

Prepared in cooperation with the San Antonio River Authority and
the Guadalupe-Blanco River Authority

Concentrations of Selected Constituents in Surface-Water and Streambed-Sediment Samples Collected From Streams In and Near an Area of Oil and Natural-Gas Development, South-Central Texas, 2011–13



Data Series 836
Version 1.1, January 2015

Front cover:

Background, A drill rig on a drill pad in Karnes County, Texas (photograph taken on January 26, 2012, by Stephen Opsahl).

Back cover:

Top, U.S. Geological Survey hydrographer collecting a streambed-sediment sample from the San Antonio River near Elmendorf, Texas (photograph taken on November 3, 2011, by Stephen Opsahl).

Middle, U.S. Geological Survey hydrographer collecting a water sample from the San Antonio River near Elmendorf, Texas (photograph taken on November 7, 2011, by Stephen Opsahl).

Bottom, U.S. Geological Survey hydrographer using a 2-millimeter sieve to process a streambed-sediment sample collected from Cibolo Creek near Falls City, Texas (photograph taken on November 7, 2011, by Stephen Opsahl).

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By Stephen P. Opsahl and Cassi L. Crow

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

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	0.00254	micrometer (μm)
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
liter (L)	0.2642	gallon (gal)
milliliter (mL)	0.03382	ounce, fluid (fl. oz.)
Flow rate		
foot per second (ft/s)	0.3048	meter per second (m/s)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)

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.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$). Concentrations of chemical constituents in streambed sediment are given in milligrams per kilogram (mg/kg), micrograms per kilogram ($\mu\text{g}/\text{kg}$), or grams per kilogram (g/kg).

Concentrations of Selected Constituents in Surface-Water and Streambed-Sediment Samples Collected From Streams In and Near an Area of Oil and Natural-Gas Development, South-Central Texas, 2011–13

By Stephen P. Opsahl and Cassi L. Crow

Abstract

During 2011–13, the U.S. Geological Survey, in cooperation with the San Antonio River Authority and the Guadalupe-Blanco River Authority, analyzed surface-water and streambed-sediment samples collected from 10 sites in the San Antonio River Basin to provide data for a broad range of constituents that might be associated with hydraulic fracturing and the produced waters that are a consequence of hydraulic fracturing. Among surface-water samples, all sulfide concentrations were less than the method detection limit of 0.79 milligrams per liter. Four glycols—diethylene glycol, ethylene glycol, propylene glycol, and triethylene glycol—were analyzed for in surface-water samples collected for this study, and none were detected. Of the 91 semivolatile organic compounds analyzed for this study, there were six detections, all but one of which were in storm-runoff samples. The base-flow sample collected at the San Antonio River at Goliad, Tex. (SAR Goliad), site contained bis(2-ethylhexyl) phthalate, a plasticizer in polyvinyl chloride and a constituent in hydraulic fracturing fluids. The storm-runoff samples collected at the San Antonio River near Elmendorf, Tex. (SAR Elmendorf), and Ecleto Creek at County Road 326 near Runge, Tex. (Ecleto 2), sites also contained bis(2-ethylhexyl) phthalate. The storm-runoff sample collected at the SAR Elmendorf site contained the plasticizer diethyl phthalate. Both storm-runoff samples collected at the Ecleto Creek near Runge, Tex. (Ecleto 1), and Ecleto 2 sites contained benzyl alcohol, a solvent commonly used in paints. Of the 67 volatile organic compounds analyzed in this study, there were a total of six detections, all of which were in base-flow samples. The surface-water sample collected at the SAR Elmendorf site contained bromodichloromethane, dibromochloromethane, and trichloromethane, all of which are disinfection byproducts associated with the chlorination of municipal water supplies and of treated municipal wastewater. The sample collected at the Cibolo Creek near Saint Hedwig, Tex. (Cibolo St. Hedwig), site contained toluene, a fuel additive, solvent, and industrial feedstock used to produce benzene and a constituent

associated with produced waters. The Cibolo St. Hedwig site is upstream from current (2014) oil and natural-gas production areas. Dichloromethane, an industrial solvent with multiple uses, was detected in surface-water samples at both the San Antonio River at State Highway 72 near Runge, Tex. (SAR 72), and SAR Goliad sites.

In streambed-sediment samples, concentrations of total saturated hydrocarbons (TSH) ranged from an estimated 260 micrograms per kilogram ($\mu\text{g}/\text{kg}$) in the less than ($<$) 2-millimeter (mm) size-fraction sample collected at the SAR Goliad site to 11,000 $\mu\text{g}/\text{kg}$ in the $<$ 2-mm size-fraction sample collected at the Ecleto 1 site. TSH concentrations were greater in the $<$ 63-micrometer (μm) size-fraction samples than in the $<$ 2-mm size-fraction samples in streambed-sediment samples collected from 5 of the 9 sites. Total polycyclic aromatic hydrocarbons (PAHs) were calculated as the sum of the individual PAHs and alkylated PAHs. Total PAH concentrations ranged from less than the method detection limit in the $<$ 2-mm size-fraction samples collected from multiple sites to 1,600 $\mu\text{g}/\text{kg}$ in the $<$ 2-mm size-fraction sample collected from the San Antonio River near McFaddin, Tex. (SAR McFaddin), site. Total PAH concentrations were greater in the $<$ 63- μm size-fraction samples than in the $<$ 2-mm size-fraction samples at 7 of the 9 sites.

During collection of streambed-sediment samples, additional samples from a subset of three sites (the SAR Elmendorf, SAR 72, and SAR McFaddin sites) were processed by using a 63- μm sieve on one aliquot and a 2-mm sieve on a second aliquot for PAH and *n*-alkane analyses. The purpose of analyzing PAHs and *n*-alkanes on a sample containing sand, silt, and clay versus a sample containing only silt and clay was to provide data that could be used to determine if these organic constituents had a greater affinity for silt- and clay-sized particles relative to sand-sized particles. The greater concentrations of PAHs in the $<$ 63- μm size-fraction samples at all three of these sites are consistent with a greater percentage of binding sites associated with fine-grained ($<$ 63 μm) sediment versus coarse-grained ($<$ 2 mm) sediment. The larger difference in total PAHs between the $<$ 2-mm and $<$ 63- μm

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size-fraction samples at the SAR Elmendorf site might be related to the large percentage of sand in the <2-mm size-fraction sample which was absent in the <63- μm size-fraction sample. In contrast, the <2-mm size-fraction sample collected from the SAR McFaddin site contained very little sand and was similar in particle-size composition to the <63- μm size-fraction sample.

Introduction

Concerns about possible environmental effects associated with the use of hydraulic fracturing processes for extracting oil and natural gas have been growing as these processes have increasingly been implemented throughout the United States in the past 10 years (U.S. Environmental Protection Agency, 2013a). Hydraulic fracturing has become a highly contentious public policy issue because of concerns about the environmental and health effects of its use (Geologic Society of America, 2013). Some of the concerns expressed by the public, staff members of State and local water resource agencies, and State and Federal regulatory agencies include the possible release of organic and inorganic constituents found in hydraulic fracturing fluids and produced waters (Mahler and Van Metre, 2001; Kresse and others, 2012; U.S. Environmental Protection Agency, 2013a). “Produced water” is the term used by the oil and gas industry to describe the mix of surface water, groundwater (or both), and hydraulic fracturing fluids injected into a well with the water naturally occurring in formation that flows to the surface throughout the development and operation lifespan of an oil or gas well (Schramm, 2011). For this report, the water-based solution that flows back to the surface after the completion of hydraulic fracturing (referred to by the oil and gas industry as “flowback”) (Schramm, 2011) is included among produced waters. Constituents of concern include those frequently used in hydraulic fracturing fluids such as glycols and surfactants and those found in produced waters such as *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) (U.S. Geological Survey, 2011; FracFocus Chemical Disclosure Registry, 2013). Individual constituents from these sources differ in their chemical, physical, and toxicological properties (U.S. Environmental Protection Agency, 2012a).

In Texas, the production rate of natural gas and oil from the Eagle Ford Shale (fig. 1) has greatly increased in recent years, from about 2 million cubic feet per day in 2008 to 3,204 million cubic feet per day in October 2013 (Railroad Commission of Texas, 2013a). Oil production also increased, from about 352 barrels per day in 2008 to 649,129 barrels per day in October 2013 (Railroad Commission of Texas, 2013b). Part of the San Antonio River Basin intersects a large area of natural-gas and oil production from the Eagle Ford Shale (fig. 1). The network of well pads, roadways, and pipelines associated with expansion of oil and natural-gas production represents potential pathways for inorganic and

organic constituents to enter surface-water systems (Kappel and others, 2013). Scant data are available pertaining to the concentrations of constituents that might be related to oil and natural-gas development in the water and sediment of streams in and near this area of oil and gas development. Therefore, there is a need to analyze different types of constituents in both water and streambed-sediment samples to effectively identify constituents that might be associated with oil and natural-gas production in Texas. The U.S. Geological Survey (USGS), in cooperation with the San Antonio River Authority and the Guadalupe-Blanco River Authority, analyzed surface-water and streambed-sediment samples collected from 10 sites in the San Antonio River Basin to provide data for a broad range of constituents that might be associated with hydraulic fracturing and the produced waters that are a consequence of hydraulic fracturing.

Purpose and Scope

This report summarizes the detections and concentrations of inorganic and organic constituents measured in surface-water and streambed-sediment samples collected from selected streams in the San Antonio River Basin in south-central Texas during 2011–13. Surface-water samples were collected during base flow and storm runoff. Streambed-sediment samples were collected twice during base flow. Several large storm events occurred between the first and second collections of streambed-sediment samples. The results from three streambed-sediment samples collected for the comparison of different sediment particle-size fractions provide data that could be used to assess whether PAHs and *n*-alkanes had a greater affinity for silt- and clay-sized particles relative to sand-sized particles.

Description of Study Area

The study area encompasses parts of Bexar, Comal, Guadalupe, Wilson, Karnes, DeWitt, Goliad, Victoria, and Refugio Counties in south-central Texas and consists of 2,150 square miles (mi^2) in the San Antonio River Basin and 2 mi^2 in the Guadalupe River Basin (fig. 1). Since 2008, rapid expansion of oil and natural-gas production with the use of hydraulic fracturing in the Eagle Ford Shale has taken place in south Texas (Railroad Commission of Texas, 2013c). A large part of three counties—Wilson, DeWitt, and Karnes Counties—is the location where most of the hydraulic fracturing for oil and natural-gas development is taking place in the study area (Railroad Commission of Texas, 2013c). Sampling site locations were chosen to provide data for a broad range of constituents that might be associated with hydraulic fracturing and the produced waters that are a consequence of hydraulic fracturing. The short names listed in table 1 for the sampling sites are used for referring to the sites throughout the text of this report. Map identifiers listed in table 1 are used in figure 1.

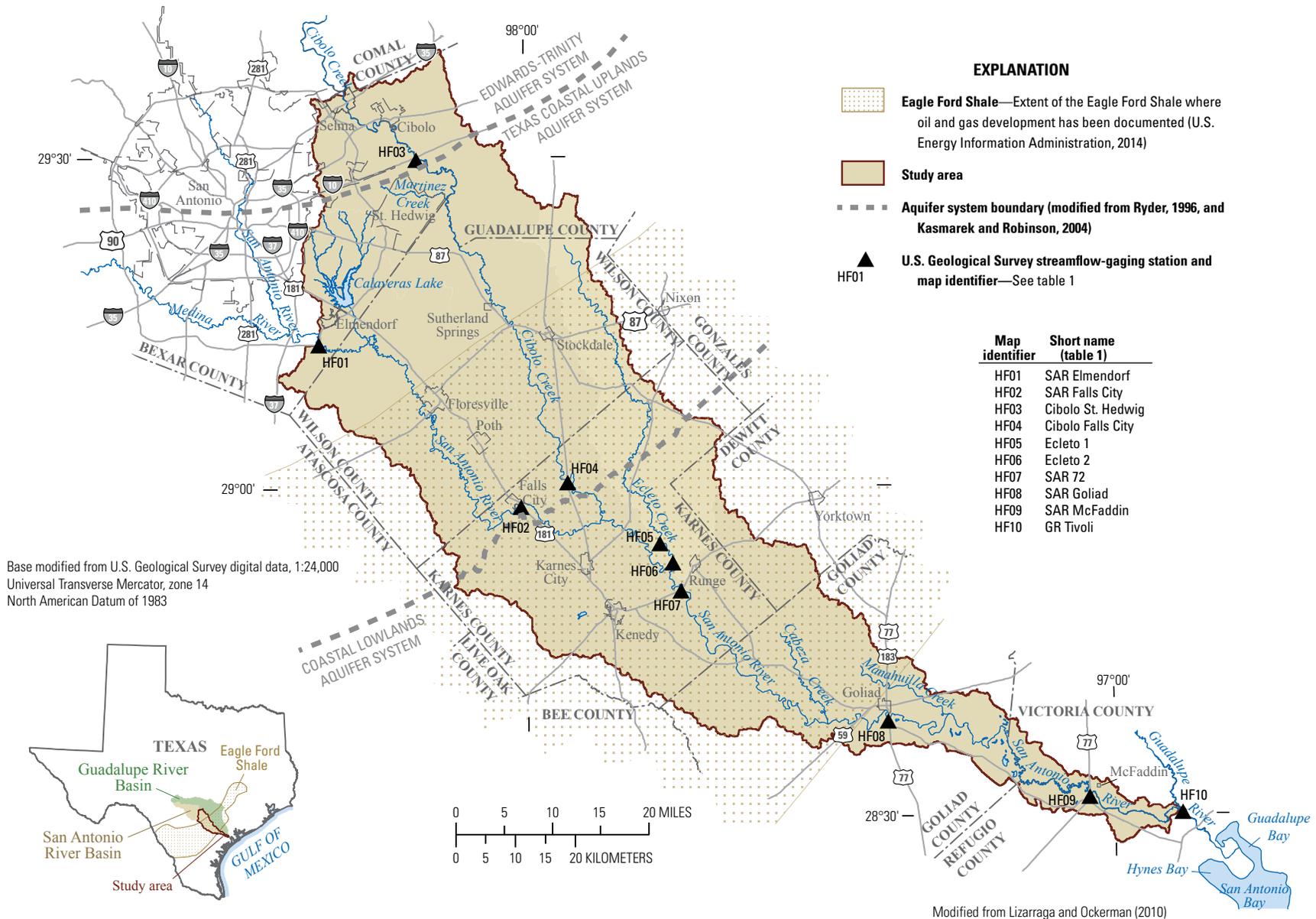


Figure 1. Locations of surface-water sampling sites in the San Antonio River Basin, Texas, 2011–13.

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Table 1. Data-collection sites in the San Antonio River Basin, Texas, 2011–13.

[USGS, U.S. Geological Survey; NAD 83, horizontal coordinate information referenced to North American Datum of 1983; dd, degrees; mm, minutes; ss, seconds; SAR, San Antonio River; St., Saint; GR, Guadalupe River]

Map identifier (as shown in fig. 1)	Short name	USGS station number	USGS station name	Latitude (NAD 83) (dd mm ss)	Longitude (NAD 83) (dd mm ss)
HF01	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	29° 13' 20"	98° 21' 21"
HF02	SAR Falls City	08183550	San Antonio River at Highway 181 near Falls City, Tex.	28° 58' 38"	98° 00' 37"
HF03	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	29° 30' 05"	98° 11' 10"
HF04	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	29° 00' 51"	97° 55' 49"
HF05	Ecleto 1	08186500	Ecleto Creek near Runge, Tex.	28° 55' 13"	97° 46' 20"
HF06	Ecleto 2	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	28° 53' 28"	97° 45' 03"
HF07	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	28° 50' 55"	97° 44' 13"
HF08	SAR Goliad	08188500	San Antonio River at Goliad, Tex.	28° 38' 57"	97° 23' 05"
HF09	SAR McFaddin	08188570	San Antonio River near McFaddin, Tex.	28° 31' 52"	97° 02' 33"
HF10	GR Tivoli	08188800	Guadalupe River near Tivoli, Tex.	28° 30' 20"	96° 53' 04"

The northern part of the study area overlies the Edwards-Trinity aquifer system (fig. 1). The remainder of the study area overlies the Texas Coastal Uplands and Coastal Lowlands aquifer systems (Ryder, 1996). The Cretaceous-age rocks of the Edwards-Trinity aquifer system primarily consist of limestone and sandstone (Ashworth and Hopkins, 1995). The Texas Coastal Uplands aquifer system is composed of formations of Paleocene and Oligocene age, with the sediments (in order of dominance) consisting mostly of sand, silt, and clay, distributed as relatively uniform sequences of predominantly fine- or coarse-grained material (Ryder, 1996). The Coastal Lowlands aquifer system is composed of younger formations from Oligocene through Holocene age that dip and thicken towards the Gulf of Mexico, with sediments that exist in complex, overlapping mixtures of sand, silt, and clay as a result of numerous oscillations of ancient shorelines (Lizárraga and Ockerman, 2010).

In the study area (fig. 1), the San Antonio River extends about 190 miles (mi) from near Elmendorf, Tex., to the confluence of the San Antonio and Guadalupe Rivers. The length of Cibolo Creek from Selma, Tex., to the confluence of Cibolo Creek and the San Antonio River is about 75 mi. The length of Ecleto Creek is about 55 mi from northern Wilson County to the confluence of Ecleto Creek and the San Antonio River in Karnes County. The San Antonio River ends at the confluence of the San Antonio and Guadalupe Rivers. From its confluence with the San Antonio River, the Guadalupe River continues southeast about 9 mi before emptying into the Guadalupe Bay in the Gulf of Mexico. The study area is composed of gently sloping, rolling terrain; the coastal uplands are somewhat more dissected and rolling compared to the coastal lowlands (Ryder, 1996). The land cover consists mostly of brush and grassland (Multi-Resolution Land Characteristics Consortium, 2013), and average annual

precipitation ranges from about 30 inches in the northern sections of the San Antonio River Basin to about 40 inches in the southern sections of the basin near the coast (National Oceanic and Atmospheric Administration, 2013).

Methods

Collection of Streamflow Data

Continuous streamflow was measured at USGS streamflow-gaging stations by using methods described by Rantz and others (1982a, b) and Turnipseed and Sauer (2010). A stage-discharge relation (rating curve) was developed on the basis of the discrete discharge and stage measurements made at each site (Kennedy, 1984; Turnipseed and Sauer, 2010). Adjustments were made to site stage-discharge ratings when discrete discharge measurements indicated changing channel conditions. From the stage-discharge ratings, stage data were used to compute continuous discharge (Kennedy, 1983). Discrete discharge measurements were made preceding surface-water sample collection in accordance with USGS methods (Rantz and others, 1982a, b; Turnipseed and Sauer, 2010). Streams were waded, and stream velocity measurements were made by using rod-mounted acoustic velocity meters (Xylem Analytics, 2012). Discharge measurements at the time of sample collection (table 2) were obtained from stage-discharge relations. Two sampling sites, San Antonio River at Highway 181 at Falls City, Tex. (SAR Falls City), and Ecleto Creek at County Road 326 near Runge, Tex. (Ecleto 2), were not equipped with continuous streamflow gages, and no discrete discharge measurements were made at the time of sample collection at these two sites.

Table 2. Summary of stream discharge and physicochemical properties in surface-water samples collected at data-collection sites from selected streams in the San Antonio River Basin, Texas, 2011–13.

[USGS, U.S. Geological Survey; mm/dd/yyyy, month/day/year; ft³/s, cubic feet per second; mg/L, milligrams per liter; μS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; FNU, formazin nephelometric units; SAR, San Antonio River; B, base flow; S, storm runoff; St., Saint; GR, Guadalupe River; E, estimated; --, not recorded]

Map identifier (as shown in fig. 1)	Short name	USGS station number	USGS station name	Date (mm/dd/yyyy)	Stream-flow condition	Dis-charge (ft ³ /s)	Dis-solved oxygen (mg/L)	pH	Specific conduc-tance (μS/cm at 25 °C)	Temper-ature (°C)	Turbid-ity (FNU)	Total dis-solved solids (mg/L)	Total sus-pended solids (mg/L)
HF01	SAR Elmendorf	08181800	San Antonio River near Elmen-dorf, Tex.	11/03/2011	B	160	7.4	8.1	1,090	22.6	11	600	42
HF01	SAR Elmendorf	08181800	San Antonio River near Elmen-dorf, Tex.	08/19/2012	S	11,600	4.5	8.0	250	24.9	1,090	170	1,500
HF02	SAR Falls City	08183550	San Antonio River at Highway 181 at Falls City, Tex.	11/07/2011	B	--	10.1	8.2	1,130	19.4	12	660	15
HF02	SAR Falls City	08183550	San Antonio River at Highway 181 at Falls City, Tex.	04/28/2013	S	--	--	--	--	--	--	750	110
HF03	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	11/02/2011	B	6.2	6.2	8.0	929	18.0	5.5	520	4.4
HF03	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	09/17/2012	S	195	5.0	7.5	846	23.4	8.0	480	12
HF04	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	11/07/2011	B	25	10.5	8.2	1,120	19.7	2.7	670	E2.8
HF04	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	09/29/2012	S	47	8.4	8.1	719	26.9	20	430	43
HF05	Ecleto 1	08186500	Ecleto Creek near Runge, Tex.	01/09/2013	S	1.1	6.8	7.5	1,180	14.2	25	720	35
HF06	Ecleto 2	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	03/20/2012	S	--	6.8	7.8	738	19.3	320	620	460
HF07	SAR 72	08188060	San Antonio River at State High-way 72 near Runge, Tex.	11/09/2011	B	110	12.4	8.7	1,250	19.2	13	750	33
HF07	SAR 72	08188060	San Antonio River at State High-way 72 near Runge, Tex.	09/30/2012	S	409	7.2	8.0	895	26.1	51	530	170
HF08	SAR Goliad	08188500	San Antonio River at Goliad, Tex.	11/09/2011	B	155	8.7	8.3	1,260	19.0	16	760	24
HF08	SAR Goliad	08188500	San Antonio River at Goliad, Tex.	01/09/2013	S	327	9.8	8.0	1,020	13.8	110	590	210
HF09	SAR McFaddin	08188570	San Antonio River near McFad-din, Tex.	11/08/2011	B	218	9.1	8.2	1,240	21.2	200	720	38
HF09	SAR McFaddin	08188570	San Antonio River near McFad-din, Tex.	01/10/2013	S	406	9.8	8.2	1,130	13.8	37	680	41
HF10	GR Tivoli	08188800	Guadalupe River near Tivoli, Tex.	11/08/2011	B	485	7.5	--	857	19.9	12	500	22
HF10	GR Tivoli	08188800	Guadalupe River near Tivoli, Tex.	01/10/2013	S	1,020	9.4	8.1	783	13.3	18	470	30

Collection and Processing of Surface-Water and Streambed-Sediment Samples

During 2011–13, 18 surface-water and 22 streambed-sediment samples were collected at 10 sites including the San Antonio River near Elmendorf, Tex. (SAR Elmendorf); SAR Falls City; Cibolo Creek near St. Hedwig, Tex. (Cibolo St. Hedwig); Cibolo Creek near Falls City, Tex. (Cibolo Falls City); Ecleto Creek near Runge, Tex. (Ecleto 1); Ecleto 2; San Antonio River at State Highway 72 near Runge, Tex. (SAR 72); San Antonio River at Goliad, Tex. (SAR Goliad); San Antonio River near McFaddin, Tex. (SAR McFaddin); and Guadalupe River near Tivoli, Tex. (GR Tivoli), sites (map identifiers HF01–HF10, respectively; fig. 1, table 1) for analysis of concentrations of selected inorganic and organic constituents (apps. 1–9). Values of physicochemical properties of surface water (dissolved oxygen concentration, pH, specific conductance, water temperature, and turbidity) were measured and recorded from the centroid of each stream site by using a YSI 6920 multiparameter water-quality monitor prior to collection of samples (table 2). Surface-water samples were collected over a variety of hydrologic conditions ranging from a minimum streamflow of 1.1 cubic feet per second (ft^3/s) at the Ecleto 1 site on January 9, 2013, to a maximum streamflow of 11,600 ft^3/s at the SAR Elmendorf site on August 19, 2012 (table 2). Ecleto Creek was an ephemeral stream. Although the sample collected at a discharge of 1.1 ft^3/s does not represent a large discharge for this creek, the sample was categorized as a storm-runoff sample because it was collected while streamflow was receding after a small rain event sufficient to create flow at this site. One of the storm-runoff samples could not be safely collected from the Ecleto 1 site at the time of sampling and was instead collected from the Ecleto 2 site, which is approximately 3.25 mi downstream from the Ecleto 1 site. Although there were two sampling sites located on Ecleto Creek, these sites were in proximity and were considered to represent the same area in figures used within this report.

Surface-water samples were collected and processed by following the methods and guidelines described in U.S. Geological Survey (variously dated) and Shelton (1997). At each sampling site, surface-water samples were collected at a minimum of 10 locations spaced at equal width increments across the stream by using samplers designed to allow water to enter the sampler with no change in speed or direction (isokinetic). When stream depths were shallow enough to be waded, surface-water samples were collected by using a US DH-81 1-liter bottle sampler (Davis, 2005) attached to a wading rod (fig. 2A). When the stream was too deep to be waded, surface-water samples were collected by using a US DH-2 1-liter collapsible bag sampler (Davis, 2005) attached to a reel and crane system (fig. 2B). Surface-water samples

collected by using the US DH-81 sampler at streamflow velocities less than ($<$) 1.5 feet per second (ft/s) and samples collected by using the US DH-2 sampler at velocities <2.0 ft/s were labeled as grab samples because the samplers are unable to collect isokinetic samples at those velocities. Surface-water samples were composited into a 14-liter Teflon (polytetrafluoroethylene) churn, and aliquots of representative whole-water (unfiltered) samples were dispensed from the churn into the appropriate sample bottles.

Two sets of streambed-sediment samples were collected during base flow. Several large storm events occurred between the first and second sets of streambed-sediment samples. Streambed-sediment samples were collected either manually with a scoop while wading (fig. 3A) or by using a ponar sampler (fig. 3B) from a watercraft or bridge by following standard USGS methods as described by Shelton and Capel (1994) and Edwards and Glysson (1999). At each site, a depositional area was identified, and a minimum of three separate samples were collected and composited into a single volume. Each sample was collected from an area at least 20 centimeters (cm) by 20 cm, and only the top 2–3 cm of streambed sediment was collected. For the first set of samples, streambed sediment was composited and put through either a stainless steel 2-millimeter (mm) sieve in preparation for the analyses of organic constituents or a 63-micrometer (μm) sieve in preparation for the analyses of inorganic constituents. Streambed-sediment samples that pass through a 2-mm sieve contain sand-, silt-, and clay-sized particles, whereas streambed-sediment samples that pass through a 63- μm sieve contain only the smaller silt- and clay-sized particles (Guy, 1969). For the second set of samples, streambed sediment was composited and put through only a 63- μm sieve in preparation for the analyses of both organic and inorganic constituents. An additional stream-bed sediment sample was collected from the Ecleto 1 site because the *n*-alkane analysis was not completed on the first stream-bed sediment sample following a sample processing error and a recollection was required (app. 7). During collection of the second sample set, additional samples from a subset of three sites (the SAR Elmendorf, SAR 72, and SAR McFaddin sites; fig. 1) were processed by using a 63- μm sieve on one aliquot and a 2-mm sieve on a second aliquot for PAH and *n*-alkane analyses. The purpose of analyzing PAHs and *n*-alkanes on a sample containing sand, silt, and clay versus a sample containing only silt and clay was to provide data that could be used determine if these organic constituents had a greater affinity for silt- and clay-sized particles relative to sand-sized particles. An unsieved portion of each of the three samples collected for the comparison of different size fractions also was analyzed for particle-size distribution (table 3).

A. US DH-81**B. US DH-2**

Figure 2. Samplers used in the collection of surface-water samples, San Antonio River Basin, Texas, 2011–13. *A*, US DH-81 1-liter bottle sampler. *B*, US DH-2 1-liter collapsible bag sampler.

A. Scoop



B. Ponar



Figure 3. Equipment and samplers used in the collection of streambed-sediment samples, San Antonio River Basin, Texas, 2011–13. *A*, Manual collection with a scoop while wading. *B*, Collection with a ponar sampler from a watercraft.

Table 3. Comparison of total polycyclic aromatic hydrocarbon and total saturated hydrocarbon concentrations and results of particle-size distribution analyses in less than 63 micrometer and less than 2 millimeter size fractions of selected streambed-sediment samples collected in June, 2012.

[USGS, U.S. Geological Survey; mm/dd/yyyy, month/day/year; PAH, polycyclic aromatic hydrocarbon; µg/kg, micrograms per kilogram; TSH, total saturated hydrocarbon; <, less than; mm, millimeter; µm, micrometer; SAR, San Antonio River; E, estimated; --, no data]

Map identifier (as shown in fig. 1)	Short name	USGS station number	USGS station name	Sample date (mm/dd/yyyy)	Total PAHs (µg/kg)		TSH (µg/kg)	
					<2 mm	<63 µm	<2 mm	<63 µm
HF01	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	06/25/2012	120	460	E3,600	E1,700
HF07	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	06/20/2012	48	160	E1,000	E2,400
HF09	SAR McFaddin	08188570	San Antonio River near McFaddin, Tex.	06/26/2012	250	340	E3,300	E2,000

Map identifier (as shown in fig. 1)	Short name	Suspended-sediment fall diameter (percentage)											
		Smaller than 0.002 mm	Smaller than 0.004 mm	Smaller than 0.008 mm	Smaller than 0.016 mm	Smaller than 0.031 mm	Smaller than 0.0625 mm	Smaller than 0.125 mm	Smaller than 0.25 mm	Smaller than 0.5 mm	Smaller than 1 mm	Smaller than 2 mm	Smaller than 4 mm
HF01	SAR Elmendorf	7	8	8	9	11	16	23	37	69	92	98	100
HF07	SAR 72	10	12	12	13	17	23	37	59	93	100	--	--
HF09	SAR McFaddin	43	57	65	75	81	86	91	99	99	100	--	--



Well pad site in Karnes County, Texas.



Drilling rig in Karnes County, Texas.

Sample Analyses

Surface-water samples were analyzed for concentrations of total dissolved solids (TDS) (app. 1), total suspended solids (TSS) (app. 1), inorganic constituents (app. 1), sulfides (app. 1), methylene blue active substances (MBAS) (app. 1), semivolatiles organic compounds (SVOCs) (app. 2), volatile organic compounds (VOCs) (app. 3), glycols (app. 4), and total organic carbon (TOC) (app. 5) by TestAmerica Laboratory (TAL) in Denver, Colorado. Streambed-sediment samples were analyzed for moisture content (app. 6) and concentrations of inorganic constituents (app. 6), *n*-alkanes (app. 7), and TOC (app. 8) by TAL. Streambed-sediment samples also were analyzed for concentrations of PAHs and alkylated PAHs (app. 9) by the USGS National Water Quality Laboratory (NWQL) in Denver. A complete list of the methods used by TAL and the NWQL to analyze the surface-water and streambed-sediment samples for chemical constituents is provided in table 4. The three streambed-sediment samples were submitted to the USGS Kentucky Water Science Center Sediment Laboratory in Louisville for particle-size analysis in accordance with methods described in Guy (1969).

For constituents analyzed by TAL in accordance with U.S. Environmental Protection Agency (EPA) methods (in which the method detection limit [MDL] is the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the concentration is greater than zero [U.S. Environmental Protection Agency, 1997]), reported values less than the MDL were considered to be nondetections as described by Glaser and others (1981). The MDL was calculated by using a minimum of seven replicate spike samples processed over a short time period (usually 2 days). TAL sets their reporting limits (RLs) as 2–10 times the MDL, depending on the constituent. Concentrations less than the MDL were considered to be nondetections and were reported as less than the MDL. Concentrations greater than the RL were reported as detections. Concentrations greater than the MDL but less than the RL were reported by TAL as estimated concentrations. Additionally, if there was a concentration of a constituent in a TAL lab blank and the concentration equated to less than 20 percent of the corresponding sample detection, the result was reported by the USGS as an estimated concentration.

For streambed-sediment samples analyzed for PAH and alkylated PAH concentrations by the NWQL, the method for censoring data was based on the long-term method detection limits (LT-MDL) and laboratory reporting limits (LRL). The LT-MDL was modified from the MDL analysis used by the EPA (Childress and others, 1999). Like the MDL, the LT-MDL also establishes the minimum concentration of a constituent that can be measured and reported with a

99-percent confidence level when the analyte concentration in the sample is greater than zero. The LT-MDL was designed to capture greater method variability than does the MDL because the LT-MDL requires a larger dataset collected over an extended period of time that incorporates more of the measurement variability that is typical for routine analyses in a laboratory, such as multiple instruments, operators, calibrations, and sample preparation events. The LT-MDL limits the risk of false positive values in a sample but does not address the possibility of false negatives in a sample when the constituent might be present in the sample but is not detected. The LRL is a laboratory quantification limit that generally is two times the LT-MDL and is designed to minimize the number of false negatives in a dataset. Because information-rich mass spectrometry methods were used to augment identification of selected PAHs and alkylated PAHs described in this report, estimated concentrations less than the LT-MDL were considered detections of the constituent. Detections were reported when the concentration of the constituent equaled or exceeded the LT-MDL, when qualified concentrations were less than the LT-MDL, and when the presence of the constituent was verified but not quantified. In this report, PAH and alkylated PAH concentrations were qualified as estimated values if the quantification of the analyte was considered by the NWQL to be highly variable; if the constituent concentration was extrapolated below the calibration curve; or if, at the discretion of the analyst, the constituent concentration was less than the LT-MDL (U.S. Geological Survey, 2010). Constituents that were verified but not quantified were qualified with an “M” remark code. Total saturated hydrocarbons (TSH) and total PAHs were calculated by summing the concentrations of individual *n*-alkanes and individual PAHs, respectively. For both TSH and total PAHs, values below the detection limit were not included in the calculation.

Quality Assurance

For quality-assurance purposes, quality-control samples were collected to qualify the precision and accuracy of the environmental samples collected. Field blank samples were collected to determine the extent of contamination that might have been introduced during sample collection, sample processing, and laboratory analysis. Split replicate samples were collected with environmental samples to determine the amount, or degree, of variability that might have resulted from the procedures used to collect, process, and analyze the samples. All quality-assurance samples were analyzed for the same analytical schedules that were used for analysis of the environmental samples.

Table 4. Analytical methods used in the chemical analyses of surface-water and streambed-sediment samples collected from selected streams in the San Antonio River Basin, Texas, 2011–13.

[W, water sample; TAL, Test America Laboratory; EPA, U.S. Environmental Protection Agency; °C, degrees Celsius; S, streambed-sediment sample; NWQL, U.S. Geological Survey National Water Quality Laboratory]

Constituents	Sample medium	Laboratory	Analysis method	Method description	Reference
Total dissolved solids	W	TAL	EPA 2540C	Dried at 180 °C	Clesceri and others (1998)
Total suspended solids	W	TAL	EPA 2540D	Dried at 103–105 °C	Clesceri and others (1998)
Methylene blue active substances	W	TAL	EPA 425.1	Color intensity	U.S. Environmental Protection Agency (1983)
Cations	W, S	TAL	EPA 6010B	Inductively coupled plasma-atomic emission spectrometry	U.S. Environmental Protection Agency (1996a)
Trace elements	W, S	TAL	EPA 6020A	Inductively coupled plasma-mass spectrometry	U.S. Environmental Protection Agency (2007)
Total organic carbon	W, S	TAL	EPA 9060	Carbonaceous analyzer	U.S. Environmental Protection Agency (1986)
Anions	W	TAL	EPA 300.0A	Ion chromatography	U.S. Environmental Protection Agency (1993)
Sulfide	W	TAL	EPA 9030B	Distillation	U.S. Environmental Protection Agency (1996b)
		TAL	EPA 9034	Distillation	U.S. Environmental Protection Agency (1996c)
Volatile organic compounds	W	TAL	EPA 8260B	Gas chromatography/mass spectrometry	U.S. Environmental Protection Agency (1996d)
Semivolatile organic compounds	W	TAL	EPA 8270C	Gas chromatography/mass spectrometry	U.S. Environmental Protection Agency (1996e)
Glycols	W	TAL	EPA 8015B	Gas chromatography/flame ionization detector	U.S. Environmental Protection Agency (1996f)
Percent moisture	S	TAL	D2216	Weighing the sample before and after drying	American Society for Testing and Materials (1992)
<i>n</i> -alkanes	S	TAL	EPA 8015C	Gas chromatography	U.S. Environmental Protection Agency (1996g)
Polycyclic aromatic hydrocarbons and alkylated polycyclic aromatic hydrocarbons	S	NWQL	Schedule 5507	Gas chromatography/mass spectrometry	Zaugg and others (2006)

Quality Assurance for Surface-Water Samples

To provide information on the bias and variability associated with constituents analyzed in surface-water samples, two field blanks were analyzed as quality-assurance samples. Field blank samples were collected and processed by using organic-free or inorganic-free deionized water obtained from the NWQL and certified to contain no detectable concentrations of the constituents that were analyzed. Field blank samples were collected on November 3, 2011, at the SAR Elmendorf site and on September 30, 2012, at the SAR 72 site (apps. 10–14). TDS concentrations were less than the MDL in both field blank samples; however, an estimated TSS concentration of 1.2 milligrams per liter (mg/L) was reported in the field blank sample collected at the SAR 72 site (app. 10). Multiple inorganic constituents were detected in both field blanks at relatively small concentrations compared to those measured in surface-water samples (app. 10). Sulfide, MBAS, and SVOCs were not detected in either field blank sample (apps. 10–11). No VOCs were detected in the field blank sample collected on November 3, 2013, but there were two detections of VOCs in the field blank sample collected on September 30, 2012, including acetone (estimated value of 2.1 micrograms per liter [$\mu\text{g/L}$]) and trichloromethane (estimated value of 0.17 $\mu\text{g/L}$) (app. 12). No glycols were detected in either field blank sample (app. 13). A relatively small concentration of TOC (estimated value of 0.22 mg/L) in comparison to environmental samples was measured in both blank samples (app. 14).

For those constituents with concentrations greater than or equal to the MDL in the field blank samples, the data were evaluated to determine if concentrations of those constituents should be rejected from the environmental-sample dataset. If the detected concentration in the field blank sample was greater than 20 percent of the detected concentration in the environmental sample, the detection in the environmental sample was rejected and not included in the calculations of summary statistics. If the detection in the blank sample was less than or equal to 20 percent of the detection in the environmental sample, the detection in the environmental sample was retained. The same criteria were applied to laboratory blank samples that TAL analyzed with the environmental samples. For those cases in which a constituent was detected in a field blank sample but was not rejected, the reported concentrations in environmental samples should be considered potentially biased high because the sampling equipment may have introduced small amounts of the given constituent to the environmental samples.

For quality assurance of surface-water samples, two split replicate samples were collected along with paired environmental samples from the SAR Elmendorf site on November 3, 2011, and from the SAR 72 site on September 30, 2012. The split replicate sample results were compared to the environmental sample results by calculating the relative percent difference (RPD) for each detected concentration pair by using the following equation:

$$\text{RPD} = |C1 - C2| / ((C1 + C2) / 2) \times 100, \quad (1)$$

where

- C1 is the detected concentration in the environmental sample, and
- C2 is the detected concentration in the split replicate sample.

RPDs were calculated for only those constituent pairs with detectable concentrations greater than or equal to the RL or LRL in both the environmental and the split replicate samples. RPDs were not computed for constituent pair concentrations that had one or more nondetected values. RPDs of less than or equal to 15 percent were considered to indicate similar environmental and split replicate sample results when concentrations were sufficiently greater than the RL or LRL. The RPDs calculated for inorganic constituents ranged from 0.0 percent for multiple constituents to 33 percent for cadmium, with a median of 1.7 percent (app. 10). RPDs for SVOCs could not be calculated because these constituents were not detected in the quality-control samples (app. 11). RPDs calculated for three paired VOC concentrations from the sample collected at the SAR Elmendorf site on November 3, 2011, ranged from 9.5 percent to 12 percent (app. 12). RPDs for glycols could not be calculated because these constituents were not detected in the split replicate samples (app. 13). RPDs calculated for TOC concentrations were 6.8 percent for the sample collected at the SAR Elmendorf site on November 3, 2011, and 2.5 percent for the sample collected at the SAR 72 site on September 30, 2012 (app. 14).

Quality Assurance for Streambed-Sediment Samples

For quality assurance of streambed-sediment samples, one split replicate sample was collected at the SAR Elmendorf site on November 3, 2013. The split replicate sample results were compared to the environmental sample results by calculating the RPD for each detected constituent pair by using equation 1. RPDs were calculated for all inorganic constituents except antimony because the antimony concentration in the environmental sample was less than the RL and the antimony concentration in the replicate sample was verified but not quantified (app. 15). RPDs among the remaining inorganic constituents ranged from 0.0 percent for multiple constituents to 39 percent for silver, with a median RPD of 12 percent (app. 15). RPDs for *n*-alkanes ranged from 0.0 percent for multiple constituents to 120 percent for hentriacontane, with a median of 52 percent (app. 16). A median of 52 percent indicates a relatively high degree of methodological variability for *n*-alkanes. The RPD for TOC was 46 percent (app. 17); however, one value was estimated and could not be reanalyzed for verification. RPDs for PAHs could not be calculated because there were no detections in either the environmental or replicate samples used for quality assurance of the streambed-sediment samples (app. 18).

Concentrations of Selected Constituents

For this report, the three-county area consisting of Wilson, Karnes, and DeWitt Counties is considered the area of active oil and natural-gas production in the study area. The SAR Elmendorf and Cibolo St. Hedwig sites were upstream from most active oil and natural-gas production. The SAR Falls City, Cibolo Falls City, Ecletto 1, Ecletto 2, and SAR 72 sites were in the area of active oil and natural-gas production. The SAR Goliad, SAR McFaddin, and GR Tivoli sites were downstream from the area of active oil and natural-gas production.

Constituents in Surface-Water Samples

Surface-water samples were analyzed for concentrations of inorganic and organic constituents in this study because of the potential usefulness of those constituents as indicators of the presence of hydraulic fracturing fluids or produced waters. Sulfide was selected because of its common occurrence in produced waters (Tibbetts and others, 1992). All sulfide concentrations were less than the MDL of 0.79 mg/L (app. 1) provided by the TestAmerica analytical laboratory. Glycols are commonly used in hydraulic fracturing fluids as scale inhibitors (FracFocus Chemical Disclosure Registry, 2013). Four glycols—diethylene glycol, ethylene glycol, propylene glycol, and triethylene glycol—were analyzed for in surface-water samples collected for this study, and none were detected at MDLs of 7.73 mg/L, 8.63 mg/L, 18.7 mg/L, and 8.45 mg/L, respectively (app. 4). The MDL for glycols for the storm-runoff sample collected at the SAR Falls City site was less than the MDLs of the other samples because it was analyzed later in the study, but there were no detections of glycols in that sample even at the lower MDLs.

Concentrations of SVOCs and VOCs also were analyzed for in this study because of their common occurrence as hydrocarbons in produced waters (Tibbetts and others, 1992). Of the 91 SVOCs analyzed for this study (app. 2), there were six detections, all but one of which were in storm-runoff samples (table 5). The base-flow sample collected at the SAR Goliad site contained bis(2-ethylhexyl) phthalate, a plasticizer in polyvinyl chloride and a constituent in hydraulic fracturing fluids (New York State Department of Environmental Conservation, 2013). The storm-runoff samples collected at the SAR Elmendorf and Ecletto 2 sites also contained bis(2-ethylhexyl) phthalate. The storm-runoff sample collected at the SAR Elmendorf site contained the plasticizer diethyl phthalate. Both storm-runoff samples collected at the Ecletto 1 and Ecletto 2 sites contained benzyl alcohol, a solvent commonly used in paints (U.S. National Library of Medicine,

2001). Of the 67 VOCs analyzed in this study, there were a total of six detections, all of which were in base-flow samples. The surface-water sample collected at the SAR Elmendorf site contained bromodichloromethane, dibromochloromethane, and trichloromethane, all of which are disinfection byproducts associated with the chlorination of municipal water supplies and of treated municipal wastewater (Munson and others, 1982; U.S. Environmental Protection Agency, 2013b; Larson and Weber, 1994). The sample collected at the Cibolo St. Hedwig site contained toluene, a fuel additive, solvent, and industrial feedstock used to produce benzene (U.S. Environmental Protection Agency, 2012b) and a constituent associated with produced waters (Tibbetts and others, 1992). The Cibolo St. Hedwig site is upstream from current (2014) oil and natural-gas production areas (fig. 1). Dichloromethane was detected in surface-water samples at both the SAR 72 and SAR Goliad sites. Dichloromethane is an industrial solvent with multiple uses (U.S. Environmental Protection Agency, 2013c).

Concentrations of selected anions (the negatively charged ions bromide, chloride, sulfate, and fluoride) were measured in surface-water samples collected at all sites during base flow and storm runoff (fig. 4). Bromide concentrations ranged from <0.11 mg/L at the SAR 72 site during storm runoff to 0.66 mg/L at the Ecletto 1 site during storm runoff. Chloride concentrations ranged from 16 mg/L at the SAR Elmendorf site during storm runoff to 200 mg/L at the Ecletto 1 site during storm runoff. Sulfate concentrations ranged from 19 mg/L at the SAR Elmendorf site during storm runoff to 160 mg/L at the SAR Falls City site during storm runoff and the Cibolo Falls City site during base flow. Fluoride concentrations ranged from an estimated 0.13 mg/L at the SAR Elmendorf site during storm runoff to 0.64 mg/L at the SAR Elmendorf site during base flow. Greater anion concentrations were measured in samples collected during base flow than in samples collected during storm runoff at most of the sites.

Concentrations of selected cations (the positively charged ions calcium, magnesium, potassium, and sodium) in surface-water samples varied substantially among sampling sites and streamflow conditions (fig. 5). Calcium concentrations ranged from 63 mg/L at the Cibolo St. Hedwig site during storm runoff to 230 mg/L at the SAR Elmendorf site during storm runoff. Magnesium concentrations ranged from 9.5 mg/L at the Ecletto 2 site during storm runoff to 20 mg/L at multiple sites during base flow. Potassium concentrations ranged from 6.7 mg/L at the GR Tivoli site during storm runoff to 15 mg/L at the SAR Falls City site during storm runoff. Concentrations of sodium were greater than potassium concentrations and ranged from 12 mg/L at the SAR Elmendorf site during storm runoff to 150 mg/L at the Ecletto 1 site during storm runoff. All major cations usually occurred at greater concentrations during base flow than during storm runoff.

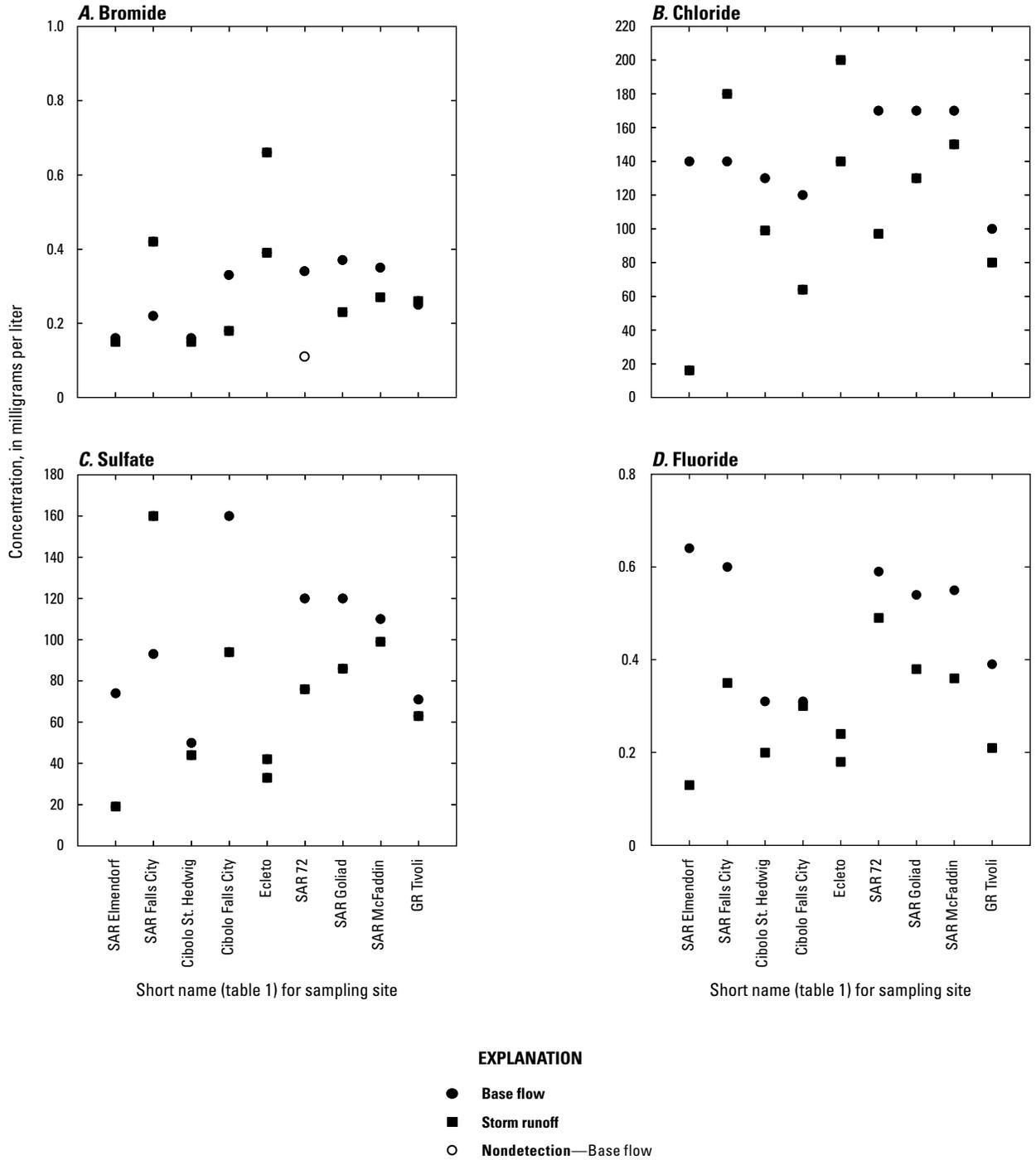


Figure 4. Concentrations of selected anions in unfiltered surface-water samples collected from the San Antonio River Basin, Texas, 2011–13. *A*, Bromide. *B*, Chloride. *C*, Sulfate. *D*, Fluoride.

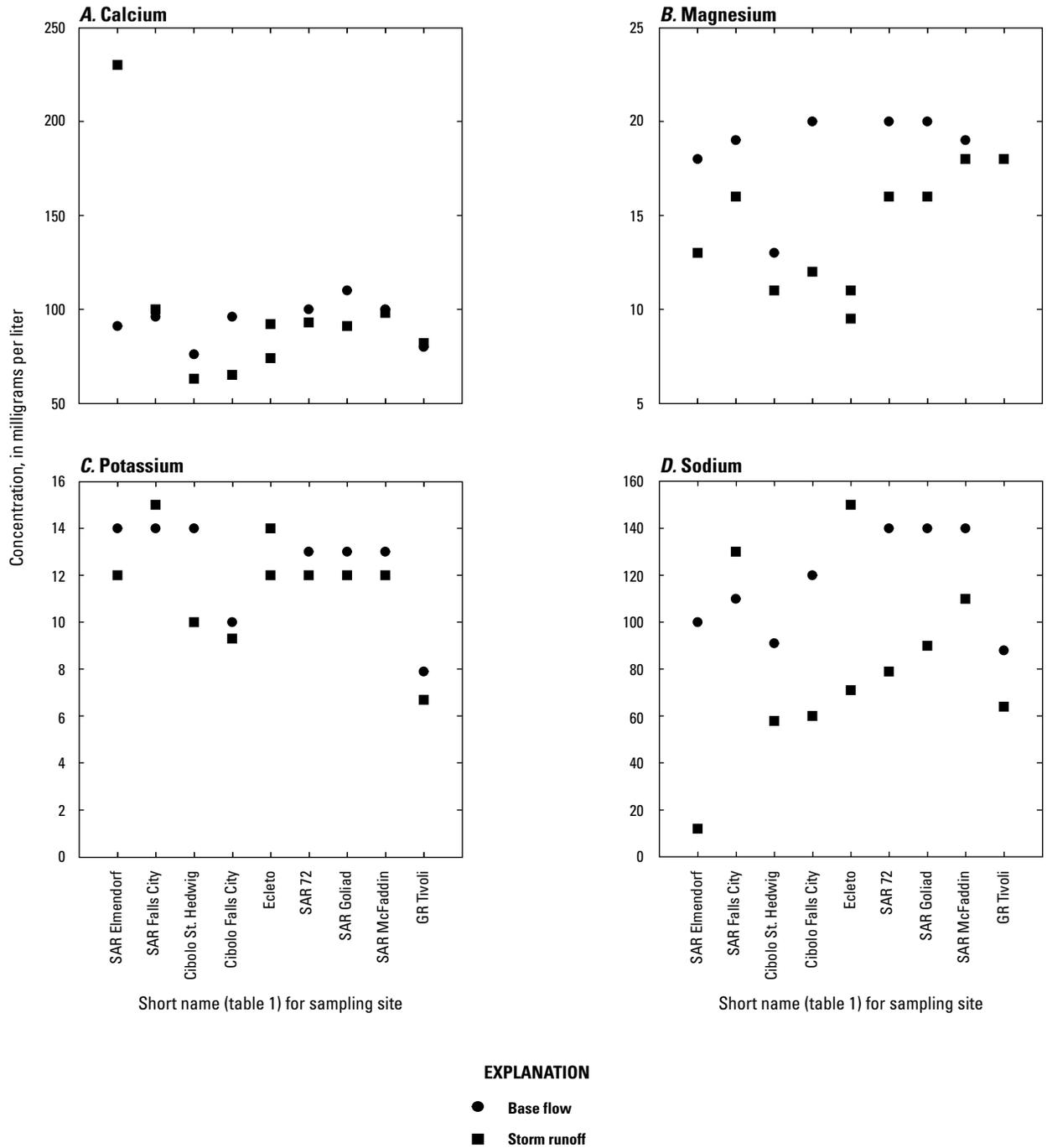


Figure 5. Concentrations of selected cations in unfiltered surface-water samples collected from the San Antonio River Basin, Texas, 2011–13. *A.* Calcium. *B.* Magnesium. *C.* Potassium. *D.* Sodium.

Concentrations of selected inorganic constituents varied widely among sampling sites and streamflow conditions (fig. 6A–L). Aluminum concentrations ranged from 110 $\mu\text{g/L}$ at the Cibolo Falls City site during base flow to 39,000 $\mu\text{g/L}$ at the SAR Elmendorf site during storm runoff. Barium concentrations ranged from 29 $\mu\text{g/L}$ during base flow at the SAR Elmendorf site to 280 $\mu\text{g/L}$ during storm runoff at the Ecletto 2 site. Chromium concentrations ranged from <0.50 $\mu\text{g/L}$ at multiple sites to 47 $\mu\text{g/L}$ during storm runoff at the SAR Elmendorf site. Copper concentrations ranged from <0.56 $\mu\text{g/L}$ at the Cibolo Falls City site during base flow to 25.0 $\mu\text{g/L}$ at the SAR Elmendorf site during storm runoff. Iron concentrations varied widely among sites ranging from 110 $\mu\text{g/L}$ at the Cibolo Falls City site during base flow to 38,000 $\mu\text{g/L}$ at the SAR Elmendorf site during storm runoff. Lead concentrations ranged from <0.18 $\mu\text{g/L}$ at the Cibolo Falls City site during base flow to 42 $\mu\text{g/L}$ at the SAR Elmendorf site during storm runoff. Lithium concentrations ranged from 13 $\mu\text{g/L}$ at the Cibolo St. Hedwig site during storm runoff to 54 $\mu\text{g/L}$ at the Cibolo Falls City site during base flow. Manganese concentrations ranged from 8.7 $\mu\text{g/L}$ at the Cibolo St. Hedwig site during base flow to 690 $\mu\text{g/L}$ at the SAR Elmendorf site during storm runoff. Strontium concentrations ranged from 400 $\mu\text{g/L}$ at the Ecletto 2 site during storm runoff to 900 $\mu\text{g/L}$ at the SAR Goliad site during base flow. Zinc concentrations ranged from an estimated 2.3 $\mu\text{g/L}$ at the Cibolo Falls City site during base flow to 130 $\mu\text{g/L}$ at the SAR Elmendorf site during storm runoff. Both

the smallest and greatest arsenic concentrations were measured at the SAR Elmendorf site, and they ranged from an estimated 0.96 $\mu\text{g/L}$ during base flow to 9.5 $\mu\text{g/L}$ during storm runoff. Boron concentrations ranged from 190 $\mu\text{g/L}$ at the Cibolo St. Hedwig and GR Tivoli sites during storm runoff to 390 $\mu\text{g/L}$ at the Ecletto 1 site during storm runoff. Inorganic constituents for which a majority of the concentrations were greater during storm runoff included aluminum, barium, chromium, copper, iron, lead, manganese, zinc, and arsenic. Inorganic constituents for which a majority of the concentrations were greater during base flow included strontium and boron. Lithium showed an equal number of concentrations that were greater during storm runoff and greater during base flow.

MBAS is a measurement of surfactants, organic substances that are used as wastewater indicators (Thomas and others, 1999) and as flowback additives during hydraulic fracturing (FracFocus Chemical Disclosure Registry, 2013). Eight of the samples analyzed for MBAS were analyzed after the recommended holding time of 48 hours had been exceeded. Analyzing samples after holding times have been exceeded could affect measured concentration. The data for these samples were included in the report for completeness. A total of five detections of MBAS were measured at the Cibolo St. Hedwig, Ecletto 1, SAR Goliad, SAR McFaddin, and GR Tivoli sites during storm runoff (fig. 7). Overall, MBAS concentrations ranged from <0.12 mg/L at multiple sites to an estimated 0.14 mg/L at the Ecletto 1 and SAR Goliad sites.



Central gathering facility in DeWitt County, Texas.

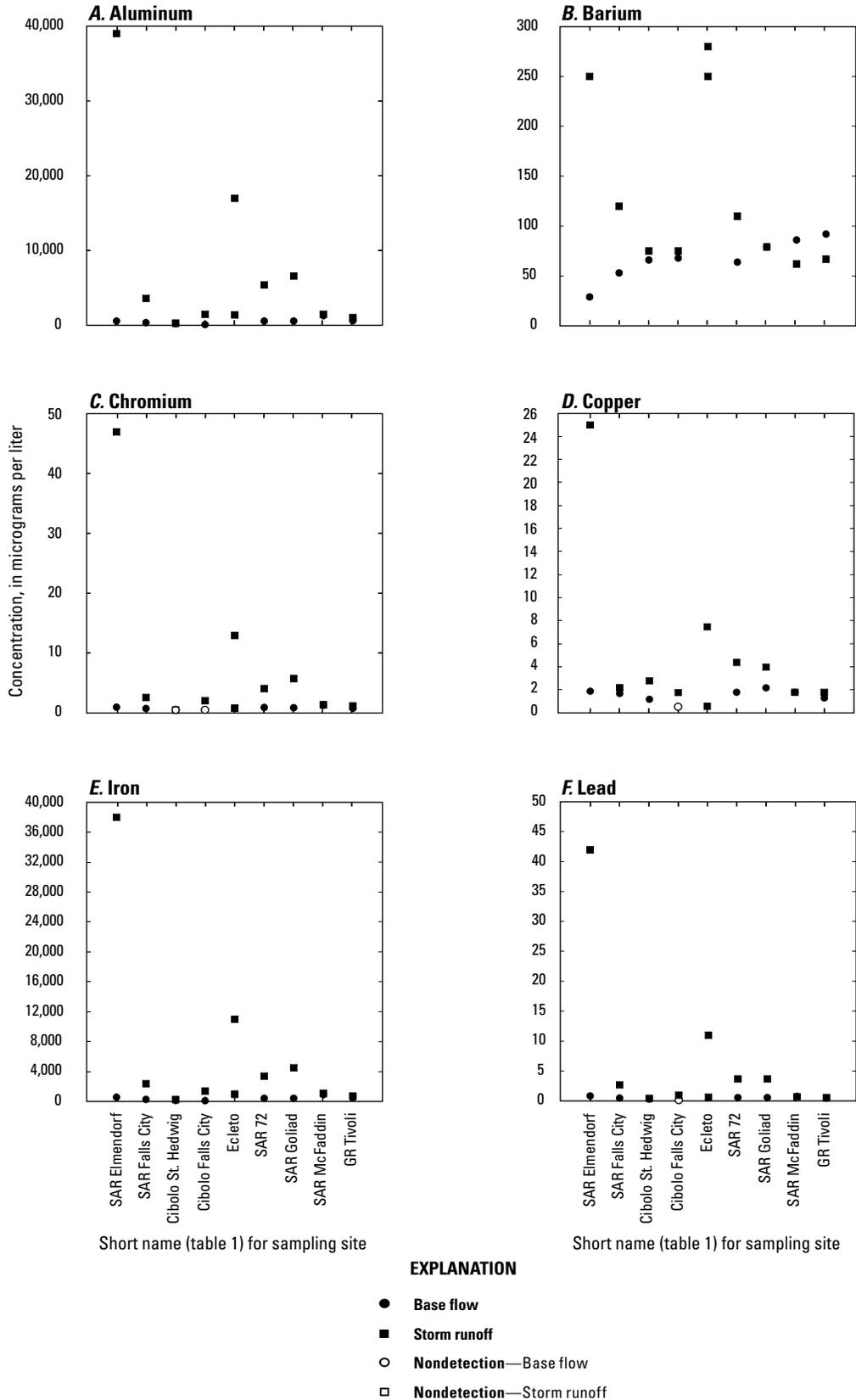


Figure 6. Concentrations of selected inorganic constituents in unfiltered surface-water samples collected from the San Antonio River Basin, Texas, 2011–13. *A*, Aluminum. *B*, Barium. *C*, Chromium. *D*, Copper. *E*, Iron. *F*, Lead. *G*, Lithium. *H*, Manganese. *I*, Strontium. *J*, Zinc. *K*, Arsenic. *L*, Boron.

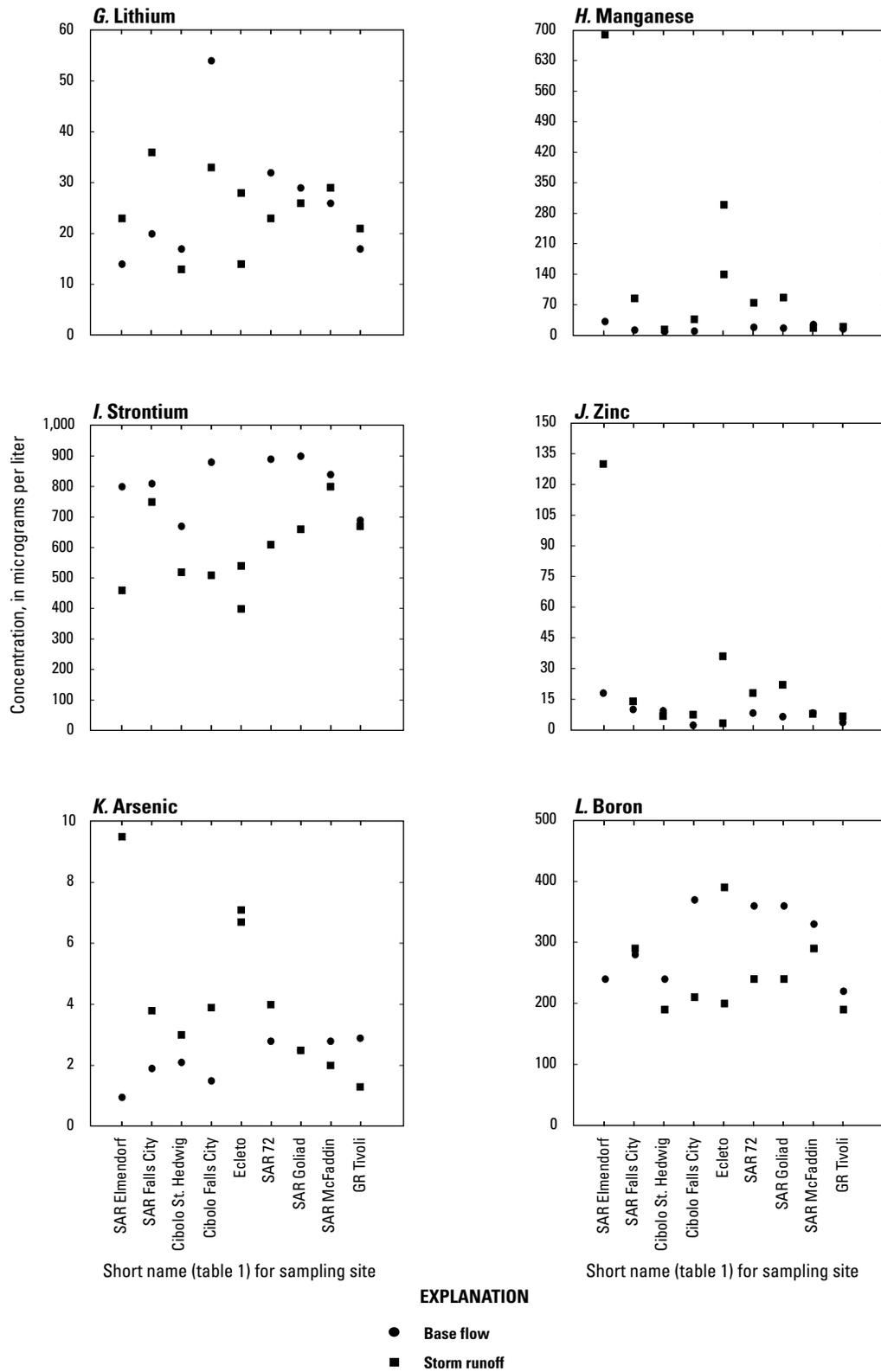


Figure 6. Concentrations of selected inorganic constituents in unfiltered surface-water samples collected from the San Antonio River Basin, Texas, 2011–13. *A*, Aluminum. *B*, Barium. *C*, Chromium. *D*, Copper. *E*, Iron. *F*, Lead. *G*, Lithium. *H*, Manganese. *I*, Strontium. *J*, Zinc. *K*, Arsenic. *L*, Boron.—Continued

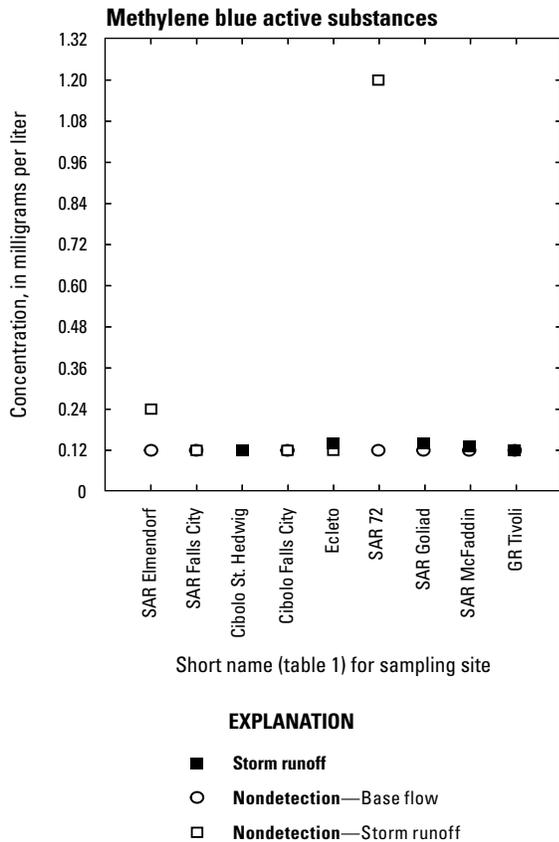


Figure 7. Concentrations of methylene blue active substances (MBAS) in unfiltered surface-water samples collected from the San Antonio River Basin, Texas, 2011–13.

Constituents in Streambed-Sediment Samples

Scant historical data are available describing inorganic constituent concentrations in streambed-sediment samples collected from the San Antonio River Basin. Inorganic constituents were measured in streambed-sediment samples to provide baseline information about the occurrence of these constituents (app. 6). Of the 28 inorganic constituents analyzed in streambed-sediment samples, all were measured in at least one sample except antimony. Antimony was not detected in any samples at MDLs that ranged from 0.01 milligrams per kilogram (mg/kg) to 0.05 mg/kg. Concentrations of the remaining inorganic constituents varied substantially. Attempting to differentiate between natural concentrations of inorganic constituents and elevated concentrations from introduced sources is not possible with such few data; however, these data provide some preliminary information about the constituents in streambed-sediment samples collected from sites upstream from, in, and downstream from the active oil and natural-gas production areas in the basin.

Selected organic constituents including *n*-alkanes and PAHs were analyzed for in streambed-sediment samples for this study because of their potential usefulness as indicators

of hydrocarbons associated with produced waters (Hostettler and others, 2013). Concentrations of individual *n*-alkanes are provided in appendix 7. Of the 38 *n*-alkanes analyzed for this study, only undecane was not detected in any of the samples (app. 7). Concentrations of TSH, which are calculated as the sum of the individual *n*-alkanes, are shown in figure 8. The <2-mm size-fraction samples include larger sand-sized particles, whereas the <63- μ m size-fraction samples exclude larger sand-sized particles. Concentrations of TSHs ranged from an estimated 260 micrograms per kilogram (μ g/kg) in the <2-mm size-fraction sample collected at the SAR Goliad site to 11,000 μ g/kg in the <2-mm size-fraction sample collected at the Ecleto 1 site (fig. 8). TSH concentrations were greater in the <63- μ m size-fraction sample than in the <2-mm size-fraction sample in streambed-sediment samples collected from 5 of the 9 sites. Concentrations of total PAHs, calculated as the sum of the individual PAHs and alkylated PAHs, are shown in figure 9. Total PAH concentrations ranged from less than the MDL in the <2-mm size-fraction samples collected from multiple sites to 1,600 μ g/kg in the <2-mm size-fraction sample collected from the SAR McFaddin site. Total PAH concentrations were greater in the <63- μ m size-fraction samples than in the <2-mm size-fraction samples at 7 of the 9 sites.

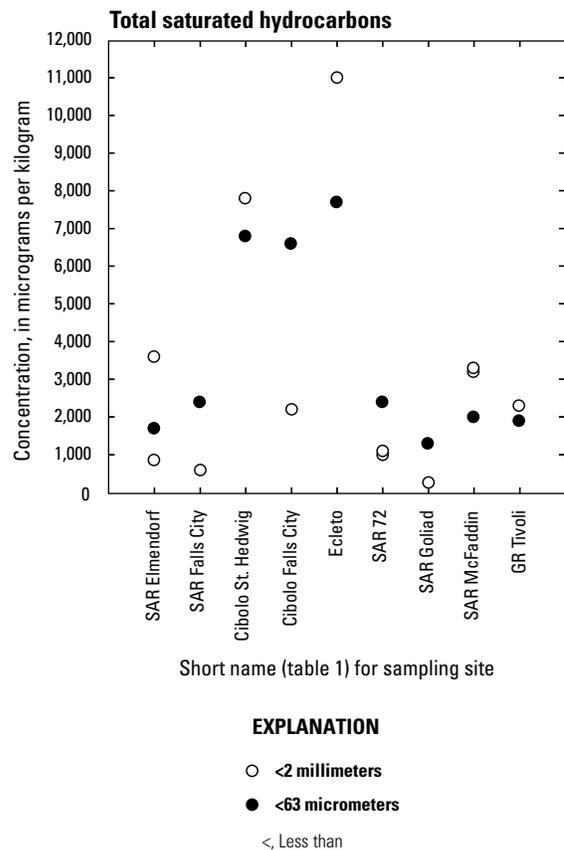


Figure 8. Concentrations of total saturated hydrocarbons in streambed-sediment samples collected from the San Antonio River Basin, Texas, 2011–13.

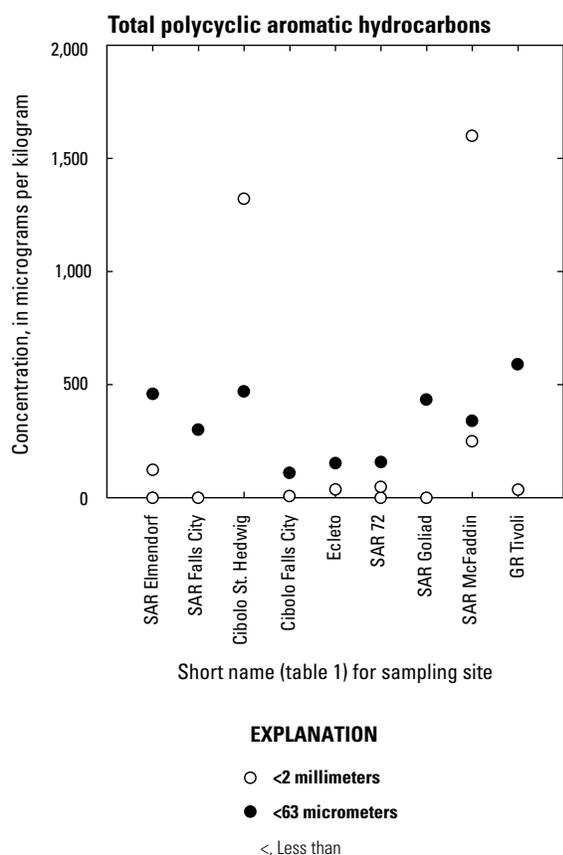


Figure 9. Concentrations of total polycyclic aromatic hydrocarbons in streambed-sediment samples collected from the San Antonio River Basin, Texas, 2011–12.

A subset of three streambed-sediment samples was analyzed for *n*-alkanes and PAHs by using both <63- μm and <2-mm size fractions from the same sample to determine whether or not there were greater concentrations of organic constituents in the <63- μm size fraction in comparison to the <2-mm size fraction (table 3). At all three sites, total PAH concentrations were greater in the <63- μm size-fraction samples than in the <2-mm size-fraction samples. In contrast, TSH concentrations were greater in the <63- μm size-fraction samples than in the <2-mm size-fraction samples at 1 of 3 sites. Particle-size analysis shows a progressively greater percentage of fine-grained sediment in the downstream direction in the San Antonio River Basin. The sample collected at the SAR Elmendorf site, the farthest upstream sampling site on the San Antonio River, contained only 16 percent of the particles smaller than the sand/fine break (0.063 mm). The sample collected at the SAR 72 site contained 23 percent of the particles smaller than the sand/fine break, and the sample collected at the SAR McFaddin site, the farthest downstream sampling site on the San Antonio River, contained 86 percent of the particles smaller than the sand/fine break. The greater concentrations of PAHs in the <63- μm size-fraction samples at

all three of these sites are consistent with a greater percentage of binding sites associated with fine-grained (<63 μm) sediment versus coarse-grained (<2 mm) sediment (Horowitz, 1991). The larger difference in total PAHs between the <2-mm and <63- μm size-fraction samples at the SAR Elmendorf site might be related to the large percentage of sand in the <2-mm size-fraction sample which is absent in the <63- μm size-fraction sample. In contrast, the <2-mm size-fraction sample collected from the SAR McFaddin site contained very little sand and was similar in particle-size composition to the <63- μm size-fraction sample.

Summary

Concerns about possible environmental effects associated with the use of hydraulic fracturing processes for extracting oil and natural gas have been growing as these processes have increasingly been implemented throughout the United States in the past 10 years. Some of the concerns expressed by the public, staff members of State and local water resource agencies, and State and Federal regulatory agencies include the possible release of organic and inorganic constituents found in hydraulic fracturing fluids and produced waters. Constituents of concern include those frequently used in hydraulic fracturing fluids such as glycols and surfactants and those found in produced waters such as *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs). Therefore, there is a need to analyze different types of constituents in both water and streambed-sediment samples to effectively identify constituents that might be associated with oil and natural-gas production in Texas. The U.S. Geological Survey, in cooperation with the San Antonio River Authority and the Guadalupe-Blanco River Authority, analyzed surface-water and streambed-sediment samples collected from 10 sites in the San Antonio River Basin to provide data for a broad range of constituents that might be associated with hydraulic fracturing and the produced waters that are a consequence of hydraulic fracturing.

During 2011–13, 18 surface-water and 22 streambed-sediment samples were collected at 10 sites including the San Antonio River near Elmendorf, Tex. (SAR Elmendorf); San Antonio River at Highway 181 at Falls City, Tex.; Cibolo Creek near St. Hedwig, Tex. (Cibolo St. Hedwig); Cibolo Creek near Falls City, Tex.; Ecleto Creek near Runge, Tex. (Ecleto 1); Ecleto Creek at County Road 326 near Runge, Tex. (Ecleto 2); San Antonio River at State Highway 72 near Runge, Tex. (SAR 72); San Antonio River at Goliad, Tex. (SAR Goliad); San Antonio River near McFaddin, Tex. (SAR McFaddin); and Guadalupe River near Tivoli, Tex. (GR Tivoli) sites for analysis of concentrations of selected inorganic and organic constituents. Surface-water samples were analyzed for concentrations of total dissolved solids, total suspended solids, inorganic constituents, sulfides, methylene blue active substances (MBAS), semivolatle organic compounds

(SVOCs), volatile organic compounds (VOCs), glycols, and total organic carbon (TOC). Streambed-sediment samples were analyzed for moisture content, inorganic constituents, *n*-alkanes, TOC, PAHs, and alkylated PAHs.

Surface-water samples were analyzed for concentrations of inorganic and organic constituents in this study because of the potential usefulness of those constituents as indicators of the presence of hydraulic fracturing fluids or produced waters. All sulfide concentrations were less than the method detection limit (MDL) of 0.79 milligrams per liter (mg/L). Four glycols—diethylene glycol, ethylene glycol, propylene glycol, and triethylene glycol—were analyzed for in surface-water samples collected for this study, and none were detected at MDLs of 7.73 mg/L, 8.63 mg/L, 18.7 mg/L, and 8.45 mg/L, respectively. Concentrations of SVOCs and VOCs also were analyzed for in this study because of their common occurrence as hydrocarbons in produced waters. Of the 91 SVOCs analyzed for this study, there were six detections, all but one of which were in storm-runoff samples. The base-flow sample collected at the SAR Goliad site contained bis(2-ethylhexyl) phthalate, a plasticizer in polyvinyl chloride and a constituent in hydraulic fracturing fluids. The storm-runoff samples collected at the SAR Elmendorf and Ecletto 2 sites also contained bis(2-ethylhexyl) phthalate. The storm-runoff sample collected at the SAR Elmendorf site contained the plasticizer diethyl phthalate. Both storm-runoff samples collected at the Ecletto 1 and Ecletto 2 sites contained benzyl alcohol, a solvent commonly used in paints. Of the 67 VOCs analyzed in this study, there were a total of six detections, all of which were in base-flow samples. The surface-water sample collected at the SAR Elmendorf site contained bromodichloromethane, dibromochloromethane, and trichloromethane, all of which are disinfection byproducts most commonly associated with the chlorination of surface waters to produce finished municipal water supplies. The sample collected at the Cibolo St. Hedwig site contained toluene, a fuel additive, solvent, and industrial feedstock used to produce benzene. The Cibolo St. Hedwig site is upstream from current (2014) oil and natural-gas production areas. Dichloromethane, an industrial solvent with multiple uses, was detected in surface-water samples at both the SAR 72 and SAR Goliad sites.

Concentrations of selected anions (the negatively charged ions bromide, chloride, sulfate, and fluoride) were measured in surface-water samples collected at all sites during base flow and storm runoff. Greater anion concentrations were measured in samples collected during base flow than in samples collected during storm runoff at most of the sites. Concentrations of selected cations (the positively charged ions calcium, magnesium, potassium, and sodium) in surface-water samples varied substantially among sampling sites and streamflow conditions. All major cations usually occurred at greater concentrations during base flow than during storm runoff. Concentrations of selected inorganic constituents varied widely among sampling sites and streamflow conditions. Inorganic constituents for which

a majority of the concentrations were greater during storm runoff included aluminum, barium, chromium, copper, iron, lead, manganese, zinc, and arsenic. Inorganic constituents for which a majority of the concentrations were greater during base flow included strontium and boron. Lithium showed an equal number of concentrations that were greater during storm runoff and greater during base flow. MBAS is a measurement of surfactants, organic substances that are used as wastewater indicators and as flowback additives during hydraulic fracturing. A total of five detections of MBAS were measured at the Cibolo St. Hedwig, Ecletto 1, SAR Goliad, SAR McFaddin, and GR Tivoli sites during storm runoff. Overall, MBAS concentrations ranged from less than (<) 0.12 mg/L at multiple sites to an estimated 0.14 mg/L at the Ecletto 1 and SAR Goliad sites.

Inorganic constituents were measured in streambed-sediment samples to provide baseline information about the occurrence of these constituents. Attempting to differentiate between natural concentrations of inorganic constituents and elevated concentrations from introduced sources is not possible with such few data. Selected organic constituents including *n*-alkanes and PAHs were analyzed for in streambed-sediment samples for this study because of their potential usefulness as indicators of hydrocarbons associated with produced waters. In streambed-sediment samples, concentrations of total saturated hydrocarbons (TSH) ranged from an estimated 260 micrograms per kilogram ($\mu\text{g}/\text{kg}$) in the <2-millimeter (mm) size-fraction sample collected at the SAR Goliad site to 11,000 $\mu\text{g}/\text{kg}$ in the <2-mm size-fraction sample collected at the Ecletto 1 site. TSH concentrations were greater in the <63-micrometer (μm) size-fraction sample than in the <2-mm size-fraction sample in streambed-sediment samples collected from 5 of the 9 sites. Concentrations of total PAHs, calculated as the sum of the individual PAHs and alkylated PAHs, ranged from less than the MDL in the <2-mm size-fraction samples collected from multiple sites to 1,600 $\mu\text{g}/\text{kg}$ in the <2-mm size-fraction sample collected from the SAR McFaddin site. Total PAH concentrations were greater in the <63- μm size-fraction samples than in the <2-mm size-fraction samples at 7 of the 9 sites.

During collection of the second sample set, additional samples from a subset of three sites (the SAR Elmendorf, SAR 72, and SAR McFaddin sites) were processed by using a 63- μm sieve on one aliquot and a 2-mm sieve on a second aliquot for PAH and *n*-alkane analyses. The purpose of analyzing PAHs and *n*-alkanes on a sample containing sand, silt, and clay versus a sample containing only silt and clay was to provide data that could be used determine if these organic constituents had a greater affinity for silt- and clay-sized particles relative to sand-sized particles. The greater concentrations of PAHs in the <63- μm size-fraction samples at all three of these sites are consistent with a greater percentage of binding sites associated with fine-grained (<63 μm) sediment versus coarse-grained (<2 mm) sediment. The larger difference in total PAHs between the <2-mm and <63- μm size-fraction samples at the SAR Elmendorf site might be related

to the large percentage of sand in the <2-mm size-fraction sample which is absent in the <63- μ m size-fraction sample. In contrast, the <2-mm size-fraction sample collected from the SAR McFaddin site contained very little sand and was similar in particle-size composition to the <63- μ m size-fraction sample.

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