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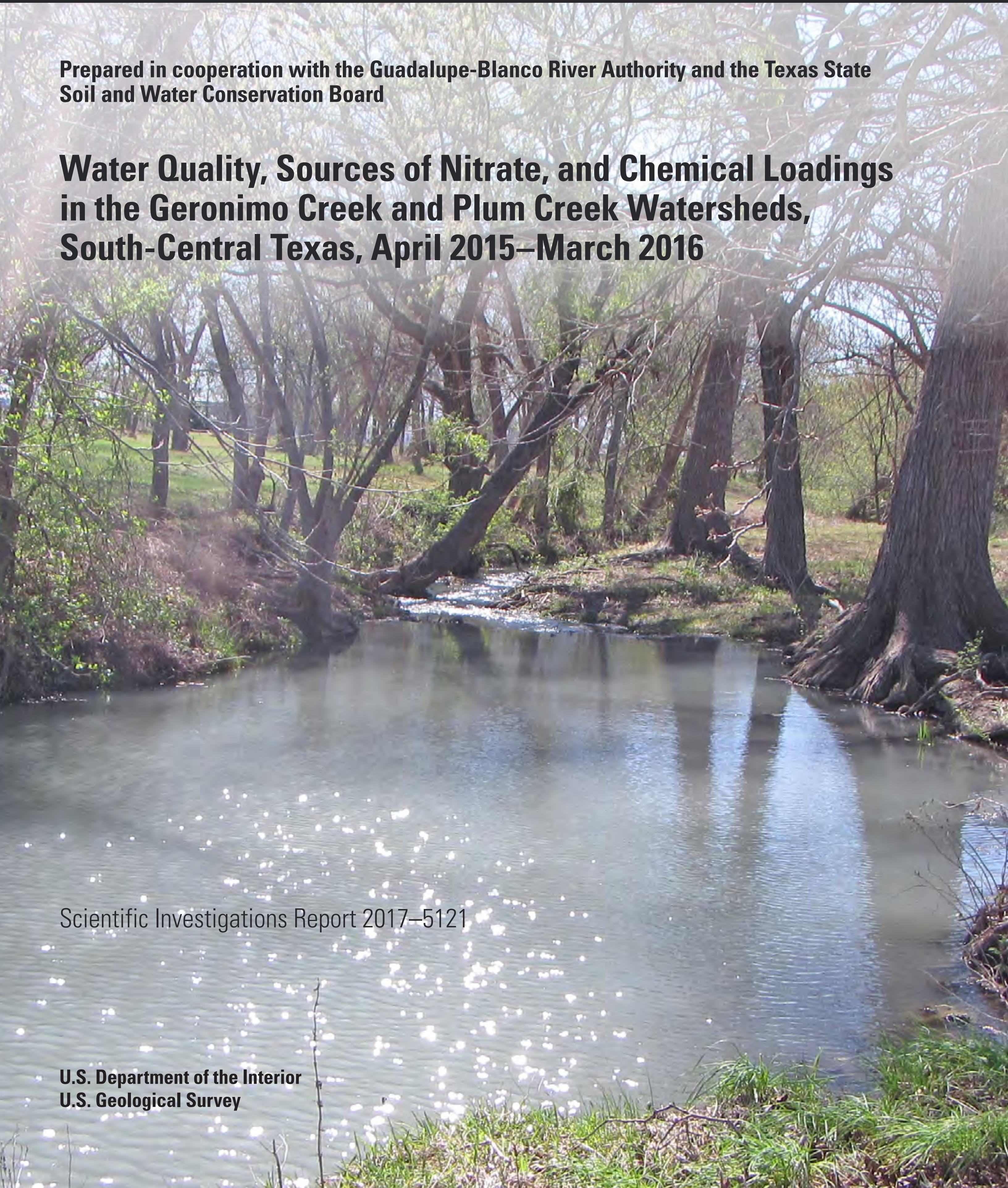

Prepared in cooperation with the Guadalupe-Blanco River Authority and the Texas State Soil and Water Conservation Board

Water Quality, Sources of Nitrate, and Chemical Loadings in the Geronimo Creek and Plum Creek Watersheds, South-Central Texas, April 2015–March 2016

Scientific Investigations Report 2017–5121

U.S. Department of the Interior
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Cover: Photograph showing Geronimo Creek at State Highway 123 near Geronimo, Tex. (photograph by Rebecca B. Lambert, March 2014).

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RYAN K. ZINKE, Secretary

U.S. Geological Survey
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U.S. Geological Survey, Reston, Virginia: 2017

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Suggested citation:
Lambert, R.B., Opsahl, S.P., and Musgrove, MaryLynn, 2017, Water quality, sources of nitrate, and chemical loadings in the Geronimo Creek and Plum Creek watersheds, south-central Texas, April 2015–March 2016: U.S. Geological Survey Scientific Investigations Report 2017–5121, 49 p., https://doi.org/10.3133/sir20175121.

ISSN 2328-0328 (online)

Acknowledgments

This study was conducted in cooperation with the Guadalupe-Blanco River Authority (GBRA) and the Texas State Soil and Water Conservation Board. Funding for this effort is provided through a Clean Water Act Section 319(h) grant from the Texas State Soil and Water Conservation Board and the U.S. Environmental Protection Agency. The authors gratefully acknowledge the assistance of Mike Urrutia (Deputy Executive Manager of Operations and Water Quality, GBRA), Debbie Magin (retired Director of Water Quality Services, GBRA), and the GBRA. Thanks also to Lee Gudgell (Water Quality Project Manager) and staff at the GBRA who helped U.S. Geological Survey field crews collect water-quality, streamflow, and water-level data and provided background information on ongoing water-quality monitoring efforts in both Geronimo Creek and Plum Creek watersheds.


Interior casing of the well at sampling site Laubach Road well (GB714) near Seguin, Tex. (USGS station number 293739097565801), in the Geronimo Creek watershed (photograph by Rebecca B. Lambert, March 2014).

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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)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m^3)
million gallons (Mgal)	3,785	cubic meter (m^3)
cubic mile (mi^3)	4.168	cubic kilometer (km^3)
acre-foot (acre-ft)	1,233	cubic meter (m^3)
acre-foot (acre-ft)	0.001233	cubic hectometer (hm^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per day (ft^3/d)	0.02832	cubic meter per day (m^3/d)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
gallon per day (gal/d)	0.003785	cubic meter per day (m^3/d)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
million gallons per day per square mile ($[Mgal/d]/mi^2$)	1,461	cubic meter per day per square kilometer ($[m^3/d]/km^2$)
mile per hour (mi/h)	1.609	kilometer per hour (km/h)
	Mass	
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	metric ton (t)
	Application rate	
pound per acre per year ([lb/acre]/yr)	1.121	kilogram per hectare per year ([kg/ha]/yr)

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

$$°F = (1.8 \times °C) + 32.$$

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 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 either milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter and micrograms per liter are units expressing the concentration of chemical constituents in solution as mass of solute (milligrams or micrograms) 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):

$$\delta X = \{(R_{sample} - R_{standard})/R_{standard}\} \times 1{,}000$$

where

δ is the “delta” notation,
X is the heavier stable isotope, and
R is ratio of the heavier, less abundant 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 ($\delta^{18}O$)	Vienna Standard Mean Ocean Water (VSMOW) (Fritz and Fontes, 1980)
Nitrogen-nitrate	Nitrogen-15/nitrogen-14 ($\delta^{15}N$-NO_3)	USGS34 potassium nitrate (KNO_3) and USGS32 KNO_3 (Böhlke and others, 2003)
Oxygen-nitrate	Oxygen-18/oxygen-16 of nitrate ($\delta^{18}O$-NO_3)	USGS34 KNO_3 and USGS35 sodium nitrate ($NaNO_3$) (Böhlke and others, 2003)

Results for measurements of stable isotopes of an element (with symbol δ) in water, solids, and dissolved constituents commonly are expressed as the relative difference in the ratio of the number of the less abundant isotope ($^{i}\delta$) to the number of the more abundant isotope of a sample with respect to a measurement standard.

Abbreviations

GBRA	Guadalupe-Blanco River Authority
LRL	laboratory reporting level
MCL	maximum contaminant level
NWQL	National Water Quality Laboratory
RPD	relative percent difference
SMCL	secondary maximum contaminant level
TCEQ	Texas Commission on Environmental Quality
TSWQS	Texas Surface-Water Quality Standards
USGS	U.S. Geological Survey

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By Rebecca B. Lambert, Stephen P. Opsahl, and MaryLynn Musgrove

Abstract

Located in south-central Texas, the Geronimo Creek and Plum Creek watersheds have long been characterized by elevated nitrate concentrations. From April 2015 through March 2016, an assessment was done by the U.S. Geological Survey, in cooperation with the Guadalupe-Blanco River Authority and the Texas State Soil and Water Conservation Board, to characterize nitrate concentrations and to document possible sources of elevated nitrate in these two watersheds. Water-quality samples were collected from stream, spring, and groundwater sites distributed across the two watersheds, along with precipitation samples and wastewater treatment plant (WWTP) effluent samples from the Plum Creek watershed, to characterize endmember concentrations and isotopic compositions from April 2015 through March 2016. Stream, spring, and groundwater samples from both watersheds were collected during four synoptic sampling events to characterize spatial and temporal variations in water quality and chemical loadings. Water-quality and -quantity data from the WWTPs and stream discharge data also were considered. Samples were analyzed for major ions, selected trace elements, nutrients, and stable isotopes of water and nitrate.

The dominant land use in both watersheds is agriculture (cultivated crops, rangeland, and grassland and pasture). The upper part of the Plum Creek watershed is more highly urbanized and has five major WWTPs; numerous smaller permitted wastewater outfalls are concentrated in the upper and central parts of the Plum Creek watershed. The Geronimo Creek watershed, in contrast, has no WWTPs upstream from or near the sampling sites.

Results indicate that water quality in the Geronimo Creek watershed, which was evaluated only during base-flow conditions, is dominated by groundwater, which discharges to the stream by numerous springs at various locations. Nitrate isotope values for most Geronimo Creek samples were similar, which indicates that they likely have a common source (or sources) of nitrate. Nitrate sources in the Geronimo Creek watershed include a predominance of nitrate from fertilizer applications, as well as a contribution from septic systems. Additional nitrate loading from these sources is ongoing. Chemical loadings of dissolved solids, chloride, and sulfate varied little among sampling events and were low at most sites because of low streamflow.

In contrast to the Geronimo Creek watershed, nitrate sources in the Plum Creek watershed are dominated by effluent discharge from the major WWTPs in the upper and central parts of the watershed. Results indicate that discharge from these WWTPs accounts for the majority of base flow in the watershed. Nitrate concentrations in Plum Creek were dependent on flow conditions, with the highest concentrations measured at lower flows, when flow is dominated by WWTP effluent discharge. In addition to WWTP effluent discharge, the Plum Creek watershed, similar to the Geronimo Creek watershed, also is affected by historical and current loading of nitrate from fertilizer applications and from septic systems in the watershed. Chemical loadings of dissolved solids, chloride, sulfate, and nitrate in Plum Creek at lower flow conditions are highest at the upstream sites and decrease downstream as distance from the WWTPs increases, which is consistent with WWTP effluent as an important control on water quality. Under higher flow conditions, however, nitrate loads to Plum Creek increased by about a factor of three. These higher nitrate loads cannot be accounted for by WWTP effluent discharge from the five major WWTPs in the watershed. This additional loading indicates that nitrate is exported from the northeastern part of the watershed. In the lower part of the Plum Creek watershed, higher concentrations of dissolved solids, chloride, and sulfate occur, which might be affected by produced water associated with oil and gas exploration, or mixing with saline groundwater.

Introduction

Nutrient species, including nitrate, nitrite, organic nitrogen, orthophosphate, and phosphorus, are common compounds found in the environment that are needed by plants and animals in low concentrations, but these compounds can have detrimental effects at relatively high concentrations. Potential concerns for human health related to elevated nitrate in drinking water include methemoglobinemia ("blue-baby syndrome"), stillbirths and premature births, and cancer (Dubrovsky and others, 2010; U.S. Environmental Protection Agency, 2012). Excess nutrients in waterways promote algal blooms and eutrophication, in which decomposition of the algae consumes dissolved oxygen and can result in the death of other aquatic life (Ansari and others, 2010). There are numerous possible natural and anthropogenic sources of nitrogen to streams, springs, and wells (Berg and others, 2008; Ling and others, 2012). These sources include fertilizers (manure, organic, and inorganic fertilizers); human and domesticated animal waste (treated wastewater effluent, septic-system drainage); wildlife animal waste (mostly from deer and feral hogs in south-central Texas); decaying plant debris and soils transported to streams by runoff; vehicle exhaust; and atmospheric deposition (Berg and others, 2008; Ling and others, 2012). With increasing urbanization, there also is the possibility of increased nitrate concentrations in groundwater and streamflow resulting from many of these sources, although nitrate sources abound in both rural and urban settings (Puckett and others, 2011; Barlow and others, 2012).

Located in south-central Texas, the Geronimo Creek and Plum Creek watersheds historically have been rural areas dominated by agricultural uses but are rapidly being urbanized as growth spreads outward along the Interstate (I) 35 and I–10 corridors connecting San Antonio, Austin, and Houston, Tex. (fig. 1). Both watersheds were identified by the Guadalupe-Blanco River Authority (GBRA) and the Texas Commission on Environmental Quality (TCEQ) as having water-quality impairments related to elevated nutrient concentrations and high bacteria counts (Berg and others, 2008; Ling and others, 2012).

From April 2015 through March 2016, an assessment was done by the U.S. Geological Survey (USGS), in cooperation with the GBRA and the Texas State Soil and Water Conservation Board, to characterize nitrate concentrations (measured in this study as nitrate as nitrogen, hereinafter referred to "nitrate-N") and to document possible sources of elevated nitrate in these two watersheds. Water-quality samples were collected by the USGS from stream, spring, and groundwater sites distributed across the two watersheds, along with precipitation samples and wastewater treatment plant (WWTP) effluent samples from the Plum Creek watershed, to characterize endmember concentrations and isotopic compositions. Stream, spring, and groundwater samples from both watersheds were collected during four synoptic sampling events to characterize spatial and temporal variations in water quality and chemical loadings. The samples collected by the USGS were analyzed for major ions, selected trace elements, nutrients, and stable isotopes of water and nitrate (fig. 1; table 1).Water-quality and -quantity data from the five major WWTPs in the study area also were obtained from the GBRA for use in the assessment (Lambert and others, 2017).

Purpose and Scope

The purpose of this report is to characterize water quality, sources of nitrate, and chemical loadings in the Geronimo Creek and Plum Creek watersheds in south-central Texas by using water-quality samples (including samples of wastewater treatment inflows) collected by the USGS during April 2015–March 2016. Additional WWTP effluent discharge data previously collected by the GBRA are used in the assessment and published as part of a companion data release to this report (Lambert and others, 2017). Nitrate-N concentrations and stable isotopes of nitrate including delta nitrogen-15 of nitrate ($\delta^{15}N\text{-}NO_3$) and delta oxygen-18 of nitrate ($\delta^{18}O\text{-}NO_3$) are used to characterize nitrate sources in each watershed. Instantaneous chemical loadings of dissolved solids, chloride, sulfate, nitrate-N, organic nitrogen, and orthophosphate are calculated for stream, spring, and WWTP samples and analyzed for spatial and temporal variability in each watershed. This report evaluates the relation of flow to the magnitude of instantaneous chemical loadings, compares loadings between sites, and analyzes spatial differences in chemical concentrations and loadings in each watershed. Concentrations of selected constituents are compared to State and Federal regulations and screening levels for general comparative purposes to provide the reader with context for the concentrations that were measured.

Description of Study Area

The study area consists of the Geronimo Creek and Plum Creek watersheds, which are relatively small watersheds in south-central Texas, east of San Antonio (fig. 1). Geronimo Creek, along with its tributary, Alligator Creek, is the smaller of the two watersheds, with a catchment of approximately 70 square miles in the study area. Geronimo Creek has been listed numerous times on the Texas Water Quality Inventory with a concern for nitrate-N and impairment of contact recreational use because of high bacteria counts (Ling and others, 2012; Texas Commission on Environmental Quality, 2014). Concentrations of nitrate-N often exceed the national primary drinking water standard of 10 milligrams per liter (mg/L) (U.S. Environmental Protection Agency, 2012).

Plum Creek is the larger of the two watersheds, with a catchment of approximately 389 square miles. Effluent discharge from WWTPs contributes base flow to Plum Creek. Spring discharge from the Leona Formation, which has elevated nitrate-N concentrations, also contributes base flow (Berg and others, 2008). Plum Creek historically has

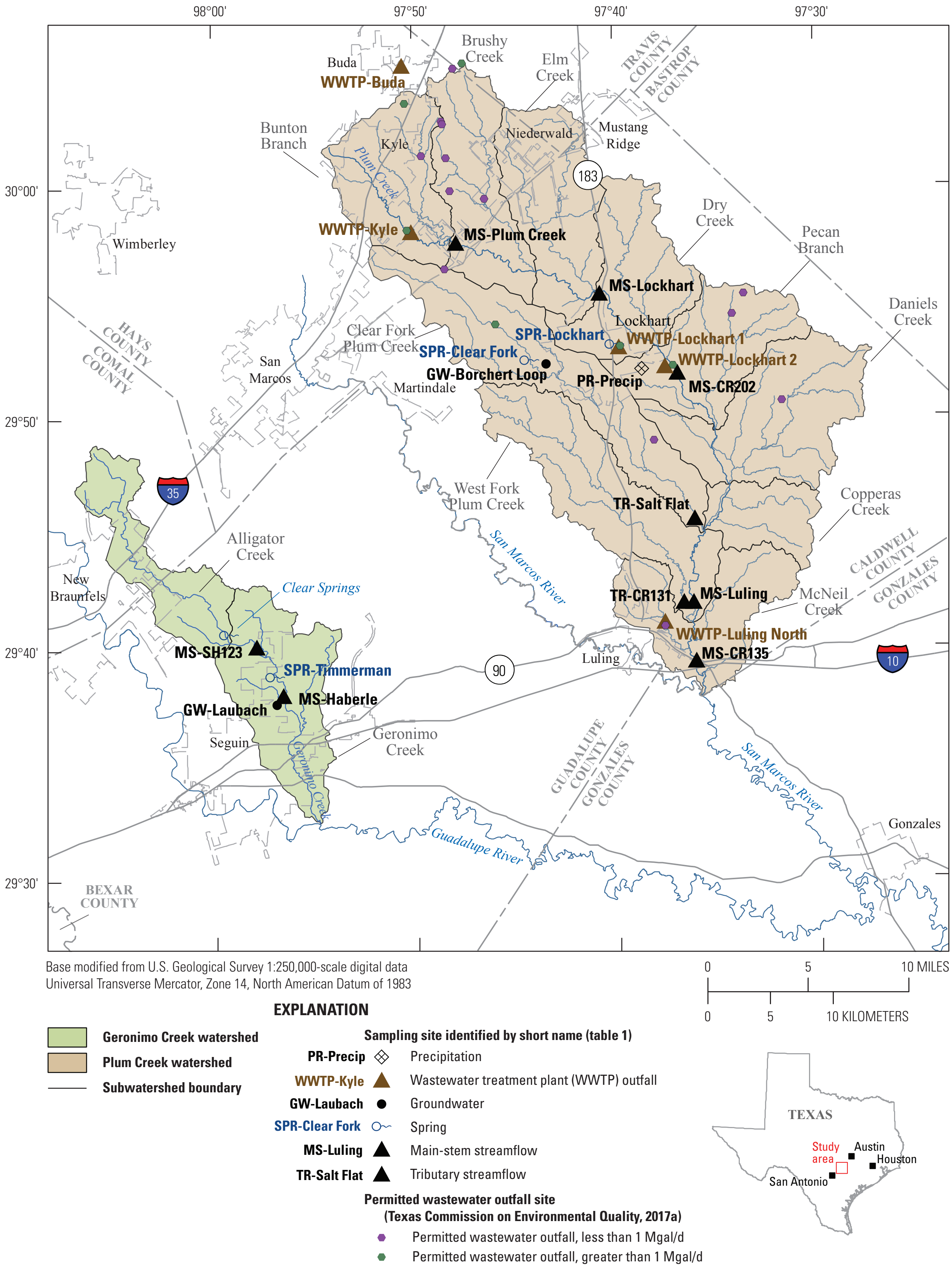

Figure 1. Locations of water-quality sampling sites in the Geronimo Creek and Plum Creek watersheds, south-central Texas, April 2015–March 2016. Permitted wastewater outfalls are in millions of gallons per day (Mgal/d).

Table 1. Water-quality sampling sites in the Geronimo Creek and Plum Creek watersheds, south-central Texas, April 2015–March 2016.

[USGS, U.S. Geological Survey; TCEQ, Texas Commission on Environmental Quality; GBRA, Guadalupe-Blanco River Authority; NAD 83, horizontal coordinate information referenced to North American Datum of 1983; PR, bulk precipitation sample collector; WW, wet deposition (precipitation); --, not applicable or not shown; SH, State Highway; Tex., Texas; MS, main stem; WS, streamflow; SPR, spring; GW, groundwater well; WG, groundwater; TR, tributary; CR, County Road; WWTP, wastewater treatment plant; WE, effluent; no., number]

USGS station number	USGS station name	Short name (fig. 1)	USGS water-quality medium code	County	TCEQ or GBRA station number	Latitude (NAD 1983) (decimal degrees)	Longitude (NAD 1983) (decimal degrees)
295204097384100	Plum Creek precipitation site	PR-Precip	WW	Caldwell	--	--	--
294011097575800	Geronimo Creek at SH 123 near Geronimo, Tex.	MS-SH123	WS	Guadalupe	14932	29.66911944	97.96582500
293851097570301	KX-67-17-808 (Timmerman Springs)	SPR-Timmerman	WS	Guadalupe	21262	29.64750000	97.95083333
293802097563800	Geronimo Creek at Haberle Road near Geronimo, Tex.	MS-Haberle	WS	Guadalupe	12576	29.63395556	97.94389167
293739097565801	Laubach Road well (GB714) near Seguin, Tex.	GW-Laubach	WG	Guadalupe	GB714	29.62738333	97.94952222
08172065	Plum Creek at Plum Creek Road near San Marcos, Tex.	MS-Plum Creek	WS	Hays	17406	29.96027778	97.79805556
[1]08172400	Plum Creek at Lockhart, Tex.	MS-Lockhart	WS	Caldwell	18343	29.92299833	97.67916669
295309097400100	Lockhart Springs at Lockhart, Tex.	SPR-Lockhart	WS	Caldwell	20509	29.88586944	97.66710556
08172475	Plum Creek at CR 202 (Old McMahan Road) near Lockhart, Tex.	MS-CR202	WS	Caldwell	12647	29.86527778	97.61527778
295228097440600	BU-67-11-104 (Clear Fork Springs)	SPR-Clear Fork	WS	Caldwell	20507	29.87500000	97.73777778
295220097432601	BU-67-11-1xx (Borchert Loop well)	GW-Borchert Loop	WG	Caldwell	--	29.87214722	97.72392778
08172980	Clear Fork Plum Creek at Salt Flat Road near Luling, Tex.	TR-Salt Flat	WS	Caldwell	12556	29.76000000	97.60222222
08173000	Plum Creek near Luling, Tex.	MS-Luling	WS	Caldwell	12642	29.69967303	97.60360823
08173080	West Fork Plum Creek at CR 131 (Biggs Road) near Luling, Tex.	TR-CR131	WS	Caldwell	20500	29.69972222	97.61166667
08173200	Plum Creek at CR 135 near Luling, Tex.	MS-CR135	WS	Caldwell	12640	29.65722222	97.60194444
300519097503100	City of Buda outfall near Buda, Tex.	WWTP-Buda	WE	Hays	99923	--	--
295805097500600	City of Kyle outfall at Kyle, Tex.	WWTP-Kyle	WE	Hays	20486	--	--
295303097394800	City of Lockhart no. 1 outfall at Lockhart, Tex.	WWTP-Lockhart 1	WE	Caldwell	20492	--	--
295212097373300	City of Lockhart no. 2 outfall near Lockhart, Tex.	WWTP-Lockhart 2	WE	Caldwell	20494	--	--
294108097374000	City of Luling outfall at Luling, Tex.	WWTP-Luling North	WE	Caldwell	20499	--	--

[1]Site used only for hydrograph comparison purposes; not sampled.

been listed on the Texas Integrated Report of Surface Water Quality (Texas Commission on Environmental Quality, 2012a, 2014) as having known contaminants of concern, impairments for high bacteria counts, and high concentrations of nitrate-N, orthophosphorus, total phosphorus, and dissolved oxygen (unsuitable for aquatic life) (Berg and others, 2008). The nitrate-N and total phosphorus concentrations at sites in the Plum Creek watershed are some of the highest in the Guadalupe-Blanco River Basin, with mean concentrations of nitrate-N ranging from 3.1 to 9.5 mg/L reported for samples collected during 2001–8 (Guadalupe-Blanco River Authority, 2017b).

Hydrogeologic Setting

Elevated nitrate concentrations have existed in the groundwater and surface water of the Plum Creek and Geronimo Creek watersheds for at least 75 years (Rasmussen, 1947; Alexander and others, 1964; Shafer, 1966; Kreitler, 1979; Lambert and others, 2017). The headwaters of Alligator Creek, a tributary to Geronimo Creek, originate in southeastern Comal County, just upstream from where Alligator Creek flows under I–35 near New Braunfels, Tex. (fig. 1). Geronimo Creek originates in northwestern Guadalupe County and flows southeast for 17 miles to its confluence with the Guadalupe River, approximately 3 miles southeast of Seguin, Tex. (fig. 1). Flow in Alligator Creek is ephemeral, with isolated pools present during much of the year. Springs issuing from the Leona Formation and fluviatile terrace deposits contribute flow to the lower part of Alligator Creek and at various locations along Geronimo Creek (Brune, 1975) (figs. 1 and 2).

The headwaters of Plum Creek originate in Hays County near Kyle, Tex. (fig. 1). Plum Creek flows southeast through Caldwell County, passing through Lockhart and Luling, Tex., before it empties into the San Marcos River north of Gonzales County. Streamflow on the main stem of Plum Creek is affected by effluent discharge from WWTPs. In the upper part of the watershed, the Buda and Kyle WWTPs (sites WWTP-Buda and WWTP-Kyle) contribute flow upstream from the MS-Plum Creek site (fig. 1). The WWTP-Buda site is located outside of the Plum Creek watershed; treated wastewater is pumped from the plant outfall to a tributary and drainage ditch that flows into the upper part of the Plum Creek watershed (fig. 1). The Lockhart 1 and Lockhart 2 WWTPs (sites WWTP-Lockhart 1 and WWTP-Lockhart 2) contribute flow to the middle part of the watershed. The Luling WWTP (site WWTP-Luling North) contributes flow to the lower part of the watershed, upstream from the confluence of Plum Creek with the San Marcos River (fig. 1). Tributaries in the subwatersheds contribute streamflow to the main stem of Plum Creek (fig. 1). Streamflow might originate from multiple sources, including spring discharge from geologic units in the study area (alluvium, fluviatile terrace deposits, and Leona Formation) (fig. 2), releases through small-capacity TCEQ-permitted wastewater outfalls (Texas Commission on Environmental Quality, 2017a), releases through culvert piping open to the base of U.S. Department of Agriculture Natural Resources Conservation Service flood-control dams (Texas State Soil and Water Conservation Board, 2017), irrigation return flows, and overland flow generated by precipitation events.

The alluvium, fluviatile terrace deposits, and Leona Formation consist of poorly sorted gravels, sands, silts, and clays and are important geologic formations in the Geronimo Creek and Plum Creek watersheds because of their water-bearing characteristics (fig. 2). The alluvium, fluviatile terrace deposits, and Leona Formation crop out along the banks of Geronimo Creek and Plum Creek. In the Geronimo Creek watershed, the fluviatile terrace deposits and the Leona Formation overlie the Edwards Limestone, Buda Limestone, Eagle Ford Formation, Austin Chalk, Pecan Gap Chalk, and Navarro Group in the upper part of the watershed and overlie the Midway Group and the Wilcox Group in the lower part of the watershed (figs. 2 and 3). In the Plum Creek watershed, the Leona Formation crops out primarily in the central part of the watershed in the Clear Fork Plum Creek subwatershed, and the fluviatile terrace deposits and alluvium are parallel to the stream channels (figs. 1 and 2). Clayey limestones and clays of the Austin Chalk, Pecan Gap Chalk, and Navarro Group crop out in the upper part of the Plum Creek watershed, whereas rocks of the Midway Group and the Wilcox Group that underlie the Leona Formation crop out in the central and lower parts of the watershed (figs. 2 and 3).

Recharge to the alluvium, fluviatile terrace deposits, and Leona Formation in both watersheds results from channel losses along streams and from the direct infiltration of precipitation. The alluvium, fluviatile terrace deposits, and Leona Formation are water-bearing deposits that function as minor aquifers by storing water that eventually issues from springs, contributing base flow to the stream channels in both watersheds and recharging underlying aquifers (Rasmussen, 1947; Hemphill, 2005). The alluvium, fluviatile terrace deposits, and Leona Formation are assumed to be hydraulically connected because the individual rock units are in proximity to one another and there are no confining layers between the units (fig. 3). Most of the groundwater in the Leona Formation, fluviatile terrace deposits, and alluvium generally flows southeast, downgradient to discharge points in stream channels (Hemphill, 2005). Discharge from the Leona Formation, fluviatile terrace deposits, and alluvium may occur along faults and fractures, where stream channels intersect the water table, and by direct infiltration into the underlying Carrizo-Wilcox aquifer, a major aquifer in Texas composed of the Wilcox Group and the hydraulically connected Carrizo Sand (fig. 3) (George and others, 2011). In areas where the Leona Formation and fluviatile terrace deposits overlie bedrock sections of impermeable clay, infiltration into the underlying Carrizo-Wilcox aquifer might be restricted by the decreased porosity and permeability associated with sections of impermeable clay (Shafer, 1966).

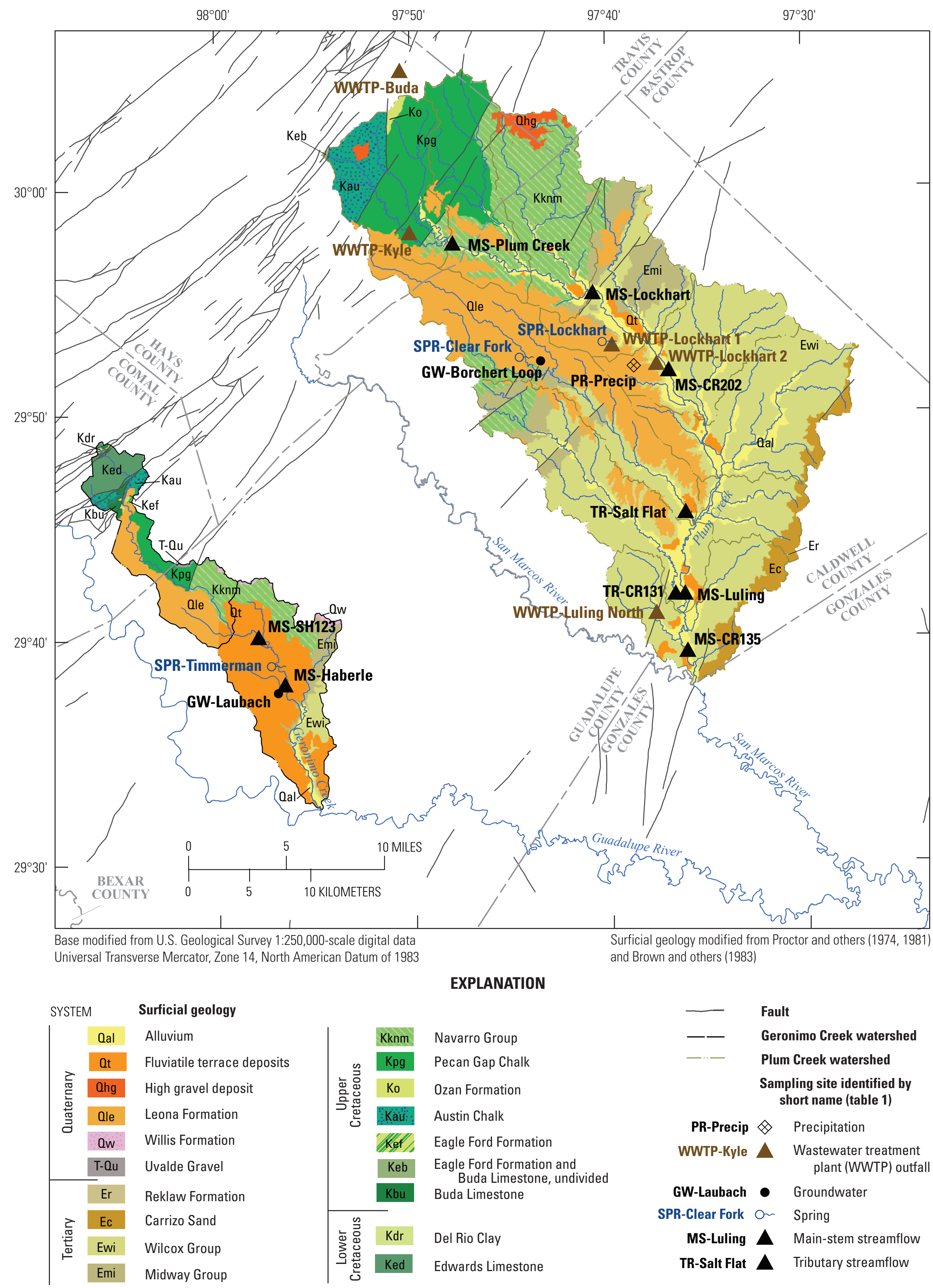

Figure 2. Surficial geology in the Geronimo Creek and Plum Creek watersheds, south-central Texas.

Geologic framework[1]					Hydrostratigraphy		
Era	Period	Epoch	Group[2]	Formation[2]	Map abbreviation and color (fig. 2)[3]	Hydrologic unit[4]	Hydrologic function[4]
Cenozoic	Quaternary	Holocene	**	Alluvium	Qal	Water bearing	Water bearing
		Pleistocene	**	Fluviatile terrace deposits	Qt	Water bearing	Water bearing
			**	High gravel deposit	Qhg	Not saturated	Water bearing
			**	Leona	Qle	Informally referred to as "Leona aquifer"	Water bearing
			**	Willis	Qw	Not saturated	Water bearing
		Pliocene/ Pleistocene	**	Uvalde Gravel	T-Qu	Not saturated	Water bearing
	Tertiary	Eocene	Claiborne	Reklaw	Er	Upper confining unit to the Carrizo-Wilcox aquifer	Confining
			Wilcox	Carrizo Sand	Ec	Carrizo-Wilcox	Aquifer
				**	Ewi		
			Midway	**	Emi	Lower confining unit to the Carrizo-Wilcox aquifer	Confining
Mesozoic	Cretaceous	Late Cretaceous	Navarro	**	Kknm	Confining unit	Confining
			Taylor	Pecan Gap Chalk	Ko		
				Ozan	Kpg		
			Austin	Austin Chalk	Kau		Water bearing
			Eagle Ford	**	Kef		Confining
			Washita	Eagle Ford and Buda, undifferentiated	Keb		Confining
		Early Cretaceous		Buda Limestone	Kbu		Confining
				Del Rio Clay	Kdr	Upper confining unit to the Edwards aquifer	Confining
				Georgetown	*	Edwards	Aquifer
			Edwards	Edwards Limestone	Ked		

[1]Era, period, and epoch are geologic time units; group and formation are geologic rock units.
[2]Double asterisks (**) indicate no further subdivision.
[3]A single asterisk (*) indicates geologic unit not present at land surface in study area.
[4]Water bearing indicates that unit locally yields small quantities of water but is not a formally designated aquifer.

Figure 3. Summary of geologic framework and hydrostratigraphy in the Geronimo Creek and Plum Creek watersheds, south-central Texas (modified from Shafer, 1966; Baker, 1995; Barker and Ardis, 1996; George and others, 2011; U.S. Geological Survey, 2017a).

Land Cover

Characterizing the land cover in a watershed can provide important information regarding possible chemical inputs into a hydrologic budget and help in the interpretation of water-quality results. Land cover for the Geronimo Creek and Plum Creek watersheds was modified from the 2011 National Land Cover Database (NLCD) for this report (fig. 4) (Homer and others, 2015). The land cover was summarized into eight main categories of open water, developed, barren, forest, rangeland, grassland and pasture, cultivated crops, and wetlands (table 2). The developed category includes open space and low-, medium-, and high-intensity subcategories (fig. 4). Deciduous forest, evergreen forest, and mixed forest subcategories were combined into a single category, as were woody wetlands and emergent herbaceous wetlands (fig. 4; table 2). The Geronimo Creek and Plum Creek watersheds each were further divided into subwatersheds (figs. 1 and 4).

In the Geronimo Creek watershed, agricultural uses (rangeland, grassland and pasture, and cultivated crops combined) are the predominant land-cover types (fig. 4; table 2). Cultivated crops account for the largest percentage of land-cover type in the total watershed (about 37 percent). Historically, the percentage of land cover represented by cultivated crops was higher than 37 percent; large amounts of cropland were converted to pasture during the 1960s and 1970s because soil fertility in parts of the watershed is relatively low (Ling and others, 2012). Corn, cotton, sorghum, and wheat are the major crops grown in the watershed (Ling and others, 2012). The sum of grassland and pasture combined with rangeland accounts for an additional approximately 36 percent of the total land cover. These three categories (cultivated crops, grassland and pasture, and rangeland) account for more than 70 percent of the total land cover in the watershed. The primary domestic animals raised on the rangeland are cattle and goats (Ling and others, 2012). Urban areas (New Braunfels and Seguin) are concentrated in the upper and lower parts of the Geronimo Creek watershed; developed land accounts for about 16 percent of the total land cover (figs. 1 and 4; table 2). More than 2,300 septic systems within 1,000 feet (ft) of streams have been documented in the Geronimo Creek watershed (Ling and others, 2012). There are no major WWTPs in the upper part of the Geronimo Creek watershed, and no water-quality samples for this study were collected from there. The WWTPs for New Braunfels and Seguin discharge to a different watershed or discharge downstream from the sampling locations for this study and thus do not affect water quality in the study area (Guadalupe-Blanco River Authority, 2017a).

In the Plum Creek watershed, cultivated crops account for only about 7 percent of the total land cover (fig. 4; table 2). Grassland and pasture combined with rangeland account for about 62 percent of the total land cover in the watershed (fig. 4; table 2). Much of the agricultural land cover is concentrated in the western and southern parts of the watershed (fig. 4; table 2). Urban areas (Buda, Kyle, and Lockhart) are concentrated in the upper and middle parts of the watershed; developed land accounts for 13 percent of the total land cover (figs. 1 and 4; table 2). In the Plum Creek watershed there are five major WWTPs (more than 1 million gallons per day [Mgal/d] capacity each) and numerous smaller permitted wastewater outfalls (less than 1 Mgal/d capacity each) (fig. 1) (Guadalupe-Blanco River Authority, 2017b). Large changes in population between the 2010 and 2016 U.S. censuses indicate rapid urbanization in this watershed; the estimated population of Kyle increased 39.4 percent (from 28,021 to 39,060), and the estimated population of Buda increased 104.6 percent (from 7,343 to 15,023) (U.S. Census Bureau, 2016a, b).

Previous Studies

Previous studies in the Geronimo Creek and Plum Creek watersheds indicate a history of elevated concentrations of nitrate associated with the geology and hydrogeology of the area (Berg and others, 2008; Ling and others, 2012). The GBRA has been monitoring and documenting nitrate-N concentrations of these two watersheds since the late 1990s (Guadalupe-Blanco River Authority, 2017a, b). Previous studies described the geology and hydrogeology of the area (Rasmussen, 1947; Hemphill, 2005) and discussed land use, fertilizer application, and possible reasons for elevated nitrate concentrations (Kreitler, 1979; Hemphill, 2005).

Rasmussen (1947) described the geology and groundwater resources of Caldwell County (including the Plum Creek watershed) and collected water-quality samples during 1943–46 for analysis of selected major ions, nitrate, and trace elements. Sample results described by Rasmussen (1947) indicated that nitrate concentrations were already elevated, ranging from 3.6 to 59 mg/L nitrate-N in samples collected from wells completed in the shallow alluvium as compared to concentrations of nitrate-N ranging from 0.11 to 32 mg/L in samples collected from wells completed in the Carrizo-Wilcox aquifer (both shallow alluvium and Carrizo-Wilcox aquifer values converted from nitrate as NO_3 concentrations reported by Rasmussen, 1947, to nitrate-N concentrations). Rasmussen (1947) noted that approximately two-thirds of Caldwell County was cultivated for a number of different crop types, with cattle, hog, and poultry ranching increasing in importance. Rasmussen (1947) also noted that oil production was substantial in the 1940s, with more than 2 million barrels of oil produced from 15 oil fields in Caldwell County during 1943–44.

Kreitler (1979) assessed the source of elevated nitrate concentrations in Caldwell County by measuring nitrate concentrations and nitrate isotope compositions in samples collected from 28 wells near Lockhart. A mix of domestic, irrigation, and public-supply wells were sampled; all of the wells were completed in the relatively shallow alluvium of the Leona Formation. Kreitler (1979) also measured nitrate isotope ratios of nonfertilized cultivated crops, fertilized cultivated crops, manure and barnyard soil samples, and alluvium samples collected from what he referred to as "alluvial fan aquifers" that are equivalent to the Leona Formation and overlying deposits in the study area. Soil nitrate $\delta^{15}N\text{-}NO_3$ values from manure and barnyard soil samples were much larger than those from samples from cultivated fields. Samples from the nonfertilized cultivated fields had $\delta^{15}N\text{-}NO_3$ values of +2 to +8 per mil with an average value of +4.9 per mil, and fertilized cultivated fields had $\delta^{15}N\text{-}NO_3$ values of +2 to +14 per mil with an average value of +8.8 per mil. In comparison, the $\delta^{15}N\text{-}NO_3$ values from samples collected from the manure and barnyard soil samples were +1 to +22 per mil, with an average $\delta^{15}N\text{-}NO_3$ value of +14.4 per mil. Kreitler (1979) also analyzed the $\delta^{15}N\text{-}NO_3$ values in fertilizer nitrogen (anhydrous ammonia and urea-ammonium-nitrate) applied to fields in the Lockhart area; these values ranged from -7.4 to +1.9 per mil. Kreitler (1979) attributed the more positive $\delta^{15}N\text{-}NO_3$ range for ammonium-fertilized cultivated fields, as compared to the unfertilized fields, to the volatilization of ammonia depleted in $\delta^{15}N\text{-}NO_3$ during fertilizer application that leaves the resulting nitrate enriched (more positive) in $\delta^{15}N\text{-}NO_3$.

Hemphill (2005) studied the hydrogeology of the shallow alluvial deposits of the Leona Formation that compose the Leona aquifer in Caldwell County. Hemphill concluded that the geologic units of the Leona Formation were produced by sedimentary processes associated with a braided stream depositional environment. The braided streams deposited heterogeneous layers of gravel, sand, silt, and clay that have different hydraulic properties, including varying degrees of porosity and permeability. Hemphill (2005) also determined the hydraulic conductivity of the soils overlying the Leona aquifer and found that the hydraulic conductivity was several orders of magnitude less than in the sands and gravels that compose the Leona aquifer. Hemphill (2005) concluded that this difference in hydraulic conductivities is a controlling factor that results in a reduction in recharge to the Leona aquifer that infiltrates through the overlying soils from precipitation.

Hemphill (2005) also evaluated the effects of cultivation furrows, soil slope, and high amounts of certain types of clays on soil permeability pertaining to the Leona Formation in Caldwell County. Hemphill (2005) noted that soil permeability increases when furrows are used in crop cultivation. He also found that soil slopes of less than 8 degrees increased the permeability of the soil, as did the presence of high amounts of shrink-swell clays, which create desiccation cracks when dry, allowing recharge to infiltrate directly.

Hemphill (2005) collected water-quality samples from 23 wells and 5 streams as part of his study and found nitrate-N concentrations in Caldwell County from 0.8 mg/L to greater than 16 mg/L with a median concentration of nearly 11 mg/L (values converted from reported concentrations of nitrate as NO_3). The highest nitrate concentrations generally were measured in samples collected from wells completed in the thickest section of the Leona Formation and fluviatile terrace deposits (Hemphill, 2005).

Methods

During April 2015–March 2016, the USGS collected water-quality samples from a combination of different types of sites distributed across the Geronimo Creek and Plum Creek watersheds (eight stream sites, five WWTP effluent outfall sites, three spring sites, two groundwater sites, and one precipitation site to characterize atmospheric deposition). The GBRA measured field parameters and made discharge and water-level measurements. Atmospheric deposition in the study area consists of precipitation (wet deposition) and the fallout of dry deposition; a bulk precipitation sampler was used to collect wet and dry deposition in one sample. Sample methods and quality-assurance and quality-control measures are documented and discussed herein. Background information on the use of nitrate isotopes as a tool in determining sources of nitrate also is discussed, as is the method for calculation of instantaneous constituent loads. Additional water-quality data were obtained from the GBRA and used to calculate instantaneous nitrate loads for the April 2015–March 2016 study period depicted in this report. Tables of water-quality data collected by the USGS from stream, spring, groundwater, and precipitation sites; instantaneous constituent loads from the stream sites; and instantaneous nitrate loads from the five major WWTPs in the Plum Creek watershed are available for download in a companion data release (Lambert and others, 2017). Additional water-quality data obtained from the GBRA are also available in the companion data release (Lambert and others, 2017).

Site Selection

A field reconnaissance was done prior to the start of sampling to select sample sites on the basis of several factors including the availability of historical data, colocation with current (2015–16) GBRA monitoring networks outlined in the Geronimo Creek and Plum Creek watershed protection plans (WPPs) (Berg and others, 2008; Ling and others, 2012), and the presence of perennial streamflow at most sites. Perennial springs were selected for sampling on the basis of their spatial distribution and amount of flow. Two wells were selected for sampling, one in the Geronimo Creek watershed and one in the Plum Creek watershed. For comparative purposes, both wells are assumed to be completed in fluviatile terrace deposits and the Leona Formation (fig. 2).

Twenty sites in the two watersheds were selected for use by the USGS for sampling or for the data available from the site (19 sites were sampled by the USGS, and 1 additional site was selected because it provided streamflow data that were useful for interpreting water-quality data). To facilitate comparisons between stream, spring, groundwater, precipitation, and WWTP samples, water-quality data in both watersheds were grouped by site type and hydrologic characteristics. The sites consisted of main-stem (MS) and tributary (TR) stream sites, spring (SPR) sites, groundwater

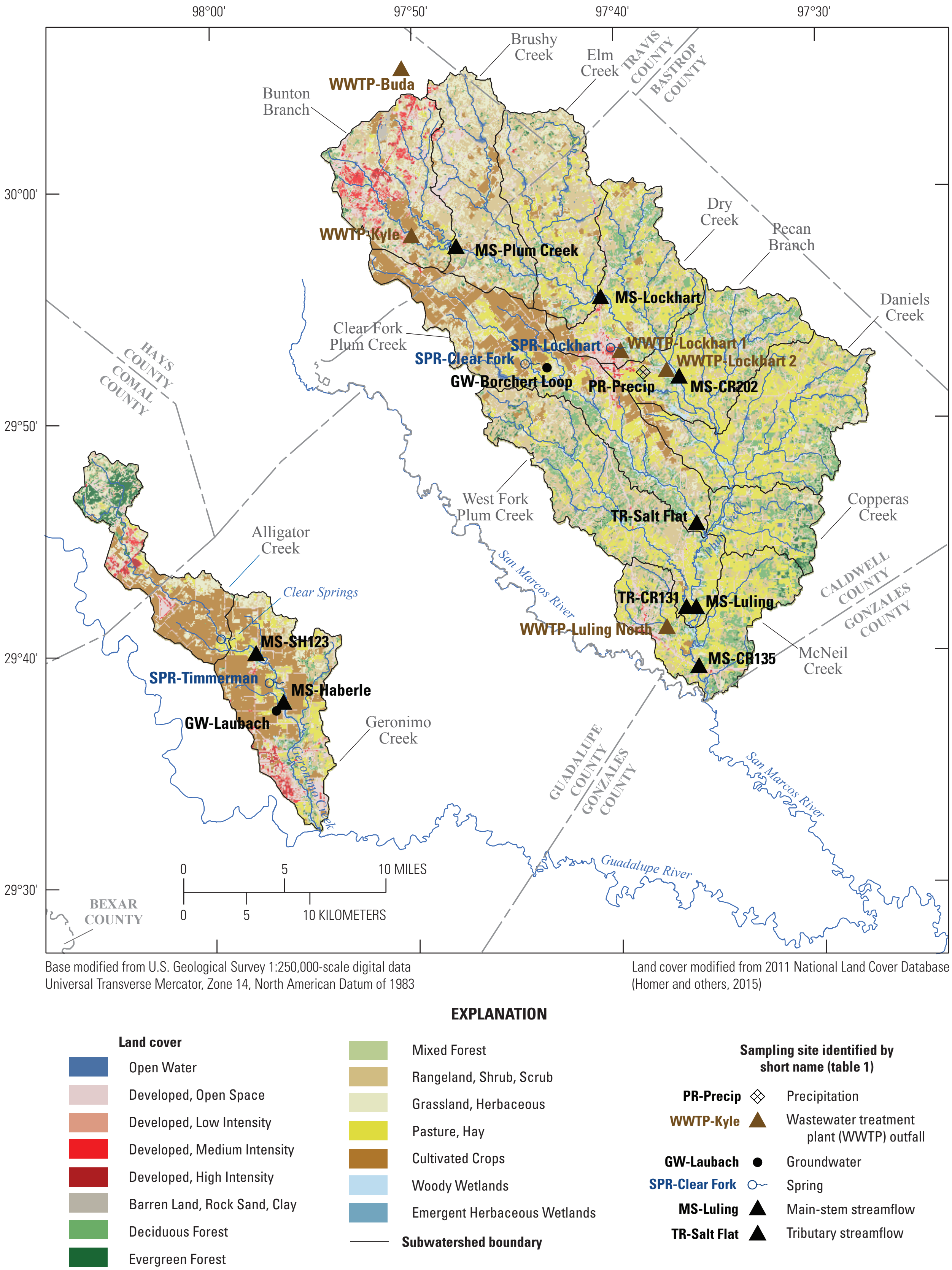

Figure 4. Land cover in the Geronimo Creek and Plum Creek watersheds, south-central Texas; modified from 2011 National Land Cover Database (Homer and others, 2015).

Table 2. Summary of land-cover acreage and percent of total watershed for Geronimo Creek and Plum Creek watersheds, south-central Texas; modified from the 2011 National Land Cover Database (Homer and others, 2015).

[Acreage, total acreage for summary category; percent, portion of total watershed for summary category; <, less than]

Watershed	Subwatershed		Summary category								
			Open water	Developed	Barren	Forest	Rangeland (shrub/scrub)	Grassland and pasture	Cultivated crops	Wetlands	Total
Geronimo Creek	Alligator Creek	Acreage	2	2,733	21	2,650	1,632	4,005	6,575	29	17,647
		Percent	0.01	15.49	0.12	15.02	9.25	22.70	37.26	0.17	100
	Geronimo Creek	Acreage	25	4,452	5	1,351	4,085	6,246	9,690	589	26,443
		Percent	0.10	16.84	0.02	5.11	15.45	23.62	36.65	2.23	100
	Total watershed	Acreage	27	7,184	26	4,002	5,717	10,251	16,265	618	44,089
		Percent	0.06	16.29	0.06	9.08	12.97	23.25	36.89	1.40	100
Plum Creek	Bunton Branch	Acreage	180	7,322	324	998	6,035	5,419	2,279	245	22,803
		Percent	0.79	32.11	1.42	4.38	26.47	23.76	10.00	1.08	100
	Brushy Creek	Acreage	275	2,614	14	1,255	9,989	6,865	1,658	351	23,020
		Percent	1.20	11.36	0.06	5.45	43.39	29.82	7.20	1.52	100
	Elm Creek	Acreage	307	2,116	74	1,692	10,958	8,982	1,173	291	25,594
		Percent	1.20	8.27	0.29	6.61	42.82	35.10	4.58	1.14	100
	Dry Creek	Acreage	68	3,182	123	3,521	6,295	7,992	1,428	1,019	23,628
		Percent	0.29	13.46	0.52	14.90	26.64	33.82	6.05	4.31	100
	Pecan Branch	Acreage	94	2,994	1	3,871	5,365	8,999	272	1,517	23,113
		Percent	0.41	12.95	<0.01	16.75	23.21	38.93	1.18	6.57	100
	Daniels Creek	Acreage	110	2,293	0	5,779	8,170	13,151	705	1,008	31,216
		Percent	0.35	7.35	0.00	18.52	26.17	42.13	2.26	3.23	100
	Copperas Creek	Acreage	31	917	0	3,274	2,726	3,860	0	284	11,092
		Percent	0.28	8.27	0.00	29.51	24.58	34.80	0.00	2.56	100
	McNeil Creek	Acreage	38	3,320	15	4,617	5,368	8,054	141	550	22,104
		Percent	0.17	15.02	0.07	20.89	24.29	36.44	0.64	2.49	100
	West Fork Plum Creek	Acreage	79	3,698	26	5,832	11,925	8,229	413	1,035	31,237
		Percent	0.25	11.84	0.08	18.67	38.18	26.34	1.32	3.31	100
	Clear Fork Plum Creek	Acreage	141	3,981	64	3,116	6,934	9,317	10,311	1,183	35,048
		Percent	0.40	11.36	0.18	8.89	19.78	26.59	29.42	3.38	100
	Total watershed	Acreage	1,324	32,437	642	33,953	73,766	80,866	18,383	7,485	248,855
		Percent	0.53	13.03	0.26	13.64	29.64	32.50	7.39	3.01	100

(GW) sites, a precipitation (PR) site, and WWTP sites (table 1). Sites were assigned a USGS station number and referred to throughout this report by their short names (fig. 1; table 1).

In the Geronimo Creek watershed, four sites were sampled: two main-stem stream sites (MS-SH123 and MS-Haberle), one spring site (SPR-Timmerman), and one groundwater site (GW-Laubach) completed in the alluvium aquifer of the Leona Formation (fig. 1; table 1). Spring discharge enters the stream channel at multiple sites along the reach between the MS-SH123 and MS-Haberle sites; one of these sites is Timmerman Springs (SPR-Timmerman), which discharges water from alluvium and Leona Formation gravels to the stream channel.

In the Plum Creek watershed, 15 sites were sampled: 6 stream sites, 5 WWTP effluent outfall sites, 2 spring sites, 1 groundwater site, and 1 precipitation site. The six stream sites consisted of four sites on the main stem—MS-Plum Creek, MS-CR202, MS-Luling (USGS streamflow-gaging station 08173000 Plum Creek near Luling, Tex.) (U.S. Geological Survey, 2017b), and MS-CR135—and two sites on tributaries (TR-Salt Flat and TR-CR131). The five WWTP effluent sites were WWTP-Buda, WWTP-Kyle, WWTP-Lockhart 1, WWTP-Lockhart 2, and WWTP-Luling North. The two spring sites were SPR-Clear Fork and SPR-Lockhart. Site GW-Borchert Loop was the one groundwater site in the Plum Creek watershed; site PR-Precip also is in the Plum Creek watershed and was the precipitation site used to characterize precipitation in the study area (fig. 1; table 1). Water from the spring sites (SPR-Clear Fork and SPR-Lockhart) and the groundwater site (GW-Borchert Loop) originates from the alluvium and Leona Formation. Two of the sites, MS-CR135 and SPR-Lockhart, were alternate sites and sampled only one time during the study because two of the primary sampling sites were dry. The MS-Lockhart site (USGS streamflow-gaging station 08172400 Plum Creek at Lockhart, Tex.) (U.S. Geological Survey, 2017b) was only used for hydrograph comparison; no water-quality samples were collected at this site, which is in the central part of the watershed upstream from where the WWTP-Lockhart 1 and WWTP-Lockhart 2 sites discharge into Plum Creek (fig. 1).

Samples of precipitation and wastewater were collected to help define sources of nitrate in the Geronimo Creek and Plum Creek watersheds. A bulk precipitation collector (site PR-Precip) was located at the Lockhart Water Plant to collect samples during precipitation events in the Plum Creek watershed, and results were assumed to represent atmospheric contributions to both the Geronimo Creek and Plum Creek watersheds (fig. 1; table 1). The five WWTP sites that were sampled represent effluent inflows from four cities (Buda, Kyle, Lockhart, and Luling) (fig. 1; table 1) (Lambert and others, 2017). The WWTP inflows of these four cities were selected for sampling because they contribute the largest quantity of effluent relative to main-stem base flows in the Plum Creek watershed (Guadalupe-Blanco River Authority, 2017b; Lambert and others, 2017).

Sample Collection and Analysis

Water-quality samples were collected from surface-water sites (streams and springs) and groundwater sites (wells) during four synoptic sampling events (S1–S4) from April to October 2015. Precipitation samples were collected from June 2015 through March 2016. WWTP samples were collected in April 2015.

In the Geronimo Creek watershed, three synoptic sampling events (S1, S2, and S3) were each completed over 1 day, on April 22, July 7, and October 2, 2015, respectively; the fourth synoptic sampling event (S4) was completed over 2 days (October 26–27, 2015). Daily mean streamflow was assessed for the entire period of sample collection, from April 2015 through March 2016. From April 2015 through March 2016, daily mean streamflow at site MS-SH123 ranged from about 1 cubic foot per second (ft^3/s) to about 500 ft^3/s (fig. 5). Instantaneous streamflow measurements ranged from 2.6 to 4.3 ft^3/s during the four sampling events (Lambert and others, 2017) in the Geronimo Creek watershed and were representative of low-flow or base-flow conditions (fig. 5).

For the Plum Creek watershed, daily mean streamflow from April 2015 through March 2016 ranged from less than 1 to about 7 ft^3/s during low-flow or base-flow conditions (generally less than 10 ft^3/s) to about 20,000 ft^3/s during storm events (fig. 6). Stream samples were collected over a range of hydrologic conditions. Synoptic sampling event S1 and synoptic sampling event S2 were done in May and July 2015, respectively, representing midrange flow conditions ranging from about 10 to 200 ft^3/s. These two synoptic sampling events (S1 and S2) each took 2 days to complete (May 1 and May 4, 2015, and July 14 and July 16, 2015, respectively). Synoptic sampling event S3 was done on October 6 and October 8, 2015, after an extended dry period at base-flow conditions when streamflow was less than 10 ft^3/s. Synoptic sampling event S4 was completed during October 25–27, 2015, after a regional storm resulting in higher flows (greater than 200 ft^3/s).

Precipitation samples were collected by using a bulk precipitation collector in the Plum Creek watershed (site PR-Precip) (fig. 1). The precipitation collector consisted of a 20-liter (L) polyethylene container mounted inside a custom stand. The top of the polyethylene container was covered with a stainless steel funnel. The funnel was about 5 ft above the ground; precipitation falling on the funnel emptied into the container. The precipitation collector was set up at the sampling location immediately prior to the beginning of a precipitation event. The sample was retrieved by USGS or GBRA personnel when the precipitation ended. The sample was placed on ice, chilled to 4 degrees Celsius, and transported to the USGS South Texas Program Office Laboratory for processing if sufficient sample volume was available to process. Additional details describing how the samples were collected and processed are outlined in the USGS national field manual (U.S. Geological Survey, variously dated). Each precipitation sample was treated as a

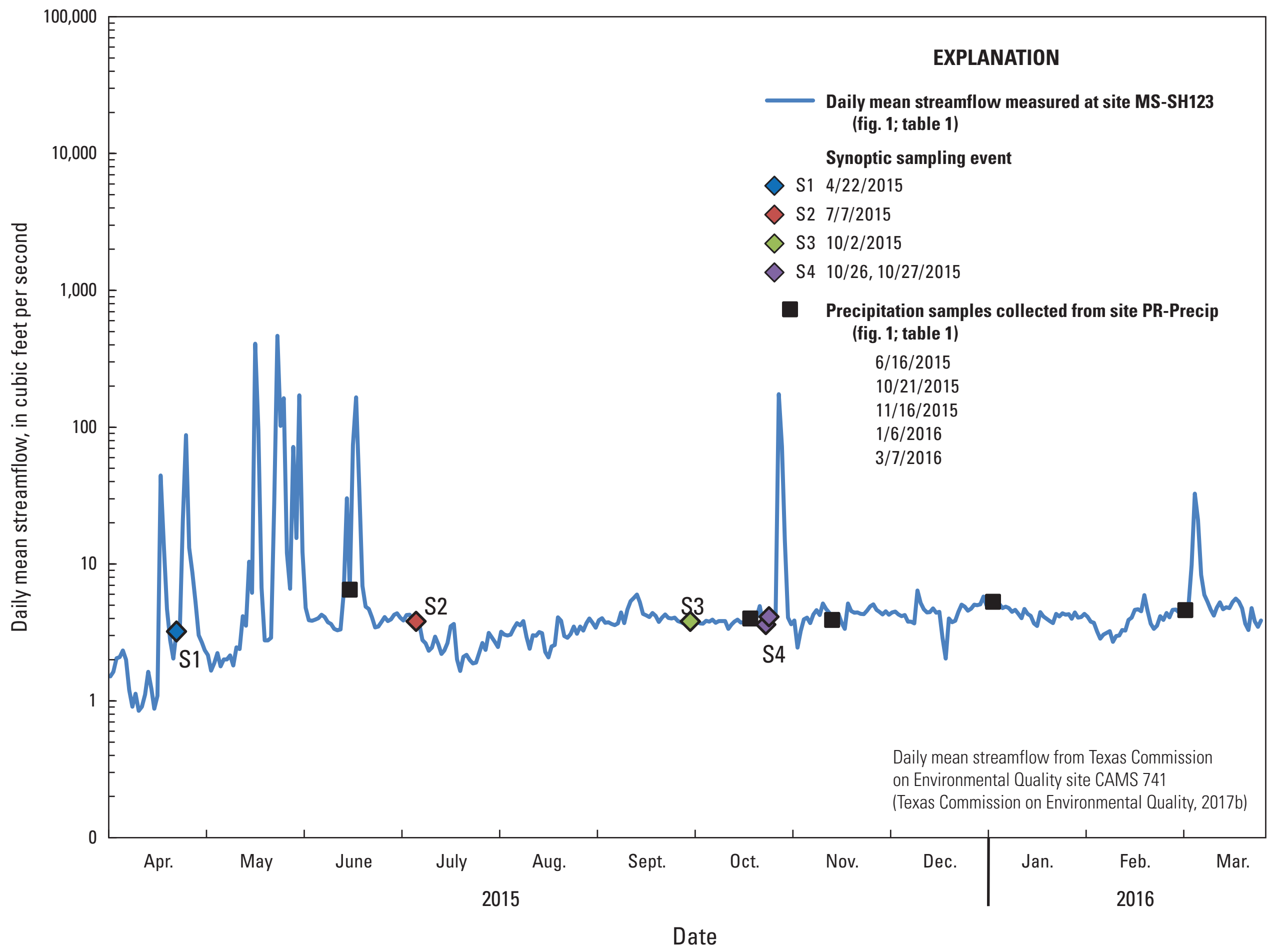

Figure 5. Daily mean streamflow and sample-collection dates at U.S. Geological Survey station 294011097575800 Geronimo Creek at State Highway 123 near Geronimo, Texas (site MS-SH123), April 2015–March 2016.

single-composite sample representing the average water quality of collected precipitation for the event. Five bulk precipitation samples were collected at site PR-Precip from June 2015 through March 2016. The precipitation sample collected on June 16, 2015, was obtained during Tropical Storm Bill (National Oceanic and Atmospheric Administration, 2015), but the resulting sample contained only enough water to analyze for stable isotopes.

Samples were collected from the five WWTPs on April 15, 2015, about the same time as synoptic sampling event S1. The WWTP samples were collected as grab samples from the WWTP outfalls by the USGS on April 15, 2015, and processed by following the procedures outlined in the USGS national field manual (U.S. Geological Survey, variously dated). The nitrate-N concentration in the WWTP-Lockhart 2 sample collected on April 15, 2015 (0.117 mg/L), was near the minimum value (0.10 mg/L) needed for analysis of nitrate isotopes (Lambert and others, 2017). The error associated with the resulting $\delta^{15}N\text{-}NO_3$ value was sufficiently large that the $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ results for this sample were not considered valid and therefore not used in the interpretation of this study.

Water-quality samples from surface-water sites (streams and springs) and groundwater sites (wells) were collected and processed by following procedures outlined in the USGS national field manual (U.S. Geological Survey, variously dated). At each surface-water sampling site with wadeable flows, surface-water (streamflow and springflow) samples were collected at a minimum of 10 locations spaced at equal width increments across the stream by using a US DH-81 1-L bottle sampler (Davis, 2005) attached to a wading rod. The US DH-81 sampler is an isokinetic sampler designed to allow water to enter the sampler with no change in speed or direction. Samples collected at streamflow velocities less than 1.5 feet per second were labeled as grab samples because the sampler is unable to collect an isokinetic sample at those

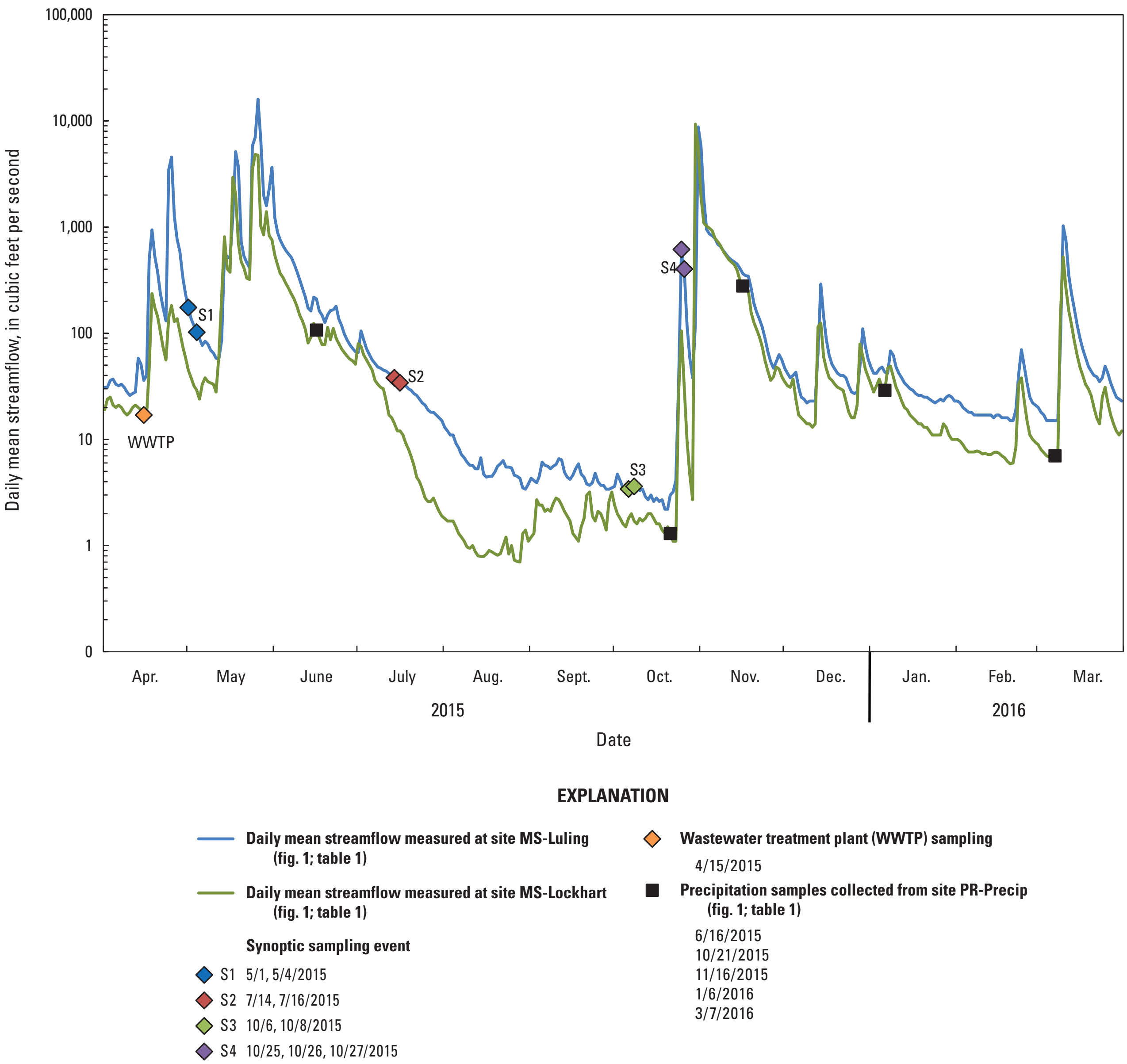

Figure 6. Daily mean streamflow and sample-collection dates at U.S. Geological Survey [USGS] streamflow-gaging station 08173000 Plum Creek near Luling, Texas (site MS-Luling), and USGS streamflow-gaging station 08172400 Plum Creek at Lockhart, Texas (site MS-Lockhart), April 2015–March 2016.

velocities. At higher flows during the stormflow event, some sites were not wadeable and could not be accessed safely because of storm conditions; in those cases a grab sample also was collected by using a 1-L Teflon (polytetrafluoroethylene) bottle. Surface-water samples were composited into a 14-L Teflon churn, and aliquots of representative whole-water (unfiltered) and filtered samples were dispensed from the churn into the appropriate sample bottles.

Groundwater samples were collected from two wells, GW-Laubach and GW-Borchert Loop. The GW-Laubach well did not have a permanently installed pump; a portable USGS groundwater sampling pump was used to collect samples by following protocols outlined in the USGS national field manual (U.S Geological Survey, variously paged). The GW-Borchert Loop well had a permanently installed pump from which the sample was collected from the raw-water spigot near the wellhead. Both of the wells were pumped each time they were sampled to remove three casing volumes of water or until the physicochemical properties of water temperature, dissolved-oxygen concentration, pH, specific conductance, and turbidity stabilized before samples were collected and processed to ensure that the samples collected were representative of water from the aquifer (U.S. Geological Survey, variously dated). Physicochemical properties were considered stable when the variation among five or more sequential field-measurement readings were within plus or minus 0.2 degrees Celsius for water temperature, 0.3 mg/L for dissolved-oxygen concentration, 0.10 unit for pH, 5 percent for specific conductance, and 10 percent for turbidity (U.S. Geological Survey, variously dated).

Water-quality properties measured in the field included water temperature, dissolved-oxygen concentration, pH, specific conductance, turbidity, and alkalinity. Where accessible, instantaneous discharge measurements and water-level measurements were made in streams and wells, respectively, at the time of sample collection.

All of the water-quality samples were analyzed for major ions, selected trace elements, and nutrients by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, by using the same analytical methods. Nutrient analysis included nitrogen components, specifically concentrations of ammonia, nitrate plus nitrite (NO_3+NO_2), nitrite, nitrate (calculated as the difference between NO_3+NO_2 and NO_2), and organic nitrogen, and phosphorus components, specifically concentrations of orthophosphate and total phosphorus (all components of phosphorus from filtered and unfiltered samples). All nitrogen compounds are reported as nitrogen. Stable isotopes of water (δD and δ^{18}O) and stable isotopes of nitrate (δ^{15}N-NO_3 and δ^{18}O-NO_3) were analyzed by the USGS Reston Stable Isotope Laboratory in Reston, Virginia.

A list of measured and calculated analytes, laboratory reporting levels (LRLs), units, method references, and analyzing laboratories for analytical methods are shown in table 3. All analytical results are available for download in a companion data release (Lambert and others, 2017). Summaries of analytical results are shown in tables 4 and 5.

Quality Assurance and Quality Control

A quality-assurance project plan was developed for this study to document the study design, sample collection, analytical methods, LRLs, laboratories used, and quality-control procedures followed during the project (Guadalupe-Blanco River Authority, 2014). Six quality-control samples were collected (Lambert and others, 2017). One field-blank sample was collected from a stream site (MS-SH123) on April 22, 2015, and one from a spring site (SPR-Timmerman) on October 27, 2015, by using blank water certified to contain concentrations of the constituents of interest that were less than the LRL. Field blanks are prepared onsite by rinsing sampling equipment with blank water so that the blank samples are exposed to the same field conditions as the environmental samples (Mueller and others, 2015). Field blanks were collected from sites MS-SH123 and SPR-Timmerman because elevated concentrations of nitrate have historically been measured in the environmental samples collected from these sites (Guadalupe-Blanco River Authority, 2017a). The field blanks from these sites thus served as a conservative (highest likely) estimate of potential contamination in the environmental samples.

Three constituents (chloride, sulfate, and phosphorus) were detected in the field blank samples; these samples were reanalyzed and the analytical results confirmed (Lambert and others, 2017). Chloride was detected in both field blanks (0.03 mg/L at site MS-SH123 and 0.22 mg/L at site SPR-Timmerman) and in NWQL laboratory blanks, indicating that the detection of chloride in the field blanks may result, in part, from chloride contamination at the NWQL. The detected concentrations of chloride, however, were much lower than the associated environmental concentrations (32.4 mg/L at site MS-SH123 and 22 mg/L at site SPR-Timmerman) and thus would not affect interpretation of the environmental results (Lambert and others, 2017). Sulfate (0.06 mg/L) and phosphorus as phosphorus (phosphorus-P), unfiltered (0.02 mg/L), also were detected in the second field blank collected from site SPR-Timmerman on October 27, 2015 (Lambert and others, 2017). Similar to chloride, the sulfate concentration in the field blank was much lower than the associated environmental concentration (38 mg/L) and thus was not considered a factor in interpretation of the environmental results. The phosphorus-P concentration in the field blank (0.02 mg/L) was similar to the associated environmental sample concentration (0.03 mg/L) (Lambert and others, 2017). A review of all phosphorus-P data collected during the study indicates that there are a number of samples collected on different dates with similar low-level concentrations of phosphorus-P, so the environmental results likely were not attributable to sample contamination.

Four split replicate sample pairs were collected from multiple site types (stream, spring, and groundwater) during three of the synoptic sampling events (S1, S2, and S3) to provide information on the reproducibility of sample processing and analysis (Lambert and others, 2017). Relative percent differences (RPDs) were calculated for each replicate pair having detectable concentrations by using the following equation:

$$RPD = [|C_1 - C_2|/((C_1 + C_2)/2)] \times 100 \quad (1)$$

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.

For each constituent, most of the calculated RPDs were less than or equal to 4 percent, indicating acceptable reproducibility associated with sample processing and laboratory analysis. Ammonia, ammonia as nitrogen, and unfiltered and filtered phosphorus-P were the only constituents with some RPDs greater than 4 percent; the RPDs for these constituents ranged from 0 to 40 percent. The concentrations of both replicate pairs of ammonia and phosphorus were low, near the LRL, which resulted in some large RPDs (Lambert and others, 2017). Whereas the RPDs for replicates with small concentrations often are large, these values did not indicate

Table 3. Measured and calculated analytes, laboratory reporting levels, units, method references, and analyzing laboratories for water-quality samples collected from the Geronimo Creek and Plum Creek watersheds, south-central Texas, April 2015–March 2016.

[µg/L, microgram per liter; NWQL, National Water Quality Laboratory of the U.S. Geological Survey; mg/L, milligram per liter; --, not applicable; N, nitrogen; TKN, total Kjeldahl nitrogen; *, nitrate as N, filtered concentration is determined by calculating the difference between the nitrate plus nitrite as N, filtered, concentration and the nitrite as N, filtered, concentration; P, phosphorus; µS/cm, microsiemens per centimeter at 25 degrees Celsius; $\delta^{18}O$, delta oxygen-18; RSIL, Reston Stable Isotope Laboratory of the U.S. Geological Survey; δD, deuterium; $\delta^{15}N\text{-}NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O\text{-}NO_3$, delta oxygen-18 in nitrate]

Analyte	Laboratory reporting level	Units	Method reference	Analyzing laboratory
Boron, filtered	2.0	µg/L	Struzeski and others, 1996	NWQL
Bromide, filtered	0.01	mg/L	Fishman and Friedman, 1989	NWQL
Calcium, filtered	0.022	mg/L	Fishman, 1993	NWQL
Chloride, filtered	0.02	mg/L	Fishman and Friedman, 1989	NWQL
Dissolved solids, filtered (calculated)	2	mg/L	--	--
Fluoride, filtered	0.01	mg/L	Fishman and Friedman, 1989	NWQL
Magnesium, filtered	0.011	mg/L	Fishman, 1993	NWQL
Ammonia as N, filtered	0.01	mg/L	Fishman, 1993	NWQL
Ammonia plus organic nitrogen as N, filtered	0.07	mg/L	Patton and Truitt, 2000	NWQL
Ammonia plus organic nitrogen as N, unfiltered (TKN)	0.07	mg/L	Patton and Truitt, 2000	NWQL
Nitrite as N, filtered	0.001	mg/L	Fishman, 1993	NWQL
Nitrate plus nitrite as N, filtered	0.01	mg/L	Patton and Kryskalla, 2011	NWQL
Nitrate as N, filtered (calculated)*	--	mg/L	--	--
pH, unfiltered, lab	0.1	pH unit	Fishman, 1993	NWQL
Orthophosphate as P, filtered	0.004	mg/L	Fishman, 1993	NWQL
Phosphorus as P, filtered	0.01	mg/L	Patton and Kryskalla, 2003	NWQL
Phosphorus as P, unfiltered	0.01	mg/L	Patton and Kryskalla, 2003	NWQL
Potassium, filtered	0.06	mg/L	American Water Works Association, 1998	NWQL
Silica, filtered	0.018	mg/L	Fishman, 1993	NWQL
Sodium, filtered	0.1	mg/L	Fishman, 1993	NWQL
Specific conductance, unfiltered, lab	5	µS/cm	Fishman and Friedman, 1989	NWQL
Strontium, filtered	0.2	µg/L	Fishman, 1993	NWQL
Sulfate, filtered	0.02	mg/L	Fishman and Friedman, 1989	NWQL
Total nitrogen, filtered	0.08	mg/L	--	--
Total nitrogen, unfiltered	0.08	mg/L	--	--
$\delta^{18}O$ in water, unfiltered	--	per mil	Révész and Coplen, 2008b	RSIL
δD in water, unfiltered	--	per mil	Révész and Coplen, 2008a	RSIL
$\delta^{15}N\text{-}NO_3$, filtered	--	per mil	Coplen and others, 2012	RSIL
$\delta^{18}O\text{-}NO_3$, filtered	--	per mil	Coplen and others, 2012	RSIL

a lack of laboratory precision. The RPD results indicated that sampling and analytical procedures were consistent and reproducible.

Nitrogen and Oxygen Isotopes of Nitrate

Stable isotopes of nitrate ($\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$) have been used in water-quality studies in conjunction with nitrate concentrations to characterize flow paths, identify sources of nitrogen, and provide information on chemical processes that potentially are relevant to tracing nitrogen sources and sinks (Clark and Fritz, 1997). These processes include nitrification and denitrification, which might influence the concentration of nitrate within the watersheds (Kendall and others, 2014). Stable isotopes are measured as the ratio of the two most abundant isotopes of a given element; higher positive values indicate enrichment of the heavier isotope, and lower, more negative values indicate depletion of the heavier isotope (Clark and Fritz, 1997). Nitrogen source studies have shown that the typical available soil nitrate $\delta^{15}N\text{-}NO_3$ values range from 0 to +9 per mil, whereas inorganic (synthetic petroleum-based) fertilizers generally have $\delta^{15}N\text{-}NO_3$ values ranging from -10 to +7 per mil (Kendall, 1998; Kendall and others, 2014). Inorganic fertilizers include ammonium nitrate, potassium nitrate, and calcium nitrate. Organic fertilizers include plant- or animal-based materials that result from naturally occurring process such as manure, leaves, and compost and urea (Kendall and others, 2014). Human and animal waste generally has a range in $\delta^{15}N\text{-}NO_3$ values of 0 to +38 per mil, ammonium in fertilizer has $\delta^{15}N\text{-}NO_3$ values of -10 to +5 per mil, precipitation has a $\delta^{15}N\text{-}NO_3$ range of about -15 to +9 per mil, and inorganic fertilizers have a range of -5 to +7 per mil (Kendall and others, 2014).

Instantaneous Constituent Loads

Constituent loads, as well as constituent concentrations, were used to characterize the chemical contribution to flow in a watershed. Instantaneous constituent loads were calculated by using the following equation:

$$CL = Q_i \times CC \times k \qquad (2)$$

where

CL is the instantaneous constituent load, in tons per day;

Q_i is the instantaneous streamflow, in cubic feet per second;

CC is the constituent concentration, in milligrams per liter; and

k is a unit conversion factor of 0.0027 in tons per day per cubic foot per second.

Instantaneous constituent loads for dissolved solids, chloride, sulfate, and nutrient species were calculated at stream sites in both Geronimo Creek and Plum Creek watersheds (Lambert and others, 2017). Instantaneous discharge measurements were made at the time that the water-quality sample was collected during each synoptic sampling event. Instantaneous WWTP effluent loads were calculated for the five major WWTPs by using effluent discharge rates and nitrate-N concentrations provided by the GBRA (Guadalupe-Blanco River Authority, 2017b; Lambert and others, 2017).

Water Quality, Sources of Nitrate, and Chemical Loadings in Geronimo Creek Watershed

Geronimo Creek from site MS-SH123 to site MS-Haberle is a gaining reach because of inflows from springs issuing from alluvium, fluviatile terrace deposits, and the Leona Formation (Brune, 1975) (fig. 2). Three of the synoptic sampling events (S1, S2, and S3) were completed during low flows, and the fourth synoptic sampling event was completed after a regional storm.

Water Quality

Water-quality data for the Geronimo Creek watershed were organized by constituent concentrations and type of site to facilitate comparisons among precipitation, groundwater, spring, and stream samples. The concentrations of dissolved solids, chloride, and sulfate in the precipitation samples were low, less than 2 mg/L, compared to the concentrations measured at the other sites (fig. 7; tables 4 and 5). In contrast, the other sites (stream, spring, and groundwater) all had higher concentrations that were similar to each other, with little variation in sample concentrations among samples or among site types (fig. 7*A*–*C*; table 4). Concentrations of dissolved solids were similar among samples collected from the groundwater (GW-Laubach), spring (SPR-Timmerman), and upstream main-stem stream (MS-SH123) sites, ranging from 447 to 501 mg/L (fig. 7*A*; table 4). The similarity in dissolved-solids concentration among these sites indicates that groundwater and springflow are dominant controls on water chemistry in the stream. Farther downstream at the MS-Haberle site, the range in dissolved-solids concentrations (350–525 mg/L; table 4) was larger compared to the range measured in samples from the well, spring, and upstream stream sites (table 4), indicating possible additional mixing of water with a different chemical composition.

Chloride and sulfate concentrations generally were lower in the GW-Laubach and SPR-Timmerman samples as compared to those in the MS-SH123 and MS-Haberle samples (figs. 7*B* and 7*C*). There was a progressive increase in chloride concentrations from the groundwater and spring samples to stream samples (fig. 7*B*). Similarly, concentrations of sulfate generally were higher in the stream samples (MS-SH123 and MS-Haberle) as compared to the groundwater and spring samples (fig. 7*C*). There was a broadening in

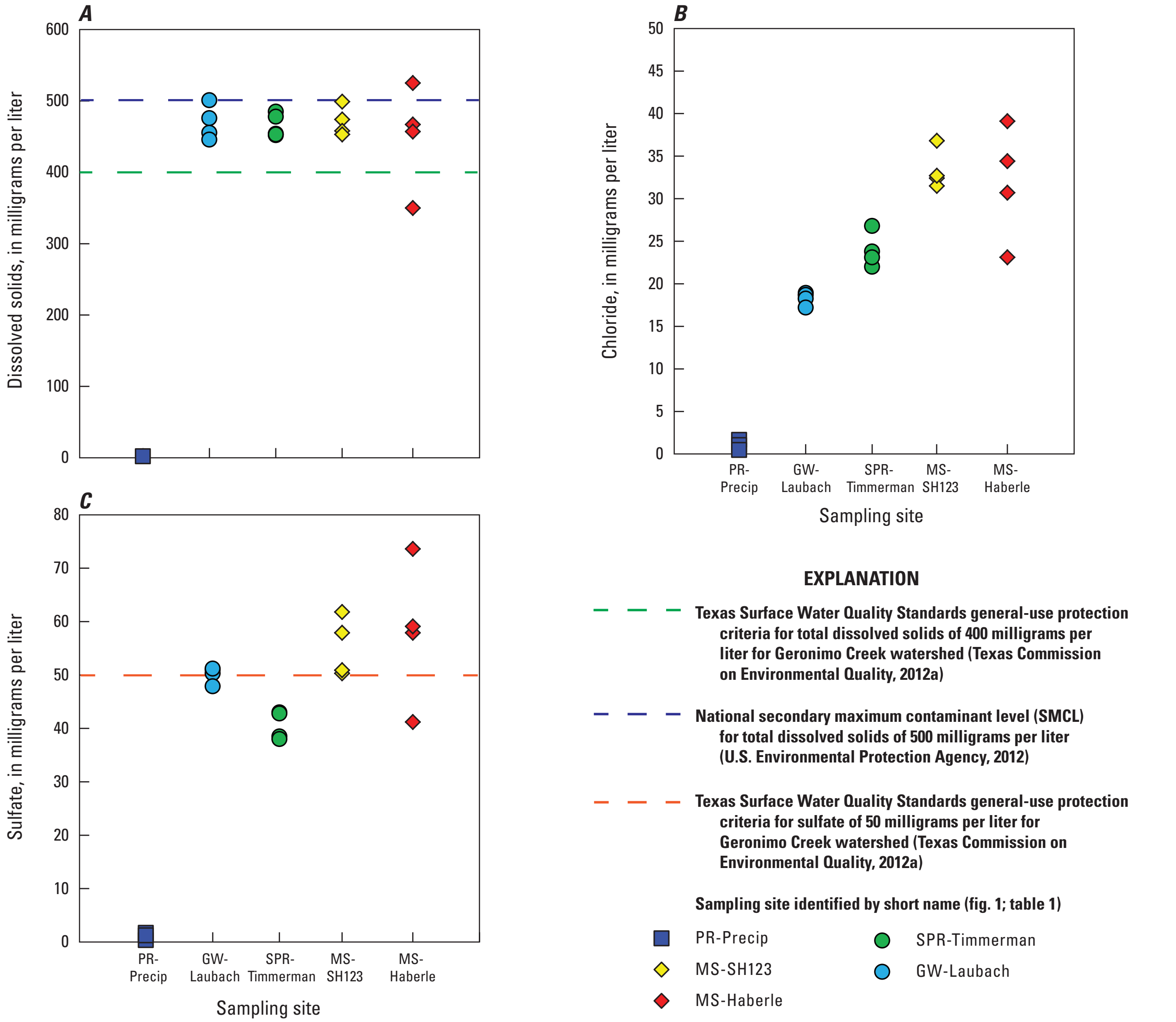

Figure 7. Concentrations of water-quality constituents measured in water-quality samples collected from a precipitation site and from groundwater, spring, and stream sites in the Geronimo Creek watershed, south-central Texas, April 2015–March 2016. *A,* Dissolved solids. *B,* Chloride. *C,* Sulfate.

range of concentration in both chloride and sulfate in the stream samples from the upstream site (MS-SH123) to the downstream site (MS-Haberle). The broadening of the concentration range likely represents increased input and additional mixing of surface water and groundwater along the stream channel from the upstream site (MS-SH123) to the downstream site (MS-Haberle). Evapotranspiration might also contribute to the observed changes, particularly during base-flow conditions.

Appreciably higher nitrate-N concentrations of 13.2–18.2 mg/L were measured in groundwater and spring samples collected from the GW-Laubach and SPR-Timmerman sites compared to the nitrate-N concentrations of 5.44–11.5 mg/L measured in stream samples collected from sites MS-SH123 and MS-Haberle (fig. 8*A*; table 4). The nitrate-N concentrations in the precipitation samples were lower than the other site types, ranging from 0.15 to 2.06 mg/L (table 5). Lower concentrations of nitrate-N in the stream samples as compared to the groundwater and spring samples likely result from mixing of different inputs including dilution from precipitation falling directly into the stream and precipitation-generated storm runoff, water originating upstream from the sampling sites, and groundwater/surface-water mixing as groundwater inflows contribute to streamflow along the length of the stream channel. Historical water-quality concentrations from 2008 to 2016 for Alligator Creek ranged from less than 0.05 to 10 mg/L (Guadalupe-Blanco River Authority, 2017a) and generally were lower than the nitrate-N concentrations measured in samples from Geronimo Creek for this study (5.44–11.5 mg/L). Springflow inflows with elevated concentrations of nitrate-N (14–25 mg/L) were documented by the GBRA to enter Geronimo Creek just upstream from site MS-SH123 (Guadalupe-Blanco River Authority, 2017a). These elevated nitrate-N values reported by the GBRA are consistent with high-nitrate input from other springs (site SPR-Timmerman) farther downstream that discharge into Geronimo Creek.

The concentrations of other nutrient species for all site types, including organic nitrogen and orthophosphate, were appreciably lower compared to the relatively high concentrations of nitrate-N measured in samples collected during this study at the Geronimo Creek sites (fig. 8; tables 4 and 5). The greatest range in concentrations of organic nitrogen and orthophosphate was observed in the precipitation samples (fig. 8; tables 4 and 5). In addition to the similarity among nitrate-N concentrations measured in samples collected from the GW-Laubach, SPR-Timmerman, and MS-SH123 sites, organic nitrogen and orthophosphate concentrations measured in samples collected from the GW-Laubach, SPR-Timmerman, and MS-SH123 sites were similar, indicating that the groundwater or surface water represented by the samples collected from these sites is of similar chemical composition (fig. 8; table 4). Concentrations of organic nitrogen and orthophosphate are higher at the MS-Haberle site compared to those measured in the samples collected from the GW-Laubach, SPR-Timmerman, and MS-SH123 sites. These results indicate that there might be additional mixing of water with a somewhat different chemical composition at the MS-Haberle site than at the upstream GW-Laubach, SPR-Timmerman, and MS-SH123 sites (figs. 8*B* and 8*C*; table 4). The highest orthophosphate (0.164 mg/L) and organic nitrogen (0.47 mg/L) concentrations at site MS-Haberle were measured in the sample collected during synoptic sampling event S1 (April 22, 2015), corresponding with the lowest nitrate-N concentration (5.44 mg/L) and also low streamflow (fig. 5; table 4). Synoptic sampling event S1 in the Geronimo Creek watershed immediately followed a runoff event. The streamflows during synoptic sampling events S2 through S4 were similar to the streamflow during synoptic sampling event S1, but because the antecedent conditions for synoptic sampling events S2 through S4 were different from the antecedent conditions for synoptic sampling event S1, the sources of streamflow were likely different. The overall hydrology and nutrient chemistry results indicate that Geronimo Creek is dominated by discharge of groundwater and springs, with the highest nitrate-N concentrations occurring in the groundwater. Springs discharging to the stream channel, as evidenced by the sample collected from site SPR-Timmerman, likely provide high-nitrate-N base flow along the length of Geronimo Creek.

Sampling site at Timmerman Springs, Tex. (USGS station number 293851097570301) (photograph by Chiquita S. Lopez, April 2015).

Table 4. Summary of results and calculated instantaneous loads of discharge, water levels, major ions, selected trace elements, nutrients, and nitrogen isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) in water samples collected from the Geronimo Creek watershed, south-central Texas, April 2015–March 2016.

[Median instantaneous loads calculated by multiplying the median concentration for a specified constituent by the median discharge. USGS, U.S. Geological Survey; all water-quality constituents were filtered; LRL, laboratory reporting level; ft^3/s, cubic foot per second; --, not measured or not calculated; mg/L, milligram per liter; µg/L, microgram per liter; <, less than; $\delta^{15}N-NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O-NO_3$, delta oxygen-18 in nitrate]

USGS station number	Short name (as identified in fig. 1 and table 1)	Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Median value	Minimum value	Maximum value	Median instantaneous load (tons/day)	Minimum instantaneous load (tons/day)	Maximum instantaneous load (tons/day)
294011097575800	MS-SH123	Discharge (ft^3/s)	4	4	3.65	2.6	4.3	--	--	--
		Dissolved solids (mg/L)	4	4	466	453	499	4.5924	3.3275	5.2593
		Chloride (mg/L)	4	4	32.55	31.5	36.8	0.3208	0.2275	0.3797
		Sulfate (mg/L)	4	4	54.4	50.3	61.8	0.5361	0.4065	0.6341
		Strontium (µg/L)	4	4	430.5	423	484	0.0042	--	--
		Boron (µg/L)	4	4	166	159	175	0.0016	--	--
		Ammonia as N (mg/L)	4	3	0.01	<0.010	0.01	0.0001	--	0.0000
		Nitrate as N (mg/L)	4	4	8.99	7.48	9.6	0.0886	0.0525	0.1021
		Nitrite as N (mg/L)	4	4	0.07	0.01	0.075	0.0007	<0.0001	0.0003
		Organic nitrogen (mg/L)	4	3	0.1	<0.09	0.17	0.0010	--	0.0012
		Orthophosphate as P (mg/L)	4	4	0.015	0.007	0.017	0.0001	0.0001	0.0002
		Phosphorus as P (mg/L)	4	3	0.01	<0.010	0.04	0.0001	--	0.0003
		$\delta^{15}N-NO_3$ (per mil)[1]	4	4	7.35	7.11	7.66	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	4	4	6.56	6.43	6.67	--	--	--
293851097570301	SPR-Timmerman	Discharge (ft^3/s)	4	4	0.27	0.19	0.32	--	--	--
		Dissolved solids (mg/L)	4	4	465	452	485	0.3393	0.2488	0.4130
		Chloride (mg/L)	4	4	32.55	22	26.8	0.0237	0.0122	0.0232
		Sulfate (mg/L)	4	4	54.4	38	43	0.0397	0.0220	0.0372
		Strontium (µg/L)	4	4	434	414	468	0.0003	--	--
		Boron (µg/L)	4	4	200.5	197	214	0.0001	--	--
		Ammonia as N (mg/L)	4	0	--	<0.010	<0.010	--	--	--
		Nitrate as N (mg/L)	4	4	15.1	14.4	16.3	0.0110	0.0084	0.0134
		Nitrite as N (mg/L)	4	0	--	<0.001	<0.001	--	--	--
		Organic nitrogen (mg/L)	4	0	--	<0.07	<0.09	--	--	--
		Orthophosphate as P (mg/L)	4	4	0.021	0.018	0.022	<0.0001	<0.0001	<0.0001
		Phosphorus as P (mg/L)	4	3	0.02	<0.01	0.02	<0.0001	--	<0.0001
		$\delta^{15}N-NO_3$ (per mil)[1]	4	4	6.03	5.79	6.13	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	4	4	5.62	5.34	5.83	--	--	--

Table 4. Summary of results and calculated instantaneous loads of discharge, water levels, major ions, selected trace elements, nutrients, and nitrogen isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) in water samples collected from the Geronimo Creek watershed, south-central Texas, April 2015–March 2016—Continued

[Median instantaneous loads calculated by multiplying the median concentration for a specified constituent by the median discharge. USGS, U.S. Geological Survey; all water-quality constituents were filtered; LRL, laboratory reporting level; ft^3/s, cubic foot per second; --, not measured or not calculated; mg/L, milligram per liter; µg/L, microgram per liter; <, less than; $\delta^{15}N\text{-}NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O\text{-}NO_3$, delta oxygen-18 in nitrate]

USGS station number	Short name (as identified in fig. 1 and table 1)	Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Median value	Minimum value	Maximum value	Median instantaneous load (tons/day)	Minimum instantaneous load (tons/day)	Maximum instantaneous load (tons/day)
293802097563800	MS-Haberle	Discharge (ft^3/s)	4	4	6.25	3.8	7.1	--	--	--
		Dissolved solids (mg/L)	4	4	462	350	525	7.7963	3.5910	10.0643
		Chloride (mg/L)	4	4	32.55	23.1	39.1	0.5493	0.2370	0.7496
		Sulfate (mg/L)	4	4	58.5	41.2	73.6	0.9872	0.4227	1.4109
		Strontium (µg/L)	4	4	426	289	509	0.0072	--	--
		Boron (µg/L)	4	4	206	146	227	0.0035	--	--
		Ammonia as N (mg/L)	4	3	0.01	<0.010	0.03	0.0002	--	0.0000
		Nitrate as N (mg/L)	4	4	10.52	5.44	11.5	0.1775	0.0558	0.2205
		Nitrite as N (mg/L)	4	4	0.023	0.016	0.036	0.0004	0.0002	0.0007
		Organic nitrogen (mg/L)	4	3	0.26	<0.18	0.47	0.0044	--	0.0048
		Orthophosphate as P (mg/L)	4	4	0.016	0.01	0.164	0.0003	0.0002	0.0003
		Phosphorus as P (mg/L)	4	4	0.01	0.01	0.17	0.0002	0.0002	0.0017
		$\delta^{15}N\text{-}NO_3$ (per mil)[1]	4	4	7.75	7.51	8.02	--	--	--
		$\delta^{18}O\text{-}NO_3$ (per mil)[1]	4	4	6.87	6.75	6.97	--	--	--
293739097565801	GW-Laubach	Water level (depth below LSD)	4	4	19.76	22.35	18.1	--	--	--
		Dissolved solids (mg/L)	4	4	466	447	501	--	--	--
		Chloride (mg/L)	4	4	18.45	17.3	18.8	--	--	--
		Sulfate (mg/L)	4	4	50.65	47.9	51.2	--	--	--
		Strontium (µg/L)	4	4	428.5	401	467	--	--	--
		Boron (µg/L)	4	4	250.5	245	276	--	--	--
		Ammonia as N (mg/L)	4	3	0.04	<0.010	0.05	--	--	--
		Nitrate as N (mg/L)	4	4	15.35	13.2	18.2	--	--	--
		Nitrite as N (mg/L)	4	4	0.003	0.001	0.007	--	--	--
		Organic nitrogen (mg/L)	4	2	0.08	<0.03	0.1	--	--	--
		Orthophosphate as P (mg/L)	4	4	0.019	0.011	0.023	--	--	--
		Phosphorus as P (mg/L)	4	3	0.01	<0.01	0.02	--	--	--
		$\delta^{15}N\text{-}NO_3$ (per mil)[1]	4	4	5.46	5.29	5.63	--	--	--
		$\delta^{18}O\text{-}NO_3$ (per mil)[1]	4	4	5.46	5.25	5.57	--	--	--

[1]Ratios of nitrogen-15 to nitrogen-14 of nitrate ($\delta^{15}N\text{-}NO_3$) are reported by using delta notation in per mil relative to USGS34 potassium nitrate (KNO_3) and USGS32 KNO_3 reference standards (Böhlke and others, 2003). Ratios of oxygen-18 to oxgyen-16 of nitrate ($\delta^{18}O\text{-}NO_3$) are reported by using delta notation in per mil relative to USGS34 and USGS35 sodium nitrate ($NaNO_3$) reference standards (Böhlke and others, 2003). The estimated uncertainty of $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ measurement results for samples with nitrate concentrations of at least 0.06 mg/L as nitrogen is ±0.5 per mil unless otherwise specified.

Table 5. Summary of results and calculated instantaneous loads of discharge, water levels, major ions, selected trace elements, nutrients, and nitrogen isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) in water samples collected from streams, springs, and wells; a bulk precipitation collector; and major wastewater treatment plants in the Plum Creek watershed, south-central Texas, April 2015–March 2016.

[Median instantaneous loads calculated by multiplying the median concentration for a specified constituent by the median discharge. USGS, U.S. Geological Survey; all water-quality constituents were filtered; LRL, laboratory reporting level; ft^3/s, cubic foot per second; --, not measured or not calculated; mg/L, milligram per liter; µg/L, microgram per liter; <, less than; $\delta^{15}N\text{-}NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O\text{-}NO_3$, delta oxygen-18 in nitrate; WWTP, wastewater treatment plant]

USGS station number	Short name (as identified in fig. 1 and table 1)	Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Median value	Minimum value	Maximum value	Median instantaneous load (tons/day)	Minimum instantaneous load (tons/day)	Maximum instantaneous load (tons/day)
08172065	MS-Plum Creek	Discharge (ft^3/s)	4	4	16.15	2.7	75	--	--	--
		Dissolved solids (mg/L)	4	4	471	384	767	20.5380	5.5914	86.2650
		Chloride (mg/L)	4	4	97.6	56.1	187	4.2558	1.2792	24.3000
		Sulfate (mg/L)	4	4	91.4	63.9	108	3.9855	0.7873	16.3418
		Strontium (µg/L)	4	4	3,460	2,530	10,100	0.1509	--	--
		Boron (µg/L)	4	4	222	171	363	0.2823	--	--
		Ammonia as N (mg/L)	4	4	0.14	0.04	0.71	0.0061	0.0005	0.0027
		Nitrate as N (mg/L)	4	4	3.53	2.49	19.7	0.1539	0.0740	0.5488
		Nitrite as N (mg/L)	4	4	0.120	0.013	0.26	0.0052	0.0009	0.0156
		Organic nitrogen (mg/L)	4	4	0.68	0.58	0.88	0.0297	0.0064	0.1397
		Orthophosphate as P (mg/L)	4	4	0.917	0.162	3.73	0.0400	0.0243	0.0328
		Phosphorus as P (mg/L)	4	4	0.91	0.16	3.69	0.0397	0.0233	0.0324
		$\delta^{15}N\text{-}NO_3$ (per mil)[1]	4	4	15.645	9.95	18.28	--	--	--
		$\delta^{18}O\text{-}NO_3$ (per mil)[1]	4	4	6.23	4.1	9.89	--	--	--
295309097400100	SPR-Lockhart	Discharge (ft^3/s)	1	1	--	2.1	2.1	--	--	--
		Dissolved solids (mg/L)	1	1	--	466	466	--	2.6422	2.6422
		Chloride (mg/L)	1	1	--	25.1	25.1	--	0.1423	0.1423
		Sulfate (mg/L)	1	1	--	65.8	65.8	--	0.3731	0.3731
		Strontium (µg/L)	1	1	--	365	365	--	--	--
		Boron (µg/L)	1	1	--	165	165	--	--	--
		Ammonia as N (mg/L)	1	0	--	<0.010	<0.010	--	--	--
		Nitrate as N (mg/L)	1	1	--	11.2	11.2	--	0.0635	0.0635
		Nitrite as N (mg/L)	1	1	--	0.005	0.005	--	<0.0001	<0.0001
		Organic nitrogen (mg/L)	1	0	--	<0.17	<0.17	--	--	--
		Orthophosphate as P (mg/L)	1	1	--	0.037	0.037	--	0.0002	0.0002
		Phosphorus as P (mg/L)	1	1	--	0.03	0.03	--	0.0002	0.0002
		$\delta^{15}N\text{-}NO_3$(per mil)[1]	1	1	--	8.72	8.72	--	--	--
		$\delta^{18}O\text{-}NO_3$ (per mil)[1]	1	1	--	7.9	7.9	--	--	--

Table 5. Summary of results and calculated instantaneous loads of discharge, water levels, major ions, selected trace elements, nutrients, and nitrogen isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) in water samples collected from streams, springs, and wells; a bulk precipitation collector; and major wastewater treatment plants in the Plum Creek watershed, south-central Texas, April 2015–March 2016—Continued

[Median instantaneous loads calculated by multiplying the median concentration for a specified constituent by the median discharge. USGS, U.S. Geological Survey; all water-quality constituents were filtered; LRL, laboratory reporting level; ft^3/s, cubic foot per second; --, not measured or not calculated; mg/L, milligram per liter; µg/L, microgram per liter; <, less than; $\delta^{15}N-NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O-NO_3$, delta oxygen-18 in nitrate; WWTP, wastewater treatment plant]

USGS station number	Short name (as identified in fig. 1 and table 1)	Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Median value	Minimum value	Maximum value	Median instantaneous load (tons/day)	Minimum instantaneous load (tons/day)	Maximum instantaneous load (tons/day)
08172475	MS-CR202	Discharge (ft^3/s)	4	4	22.5	5	306	--	--	--
		Dissolved solids (mg/L)	4	4	453.5	154	608	27.5501	8.2080	127.2348
		Chloride	4	4	64.9	15.5	127	3.9427	1.7145	12.8061
		Sulfate	4	4	67	21.4	87.9	4.0703	1.0598	17.6807
		Strontium (µg/L)	4	4	1,755	635	2,070	0.1066	--	--
		Boron (µg/L)	4	4	198.5	73	258	0.0121	--	--
		Ammonia as N (mg/L)	4	4	0.02	0.02	0.03	0.0012	0.0001	0.0002
		Nitrate as N	4	4	4.355	1.93	14.3	0.2646	0.1931	1.5946
		Nitrite as N	4	4	0.0165	0.013	0.065	0.0010	0.0003	0.0537
		Organic nitrogen (mg/L)	4	4	0.55	0.42	1.2	0.0334	0.0073	0.9914
		Orthophosphate as P (mg/L)	4	4	0.756	0.368	1.73	0.0459	0.0234	0.3040
		Phosphorus as P (mg/L)	4	4	0.79	0.36	1.64	0.0480	0.0221	0.2974
		$\delta^{15}N-NO_3$ (per mil)[1]	4	4	12.605	8.79	16.55	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	4	4	8.06	7.82	9.14	--	--	--
295228097440600	SPR-Clear Fork	Discharge (ft^3/s)	4	4	2.2	1.2	10	--	--	--
		Dissolved solids (mg/L)	4	4	443	348	479	2.6314	1.4288	9.3960
		Chloride (mg/L)	4	4	24.5	21.6	28.9	0.1455	0.0719	0.7803
		Sulfate (mg/L)	4	4	82.9	68.2	86.3	0.4924	0.2592	2.3301
		Strontium (µg/L)	4	4	344	279	401	0.0770	--	--
		Boron (µg/L)	4	4	149	134	165	0.1384	--	--
		Ammonia as N (mg/L)	4	2	0.025	<0.010	0.04	0.0001	<0.0001	<0.0001
		Nitrate as N (mg/L)	4	4	5.9	11.9	35	0.0350	0.0256	0.0726
		Nitrite as N (mg/L)	4	4	0.06	0.034	0.105	0.0004	0.0000	0.0009
		Organic nitrogen (mg/L)	4	2	0.41	<0.21	0.62	0.0024	0.0012	0.0037
		Orthophosphate as P (mg/L)	4	4	0.05	0.008	0.136	0.0003	0.0001	0.0227
		Phosphorus as P (mg/L)	4	3	0.1	<0.01	0.19	0.0006	<0.0001	0.0027
		$\delta^{15}N-NO_3$ (per mil)[1]	4	4	9.2	8.64	9.85	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	4	4	7.2	6.8	8.27	--	--	--

Table 5. Summary of results and calculated instantaneous loads of discharge, water levels, major ions, selected trace elements, nutrients, and nitrogen isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) in water samples collected from streams, springs, and wells; a bulk precipitation collector; and major wastewater treatment plants in the Plum Creek watershed, south-central Texas, April 2015–March 2016—Continued

[Median instantaneous loads calculated by multiplying the median concentration for a specified constituent by the median discharge. USGS, U.S. Geological Survey; all water-quality constituents were filtered; LRL, laboratory reporting level; ft³/s, cubic foot per second; --, not measured or not calculated; mg/L, milligram per liter; µg/L, microgram per liter; <, less than; $\delta^{15}N-NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O-NO_3$, delta oxygen-18 in nitrate; WWTP, wastewater treatment plant]

USGS station number	Short name (as identified in fig. 1 and table 1)	Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Median value	Minimum value	Maximum value	Median instantaneous load (tons/day)	Minimum instantaneous load (tons/day)	Maximum instantaneous load (tons/day)
295220097432601	GW-Borchert Loop	Water level (depth below LSD)	4	4	--	--	--	--	--	--
		Dissolved solids (mg/L)	4	4	394.5	378	401	--	--	--
		Chloride (mg/L)	4	4	11.5	10.9	11.7	--	--	--
		Sulfate (mg/L)	4	4	45.5	44.9	51.4	--	--	--
		Strontium (µg/L)	4	4	310	288	323	--	--	--
		Boron (µg/L)	4	4	117.5	113	120	--	--	--
		Ammonia as N (mg/L)	4	0	--	<0.010	<0.010	--	--	--
		Nitrate as N (mg/L)	4	4	13.4	12.6	15.5	--	--	--
		Nitrite as N (mg/L)	4	0	--	<0.001	<0.001	--	--	--
		Organic nitrogen (mg/L)	4	0	--	<0.070	<0.070	--	--	--
		Orthophosphate as P (mg/L)	4	4	0.014	0.012	0.016	--	--	--
		Phosphorus as P (mg/L)	4	4	0.03	<0.010	0.01	--	--	--
		$\delta^{15}N-NO_3$ (per mil)[1]	4	4	5.5	4.68	5.62	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	4	4	5	4.88	5.1	--	--	--
08172980	TR-Salt Flat	Discharge (ft³/s)	3	3	18	13	73	--	--	--
		Dissolved solids (mg/L)	3	3	249	181	332	12.1014	11.6532	35.6751
		Chloride (mg/L)	3	3	25.3	17.4	45.5	1.2296	1.2296	3.4295
		Sulfate (mg/L)	3	3	26.7	20.8	33.8	1.2976	1.0109	5.2626
		Strontium (µg/L)	3	3	235	129	296	0.0114	--	--
		Boron (µg/L)	3	3	84	82	110	0.0041	--	--
		Ammonia as N (mg/L)	3	3	0.02	0.02	0.03	0.0010	<0.0001	0.0004
		Nitrate as N (mg/L)	3	3	0.86	0.766	1.33	0.0418	0.0416	0.2621
		Nitrite as N (mg/L)	3	3	0.009	0.007	0.037	0.0004	0.0003	0.0073
		Organic nitrogen (mg/L)	3	3	0.53	0.47	0.82	0.0258	0.0186	0.1616
		Orthophosphate as P (mg/L)	3	3	0.079	0.143	0.757	0.0038	0.0023	0.0487
		Phosphorus as P (mg/L)	3	3	0.09	0.04	0.27	0.0044	0.0019	0.0532
		$\delta^{15}N-NO_3$ (per mil)[1]	3	3	9.74	9.11	9.87	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	3	3	7.15	5.75	8.58	--	--	--

Table 5. Summary of results and calculated instantaneous loads of discharge, water levels, major ions, selected trace elements, nutrients, and nitrogen isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) in water samples collected from streams, springs, and wells; a bulk precipitation collector; and major wastewater treatment plants in the Plum Creek watershed, south-central Texas, April 2015–March 2016—Continued

[Median instantaneous loads calculated by multiplying the median concentration for a specified constituent by the median discharge. USGS, U.S. Geological Survey; all water-quality constituents were filtered; LRL, laboratory reporting level; ft^3/s, cubic foot per second; --, not measured or not calculated; mg/L, milligram per liter; µg/L, microgram per liter; <, less than; $\delta^{15}N-NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O-NO_3$, delta oxygen-18 in nitrate; WWTP, wastewater treatment plant]

USGS station number	Short name (as identified in fig. 1 and table 1)	Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Median value	Minimum value	Maximum value	Median instantaneous load (tons/day)	Minimum instantaneous load (tons/day)	Maximum instantaneous load (tons/day)
08173000	MS-Luling	Discharge (ft^3/s)	4	4	54.5	4.6	437	--	--	--
		Dissolved solids (mg/L)	4	4	359	144	750	52.8269	9.3150	169.9056
		Chloride (mg/L)	4	4	65.2	15.7	196	9.5942	2.4343	18.5244
		Sulfate (mg/L)	4	4	40.4	17.7	81.8	5.9449	1.0160	20.8842
		Strontium (µg/L)	4	4	941.5	418	2,060	0.1385	--	--
		Boron (µg/L)	4	4	161	72	462	0.0237	--	--
		Ammonia as N (mg/L)	4	4	0.025	0.02	0.03	0.0037	0.0001	0.0017
		Nitrate as N (mg/L)	4	4	1.62	0.757	4.36	0.2384	0.0542	1.6873
		Nitrite as N (mg/L)	4	4	0.022	0.01	0.041	0.0032	0.0003	0.0484
		Organic nitrogen (mg/L)	4	4	0.6	0.47	1.2	0.0883	0.0066	1.4159
		Orthophosphate as P (mg/L)	4	4	0.289	0.26	1.14	0.0425	0.0142	0.3481
		Phosphorus as P (mg/L)	4	4	0.31	0.27	1.1	0.0456	0.0137	0.3540
		$\delta^{15}N-NO_3$ (per mil)[1]	4	4	12.645	8.21	21.8	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	4	4	8.42	5.91	14.1	--	--	--
08173080	TR-CR131	Discharge (ft^3/s)	3	3	0.07	0.04	0.1	--	--	--
		Dissolved solids (mg/L)	3	3	1,360	799	1,870	0.2570	0.1469	0.3534
		Chloride (mg/L)	3	3	551	236	667	0.1041	0.0595	0.1261
		Sulfate (mg/L)	3	3	25.3	24.8	93.3	0.0048	0.0047	0.0101
		Strontium (µg/L)	3	3	416	243	463	0.0001	--	--
		Boron (µg/L)	3	3	1,890	924	2,390	0.0004	--	--
		Ammonia as N (mg/L)	3	2	0.085	<0.010	0.1	<0.0001	--	0.0001
		Nitrate as N (mg/L)	3	2	0.4925	<0.010	0.969	0.0001	--	0.0001
		Nitrite as N (mg/L)	3	1	0.169	<0.003	0.554	<0.0001	--	<0.0001
		Organic nitrogen (mg/L)	3	2	1.3	<0.92	1.4	0.0002	0.0002	0.0002
		Orthophosphate as P (mg/L)	3	3	0.183	0.056	0.266	<0.0001	<0.0001	0.0001
		Phosphorus as P (mg/L)	3	3	0.46	0.08	0.28	0.0001	0.0000	0.0001
		$\delta^{15}N-NO_3$ (per mil)[1]	3	1	8.28	8.28	8.28	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	3	1	6.48	6.48	6.48	--	--	--

Table 5. Summary of results and calculated instantaneous loads of discharge, water levels, major ions, selected trace elements, nutrients, and nitrogen isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) in water samples collected from streams, springs, and wells; a bulk precipitation collector; and major wastewater treatment plants in the Plum Creek watershed, south-central Texas, April 2015–March 2016—Continued

[Median instantaneous loads calculated by multiplying the median concentration for a specified constituent by the median discharge. USGS, U.S. Geological Survey; all water-quality constituents were filtered; LRL, laboratory reporting level; ft^3/s, cubic foot per second; --, not measured or not calculated; mg/L, milligram per liter; µg/L, microgram per liter; <, less than; $\delta^{15}N-NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O-NO_3$, delta oxygen-18 in nitrate; WWTP, wastewater treatment plant]

USGS station number	Short name (as identified in fig. 1 and table 1)	Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Median value	Minimum value	Maximum value	Median instantaneous load (tons/day)	Minimum instantaneous load (tons/day)	Maximum instantaneous load (tons/day)
08173200	MS-CR135	Discharge (ft^3/s)	1	1	--	4	4	--	--	--
		Dissolved solids (mg/L)	1	1	--	864	864	--	9.3312	9.3312
		Chloride (mg/L)	1	1	--	253	253	--	2.7324	2.7324
		Sulfate (mg/L)	1	1	--	91.3	91.3	--	0.9860	0.9860
		Strontium (µg/L)	1	1	--	1,900	1,900	--	--	--
		Boron (µg/L)	1	1	--	621	621	--	--	--
		Ammonia as N (mg/L)	1	1	--	0.03	0.03	--	0.0001	0.0001
		Nitrate as N (mg/L)	1	1	--	2	2	--	0.0216	0.0216
		Nitrite as N (mg/L)	1	1	--	0.052	0.052	--	0.0002	0.0002
		Organic nitrogen (mg/L)	1	1	--	0.46	0.46	--	0.0050	0.0050
		Orthophosphate as P (mg/L)	1	1	--	0.85	0.85	--	0.0092	0.0092
		Phosphorus as P (mg/L)	1	1	--	0.85	0.85	--	0.0092	0.0092
		$\delta^{15}N-NO_3$ (per mil)[1]	1	1	--	24.32	24.32	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	1	1	--	15.83	15.83	--	--	--
295204097384100	PR-Precip	Discharge (ft^3/s)	--	--	--	--	--	--	--	--
		Dissolved solids (mg/L)	1	0	--	<2.0	<2.0	--	--	--
		Chloride (mg/L)	4	4	0.81	0.47	1.65	--	--	--
		Sulfate (mg/L)	4	4	1.2	0.35	1.68	--	--	--
		Strontium (µg/L)	4	4	0.85	0.3	2.1	--	--	--
		Boron (µg/L)	4	2	4.3	<2.0	4.9	--	--	--
		Ammonia as N (mg/L)	4	4	0.29	0.07	0.41	--	--	--
		Nitrate as N (mg/L)	4	4	0.094	0.15	2.06	--	--	--
		Nitrite as N (mg/L)	4	3	0.002	<0.003	0.016	--	--	--
		Organic nitrogen (mg/L)	4	2	0.7	0.7	0.73	--	--	--
		Orthophosphate as P (mg/L)	4	2	0.07	<0.004	0.077	--	--	--
		Phosphorus as P (mg/L)	4	2	0.07	<0.010	0.08	--	--	--
		$\delta^{15}N-NO_3$ (per mil)[1]	4	4	-1.765	-4.91	-1.14	--	--	--
		$\delta^{18}O-NO_3$ (per mil)[1]	4	4	63.9	55	79.98	--	--	--

Table 5. Summary of results and calculated instantaneous loads of discharge, water levels, major ions, selected trace elements, nutrients, and nitrogen isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$) in water samples collected from streams, springs, and wells; a bulk precipitation collector; and major wastewater treatment plants in the Plum Creek watershed, south-central Texas, April 2015–March 2016—Continued

[Median instantaneous loads calculated by multiplying the median concentration for a specified constituent by the median discharge. USGS, U.S. Geological Survey; all water-quality constituents were filtered; LRL, laboratory reporting level; ft^3/s, cubic foot per second; --, not measured or not calculated; mg/L, milligram per liter; µg/L, microgram per liter; <, less than; $\delta^{15}N\text{-}NO_3$, delta nitrogen-15 in nitrate; $\delta^{18}O\text{-}NO_3$, delta oxygen-18 in nitrate; WWTP, wastewater treatment plant]

USGS station number	Short name (as identified in fig. 1 and table 1)	Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Median value	Minimum value	Maximum value	Median instantaneous load (tons/day)	Minimum instantaneous load (tons/day)	Maximum instantaneous load (tons/day)
300519097503100, 295805097500600, 295303097394800, 295212097373300, 294108097374000	WWTP-Buda,[2] WWTP-Kyle, WWTP-Lockhart 1, WWTP-Lockhart 2, WWTP-Luling North	Discharge (ft^3/s)	5	5	1.1	0.25	2.6	--	--	--
		Dissolved solids (mg/L)	5	5	598	480	828	1.7761	0.4037	4.8719
		Chloride (mg/L)	5	5	130	97.3	144	0.3861	0.0878	1.0109
		Sulfate (mg/L)	5	5	67.3	10.9	114	0.1999	0.0400	0.7160
		Strontium (µg/L)	5	5	880	482	4,660	0.0026	--	--
		Boron (µg/L)	5	5	260	222	304	0.0008	--	--
		Ammonia as N (mg/L)	5	5	0.05	0.02	7.21	0.0001	<0.0001	0.0066
		Nitrate as N (mg/L)	5	5	8.07	0.117	29.1	0.0240	0.0007	0.0567
		Nitrite as N (mg/L)	5	5	0.002	0.001	0.239	0.0000	<0.0001	0.0007
		Organic nitrogen (mg/L)	5	5	1.1	0.65	1.5	0.0033	0.0006	0.0045
		Orthophosphate as P (mg/L)	5	5	2.91	0.963	4.49	0.0086	0.0030	0.0204
		Phosphorus as P (mg/L)	5	5	2.82	0.96	4.55	0.0084	0.0031	0.0209
		$\delta^{15}N\text{-}NO_3$ (per mil)[1]	5	4	12.735	11.99	15.57	--	--	--
		$\delta^{18}O\text{-}NO_3$ (per mil)[1]	5	4	5.795	2.52	7.56	--	--	--

[1]Ratios of nitrogen-15 to nitrogen-14 of nitrate ($\delta^{15}N\text{-}NO_3$) are reported by using delta notation in per mil relative to USGS34 potassium nitrate (KNO_3) and USGS32 KNO_3 reference standards (Böhlke and others, 2003). Ratios of oxygen-18 to oxgyen-16 of nitrate ($\delta^{18}O\text{-}NO_3$) are reported by using delta notation in per mil relative to USGS34 and USGS35 sodium nitrate ($NaNO_3$) reference standards (Böhlke and others, 2003). The estimated uncertainty of $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ measurement results for samples with nitrate concentrations of at least 0.06 mg/L as nitrogen is ±0.5 per mil unless otherwise specified.

[2]Data from all five WWTPs (listed individually) were compiled into a combined dataset, and minimum, maximum, and median values were calculated for each constituent reported from the combined dataset.

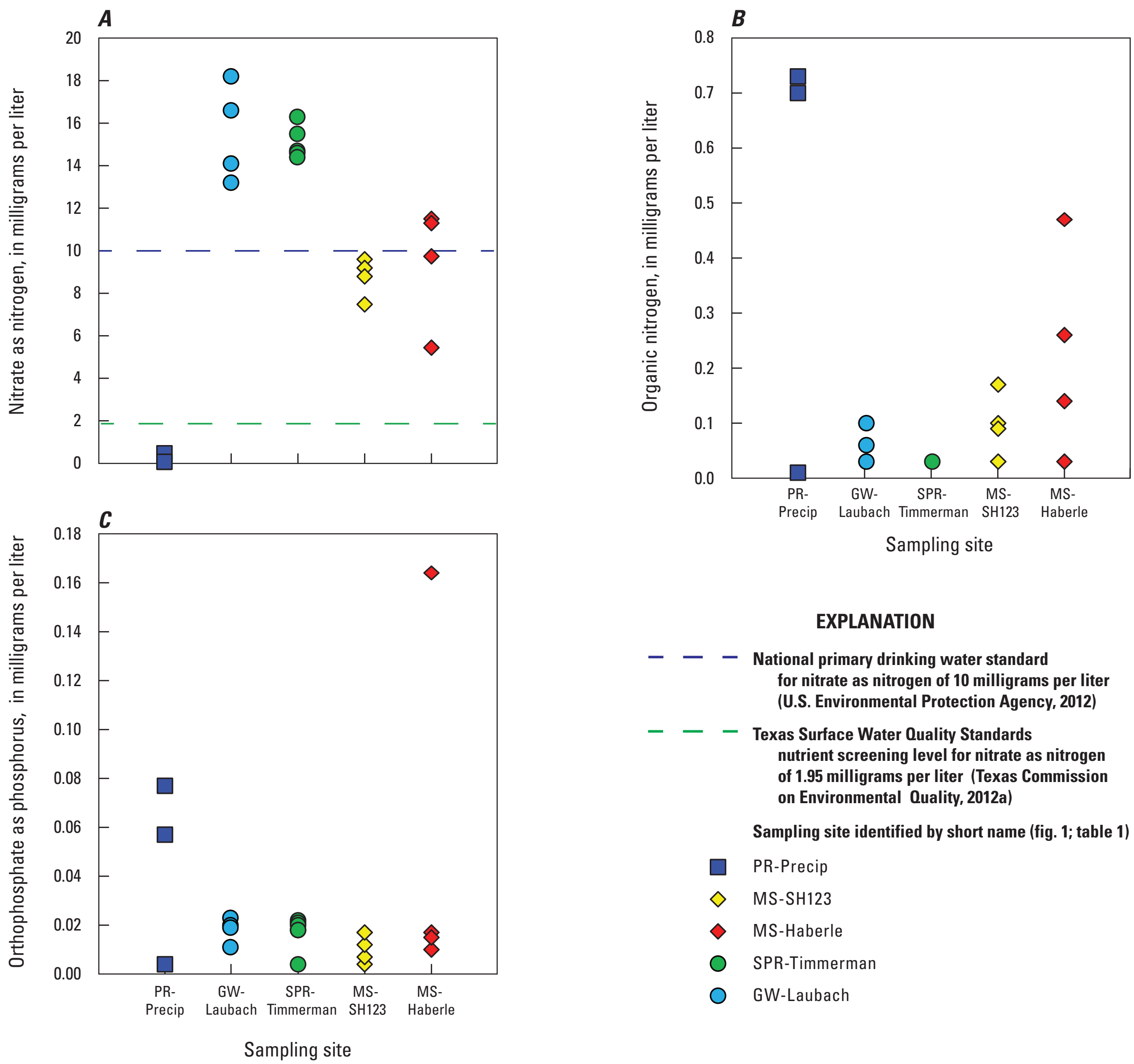

Figure 8. Concentrations of nutrients measured in water-quality samples collected from a precipitation site and from groundwater, spring, and stream sites in the Geronimo Creek watershed, south-central Texas, April 2015–March 2016. *A,* Nitrate as nitrogen. *B,* Organic nitrogen. *C,* Orthophosphate.

Sources of Nitrate

Nitrogen and oxygen isotopes of nitrate provide insight into potential sources of nitrate. The ranges in isotopic compositions were narrow; $\delta^{15}N\text{-}NO_3$ values in the GW-Laubach and SPR-Timmerman samples ranged from 5.29 to 6.13 per mil, and $\delta^{18}O\text{-}NO_3$ values ranged from 5.25 to 5.83 per mil (table 4). $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ values for stream samples (MS-SH123 and MS-Haberle) also were narrow in range, but were characterized by higher $\delta^{15}N\text{-}NO_3$ values, ranging from 7.11 to 8.02 per mil, and $\delta^{18}O\text{-}NO_3$ values, ranging from 6.43 to 6.97 (fig. 9; table 4). Compared to the $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ values measured in groundwater, spring, and stream samples, values for nitrate in precipitation were markedly different ($\delta^{15}N\text{-}NO_3$ = -4.91 to -1.14 per mil and $\delta^{18}O\text{-}NO_3$ = 55 to 79.98 per mil). The nitrate-N concentrations measured in the precipitation samples (0.15–2.06 mg/L) (table 5) were lower than those in groundwater, spring, and stream samples (5.44–18.2 mg/L) (table 4). Although atmospheric deposition contributes nitrate to the watershed, these results indicate that the direct contribution is relatively minor and is not a primary source of elevated nitrate in the Geronimo Creek watershed during low-flow or base-flow conditions.

The observed $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ values for groundwater and surface-water samples are more closely associated with nitrate sources such as soil nitrate, as well as human and animal waste, rather than precipitation (fig. 9).

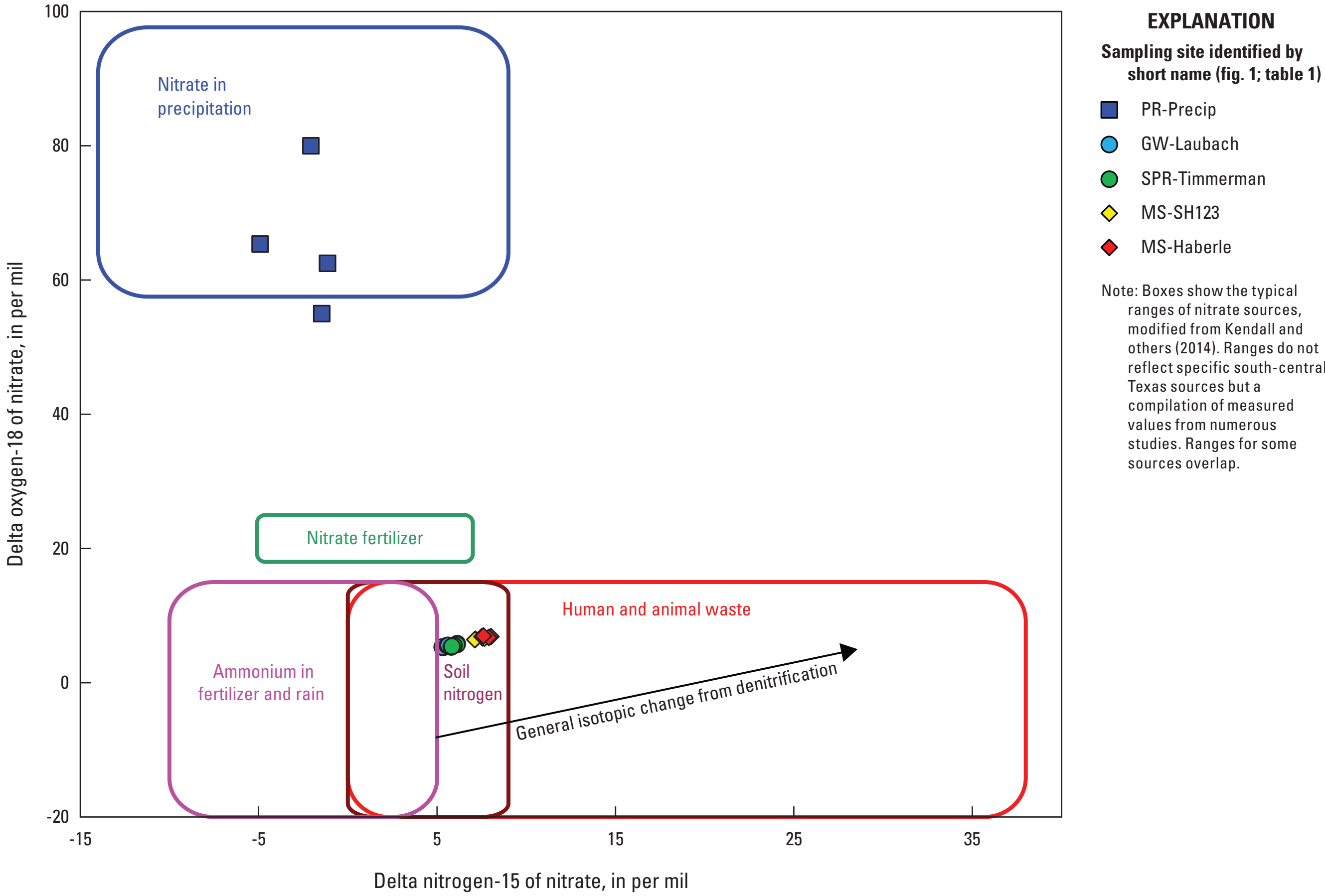

Figure 9. Values for stable nitrogen and oxygen isotopes of nitrate (delta nitrogen-15 of nitrate [$\delta^{15}N-NO_3$] and delta oxygen-18 of nitrate [$\delta^{18}O-NO_3$]) measured in water samples collected from a precipitation site and from groundwater, spring, and stream sites in the Geronimo Creek watershed, south-central Texas, 2015–16.

For example, soil nitrate might have a natural source or might be amended by the application of manure, organic fertilizers, and inorganic fertilizers to the soil. Although the $\delta^{15}N$ values for NO_3 and ammonium in inorganic fertilizer are largely outside the range of observed groundwater values (fig. 9), inorganic fertilizer is transformed in soils through a variety of processes (for example, nitrification, denitrification, and ammonium volatilization) with a net effect that the nitrate isotope composition of the resulting soil nitrate increases relative to the isotopic concentration of the precursor fertilizer. This pathway for converting inorganic fertilizer to soil nitrate was described by Kreitler (1975, 1979), who found that fertilized soils collected in the study area had a $\delta^{15}N-NO_3$ range of 2.0–14 per mil and that the average value 8.8 per mil was higher than that of unfertilized soils ($\delta^{15}N-NO_3$ = 4.9 per mil). These $\delta^{15}N-NO_3$ values for both fertilized and unfertilized soils (Kreitler, 1979) are similar to those measured in samples collected for this study from the Geronimo Creek watershed. The $\delta^{15}N-NO_3$ values in groundwater and spring samples collected for this study ranged from 5.29 to 6.13 per mil, whereas the stream samples ranged from 7.11 to 8.02 per mil (fig. 9; table 4).

More than 70 percent of the 2011 total land cover in the watershed is agricultural related, with cultivated crop acreage accounting for slightly less than 37 percent of the total area (Homer and others, 2015) (fig. 4; table 2). Historical reports from nearby counties indicate that cultivated crop acreages were a dominant land cover dating back to the early 1900s and that agriculture accounted for about two-thirds of the land use in Caldwell County (Rasmussen, 1947). Kreitler (1979) reported a historical fertilizer application rate of 40 kilograms per hectare annually (35.7 pounds per acre annually) in the Lockhart area in Caldwell County. The fertilizers applied at that time were inorganic and included ammonium phosphate, ammonium phosphate sulfate, urea-ammonium nitrate (liquid), and aqua-ammonia (Kreitler, 1979). Current (2017) fertilizers applied are similar to the inorganic fertilizers reported by Kreitler (1979), but application rates are higher—ranging from 300 to 350 pounds per acre annually in the Geronimo Creek watershed (Mike Urrutia, Director of Water Quality Services, Guadalupe-Blanco River Authority, written commun., 2017).

For the cultivated crop acreage in the Geronimo Creek watershed (16,265 acres; table 2) this would result in an estimated range of about 2,400–2,800 tons of fertilizer applied during a single growing season, part of which is converted to soil nitrate-N. Given the linkage between inorganic fertilizer and soil nitrate and the continued application of fertilizer in the watershed, inorganic fertilizer likely leaches from soils and contributes to groundwater nitrate-N concentrations (Puckett and others, 2011).

The $\delta^{15}N\text{-}NO_3$ data are consistent with a contribution from human and animal waste; manure application and septic systems are likely sources of nitrate-N in the Geronimo Creek watershed. Median $\delta^{15}N\text{-}NO_3$ values from groundwater (5.46 per mil) and springs (6.03 per mil) were lower than those measured from the upstream and downstream sites in Geronimo Creek (7.35 and 7.75 per mil, respectively), indicating additional mixing of nitrate with a higher $\delta^{15}N\text{-}NO_3$ value with the lower $\delta^{15}N\text{-}NO_3$ groundwater discharging to surface water, which resulted in the higher values measured for the stream samples (fig. 8; table 4). Although the differences in $\delta^{15}N\text{-}NO_3$ values for these sites were small, they are consistent with contributions from a nitrate source with a waste component. In support of this, Kreitler (1979) reported that soil $\delta^{15}N\text{-}NO_3$ values in agricultural fields fertilized with manure ranged from 10 to 22 per mil (average = 14.4 per mil) and were much higher than the values in fields fertilized with inorganic fertilizer (average = 8.8 per mil) or in unfertilized fields (average = 4.9 per mil). When manure is applied as fertilizer, it likely would be converted to nitrate in soils in a manner similar to inorganic fertilizer, in which soil transformation serves as an intermediate step in the conversion of manure applied as fertilizer to nitrate in groundwater. Manure, however, cannot be isotopically distinguished from human waste solely by using $\delta^{15}N\text{-}NO_3$ values (fig. 9) (Cravotta, 2002), and there are a large number of septic systems in the Geronimo Creek watershed.

In 2012, there were approximately 2,300 septic systems estimated to be in use within 1,000 ft of a stream in the Geronimo Creek watershed (Ling and others, 2012). Although the amount of human waste leaching into streams as groundwater inflows from septic systems was not examined in this study, Wakida and Lerner (2005) estimated a loss of approximately 9.5 kilograms (about 21 pounds) of nitrate per home per year to account for human waste leaching into the groundwater system. If this value is used for the approximately 2,300 septic systems in the Geronimo Creek watershed, then the estimated load from septic systems to shallow groundwater would be about 24 tons per year (ton/yr), which is about two orders of magnitude less than estimated fertilizer application rates. The density of the septic systems in the Geronimo Creek watershed was estimated to be about 19 acres per septic system based on a total acreage of 44,089 acres (table 2). Although neither of these estimates represents actual contributions from these different sources to Geronimo Creek because transport processes and the degree of attenuation in soils and shallow groundwater are unknown, they provide insight into the role of potential sources and indicate that the amount of introduced nitrogen from fertilizers likely greatly exceeds that of septic systems.

The role of soils as an intermediary in the formation and transport of groundwater nitrate is supported by a comparison of the observed groundwater and spring $\delta^{15}N\text{-}NO_3$ values in this study with those reported by Kreitler (1979). Average groundwater $\delta^{15}N\text{-}NO_3$ values reported by Kreitler (1979) for irrigation wells ranged from 3.3 per mil to 10.8 per mil (average of 7.3 per mil), and the range of values from the stream samples (MS-SH123 and MS-Haberle) collected for this study in the Geronimo Creek watershed were similar (range of 7.11–8.02 per mil; average of 7.6 per mil), which is consistent with a source of nitrate from fields cultivated with inorganic fertilizer. Kreitler (1979) also reported that domestic wells in the area were contaminated with animal waste on the basis of higher average $\delta^{15}N\text{-}NO_3$ values in domestic wells (11.1 per mil) in comparison to irrigation wells (7.3 per mil). The $\delta^{15}N\text{-}NO_3$ values in groundwater and spring samples collected from the Geronimo Creek watershed were not as high as those reported by Kreitler (1979), although the number of samples analyzed for this study was considerably less than the number of samples analyzed by Kreitler (1979). The results from this study are consistent with a predominance of nitrate derived from inorganic fertilizer but with an additional component of nitrate-N derived from human or animal waste.

Chemical Loadings

Calculation of chemical loads provides information regarding total transport of specific constituents with respect to hydrologic conditions and can provide information about sources of constituents in combination with other chemical measurements. Instantaneous loads of selected constituents were calculated for the MS-SH123, SPR-Timmerman, and MS-Haberle sites (table 4) (Lambert and others, 2017). The concentrations and loads for dissolved solids, chloride, sulfate, and nitrate-N remained relatively consistent during the study period for all sites, although the greatest range in nitrate-N concentrations and loads of these constituents was at the downstream MS-Haberle site (fig. 10; table 4). Loads for the SPR-Timmerman samples were smaller than the stream loads (fig. 10). Although individual concentrations of these constituents were relatively high in Geronimo Creek overall, the daily loads generally were small because streamflow varied little during the periods of sample collection (fig. 5). The consistency in the load values is a result, in part, of collection of samples mostly at, or near, base-flow conditions during each synoptic sampling event. Constituent loads during stormwater runoff events would likely be greater.

Nitrate-N loads at the downstream MS-Haberle site ranged from about 0.056 to 0.221 tons per day (ton/d), or a range of about 20–80 ton/yr of nitrate-N moving through the watershed during base-flow conditions. These estimates are conservative because they do not account for higher loads that might be transported during storm events or for losses

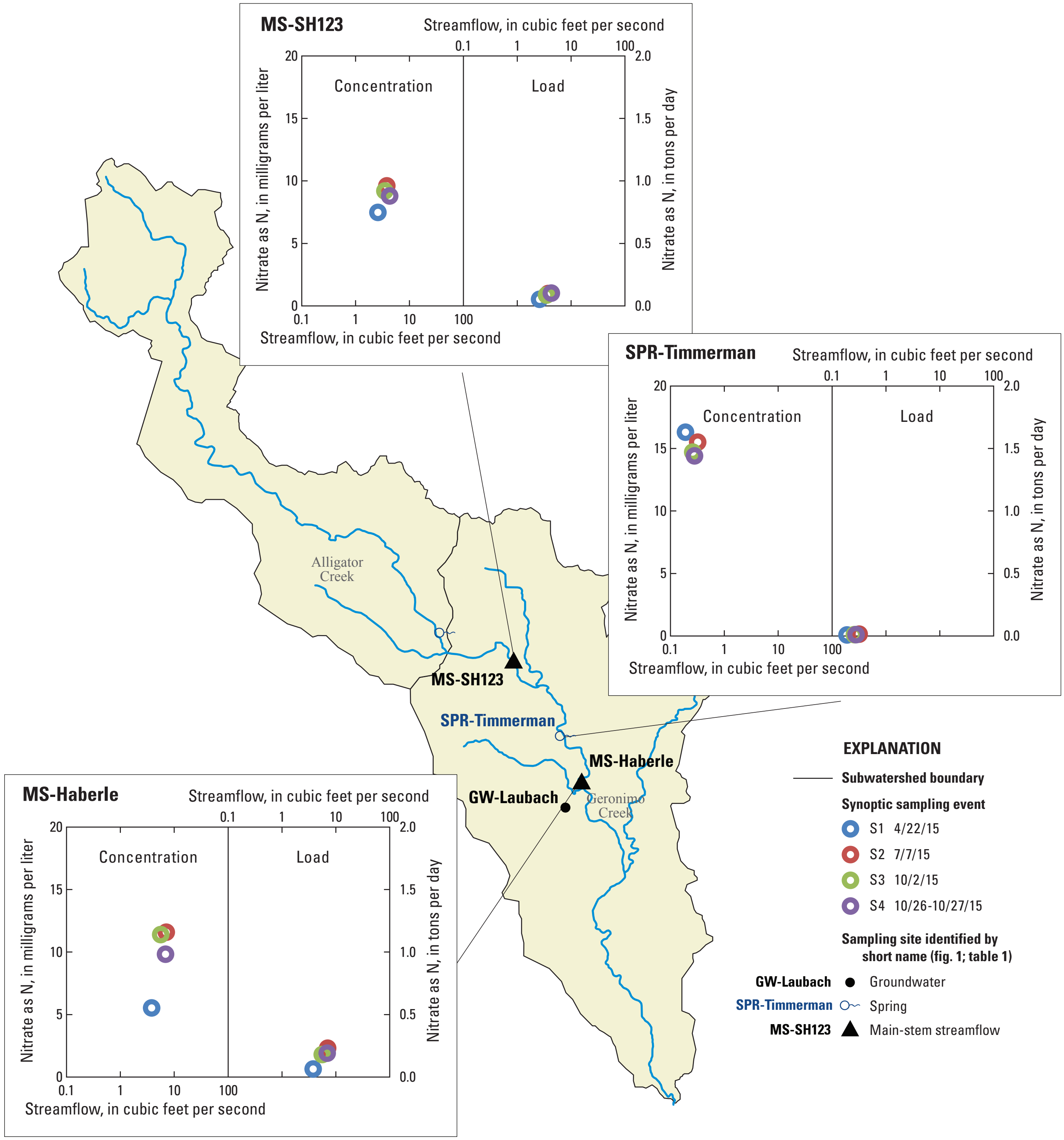

Figure 10. Relation of nitrate as nitrogen (N) concentrations and loads from main-stem (MS) stream and spring (SPR) sampling sites to streamflow during four synoptic sampling events (S1–S4) in the Geronimo Creek watershed, south-central Texas, April–October 2015.

that might occur during transport as a result of uptake by plants and breakdown by microbes. The continued application of agricultural fertilizers and, to a lesser degree, ongoing inputs from leaking septic systems likely will result in continued loading of nitrate-N to Geronimo Creek, as well as likely provide legacy accumulations of nitrate (Puckett and others, 2011).

Water Quality, Sources of Nitrate, and Chemical Loadings in Plum Creek Watershed

Streamflow in Plum Creek varied considerably during the study. Regional storms resulted in higher streamflow, exceeding 1,000 ft^3/s, during April–June 2015 and again in late October 2015 (fig. 6). During an extended drought period from mid-July through early October 2015, streamflow decreased to between 1 and 10 ft^3/s. The reach of Plum Creek from which samples were collected generally is a gaining reach because of input from the WWTPs and as indicated by the comparison of streamflow at sites MS-Luling and MS-Lockhart (fig. 6). Discharge records (Guadalupe-Blanco River Authority, 2017b) indicate that effluent discharge from the major WWTPs in the Plum Creek watershed accounted for much of the base flow during July through early October 2015 (figs. 6 and 11). The Kyle and Buda WWTPs were the two largest contributors during the study period, followed by the Lockhart 2, Lockhart 1, and Luling North WWTPs (fig. 11). There were notable increases in WWTP effluent discharge during periods of higher streamflow, which is consistent with typical WWTP operations where treated water might be held back during lower flows and then released during higher flows to allow for dilution (Mike Urrutia, Director of Water Quality Services, Guadalupe-Blanco River Authority, written commun., 2017). Comparing streamflows over the period of this study indicates that the total contribution of effluent discharge from all five WWTPs to the Plum Creek watershed ranged from 6 to 19 ft^3/s (fig. 11), representing a substantial part of the total flow in Plum Creek, especially during periods of low streamflow.

Water Quality

To facilitate comparisons between precipitation, groundwater, spring, stream, and WWTP samples, water-quality data in the Plum Creek watershed were grouped by constituent concentration and site type. The dissolved-solids, chloride, and sulfate concentrations in the precipitation samples were low compared to most other site types (generally less than 2 mg/L) (fig. 12; table 5). The dissolved-solids and chloride concentrations associated with the groundwater (GW-Borchert Loop) and the spring (SPR-Lockhart and SPR-Clear Fork) sites were similar, and their concentration values were generally lower than for those samples collected from the stream and WWTP sites (fig. 12; table 5). The dissolved-solids concentrations for the main-stem stream sites (MS-Plum Creek, MS-CR202, and MS-Luling) and the tributary stream site (TR-Salt Flat) ranged from 144 to 767 mg/L and generally decreased from upstream to downstream by sampling location (fig. 12; table 5). The dissolved-solids concentrations for the WWTP sites ranged from 480 to 828 mg/L, comparable to concentrations measured for the main-stem stream sites, which is consistent with main-stem flow dominated by WWTP effluent discharge at lower flows (fig. 12; table 5). The dissolved-solids concentrations measured in the samples collected from stream sites TR-CR131 and MS-CR135 in the downstream part of the watershed ranged from 799 to 1,870 mg/L. These dissolved-solids concentrations were substantially higher than concentrations from samples collected from other stream sites in the Plum Creek watershed, indicative of differences in water chemistry that are discussed further in the “Additional Water-Quality Observations” section of this report.

Similar to the patterns observed for dissolved-solids concentrations, chloride concentrations were lower in the groundwater and spring samples (10.9–28.9 mg/L) and generally somewhat higher, with greater variability, in most stream (main-stem and tributary) samples (15.5–196 mg/L). The exceptions to this pattern were with the TR-CR131 and MS-CR135 samples collected in the southern part of the watershed, where the chloride concentrations were substantially higher (236–667 mg/L) than those measured in other stream samples (fig. 12; table 5). Chloride concentrations in the WWTP samples ranged from 97.3 to 144 mg/L (table 5), which are comparable to, though slightly higher overall than, concentrations for most main-stem stream sites. There was an overall decrease in chloride concentration downstream from the Kyle and Buda WWTPs (Lambert and others, 2017); these decreasing concentrations might indicate that effluent discharge is diluted downstream by lower concentration inflows from groundwater discharging to the stream, by tributary inflows, or by both (fig. 12).

Sulfate concentrations ranged from 10.9 to 114 mg/L in the Plum Creek watershed for WWTP, groundwater, spring, and stream samples (table 5). The two highest sulfate concentrations were measured at sites WWTP-Buda (114 mg/L) and MS-Plum Creek (108 mg/L) (Lambert and others, 2017). Among all groundwater, spring, and stream samples, sulfate concentrations generally were lower in the samples collected from tributary stream site TR-Salt Flat; among all main-stem stream sites, lower sulfate concentrations were generally measured in the samples collected from the MS-Luling site, which is relatively far downstream from WWTPs compared to other main-stem stream sites (figs. 1 and 12). Consistent with the concentration patterns for dissolved solids and chloride, sulfate concentrations during lower flow conditions were generally higher in samples collected from main-stem stream sites in the upper part of the watershed where the streamflow was dominated by effluent discharge from the WWTPs.

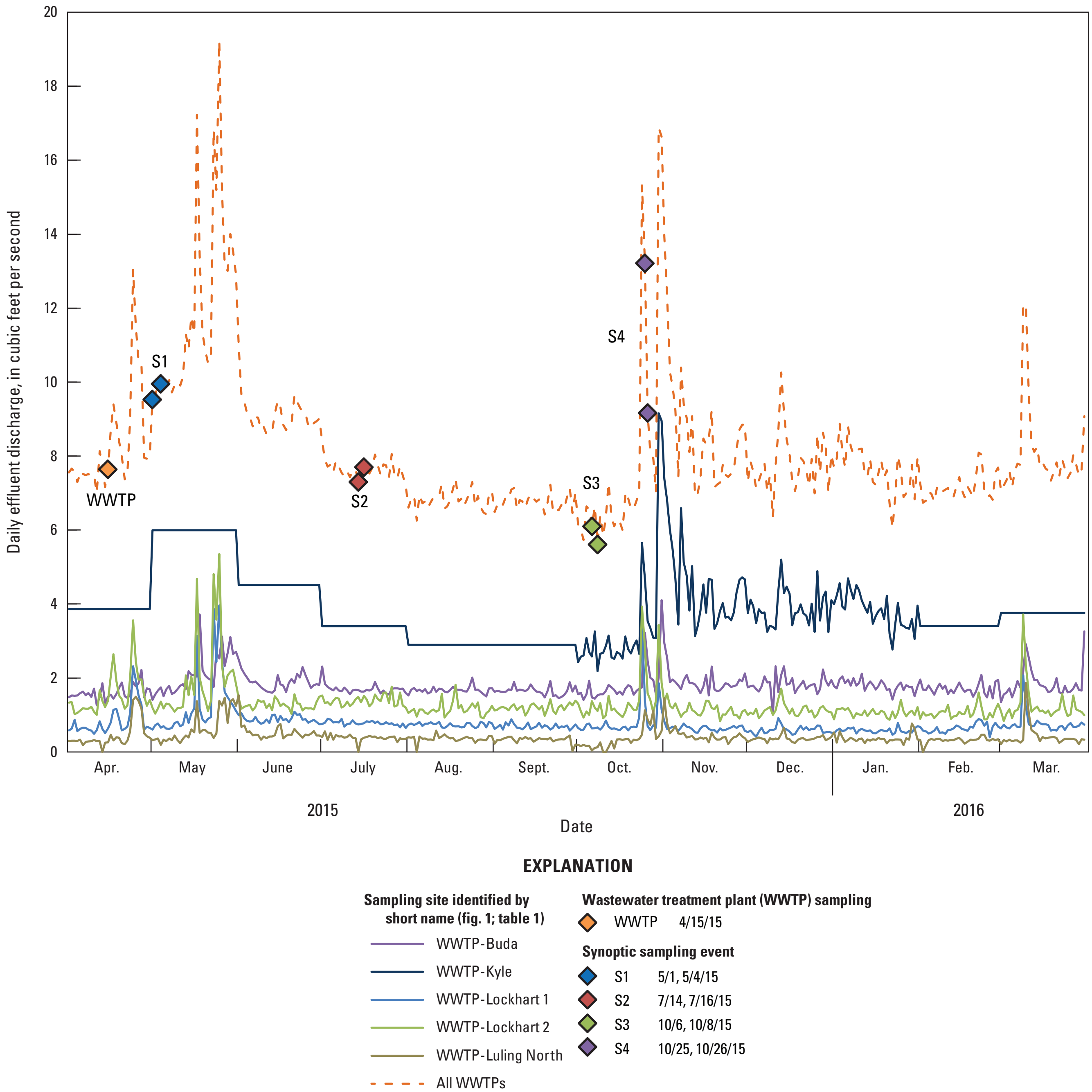

Figure 11. Daily effluent discharge from wastewater treatment plants (WWTPs) and summation of all WWTP flows in the Plum Creek watershed from April 2015 through March 2016. All effluent discharge values are average daily values with the exception of the average daily value by month for the Kyle WWTP for April 1–September 30, 2015, and February 1–March 31, 2016. Data collection periods for synoptic sampling events and WWTP samplings also are shown.

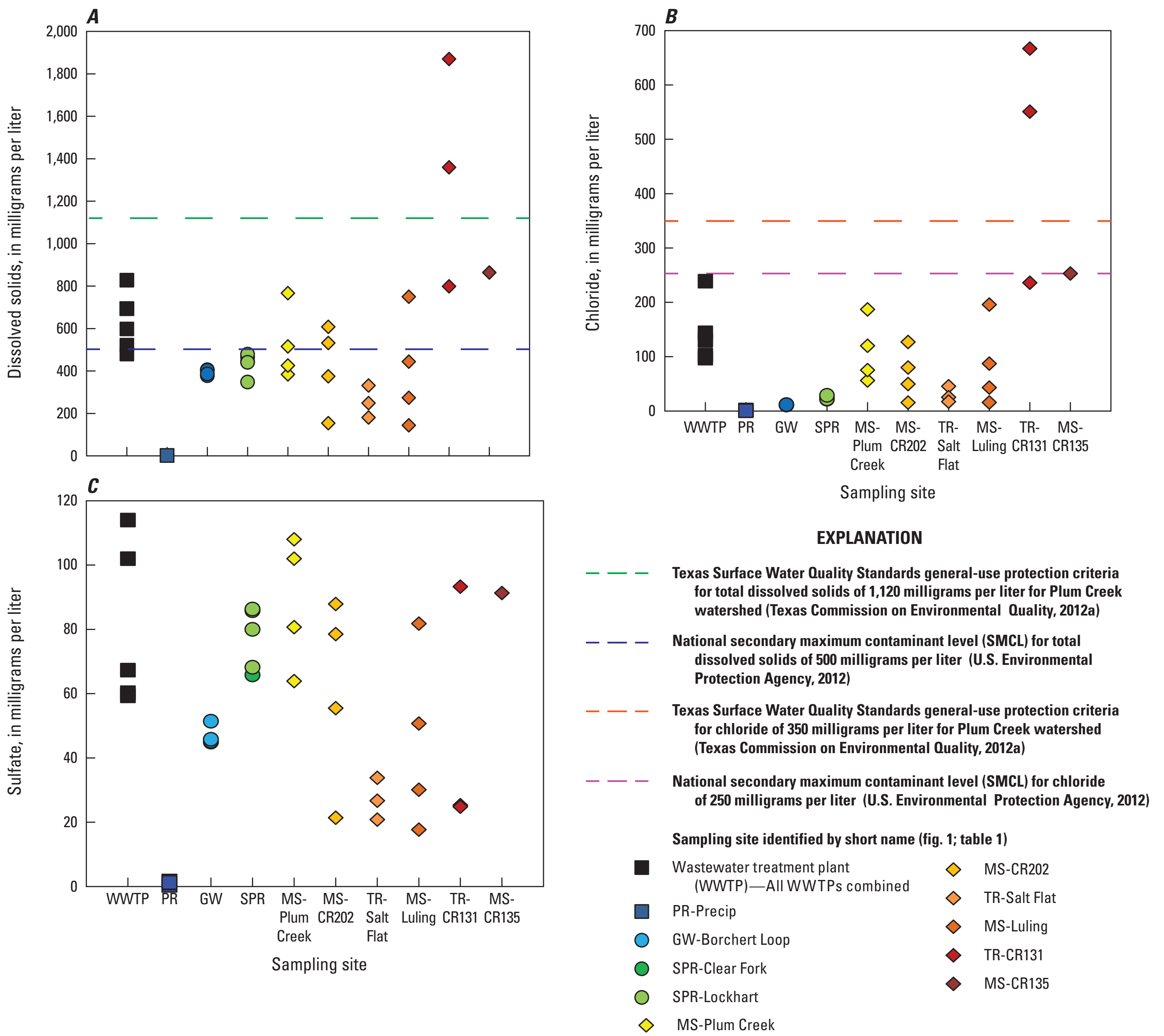

Figure 12. Concentrations of water-quality constituents measured in water-quality samples collected from wastewater treatment plants; a precipitation site; and groundwater, spring, and stream sites in the Plum Creek watershed, south-central Texas, April 2015–March 2016. *A,* Dissolved solids. *B,* Chloride. *C,* Sulfate.

Relatively high nitrate-N concentrations that sometimes exceeded 10 mg/L were measured in samples collected from groundwater, spring, and main-stem stream sites (GW-Borchert Loop, SPR-Lockhart, SPR-Clear Fork, MS-Plum Creek, and MS-CR202) in the upper and central parts of the watershed compared to relatively low nitrate-N concentrations that were consistently less than 10 mg/L in samples collected from main-stem and tributary stream sites (TR-Salt Flat, MS-Luling, TR-CR131, and MS-CR135) in the lower part of the watershed (figs. 1 and 13). Nitrate-N concentrations for samples collected from the main-stem and tributary stream sites in the Plum Creek watershed generally decreased downstream from the Kyle and Buda WWTPs (Lambert and others, 2017). Relatively high nitrate-N concentrations (12.6–15.5 mg/L) were measured in the groundwater samples, but they varied little compared to the wide range in nitrate-N concentrations measured in WWTP samples (0.117–29.1 mg/L) (table 5). More variable nitrate-N concentrations (11.2–35 mg/L) also were measured in the spring samples compared to the groundwater samples (table 5). The highest nitrate-N concentration in Plum Creek of 19.7 mg/L was measured at site MS-Plum Creek during low-flow conditions, when WWTP effluent discharges are a large component of streamflow (table 5) (Lambert and others, 2017).

Organic nitrogen and orthophosphate concentrations measured in groundwater and spring samples collected in the Plum Creek watershed generally were lower than those measured in most stream (main-stem and tributary) and WWTP samples but were similar to the concentrations measured in precipitation (fig. 13). Organic nitrogen and orthophosphate concentrations measured in the stream samples differed depending on flow conditions—higher concentrations of organic nitrogen and orthophosphate were measured during the lower to midrange flows (synoptic sampling events S1, S2, and S3; fig. 6), whereas lower concentrations were measured in the stormwater runoff sample (synoptic sampling event S4; fig. 6). Whereas these differences might result, in part, from seasonal differences from fresh applications of fertilizers, WWTP effluent discharge likely dominates streamflow and water chemistry during lower to midrange flows and especially at lower flows.

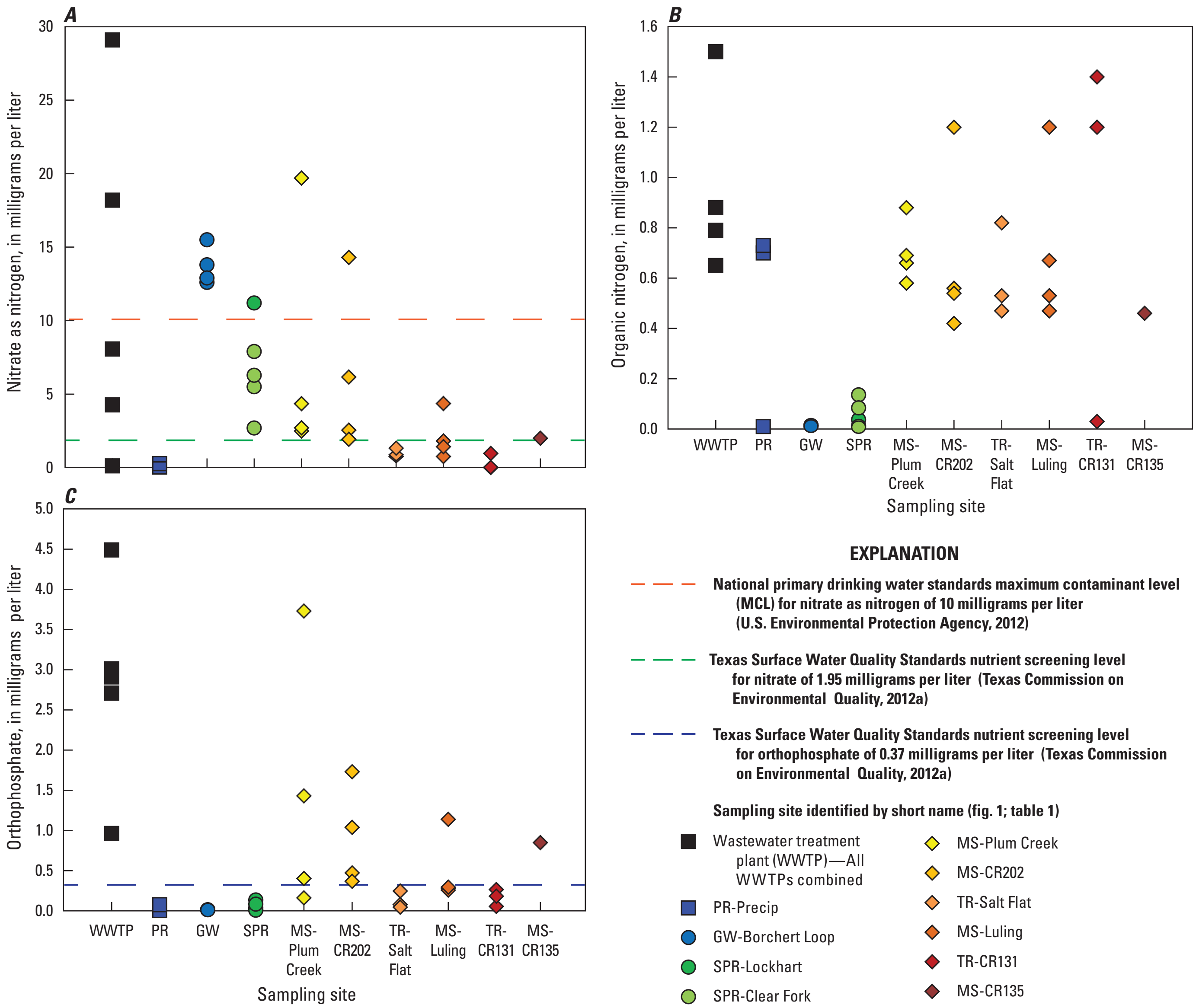

Figure 13. Concentrations of nutrients measured in water-quality samples collected from wastewater treatment plants; a precipitation site; and groundwater, spring, and stream sites in the Plum Creek watershed, south-central Texas, April 2015–March 2016. *A,* Nitrate as nitrogen. *B,* Organic nitrogen. *C,* Orthophosphate.

Sources of Nitrate

Water-quality and nitrate isotope data indicate that, similar to the Geronimo Creek watershed, the dominant source of nitrate to the Plum Creek watershed is not atmospheric in origin; $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ values measured in precipitation samples are different from those measured in Plum Creek watershed samples (fig. 14). Precipitation might be a minor source of additional nitrate during storm events and higher flows as evidenced by higher $\delta^{18}O\text{-}NO_3$ values in samples collected during synoptic sampling event S4 (Lambert and others, 2017). Nitrate isotope ($\delta^{15}N\text{-}NO_3$) values for groundwater samples (table 5) collected from the GW-Borchert Loop well in the Plum Creek watershed (median of 5.5 per mil) are similar to those measured in the Geronimo Creek watershed, both for the GW-Laubach well (median of 5.46 per mil) and the SPR-Timmerman site (median of 6.03 per mil). Similar to groundwater values for the Geronimo Creek watershed, these values for groundwater from the Plum Creek watershed are consistent with an inorganic fertilizer source of nitrate (Kreitler, 1979). This similarity in values indicates that the source(s) of nitrate in the groundwater and spring samples collected in Plum Creek also might be derived from diffuse, mixed nitrate from fertilizer, manure, and septic systems that result in composite $\delta^{15}N$ and $\delta^{18}O$ isotope values indicating a soil nitrate source. Median $\delta^{15}N\text{-}NO_3$ values in spring samples collected in the Plum Creek watershed, however, were notably higher for samples collected from site SPR-Clear Fork (median of 9.2 per mil) and the sample collected from site SPR-Lockhart (8.72 per mil) than for the

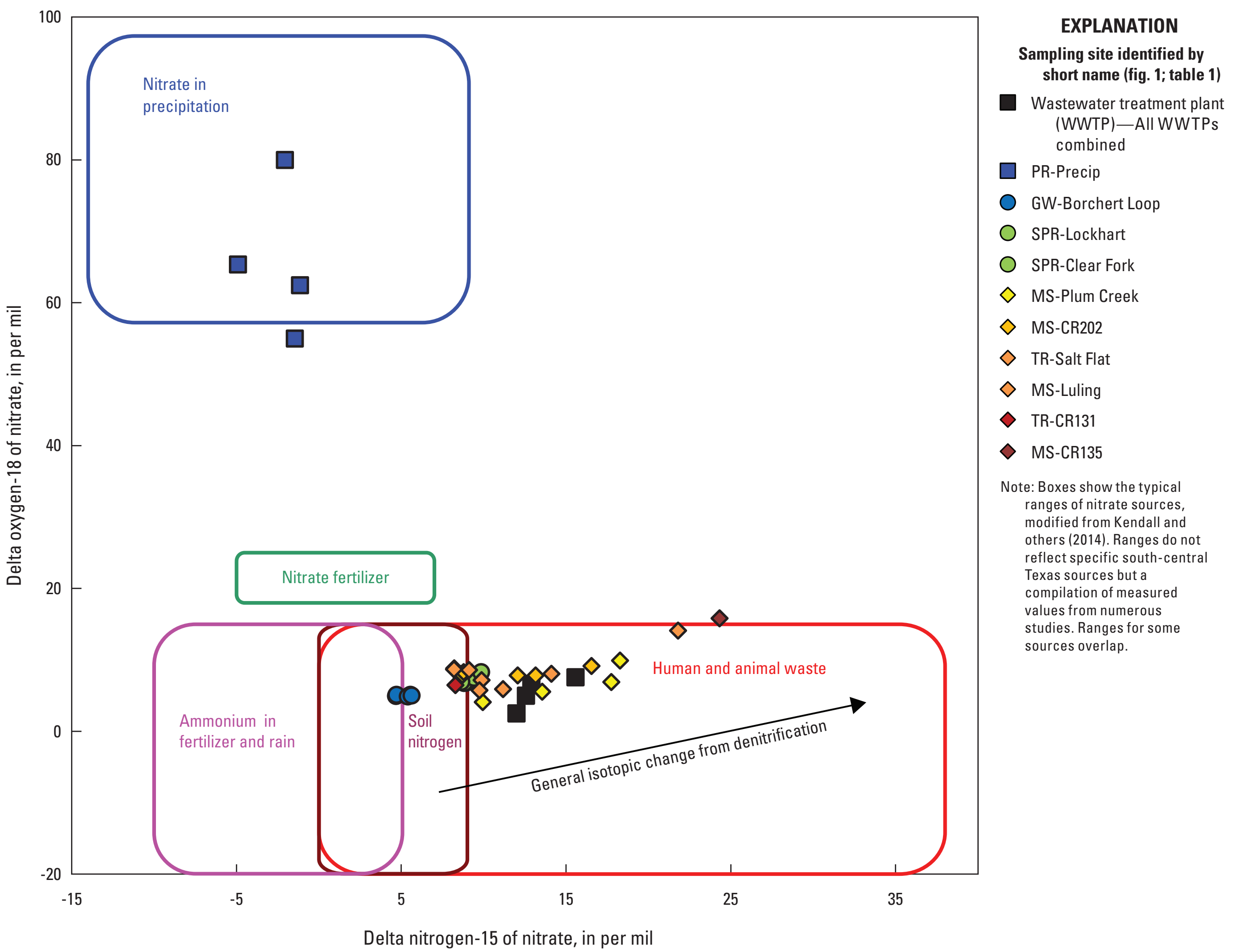

Figure 14. Values of stable nitrogen and oxygen isotopes of nitrate (delta nitrogen-15 of nitrate [$\delta^{15}N\text{-}NO_3$] and delta oxygen-18 of nitrate [$\delta^{18}O\text{-}NO_3$]) measured in water-quality samples collected in the Plum Creek watershed, south-central Texas, 2015–16.

other groundwater samples. These differences in $\delta^{15}N\text{-}NO_3$ values between the groundwater (well) and spring sites in the Plum Creek watershed indicate that nitrate-N concentrations in the spring samples from Plum Creek likely have a contribution from human or animal waste sources.

Lower nitrate-N concentrations (less than 0.010 to 1.33 mg/L) were measured for the tributary stream sites (TR-Salt Flat and TR-CR131) compared to the main-stem stream sites (fig. 13; table 5). These relatively low nitrate-N concentrations are associated with lower or intermittent flows and indicate that tributary flows likely have not been affected by WWTP effluent discharge; there are no major WWTPs discharging to the sampled tributaries in the upper part of the watershed. Only site WWTP-Luling North, in the southern part of the watershed, discharges to a tributary, but this site is downstream from all of the sampling sites with the exception of site MS-CR135. Furthermore, samples from these tributary stream sites have relatively high $\delta^{15}N\text{-}NO_3$ values that implicate a likely human or animal waste source (Kreitler and Browning, 1983) (fig. 14). Similar to the Geronimo Creek watershed, manure application and septic systems are also likely sources of nitrate-N in the Plum Creek watershed.

The geologic and hydrogeologic characteristics and historical land cover in the Plum Creek watershed are similar to those in the Geronimo Creek watershed. Fertilizers applied to the soils overlying the Leona Formation and the fluviatile terrace deposits might have contributed to legacy accumulation of nitrate (Puckett and others, 2011) in the Plum Creek watershed from past agricultural practices, especially in the Clear Fork Plum Creek subwatershed (fig. 4). The 2011 cultivated crop acreage in the Plum Creek watershed was 18,383 acres (table 2). Using the same method and application rates of 300–350 pounds per acre as was used in the Geronimo Creek estimates (Mike Urrutia, Director of Water Quality Services, Guadalupe-Blanco River Authority, written commun., 2017), the estimated amount of fertilizer applied during a single growing season in the Plum Creek watershed would range from about 2,800 to 3,200 ton/yr of fertilizer. Additionally, contribution of nitrate from leaking septic systems in the Plum Creek watershed is likely. An estimated 5,900 permitted septic systems were installed from 1978 through May 2017 in Caldwell County, which makes up a large part of the Plum Creek watershed (Kasi Miles, Director of Sanitation, Caldwell County, Texas, written commun., 2017). Using the estimated loss of 9.5 kilograms (about 21 pounds) of nitrate per home per year proposed by Wakida and Lerner (2005), the estimated nitrate input into the groundwater system associated with the 5,900 septic systems in Caldwell County is approximately 62 ton/yr of nitrate. The density of the septic systems in the Plum Creek watershed was estimated to be about 42 acres per septic system on the basis of a total acreage of 248,855 acres (table 2), or approximately one-half the density of septic systems estimated in the Geronimo Creek watershed.

Nitrate isotopes measured in spring, stream (main-stem and tributary), and WWTP samples from the Plum Creek watershed generally depict increasing $\delta^{15}N\text{-}NO_3$ values with increasing $\delta^{18}O\text{-}NO_3$ values, which is consistent with isotopic changes that occur with denitrification (a microbial process by which nitrate is reduced to nitrogen gas) (fig. 14). Denitrification occurs along a predictable pattern of isotopic increases as nitrate decomposes under anaerobic conditions and accounts for elevated isotopic values commonly observed in environmental samples (Kendall, 1998). Although denitrification requires anoxic conditions, the WWTPs sampled in this study use an aerobic process for wastewater treatment. Nonetheless, denitrification might occur in anoxic zones in onsite holding ponds, in anaerobic microsites (small areas within the soil zone where anaerobic conditions develop) (Koba and others, 1997), in anoxic zones in the streambed (Mulholland and others, 2008), or in association with other unidentified processes. Instream mixing of streamflow with WWTP effluent discharge is consistent with the range of $\delta^{15}N\text{-}NO_3$ values and nitrate-N concentrations measured in Plum Creek. The relatively high $\delta^{15}N\text{-}NO_3$ values and nitrate-N concentrations measured in WWTP effluent samples, and the similar range observed in samples from main-stem Plum Creek sites, indicate that WWTP effluent discharge is an important source of nitrate in the Plum Creek watershed (figs. 14 and 15).

Although discharge from the WWTPs was somewhat higher during periods of higher flow, dilution of the WWTP effluent discharge by higher streamflow also likely occurred (fig. 16). For example, $\delta^{15}N\text{-}NO_3$ values for the MS-CR202 and MS-Luling sites were substantially lower (8.79 and 8.21 per mil, respectively; table 5) during the higher flow synoptic sampling event S4 compared to those measured for these sites during the other sampling events (fig. 16) (Lambert and others, 2017). Both $\delta^{15}N\text{-}NO_3$ values and nitrate-N concentrations generally decreased with increasing streamflow (fig. 16), which is consistent with dilution of the WWTP effluent discharge source. A relatively high $\delta^{15}N\text{-}NO_3$ value (18.28 per mil) was measured in the sample collected from the most upstream main-stem stream site (MS-Plum Creek) during the same higher flow (synoptic sampling event S4), indicative of a predominantly WWTP nitrate source; this $\delta^{15}N\text{-}NO_3$ value indicates that dilution of WWTP effluent discharged to the stream likely increases downstream from the WWTP effluent sources (fig. 16).

Although additional nitrate sources including cattle waste and septic systems were not directly assessed in this study, results indicate that they might be contributing some nitrate to the Plum Creek watershed. Whereas WWTP effluent is likely the dominant nitrate source, its dominance as a source is less apparent during higher flow conditions, when the higher nitrate load indicates there might be appreciable contributions from other nitrate sources in the watershed.

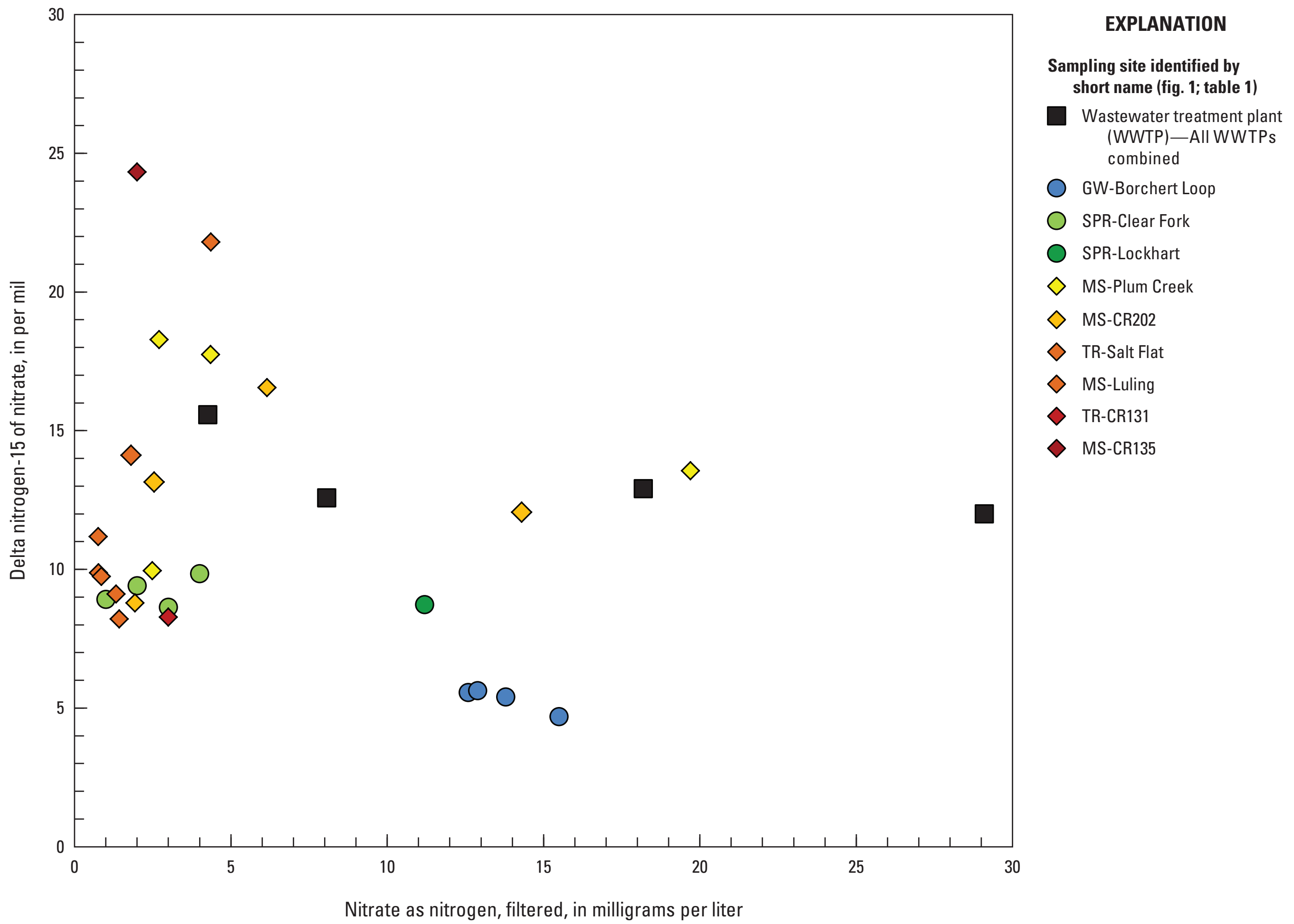

Figure 15. Relation of nitrate as nitrogen to stable nitrogen isotopes of nitrate (delta nitrogen-15 of nitrate [$\delta^{15}N\text{-}NO_3$]) measured in samples collected in the Plum Creek watershed, south-central Texas, April 2015–March 2016.

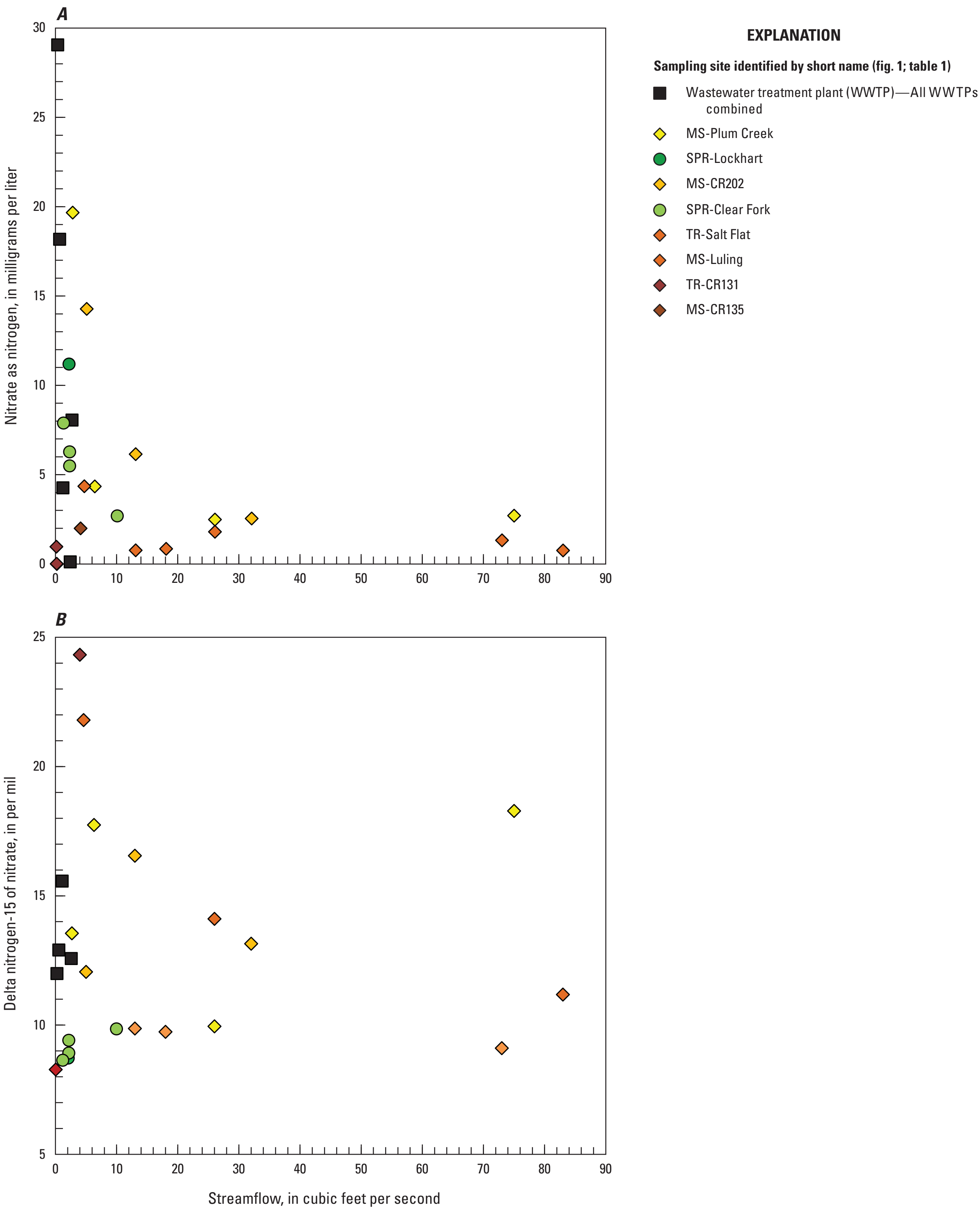

Figure 16. Relation of streamflow compared to *A*, nitrate as nitrogen concentrations and *B*, values of stable nitrogen isotopes of nitrate (delta nitrogen-15 of nitrate [$\delta^{15}N\text{-}NO_3$]) measured in samples collected from the Plum Creek watershed, south-central Texas, April–October 2015.

Chemical Loadings

The amount of chemical loading of dissolved solids, chloride, sulfate, and nitrate-N to the Plum Creek watershed varied with flow conditions and the contribution of WWTP effluent discharge (Lambert and others, 2017). Whereas nitrate concentrations in WWTP effluent discharge might be quite high (as high as 29.1 mg/L at site WWTP-Luling North on April 15, 2015; Lambert and others, 2017), compared to instantaneous loads in the stream (fig. 17), the instantaneous loads for nitrate-N from the WWTPs (fig. 18) tended to be relatively low because of the relatively low volume of WWTP effluent discharged to the stream. Summing the instantaneous loads for all WWTPs discharging to Plum Creek provides insight into the amount of the nitrate-N load in the stream that can be attributed to the WWTPs (fig. 18) (Lambert and others, 2017).

The instantaneous dissolved-solids loads for the WWTPs in the Plum Creek watershed ranged from about 0.4 to nearly 4.9 ton/d (table 5), with the highest dissolved-solids loads (2.5–4.9 ton/d) contributed by the WWTP-Kyle, WWTP-Lockhart 2, and WWTP-Buda sites as calculated from samples collected in April 2015 (Lambert and others, 2017). These three WWTPs also contributed the highest loads for chloride and sulfate, with loads ranging from about 0.64 to about 1.0 ton/d for chloride and 0.34 to 0.72 ton/d for sulfate (Lambert and others, 2017). The dissolved-solids loads in the main stem increased downstream from the MS-Plum Creek site to the MS-Luling site for all synoptic sampling events; the highest loads were calculated at the MS-Luling site in the central part of the watershed downstream from four WWTPs (fig.1; table 5). Smaller loads of dissolved solids, chloride, and sulfate were calculated at the tributary stream and spring sites compared to the loads calculated for these constituents at the main-stem stream sites (fig. 1; table 5).

The combined total instantaneous nitrate-N loads for the WWTPs during the study period in the Plum Creek watershed ranged from approximately 0.10 to 0.50 ton/d, with an average of approximately 0.32 ton/d (the data used to calculate instantaneous nitrate-N loads for the WWTPs were provided by the GBRA and are available in the companion data release [Lambert and others, 2017]) (fig. 18). Generally the highest loads were discharged from sites WWTP-Kyle and WWTP-Buda because of their large wastewater treatment capacities, followed by sites WWTP-Lockhart 1 and WWTP-Luling North (fig. 18). The loads from site WWTP-Lockhart 2 varied more but often were lower compared to the loads at the other WWTPs (fig. 18). Higher nitrate concentrations were measured in samples collected from the main-stem stream sites during the S1, S2, and S3 synoptic sampling events when the streamflow was relatively low compared to the lower nitrate concentrations during the S4 synoptic sampling event when the streamflow was relatively high (fig. 17). The nitrate loads during the S1, S2, and S3 synoptic sampling events were relatively low (fig. 17) and can be accounted for by the WWTP loadings to the stream channel (figs. 17 and 18).

At higher streamflows, WWTP effluent discharge is no longer the dominant source of flow or of nitrate. Nitrate from other sources, however, might be transported by tributaries in subwatersheds into the main stem during higher streamflows and runoff events (fig. 17). During higher streamflow conditions (synoptic sampling event S4), the nitrate concentration decreased, whereas the overall nitrate load increased by about a factor of 3—the load was much higher than could be accounted for solely from WWTP effluent discharge (figs. 17 and 18). Nitrate-N loads for synoptic sampling event S4 increased from about 0.55 ton/d at the MS-Plum Creek site to nearly 1.6 ton/d at the MS-CR202 site. The total WWTP load for synoptic sampling event S4 accounted for approximately 0.5 ton/d (fig. 18), indicating that additional nitrate from sources other than the WWTPs contributed to the nitrate-N load in the main-stem stream channel between sites MS-Plum and MS-CR202 at a rate of approximately 1 ton/d during a runoff event of this magnitude (fig. 17). This part of the watershed also receives input from the WWTP-Lockhart 1 and WWTP-Lockhart 2 sites, but the combined discharge from these WWTPs is not enough to account for the increased nitrate-N load to the main stem between the MS-Plum Creek and MS-CR202 sites.

The source of the higher nitrate-N loads that occurred during higher streamflow (synoptic sampling event S4) is from the subwatersheds (Brushy Creek, Elm Creek, or Dry Creek) located in the northeastern part of the watershed (fig. 17). The range of $\delta^{15}N\text{-}NO_3$ values for Plum Creek sites during synoptic sampling event S4 (8.20–21.8 per mil; Lambert and others, 2017) is consistent with a combination of sources such as soil-derived nitrate from fertilized soils and human or animal waste, corroborating that there are other nitrate sources in addition to the WWTPs. The upper part of the Plum Creek watershed is rapidly urbanizing, but there were an estimated 33,000 cattle in the Brushy Creek subwatershed as of 2008 (Berg and others, 2008). Downstream from site MS-CR202, there was a relatively small increase in the nitrate-N load with little change in the $\delta^{15}N\text{-}NO_3$ values during synoptic sampling event S4 (fig. 17) (Lambert and others, 2017). A relatively small increase in the nitrate-N load might result when there is streamflow from one of the other subwatersheds with a similar nitrate-N concentration into the main stem, or might result from collecting the sample on the hydrograph recession, which might not be representative of the total nitrate-N load during peak streamflow conditions.

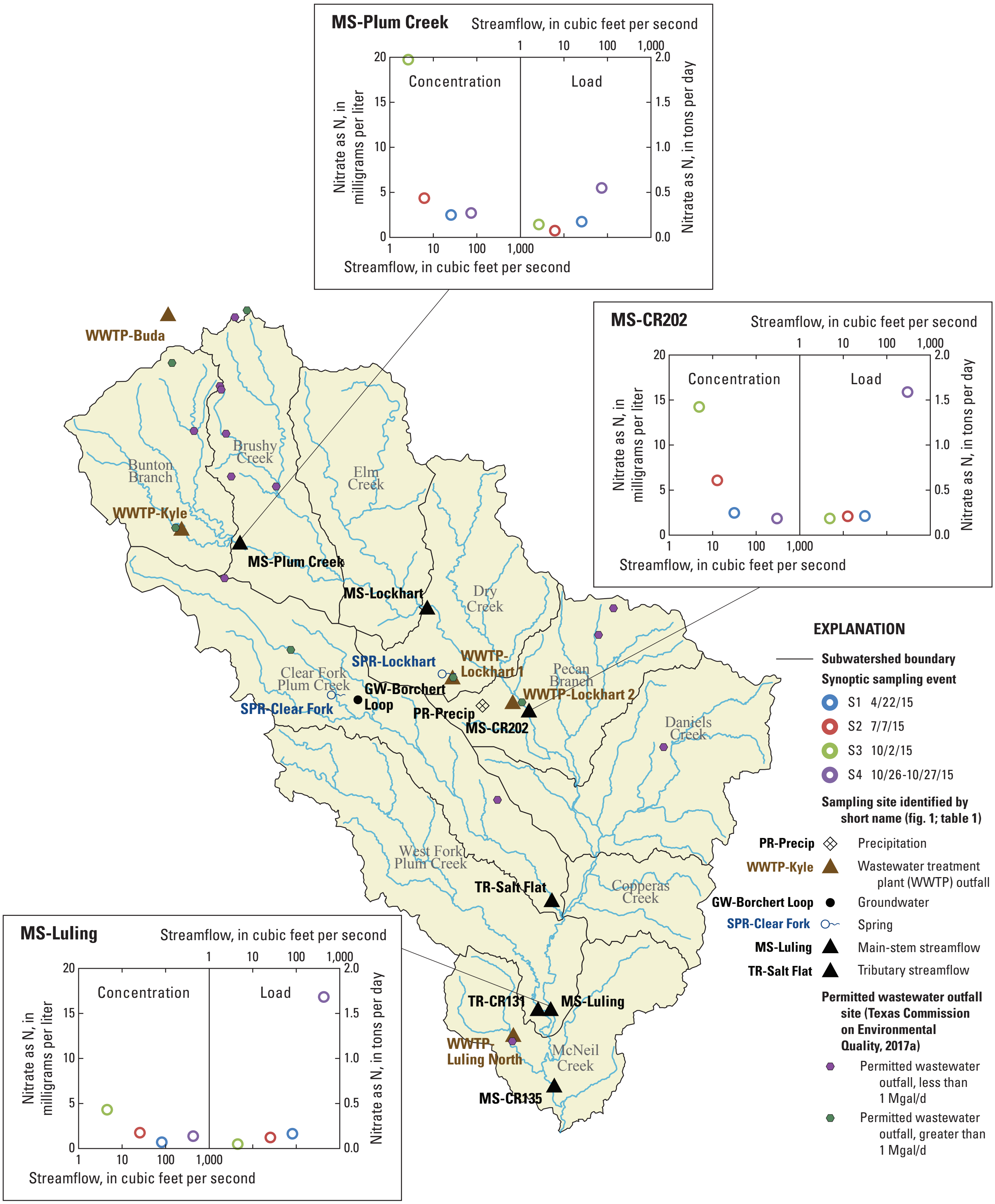

Figure 17. Relation of nitrate as nitrogen (N) concentrations and loads from main-stem (MS) stream sampling sites to streamflow during four synoptic sampling events (S1–S4) in the Plum Creek watershed, south-central Texas, April–October 2015.

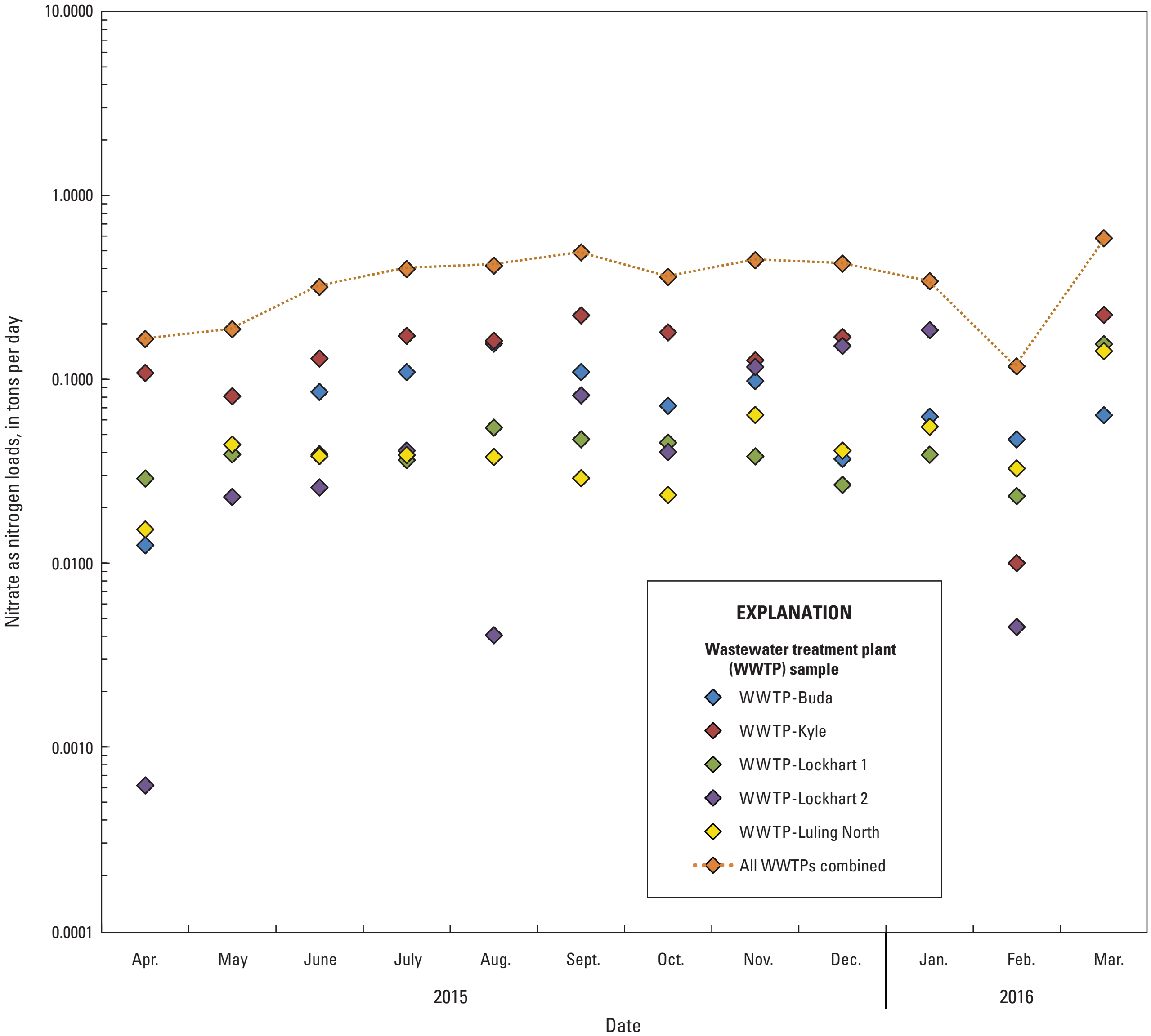

Figure 18. Instantaneous wastewater treatment plant nitrate as nitrogen loads to the Plum Creek watershed, south-central Texas, April 2015–March 2016. Data from the Plum Creek Watershed Monitoring Program (Guadalupe-Blanco River Authority, 2017b).

Additional Water-Quality Observations

Concentrations of dissolved solids, chloride, and sulfate in the lower part of the Plum Creek watershed (sites TR-CR131 and MS-CR135) indicate that water quality in this area differs from elsewhere in the watershed (fig. 12). Explanations for high concentrations of these constituents at these sites include the influx of produced waters associated with oil and gas exploration or saline groundwater. Historical records and reports (Berg and others, 2008) indicate that there was extensive oil and gas exploration in the Luling area, and brines that were coproduced were stored in surface disposal pits until streamflows in the surrounding rivers were substantial enough to dilute the brine. There are also historical accounts of springs producing saline water in this area (Rasmussen, 1947).

Comparison With Regulatory Standards

Water-quality results from both watersheds were compared to national drinking water regulations and guidelines (U.S. Environmental Protection Agency, 2012) and TCEQ's Texas Surface-Water Quality Standards (TSWQS) general-use criteria and nitrate screening levels. Water-quality results were compared to national drinking water regulations for comparative purposes only; these standards apply only to finished drinking water supplies distributed through a municipal water-supply system and may differ in quality from raw, ambient water samples. The goal of TCEQ's water management programs are to protect Texas water resources and water uses including the support of aquatic life, recreation, fishing, and drinking water supplies (Texas Commission on Environmental Quality, 2014). TCEQ's general-use criteria are site-specific numerical criteria developed for classified river segments, not unclassified water bodies, to quantitatively evaluate general uses including water temperature, pH, chloride, sulfate, and total dissolved solids (Texas Commission on Environmental Quality, 2014). These criteria are "used as maximum or minimum instream concentrations that may result from permitted discharge and nonpoint sources" (Texas Commission on Environmental Quality, 2014). Nutrient screening levels are not regulatory in nature; they are used to help evaluate the "health" of surface water in the State of Texas (Texas Commission on Environmental Quality 2012a, 2012b, 2014). The screening levels are targeted instream concentrations for nutrient constituents that can be directly compared to monitoring data (Texas Commission on Environmental Quality, 2014). The screening levels are "statistically derived from long-term monitoring data or published levels of concern," and monitoring data are "compared to the screening levels to identify areas where elevated concentrations are causes for concern" (Texas Commission on Environmental Quality, 2014).

Geronimo Creek

All of the water-quality samples collected from the Geronimo Creek watershed—with one exception from the MS-Haberle site—exceeded the TSWQS general-use criteria of 400 mg/L for dissolved-solids concentrations (fig. 7; table 6). One sample from each of the GW-Laubach and MS-Haberle sites exceeded the national drinking water guidelines secondary maximum contaminant level (SMCL) of 500 mg/L for dissolved-solids concentrations (fig. 7; table 6). Most of the samples collected from the GW-Laubach, MS-SH123, and MS-Haberle sites also exceeded the TSWQS 50-mg/L general-use criteria for sulfate (fig. 7; table 6). All of the samples from the GW-Laubach and SPR-Timmerman sites exceeded the TSWQS nitrate-N screening criteria of 1.95 mg/L (Texas Commission on Environmental Quality, 2012b, 2014) and the national primary drinking water standards maximum contaminant level (MCL) of 10 mg/L nitrate-N (fig. 8; table 6). All stream samples (sites MS-SH123 and MS-Haberle) also exceeded the TSWQS nitrate-N screening criteria of 1.95 mg/L, and two of four samples from the MS-Haberle site also exceeded the MCL of 10 mg/L.

Plum Creek

Samples collected from the upper main-stem stream sites (Plum Creek and MS-CR202), the WWTP sites, and the lowermost sites (MS-CR135 and TR-CR131) had the poorest water quality with respect to existing standards. Samples from five sites (MS-Plum Creek, MS-CR202, MS-Luling, TR-CR131, and TR-CR135) exceeded the SMCL of 500 mg/L, and two samples from the TR-CR131 site exceeded the TSWQS general-use protection criteria of 1,120 mg/L for dissolved solids (fig. 12; table 6). The TR-CR131 site also exceeded the TSWQS general-use protection criteria of 350 mg/L and the SMCL of 250 mg/L for chloride (fig. 12; table 6). Samples collected from the GW-Borchert Loop, SPR-Lockhart, SPR-Clear Fork, MS-Plum Creek, MS-CR202, WWTP-Lockhart 1, and WWTP-Luling North sites in the upper and central parts of the watershed exceeded the MCL for nitrate-N of 10 mg/L; most of the remaining samples also exceeded the TSWQS 1.95-mg/L nitrate-N screening criteria (fig. 13).

Table 6. Texas Surface-Water Quality Standards general-use criteria and nutrient screening levels used to assess surface-water quality in Geronimo Creek and Plum Creek, south-central Texas; national primary drinking water standards; and national secondary drinking water guidelines for finished water from public water supply systems.

[TSWQS, Texas Surface Water Quality Standard; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; --, not applicable; °F, degree Fahrenheit; mg/L, milligram per liter; µg/L, microgram per liter; nitrate-N, nitrate as nitrogen; *, dissolved solids is the term used by the U.S. Geological Survey but is equivalent to Total Dissolved Solids (TDS) used in TSWQS general-use criteria and national (U.S. Environmental Protection Agency) drinking water standards and secondary drinking water guidelines; ammonia-N, ammonia as nitrogen]

Constituent	TSWQS general-use criteria[1]		TSWQS nutrient screening levels[2]	National primary drinking water standards (MCLs)[3]	National secondary drinking water guidelines (SMCLs)[4]
	Geronimo Creek	Plum Creek	Both watersheds		
pH (units)	6.5–9.0	6.5–9.0	--	--	--
Temperature (°F)	90	90	--	--	--
Dissolved oxygen (mg/L)	5.0	5.0	--	--	--
Chloride (mg/L)	100	350	--	--	250
Sulfate (mg/L)	50	150	--	--	250
Nitrate-N (mg/L)	--	--	--	10.0	--
Dissolved solids (mg/L)*	400	1,120	--	--	500
Fluoride (mg/L)	--	--	--	4.0	2.0
Total phosphorus (mg/L)	--	--	0.69	--	--
Orthophosphorus (mg/L)	--	--	0.37	--	--
Nitrate-N (mg/L)	--	--	1.95	10	--
Ammonia-N (mg/L)	--	--	0.33	--	--

[1]Water-quality criteria established in Texas Surface Water Quality Standards (TSWQS) to safeguard general water quality, rather than protection of specific use; dissolved oxygen criterion is the exception and is related to aquatic life-use protection (Texas Commission on Environmental Quality, 2012a).

[2]Statistically derived from 10 years of surface-water-quality monitoring data using the 85th percentile; used in the absence of established criteria to denote a concern (Texas Commission on Environmental Quality, 2012b, 2014).

[3]MCL (maximum contaminant level) is an enforceable standard regulating the highest level of a contaminant that is legally allowed in finished drinking water from public water supply systems (U.S. Environmental Protection Agency, 2012).

[4]SMCL (secondary maximum contaminant level) regulations are nonenforceable guidelines regarding contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water (U.S. Environmental Protection Agency, 2012).

Summary

Located in south-central Texas, the Geronimo Creek and Plum Creek watersheds have been identified by the Guadalupe-Blanco River Authority and the Texas Commission on Environmental Quality as having water-quality impairments related to elevated nutrient concentrations and high bacteria counts. Historical data reveal a long history of problems with nitrate and possible sources that might contribute to elevated concentrations of nitrate. Agriculture (cultivated crops, rangeland, and grassland and pasture) is the predominant land use in the Geronimo Creek watershed, accounting for more than 70 percent of the 2011 total land cover. By comparison, agricultural uses in the Plum Creek watershed also account for about 70 percent of the 2011 total land cover, but the cultivated crop land cover was higher in the Geronimo Creek watershed (about 37 percent) as compared to Plum Creek watershed (about 7 percent). The upper and central parts of the Plum Creek watershed are more highly urbanized; four of the five major wastewater treatment plants (WWTPs) in this watershed and numerous smaller permitted outfalls are concentrated in the upper and central parts of the watershed.

Water-quality samples were collected from stream, spring, and groundwater sites distributed across the two watersheds, along with precipitation samples and WWTP effluent samples from the Plum Creek watershed to characterize endmember concentrations and isotopic compositions from April 2015 through March 2016. The water-quality samples were analyzed for selected major ions, trace elements, and nutrient species, as well as stable isotopes of nitrate ($\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3). Water-quality data from effluent discharge samples from the five WWTPs collected by the Guadalupe-Blanco River

Authority were analyzed in conjunction with the other datasets. Chemical loadings were calculated for selected major ions and nutrient species. The data collected in association with the stable isotopes of nitrate ($\delta^{15}N-NO_3$ and $\delta^{18}O-NO_3$) were interpreted to characterize water quality and to determine possible sources of nitrate in both watersheds.

Six quality-control samples were collected for this study. Two field-blank samples were collected; chloride was detected in both field blanks, whereas sulfate and phosphorus were detected in the second field blank. The detected concentrations of chloride, sulfate, and phosphorus were much lower than the environmental concentrations and thus are not considered factors influencing the concentrations. Four split replicate samples were collected from multiple site types, and relative percent differences were calculated for each replicate pair having detectable concentrations. The relative percent differences indicated that the sampling procedures used to collect the samples were representative and comparable.

Water quality in the Geronimo Creek watershed is dominated by the groundwater chemistry with minimal variation in concentrations likely resulting, in part, from the collection of water-quality samples primarily at lower streamflow. The largest variation in concentrations of dissolved solids, chloride, sulfate, and nutrients was measured in samples collected at the downstream main-stem stream site MS-Haberle. The largest input to the system occurs in conjunction with groundwater inflow that enters the stream channel upstream from site MS-SH123. Nitrate as nitrogen (Nitrate-N) concentrations were highest in the groundwater (site GW-Laubach) and spring (site SPR-Timmerman) samples and two of the stream samples (site MS-Haberle). Nitrate-N concentrations of precipitation samples were very low as compared to other site types.

The nitrogen isotope ($\delta^{15}N-NO_3$ and $\delta^{18}O-NO_3$) values indicate that all of the sites in the Geronimo Creek watershed share one or more common sources of elevated nitrate. The sources of elevated nitrate in groundwater and spring discharge most likely are diffuse sources that occur in conjunction with the mixing of nitrate from fertilizer applications and septic systems, resulting in a homogenized $\delta^{15}N-NO_3$ composition. In the Geronimo Creek watershed there has likely been substantial historical and ongoing nitrate-N loading, as evidenced by the continued high nitrate concentrations, with an estimated range of about 2,400–2,800 tons of fertilizer applied (2017) during a single growing season. Another possible source of nitrate is leaking septic systems; approximately 2,300 septic systems within 1,000 feet of a stream have been identified in the Geronimo Creek watershed that might contribute an estimated 24 tons per year; this is about two orders of magnitude less than the amount estimated from inorganic fertilizer application rates. The continued loading of nitrate-N from application of agricultural fertilizers and possible leaks from septic systems might result in ongoing accumulations and continued elevated concentrations of nitrate-N.

Instantaneous chemical loads were calculated for selected major ions and nutrient species and compared to constituent concentrations from the Geronimo Creek spring and stream sites. Although individual concentrations are elevated, overall the dissolved solids, chloride, sulfate, and nitrate-N loads generally were consistent in value and very low at most sites because of low streamflow. The highest loads and greatest range in concentrations and loads were measured in samples collected at the MS-Haberle site. Nitrate loads ranged from about 0.056 to 0.221 tons per day or about 20–80 tons per year of nitrate moving through the system under lower streamflow conditions.

Results from the Geronimo Creek watershed indicate that during lower streamflow conditions (1) water quality is groundwater dominated although the influence of a surface-water component increases from upstream to downstream; (2) nitrate-N concentrations are high throughout the Geronimo Creek watershed where the sample sites are located; (3) the sources of nitrate-N likely include inorganic fertilizer, human waste, and animal waste; and (4) nitrate-N loads are most likely dominated by inorganic fertilizer.

The Plum Creek watershed is dominated by effluent discharged from the major WWTPs, which accounts for a majority of base flow in the watershed. Generally, the highest loads were discharged from sites WWTP-Kyle and WWTP-Buda because of their large wastewater treatment capacities, followed by sites WWTP-Lockhart 1 and WWTP-Luling North. The overall contribution of WWTP effluent discharge to the Plum Creek watershed during base-flow conditions is fairly consistent, with total contributions ranging from about 6 to 19 cubic feet per second.

The concentrations of dissolved solids, chloride, and sulfate at lower streamflows in the main-stem samples (sites MS-Plum Creek, MS-CR202, and MS-Luling) are similar in composition to the WWTP samples, indicating that WWTP effluent discharge in the upper and central parts of the watershed dominates the streamflow water chemistry. Concentrations decrease downstream from sites WWTP-Kyle and WWTP-Buda as additional flow enters the main-stem channel. The higher concentrations of dissolved solids, chloride, and sulfate in the lower part of the watershed indicate that the water chemistry in this area likely differs from the water chemistry in samples collected throughout the remainder of the watershed; these higher concentrations are influenced by saline water, such as produced waters associated with oil and gas exploration or saline springs.

The highest concentrations of nitrate-N in the Plum Creek watershed were measured in WWTP, groundwater, and spring samples. Samples collected from the main-stem and tributary stream sites in the Plum Creek watershed show an overall decrease in nitrate concentration relative to the downstream distance from the WWTPs. Nitrate concentrations were dependent on streamflow conditions, with the highest concentrations measured in samples collected at lower flows. Groundwater samples (site GW-Borchert Loop) had relatively high concentrations (12.6–15.5 milligrams per liter [mg/L]), but were lower on average than the WWTP samples. Nitrate-N concentrations in spring samples (sites SPR-Clear Fork and SPR-Lockhart) were variable, ranging from 11.2 to 35 mg/L. Organic nitrogen and orthophosphate concentrations were higher in main-stem and tributary stream samples and WWTP samples than in groundwater and spring samples. Higher concentrations of organic nitrogen and orthophosphate were measured in samples collected from low to midrange streamflows; the lowest concentrations were measured in samples collected from the highest (stormwater runoff) flow and from precipitation.

There are different (multiple) sources of nitrate in the Plum Creek watershed whose contributions are dependent on the type of site and the streamflow conditions. The $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ values in groundwater samples from the Plum Creek watershed are similar to values measured in the groundwater and spring samples from the Geronimo Creek watershed. This similarity in values indicates that the source(s) of nitrate in the groundwater and spring samples collected in Plum Creek also might be derived from diffuse, mixed nitrate from fertilizer, manure, and septic systems that result in composite $\delta^{15}N$ and $\delta^{18}O$ isotope values indicating a soil nitrate source.

As the geologic and hydrogeologic characteristics and historical land use in the Plum Creek watershed are similar to those currently noted in the Geronimo Creek watershed, there are historical and ongoing inputs of nitrate-N to the soil that provide legacy accumulations of nitrate-N in the Plum Creek watershed. Using the same method and values used for Geronimo Creek, the estimated amount of fertilizer applied (2017) during a single growing season in the Plum Creek watershed would range from about 2,800 to 3,200 tons of fertilizer. There are an estimated 5,900 permitted septic systems in Caldwell County, in which much of the Plum Creek watershed is located. Using an estimated loss of 9.5 kilograms (about 21 pounds) of nitrate per home per year, the estimated nitrate input into the groundwater system is nearly 62 tons of nitrate per year.

Nitrate isotopes measured in spring, stream (main-stem and tributary), and WWTP samples from the Plum Creek watershed generally depict increasing $\delta^{15}N\text{-}NO_3$ values with increasing $\delta^{18}O\text{-}NO_3$ values, which is consistent with isotopic changes that occur with denitrification (a microbial process by which nitrate is reduced to nitrogen gas). Instream mixing of streamflow with WWTP effluent discharge is consistent with the range of $\delta^{15}N\text{-}NO_3$ values and nitrate-N concentrations measured in Plum Creek. The relatively high $\delta^{15}N\text{-}NO_3$ values and nitrate-N concentrations measured in WWTP effluent samples, and the similar range observed in samples from main-stem Plum Creek sites, indicate that WWTP effluent discharge is an important source of nitrate in the Plum Creek watershed.

The loads of dissolved solids, chloride, sulfate, and nitrate vary depending on the amount of streamflow, likely because the sources of these constituents also vary as hydrologic conditions change. The chemical loads calculated for selected constituents from stream sites indicate that the main-stem loads differ from the tributary and spring loads. The dissolved-solids, chloride, sulfate, and nitrate-N loads are highest at the MS-Plum Creek, MS-CR202, and MS-Luling sites in the upper part of the Plum Creek watershed. During lower flows the loads decrease downstream as distance from WWTPs increases. The nitrate-N loads calculated for the spring and tributary stream samples tend to be very low and are the result of lower flows that may or may not reach the main-stem stream channel. The combined total instantaneous nitrate-N loads from the WWTPs in the Plum Creek watershed ranged from approximately 0.10 to 0.50 tons per day, with an average of approximately 0.32 tons per day, and nitrate-N loads in main-stem samples collected at lower flows can be accounted for by WWTP effluent discharges to the stream.

During higher flows, however, nitrate-N concentrations decreased, whereas the overall loads increased and the loads were much higher than could be accounted for solely from WWTP effluent discharges. The nitrate-N loads increased from about 0.55 tons per day at the MS-Plum Creek site to nearly 1.6 tons per day at the MS-CR202 site. The total WWTP loads can only account for approximately 0.5 tons per day, leaving an additional 1 ton per day that is entering the stream channel between the MS-Plum and MS-CR202 sites. This additional loading indicates that nitrate-N might be transported as flood flows from one of the subwatersheds (Brushy Creek, Elm Creek, or Dry Creek) located in the northeastern part of the watershed. The upper part of the Plum Creek watershed is rapidly becoming urbanized, but there were an estimated 33,000 cattle in the Brushy Creek subwatershed as of 2008. Thus at higher flows, much larger nitrate loads are being transported through the watershed during stormwater runoff conditions. These larger loadings have $\delta^{15}N\text{-}NO_3$ values indicative of human and animal waste.

Results from the Plum Creek watershed indicate that (1) water quantity and quality are surface-water dominated; (2) nitrate concentrations vary widely, with concentrations highest in WWTP samples, groundwater samples, and stream samples collected at sites downstream from WWTPs and lowest in stream samples collected from the tributaries; (3) under low-flow conditions the predominant source of flow and nitrate is WWTPs, and nitrate loads are relatively low; and (4) during higher flow storm events the source of nitrate is no longer dominated by the WWTP contribution.

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For more information about this publication, contact

Director, Texas Water Science Center
U.S. Geological Survey
1505 Ferguson Lane
Austin, TX 78754–4501

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Publishing support provided by
Lafayette Publishing Service Center

Lambert and others—**Water Quality, Sources of Nitrate, and Chemical Loadings in the Geronimo Creek and Plum Creek Watersheds, Texas, April 2015–March 2016**—SIR 2017–5121

ISSN 2328-0328 (online)
https://doi.org/10.3133/sir20175121