites transitions from a more variable distribution in stormwater runoff to a more uniform distribution in groundwater in which the dominant form is nitrate. Differences in nitrate isotopic composition and concentration in groundwater across the study area are likely controlled by the relative contributions of natural and anthropogenic nitrogen (with the anthropogenic nitrogen component including a wastewater source) and by the process of nitrification. Among all measured constituents, pesticides detected in discrete stormwater-runoff samples provided the clearest indication that urbanization was adversely affecting water quality; specifically, the more urbanized surface-water site had a greater number of detections and greater variety of detected pesticides. Though temporal variability in the numbers and types of pesticides was evident, the overall proportion of pesticides was dominated by triazine herbicides including atrazine, atrazine degradates, and simazine. The observed hydrologic responses to rainfall and corresponding changes in water quality in wells are thought to result from the direct hydrologic connectivity of surface water and unconfined groundwater; however, patterns of groundwater-quality change indicate mixing from multiple sources such as ambient groundwater, recent surface-derived recharge, and possibly inflow from other aquifers. Therefore, understanding the connection between urbanization and groundwater quality cannot be inferred from the input of stormwater runoff alone as changes related to local and regional hydrologic conditions also need to be considered. It should be noted that a single study comparing the results from two site pairs is not able to support definitive conclusions about the full effect of urbanization on surface water/groundwater quality; however, this study does provide useful insights about the spatial and temporal variability of both stormwater runoff and unconfined groundwater that are consistent with expectations based on the current conceptual model that depicts the Edwards aquifer surface-water/groundwater system as a single water resource.

Introduction

Widespread urbanization in south-central Texas raises concerns about the potential adverse effects of residential and commercial development on water quality of the Edwards aquifer. The San Antonio segment of the Edwards aquifer (hereinafter referred to as the "Edwards aquifer"), in south-central Texas (fig. 1), is a designated sole-source aquifer (U.S. Environmental Protection Agency, 2019a) and the primary water supply for more than 1.7 million people in San Antonio and the surrounding area (Tremallo and others, 2015; Greater Edwards Aquifer Alliance, 2020). The Edwards aquifer is a karst aquifer consisting primarily of carbonate rock (limestone) that has partially dissolved and is able to hold and transport substantial volumes of water within its matrix (White, 1988). Groundwater recharge occurs primarily in the unconfined zone of the Edwards aquifer (fig. 1) (Puente, 1978; Maclay and Land, 1988), though leakage from the underlying Trinity aquifer might also contribute to the Edwards aquifer (Lindgren and others, 2004). The porous nature of the Edwards aquifer recharge zone makes the system vulnerable to contamination from sources at the land surface because the rapid transport of surface-water recharge through sinkholes and losing reaches of streams provides little opportunity for subsurface filtration, sorption, or degradation of the contaminants (White, 1988). Ongoing residential and commercial development in Bexar County, Tex., on the Edwards aquifer recharge zone has the potential to increase the diversity and concentration of contaminants in stormwater runoff and, thereby, in water recharging the aquifer (Musgrove and others, 2016; Opsahl and others, 2018a).

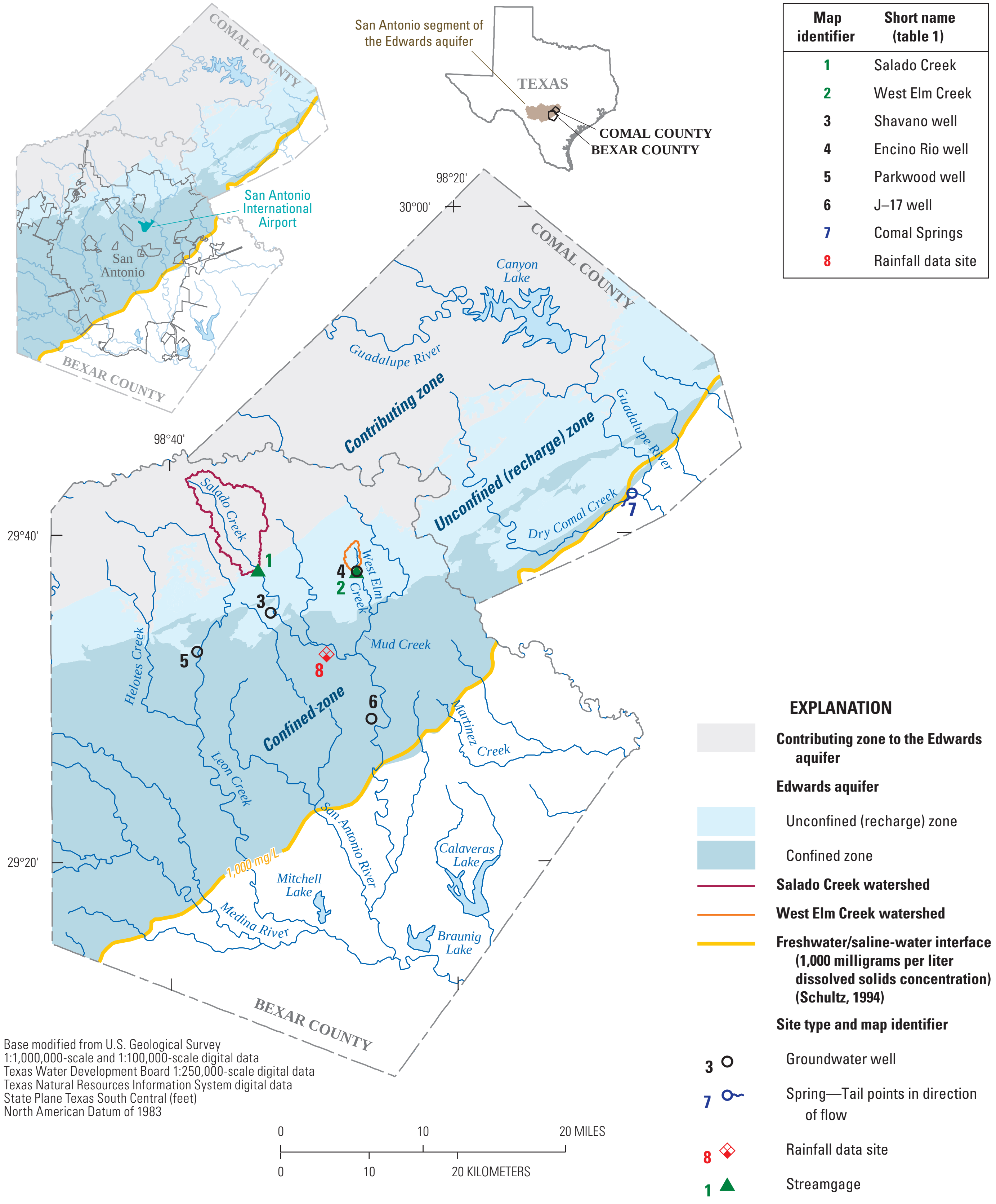
Nutrients such as nitrogen (N) and phosphorus (P) are essential elements for plant and animal life but can be detrimental at concentrations considerably above natural levels (U.S. Environmental Protection Agency, 2019b). Nitrate-N (hereinafter referred to as "NO_3") is a nutrient of concern to human health and ecosystems and has a maximum contaminant level in drinking water of 10 milligrams per liter (mg/L) (U.S. Environmental Protection Agency, 2019b). Concentrations of NO_3 in groundwater at some locations in the San Antonio segment of the Edwards aquifer have approximately doubled since the 1930s (Musgrove and others, 2016), though current (2020) concentrations are generally well below the maximum contaminant level. In recent studies (Opsahl, 2012; Opsahl and others, 2018a), the temporal and spatial patterns of NO_3 concentrations in regional recharge streams of the Edwards aquifer showed considerable variability in source waters to the aquifer. Given the presence of many recharge streams in and around the urbanizing areas of San Antonio, more focused studies of the spatial and temporal variability of NO_3 are needed to distinguish natural from anthropogenic NO_3 sources to the aquifer and to determine how urbanization might affect NO_3 contributions to the deeper aquifer system.

The term "pesticides," as used in this study, refers to anthropogenic organic compounds that are widely used in urban and agricultural settings to kill or control plants (herbicides), insects (insecticides), fungi (fungicides), or other organisms, and to the degradates of these compounds. Between 1992 and 2001, the herbicides most commonly detected in streams and groundwater at urban areas in the United States were prometon (streams) and atrazine (groundwater), and the insecticides most commonly detected in urban areas were diazinon (streams) and dieldrin (groundwater) (Gilliom and others, 2006). Previous studies of the Edwards aquifer have documented the occurrence, distribution, and temporal variability of these and other pesticides in recharge streams and groundwater (Bush and others, 2000; Fahlquist and Ardis, 2004; Musgrove and others, 2010; Opsahl and others, 2018a). Types of pesticides, however, have changed over time, with relatively new pesticides continually made available to consumers, which have the potential for being introduced into the environment.

Water-resource managers working on the Edwards aquifer have implemented management practices for aquifer protection such as the creation of conservation easements to protect water quality and the long-term health of the region's public water supply (City of San Antonio, 2020; Edwards Aquifer Authority, 2020a; San Antonio Water System, 2020). Surface-water/groundwater interactions along the Edwards aquifer recharge zone are complex, and tracing the potential connections between stormwater runoff and the groundwater system is challenging. Nevertheless, a better understanding of the sources and transport of common urban contaminants—in particular, nutrients and pesticides—is needed to assess the potential effects of urban development on regional water quality in the Edwards aquifer. To address these challenges, the U. S. Geological Survey (USGS), in cooperation with the City of San Antonio, studied patterns of temporal change in water quality at selected surface-water and groundwater sites in the Edwards aquifer recharge zone, with an emphasis on changes during periods of groundwater recharge.

Purpose and Scope

This report provides information for water managers and the scientific community on the possible effects of urbanization on water quality in the Edwards aquifer recharge zone. The report assesses the temporal and spatial variability of water quality in the San Antonio segment of the Edwards aquifer recharge zone, with an emphasis on periods of groundwater recharge during the period September 2017–July 2019. Continuous and discrete water-quality data were collected at paired urban stormwater runoff and unconfined groundwater sites in the recharge zone of the Edwards aquifer, and these data were evaluated to gain insights into the relation between surface-water and groundwater quality at sites representing different degrees of urbanization. Differences in selected water-quality constituents and hydrologic properties at the paired sites are described during relative dry conditions and after a large recharge event. Hydrologic connectivity between the water quality of stormwater runoff and recharge was evaluated in terms of which constituents were most likely affected by urbanization in the study area.



Map identifier	Short name (table 1)
1	Salado Creek
2	West Elm Creek
3	Shavano well
4	Encino Rio well
5	Parkwood well
6	J–17 well
7	Comal Springs
8	Rainfall data site

Base modified from U.S. Geological Survey
1:1,000,000-scale and 1:100,000-scale digital data
Texas Water Development Board 1:250,000-scale digital data
Texas Natural Resources Information System digital data
State Plane Texas South Central (feet)
North American Datum of 1983

Figure 1. Hydrogeologic setting and study site locations in the San Antonio segment of the Edwards aquifer, Bexar and Comal Counties, south-central Texas.

Hydrogeologic Setting

The Edwards aquifer consists of heavily faulted, fractured, and karstified Early Cretaceous-aged limestone and dolomitic rocks with extensive dissolution that yielded a porous matrix (Barker and Ardis, 1996). The northern and central parts of Bexar County include parts of the Edwards aquifer contributing zone, unconfined (recharge) zone, and confined zone (fig. 1). The recharge zone consists of Edwards Group limestone exposed at the land surface (Hamilton and others, 2008). Downdip from the recharge zone, the aquifer becomes confined and is artesian in places. Most public-supply wells withdraw water from the confined zone of the Edwards aquifer. The aquifer is bounded to the south by the freshwater/saline-water interface, downgradient from which the salinity of the water rises rapidly (dissolved solids concentration exceeds 1,000 mg/L), and the water is considered unpotable (Schultz, 1994).

Most of the recharge to the Edwards aquifer takes place by direct infiltration from streams that drain the contributing zone (fig. 1) as they cross the recharge zone and enter the aquifer through solution-enlarged conduits and sink holes in the channel bed (Puente, 1978; Maclay and Land, 1988). Intense storms with heavy rainfall are common, and flash flooding in streams greatly enhances groundwater recharge following such storms. Additional recharge to the Edwards aquifer comes from a combination of diffuse seepage and leakage from adjacent aquifers (Sharp and Banner, 1997; Lindgren and others, 2004). Water-level altitudes (WLAs) in the aquifer can rise rapidly in response to rainfall and corresponding recharge; conversely, WLAs decrease during periods of low rainfall and corresponding lack of recharge. The flow paths of recharge and regional groundwater in the Edwards aquifer were described by Lindgren and others (2009). Recharge water in the unconfined zone flows downdip to the confined zone (fig. 1). Regional groundwater flow is generally from west to east through Bexar County and shifts to northeasterly flow through Comal County, where considerable discharge occurs at Comal Springs. WLA at the Bexar County index well, J–17 (site 6 on fig. 1), and the discharge at Comal Springs (site 7 on fig. 1) are considered to be representative of regional hydrologic conditions in the Edwards aquifer and thus are continuously monitored (Edwards Aquifer Authority, 2020b) and used for regulatory purposes and the development of water-management strategies.

Regional Geography and Demographics

As of 2018, there were approximately 461 square miles of urbanized area in Bexar County in south-central Texas, and neighboring Comal County ranked as one of the 10 fastest growing counties in the Nation among counties with a population of at least 10,000 (U.S. Census Bureau, 2019). In 2018, San Antonio was the seventh largest city in the United States, with a population of about 1.53 million (U.S. Census Bureau, 2019). San Antonio is the principal urban area overlying and supplied by the Edwards aquifer. Between 2010 and 2018, the population of Bexar County increased from 1.72 million to 1.99 million people (approximately a 16 percent increase), while the population of Comal County increased from 108,472 to 148,373 people (approximately a 37 percent increase) (U.S. Census Bureau, 2019). Most of the growth in the greater San Antonio area is occurring on the Edwards aquifer contributing and recharge zones (fig. 1), and the land-use changes associated with urban development are altering surface topography.

Study Methods

Hydrologic and water-quality data were collected for a 2-year period at two sets of paired surface-water and groundwater sites. Ancillary climatic and hydrologic data available from other monitoring sites and networks also were used in the analyses and interpretations made in this study (fig. 1; table 1). Hydrologic data, including WLAs, water temperature, specific conductance (SC), and NO_3 concentrations were continuously monitored. All sites will hereinafter be referred to by their short names (table 1).

Study Design

The study design was based on previous and ongoing work in and around the San Antonio area (Musgrove and others, 2010, 2011; Opsahl, 2012; Opsahl and others, 2018a; Musgrove and others, 2019). Data were collected at two sets of paired sites to provide a detailed comparison of the chemical quality of stormwater runoff in recharging (losing) streams and the water within the unconfined Edwards aquifer. The first site pair was the Salado Creek site and the Shavano well (fig. 1; table 1). This site pair was selected because of minimal urban development in the catchment area of this watershed. Salado Creek is an ephemeral stream that typically flows only in response to substantial rain events, and some stormwater runoff from Salado Creek contributes to local groundwater recharge. The Shavano well was paired with the Salado Creek site because a general hydrologic connection between groundwater recharge from specific karstic features in the northwestern part of the contributing and recharge zones with monitoring wells further south has been recognized (Johnson and others, 2010). Although considered a site pair in this study, the degree of hydrologic connectivity between Salado Creek and the Shavano well has not been established.

The second site pair was the West Elm Creek site and the Encino Rio well in northern San Antonio (fig. 1; table 1), an area in the recharge zone that is undergoing considerable urban development. The drainage area of the West Elm Creek site is much smaller than that of the Salado Creek site (fig. 1), and the chemical characteristics of stormwater runoff from West Elm Creek, also an ephemeral stream, is likely to be more influenced by urban processes. The degree of hydrologic connectivity between West Elm Creek and the Encino Rio well has not been established.

Table 1. Sites at which hydrologic data were obtained and water-quality samples were collected in the San Antonio segment of the Edwards aquifer recharge zone, south-central Texas, 2017–19.

[USGS, U.S. Geological Survey; EAA, Edwards Aquifer Authority; GHCN, Global Historical Climatology Network; dd, decimal degrees referenced to North American Datum of 1983; ft, foot; NAVD 88, North American Vertical Datum of 1988; NA, not applicable; QWs, stormflow-runoff water quality; WLA, water-level altitude; QWp, periodic water quality; QWc, continuous water quality; QWn, continuous nitrate water quality; SF, streamflow; US, United States; RF, rainfall]

Map identifier (fig. 1)	Site type	USGS, EAA, or GHCN station number	USGS, EAA, or GHCN station name	Short name (fig. 1)	Latitude (dd)	Longitude (dd)	Elevation of land surface (ft above NAVD 88)	Well depth (ft below land surface)	Water-quality sensor depth (ft below land surface)	Nitrate sensor depth (ft below land surface)	Data type
1	Streamgaging station	08178585	Salado Creek at Wilderness Road, San Antonio, Texas[1]	Salado Creek	29.630	98.565	NA	NA	NA	NA	QWs
2	Streamgaging station	08178638	West Elm Creek at Encino Rio at San Antonio, Texas[1]	West Elm Creek	29.629	98.449	NA	NA	NA	NA	QWs
3	Groundwater well-unconfined	293516098325501	Shavano Park at Fawn Drive[1]	Shavano well	29.588	98.549	975	300	270	295	WLA, QWp, QWc, QWn
4	Groundwater well-unconfined	293746098265401	Encino Rio[1]	Encino Rio well	29.629	98.448	845	290	265	275	WLA, QWp, QWc, QWn
5	Groundwater well-unconfined	293252098380801	AY-68-27-610 (Parkwood Park)[1]	Parkwood well	29.548	98.636	896	229	NA	NA	NA
6	Groundwater well-confined	6837203	Bexar County index well J–17[2,3]	J–17 well	29.479	98.433	730.8	874	NA	NA	WLA
7	Spring	08168710	Comal Springs[1]	Comal Springs	29.706	98.123	NA	NA	NA	NA	SF
8	Weather station	USW00012921	San Antonio International Airport TX US[4]	Rainfall data site	29.544	98.484	NA	NA	NA	NA	RF

[1] USGS station.

[2] EAA station.

[3] Bexar County index well (J–17) water-level altitudes are reported and referenced to the National Geodetic Vertical Datum of 1929.

[4] GHCN station.

Continuous Monitoring of Hydrologic Data

Continuous monitoring of various types of hydrologic data began in September 2017 and continued through July 2019. Stage refers to the altitude of the water surface in a stream above an arbitrary reference point (Rantz and others, 1982a, b). Stage at the Salado Creek and West Elm Creek sites was recorded every 15 minutes and transmitted hourly by the Geostationary Operational Environmental Satellite (GOES) transmitter to the USGS National Water Information System (NWIS) database (U.S. Geological Survey, 2019). The sites were visited periodically to verify the recorded stage (Rantz and others, 1982a; Turnipseed and Sauer, 2010). The information obtained during the site visits was applied to update the stage record (Rantz and others, 1982b; Kennedy, 1983, 1984; Sauer and Turnipseed, 2010), which is stored in the NWIS database (U.S. Geological Survey, 2019). Continuous WLA data were collected from the Shavano and Encino Rio wells (fig. 1; table 1) using methods described by Cunningham and Schalk (2011). At each well, water-level data were recorded in feet below a known land-surface datum at 15-minute intervals and periodically verified with discrete measurements by using a calibrated water-level tape. The 15-minute water-level data were transmitted hourly by the GOES transmitter to the NWIS database (U.S. Geological Survey, 2019). In NWIS, the water-level data were then converted to WLA data by using either the National Geodetic Vertical Datum of 1929 (NGVD 1929) or the North American Vertical Datum of 1988 (NAVD 1988) reference datum. Water-quality sensors were placed near the bottom of the Shavano and Encino Rio wells (at approximate depths shown in table 1), where available stratigraphic data and geophysical logs indicated that the most productive water-bearing zones were likely present. Prior studies have indicated that the water in wells in this area generally is vertically well mixed (Lindgren, 2006; Musgrove and others, 2011; Opsahl and others, 2017). The wells were instrumented with multiparameter EXO 1 water-quality sensors (YSI Incorporated) to collect water temperature and SC data. The 15-minute water-quality data were transmitted hourly via GOES to the NWIS database (U.S. Geological Survey, 2019). A longer record of continuous water-quality monitoring at the Shavano well is also available (U.S. Geological Survey, 2019); historical data are available for context and are discussed in more detail by Musgrove and others (2019).

NO_3 was continuously monitored at the Shavano and Encino Rio wells by a Submersible Ultraviolet Nitrate Analyzer (SUNA) (Sea-Bird Scientific, 2020). The measuring principle of the SUNAs used in this study is based on optical absorption (Pellerin and others, 2013). NO_3 and nitrite (NO_2) have similar absorption properties, and the SUNAs detect both constituents in a composite measurement. Because NO_2 concentrations in the types of water monitored in this study are uniformly low and account for little of the TN (Opsahl and others, 2017), the composite NO_3 and NO_2 measurements made with the SUNAs and reported in this study are hereinafter referred to as “NO_3 concentrations.” The water-quality sensors were maintained during periodic field visits to clean and verify the calibration, using methods described by Pellerin and others (2013). The precision of the NO_3 sensor measurement in Edwards aquifer groundwater is plus or minus 0.07 mg/L with a 95-percent confidence interval (Opsahl and others, 2017). Concentrations of NO_3 were measured hourly and transmitted via GOES to the NWIS database (U.S. Geological Survey, 2019).

Additional hydrologic data used in this assessment included daily rainfall data, continuous WLA data from the J–17 index well, and records of continuous discharge at Comal Springs (table 1). Daily rainfall data for the San Antonio International Airport were acquired from the Global Historical Climatology Network (Menne and others, 2012; National Oceanic and Atmospheric Administration, 2020). WLA data for the J–17 index well were obtained from the Edwards Aquifer Authority’s online database (Edwards Aquifer Authority, 2020b). Comal Springs discharge data were obtained from the NWIS database (U.S. Geological Survey, 2019).

Collection and Analyses of Discrete Water Samples

Samples for chemical analyses were collected at surface-water sites intermittently between August 2017 and December 2018. On August 8, 2017, stormwater-runoff samples were collected from Salado Creek and West Elm Creek (fig. 1) prior to the beginning of continuous monitoring; Salado Creek and West Elm Creek are ephemeral streams that flow for short periods following storm events, which means there are few opportunities to collect any samples from these normally dry sites. All 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). Stormwater-runoff samples were collected by using ISCO 6712 autosamplers (Teledyne ISCO, 2020). For samples collected with the autosampler, flow-weighted samples were composited by using a point-integrated sampling method (Burkham, 1985). Each sample was drawn through a fixed intake mounted at the midpoint of the stream channel. Autosamplers were triggered at predetermined water levels that were indicative of the onset of streamflow. The autosampler was programmed to collect 450-milliliter samples every 15 minutes and sequentially fill each of four 3.6-liter bottles during the runoff event. The samples were retrieved within 4 hours following the runoff event, immediately placed on ice, and transported to the USGS South Texas Program Office laboratory in San Antonio for processing. The four 3.6-liter samples collected by the autosampler were stage-weighted and composited into a single sample to represent mean concentration values during the event. Not all stormwater-runoff samples could be collected as stage-weighted composites because of the occurrence of multiple streamflow peaks or mechanical problems with autosamplers. In some instances, multiple grab samples (about four bottles over a period of 15 minutes) were collected from the edge of the stream or bridge and composited into a single sample. Constituent concentrations from multiple grab samples are considered to represent instantaneous event concentrations. Samples collected either with autosamplers or as grab samples were composited in a Teflon churn. Subsamples for specific analysis were withdrawn from the churn and preserved as required by the analyzing laboratory. For the purposes of this report, all stormwater-runoff samples are considered to represent instantaneous event concentrations and are not used to compute loadings of individual constituents.

Water samples were collected from the Shavano and Encino Rio wells approximately every 8 weeks between September 2017 and July 2019. These were considered “routine samples,” in that they were collected without regard to hydrologic conditions. Additional samples were collected in response to recharge-generating storms and corresponding rises in WLAs to characterize the aquifer response during suspected groundwater recharge events. Groundwater samples were collected as described in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). A Grundfos Redi-Flo2 pump equipped with Teflon tubing (Geotech, 2020) was used to sample water from the Encino Rio well. At the Shavano well, a Grundfos Redi-Flo3 pump (Geotech, 2020) was permanently installed in situ and used to collect the samples. Because the Shavano well is purged daily by USGS personnel, only a short purge time is required to achieve stability of field properties (water temperature, dissolved-oxygen concentration, pH, turbidity, and SC). Prior to sample collection at the Encino Rio well, three casing volumes were purged to ensure the sampled water was representative of that in the surrounding formation. Field properties were monitored until they had stabilized and were recorded just prior to sample collection (Wilde, variously dated).

Filtered and unfiltered water-quality samples were collected and processed immediately in the field, placed on ice, and shipped to the appropriate laboratory. The samples were analyzed for major ions, trace ions, nutrients, pesticides, and pesticide degradates by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Measured nutrient species included NO_3 plus NO_2, NO_2, ammonia (NH_4) plus organic N, orthophosphate (ortho-P), and P on filtered samples, and P and NH_4 plus organic N on unfiltered samples. Calculated nutrient species included NO_3 (measured NO_3 plus NO_2 concentration minus the measured NO_2 concentration), dissolved organic nitrogen (DON; measured NH_4 plus organic N concentration minus the measured NH_4 concentration from filtered water samples), total dissolved nitrogen (TDN; sum of the measured concentrations of NO_3, NO_2, and NH_4 plus organic N), total nitrogen (TN; sum of unfiltered NH_4 plus organic N, and filtered NO_3, and NO_2), and total organic nitrogen (TON; sum of unfiltered NH_4 plus organic N, filtered NO_3, and filtered NO_2). Unfiltered NO_3 and NO_2 were not measured in this study but filtered NO_3 and NO_2 values were considered representative of unfiltered NO_3 and NO_2 as these constituents are readily soluble in water (Hem, 1985). Dissolved solids were calculated as the sum of the measured major ions (calcium [Ca], magnesium [Mg], sodium [Na], potassium [K], silica [SiO_2], chloride [Cl], sulfate [SO_4], and alkalinity [carbonate/bicarbonate (HCO_3) expressed as carbonate equivalent]), plus the sum of all other measured dissolved constituents. Major ions typically make up the bulk of the dissolved constituents in a sample (Hem, 1985). All N species are reported in units of milligrams per liter as N and discussed as N. Ortho-P is reported in units of milligrams per liter as P and discussed as P. Stable isotopes of water (deuterium [δD] and delta oxygen-18 [$\delta^{18}O$]) and stable isotopes of NO_3 (delta nitrogen-15 of nitrate [$\delta^{15}N\text{-}NO_3$] and delta oxygen-18 of nitrate [$\delta^{18}O\text{-}NO_3$]) were analyzed by the USGS Reston Stable Isotope Laboratory in Reston, Virginia. Strontium (Sr) isotopes (strontium-87/strontium-86 [$^{87}Sr/^{86}Sr$]) were analyzed by the USGS Metal and Metalloid Isotope Laboratory in Menlo Park, California. Alkalinity was titrated either in the field or at the USGS South Texas Program Office shortly after sampling and also was measured on samples sent to the NWQL. Laboratory methods and reporting levels for analysis of major and trace ions, nutrients, and selected environmental isotopes are previously described (table 2 in Opsahl and others, 2018a).

Pesticides were analyzed by using the method described in Sandstrom and others (2015). This method analyzes for 226 pesticides and pesticide degradates using liquid chromatography-tandem mass spectrometry. Mass spectrometry provides positive identification of individual pesticides at very low levels, and concentrations are reported in units of nanograms per liter (ng/L). Reporting of results is described in detail by Sandstrom and others (2015). Briefly, the method detection level (MDL) is the minimum concentration of an analyte that can be identified, measured, and reported with 99-percent confidence that the analyte concentration is greater than zero. At the MDL, the risk of a false positive (reporting a detection when no analyte is present) is predicted to be less than 1 percent (Childress and others, 1999). The laboratory reporting level (LRL) is set at twice the MDL. An LRL is the less-than (<) value reported to data users when the pesticide is not detected. The LRL is used to control false-negative error; the risk of a false negative (not detecting an analyte when present) is less than 1 percent at the LRL (Childress and others, 1999). Pesticide data occasionally contain raised reporting levels (RRLs). An RRL is a less-than value reported at a concentration higher than the LRL. RRLs can vary in magnitude above the standard LRL and can result from a variety of environmental and analytical circumstances (Shoda and others, 2018). In pesticide analyses of previously used laboratory schedules, RRLs have been retained in the dataset as nondetected values (Martin and Eberle, 2011; Oelsner and others, 2017), treated as missing values and not used in data interpretation (Ryberg and others, 2010), or screened at user-defined levels (Gilliom and others, 2006).

The NWQL routinely reports pesticide concentrations below the LRL and MDL, which increases the likelihood of false-negative and false-positive results and adds greater uncertainty to the results. The laboratory also provides other qualifying information that indicates the relative degree of uncertainty to which reported concentrations are subject. Such information is important to consider, especially when comparing nondetected values for individual compounds with compounds having different LRLs and MDLs. Greater uncertainty, which typically is associated with low (near or below the LRL) concentrations but can also be caused by certain analytical conditions or aspects of method performance, needs to be considered during data analysis and interpretation. Care also must be taken when RRLs are associated with specific detections, especially when comparing a nondetection reported with an RRL to a measured concentration reported at a level below that RRL for the same compound or to a nondetection reported at the standard (lower) LRL for that compound. Some pesticide results were qualified as estimated (“E”) if the compound has inherently high analytical variability or if there were instances of laboratory blank contamination (Shoda and others, 2018). Recognizing these methodological caveats for reporting results, the analysis and interpretation of pesticides in this study are based primarily on the occurrence of pesticide detections rather than pesticide concentrations, regardless of differences in reporting levels; however, all pesticide-concentration data and associated laboratory qualifiers for each value are available in NWIS (U.S. Geological Survey, 2019). All pesticide detections reported by the NWQL, including those reported below the MDL, are considered as detections in this study.

Median concentrations were reported for nutrients, major ions, trace ions, and environmental isotopes based on simple ranking of individual values. Nondetections were included in this ranking, and constituents having more than half of reported values as nondetections were assigned the nondetection value as its median concentration. The Mann-Whitney U test was used to test for differences between medians of constituent concentrations; differences were considered statistically significant for *p*-values less than 0.05. All data collected as part of this study are available in NWIS (U.S. Geological Survey, 2019).

Quality Assurance of Water Samples

Quality-assurance (QA) samples, including field-equipment blanks and sequential-replicate environmental samples, were collected and analyzed to evaluate bias and variability of environmental samples. Bias is the systematic error inherent in a method or caused by some artifact of the measurement system. Variability is the extent to which data points in a statistical distribution or dataset diverge from the average (or median) value, as well as the extent to which these data points differ from each other (Mueller and others, 2015). All replicate and blank QA samples were analyzed for major ions, nutrients, trace ions, and pesticide compounds. Isotopes were analyzed in replicate QA samples but were not analyzed in blank QA samples. In addition to the QA samples submitted from the field, the USGS NWQL provides internal QA data for laboratory blanks, replicates, and spikes. NWQL personnel screen these internal QA data for potential errors prior to making the environmental sample data publicly available (Medalie and others, 2019).

Constituents detected in autosampler field-equipment blanks (number [n] = 2) included two detections of Cl and one detection of the pesticide disulfoton oxon sulfone (table 2). Cl concentrations were 0.11 mg/L and 0.36 mg/L in the blank samples, and the lowest environmental concentration reported in this study was 1.23 mg/L (table 3). On the basis of these concentrations, Cl contamination could result in as much as 26 percent positive bias in the Cl concentrations measured in samples collected using the autosampler. Although disulfoton oxon sulfone was detected in one of the autosampler blank QA samples, it was not detected in any environmental samples and is not discussed further in this report.

The groundwater-pump field-equipment blank was not collected at either of the sites specific to this study, but it was collected at the Parkwood well, an unconfined groundwater site (fig. 1; table 1) with similar hydrogeological properties and at which the same sample collection procedures are used that were used for samples collected in this study. There was one detection of Ca in the groundwater-pump field-equipment blank and no detections of pesticides. The Ca concentration was 0.025 mg/L in this blank sample, a negligible concentration compared to the lowest measured value in groundwater (96.6 mg/L) (table 4); therefore, it was likely that any Ca contamination bias associated with the groundwater pump was negligible. No environmental Ca data were censored (removed from the dataset) in this study on the basis of the groundwater-pump field-equipment blank sample results.

Table 2. Quality-assurance data for selected constituents detected in field-equipment blank water samples and sequential-replicate samples.

[LRL, laboratory reporting level; n, number of samples; mg/L, milligram per liter; ng/L, nanogram per liter; RPD, relative percent difference; %, percent; ND, not determined]

Quality assurance data for field-equipment blank samples		
Constituent	**LRL**	**Blank sample concentration**
Autosampler field-equipment blanks (n=2)		
Chloride, filtered (mg/L)	0.02	0.11, 0.36
Disulfoton oxon sulfone, filtered (ng/L)	6.00	2.69
Groundwater pump field-equipment blank (n=1)		
Calcium, filtered (mg/L)	0.022	0.025

Quality-assurance data for sequential-replicate samples		
Constituent	**LRL**	**RPD (%)**
Selected split replicate RPDs from three replicate sample pairs[1]		
Ammonia plus organic nitrogen, filtered (mg/L as N)	0.07	36
Ammonia plus organic nitrogen, unfiltered (mg/L as N)	0.07	29
Organic carbon, filtered (mg/L)	0.23	11, 12
2-Chloro-4-isopropylamino-6-amino-s-triazine (CIAT), filtered (ng/L)	11.0	7
2-Hydroxy-4-isopropylamino-6-amino-s-triazine (OIAT), filtered (ng/L)	4.00	8, 4
Atrazine, filtered (ng/L)	6.80	22
Chlorodiamino-s-triazine (CAAT), filtered (ng/L)	24.0	8, 17
Imidacloprid, filtered, (ng/L)[2]	16.0	ND
Propoxur, filtered (ng/L)[2]	3.20	ND
Simazine, filtered (ng/L)	7.20	23

[1] Only replicate sample differences calculated as greater than 5 percent are shown.

[2] Constituent was only detected in either the environmental or sequential-replicate sample; therefore, a corresponding RPD could not be calculated.

Sequential-replicate samples were collected to evaluate variability resulting from the sample collection and analytical processes. A relative percent difference (RPD) was calculated for replicate pairs as follows:

$$RPD = |C_1 - C_2| / ((C_1 + C_2)/2) \times 100, \qquad (1)$$

where

C_1 is the constituent concentration, in milligrams per liter, from the environmental sample; and

C_2 is the constituent concentration, in milligrams per liter, from the replicate sample.

RPDs were calculated for all major and trace ions, nutrients, isotopes, and pesticides and almost all values were below 5 percent. All constituents for which RPDs were greater than 5 percent are indicated in table 2. NH_4 plus organic-N in filtered and unfiltered samples and dissolved organic carbon (DOC) had RPDs greater than 5 percent, but these occurred in groundwater samples in which measured concentrations of these constituents are near the LRL, where higher percent deviations would be expected. Only a few RPDs for pesticides were greater than 5 percent. RPDs for the pesticides imidacloprid and propoxur could not be calculated; these two pesticides were detected in only one sample of the replicate pair (either in the environmental sample or sequential-replicate sample, but not in both). Small RPDs for most constituents indicate little variability associated with sampling and analytical processes.

Table 3. Summary of analyses for selected constituents measured in discrete water samples collected from Salado Creek and West Elm Creek, 2017–19.

[LRL, laboratory reporting level; Ca, calcium; mg/L, milligram per liter; Mg, magnesium; Na, sodium; HCO_3, bicarbonate; Cl, chloride; SO_4, sulfate; NH_4, ammonia as nitrogen; mg N/L, milligram nitrogen per liter; <, less than; NO_3, nitrate as nitrogen; NO_2, nitrite as nitrogen; DON, dissolved organic nitrogen; TON, total organic nitrogen; Ortho-P, orthophosphate as phosphorus; mg P/L, milligram phosphate per liter; TDN, total dissolved nitrogen; TN, total nitrogen; Sr, strontium; µg/L, microgram per liter; δD, delta deuterium in water; δ^{18}O, delta oxygen-18 in water; δ^{15}N-NO_3, delta nitrogen-15 in nitrate; δ^{18}O-NO_3, delta oxygen-18 in nitrate]

Map identifier (fig. 1; table 1)	Short name (fig. 1; table 1)	Constituent (and units of measurement)	Number of samples	Number of concentrations equal to or greater than the LRL	Minimum value	Maximum value	Median value
1	Salado Creek	Ca (mg/L)	4	4	16.5	34.4	20.4
		Mg (mg/L)	4	4	1.66	4.31	2.22
		Na (mg/L)	4	4	0.69	2.50	1.13
		HCO_3 (mg/L)	4	4	47.2	113	57.5
		Cl (mg/L)	4	4	1.28	3.48	1.78
		SO_4 (mg/L)	4	4	2.23	13.4	5.04
		NH_4 (mg N/L)	4	3	<0.01	0.46	0.10
		NO_3 (mg N/L)	4	4	0.139	0.913	0.352
		NO_2 (mg N/L)	4	4	0.004	0.049	0.020
		DON (mg/L)	4	3	<0.23	0.64	0.61
		TON (mg/L)	4	3	<0.42	2.4	1.0
		Ortho-P (mg P/L)	4	4	0.038	0.178	0.153
		TDN (mg/L)	4	4	0.37	1.60	1.19
		TN, unfiltered (mg/L)	4	4	0.56	3.20	1.65
		Sr (µg/L)	4	4	16.1	72.9	29.2
		Dissolved organic carbon (mg/L)	4	4	3.43	11.6	8.6
		δD-water (per mil)	4	4	−49.00	−8.80	−18.90
		δ^{18}O-water (per mil)	4	4	−8.01	−2.85	−4.14
		δ^{15}N-NO_3 (per mil)	4	4	0.36	3.77	2.38
		δ^{18}O-NO_3 (per mil)	4	4	8.16	23.14	12.65
2	West Elm Creek	Ca (mg/L)	4	4	18.2	36.9	28.6
		Mg (mg/L)	4	4	0.82	0.93	0.86
		Na (mg/L)	4	4	1.30	1.89	1.33
		HCO_3 (mg/L)	4	4	49.4	114	76.9
		Cl (mg/L)	4	4	1.23	1.91	1.74
		SO_4 (mg/L)	4	4	1.96	3.47	2.54
		NH_4 (mg N/L)	4	4	0.02	0.16	0.04
		NO_3 (mg N/L)	4	4	0.615	0.885	0.751
		NO_2 (mg N/L)	4	4	0.015	0.049	0.020
		DON (mg/L)	4	4	0.23	0.42	0.39
		TON (mg/L)	4	4	0.63	1.8	1.6
		Ortho-P (mg P/L)	4	4	0.040	0.079	0.072
		TDN (mg/L)	4	4	0.89	1.40	1.25
		TN, unfiltered (mg/L)	4	4	1.50	2.80	2.35
		Sr (µg/L)	4	4	37.8	44.4	40.3
		Dissolved organic carbon (mg/L)	4	4	5.47	8.96	5.95
		δD-water (per mil)	4	4	−46.00	−9.20	−28.10
		δ^{18}O-water (per mil)	4	4	−7.30	−2.75	−4.72
		δ^{15}N-NO_3 (per mil)	4	4	1.91	2.81	2.23
		δ^{18}O-NO_3 (per mil)	4	4	8.22	17.24	12.65

Table 4. Summary of analyses for selected constituents in water samples collected from Shavano and Encino Rio wells, 2017–19.

[LRL, laboratory reporting level; Ca, calcium; mg/L, milligram per liter; Mg, magnesium; Na, sodium; HCO_3, bicarbonate; Cl, chloride; SO_4, sulfate; NH_4, ammonia as nitrogen; mg N/L, milligram nitrogen per liter; <, less than; NO_3, nitrate as nitrogen; NO_2, nitrite as nitrogen; DON, dissolved organic nitrogen; TON, total organic nitrogen; Ortho-P, orthophosphate as phosphorus; mg P/L, milligram phosphate per liter; TDN, total dissolved nitrogen; TN, total nitrogen; Sr, strontium; µg/L, microgram per liter; δD, delta deuterium in water; $\delta^{18}O$, delta oxygen-18 in water; $\delta^{15}N\text{-}NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O\text{-}NO_3$, delta oxygen-18 in nitrate]

Map identifier (fig. 1; table 1)	Short name (fig. 1; table 1)	Constituent (and units of measurement)	Number of samples	Number of concentrations equal to or greater than the LRL	Minimum value	Maximum value	Median value
3	Shavano well	Ca (mg/L)	14	14	96.6	116	112
		Mg (mg/L)	14	14	6.39	14.8	6.94
		Na (mg/L)	14	14	7.02	14.8	10.1
		HCO_3 (mg/L)	14	14	277	346	325
		Cl (mg/L)	14	14	12.7	26.6	19.6
		SO_4 (mg/L)	14	14	15.6	55.1	18.8
		NH_4 (mg N/L)	14	1	<0.01	0.01	<0.01
		NO_3 (mg N/L)	14	14	1.61	2.06	1.86
		NO_2 (mg N/L)	14	0	<0.001	<0.001	<0.001
		DON (mg/L)	14	0	<0.04	<0.04	<0.04
		TON (mg/L)	12	0	<0.06	<0.06	<0.06
		Ortho-P (mg P/L)	14	13	<0.004	0.018	0.015
		TDN (mg/L)	12	2	<1.7	2.0	<1.7
		TN, unfiltered (mg/L)	12	1	<1.7	2.0	<1.7
		Sr (µg/L)	14	14	137	292	154
		Tritium (picocuries per liter)	3	3	3.40	4.10	4.01
		Dissolved organic carbon (mg/L)	14	14	0.32	2.02	0.64
		δD-water (per mil)	14	14	−26.0	−22.3	−24.6
		$\delta^{18}O$-water (per mil)	14	14	−4.54	−4.12	−4.36
		$\delta^{15}N\text{-}NO_3$ (per mil)	14	14	5.37	8.51	6.67
		$\delta^{18}O\text{-}NO_3$ (per mil)	14	14	5.07	6.51	6.09
		$^{87}Sr/^{86}Sr$ (ratio)	2	2	0.7084	0.7086	0.7085
4	Encino Rio well	Ca (mg/L)	14	14	102	119	112
		Mg (mg/L)	14	14	1.56	6.82	4.66
		Na (mg/L)	14	14	3.66	18.4	13.6
		HCO_3 (mg/L)	14	14	260	316	301
		Cl (mg/L)	14	14	5.73	24.6	20.8
		SO_4 (mg/L)	14	14	7.46	47.9	40.6
		NH_4 (mg N/L)	14	0	<0.01	<0.01	<0.01
		NO_3 (mg N/L)	14	14	1.30	2.01	1.58
		NO_2 (mg N/L)	14	1	<0.001	0.004	<0.001
		DON (mg/L)	14	0	<0.07	<0.07	<0.07
		TON (mg/L)	13	0	<0.07	<0.07	<0.07
		Ortho-P (mg P/L)	14	13	<0.004	0.010	0.007
		TDN (mg/L)	14	1	<1.4	1.6	<1.4
		TN, unfiltered (mg/L)	13	1	<1.4	1.8	<1.4
		Sr (µg/L)	14	14	44.7	327	177
		Tritium (picocuries per liter)	2	2	3.80	4.88	4.34
		Dissolved organic carbon (mg/L)	14	14	0.24	0.84	0.34
		δD-water (per mil)	14	14	−25.6	−21.8	−24.7
		$\delta^{18}O$-water (per mil)	14	14	−4.60	−4.31	−4.44
		$\delta^{15}N\text{-}NO_3$ (per mil)	14	14	5.36	7.64	6.92
		$\delta^{18}O\text{-}NO_3$ (per mil)	14	14	4.09	5.35	4.92
		$^{87}Sr/^{86}Sr$ (ratio)	1	1	0.7083	0.7083	0.7083

Additional sources of QA data provided relevant information for interpretation of environmental data in this study. This report includes environmental data from two surface-water and two groundwater monitoring sites that are part of a much larger sampling network in and around the Edwards aquifer recharge zone in Bexar County. Sampling from surface-water and groundwater sites within this network has been ongoing since 1997, and extensive QA results obtained by using comparable field sampling protocols and analytical methods have been previously published. Opsahl (2012) provided a detailed evaluation of autosampler blank contamination by testing for contamination before and after cleaning autosamplers that had been in the field for various periods of time. That evaluation showed a few more detections of major and trace ions that were not observed in the current study (see app. 2 in Opsahl and others, 2012); however, most of these detections were close to the LRL, indicating potential contamination from autosamplers is not likely to substantially affect environmental sample results. Concentrations of Ca above the LRL were measured in the field-blank samples for several environmental samples, which is not surprising given the karst limestone stream beds in which the autosamplers are installed. Nevertheless, potential Ca contamination from samplers would represent less than 5 percent of Ca concentrations measured in typical surface-water samples. The other notable exception was the occurrence of NH_4 in multiple autosampler field blank samples. Though not detected in autosampler blanks in this study, low-level NH_4 contamination might be important relative to concentrations in environmental samples and need to be considered in the interpretation of data collected from autosamplers. Additionally, a more extensive QA dataset of 75 samples, including field-equipment blanks and sequential replicates, was produced from the same sampling network (Opsahl and others, 2018a, 2018b). In summary, QA results from these reports show sporadic detections of various major and trace ions, but the potential for bias was low as concentrations were substantially lower than in any surface-water or groundwater environmental sample concentrations.

The pesticide analytical method used in this study (Sandstrom and others, 2015) differs from the pesticide methods previously used for sites within the San Antonio segment of the Edwards aquifer. With 226 analytes and low detections limits, added scrutiny of QA data is necessary to avoid false-positive and false-negative values. Pesticide results presented in this study were evaluated by the NWQL prior to their release. Details of additional evaluations of QA data for this pesticide method are described in prior publications. For example, Shoda and others (2018) discuss analytical recoveries using field-matrix spikes and their paired environmental samples. Figure 4 in Shoda and others (2018, p. 37–93) provides analytical-recovery information for each individual pesticide. Additional QA information focused specifically on surface-water samples and associated analytical considerations is provided by Martin and others (2017). Medalie and others (2019) describe NWQL-established criteria for removing poor-quality data on the basis of results from laboratory instrument blanks and data from laboratory set blanks used during analysis. Examination of laboratory instrument-blank and set-blank data for each detected compound over the course of this study indicated that there is likely little positive bias resulting from detections of constituents during laboratory analysis. Examination of laboratory matrix-spike data for environmental samples indicated that there is little negative or positive bias that results from substantially lower (less than 70 percent) or higher (greater than 130 percent) spike recoveries during analysis. On the basis of low-level detections of some pesticides in laboratory blanks, however, two acetochlor oxanilic acid detections, one alachlor oxanilic acid detection, four atrazine detections, one etoxazole detection, one metolachlor detection, and one metribuzin DK detection were further censored from the dataset. No laboratory-censored values were added back to the dataset.

Climatic and Hydrologic Conditions During Study Period

The study area is prone to climatic and hydrologic extremes (Griffiths and Strauss, 1985; Jones, 1991). The study began in September 2017, when the region was receiving only periodic rainfall and hydrologic conditions were relatively stable, as indicated by the WLAs at the J–17 index well and discharge at Comal Springs (fig. 2). Drier conditions prevailed from about April through August 2018, and WLAs at the J–17 index well and discharge at Comal Springs both dropped below their long-term median values. In September 2018, more than 16 inches of rainfall was measured at the San Antonio International Airport (National Oceanic and Atmospheric Administration, 2020); the increase in regional groundwater recharge that this large amount of rainfall caused resulted in a rapid rise in WLAs at the J–17 index well and in the discharge at Comal Springs (fig. 2). Rapid upward changes in the J–17 index well WLAs and Comal Springs discharge (indicators of regional hydrologic conditions) continued through most of October 2018, and the period September through October 2018 is hereinafter referred to as the “large recharge event.” After this event, WLA at the J–17 index well and discharge at Comal Springs remained above long-term median values for the remainder of the study period.

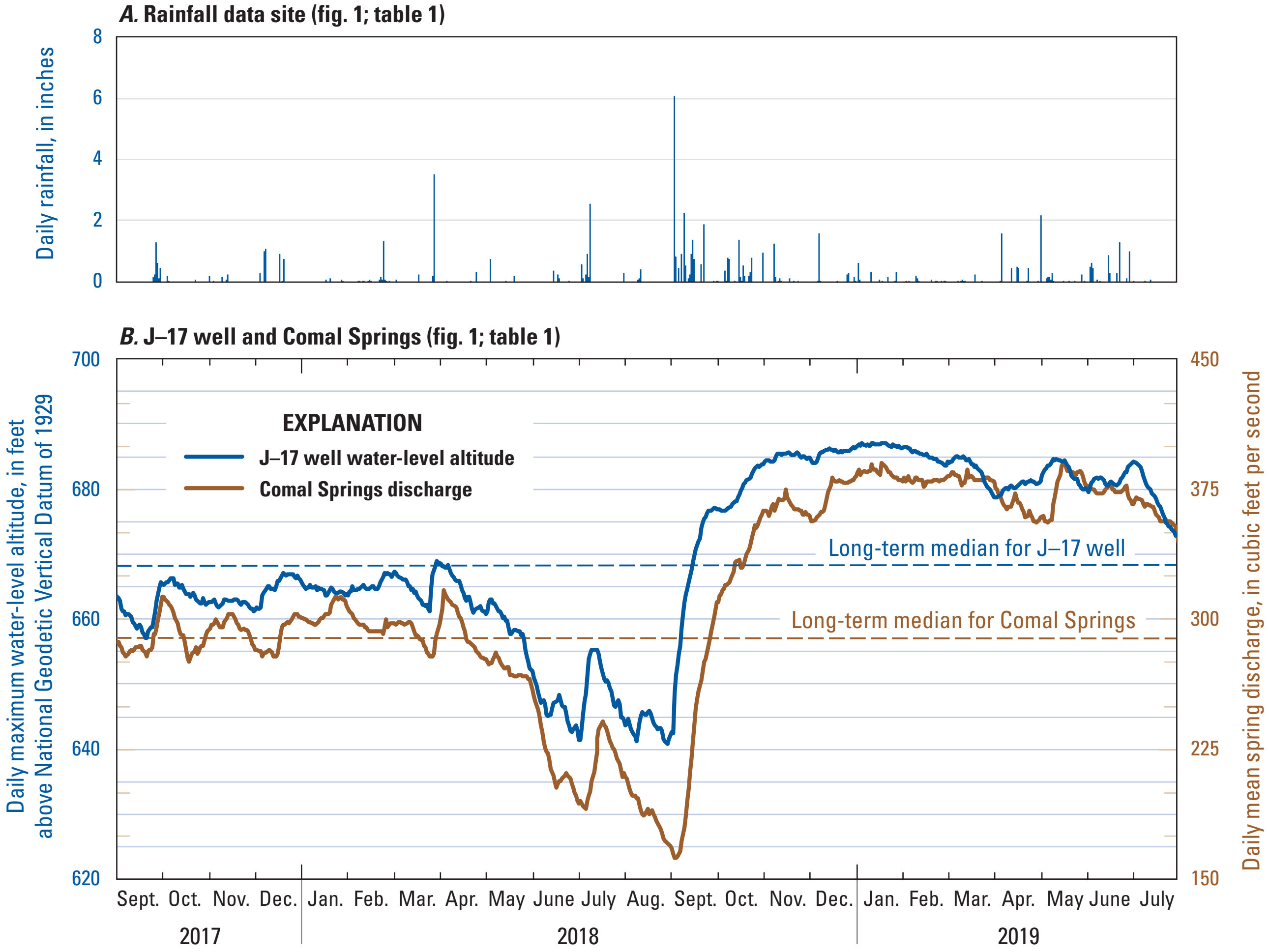
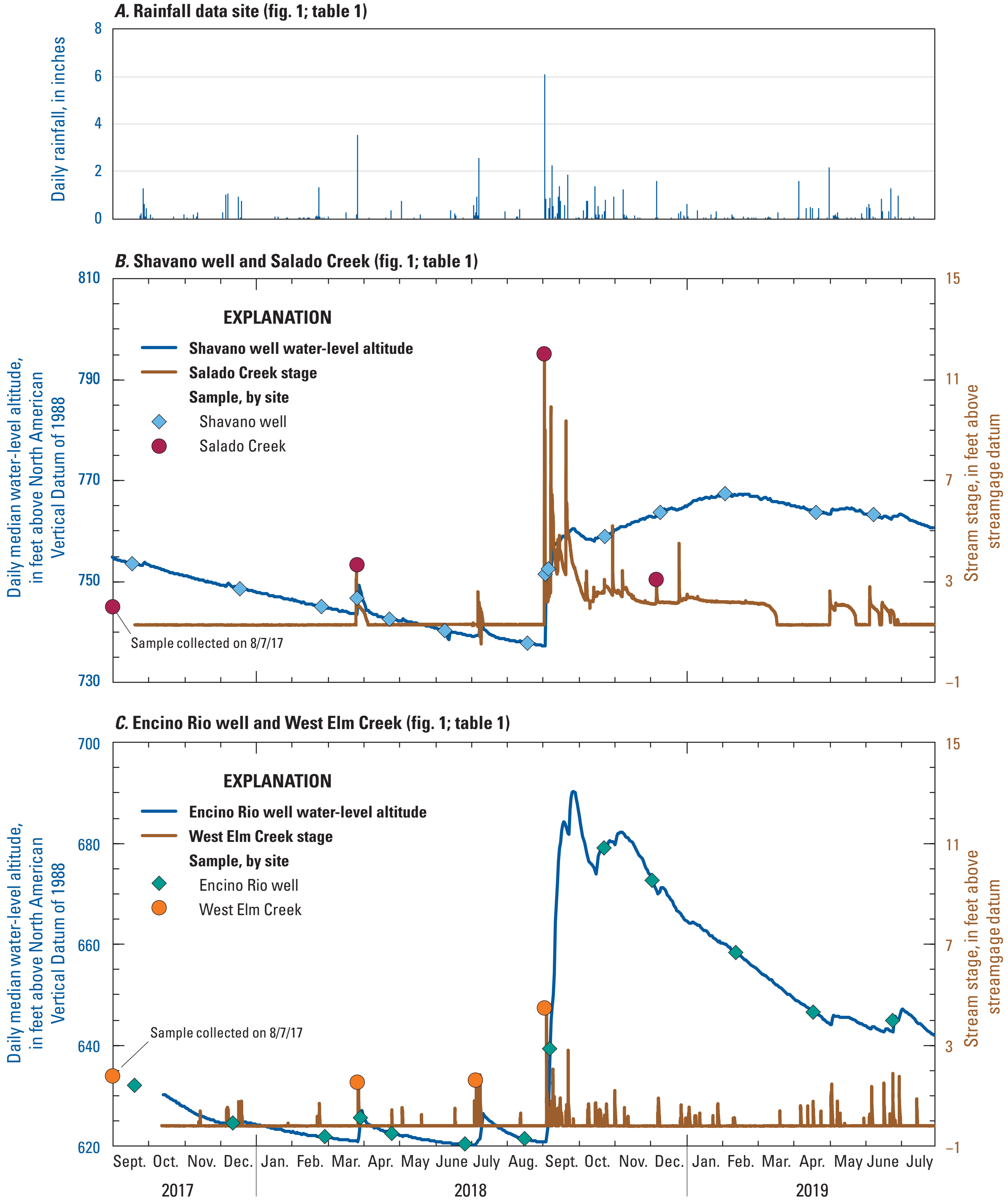


Figure 2. Time series (September 2017–July 2019) of *A*, daily rainfall recorded at the rainfall data site (National Oceanic and Atmospheric Administration, 2020) and *B*, water-level altitude for the J–17 index well (Edwards Aquifer Authority, 2020b) and discharge at Comal Springs (U.S. Geological Survey, 2019). Horizontal lines are long-term median values.

Streamflow characteristics at the study sites (fig. 3) were responsive to differences in climatic conditions. Stage records indicate that West Elm Creek flowed more frequently than Salado Creek. When Salado Creek did flow, however, the stage was generally higher, and streamflow persisted for a longer period than at West Elm Creek. Many variables are likely to influence the frequency of flow in these two streams, but one notable difference is that West Elm Creek drains a watershed that is more urbanized, or otherwise developed, than the watershed drained by Salado Creek, and rapid runoff is associated with impervious surfaces found in urbanized watersheds (Huang and others, 2008; Miller and others, 2014). Impervious land-surface cover in the urbanized West Elm watershed therefore likely contributes to the “flashiness” of the flow in West Elm Creek as rain rapidly runs off rather than soaks into the ground. Small rainfall events insufficient to generate flow in the relatively undeveloped Salado Creek watershed are more likely to generate short periods of flow in the urbanized watershed of West Elm Creek. Of the two watersheds, the Salado Creek drainage area is larger, which contributes to periods of large stage increases, particularly in response to large rainfall events such as that in September 2018. The influence of differences in land-surface characteristics in the watersheds of West Elm Creek and Salado Creek demonstrates how the flow of each stream responds differently to rainfall, leading to differences in their respective recharge contributions to the Edwards aquifer.



A. Rainfall data site (fig. 1; table 1)

B. Shavano well and Salado Creek (fig. 1; table 1)

C. Encino Rio well and West Elm Creek (fig. 1; table 1)

Figure 3. *A*, Rainfall at the San Antonio International Airport, *B*, continuous water-level altitude, stage data, and sampling dates for the Salado Creek and Shavano well site pair, and *C*, continuous water-level altitude, stage data, and sampling dates for the West Elm Creek and Encino Rio well site pair. Scales on both y-axes have the same ranges so that water-level altitude and stage data can be directly compared between sites.

Patterns of WLAs in the Shavano and Encino Rio wells (fig. 3*B*, *C*) contrast with the WLAs at the J–17 index well (fig. 2*B*). At the onset of the study (September 2017), Shavano and Encino Rio WLAs were declining whereas J–17 index well WLA was initially stable then declined from about April 2018 through September 2018. Following the large recharge event in September 2018, the response at each well was different. Initial rises in WLA were approximately 25, 45, and 70 feet at the Shavano, J–17 index, and Encino Rio wells, respectively, and the initial rises occurred more rapidly at the Shavano and Encino Rio wells, where the Edwards aquifer is unconfined. The higher WLAs persisted for longer periods at both the J–17 index and Shavano wells than at the Encino Rio well, where WLA progressively declined beginning in late 2018. The early (September 2017 through mid-2018) WLA declines and rapid response to recharge observed at the Shavano and Encino Rio wells indicate that these wells were largely influenced by local climatic and hydrologic conditions. Stormwater runoff in nearby recharge streams likely contributed to rapid rises in WLA in the unconfined zone of the Edwards aquifer during the study period.

The hydrologic response of wells in the unconfined zone of the aquifer (the Shavano and Encino Rio wells) compared to that of regional hydrologic indicators (J–17 index well and Comal Springs), demonstrates how groundwater flow in the confined zone differs from that in the unconfined recharge zone. At the onset of the study (September 2017 through mid-2018), little rainfall or runoff occurred (figs. 2 and 3) and WLAs were declining at the Shavano and Encino Rio wells. At the same time, the regional hydrologic indicators were relatively stable (fig. 2), which is consistent with the regional flow path in the deeper aquifer that originates predominantly from the west. Following the large recharge event, rapid increases were evident in discharge at Comal Springs and WLAs at the J-17 index well and at the Shavano and Encino Rio wells, although a more rapid initial response in WLAs was apparent in the unconfined aquifer at Shavano and Encino Rio wells than in WLAs at the J–17 index well or Comal Springs discharge (figs. 2 and 3). WLAs at the Encino Rio well declined within a few days following the large recharge event, which is consistent with local climatic/hydrologic conditions (that is, reduction in local recharge) controlling its response. In contrast, the Shavano well maintained a higher WLA for months subsequent to its response to the large recharge event. The Shavano and Encino Rio wells were subject to similar climatic/hydrologic conditions during this period, with each site receiving 15–20 inches of rain in September 2018. The pattern in WLA at the Shavano well could have resulted from continued local recharge as evidenced by sustained flow at Salado Creek, though contributions from other groundwater flow paths might also be contributing to the prolonged WLA increases at the Shavano well.

Temporal and Spatial Variability in Continuously Monitored Water-Quality Data

Unlike the analysis of discrete water-quality samples that provides insights into the water quality of a stream or groundwater system at a point in time, continuous monitoring provides insights into the water quality on an ongoing basis. The complete continuum of hydrology conditions affecting a stream or groundwater system is reflected in continuous water-quality data.

Specific Conductance

Continuous monitoring of SC in groundwater serves as an indicator of how different hydrologic conditions affect the overall chemical quality of recharge water. Large changes and substantially different responses in SC were observed at the Shavano and Encino Rio wells over the range of hydrologic conditions that occurred during the study (fig. 4). During the relatively dry conditions in the early part of the study, the gradual decline in WLAs at both sites was accompanied by fluctuations in SC at the Shavano well and a gradual decrease with smaller fluctuations in SC at the Encino Rio well. The gradual decrease in SC at the Encino Rio well cannot be explained by contributions of dilute surface-derived recharge because of the relatively dry conditions at this time. The SC decrease may have resulted from an increasing proportion of dilute inflow of groundwater from an adjacent area or perhaps from recharge originating west of the study area. The fluctuations in SC at the Shavano well during small recharge events in March 2018 and July 2018 were more pronounced than at the Encino Rio well. A large decrease in SC of about 80–100 microsiemens per centimeter at 25 degrees Celsius (µS/cm) was observed at both of these wells in response to the large recharge event in September 2018, which is again consistent with mixing of ambient groundwater with relatively dilute water from surface-derived recharge. The decrease in SC at the Shavano well was rapid (occurring over about 5 days) relative to that at the Encino Rio well (occurring over about 3 weeks). Almost immediately after this initial decrease, SC at the Shavano well then rapidly increased by about 50 µS/cm within 3 days, whereas at the Encino Rio well SC remained low for several weeks. In the months following the large recharge event, the WLA at the Encino Rio well gradually declined, accompanied by an increase in SC. In contrast, the pattern of SC and WLA at the Shavano well was markedly different; several distinct peaks in SC occurred, increasing to values that exceeded the baseline at the beginning of the study. Concurrently, WLA at the Shavano well did not gradually decline but remained relatively stable and even increased slightly in early 2019.

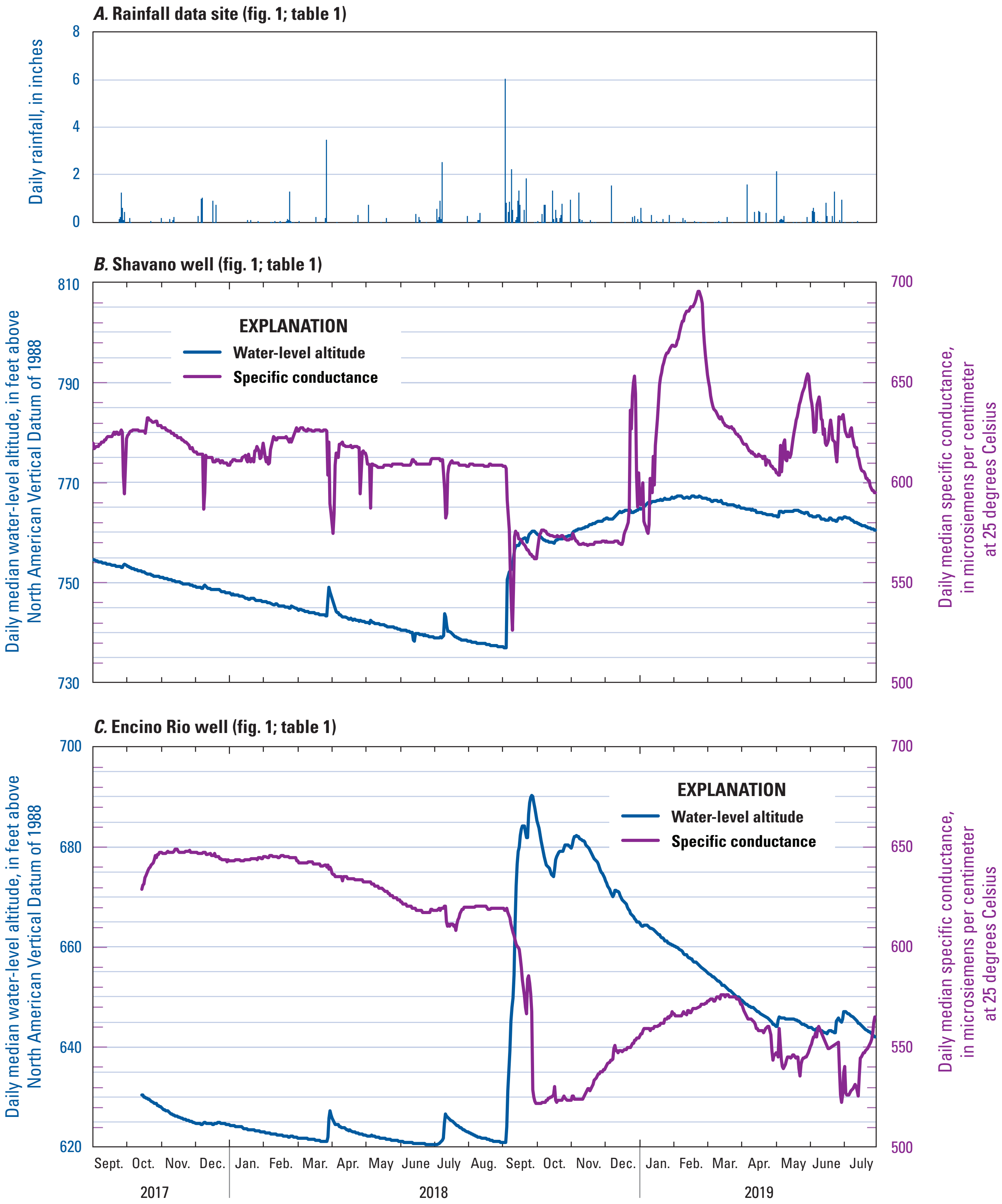


Figure 4. *A*, Rainfall at the San Antonio International Airport, *B*, continuous water-level altitude and continuous specific conductance data for the Shavano well, and *C*, continuous water-level altitude and continuous specific conductance data for the Encino Rio well. Scales on the y-axes for graphs *B* and *C* have the same ranges so that water-level altitude and specific conductance data can be directly compared between sites.

In the late spring and early summer months, prior to the end of data collection in July 2019, rises in WLA at both wells were small but measurable in response to a series of rain events, but the accompanying changes in SC were in opposite directions at the two sites. The decrease in SC at the Encino Rio well is consistent with an influx of dilute water derived from surface-water recharge. At the Shavano well, however, SC increased when slight rises in WLA were observed, which is consistent with a source of more saline, higher SC water. The source of this relatively high SC water in the Shavano well is uncertain but might be accounted for in part by the mixing in of additional Edwards aquifer water with higher SC values, which might have included a wastewater component, or introduction of higher SC water from still another source, such as the underlying Trinity aquifer.

Nitrate

Continuous monitoring of NO_3 concentrations provides more insight into temporal NO_3 variability and sources than do periodically collected discrete samples. Initial (September to December 2017) NO_3 concentrations (about 1.6–1.7 mg/L) were similar at the Shavano and Encino Rio wells (fig. 5). For context, historical background NO_3 concentrations in the San Antonio segment of the Edwards aquifer were approximately 1.0 mg/L but have increased to approximately 2.0 mg/L (Musgrove and others, 2016). Other wells within the same general area that are completed in the unconfined zone of the Edwards aquifer yield water with higher ambient NO_3 concentrations (3–5 mg/L) than the Shavano and Encino Rio wells (Musgrove and others, 2016; Opsahl and others, 2018a). NO_3 concentrations were variable at both wells during the study period, with values ranging from about 1.1 to 2.1 mg/L. Following the large recharge event in September 2018, NO_3 concentrations decreased at both wells by about 0.2–0.3 mg/L through early November, which is consistent with an influx of recent surface-water recharge that has relatively low NO_3 concentrations. With the exception of December 2018 through March 2019, decreases in concentrations of NO_3 in the Shavano well following recharge events (fig. 5*B*) were generally consistent with the decreases in SC (fig. 4*B*), which is indicative of mixing with more dilute surface-water recharge. At the Encino Rio well, the concentration of NO_3 increased by about 0.8 mg/L between December 2018 and March 2019 while the WLA was steadily declining (fig. 5*C*). The progressive increase in NO_3 in the Encino Rio well during these 4 months likely results from a decreasing proportion of surface-derived recharge water and an increasing proportion of ambient groundwater, which is consistent with the corresponding increase in SC (fig. 4*C*). Additionally, in the last few months of the study (May through July 2019), small rises in WLA occurred in response to multiple rain and recharge events; corresponding decreases in NO_3 concentrations were similar to or larger than in response to the large recharge event (the lowest continuous NO_3 concentrations were measured at both wells in 2019). The observed fluctuation in NO_3 concentrations outside of periods of rapid recharge is indicative of mixing with different water sources or of additional processes affecting NO_3 concentrations, such as nitrification (Musgrove and others, 2016), the relative contributions of which are uncertain.

Results of Analyses of Discrete Water Samples

Changes in concentrations of specific constituents in groundwater in response to mixing with surface-derived recharge and other source inputs can provide insight into urban influences on surface-water/groundwater interactions in the Edwards aquifer. The collection of discrete samples at both surface-water and groundwater sites and their analyses for a suite of constituents can shed light on source inputs and the distribution of both naturally occurring constituents and anthropogenic contaminants in the aquifer's recharge zone.

U.S. Geological Survey hydrographers processing a groundwater sample for pesticide analysis at the Encino Rio site.

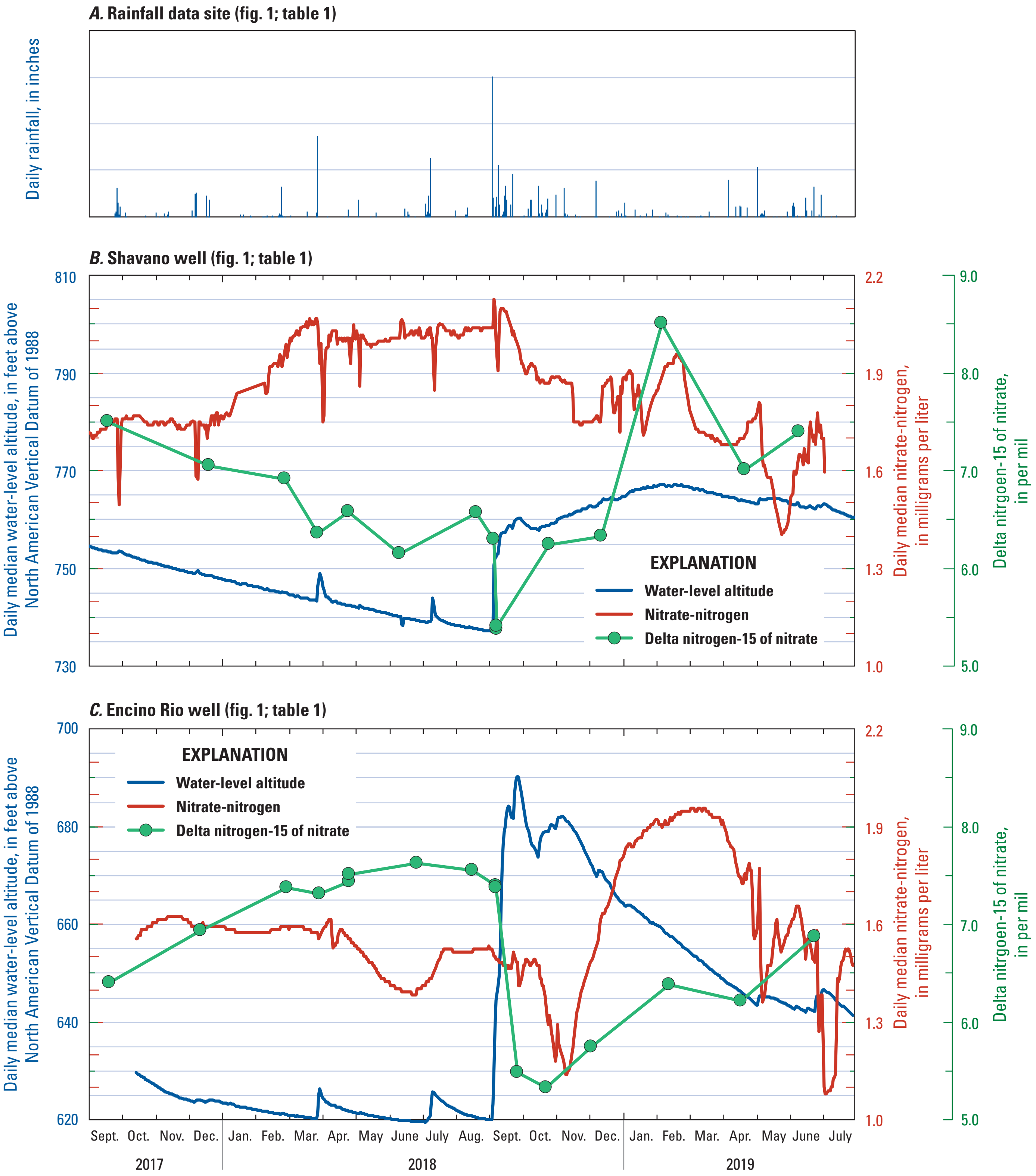


Figure 5. *A*, Rainfall at the San Antonio International Airport and *B* and *C*, continuous water-level altitude, continuous nitrate concentrations, and discrete delta nitrogen-15 of nitrate values for the Shavano and Encino Rio wells, respectively. Scales on the y-axes for graphs *B* and *C* have the same ranges so that water-level altitude, nitrate concentrations, and delta nitrogen-15 values can be directly compared between sites.

Deuterium/Oxygen Isotopes

Measurements of the stable isotopic composition of oxygen and hydrogen ($\delta^{18}O$ and δD) in surface-water and groundwater samples provide insights into water sources, processes such as mixing and evaporation, and the movement of stormwater runoff into the Edwards aquifer. Stable isotope values for groundwater samples are tightly clustered with little variability, whereas values for surface-water samples are more broadly distributed (fig. 6). All samples lie along or close to the global and local meteoric lines, which represent the isotopic compositions of rainfall around the globe (Craig, 1961) and in central Texas (Pape and others, 2010), respectively, indicating that surface-water runoff and groundwater consist primarily of meteoric water (water derived from precipitation). Although there is a broad range in the isotope values for stormwater runoff, data obtained from the two streams (Salado Creek and West Elm Creek) are similar for each of the storm events during which samples were collected. For example, on March 28, 2018, the stormwater-runoff samples collected from each stream are both relatively isotopically heavier (higher isotope values) than other "non-storm" samples, whereas those collected on August 7, 2017, are appreciably isotopically lighter (lower isotope values). Isotopically lighter stable isotope values might originate from rainfall associated with tropical cyclone storms (Lawrence and Gedzelman, 1996; Lawrence, 1998). Recharge to the Edwards aquifer in response to these rainfall/runoff events would likely reflect lower isotopic values and provide a tracer of recent recharge; this has been previously demonstrated in the unconfined zone of the Edwards aquifer by Musgrove and others (2010). Sample collection at the wells, however, had not yet started on August 7, 2017, so groundwater $\delta^{18}O$ and δD during this event cannot be compared to the isotopically light stormwater-runoff samples. A broad range in measured values of the stable isotopes of water expressed as δD and $\delta^{18}O$ in the water samples collected from two streams (Salado and West Elm Creeks), in comparison to the tight clustering of the values of these isotopes in groundwater samples, indicates that source waters (surface waters) of widely varying chemical characteristics become homogenized within the aquifer system. Previous attempts to compare stable isotope values for the unconfined and confined zones of the Edwards aquifer indicate that water in the confined zone is chemically less variable than water in the unconfined zone, which is consistent with further mixing and homogenization of multiple aquifer recharge sources in the deeper confined zone of the aquifer (Musgrove and others, 2010; Opsahl and others, 2018a).

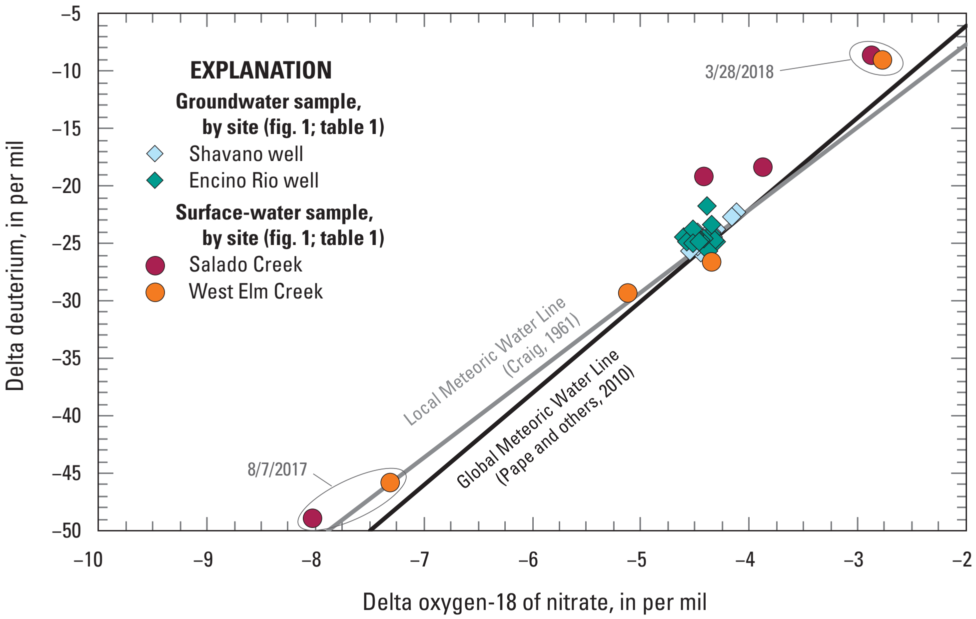


Figure 6. Relation between deuterium and oxygen-18 isotopes measured in stormwater-runoff and groundwater samples collected from the San Antonio segment of the Edwards aquifer, south-central Texas, 2017–19. Local (Pape and others, 2010) and global (Craig, 1961) meteoric water lines are shown for comparison.

Composition of Inorganic Constituents

Concentrations of major ions, trace ions, and nutrient concentrations in stormwater runoff indicate a combination of land-derived and rainfall-derived constituents. Median concentrations of major and trace ions (Ca, Mg, Na, HCO_3, Cl, SO_4, and Sr) at surface-water sites (table 3) were similar to those previously reported for other surface-water sites where streams contribute recharge to the Edwards aquifer within the same general area (Opsahl, 2012; Musgrove and others, 2016; Opsahl and others, 2018a). A comparison of major and trace-ion concentrations in stormwater runoff and rainfall samples collected previously indicates that the runoff generally contains higher concentrations of these ions than does rainfall; thus, most of the major ions in stormwater runoff are derived from the land surface rather than from precipitation. Concentrations of nutrients (NH_4, NO_3, NO_2, DON, TON, ortho-P, TDN, TN) at surface-water sites also were similar to previously reported concentrations in samples collected from recharging streams (Opsahl, 2012; Musgrove and others, 2016; Opsahl and others, 2018a). Median concentrations reported for some nutrients in urban rainfall were considerable, specifically NH_4 (0.18–0.25 mg/L), NO_3 (0.11–0.12 mg/L), and TDN (0.30–0.49 mg/L) (Opsahl and others, 2018a), indicating that a substantial proportion of these nutrients in stormwater-runoff samples might originate from rainfall.

Median concentrations in major and trace ions (Ca, Mg, Na, HCO_3, Cl, SO_4, Sr) in samples from the Shavano and Encino Rio wells (table 4) were similar to previously reported concentrations from other wells within the same general area where the Edwards aquifer is unconfined (Opsahl, 2012; Musgrove and others, 2016; Opsahl and others, 2018a). Most constituents in samples collected from these two wells had a broad range in concentration, and only the median values for Mg, HCO_3, NO_3, ortho-P, DOC, and $\delta^{18}O\text{-}NO_3$ were statistically significantly different between the two wells (*p*-value less than 0.05); thus, differences in the composition of inorganic constituents based on median concentrations between the two wells were difficult to discern (table 4). Although fewer stormwater-runoff samples were collected (n=4) compared to groundwater samples (n=14), considerable differences between stormwater-runoff and groundwater composition were apparent. Major and trace-ion concentrations were substantially lower in stormwater-runoff samples, however, than in groundwater samples. Concentrations of NO_3 were higher in groundwater samples than in surface-water samples, whereas the opposite was true for concentrations of NH_4, NO_2, DON, and ortho-P. The concentration of TN is a computed value and thus could not be determined for groundwater samples because nondetections in those samples could not be used for computations.

Time series graphs for concentrations of selected major and trace ions in water samples from the Shavano and Encino Rio wells had both similarities and differences between the wells over the broad range of hydrologic conditions during the study (fig. 7*A–D*). From the onset of the study in September 2017, through August 2018, Na, Cl, and Sr concentrations increased, and the concentration of SO_4 changed little at the Encino Rio well as WLA gradually declined. The increases in Na and Cl concentrations during that period contrast with the gradual decrease in total SC, indicating that changes in other major and trace ion concentrations are responsible for the observed decrease in SC. In contrast to the Encino Rio well, concentration of Na, Cl, and SO_4 changed little and Sr decreased at the Shavano well. On the basis of the generally smaller concentrations of major and trace ions in stormwater runoff relative to those in unconfined groundwater (tables 3 and 4), the gradual changes early in the study period are generally consistent with a decreasing proportion of more dilute surface-water recharge, primarily at the Encino Rio well. During and shortly after the large recharge event in September 2018, large decreases in concentrations of Na, Cl, Sr, and SO_4 were observed in samples from the Encino Rio well, while only small decreases in Na and Cl and very small decreases in Sr and SO_4 were observed in samples from the Shavano well. The large decreases in constituent concentrations at the Encino Rio well in response to recharge are consistent with a rapid influx of more dilute surface-derived recharge, specifically for lower concentrations of major and trace ions. Less variability in major and trace-ion concentrations as well as a smaller rise in WLA (fig. 3*B*) at the Shavano well in response to the large recharge event indicates that less mixing with recent surface-derived recharge occurred relative to mixing at the Encino Rio well (tables 3 and 4). After the initial response to the large recharge event and during the latter part of the study throughout 2019, variability in major and trace-ion concentrations was similar at both wells as the general pattern in all measured constituents was a gradual increase. As during the early part of the study (September 2017 through August 2018), the increase is interpreted to partially result from a decreased proportion of dilute surface-derived recharge, along with increased water-rock interactions, and contributions from upgradient water sources. Relatively large and abrupt increases in major and trace-ion concentrations occurred at the Shavano well in February 2019, coincident with high SC values (fig. 4*B*). WLA at the Shavano well in February 2019 was near the highest values measured during the study period and these elevated major and trace-ion concentrations are inconsistent that has surface-derived recharge. The addition of Edwards aquifer water with higher SC values, perhaps derived from wastewater, or the mixing of Edwards aquifer water with water that has a higher SC from the underlying Trinity aquifer might account for the groundwater composition observed under these hydrologic conditions.

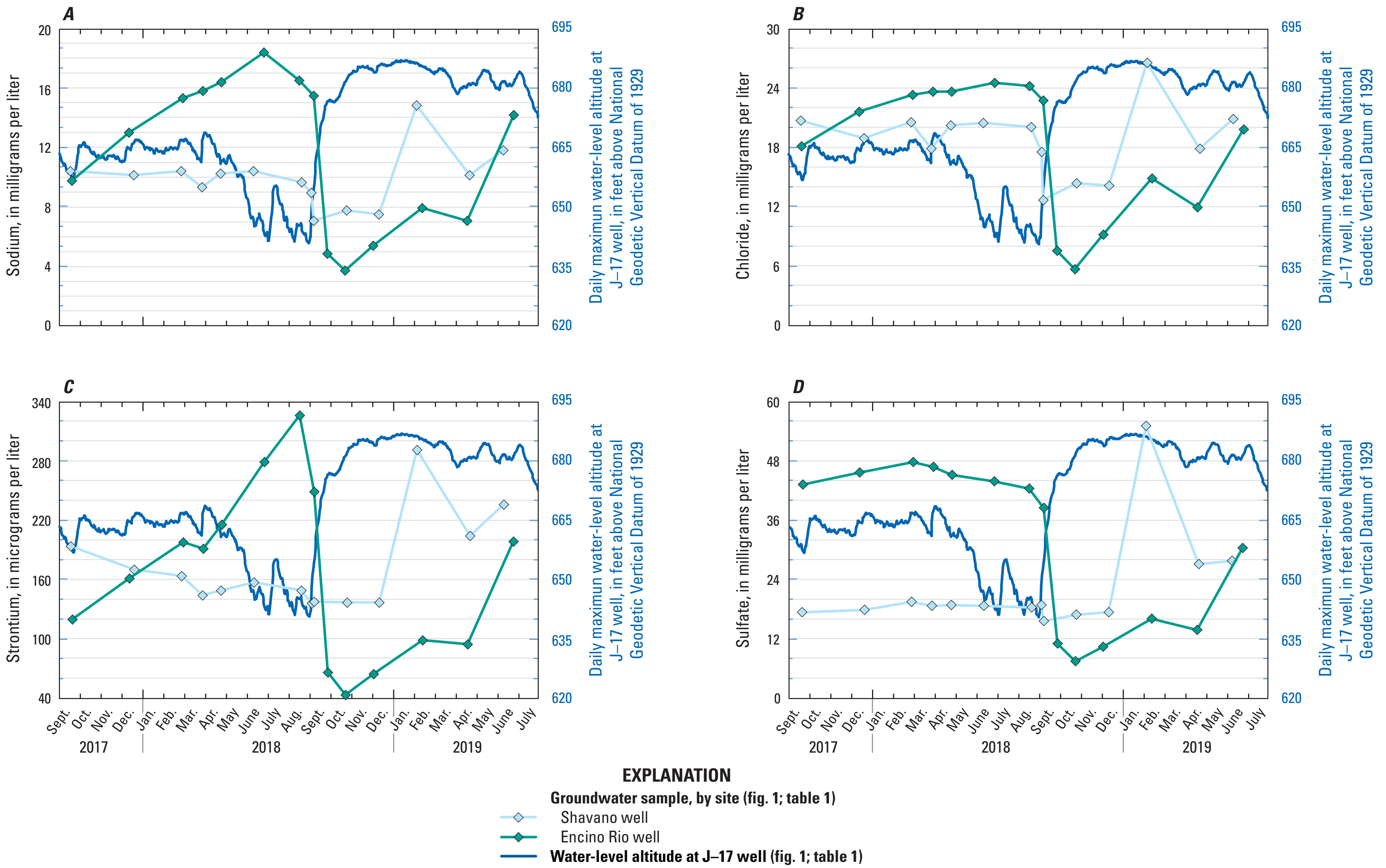


Figure 7. Concentrations of *A*, sodium, *B*, chloride, *C*, strontium, and *D*, sulfate measured in water samples collected from the Shavano and Encino Rio wells, September 2017–July 2019.

Nutrient Dynamics

Stormwater runoff carries both rainfall-derived and land-derived nutrients from the land surface into the aquifer, where environmental conditions and biogeochemical processes likely affect nutrient concentrations. Median concentrations of ortho-P were relatively low (less than 0.200 mg/L) in all samples and lower in groundwater samples than in surface-water samples (tables 3 and 4). Median concentrations of ortho-P exceeded estimated background concentrations for streams (0.010 mg/L) but were within the range of concentrations for streams in urban settings studied across the Nation (Dubrovsky and others, 2010). Median groundwater ortho-P concentrations were lower than estimated background concentrations for groundwater (0.030 mg/L) (Dubrovsky and others, 2010). P is commonly the nutrient in most limited supply in aquatic systems (Hem, 1985), and biological uptake might partly explain lower concentrations of ortho-P in groundwater. P also tends to sorb onto the surfaces of minerals (Litke, 1999); thus P associated with suspended sediments that become trapped before reaching the aquifer might also explain the lower ortho-P concentrations in groundwater.

The distribution of concentrations of N species (NO_2, NO_3, and NH_4) among sampling sites transitions from a more variable distribution in stormwater runoff to a more uniform distribution in groundwater in which the dominant form is NO_3. In stormwater runoff, measurable concentrations of NH_4, NO_3, NO_2, and DON were typically present (table 3), whereas the primary form of N in groundwater samples was NO_3, with only two detections of other N species at small concentrations for all groundwater samples (table 4). In most cases, TN concentrations could not be calculated in groundwater samples because of numerous nondetections in the samples from each site; however, NO_3 concentrations, which accounted for almost all measurable N, are likely representative of the TN in groundwater samples. Distributional patterns of N species reported in this study are similar to those found by Musgrove and others (2010, 2011, and 2016), who reported that NO_3 concentrations in Edwards aquifer water were elevated relative to those in surface-water recharge.

Patterns of nutrient concentrations in stormwater-runoff and unconfined groundwater samples provide insights into processes, such as biogeochemical transformations, that affect nutrient concentrations during groundwater recharge or within the aquifer. Individual nutrients, including NH_4, NO_2, NO_3, and DON, are chemically and biologically reactive and can be produced or consumed in water and soils. For example, NH_4 from rainfall and runoff is nearly absent in groundwater. NH_4 in aquatic systems is typically in high demand (Vitousek and Howarth, 1991; Geisseler and others, 2010) and biological utilization likely accounts for at least some NH_4 removal. Similarly, DON also is readily broken down by microorganisms (Neff and others, 2003), which is consistent with an absence of DON in groundwater. As described by Musgrove and others (2016), the removal of NH_4 and DON along with the corresponding enrichment in NO_3 as stormwater runoff transitions into unconfined groundwater is consistent with the process of nitrification. Nitrification typically occurs under aerobic (oxygenated) conditions in the presence of natural organic matter in the form of DON and DOC (Kendall and others, 2007), both of which were present at higher concentrations in stormwater runoff than in groundwater (tables 3 and 4). DOC does not contain N, but its presence in high concentrations in stormwater runoff represents an energy source for nitrifying bacteria to metabolize NH_4 and DON into NO_3 (Kendall and others, 2007). Additional support for the occurrence of nitrification is provided by using a mass balance approach. The median TDN concentration for all stormwater-runoff samples was 1.25 mg/L, and the median TN concentration for all stormwater-runoff samples was 2.10 mg/L, somewhat higher than TDN because of the presence of particulate N. The median NO_3 concentration for all groundwater samples was 1.72 mg/L, similar to and intermediate between TDN and TN concentrations in stormwater-runoff samples. This similarity between TDN and TN concentrations in stormwater runoff and NO_3 concentrations in groundwater is generally consistent with the production of NO_3 caused by the nitrification of most NH_4 and DON from stormwater runoff, which results in a similar amount of NO_3 accumulating in groundwater compared to NO_3 concentrations in surface-water runoff. NO_3 concentrations in groundwater and stormwater runoff are subject to considerable uncertainty because of the spatial and temporal variability in N concentrations and nitrification processes in stormwater runoff and unconfined groundwater; nevertheless, antecedent conditions in the unconfined zone of an aquifer, including oxygenated water and an abundant energy source for microorganisms in the form of DOC in stormwater runoff, support nitrification as a mechanism for various N species into NO_3 in the aquifer. While the specific timing of this process is unclear, the data indicate that nitrification is largely complete in unconfined aerobic (oxygenated) groundwater in the study area.

Stable isotope values of N ($\delta^{15}N\text{-}NO_3$) and O ($\delta^{18}O\text{-}NO_3$) in NO_3 (fig. 8) provide further insight into sources and transformations of N species during the transition from stormwater runoff to unconfined groundwater. Potential NO_3 sources that are consistent with the range of isotope values in samples of stormwater runoff collected in this study include NO_3 in fertilizer, NH_4 in fertilizer that has subsequently been nitrified to NO_3, NO_3 derived from human and animal waste, soil-derived NO_3, NO_3 in rainfall, and NH_4 in rainfall that has been subsequently nitrified to NO_3 (fig. 8). On the basis of low NH_4 and NO_3 concentrations (less than 1.0 mg/L) in stormwater runoff (table 3), contributions of

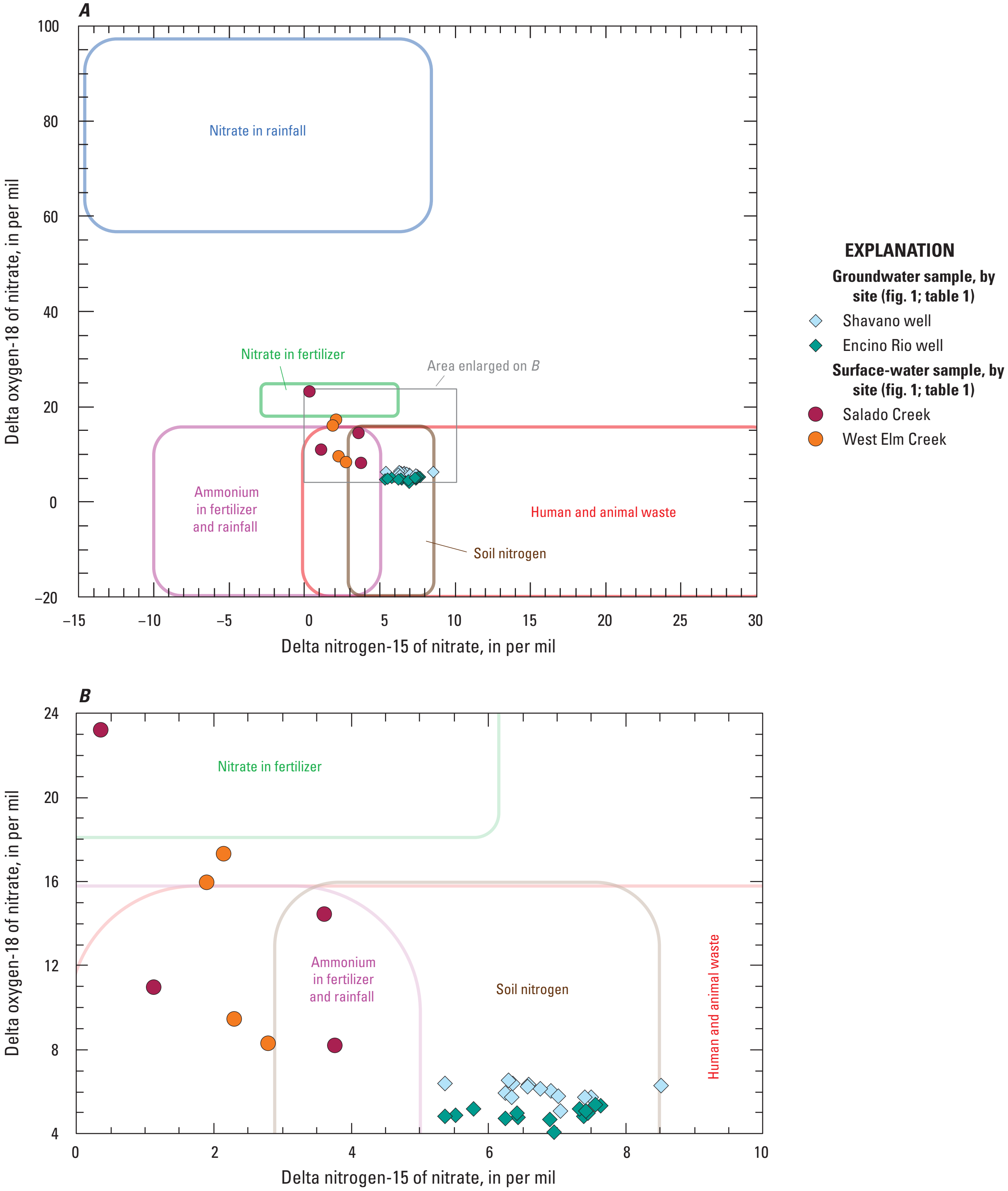


Figure 8. Stable nitrogen and oxygen isotopes of nitrate (delta nitrogen-15 of nitrate [δ^{15}N-nitrate] and delta oxygen-18 of nitrate [δ^{18}O-nitrate]) measured in water samples collected from stormwater-runoff and groundwater sites in the San Antonio segment of the Edwards aquifer, south-central Texas, 2017–19, for *A*, all samples plotted relative to boxes showing the typical δ^{15}N and δ^{18}O ranges of nitrate sources (modified from Kendall and others, 2014) and *B*, samples within a δ^{15}N-nitrate range between 0 and 10 per mil and a δ^{18}O-nitrate range between 4 and 24 per mil. Ranges do not reflect specific south-central Texas sources but rather a compilation of measured values from numerous studies.

excess N from fertilizer or human and animal waste sources are likely small. The observed δ^{15}N-NO$_3$ and O δ^{18}O-NO$_3$ values for stormwater-runoff samples likely result from a mixture of rainfall and soil-derived N sources, which is consistent with the major and trace ion composition of stormwater runoff as previously described. Groundwater had more positive δ^{15}N-NO$_3$ values and more negative δ^{18}O-NO$_3$ values than stormwater runoff. Median values for δ^{15}N-NO$_3$ (6.67 and 6.92 per mil for the Shavano and Encino Rio wells, respectively) and for δ^{18}O-NO$_3$ (6.09 and 4.92 per mil for the Shavano and Encino Rio wells, respectively) are consistent with a shift further away from values expected for rainfall sources and closer to values expected for soil-derived and human or animal waste sources. The large range of values for human and animal waste from Kendall and others (2014) was derived from a broad range of study areas and is not necessarily representative of the Edwards aquifer. Prior data, specifically from the San Antonio segment of the Edwards aquifer (Opsahl and others, 2018), shows that δ^{15}N-NO$_3$ values of less than about 8 per mil are primarily from soil-derived (natural) NO$_{3,}$ and δ^{15}N-NO$_3$ values greater than 8 per mil likely have a wastewater component based on the relation between δ^{15}N-NO$_3$ and NO$_3$ concentration. The clustering of δ^{15}N-NO$_3$ values between 5.36 and 8.51 per mil in groundwater (the value in only one sample was greater than 8 per mil) indicates that groundwater NO$_3$ is primarily soil-derived at both sites, though a component of wastewater-derived NO$_3$ might be present (fig. 8). The single δ^{15}N-NO$_3$ value greater than 8.0 per mil at the Shavano well is indicative of mixing with a small component of wastewater-derived NO$_3$ or another NO$_3$ source with elevated δ^{15}N-NO$_3$ values. Median NO$_3$ concentrations measured in the samples from the Shavano and Encino Rio wells (1.86 and 1.58 mg/L for the Shavano and Encino Rio wells, respectively) were similar, as were median δ^{15}N-NO$_3$ values (6.67 and 6.92 per mil for the Shavano and the Encino Rio wells, respectively), which does not provide clear evidence of a contribution of anthropogenically sourced N to the groundwater at the more urbanized Encino Rio well site.

Concentrations of NO$_3$ and isotopic values (δ^{15}N-NO$_3$) vary temporally in groundwater in response to changes in hydrologic conditions (fig. 5). At the onset of the study, when WLAs were not fluctuating very much, gradual changes in δ^{15}N-NO$_3$ occurred at both sites but in opposite directions. Small shifts in δ^{15}N-NO$_3$ over time likely indicate small changes in the proportions of different NO$_3$ sources. As with other constituents, notable decreases in δ^{15}N-NO$_3$ and NO$_3$ concentrations occurred at both groundwater sites in response to the large recharge event in September 2018; the response at the Encino Rio well was larger than the response at the Shavano well. The decrease in both δ^{15}N-NO$_3$ and NO$_3$ in response to recharge with a concurrent rapid WLA rise is consistent with an influx of stormwater runoff with lower δ^{15}N-NO$_3$ values and NO$_3$ concentrations (table 3). The larger response at the Encino Rio well might result from a more direct connection to stormwater runoff than at the Shavano well, perhaps driven by more conduit flow from recharge streams. Alternatively, the Shavano well might have other less dilute sources of water mixing in at the same time. Following the large recharge event, δ^{15}N-NO$_3$ values gradually increased at both groundwater sites, returning to values similar to those prior to the event. The February 2019 δ^{15}N-NO$_3$ value (8.51 per mil) at the Shavano well, however, was shifted appreciably higher and outside the range of other values for this site. This difference is consistent with changes in other constituents previously described for this period and indicates that a different NO$_3$ source was likely present. The higher isotopic value is consistent with mixing with a water source that is at least partly influenced by wastewater. It is possible that water with a higher δ^{15}N-NO$_3$ value was introduced from another zone of the Edwards aquifer, although exchange of water with the underlying Trinity aquifer (Lindgren and others, 2004) might also account for this shift in chemistry at the Shavano well in February 2019 (δ^{15}N-NO$_3$ values of the Trinity aquifer in this general area are not available for comparison).

The relation between δ^{15}N-NO$_3$ composition and NO$_3$ concentration (fig. 9) illustrates the variability associated with changing NO$_3$ sources as stormwater runoff moves into the aquifer. Samples with lower concentrations of NO$_3$ (stormwater runoff) had isotopic signatures indicative of mixing with rainwater, as would be expected in runoff samples collected shortly (within hours) following rain events (fig. 8). The higher concentrations of NO$_3$ in groundwater relative to those in stormwater runoff are consistent with the transformation of NH$_4$ and DON into NO$_3$ by nitrification. Groundwater δ^{15}N-NO$_3$ values are likely controlled by a combination of factors including the isotopic composition of ambient groundwater and that of NO$_3$ introduced in stormwater runoff, other groundwater sources from the Edwards or Trinity aquifers, and isotopic evolution from nitrification processes. Similar relations between δ^{15}N-NO$_3$ and NO$_3$ have been reported for other wells in the Edwards aquifer (Musgrove and others, 2016; Opsahl and others, 2018a) and collectively indicate that NO$_3$ varies in both concentration and isotopic composition across the aquifer. Values outside a typical range for unconfined groundwater (5–8 per mil) are likely associated with periods of groundwater recharge (Opsahl and others, 2018a), mixing with other aquifer water, or inputs from local sources of anthropogenic NO$_3$ with a wastewater source. Differences in nitrate isotopic composition and concentration in groundwater across the study area are likely controlled by the relative contributions of natural and anthropogenic N (with the anthropogenic N component including a wastewater source) and by the process of nitrification.

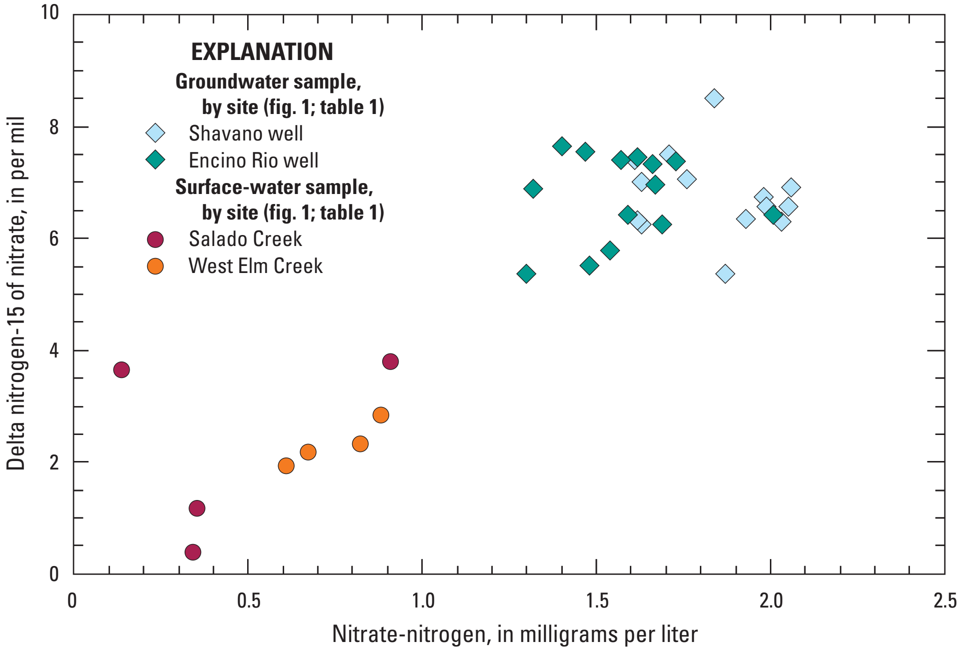


Figure 9. Stable nitrogen isotopes of nitrate (delta nitrogen-15 of nitrate) versus nitrate-nitrogen concentration measured in groundwater samples collected from stormwater-runoff and groundwater sites in the San Antonio segment of the Edwards aquifer, south-central Texas, 2017–19.

Pesticide Dynamics

The occurrence of pesticides in stormwater runoff and unconfined groundwater provides insight into inputs and transport of anthropogenic compounds within the Edwards aquifer. Among all samples, 33 different pesticides (or pesticide degradates) were detected at least once (table 5). The detection frequency of individual pesticides for all samples ranged from about 3 percent (1 detection in 36 samples), which occurred for multiple pesticides, to 75 percent (27 detections in 36 samples) for the atrazine degradate 2-chloro-4-isopropylamino-6-amino-s-triazine (CIAT). There were large differences in the number of pesticides detected at the two surface-water sites: 7 different pesticides were detected at Salado Creek, whereas 25 were detected at West Elm Creek (table 5). Both the total number of pesticide detections per site (50 versus 10) and the average number of detections per sample (12.5 versus 2.5) were five times higher in samples collected from West Elm Creek than in samples collected from Salado Creek. All seven pesticides detected in samples from Salado Creek were herbicides or herbicide degradates. In contrast, a combination of herbicides and herbicide degradates (12), insecticide and insecticide degradates (8), and fungicides (5) were detected in West Elm Creek. Pesticide concentrations greater than 100 ng/L were considered high for the purposes of this study and are discussed for each occurrence. In Salado Creek, there was one detection of triclopyr at a concentration of 2,850 ng/L (table 6). At West Elm Creek, there was one detection of 2,4-D at 116 ng/L, one detection of atrazine at 118 ng/L, and one detection of triclopyr at 101 ng/L. All four pesticides that occurred at concentrations above 100 ng/L were herbicides. Distinct differences in the number of pesticides detected and the total number of detections for the two surface-water sites are consistent with use of a wider variety and greater quantity of pesticides in more urbanized watersheds on the Edwards aquifer recharge zone.

Table 5. Summary of pesticide (or pesticide degradate) detections in surface-water and groundwater samples collected at sites in the San Antonio segment of the Edwards aquifer, 2017–19.

[ng/L, nanogram per liter; SW, surface water; GW, groundwater; NA, not applicable; F, fungicide; H, herbicide; Hd, herbicide degradate; Fd, fungicide degradate; I, insecticide; Id, insecticide degradate]

	Type of pesticide	Laboratory reporting level (ng/L)	Surface water sites (fig. 1; table 1)		Groundwater sites (fig. 1; table 1)		SW detection frequency (percent)[1]	GW detection frequency (percent)[1]
			Salado Creek	West Elm Creek	Shavano well	Encino Rio well		
Number of samples (n)	NA	NA	4	4	14	14	NA	NA
Pesticide compounds	Number of detections[2]							
1H-1,2,4-Triazole	F	22	0	0	1	0	0	4
2,4-D	H	62	0	3	0	1	38	4
2-Chloro-4-isopropylamino-6-amino-s-triazine (CIAT)	Hd	11	1	2	11	13	38	86
2-Chloro-6-ethylamino-4-amino-s-triazine (CEAT)	Hd	20	0	0	2	5	0	25
2-Hydroxy-4-isopropylamino-6-amino-s-triazine (OIAT)	Hd	4.0	1	3	0	9	50	32
2-Hydroxy-4-isopropylamino-6-ethylamino-s-triazine (OIET)	Hd	8.0	0	3	2	6	38	29
4-Hydroxychlorothalonil	Fd	98	0	0	3	2	0	18
Acephate	I	10	0	1	0	0	13	0
Atrazine	H	6.8	2	3	4	11	63	54
Azoxystrobin	F	3.0	0	2	0	0	25	0
Carbaryl	I	5.6	0	2	0	0	25	0
Carbendazim	F	10	0	3	1	2	38	11
Chlorodiamino-s-triazine (CAAT)	Hd	24	0	0	9	10	0	68
Desulfinylfipronil	Id	3.8	0	1	0	0	13	0
Dimethenamid	H	3.0	0	0	1	0	0	4
Diuron	H	5.0	0	3	0	0	38	0
Fipronil amide	Id	9.2	0	1	0	2	13	7
Fipronil sulfone	Id	5.6	0	3	0	0	38	0
Fipronil	I	4.0	0	3	0	1	38	4
Imazaquin	H	18	0	1	0	0	13	0
Imidacloprid	I	16	0	2	1	0	25	4
Malathion	I	5.4	0	1	0	0	13	0
Metolachlor	H	3.2	2	1	0	0	38	0
Myclobutanil	F	7.0	0	1	0	0	13	0
N-(3,4-Dichlorophenyl)-N'-methylurea	H	5.0	1	2	0	0	38	0
Prometon	H	4.0	1	0	0	3	13	11
Propazine	H	3.2	0	1	0	0	13	0

Table 5. Summary of pesticide (or pesticide degradate) detections in surface-water and groundwater samples collected at sites in the San Antonio segment of the Edwards aquifer, 2017–19.—Continued

[ng/L, nanogram per liter; SW, surface water; GW, groundwater; NA, not applicable; F, fungicide; H, herbicide; Hd, herbicide degradate; Fd, fungicide degradate; I, insecticide; Id, insecticide degradate]

	Type of pesticide	Laboratory reporting level (ng/L)	Surface water sites (fig. 1; table 1)		Groundwater sites (fig. 1; table 1)		SW detection frequency (percent)[1]	GW detection frequency (percent)[1]
			Salado Creek	West Elm Creek	Shavano well	Encino Rio well		
Propiconazole	F	6.0	0	3	0	0	38	0
Propoxur	I	3.2	0	0	1	0	0	4
Simazine	H	7.2	0	0	5	9	0	50
Sulfosulfuron	H	11	0	3	1	0	38	4
Tebuconazole	F	5.0	0	1	0	0	13	0
Triclopyr	H	88	2	1	0	0	38	0
Number of different pesticides detected	NA	NA	7	25	13	13	NA	NA
Total number of detections per site	NA	NA	10	50	42	74	NA	NA
Average number of detections per sample[3]	NA	NA	2.5	12.5	3.0	5.3	NA	NA

[1] Calculated for each compound as the total number of detections divided by the total number of samples (n=36) expressed as a percentage.

[2] Estimated pesticide concentrations less than the laboratory reporting level were considered detections.

[3] Calculated for each site as the total number of detections of all pesticides divided by the number of samples.

Table 6. Summary of maximum concentrations of pesticides (or pesticide degradates) in surface-water and groundwater samples collected at sites in the San Antonio segment of the Edwards aquifer, 2017–19.

[F, fungicide; --, not detected in any samples at the corresponding site; H, herbicide; Hd, herbicide degradate; Fd, fungicide degradate; I, insecticide; Id, insecticide degradate]

Pesticide compounds	Type of pesticide	Laboratory reporting level (nanograms per liter)	Concentrations measured in nanograms per liter in samples collected at surface-water sites[1] (fig. 1; table 1)		Concentrations measured in nanograms per liter is samples collected at groundwater well sites[1] (fig. 1; table 1)	
			Salado Creek (n=4)	West Elm Creek (n=4)	Shavano well (n=14)	Encino Rio well (n=14)
1H-1,2,4-Triazole	F	22	--	--	28.2	--
2,4-D	H	62	--	116	--	9.9
2-Chloro-4-isopropylamino-6-amino-s-triazine (CIAT)	Hd	11	10.3	8.67	22.5	41.4
2-Chloro-6-ethylamino-4-amino-s-triazine (CEAT)	Hd	20	--	--	5.7	18
2-Hydroxy-4-isopropylamino-6-amino-s-triazine (OIAT)	Hd	4.0	4.36	12.1	--	7.96
2-Hydroxy-4-isopropylamino-6-ethylamino-s-triazine (OIET)	Hd	8.0	--	57.3	12.4	19.2
4-Hydroxychlorothalonil	Fd	98	--	--	130	51.9
Acephate	I	10	--	13.2	--	--
Atrazine	H	6.8	25.5	118	93.4	18.9
Azoxystrobin	F	3.0	--	2.1	--	--
Carbaryl	I	5.6	--	11.6	--	--
Carbendazim	F	10	--	27.3	--	3.23
Chlorodiamino-s-triazine (CAAT)	Hd	24	--	--	31.3	69.4
Desulfinylfipronil	Id	3.8	--	1.49	--	--
Dimethenamid	H	3.0	--	--	28.2	--
Diuron	H	5.0	--	37.4	--	--
Fipronil amide	Id	9.2	--	5.84	--	4.56
Fipronil sulfone	Id	5.6	--	6	--	--
Fipronil	I	4.0	--	12.4	--	1.63
Imazaquin	H	18	--	8.01	--	--
Imidacloprid	I	16	--	56.1	12.8	--
Malathion	I	5.4	--	6.88	--	--
Metolachlor	H	3.2	12.2	--	--	--
Myclobutanil	F	7.0	--	5.1	--	--
N-(3,4-Dichlorophenyl)-N'-methylurea	H	5.0	3.08	9.16	--	--
Prometon	H	4.0	1.11	--	--	1.77
Propazine	H	3.2	--	2.52	--	--
Propiconazole	F	6.0	--	11.5	--	--
Propoxur	I	3.2	--	--	2.13	--
Simazine	H	7.2	--	--	10.1	10.6
Sulfosulfuron	H	11	--	8.07	1.88	--
Tebuconazole	F	5.0	--	13.7	--	--
Triclopyr	H	88	2,850	101	--	--

[1] Reported concentrations for estimated values that were less than the laboratory reporting level or method detection level are included.

The occurrence and concentrations of pesticides in samples collected at the Encino Rio and Shavano wells were different, and pesticide concentrations in groundwater differed from those in surface water (table 5). Thirteen different pesticides were detected at each groundwater site, but the detection frequency was much higher at the Encino Rio well (n=74) than at the Shavano well (n=42), as was the average number of detections per sample (5.3 and 3.0, respectively). A mixture of herbicides, fungicides, insecticides, and associated degradates occurred at both groundwater sites. Several pesticide compounds occurred in multiple samples from both groundwater sites that were not detected at surface-water sites: the herbicide atrazine degradate 2-chloro-6-ethylamino-4-amino-s-triazine (CEAT), the fungicide degradate 4-hydroxychlorothalanil, the herbicide atrazine degradate chlorodiamino-s-triazine (CAAT), and the herbicide simazine. The presence of pesticide degradates in groundwater but not of the parent pesticide in surface water can be explained by the presence of a component of older groundwater sufficient in age to allow accumulation of the degradates. A near lack of simazine in surface-water samples compared to its widespread occurrence in groundwater is consistent with results from a prior study of the same general study area (Opsahl and others, 2018). The reason for this observation remains unknown. Pesticide concentrations greater than 100 ng/L were considered high for the purposes of this study and are discussed for each occurrence. One of the detections of the fungicide degradate 4-hydroxychlorothalonil at the Shavano well had a concentration of 130 ng/L, whereas no pesticide detections greater than 100 ng/L occurred at the Encino Rio well. Overall, a diverse assortment of pesticides was present in samples from both wells, but the more frequent occurrences at the Encino Rio well are consistent with a larger urban stormwater-runoff component in recharge source water.

The total number of pesticide detections in groundwater samples shows temporal variability associated with changing hydrologic conditions. As WLAs were generally declining at the onset of the study, the total number of pesticides detected in samples collected at the Shavano well ranged from one to three except for a sample collected on March 28, 2018, during a relatively small recharge event; five pesticides were detected in this sample (fig. 10*A*). Following the large recharge event, increases in the total number of detections were evident in three subsequent samples as WLAs at the Shavano well remained relatively high. Thereafter, the number of total pesticide detections decreased to one (April 22, 2019) and then increased to eight (June 10, 2019). The sample with eight detections followed another relatively small recharge event, consistent with the increase in pesticide detections in the sample collected during a small recharge event on March 28, 2018. At the Encino Rio well (fig. 10*B*), the total number of pesticide detections was more variable than at the Shavano well prior to the large recharge event. Similarly, for the Shavano well, the total number of pesticide detections increased in most samples from before the large recharge event relative to the first three samples following the event. WLA then progressively declined at the Encino Rio well as did the total number of pesticide detections. Increases in the number of total pesticide detections following groundwater recharge events observed at both wells are consistent with previous observations (Musgrove and others, 2010; Opsahl and others, 2018a) and further supports the general relation between elevated pesticide detections and contributions of stormwater runoff to groundwater recharge in the Edwards aquifer.

Grouping pesticides into specific categories (herbicides, insecticides, and fungicides) shows a predominance of herbicides relative to insecticides and fungicides in groundwater (fig. 10). Though temporal variability in the numbers and types of pesticides was evident, the overall proportion of pesticides was dominated by triazine herbicides including atrazine, atrazine degradates (CIAT, CEAT, 2-hydroxy-4-isopropylamino-6-amino-s-triazine [OIAT], 2-hydroxy-4-isopropylamino-6-ethylamino-s-triazine [OIET], and CAAT), and simazine (table 5). Most samples had either zero or one detection of insecticides or fungicides (fig. 10) except for three samples collected from the Encino Rio well following the large recharge event. In these three samples, there were two occurrences of each of the following compounds: the fungicide degradate 4-hydroxychlorothalonil, the fungicide (and fungicide degradate) carbendazim, and the insecticide degradate fipronil amide. The occurrence of these pesticides in samples collected from the Encino Rio well following the large recharge event is consistent with an influx of surface-derived recharge having a substantial urban stormwater-runoff component with a higher abundance of pesticides than does ambient groundwater.

Concentrations of pesticides were generally low (less than 100 ng/L) in all samples relative to existing water-quality benchmarks, though four detections exceeded 100 ng/L (0.1 µg/L) and one detection exceeded 2,000 ng/L (2 µg/L). Not all pesticides have regulatory standards, but for those that do, there were no exceedances of individual pesticide concentrations relative to current (2020) drinking water standards (U.S. Environmental Protection Agency, 2019b). Aquatic life benchmarks (U.S. Environmental Protection Agency, 2019c) are not regulatory, but are used to evaluate potential effects of pesticides on aquatic life including fish, invertebrates, vascular plants, and nonvascular plants. In this study, aquatic life benchmarks were exceeded by imidacloprid, which has 0.01 µg/L (10 ng/L) as an invertebrate chronic benchmark (concentrations were 56.1 ng/L and 35.4 ng/L for two samples at West Elm Creek and 12.1 ng/L in one sample at the Shavano well), and by fipronil, which has 0.011 µg/L (11 ng/L) as the invertebrate chronic benchmark (one sample at West Elm Creek had a fipronil concentration of 12.4 ng/L). On the basis of these results, potential effects on aquatic life would be primarily for invertebrate communities in streams. If elevated insecticide concentrations persist in groundwater, groundwater invertebrate communities also might be affected.

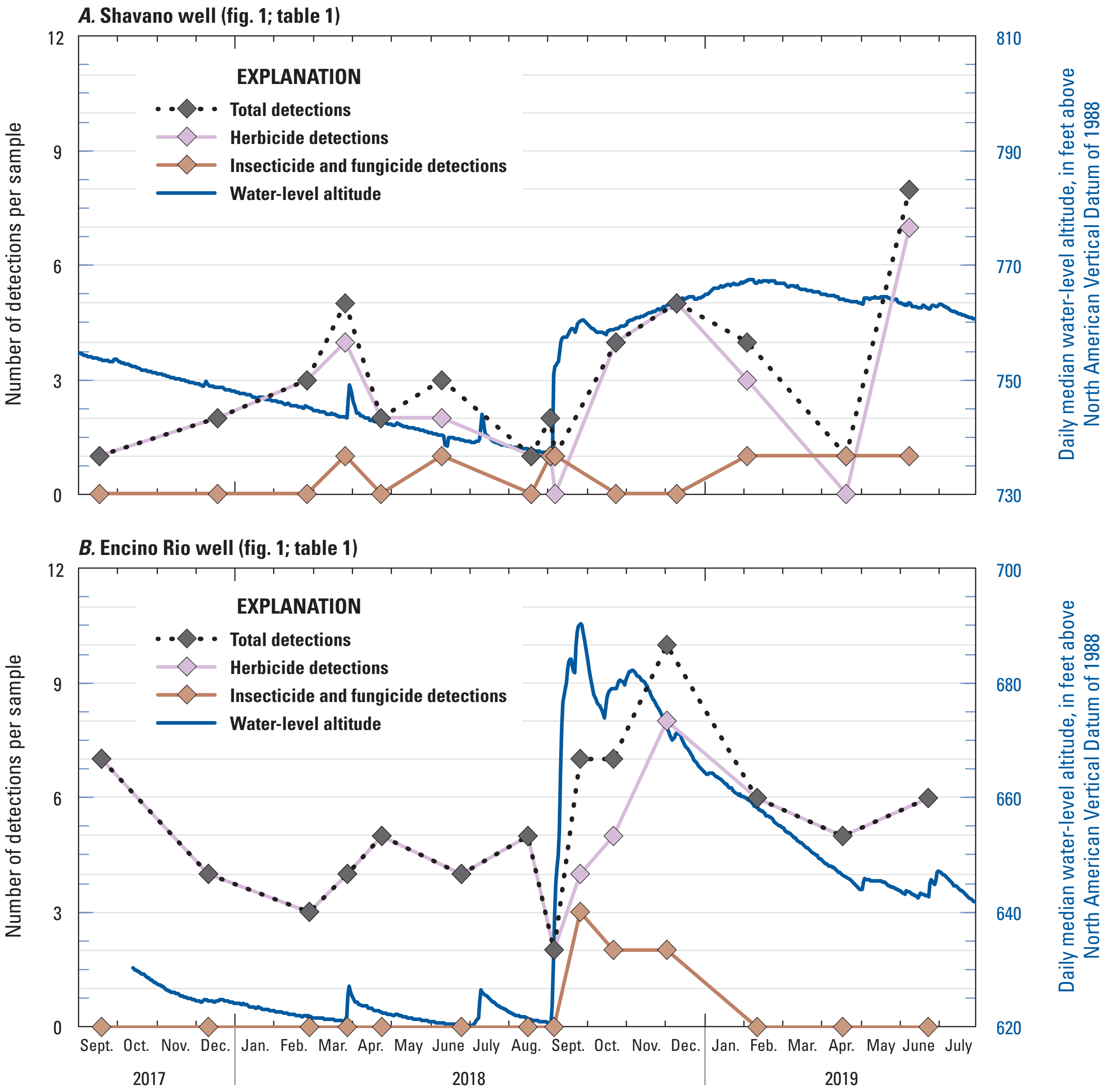


Figure 10. Water-level altitude and the number of detections of herbicides, insecticides plus fungicides, and the total number of detections in samples collected from *A*, the Shavano well and *B*, the Encino Rio well.

Implications of Study Results for Edwards Aquifer Water Quality

This study was designed to monitor and compare water quality at both surface-water and unconfined groundwater sites with different degrees of urbanization. Continuous monitoring of WLA, SC, and concentrations of NO_3 in two wells provided high-resolution data showing detailed changes in water quality across a broad range of hydrologic conditions. The two wells responded differently to the large recharge event in September 2018, with the Encino Rio well in the more urbanized area showing a larger rise in WLA and a greater influx of surface-derived recharge (indicated by decreases in SC and NO_3 concentrations) than at the Shavano well. Among all measured constituents, pesticides detected in discrete stormwater-runoff samples provided the clearest indication that urbanization was adversely affecting water quality; specifically, the more urbanized surface-water site had a greater number of detections and greater variety of detected pesticides. Spatial and temporal variability of nutrients (NO_3, NH_4, DON, and ortho-P) was evident among the surface-water and groundwater sites, but there were no clear associations between nutrient concentrations and degree of urbanization. Prior studies in the same general area as this study have, however, shown elevated levels of NO_3 in groundwater, with a probable wastewater source (Musgrove and others, 2016; Opsahl and others, 2018a) indicating that urbanization effects on groundwater quality vary spatially, with considerable heterogeneity even within the urban area.

A second objective of this study was to determine the extent to which surface-water/groundwater site pairs exhibited hydrologic connectivity between stormwater runoff and recharge. Water levels in the wells responded rapidly (within hours to days) to recharge from both small and large rainfall and runoff events; changes in groundwater quality as a consequence of the influx of surface-derived recharge were indicated by changes in values of the monitored characteristics. The observed hydrologic responses to rainfall and corresponding changes in water quality in wells are thought to result from the direct hydrologic connectivity of surface water and unconfined groundwater; however, patterns of groundwater-quality change indicate mixing from multiple sources such as ambient groundwater, recent surface-derived recharge, and possibly inflow from other aquifers. Therefore, understanding the connection between urbanization and groundwater quality cannot be inferred from the input of stormwater runoff alone as changes related to local and regional hydrologic conditions also need to be considered.

Refined estimates of the spatial and temporal variability in the chemical quality of both stormwater runoff and unconfined groundwater will better constrain inputs into the aquifer and better distinguish the urban-source component. This in turn will help provide insights into the extent to which urban contamination affects the quality of water in the deeper confined zone of the Edwards aquifer, which currently (2020) represents a high-quality public supply to the greater San Antonio area. The deeper, confined zone of the aquifer, which is downgradient from the unconfined zone, is still susceptible to contamination from urban sources, though changes in water quality in this confined zone would likely occur over longer timescales (Musgrove and others, 2019). It should be noted that a single study comparing the results from two site pairs is not able to support definitive conclusions about the full effect of urbanization on surface water/groundwater quality; however, this study does provide useful insights about the spatial and temporal variability of both stormwater runoff and unconfined groundwater that are consistent with expectations based on the current conceptual model that depicts the Edwards aquifer surface-water/groundwater system as a single water resource.

Summary

The San Antonio segment of the Edwards aquifer, in south-central Texas, is a designated sole-source aquifer and the primary water supply for more than 1.7 million people in the city of San Antonio and the surrounding area. The porous nature of the Edwards aquifer recharge zone makes the system vulnerable to contamination from sources at the land surface because the rapid transport of surface-water recharge through sinkholes and losing reaches of streams provides little opportunity for subsurface filtration, sorption, or degradation of the contaminants. Ongoing residential and commercial development in Bexar County, on the Edwards aquifer recharge zone, has the potential to increase the diversity and concentration of contaminants in stormwater runoff and thereby in water recharging the aquifer. To address these challenges, the U.S. Geological Survey (USGS), in cooperation with the City of San Antonio, studied patterns of temporal change (from 2017 to 2019) in water quality at selected surface-water and groundwater sites in the Edwards aquifer recharge zone, with an emphasis on changes during periods of groundwater recharge.

The study design was based on previous and ongoing work in and around the San Antonio area. Water-level altitude (WLA) was measured and water samples were collected at paired surface-water and groundwater sites (wells) during the 2-year study period. WLA, water temperature, specific conductance (SC), and nitrate (NO_3) concentrations were continuously monitored. In addition, discrete water-quality samples were collected from wells and at surface-water sites. The samples were analyzed for major ions, trace ions, nutrients, pesticides, and pesticide degradates. Ancillary climatic and hydrologic data available from other monitoring sites and networks also were used in the analyses and interpretations made in this study.

The study began in September 2017, when the region was receiving only periodic rainfall and hydrologic conditions were relatively stable. Drier conditions prevailed from about April through August 2018, and WLAs at the J–17 index well and discharge at Comal Springs, two regional indicators of hydrologic conditions in the San Antonio segment of the Edwards aquifer, dropped below their long-term median values. In September 2018, more than 16 inches of rainfall was measured at the San Antonio International Airport, resulting in a rapid rise in WLAs at the J–17 index well and in the discharge at Comal Springs. Rapid upward changes in the WLAs at the J–17 index well and in the discharge of Comal Springs were referred to as the “large recharge event.”

Continuous monitoring of SC in groundwater serves as an indicator of how different hydrologic conditions affect the overall chemical quality of recharge water. Large changes and substantially different responses in SC were observed at the Shavano and Encino Rio wells (wells located in the Edwards aquifer recharge zone) over the range of hydrologic conditions that occurred during the study. During the relatively dry condition in the early part of the study, the gradual decline in WLAs at both sites was accompanied by fluctuations in SC at the Shavano well and a gradual decrease with smaller fluctuations in SC at the Encino Rio well. A large decrease in SC of about 80–100 microsiemens per centimeter at 25 degrees Celsius was observed at both of these wells in response to the large recharge event, which is again consistent with mixing of ambient groundwater with relatively dilute water from surface-derived recharge. At the Shavano well, SC increased when slight rises in WLA were observed, which is consistent with a source of more saline, higher SC water. The source of this relatively high SC water in the Shavano well is uncertain but might be accounted for in part by mixing with Edwards aquifer water with higher SC values, which might have included a wastewater component, or introduction of higher SC water from still another source, such as the underlying Trinity aquifer.

Continuous monitoring of NO_3 concentrations provides more insight into their temporal variability and sources compared to periodically collected discrete samples. Initial (September to December 2017) NO_3 concentrations (about 1.6–1.7 mg/L) were similar at the Shavano and Encino Rio wells. NO_3 concentrations were variable at both wells during the study period, with values ranging from about 1.1 to 2.1 mg/L. Following the large recharge event in September 2018, NO_3 concentrations decreased at both wells by about 0.2 to 0.3 mg/L through early November 2018, which is consistent with an influx of recent surface-water recharge that has relatively low NO_3 concentrations. The observed fluctuation in NO_3 concentrations outside of periods of rapid recharge is indicative of mixing with different water sources or of additional processes affecting NO_3 concentrations such as nitrification, the relative contributions of which are uncertain.

Changes in concentrations of specific constituents in groundwater in response to mixing with surface-derived recharge and other source inputs can provide insight into urban influences on surface-water/groundwater interactions in the Edwards aquifer. A broad range in measured values of the stable isotopes of water expressed as delta deuterium (δD) and delta oxygen-18 ($\delta^{18}O$) in the water samples collected from two streams located in the Edwards aquifer recharge zone (Salado and West Elm Creeks), in comparison to the tight clustering of the values of these isotopes in groundwater samples, indicates that source waters (surface waters) of widely varying chemical characteristics likely become homogenized within the aquifer system.

A comparison of major and trace-ion concentrations in stormwater runoff and rainfall samples collected previously indicates that the runoff generally contains higher concentrations of these ions than does rainfall; thus, most of the major ions in stormwater runoff are derived from the land surface rather than from precipitation. Major and trace-ion concentrations were substantially lower in stormwater-runoff samples, however, than in groundwater samples. Time series graphs for concentrations of selected major and trace ions in water samples from the Shavano and Encino Rio wells had both similarities and differences between the wells over the broad range of hydrologic conditions during the study. On the basis of the generally smaller concentrations of major and trace ions in stormwater runoff relative to those in unconfined groundwater (tables 3 and 4), the gradual changes early in the study period are generally consistent with a decreasing proportion of more dilute surface-water recharge, primarily at the Encino Rio well. During and shortly after the large recharge event in September 2018, large decreases in concentrations of sodium, chloride, strontium, and sulfate were observed in samples from the Encino Rio well, while only small decreases in sodium and chloride and very small decreases in strontium and sulfate were observed in samples from the Shavano well. The large decreases in constituent concentrations at the Encino Rio well in response to recharge are consistent with a rapid influx of more dilute surface-derived recharge, specifically with lower concentrations of major and trace ions. Less variability in major and trace-ion concentrations, as well as a smaller rise in WLA at the Shavano well in response to the large recharge event, indicates that less mixing with recent surface-derived recharge occurred relative to mixing at the Encino Rio well.

Stormwater runoff carries both rainfall-derived and land-derived nutrients from the land surface into the aquifer, where environmental conditions and biogeochemical processes likely affect nitrogen (N) concentrations. The distribution of concentrations of N species (NO_3, nitrite [NO_2], and ammonia [NH_4]) among sampling sites transitions from a more variable distribution in stormwater runoff to a more uniform distribution in groundwater in which the dominant form is NO_3. NO_3 concentrations in groundwater and stormwater runoff are subject to considerable uncertainty because of the spatial and temporal variability in N concentrations and nitrification processes in stormwater runoff and unconfined groundwater; nevertheless, antecedent conditions in the unconfined zone of an aquifer, including oxygenated water and an abundant energy source for microorganisms in the form of dissolved organic carbon in stormwater runoff, support nitrification as a mechanism for various N species into NO_3 in the aquifer.

Stable isotope values of N ($\delta^{15}N\text{-}NO_3$) and O ($\delta^{18}O\text{-}NO_3$) in NO_3 provide further insight into sources and transformations of N species during the transition from stormwater runoff to unconfined groundwater. The observed $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ values for stormwater-runoff samples likely result from a mixture of rainfall and soil-derived N sources. Median values for $\delta^{15}N\text{-}NO_3$ (6.67 and 6.92 per mil for the Shavano and Encino Rio wells, respectively) and for $\delta^{18}O\text{-}NO_3$ (6.09 and 4.92 per mil for the Shavano and Encino Rio wells, respectively) are consistent with a shift further away from values expected for rainfall sources and closer to values expected for soil-derived and human or animal waste sources. The clustering of $\delta^{15}N\text{-}NO_3$ values between 5.36 and 8.51 per mil in groundwater (the value in only one sample was greater than 8 per mil) indicates that groundwater NO_3 is primarily soil derived at both sites though a component of wastewater-derived NO_3 might be present. Groundwater $\delta^{15}N\text{-}NO_3$ values are likely controlled by a combination of factors, including the isotopic composition of ambient groundwater and that of NO_3 introduced in stormwater runoff, other groundwater sources from the Edwards or Trinity aquifers, and isotopic evolution from nitrification processes.

The occurrence of pesticides in stormwater runoff and unconfined groundwater provides insight into inputs and transport of anthropogenic compounds within the Edwards aquifer.

Among all samples, 33 different pesticides (or pesticide degradates) were detected at least once. There were large differences in the number of pesticides detected at the two surface-water sites: 7 different pesticides were detected at Salado Creek, whereas 25 were detected at West Elm Creek. Both the total number of pesticide detections (50 versus 10) and the average number of detections per sample (12.5 versus 2.5) were five times higher in samples collected from West Elm Creek than in samples collected from Salado Creek. Distinct differences in the number of pesticides detected and the total number of detections for the two surface-water sites are consistent with use of a wider variety and greater quantity of pesticides in more urbanized watersheds on the Edwards aquifer recharge zone.

The occurrence and concentrations of pesticides in samples collected at the Encino Rio and Shavano wells were different, and pesticide concentrations in groundwater differed from those in surface water. Thirteen different pesticides were detected at each groundwater site, but the detection frequency was much higher at the Encino Rio well (number of samples=74) than at the Shavano well (number of samples=42), as was the average number of detections per sample (5.3 and 3.0, respectively). Increases in the number of total pesticide detections following groundwater recharge events observed at both wells is consistent with previous observations and further supports the general relation between elevated pesticide detections and contributions of stormwater runoff to groundwater recharge in the Edwards aquifer.

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