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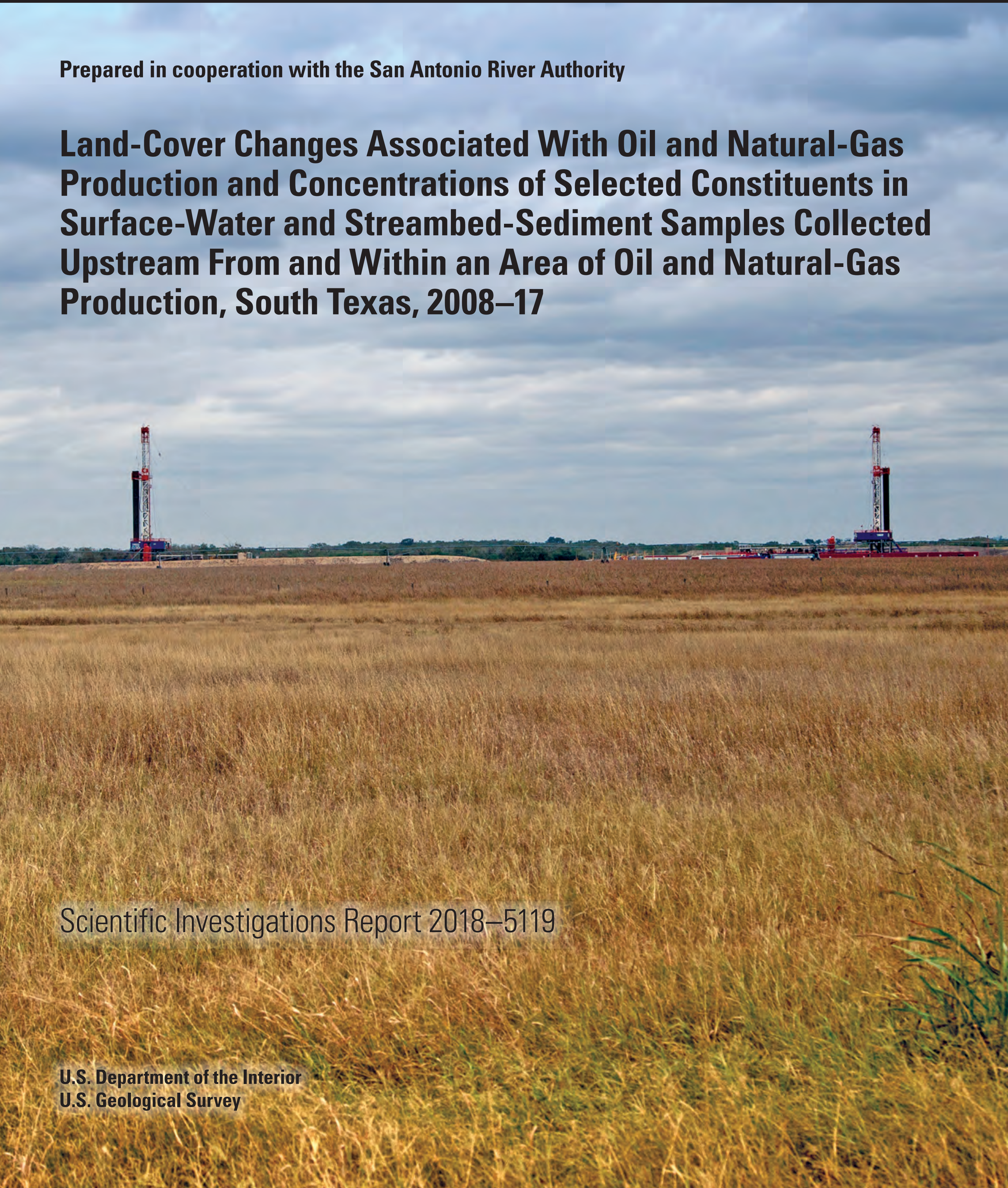
Land-Cover Changes Associated With Oil and Natural-Gas Production and Concentrations of Selected Constituents in Surface-Water and Streambed-Sediment Samples Collected Upstream From and Within an Area of Oil and Natural-Gas Production, South Texas, 2008–17



Scientific Investigations Report 2018–5119

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

Front cover, Oil and natural-gas drilling rigs near U.S. Geological Survey sampling site 08186550 Ecleto Creek at County Road 326 near Runge, Texas. Photograph by Cassi L. Crow, U.S. Geological Survey.

Back cover:

Top left, Kayak containing streambed-sediment sampling equipment and samples. Photograph by Michael L. Willis, U.S. Geological Survey.

Top right, U.S. Geological Survey personnel kayaking to collect streambed-sediment samples. Photograph by Michael L. Willis, U.S. Geological Survey.

Middle left, U.S. Geological Survey personnel processing streambed-sediment sample through 63-micrometer plastic sieve fabric. Photograph by Cassi L. Crow, U.S. Geological Survey.

Middle right, U.S. Geological Survey personnel processing streambed-sediment sample through 2-millimeter sieve. Photograph by Cassi L. Crow, U.S. Geological Survey.

Bottom, Equipment and various stages of streambed-sediment sample processing. Photograph by Cassi L. Crow, U.S. Geological Survey.

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U.S. Department of the Interior
RYAN K. ZINKE, Secretary

U.S. Geological Survey
James F. Reilly II, Director

U.S. Geological Survey, Reston, Virginia: 2018

Suggested citation:
Crow, C.L., Opsahl, S.P., Pedraza, D.E., Pease, E.C., and Kushnereit, R.K., 2018, Land-cover changes associated with oil and natural-gas production and concentrations of selected constituents in surface-water and streambed-sediment samples collected upstream from and within an area of oil and natural-gas production, south Texas, 2008–17: U.S. Geological Survey Scientific Investigations Report 2018–5119, 52 p., https://doi.org/10.3133/sir20185119.

ISSN 2328-031X (print)
ISSN 2328-0328 (online)

ISBN 978-1-4113-4261-3

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Conversion Factors

U.S. customary units to International System of Units

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	
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm^2)
acre	0.004047	square kilometer (km^2)
square mile (mi^2)	2.590	square kilometer (km^2)
	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)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
micrometer (µm)	0.00003937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
meter (m)	1.094	yard (yd)
	Volume	
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in^3)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)

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

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

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). Concentrations of chemical constituents in streambed sediment are given in either milligrams per kilogram (mg/kg) or micrograms per kilogram (µg/kg).

Abbreviations

<	less than
BTEX	benzene, toluene, ethylbenzene, and all isomers of xylene
CFR	Code of Federal Regulations
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
GIS	geographic information system
LRL	laboratory reporting limit
LT-MDL	long-term method detection level
MBAS	methylene blue active substances
MCL	maximum contaminant level
MDL	method detection limit
NAIP	National Agricultural Imagery Program
NWQL	National Water Quality Laboratory (USGS)
PAHs	polycyclic aromatic hydrocarbons
PEC	probable effect concentration
QC	quality control
RPD	relative percent difference
RTI	RTI Laboratories, Inc.
SQG	sediment quality guideline
SVOC	semivolatile organic compound
TEC	threshold effect concentration
TNRIS	Texas Natural Resources Information System
TOC	total organic carbon
TSS	total suspended solids
USGS	U.S. Geological Survey
VOC	volatile organic compound

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By Cassi L. Crow, Stephen P. Opsahl, Diana E. Pedraza, Emily C. Pease, and Ross K. Kushnereit

Abstract

The extensive development of oil and natural-gas resources in south Texas during the past 10 years has led to questions regarding possible environmental effects of processes associated with oil and natural-gas production, in particular the process of hydraulic fracturing, on water and other natural resources. Part of the lower San Antonio River watershed intersects an area of oil and natural-gas production from the sedimentary rocks that compose the Eagle Ford Group.

The rapid expansion of infrastructure associated with oil and natural-gas production increases potential pathways for inorganic and organic contaminants to enter surface-water systems. The U.S. Geological Survey, in cooperation with the San Antonio River Authority, analyzed geospatial data from different years (2008 and 2015) to evaluate changes in land cover associated with oil and natural-gas production activities in the lower San Antonio River watershed. Impervious surface in this study is defined as land cover consisting of well pads, oil- and gas-related features, or roads. The areal coverage associated with impervious surface increased from 201 acres to 5,390 acres (net increase of 5,189 acres) between 2008 and 2015. The total percentage of the study area accounted for by impervious surface resulting from oil and natural-gas production activities increased from 0.034 percent to 0.912 percent, which is an increase of approximately 27-fold. Collectively, 0.878 percent of the study area was converted to new impervious surface between 2008 and 2015. If the area associated with new storage ponds (0.066 percent) is added to the estimate of total land-cover changes as a result of oil and natural-gas production, then 0.944 percent of the study area was altered.

During 2015–17, surface-water samples collected from 5 sites and streambed-sediment samples collected from 17 sites in the lower San Antonio River watershed were analyzed for a broad range of constituents that might be associated with oil and natural-gas production. All major elements, trace elements, semivolatile organic compounds (SVOCs), and volatile organic compounds (VOCs) measured in surface-water samples were detected at concentrations less than any of the U.S. Environmental Protection Agency's water-quality standards. In general, the greatest SVOC and VOC concentrations were observed in samples collected from sites upstream from the area of active oil and natural-gas production and just downstream from urban areas. The lack of benzene, toluene, ethylbenzene, and all isomers of xylene (hereinafter referred to as BTEX) for most sites within the area of active oil and natural-gas production indicates that little, if any, local runoff associated with the area of active oil and natural-gas production has contaminated the surface water with BTEX compounds. Glycols, which are commonly used in hydraulic fracturing fluids as scale inhibitors, were detected in one surface-water sample from Ecleto Creek within the area of oil and natural-gas production; however, the presence of glycols does not necessarily indicate contamination from hydraulic fracturing fluid. The glycols detected also have other potential sources including the use of diethylene and ethylene glycols in antifreeze used in vehicles and the use of triethylene glycol in antibacterial air sanitizers.

The concentrations of select constituents in the streambed-sediment samples were compared to sediment quality guidelines (SQGs). The SQGs evaluate the potential toxicity of bed sediments to sediment-dwelling organisms. Two SQG concentration levels are used: (1) a lower level, called the threshold effect concentration (TEC), below which harmful effects to benthic biota are not expected, and (2) a higher level, the probable effect concentration (PEC), above which harmful effects are expected to occur frequently. The PEC for arsenic was exceeded in a sample collected from one site on Ecleto Creek. The origin of the elevated arsenic concentration is unknown; the contamination likely is not related to oil and natural-gas production because the site of the sample collection is located upstream from the area of active oil and natural-gas production. Streambed-sediment samples were analyzed for selected polycyclic aromatic hydrocarbons (PAHs) because PAHs can be used as indicators of petroleum hydrocarbons associated with produced waters. Each streambed-sediment sample was analyzed for two size fractions of PAHs: less than (<) 63 micrometers (µm) and < 2 millimeters (mm). Total PAH concentrations in all samples, regardless of size fraction, were less than the TEC for total PAHs of 1,610 micrograms per kilogram. Total PAH concentrations generally were greater in the <63-µm size-fraction samples than in the <2-mm size-fraction samples, indicating that PAHs could potentially sorb more readily to the exclusively silt- and clay-sized particles that compose <63-µm size-fraction samples than to the mixture of silt and clay and larger sized particles that compose the <2-mm size-fraction samples. Total PAH concentrations typically were greater in the samples collected from the sites upstream from the area of active oil and natural-gas production compared to those collected from sites within the area in both the <2-mm and <63-µm size-fraction samples. The smaller PAH concentrations measured in samples collected from within the area of active oil and natural-gas production in comparison to the upstream urbanized areas indicate relatively minor additional local contributions of PAHs of uncertain origin to the watershed.

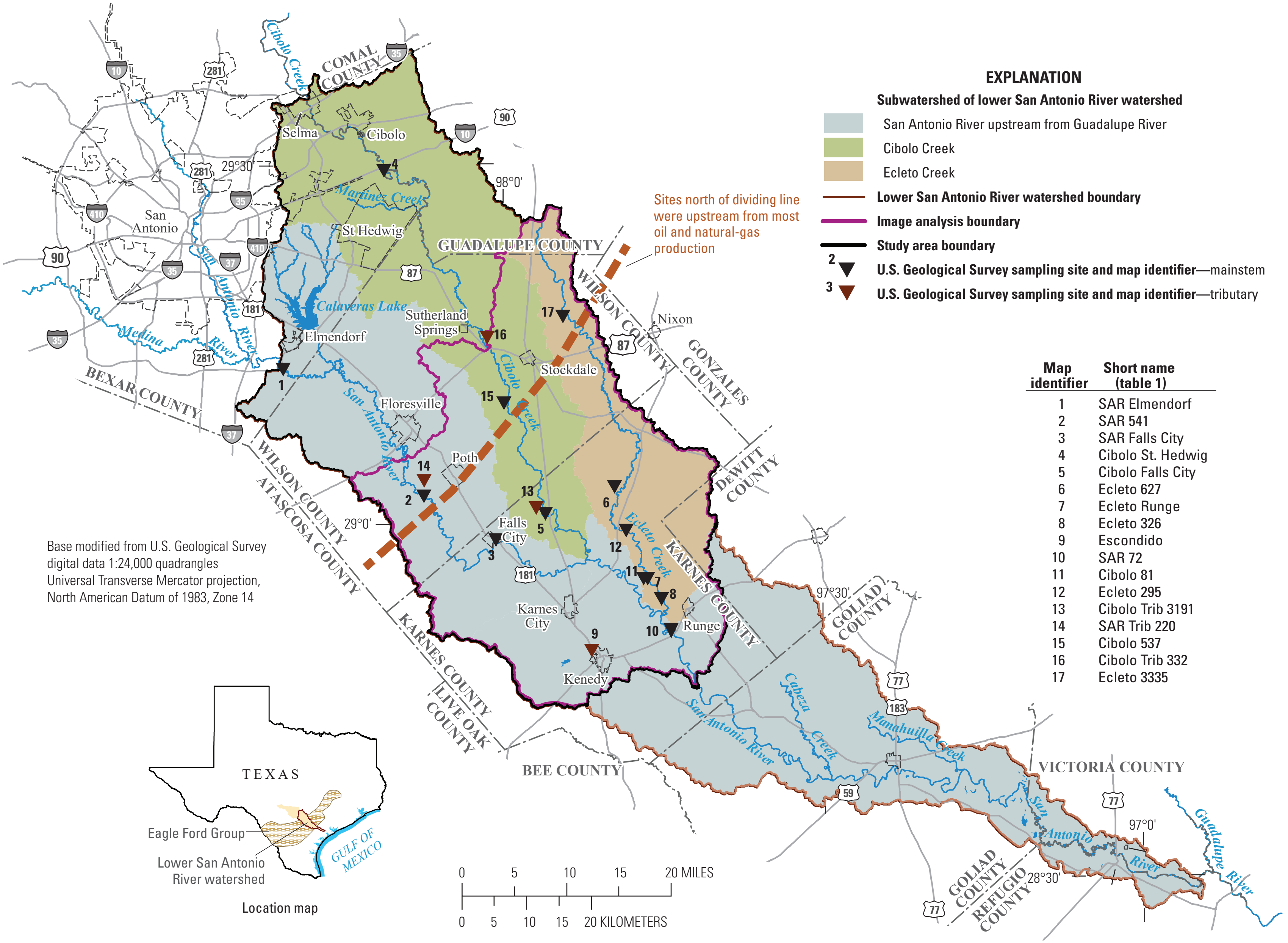
Introduction

The Eagle Ford Group is an important source of oil and natural gas in south Texas and contributes greatly to the energy production of the United States. Oil and natural-gas production from shale formations such as those present in the Eagle Ford Group in south Texas represented about 50 percent of U.S. crude oil production in 2017 (U.S. Energy Information Administration, 2018). The extensive development of oil and natural-gas resources in south Texas during the past 10 years has led to questions regarding possible environmental effects of processes associated with oil and natural-gas production, in particular the process of hydraulic fracturing, on water and other natural resources. In addition to the water required for initial well drilling, hydraulic fracturing of a typical well completed in shale formations in Texas requires an average 4.3 million gallons of water (Nicot and Scanlon, 2012). This water, along with a proppant (typically sand) and various chemicals, are pumped into a well completed in a shale formation under increased pressure to fracture the oil reservoir. The fractures, held open by the proppant, facilitate oil and natural-gas flow into the well (Veatch, 1983). Flowback water, which is water that “flows back” from the shale into the well during the hydraulic fracturing process, is a mixture of the hydraulic fracturing fluid and water that exists naturally in the shale. Once the water flowing out of the well no longer contains any traces of hydraulic fracturing fluid and contains only natural formation water, the water is called produced water. Produced water can continue to be generated along with oil and natural gas for as long as the well is in operation (Schramm, 2011).

Water for the initial well drilling and hydraulic fracturing typically is sourced locally and can sometimes come from the same sources that provide water for domestic, agricultural, and industrial use (Nicot and Scanlon, 2012). Concerns about water availability, coupled with technological improvements, have led to increased use of brackish groundwater and recycled flowback and produced water in the hydraulic fracturing process in some areas (Nicot and Scanlon, 2012). Concerns about possible environmental effects from releases of inorganic and organic constituents found in flowback and produced waters have been expressed by the public leading to previous assessments such as Mahler and Van Metre (2001), Kresse and others (2012), and U.S. Environmental Protection Agency (2018a).

Oil and natural-gas production from the Eagle Ford Group involves moving large amounts of equipment into mostly rural areas for the construction of new well pads. Oil- and gas-related equipment often involves heavy machinery, trucks, pipe, large warehouses, storage tanks, fluids, and parking areas to support oil and natural-gas production activities. New roads are constructed to access and service newly constructed well pads. Storage ponds are created to provide water to support drilling and oil and natural-gas production activities. Temporary runoff ponds are constructed adjacent to well pads during the drilling process to capture runoff from the well pad during the drilling phase of oil and natural-gas production. Together, these activities could result in alterations to regional land cover within the area of development.

Part of the lower San Antonio River watershed intersects an area of oil and natural-gas production from the Eagle Ford Group (Opsahl and Crow, 2015). The rapid expansion of infrastructure associated with oil and natural-gas production increases potential pathways for inorganic and organic contaminants to enter surface-water systems (Kappel and others, 2013). The U.S. Geological Survey (USGS), in cooperation with the San Antonio River Authority, analyzed geospatial data from different years (2008 and 2015) to evaluate changes in land cover associated with oil and natural-gas production activities in the lower San Antonio River watershed. Additionally, surface-water samples collected from 5 sites and streambed-sediment samples collected from 17 sites in the lower San Antonio River watershed during 2015–17 (fig. 1; table 1) were analyzed for a broad range of constituents that might be associated with oil and natural-gas production activities. The surface-water sample collection effort was intended to serve as a follow-up to the more extensive surface-water sampling that was done in 2011–13 (Opsahl and Crow, 2015); therefore, only a few samples were collected from a subset of sites which may be used to develop a long-term (years to decades) monitoring record.



Map identifier	Short name (table 1)
1	SAR Elmendorf
2	SAR 541
3	SAR Falls City
4	Cibolo St. Hedwig
5	Cibolo Falls City
6	Ecleto 627
7	Ecleto Runge
8	Ecleto 326
9	Escondido
10	SAR 72
11	Cibolo 81
12	Ecleto 295
13	Cibolo Trib 3191
14	SAR Trib 220
15	Cibolo 537
16	Cibolo Trib 332
17	Ecleto 3335

Figure 1. Location of surface-water and streambed-sediment sampling sites in the lower San Antonio River watershed, Texas, 2015–17.

Table 1. Data-collection sites in the lower San Antonio River watershed, Texas, 2015–17.

[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; Trib, tributary]

Map identifier (fig. 1)	Short name	USGS station number	USGS station name	Latitude (NAD 83) (dd mm ss)	Longitude (NAD 83) (dd mm ss)	Sample type(s) collected	Sampled during 2011–13?
1	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	29° 13′ 19"	98° 21′ 20"	Water/bed sediment	Yes
2	SAR 541	08183300	San Antonio River at Farm to Market Road 541 near Poth, Tex.	29° 02′ 22"	98° 07′ 31.8"	Bed sediment	No
3	SAR Falls City	08183550	San Antonio River at Highway 181 at Falls City, Tex.	28° 58′ 38.46"	98° 00′ 36.51"	Bed sediment	Yes
4	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	29° 30′ 05.2"	98° 11′ 10.5"	Water/bed sediment	Yes
5	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	29° 00′ 50"	97° 55′ 48"	Water/bed sediment	Yes
6	Ecleto 627	08186450	Ecleto Creek at Farm to Market Road 627 near Gillett, Tex.	29° 03′ 04"	97° 49′ 00"	Bed sediment	No
7	Ecleto Runge	08186500	Ecleto Creek near Runge, Tex.	28° 55′ 12"	97° 46′ 19"	Bed sediment	Yes
8	Ecleto 326	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	28° 53′ 28.4"	97° 45′ 03.4"	Water/bed sediment	Yes
9	Escondido	08187500	Escondido Creek at Kenedy, Tex.	28° 49′ 11"	97° 51′ 32"	Bed sediment	No
10	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	28° 50′ 55.3"	97° 44′ 13.7"	Water/bed sediment	Yes
11	Cibolo 81	285515097462400	Cibolo Creek at Farm to Market Road 81 near Runge, Tex.	28° 55′ 14.87"	97° 46′ 23.81"	Bed sediment	No
12	Ecleto 295	285920097475800	Ecleto Creek at County Road 295 near Gillett, Tex.	28° 59′ 20.32"	97° 47′ 58.35"	Bed sediment	No
13	Cibolo Trib 3191	290055097563400	Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.	29° 00′ 54.67"	97° 56′ 33.71"	Bed sediment	No
14	SAR Trib 220	290340098074500	Unnamed tributary to San Antonio River at Farm to Market Road 220 near Poth, Tex.	29° 03′ 40.47"	98° 07′ 44.86"	Bed sediment	No
15	Cibolo 537	291014097594200	Cibolo Creek at Farm to Market Road 537 near Stockdale, Tex.	29° 10′ 13.66"	97° 59′ 42.01"	Bed sediment	No
16	Cibolo Trib 332	291533098011600	Unnamed tributary to Cibolo Creek at Farm to Market Road 332 near Sutherland Springs, Tex.	29° 15′ 32.86"	98° 01′ 16.48"	Bed sediment	No
17	Ecleto 3335	291733097535800	Ecleto Creek at Farm to Market Road 3335 near Pandora, Tex.	29° 17′ 33.32"	97° 53′ 57.83"	Bed sediment	No

Purpose and Scope

This report summarizes changes in land cover associated with oil and natural-gas production between 2008 and 2015 and describes detections and concentrations of inorganic and organic constituents measured in surface-water and streambed-sediment samples collected during 2015–17 from selected stream sites located upstream from and within the area evaluated for land-cover change in the lower San Antonio River watershed in south Texas. The results from surface-water and streambed-sediment samples were used to evaluate inorganic and organic constituents which might be associated with oil and natural-gas production activities. Streambed-sediment samples also were collected for a comparison of different sediment particle-size fractions to determine if PAHs would more readily sorb to silt- and clay-sized particles than to larger sand-sized particles. To determine if any constituent concentrations had changed since the previous study, surface-water and sediment analytical results, where possible, were compared to results from Opsahl and Crow (2015), a study that summarized the detections and concentrations of inorganic and organic constituents in surface-water and streambed-sediment samples during 2011–13 in the lower San Antonio River watershed. All analytical data collected in this study are presented in Crow and others (2018). Possible effects associated with oil and natural-gas production activities on groundwater were not evaluated in this study.

Description of Study Area

The study area encompasses parts of Bexar, Comal, Guadalupe, Wilson, Karnes, and DeWitt Counties in south Texas and consists of 1,593 square miles (mi^2) in the lower San Antonio River watershed (fig. 1). Since 2008, rapid expansion of oil and natural-gas production with the use of hydraulic fracturing in the Eagle Ford Group has taken place in south Texas (Railroad Commission of Texas, 2018). Most of the hydraulic fracturing activity for oil and natural-gas production in the study area is taking place in an area encompassing parts of three counties—Wilson, DeWitt, and Karnes (Railroad Commission of Texas, 2018).

The upper part of the Eagle Ford Group extends approximately 400 miles (mi) from the Maverick Basin in the southwest of the State to the East Texas Basin in the northeast of the State (Bureau of Economic Geology, 2018). The Eagle Ford Group consists primarily of carbonaceous marls and interbedded sandstones, silts, and shale, and it is divided into three formations bounded by major unconformities (Surles, 1987). Deposition of the Eagle Ford Group recorded a north-northwestward transgression of Cretaceous seas along the ancestral Gulf of Mexico during periods when the sea level rose, followed by regressions caused by the prograding of deltaic complexes during periods when the sea level fell (Surles, 1987; Dawson, 2000). In general, lower strata in the Eagle Ford Group represent low-energy, poorly oxygenated, deep-water environments, whereas the upper strata represent high-energy, well-oxygenated, shallow marine environments (Dawson, 1997, 2000). The Eagle Ford Group occurs in the subsurface of south Texas where, in addition to producing oil and natural gas through hydraulic fracturing, it is the source rock for oil found in the Austin Chalk and the Buda Limestone (Surles, 1987).

Three main streams flow through the area of oil and natural-gas production in the study area (fig. 1). The longest of the three streams is the San Antonio River. The San Antonio River flows about 90 mi through the study area, from near Elmendorf, Tex., to just beyond the most downstream site in the study area at SAR 72. The second longest stream is Cibolo Creek which flows into the San Antonio River approximately 3 mi northeast of Karnes City, Tex. The length of Cibolo Creek from Selma, Tex., to the confluence with the San Antonio River is about 75 mi. The third stream, Ecleto Creek, flows into the San Antonio River approximately 1 mi west of Runge, Tex. 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 study area is composed of gently sloping, rolling terrain, with the upper part of the watershed more dissected and rolling compared to the lower part of the watershed (Ryder, 1996). The land cover consists mostly of brush and grassland (Homer and others, 2015), and average annual precipitation ranges from about 30 inches in the northern part of the lower San Antonio River watershed to about 40 inches in the southern part of the watershed near the coast (National Oceanic and Atmospheric Administration, 2018a, b).

Methods

The study entailed a two-part effort to (1) quantify the change in oil and natural gas-associated land-use in the lower San Antonio River watershed by analyzing aerial imagery data and (2) to determine to what degree, if any, land-cover changes might have resulted in changes in the concentrations of selected constituents in surface-water and streambed-sediment samples. The imagery data and the environmental data were analyzed independently to determine changes in each data type prior to completing analyses that included all of the data.

Computation of Land-Cover Changes Associated with Oil and Natural-Gas Production

Land-cover changes associated with oil and natural-gas production activities were quantified by comparing aerial imagery data collected during 2008 and 2015. Oil and natural-gas features were identified on the aerial imagery so that total area covered by each feature could be calculated to provide an estimate of change in each feature between 2008 and 2015.

The study area used for geographic information system (GIS) analysis (fig. 1), a subsection of the study area from which surface-water and streambed-sediment samples were collected, was estimated to be 591,049 acres and was used to estimate the percentage change for each land-use category.

Aerial Imagery Collection

Aerial imagery (hereinafter referred to as “imagery”) from the National Agricultural Imagery Program (NAIP) (U.S. Department of Agriculture, Natural Resources Conservation Service, 2011) was used for the 2008 analysis. NAIP imagery provides high-resolution data (1-meter [m] by 1-m resolution), suitable for detailed analysis of the landscape, that are available for download from the U.S. Department of Agriculture Geospatial Data Gateway website (U.S. Department of Agriculture, Natural Resources Conservation Service, 2011). High-resolution imagery from the Texas Natural Resources Information System (TNRIS) was used for the 2015 analysis and is available for download from the TNRIS website (Texas Natural Resources Information System, 2018). The imagery from TNRIS is 6-inch by 6-inch (0.1524-m by 0.1524-m) resolution and was recorded during January and February 2015. The higher spatial resolution and appropriate temporal resolution of the TNRIS imagery compared to the 2008 NAIP imagery allowed for increased detail and precision during imagery interpretation for the 2015 analysis. The amount of error introduced to the spatial data analysis from comparing imagery with different resolutions was not quantified but was expected to be negligible considering the small number of features available for digitization during the 2008 analysis when most of the land in the study area was undeveloped compared to the large number of man-made features available for digitizing during the 2015 analysis. The 2008 NAIP imagery and 2015 TNRIS imagery will hereinafter be referred to as the 2008 imagery and 2015 imagery, respectively.

Imagery Interpretation and Data Analysis

The 2008 imagery and 2015 imagery data were visualized and analyzed by using ArcMap (Esri, 2018a). To evaluate differences in the 2008 and 2015 imagery, a process referred to as “heads-up digitizing” was used to assess differences in land-cover attributes associated with oil and natural-gas features in 2015 compared to 2008. Heads-up digitizing involves manually tracing features on a computer monitor from another dataset, usually aerial or satellite imagery, and saving the traced features to a new shapefile for use in GIS applications (Esri, 2018b). Polygons were drawn around five types of oil- and gas-related land-cover attributes based on visual interpretation of the 2008 and 2015 imagery data, and total areas were calculated from the polygons that were delineated from the imagery. The five types of land-cover attributes classified from the imagery are the following:

1. Well pads – Well pads were digitized if clearly identifiable well location or pump jack was onsite (fig. 2*A*). Well pads that were digitized in the 2008 imagery but were overgrown by vegetation in the 2015 imagery were not included in the estimate of the total number of new well pads constructed between 2008 and 2015. Well pads that were identified in the 2008 imagery but were classified as a different attribute in the 2015 imagery (for example, a well pad that was converted to a storage pond) were included in total area estimate for the new attribute identified in 2015.

2. Oil- and gas-related features – Areas with no apparent wells or drilling activity that had been cleared and were being used for storing equipment, trucks, chemicals, or other materials were considered oil- and gas-related features (fig. 2*B*).

3. New roads – Roads that run directly from new well pads to a main road that were not present in 2008 but were present in 2015 were considered new roads (fig. 2*C*). Based on visual inspection of the imagery, new roads in this region were generally constructed with a caliché base material. Highways, county roads, city streets, and other roads commonly associated with population centers were not included in this analysis.

4. Storage ponds – Storage ponds were typically observed near multiple well pads and usually had a visible lining on the bottom (fig. 2*D*). Pumps and hoses were often present near storage ponds.

5. Runoff ponds – Runoff ponds were located immediately adjacent to a well pad (fig. 2*E*) and were constructed to capture the well cuttings (broken fragments of rock produced during drilling) and any runoff from the well pad during drilling.

Imagery Quality Assurance

Visual inspection of the delineations of oil and natural-gas related land-cover features and attributes were done by using GIS. The topology tool was used to locate and correct potential topological errors such as dangles and overlapping lines created during the digitization process. The 2008 imagery used for delineations was visually compared to Google Earth imagery from the same time period to ensure that no features were missed. The 2015 imagery was not compared to Google Earth imagery because the 2015 imagery was of higher resolution than the Google Earth imagery.

Figure 2. Examples of land-cover attributes that were classified by using 2008 imagery from the National Agricultural Imagery Program (U.S. Department of Agriculture, Natural Resources Conservation Service, 2011) and 2015 imagery from the Texas Natural Resources Information System (Texas Natural Resources Information System, 2018): *A*, well pads; *B*, oil- and gas-related features; *C*, new roads; *D*, a storage pond; and *E*, a runoff pond. All images shown in this figure were obtained from the 2015 imagery.

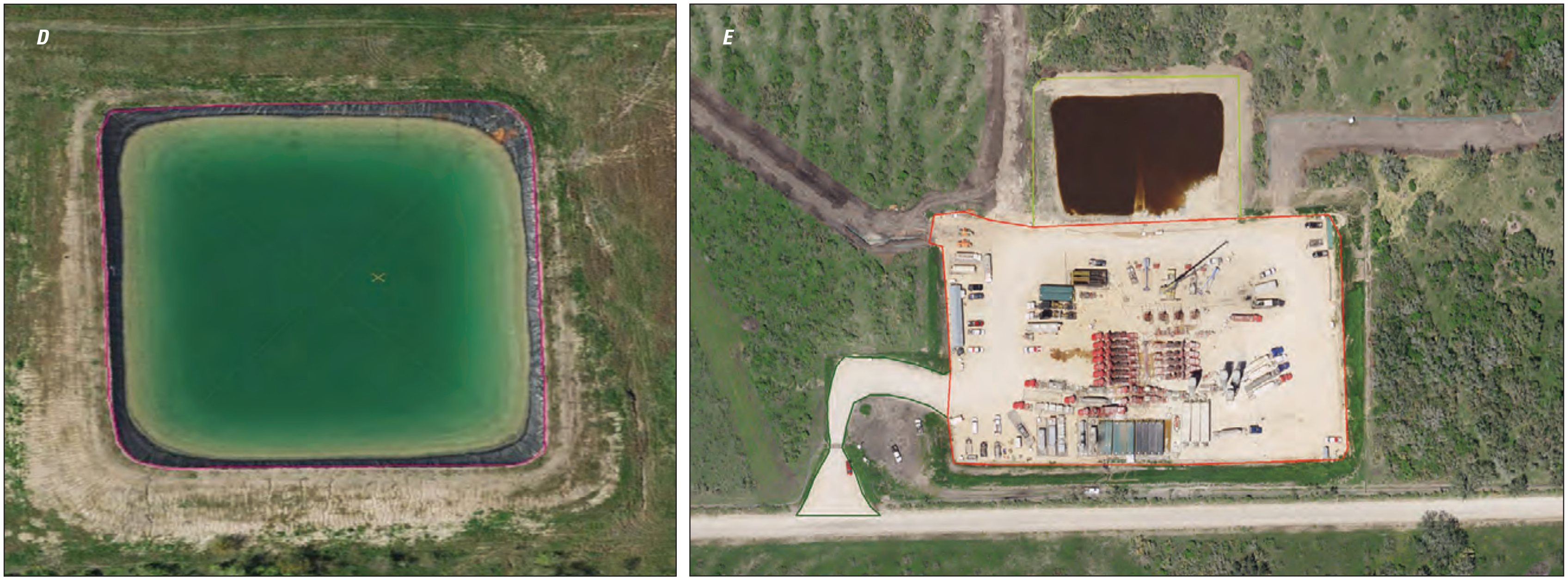


Figure 2. Examples of land-cover attributes that were classified by using 2008 imagery from the National Agricultural Imagery Program (U.S. Department of Agriculture, Natural Resources Conservation Service, 2011) and 2015 imagery from the Texas Natural Resources Information System (Texas Natural Resources Information System, 2018): *A*, well pads; *B*, oil- and gas-related features; *C*, new roads; *D*, a storage pond; and *E*, a runoff pond. All images shown in this figure were obtained from the 2015 imagery.—Continued

Collection of Streamflow Data

The methods described here for streamflow-data collection are modified from Opsahl and Crow (2015). Continuous streamflow was measured at USGS streamflow-gaging stations (sites 1, 4, 5, and 10) by using methods described by Rantz and others (1982a, b) and Turnipseed and Sauer (2010). A stage-discharge relation (rating curve) was developed from the discrete discharge and stage measurements made at each streamflow-gaging station (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). Discharge measurements at the time of surface-water sample collection (table 2) were obtained from the site stage-discharge relations. Stage at each streamflow-gaging station was recorded every 15 minutes and transmitted hourly by the Geostationary Operational Environmental Satellite transmitter to the USGS National Water Information System database (U.S. Geological Survey, 2017). The sampling site Ecleto 326 was not equipped with a continuous streamflow gage, and discrete discharge measurements were not made at the time that surface-water samples were collected from this site. Discrete discharge measurements were not made at the time of streambed-sediment sample collection at any of the 17 sites.

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

Five surface-water samples and 34 streambed-sediment samples were collected from 17 sites in the lower San Antonio River watershed during 2015–17 (fig. 1; table 1). Sampling sites included a subset of seven sites that were previously sampled for surface water or sediment during 2011–2013 (Opsahl and Crow, 2015; sites 1, 3, 4, 5, 7, 8, and 10). During the 2015–17 study, streambed-sediment samples were collected from all seven of these sites, and surface-water samples from five of these seven sites were collected during stormflow-runoff conditions for analysis of water-quality constituents.

Surface-water samples were collected and processed by following the methods and guidelines described in U.S. Geological Survey (variously dated) and Shelton (1997). 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 model 6920 multiparameter water-quality sonde (Xylem Analytics, 2018) prior to collection of surface-water samples (table 2). At each sampling site, surface-water samples were collected from 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 (L) bottle sampler (Davis, 2005) attached to a wading rod. When the stream was too deep to be waded, surface-water samples were collected by using either a US DH-2 1-L collapsible bag sampler or a US DH-95 1-L bottle sampler (Davis, 2005) attached to a reel and crane system. 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-95 sampler at velocities <2.0 ft/s were labeled as being collected by using the multiple vertical method because the samplers are unable to collect isokinetic samples at those velocities. Surface-water samples were composited into a 14-L Teflon (polytetrafluoroethylene) churn, and aliquots of representative whole-water (unfiltered) samples were dispensed from the churn into the appropriate sample bottles for analysis of total suspended solids (TSS), sulfide, glycols, and methylene blue active substances (MBAS). Unfiltered samples for analysis of semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs) were collected directly from the centroid of the stream to avoid aeration of the samples which would allow the constituents to volatize. Additional water samples for dissolved solids and inorganics were collected by passing water from the churn through a 0.45-micrometer (µm) filter into the appropriate sample collection bottles.

Streambed-sediment samples were collected twice from all sampling sites (table 1), once during base flow (hereinafter referred to as 2015 samples) and again during base flow shortly after multiple stormwater-runoff events (hereinafter referred to as 2016 samples). Both sets of streambed-sediment samples (2015 and 2016 samples) were collected either manually with a scoop while wading or by using a ponar sampler (fig. 3) from a watercraft 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. The streambed sediment was composited and put through a stainless steel 2-millimeter (mm) sieve in preparation for the analyses of polycyclic aromatic hydrocarbons (PAHs), total organic carbon (TOC), radium-226, and radium-228; instead of the 2-mm sieve, a 63-µm plastic sieve fabric was used in preparation for the analyses of major and trace elements and for additional analyses of PAHs and TOC. 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). The purpose of analyzing PAHs from samples passed through two different sieve sizes (2 mm and 63 µm) was to determine if PAHs would more readily sorb to silt- and clay-sized particles than to larger sand-sized particles. An unsieved portion of each of the streambed-sediment samples also was analyzed for particle-size distribution.

Table 2. Summary of stream discharge and physicochemical properties in surface-water samples collected at sites from selected streams in the lower San Antonio River watershed, Texas, 2015–17.

[USGS, U.S. Geological Survey; ft^3/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; St., Saint; --, not recorded. Dates are formatted as month-day-year]

Map identifier (fig. 1)	Short name	USGS station number	USGS station name	Date	Discharge (ft^3/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm at 25 °C)	Temperature (°C)	Turbidity (FNU)	Dissolved solids (mg/L)	Total suspended solids (mg/L)
1	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	08-07-2017	4,800	6.1	7.9	224	25.1	590	124	910
4	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	10-25-2015	48.4	7.5	7.5	305	21.5	35	184	34
5	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	10-25-2015	100	7.1	7.1	492	20.3	78	302	94
8	Ecleto 326	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	05-20-2016	--	6.2	7.7	213	20.4	420	135	820
10	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	08-03-2017	506	5.8	7.9	346	26.2	1,120	205	2,340

Figure 3. A ponar sampler used to collect streambed-sediment samples at sites from selected streams in the lower San Antonio River watershed, Texas, 2015–16.

Sample Analyses

A complete list of the analytical methods and laboratories used to analyze the surface-water and streambed-sediment samples for chemical constituents and physical properties is provided in table 3. Surface-water samples were analyzed for concentrations of dissolved solids, TSS, MBAS, major and trace elements, SVOCs, and VOCs by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Glycol and sulfide concentrations were analyzed in surface-water samples by RTI Laboratories, Inc. (RTI), in Livonia, Michigan. Streambed-sediment samples were analyzed for moisture content and concentrations of major and trace elements by the NWQL, and for TOC and PAH concentrations by RTI. Streambed-sediment samples also were analyzed for concentrations of radium-226 and radium-228 by ALS Environmental Laboratory in Fort Collins, Colorado. Radium data are not evaluated in this report because detected concentrations were not distinguishable from background sources, but the data are available in Crow and others (2018). Thirty-four streambed-sediment samples were submitted to the USGS Kentucky Water Science Center Sediment Laboratory in Louisville for particle-size analysis. Following an analytical issue that involved the exceedance of sample holding times that occurred at the NWQL, major and trace element data associated with streambed-sediment samples collected in 2015 were thoroughly reviewed. After review, the data were rejected because it could not be verified that the holding-time exceedances did not affect the results. All major and trace element data for samples collected in 2015 are not used in this report, but major and trace element data for samples collected in 2016 did not have any issues, and those data are included in this report.

Values reported for samples analyzed by the NWQL and RTI are censored by using a laboratory reporting limit (LRL) established by each analytical laboratory. For trace elements, the NWQL sets the LRL equal to the long-term method detection level (LT-MDL) (Childress and others, 1999). The LRL for organic constituents analyzed by the NWQL is calculated as twice the LT-MDL, which is a modification of the U.S. Environmental Protection Agency (EPA) definition of the method detection limit (MDL) provided in the Code of Federal Regulations (CFR) Title 40 Part 136 (EPA, 1992). The LRLs for constituents analyzed by RTI are usually established at levels corresponding to the lowest calibration standard used to determine an MDL using methods described in CFR Title 40 Part 136.

For this report, concentrations equal to or greater than the LRL hereinafter are referred to as “detections” or “detected concentrations.” Concentrations less than the LRL that were reported as less than the LRL by the laboratory hereinafter are referred to as “nondetections” or were said to be “not detected.” Concentrations less than the LRL but greater than the LT-MDL were typically reported by the NWQL as estimated concentrations and denoted with the “E” remark code. For information-rich analyses, the NWQL can report concentrations less than the LT-MDL if the analyte is determined to be positively identified (Childress and others, 1999). Constituents that were verified as present but not quantified in a sample (that is, less than the LRL) were qualified by the NWQL with an “M” remark code. Likewise, RTI considered a value estimated and denoted with the “E” remark code any constituent for which the value was greater than the MDL but less than the LRL. Total PAH concentrations were computed as the sum of the detected values of 13 individual PAH compounds: 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene (Ingersoll and others, 2001).

Quality Assurance

Quality-control (QC) samples were collected and analyzed to estimate the amount of variability and bias found in the environmental sample results. Variability is the extent to which data points in a statistical distribution or dataset diverge from the average, or mean, value as well as the extent to which these data points differ from each other. Bias is the systematic error inherent in a method or caused by some artifact of the

Table 3. Analyzing laboratories and analytical methods used in the chemical and physical analysis of surface-water and streambed-sediment samples collected from select streams in the lower San Antonio River watershed, Texas, 2015–17.

[NWQL, U.S. Geological Survey National Water Quality Laboratory; RTI, RTI Laboratories, Inc.; ALS, ALS Environmental Laboratory; KY-WSC, Kentucky Water Science Center Sediment Laboratory]

Constituent	Analyzing laboratory	Method reference(s)
Surface-water samples		
Dissolved solids	NWQL	Fishman and Friedman (1989)
Total suspended solids	NWQL	Fishman and Friedman (1989)
Methylene blue active substances	NWQL	Burkhardt and others (1995)
Major and trace elements	NWQL	Fishman and Friedman (1989) Fishman (1993) Struzeski and others (1996) Garbarino (1999) Garbarino and others (2006)
Semivolatile organic compounds	NWQL	Fishman (1993)
Volatile organic compounds	NWQL	Rose and others (2016)
Glycols	RTI	U.S. Environmental Protection Agency (1996a)
Sulfide	RTI	American Public Health Association (1998)
Stream-sediment samples		
Percent moisture	NWQL	American Society for Testing and Materials (1992)
Major and trace elements	NWQL	Fishman and Friedman (1989) Garbarino and Struzeski (1998) U.S. Environmental Protection Agency (1998) Garbarino and others (2006)
Total organic carbon	RTI	U.S. Environmental Protection Agency (2004)
Polycyclic aromatic hydrocarbons	RTI	U.S. Environmental Protection Agency (1996b)
Radium-226, radium-228	ALS	U.S. Environmental Protection Agency (1980)
Particle-size distribution	KY-WSC	Guy (1969)

measurement system (Mueller and others, 2015). The QC samples submitted to the analytical laboratories included streambed-sediment sample replicates and matrix spikes. All QC samples were analyzed by using the same analytical methods that were used for analysis of the environmental samples. In addition to the QC samples submitted from the field, the NWQL analyzed internal laboratory blanks, replicates, and spikes.

Replicate samples are used to evaluate variability in measurements associated with analytical processes, sample processing protocols, or natural variation, and to provide information on the reproducibility and precision of sample processing and analysis. In this study, split replicate samples were used to evaluate sample processing and analytical variability. Split replicate samples are duplicate samples that are collected from a single sample container by using identical methodology (Horowitz and others, 1994). Variability can be evaluated by comparing concentrations between environmental and replicate analyte pairs and expressed as relative percent differences (RPDs). The RPD was calculated between each pair of replicate analyses to provide a measure of variability by using the following equation:

$$RPD = |C1 - C2|/((C1 + C2)/2) \times 100, \qquad (1)$$

where

$C1$ is the constituent concentration in the environmental sample, and

$C2$ is the constituent concentration in the duplicate sample.

RPDs calculated for each replicate pair of analytes having detectable concentrations are summarized in table 4 and listed in tables 5–7. RPDs were not computed for analyte pairs where either one or both concentrations were nondetected values.

Table 4. Statistical summary of relative percent difference between environmental and replicate streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

[RPD, relative percent difference; <, less than; mm, millimeter; µm, micrometer]

Category	Number of samples	Total number of analyte pairs	Number of analyte pairs where both samples yielded nondetections	Number of analyte pairs yielding one nondetection	Number of computed RPDs	Minimum RPD (percent)	Maximum RPD (percent)	Mean RPD (percent)	Median RPD (percent)
Trace elements	3	45	2	1	42	0.0	54	11	8.4
Polycyclic aromatic hydrocarbons	12	204	153	8	43	1.9	120	46	48
<2-mm size fraction	6	102	79	7	16	1.9	120	41	22
<63-µm size fraction	6	102	74	1	27	16	75	46	49
Organic carbon	12	12	0	2	10	0.0	55	20	21
<2-mm size fraction	6	6	0	2	4	21	35	26	23
<63-µm size fraction	6	6	0	0	6	0.0	55	17	8.0

Table 5. Relative percent differences between environmental samples and replicate samples for trace elements measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2016.

[USGS, U.S. Geological Survey; mm, millimeter; mg/kg, milligrams per kilogram; ENV, environmental sample concentration; REP, replicate sample concentration; RPD, relative percent difference; <, less than; --, no data; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and replicate sample information by USGS station number								
USGS station number	**08186500**			**08188060**			**290055097563400**		
USGS station name	**Ecleto Creek near Runge, Tex.**			**San Antonio River at State Highway 72 near Runge, Tex.**			**Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.**		
Short name	**Ecleto Runge**			**SAR 72**			**Cibolo Trib 3191**		
Map identifier (fig. 1)	**7**			**10**			**13**		
Sample date	**6/24/2016**			**7/26/2016**			**6/22/2016**		
Sieve size (mm)	**0.063**			**0.063**			**0.063**		
Sample type	**ENV (mg/kg)**	**REP (mg/kg)**	**RPD (percent)**	**ENV (mg/kg)**	**REP (mg/kg)**	**RPD (percent)**	**ENV (mg/kg)**	**REP (mg/kg)**	**RPD (percent)**
Calcium	42,100	44,100	4.6	100,000	103,000	3.0	84,800	84,600	0.2
Sodium	661	615	7.21	389	416	6.7	2,230	2,300	3.1
Aluminum	15,000	12,000	22.2	8,900	9,600	7.6	11,000	12,000	8.7
Barium	310	300	3.3	97	100	3.0	110	120	8.7
Cadmium	0.221	0.253	13.5	0.189	0.211	11.0	0.324	0.297	8.7
Chromium	12	8.9	29.7	14	15	6.9	13	13	0.0
Iron	13,000	11,000	16.7	10,000	11,000	9.5	12,000	13,000	8.0
Lead	20	18	10.5	12	14	15.4	15	15	0.0
Lithium	9.5	8	17.1	8.5	9.2	7.9	11	12	8.7
Manganese	610	570	6.8	280	340	19.4	370	380	2.7
Molybdenum	E0.130	0.226	53.9	<0.100	<0.100	--	10	7.3	31.2
Nickel	8.5	7.7	9.9	8.8	9.8	10.8	12.3	12	2.5
Zinc	43	36	17.7	33	38	14.1	47	51	8.2
Arsenic	8.3	8.2	1.2	4.3	4.6	6.7	6.8	6.1	10.9
Boron	4.9	<4.8	--	<9.6	<9.6	--	6.6	7.1	7.3

Table 6. Relative percent differences between environmental samples and replicate samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; REP, replicate sample concentration; RPD, relative percent difference; <, less than; --, no data; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and replicate sample information by USGS station number											
USGS station number	**08186500**											
USGS station name	**Ecleto Creek near Runge, Tex.**											
Short name	**Ecleto Runge**											
Map identifier (fig. 1)	**7**											
Sample date	**4/3/2015**			**4/3/2015**			**6/24/2016**			**6/24/2016**		
Sieve size (mm)	**2**			**0.063**			**2**			**0.063**		
Sample type	**ENV (µg/kg)**	**REP (µg/kg)**	**RPD (percent)**	**ENV (µg/kg)**	**REP (µg/kg)**	**RPD (percent)**	**ENV (µg/kg)**	**REP (µg/kg)**	**RPD (percent)**	**ENV (µg/kg)**	**REP (µg/kg)**	**RPD (percent)**
2-Methylnaphthalene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
9H-Fluorene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Acenaphthene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Acenaphthylene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Anthracene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Benzo[a]anthracene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Benzo[a]pyrene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Benzo[b]fluoranthene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Benzo[ghi]perylene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Benzo[k]fluoranthene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Chrysene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Dibenzo[a,h]anthracene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Fluoranthene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Indeno[1,2,3-cd]pyrene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Naphthalene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Phenanthrene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--
Pyrene	<0.79	<0.80	--	<3.3	<3.8	--	<0.84	<0.83	--	<4.0	<4.1	--

Table 6. Relative percent differences between environmental samples and replicate samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; REP, replicate sample concentration; RPD, relative percent difference; <, less than; --, no data; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and replicate sample information by USGS station number											
USGS station number	08188060											
USGS station name	San Antonio River at State Highway 72 near Runge, Tex.											
Short name	SAR 72											
Map identifier (fig. 1)	10											
Sample date	4/6/2015			4/6/2015			7/26/2016			7/26/2016		
Sieve size (mm)	2			0.063			2			0.063		
Sample type	ENV (µg/kg)	REP (µg/kg)	RPD (percent)	ENV (µg/kg)	REP (µg/kg)	RPD (percent)	ENV (µg/kg)	REP (µg/kg)	RPD (percent)	ENV (µg/kg)	REP (µg/kg)	RPD (percent)
2-Methylnaphthalene	<0.79	<0.88	--	<2.0	<2.3	--	<0.94	<0.94	--	<1.8	<2.0	--
9H-Fluorene	<0.79	<0.88	--	<2.0	<2.3	--	<0.94	<0.94	--	<1.8	<2.0	--
Acenaphthene	<0.79	<0.88	--	<2.0	<2.3	--	<0.94	<0.94	--	<1.8	<2.0	--
Acenaphthylene	<0.79	<0.88	--	<2.0	<2.3	--	<0.94	<0.94	--	<1.8	<2.0	--
Anthracene	<0.79	<0.88	--	<2.0	<2.3	--	<0.94	<0.94	--	<1.8	<2.0	--
Benzo[a]anthracene	<0.79	<0.88	--	11	16	37	2.5	2.3	8.3	4.9	7.4	41
Benzo[a]pyrene	<0.79	<0.88	--	13	17	27	2.9	2.6	11	6.0	9.6	46
Benzo[b]fluoranthene	0.97	1.0	3.0	22	31	34	5.8	4.7	21	11	19	53
Benzo[ghi]perylene	0.87	1.1	23	13	20	42	3.0	1.8	50	<1.8	<2.0	--
Benzo[k]fluoranthene	<0.79	<0.88	--	8.3	9.8	17	1.7	1.9	11	3.4	6.9	68
Chrysene	<0.79	<0.88	--	16	19	17	3.2	2.9	9.8	6.1	11	57
Dibenzo[a,h]anthracene	<0.79	<0.88	--	3.2	7.0	75	<0.94	<0.94	--	<1.8	<2.0	--
Fluoranthene	<0.79	1.0	--	23	30	26	5.3	5.2	1.9	9.8	16	48
Indeno[1,2,3-cd]pyrene	<0.79	1.0	--	11	21	63	3.0	2.0	40	<1.8	<2.0	--
Naphthalene	<0.79	<0.88	--	<2.0	<2.3	--	<0.94	<0.94	--	<1.8	<2.0	--
Phenanthrene	<0.79	<0.88	--	7.3	8.6	16	<0.94	<0.94	--	<1.8	<2.0	--
Pyrene	<0.79	<0.88	--	19	24	23	4.5	4.3	4.5	8.2	13	45

Table 6. Relative percent differences between environmental samples and replicate samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; REP, replicate sample concentration; RPD, relative percent difference; <, less than; --, no data; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and replicate sample information by USGS station number											
USGS station number	**290055097563400**											
USGS station name	**Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.**											
Short name	**Cibolo Trib 3191**											
Map identifier (fig. 1)	**13**											
Sample date	**4/2/2015**			**4/2/2015**			**6/22/2016**			**6/22/2016**		
Sieve size (mm)	**2**			**0.063**			**2**			**0.063**		
Sample type	**ENV (µg/kg)**	**REP (µg/kg)**	**RPD (percent)**	**ENV (µg/kg)**	**REP (µg/kg)**	**RPD (percent)**	**ENV (µg/kg)**	**REP (µg/kg)**	**RPD (percent)**	**ENV (µg/kg)**	**REP (µg/kg)**	**RPD (percent)**
2-Methylnaphthalene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	<1.5	--	<2.0	<3.2	--
9H-Fluorene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	<1.5	--	<2.0	<3.2	--
Acenaphthene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	<1.5	--	<2.0	<3.2	--
Acenaphthylene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	<1.5	--	<2.0	<3.2	--
Anthracene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	<1.5	--	<2.0	<3.2	--
Benzo[a]anthracene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	3.3	--	3.1	5.9	62
Benzo[a]pyrene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	19	--	16	27	51
Benzo[b]fluoranthene	1.2	<1.1	--	<1.8	<1.8	--	3	10	108	8.2	17	70
Benzo[ghi]perylene	<1.0	<1.1	--	<1.8	<1.8	--	2	3.9	64	3.9	6.4	49
Benzo[k]fluoranthene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	1.9	--	2.9	<3.2	--
Chrysene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	4.8	--	4.5	8.2	58
Dibenzo[a,h]anthracene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	<1.5	--	<2.0	<3.2	--
Fluoranthene	<1.0	<1.1	--	1.8	<1.8	--	1.7	6.5	117	6.3	11	54
Indeno[1,2,3-cd]pyrene	<1.0	<1.1	--	<1.8	<1.8	--	1.7	3.9	79	3.9	6.4	49
Naphthalene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	<1.5	--	<2.0	<3.2	--
Phenanthrene	<1.0	<1.1	--	<1.8	<1.8	--	<1.2	2.5	--	2.3	4.3	61
Pyrene	<1.0	<1.1	--	<1.8	<1.8	--	1.8	6.2	110	5.8	11	62

Table 7. Relative percent differences between environmental samples and replicate samples for organic carbon concentrations measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

[USGS, U.S. Geological Survey; mm, millimeter; mg/kg, milligrams per kilogram; ENV, environmental sample concentration; REP, replicate sample concentration; RPD, relative percent difference; <, less than; --, no data; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and replicate sample information by USGS station number											
USGS station number	08186500											
USGS station name	Ecleto Creek near Runge, Tex.											
Short name	Ecleto Runge											
Map identifier (fig. 1)	7											
Sample date	4/3/2015			4/3/2015			6/24/2016			6/24/2016		
Sieve size (mm)	2			0.063			2			0.063		
Sample type	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)
Organic carbon	770	<1,600	--	20,000	21,000	4.9	1,100	860	24	24,000	27,000	12

	Environmental and replicate sample information by USGS station number											
USGS station number	08188060											
USGS station name	San Antonio River at State Highway 72 near Runge, Tex.											
Short name	SAR 72											
Map identifier (fig. 1)	10											
Sample date	4/6/2015			4/6/2015			7/26/2016			7/26/2016		
Sieve size (mm)	2			0.063			2			0.063		
Sample type	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)
Organic carbon	<1,900	730	--	13,000	13,000	0.0	9,100	7,300	22	19,000	15,000	24

Table 7. Relative percent differences between environmental samples and replicate samples for organic carbon concentrations measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; mg/kg, milligrams per kilogram; ENV, environmental sample concentration; REP, replicate sample concentration; RPD, relative percent difference; <, less than; --, no data; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and replicate sample information by USGS station number											
USGS station number	290055097563400											
USGS station name	Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.											
Short name	Cibolo Trib 3191											
Map identifier (fig. 1)	13											
Sample date	4/2/2015			4/2/2015			6/22/2016			6/22/2016		
Sieve size (mm)	2			0.063			2			0.063		
Sample type	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)	ENV (mg/kg)	REP (mg/kg)	RPD (percent)
Organic carbon	9,800	14,000	35	12,000	21,000	55	13,000	16,000	21	21,000	22,000	4.7

Replicate streambed-sediment samples were collected from the same three sites (Ecleto Runge, SAR 72, and Cibolo Trib 3191) in 2015 and 2016. Replicates consisted of 3 samples for trace elements, 12 samples for PAHs (6 for the <2-mm size fraction and 6 for the <63-µm size fraction), 12 samples for organic carbon (6 for the <2-mm size fraction and 6 for the <63-µm size fraction), and 6 samples for sediment size analysis. RPDs were computed for trace elements, PAHs, and organic carbon for 95 of the total 261 analyte pairs. The remaining 166 analyte pairs included results in which one or both values were nondetections. Data for sediment size analysis replicates were evaluated by preparing scatterplots to graphically assess differences between paired values. The QC data for major and trace elements in the 2015 samples were affected by the same holding-time exceedance at the NWQL as the environmental samples and were, therefore, not used to evaluate variability in this study.

The median value for the 42 RPDs computed for trace elements was 8.4 percent (table 4); RPDs ranged from 0.0 percent for chromium and lead in the 2016 sample collected from the Cibolo Trib 3191 site to 54 percent for molybdenum in the 2016 sample collected from the Ecleto Runge site (table 5). The median value for the 43 RPDs computed for all PAHs was 48 percent (table 4); RPDs ranged from 1.9 percent for fluoranthene in the <2-mm size-fraction 2016 sample collected from the SAR 72 site to 117 percent for fluoranthene in the <2-mm size-fraction 2016 sample collected from the Cibolo Trib 3191 site (table 6). When evaluated by size fraction, more analytical variability in PAHs was observed in the <2-mm size fraction compared to the <63-µm size fraction. The median value for the <2-mm size-fraction RPDs was 22 percent, and the range of these RPDs was similar to the range of the RPDs computed for all PAHs (table 4).

Replicate sample results can be affected by sample heterogeneity, particularly when sediment is the sample medium (Pirkey and Glodt, 1998). Additionally, when constituent concentrations are small, minor differences in analyte pair concentrations can cause large RPDs. For example, the RPD computed for fluoranthene in the <2-mm size-fraction 2016 sample collected from the Cibolo Trib 3191 site was 117 percent, but the actual concentrations only differed by 4.8 micrograms per kilogram (µg/kg) (table 6). Based on replicate analysis, no adjustment to interpretation of environmental major or trace element, PAH, or organic carbon data or rejection of individual values was needed due to variability.

Twelve environmental and replicate analyte pairs were analyzed for organic carbon concentration from samples collected at the Ecleto Runge, SAR 72, and Cibolo Trib 3191 sites in 2015 and 2016 (table 7). The RPDs for analytes in the <2-mm size fraction ranged from 21 to 35 percent (4 analyte pairs), and the RPDs for analytes in the <63-µm size fraction ranged from 0.0 to 55 percent (6 analyte pairs). The median RPD was 23 percent in the <2-mm size fraction and 8.0 percent in the <63-µm size fraction (table 4).

Six environmental and replicate analyte pairs were analyzed for streambed-sediment sample size distribution. Three analyte pairs were collected during 2015 from the Ecleto Runge, SAR 72, and Cibolo Trib 3191 sites, and three pairs were collected during 2016 from the same three sites (table 8). Overall, the size fractions associated with environmental and replicate sample pairs were similar. The small amount of variability observed in the replicate data did not affect the ability to evaluate the environmental data; therefore, no environmental streambed-sediment size data were rejected based on RPDs from this study.

Laboratory matrix spikes (hereinafter referred to as “matrix spikes”) are used to assess bias from method performance or the effects of the sample matrix (Mueller and others, 2015). Matrix spikes are environmental samples to which a laboratory adds a known volume and concentration of an analyte before analysis; analytical recoveries of the spiked analytes are expressed as percentages of expected concentrations. Computed spike recoveries are compared to expected and laboratory recoveries to evaluate matrix interferences or degradation of analytes.

Streambed-sediment samples for matrix spike analysis were collected from the same three sites (Ecleto Runge, SAR 72, and Cibolo Trib 3191) in 2015 and 2016 (tables 9 and 10). Samples in both years included <2-mm and <63-µm size-fraction samples, resulting in a total of 12 matrix spikes. Each sample was spiked with known concentrations of 17 PAHs and dissolved organic carbon (DOC) prior to analysis. Bias can be evaluated by computing percent recovery using the known spike concentration, environmental concentration in each environmental sample, and the concentration recovered from each matrix spike. The percent recovery was calculated for each matrix spike sample by using the following equation:

$$R = ((C_{spike} - C_{env})/C_{expected}) \times 100, \qquad (2)$$

where

R is recovery, in percent

C_{spike} is the concentration of the analyte in the spiked matrix sample,

C_{env} is the concentration of the analyte in the background environmental sample, and

$C_{expected}$ is the concentration of the spiked analyte expected in the sample.

When the constituent concentration in the environmental sample was a nondetected value, instead of a single percent recovery value, a possible range of percent recoveries had to be computed. The lower end of the range was the “minimum nondetection recovery” (NDRMIN in tables 9 and 10), which is computed by using the LRL (the greatest concentration of the constituent that could have been contributed by the environmental sample) as the C_{env} value in equation 2. The upper end of the range was the “maximum nondetection recovery” (NDRMAX in tables 9 and 10), which is computed by using zero (meaning the environmental sample contributed none of the constituent to the final concentration) as the C_{env} value.

Table 8. Environmental samples and replicate data for size analysis measured in streambed-sediment samples collected from three sites in the lower San Antonio River watershed, Texas, 2015–16.

[USGS, U.S. Geological Survey; mm, millimeter; ENV, environmental sample; REP, replicate sample; --, no data; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month-day-year]

USGS station number	USGS station name	Short name	Map identifier (fig. 1)	Sample date	Sample type	Bed sediment, percent smaller than 0.002 mm	Bed sediment, percent smaller than 0.004 mm	Bed sediment, percent smaller than 0.008 mm	Bed sediment, percent smaller than 0.016 mm	Bed sediment, percent smaller than 0.0625 mm	Bed sediment, percent smaller than 0.125 mm	Bed sediment, percent smaller than 0.25 mm
08186500	Ecleto Creek near Runge, Tex.	Ecleto Runge	7	04-03-2015	ENV	1	1	1	1	2	3	14
					REP	1	1	1	2	2	3	17
				06-24-2016	ENV	0.0	1	1	1	1	2	9
					REP	1	1	1	1	1	2	11
08188060	San Antonio River at State Highway 72 near Runge, Tex.	SAR 72	10	04-06-2015	ENV	4	5	5	5	9	12	21
					REP	3	3	4	4	6	9	28
				07-26-2016	ENV	16	18	19	22	47	76	97
					REP	19	21	22	25	50	84	98
290055097563400	Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.	Cibolo Trib 3191	13	04-02-2015	ENV	24	28	30	33	41	49	62
					REP	25	26	28	31	39	44	53
				06-22-2016	ENV	30	38	45	48	59	70	77
					REP	38	48	53	61	71	78	86

USGS station number	USGS station name	Short name	Map identifier (fig. 1)	Sample date	Sample type	Bed sediment, percent smaller than 0.5 mm	Bed sediment, percent smaller than 1 mm	Bed sediment, percent smaller than 2 mm	Bed sediment, percent smaller than 4 mm	Bed sediment, percent smaller than 8 mm	Bed sediment, percent smaller than 16 mm
08186500	Ecleto Creek near Runge, Tex.	Ecleto Runge	7	04-03-2015	ENV	61	88	98	100	--	--
					REP	68	90	98	100	--	--
				06-24-2016	ENV	56	85	93	96	97	100
					REP	62	91	98	99	99	100
08188060	San Antonio River at State Highway 72 near Runge, Tex.	SAR 72	10	04-06-2015	ENV	81	99	100	--	--	--
					REP	84	98	100	--	--	--
				07-26-2016	ENV	99	99	100	--	--	--
					REP	100	--	--	--	--	--
290055097563400	Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.	Cibolo Trib 3191	13	04-02-2015	ENV	77	88	97	98	100	--
					REP	69	82	92	95	100	--
				06-22-2016	ENV	83	87	93	96	100	--
					REP	93	96	98	100	--	--

Table 9. Percent recovery values for matrix spike samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	**08186500**									
USGS station name	**Ecleto Creek near Runge, Tex.**									
Short name	**Ecleto Runge**									
Map identifier (fig. 1)	**7**									
Sample date	**4/3/2015**					**4/3/2015**				
Sieve size (mm)	**2**					**0.063**				
Spike concentration (µg/kg)	**15.70**					**62.91**				
Sample type	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
2-Methylnaphthalene	<0.79	11	--	66.7	70.1	<3.3	52	--	78.5	82.7
9H-Fluorene	<0.79	13	--	78.8	82.8	<3.3	47	--	71.0	74.7
Acenaphthene	<0.79	11	--	66.7	70.1	<3.3	47	--	71.0	74.7
Acenaphthylene	<0.79	13	--	78.8	82.8	<3.3	57	--	86.1	90.6
Anthracene	<0.79	13	--	78.8	82.8	<3.3	56	--	84.6	89.0
Benzo[a]anthracene	<0.79	15	--	91.0	95.5	<3.3	61	--	92.1	97.0
Benzo[a]pyrene	<0.79	13	--	78.8	82.8	<3.3	61	--	92.1	97.0
Benzo[b]fluoranthene	<0.79	13	--	78.8	82.8	<3.3	53	--	80.0	84.2
Benzo[ghi]perylene	<0.79	10	--	60.6	63.7	<3.3	42	--	63.4	66.8
Benzo[k]fluoranthene	<0.79	9.8	--	59.4	62.4	<3.3	40	--	60.4	63.6
Chrysene	<0.79	11	--	66.7	70.1	<3.3	49	--	74.0	77.9
Dibenzo[a,h]anthracene	<0.79	13	--	78.8	82.8	<3.3	53	--	80.0	84.2
Fluoranthene	<0.79	15	--	91.0	95.5	<3.3	62	--	93.6	98.6
Indeno[1,2,3-cd]pyrene	<0.79	13	--	78.8	82.8	<3.3	54	--	81.6	85.8
Naphthalene	<0.79	11	--	66.7	70.1	<3.3	48	--	72.5	76.3
Phenanthrene	<0.79	13	--	78.8	82.8	<3.3	52	--	78.5	82.7
Pyrene	<0.79	13	--	78.8	82.8	<3.3	55	--	83.1	87.4

Table 9. Percent recovery values for matrix spike samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	08186500									
USGS station name	Ecleto Creek near Runge, Tex.—Continued									
Short name	Ecleto Runge									
Map identifier (fig. 1)	7									
Sample date	6/24/2016					6/24/2016				
Sieve size (mm)	2					0.063				
Spike concentration (µg/kg)	16.71					78.92				
Sample type	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
2-Methylnaphthalene	<0.84	13	--	74.1	77.8	<4.0	54	--	65.1	68.4
9H-Fluorene	<0.84	13	--	74.1	77.8	<4.0	53	--	63.9	67.2
Acenaphthene	<0.84	13	--	74.1	77.8	<4.0	52	--	62.7	65.9
Acenaphthylene	<0.84	13	--	74.1	77.8	<4.0	52	--	62.7	65.9
Anthracene	<0.84	13	--	74.1	77.8	<4.0	51	--	61.5	64.6
Benzo[a]anthracene	<0.84	17	--	96.9	101.7	<4.0	67	--	80.8	84.9
Benzo[a]pyrene	<0.84	13	--	74.1	77.8	<4.0	52	--	62.7	65.9
Benzo[b]fluoranthene	<0.84	15	--	85.5	89.8	<4.0	61	--	73.6	77.3
Benzo[ghi]perylene	<0.84	14	--	79.8	83.8	<4.0	58	--	69.9	73.5
Benzo[k]fluoranthene	<0.84	12	--	68.4	71.8	<4.0	51	--	61.5	64.6
Chrysene	<0.84	12	--	68.4	71.8	<4.0	46	--	55.5	58.3
Dibenzo[a,h]anthracene	<0.84	15	--	85.5	89.8	<4.0	61	--	73.6	77.3
Fluoranthene	<0.84	12	--	68.4	71.8	<4.0	47	--	56.7	59.6
Indeno[1,2,3-cd]pyrene	<0.84	12	--	68.4	71.8	<4.0	49	--	59.1	62.1
Naphthalene	<0.84	12	--	68.4	71.8	<4.0	51	--	61.5	64.6
Phenanthrene	<0.84	15	--	85.5	89.8	<4.0	60	--	72.4	76.0
Pyrene	<0.84	14	--	79.8	83.8	<4.0	56	--	67.5	71.0

Table 9. Percent recovery values for matrix spike samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	08188060									
USGS station name	San Antonio River at State Highway 72 near Runge, Tex.									
Short name	SAR 72									
Map identifier (fig. 1)	10									
Sample date	4/6/2015					4/6/2015				
Sieve size (mm)	2					0.063				
Spike concentration (µg/kg)	15.45					40.25				
Sample type	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
2-Methylnaphthalene	<0.79	11	--	67.7	71.2	<2.0	23	--	54.4	57.1
9H-Fluorene	<0.79	13	--	80.0	84.1	<2.0	29	--	68.6	72.0
Acenaphthene	<0.79	12	--	73.9	77.7	<2.0	26	--	61.5	64.6
Acenaphthylene	<0.79	13	--	80.0	84.1	<2.0	28	--	66.3	69.6
Anthracene	<0.79	13	--	80.0	84.1	<2.0	25	--	59.2	62.1
Benzo[a]anthracene	<0.79	17	--	105	110	11	51	99.5	--	--
Benzo[a]pyrene	<0.79	13	--	80.0	84.1	13	44	82.6	--	--
Benzo[b]fluoranthene	0.97	14	85.3	--	--	22	49	78.7	--	--
Benzo[ghi]perylene	0.87	16	98.0	--	--	13	37	69.5	--	--
Benzo[k]fluoranthene	<0.79	12	--	73.9	77.7	8.3	40	82.4	--	--
Chrysene	<0.79	12	--	73.9	77.7	16	40	71.1	--	--
Dibenzo[a,h]anthracene	<0.79	18	--	111	117	3.2	33	75.9	--	--
Fluoranthene	<0.79	15	--	92.4	97.1	23	54	85.4	--	--
Indeno[1,2,3-cd]pyrene	<0.79	17	--	105	110	11	39	76.1	--	--
Naphthalene	<0.79	11	--	67.7	71.2	<2.0	25	--	59.2	62.1
Phenanthrene	<0.79	13	--	80.0	84.1	7.3	42	88.3	--	--
Pyrene	<0.79	14	--	86.2	90.6	19	49	82.7	--	--

Table 9. Percent recovery values for matrix spike samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	08188060									
USGS station name	San Antonio River at State Highway 72 near Runge, Tex.—Continued									
Short name	SAR 72									
Map identifier (fig. 1)	10									
Sample date	7/26/2016					7/26/2016				
Sieve size (mm)	2					0.063				
Spike concentration (µg/kg)	18.85					35.65				
Sample type	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
2-Methylnaphthalene	<0.94	16	--	80.8	84.9	<1.8	18	--	48.1	50.5
9H-Fluorene	<0.94	17	--	85.9	90.2	<1.8	20	--	54.7	56.1
Acenaphthene	<0.94	17	--	85.9	90.2	<1.8	20	--	54.7	56.1
Acenaphthylene	<0.94	17	--	85.9	90.2	<1.8	21	--	57.4	58.9
Anthracene	<0.94	20	--	101	106	<1.8	23	--	62.9	64.5
Benzo[a]anthracene	2.5	24	112	--	--	4.9	26	64.1	--	--
Benzo[a]pyrene	2.9	22	101	--	--	6	27	64.8	--	--
Benzo[b]fluoranthene	5.8	29	118	--	--	11	37	79.3	--	--
Benzo[ghi]perylene	3	19	87.0	--	--	<1.8	18	--	49.2	50.5
Benzo[k]fluoranthene	1.7	19	92.5	--	--	3.4	24	61.5	--	--
Chrysene	3.2	22	99.8	--	--	6.1	27	64.7	--	--
Dibenzo[a,h]anthracene	<0.94	18	--	91.0	95.5	<1.8	18	--	49.2	50.5
Fluoranthene	5.3	26	108	--	--	9.8	31	68.2	--	--
Indeno[1,2,3-cd]pyrene	3	19	87.0	--	--	<1.8	24	--	65.6	67.3
Naphthalene	<0.94	15	--	75.8	79.6	<1.8	18	--	49.2	50.5
Phenanthrene	<0.94	19	--	96.0	101	<1.8	22	--	60.1	61.7
Pyrene	4.5	24	103	--	--	8.2	29	66.1	--	--

Table 9. Percent recovery values for matrix spike samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	290055097563400									
USGS station name	Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.									
Short name	Cibolo Trib 3191									
Map identifier (fig. 1)	13									
Sample date	4/2/2015					4/2/2015				
Sieve size (mm)	2					0.063				
Spike concentration (µg/kg)	20.68					35.39				
Sample type	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
2-Methylnaphthalene	<1.0	16	--	73.8	77.4	<1.8	28	--	75.3	79.1
9H-Fluorene	<1.0	16	--	73.8	77.4	<1.8	30	--	80.7	84.8
Acenaphthene	<1.0	15	--	69.2	72.5	<1.8	26	--	69.9	73.5
Acenaphthylene	<1.0	18	--	83.0	87.0	<1.8	31	--	83.4	87.6
Anthracene	<1.0	18	--	83.0	87.0	<1.8	32	--	86.0	90.4
Benzo[a]anthracene	<1.0	19	--	87.6	91.9	<1.8	39	--	105	110
Benzo[a]pyrene	<1.0	20	--	92.3	96.7	<1.8	36	--	96.8	102
Benzo[b]fluoranthene	1.2	18	82.3	--	--	<1.8	30	--	80.7	84.8
Benzo[ghi]perylene	<1.0	14	--	64.6	67.7	<1.8	24	--	64.5	67.8
Benzo[k]fluoranthene	<1.0	13	--	60.0	62.9	<1.8	25	--	67.2	70.6
Chrysene	<1.0	15	--	69.2	72.5	<1.8	28	--	75.3	79.1
Dibenzo[a,h]anthracene	<1.0	17	--	78.4	82.2	<1.8	30	--	80.7	84.8
Fluoranthene	<1.0	21	--	96.9	102	1.8	35	94.1	--	--
Indeno[1,2,3-cd]pyrene	<1.0	17	--	78.4	82.2	<1.8	30	--	80.7	84.8
Naphthalene	<1.0	15	--	69.2	72.5	<1.8	26	--	69.9	73.5
Phenanthrene	<1.0	16	--	73.8	77.4	<1.8	29	--	78.0	81.9
Pyrene	<1.0	17	--	78.4	82.2	<1.8	31	--	83.4	87.6

Table 9. Percent recovery values for matrix spike samples for polycyclic aromatic hydrocarbons measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; µg/kg, micrograms per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	290055097563400									
USGS station name	Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.—Continued									
Short name	Cibolo Trib 3191									
Map identifier (fig. 1)	13									
Sample date	6/22/2016					6/22/2016				
Sieve size (mm)	2					0.063				
Spike concentration (µg/kg)	24.86					39.65				
Sample type	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (µg/kg)**	**SPK (µg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
2-Methylnaphthalene	<1.2	18	--	69.1	72.4	<2.0	21	--	50.4	53.0
9H-Fluorene	<1.2	19	--	72.9	76.4	<2.0	21	--	50.4	53.0
Acenaphthene	<1.2	18	--	69.1	72.4	<2.0	22	--	52.8	55.5
Acenaphthylene	<1.2	18	--	69.1	72.4	<2.0	21	--	50.4	53.0
Anthracene	<1.2	18	--	69.1	72.4	<2.0	25	--	60.0	63.1
Benzo[a]anthracene	<1.2	25	--	95.9	101	3.1	27	63.2	--	--
Benzo[a]pyrene	<1.2	19	--	72.9	76.4	16	25	44.9	--	--
Benzo[b]fluoranthene	3	26	93.3	--	--	8.2	33	69.0	--	--
Benzo[ghi]perylene	2	21	78.2	--	--	3.9	26	59.7	--	--
Benzo[k]fluoranthene	<1.2	16	--	61.4	64.4	2.9	24	56.4	--	--
Chrysene	<1.2	17	--	65.2	68.4	4.5	26	58.9	--	--
Dibenzo[a,h]anthracene	<1.2	20	--	76.7	80.5	<2.0	24	--	57.6	60.5
Fluoranthene	1.7	19	71.5	--	--	6.3	30	65.3	--	--
Indeno[1,2,3-cd]pyrene	1.7	18	67.8	--	--	3.9	26	59.7	--	--
Naphthalene	<1.2	17	--	65.2	68.4	<2.0	21	--	50.4	53.0
Phenanthrene	<1.2	22	--	84.4	88.5	2.3	23	54.8	--	--
Pyrene	1.8	21	78.8	--	--	5.8	29	63.8	--	--

Table 10. Percent recovery values for matrix spike samples for organic carbon measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

[USGS, U.S. Geological Survey; mm, millimeter; mg/kg, milligrams per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	**08186500**									
USGS station name	**Ecleto Creek near Runge, Tex.**									
Short name	**Ecleto Runge**									
Map identifier (fig. 1)	**7**									
Sample date	**4/3/2015**					**4/3/2015**				
Sieve size (mm)	**2**					**0.063**				
Spike concentration (mg/kg)	**19,740**					**38,430**				
Sample type	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
Organic carbon	770	22,000	107	--	--	20,000	58,000	99.3	--	--

	Environmental and spike sample information by USGS station number									
USGS station number	**08186500**									
USGS station name	**Ecleto Creek near Runge, Tex.—Continued**									
Short name	**Ecleto Runge**									
Map identifier (fig. 1)	**7**									
Sample date	**6/24/2016**					**6/24/2016**				
Sieve size (mm)	**2**					**0.063**				
Spike concentration (mg/kg)	**19,860**					**33,110**				
Sample type	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
Organic carbon	1,100	20,000	95.4	--	--	24,000	58,000	102	--	--

Table 10. Percent recovery values for matrix spike samples for organic carbon measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; mg/kg, milligrams per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	08188060									
USGS station name	San Antonio River at State Highway 72 near Runge, Tex.									
Short name	SAR 72									
Map identifier (fig. 1)	10									
Sample date	4/6/2015					4/6/2015				
Sieve size (mm)	2					0.063				
Spike concentration (mg/kg)	19,520					31,930				
Sample type	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
Organic carbon	<1,900	20,000	--	93.4	102	13,000	43,000	95.7	--	--

	Environmental and spike sample information by USGS station number									
USGS station number	08188060									
USGS station name	San Antonio River at State Highway 72 near Runge, Tex.—Continued									
Short name	SAR 72									
Map identifier (fig. 1)	10									
Sample date	7/26/2016					7/26/2016				
Sieve size (mm)	2					0.063				
Spike concentration (mg/kg)	32,320					32,590				
Sample type	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
Organic carbon	9,100	40,000	96.6	--	--	19,000	47,000	91.1	--	--

Table 10. Percent recovery values for matrix spike samples for organic carbon measured in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.—Continued

[USGS, U.S. Geological Survey; mm, millimeter; mg/kg, milligrams per kilogram; ENV, environmental sample concentration; SPK, spike sample concentration; NDRMIN, nondetection percent recovery minimum; NDRMAX, nondetection percent recovery maximum; <, less than; --, not calculated; SAR, San Antonio River; Trib, tributary. Sample dates are formatted as month/day/year]

	Environmental and spike sample information by USGS station number									
USGS station number	290055097563400									
USGS station name	Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.									
Short name	Cibolo Trib 3191									
Map identifier (fig. 1)	13									
Sample date	4/2/2015					4/2/2015				
Sieve size (mm)	2					0.063				
Spike concentration (mg/kg)	37,980					35,340				
Sample type	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
Organic carbon	9,800	49,000	103	--	--	12,000	47,000	99.3	--	--

	Environmental and spike sample information by USGS station number									
USGS station number	290055097563400									
USGS station name	Unnamed tributary to Cibolo Creek at Farm to Market Road 3191 near Falls City, Tex.—Continued									
Short name	Cibolo Trib 3191									
Map identifier (fig. 1)	13									
Sample date	6/22/2016					6/22/2016				
Sieve size (mm)	2					0.063				
Spike concentration (mg/kg)	44,170					39,950				
Sample type	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**	**ENV (mg/kg)**	**SPK (mg/kg)**	**Recovery (percent)**	**NDRMIN (percent)**	**NDRMAX (percent)**
Organic carbon	13,000	56,000	98.0	--	--	21,000	56,000	91.9	--	--

Mean recoveries for each PAH and for DOC were computed by averaging all percent recovery values for each analyte (table 11). The average of the nondetection percent recovery range [(NRDMIN + NDRMAX)/2] was used if the environmental sample concentration was a nondetection. Based on the range of mean recoveries (66.2 to 92.7 percent) calculated for each PAH, method accuracy appears to be generally consistent to varying degrees for all analytes in both streambed-sediment size fractions. Given the consistency of percent recovery values, potential corrections to the PAH concentration data were considered to be minor and unnecessary for the purposes of this study. The mean recovery for DOC (98.0 percent) was much closer to expected recoveries, indicating little bias in the DOC measurements; therefore, no recovery corrections were applied to the DOC data.

Land-Cover Changes Associated with Oil and Natural-Gas Production

Changes in oil and natural-gas production-related land-cover features during the study period can be seen by comparing the 2008 and 2015 imagery. Examples of the land-cover features of interest described in this section are labeled on figure 2. In one 6.8-mi^2 area, more than 20 well pads were added between 2008 and 2015 (fig. 4). Imagery of a smaller area near the San Antonio River (approximately 1 mi^2) shows the addition of eight well pads, one storage pond, three runoff ponds, one recently removed runoff pond, and multiple new roads (fig. 5). Summary statistics derived from the 2008 and 2015 imagery (table 12) were used to characterize changes in land cover resulting from the increase in oil and natural-gas production activities within the image analysis boundary (fig. 1).

Table 11. Mean recovery by analyte in matrix spike analysis of streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

[<, less than; mm, millimeter; µm, micrometer]

Analyte	Mean recovery with standard deviation (percent)					
	All samples	Standard deviation	<2-mm size fraction	Standard deviation	<63-µm size fraction	Standard deviation
2-Methylnaphthalene	68.7	11.1	73.8	5.4	63.6	13.4
9H-Fluorene	73.0	10.9	79.5	5.2	66.4	11.5
Acenaphthene	69.3	9.3	75.0	7.1	63.6	7.9
Acenaphthylene	74.9	12.3	80.4	6.3	69.3	14.7
Anthracene	76.8	13.3	83.0	11.3	70.7	13.1
Benzo[a]anthracene	92.7	15.8	100	8.5	85.3	18.6
Benzo[a]pyrene	80.0	16.5	84.9	10.6	75.1	20.7
Benzo[b]fluoranthene	84.5	12.1	91.2	13.7	77.9	5.1
Benzo[ghi]perylene	71.3	13.1	78.9	13.3	63.7	7.9
Benzo[k]fluoranthene	68.1	10.6	70.6	12.2	65.7	9.1
Chrysene	71.4	11.0	75.3	12.4	67.5	8.6
Dibenzo[a,h]anthracene	80.0	15.9	89.0	13.3	70.9	13.4
Fluoranthene	83.6	16.1	89.4	15.3	77.9	16.1
Indeno[1,2,3-cd]pyrene	76.9	13.3	82.2	14.3	71.5	10.8
Naphthalene	66.2	8.5	70.6	3.8	61.9	10.0
Phenanthrene	79.2	11.9	85.2	7.8	73.1	12.8
Pyrene	80.5	10.6	85.5	9.1	75.4	10.1
Organic carbon	98.0	4.5	99.6	4.5	96.5	4.3

Figure 4. Examples of land-cover changes associated with oil and natural-gas production in the lower San Antonio River watershed based on *A*, 2008 imagery from the National Agricultural Imagery Program (U.S. Department of Agriculture, Natural Resources Conservation Service, 2011) and *B*, 2015 imagery from the Texas Natural Resources Information System (Texas Natural Resources Information System, 2018). The area in this figure is approximately 7 square miles.

Figure 5. Examples of land-cover changes associated with oil and natural-gas production in the lower San Antonio River watershed based on *A*, 2008 imagery from the National Agricultural Imagery Program (U.S. Department of Agriculture, Natural Resources Conservation Service, 2011) and *B*, 2015 imagery from the Texas Natural Resources Information System (Texas Natural Resources Information System, 2018). The area in this figure is approximately 1 square mile.

Table 12. Summary statistics for oil- and natural-gas-related attributes delineated using 2008 imagery from the National Agricultural Imagery Program (U.S. Department of Agriculture, Natural Resources Conservation Service, 2011) and 2015 imagery from the Texas Natural Resources Information System (TNRIS) (Texas Natural Resources Information System, 2018) for the lower San Antonio River watershed, Texas.

[NA, not applicable]

	Number identified	Surface area (acres)	Average individual size (acres)	Percentage of land covered in the study area[1]
2008				
Well pads	75	128	1.71	0.022
Oil- and natural-gas-related features	12	35	2.90	0.006
Roads	67	38	0.56	0.006
Storage ponds	1	1	0.96	0.000
Runoff ponds	5	3	0.52	0.000
Total impervious surface associated with oil- and natural-gas production[2]	NA	201	NA	0.034
2015				
Well pads	1,340	3,920	2.93	0.663
Oil- and natural-gas-related features	247	897	3.63	0.152
Roads	1,182	573	0.48	0.097
Storage ponds	127	393	3.09	0.066
Runoff ponds	112	120	1.07	0.020
Total impervious surface associated with oil- and natural-gas production[2]	NA	5,390	NA	0.912

[1] Study area is 591,049 acres.

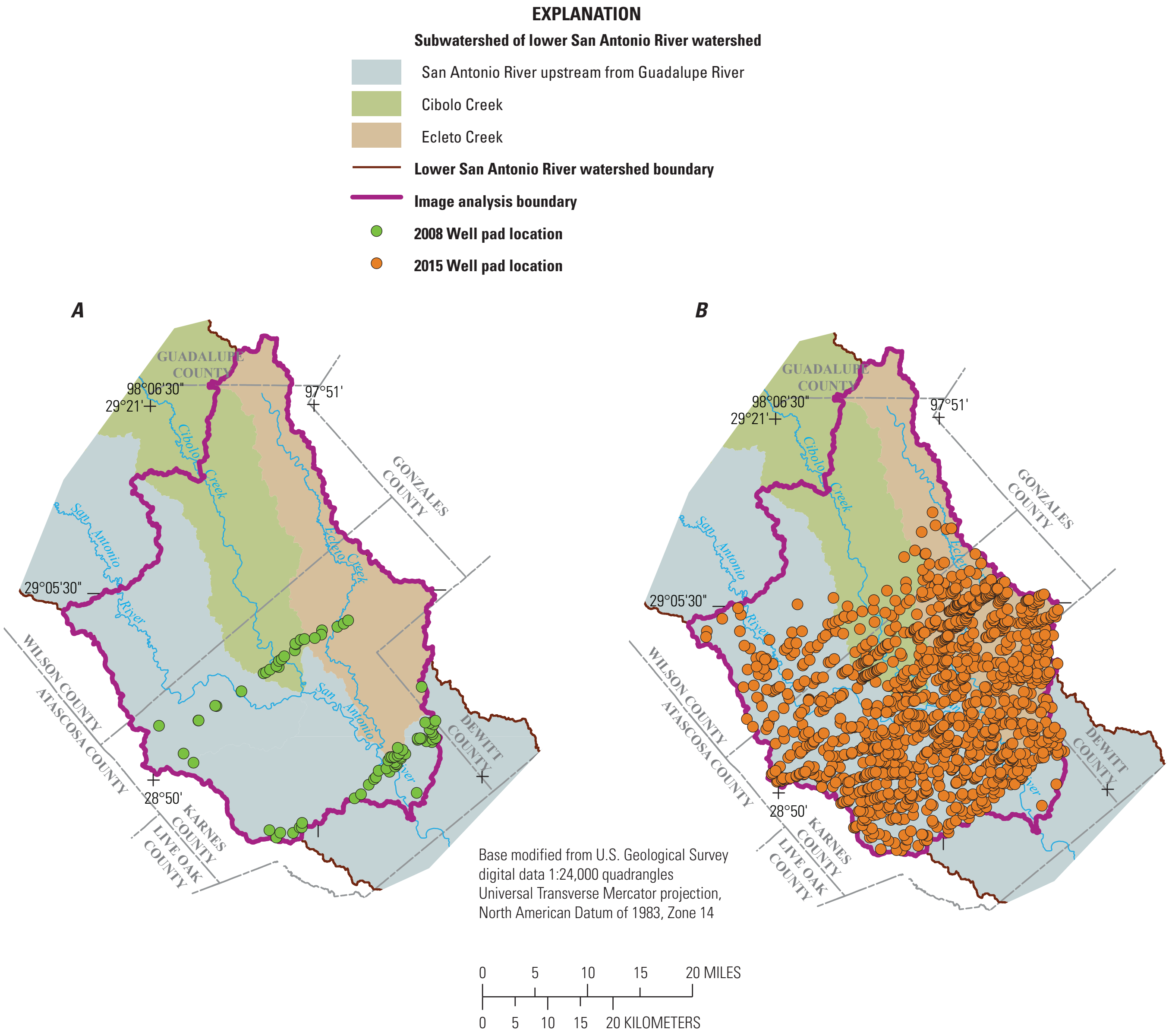
[2] Total impervious surface associated with oil and natural-gas production was calculated as the sum of the areas of all well pads, oil- and natural-gas-related features, and roads.

Well Pads

Well pads accounted for the largest land-cover change among the categories defined and delineated within the study area (fig. 6; table 12). The total number of well pads increased from 75 to 1,340 (net increase of 1,265) between 2008 and 2015. The number of new well pads (1,275) is slightly greater than the net increase in well pads (1,265) because 10 of the 75 well pads delineated in the 2008 imagery either had returned to a vegetated state or were converted to another attribute in the 2015 imagery. The surface area associated with well pads increased from 128 acres to 3,920 acres (net increase of 3,792 acres) between 2008 and 2015. The average size of a well pad was smaller in 2008 (1.71 acres) than in 2015 (2.93 acres). The total percentage of the study area accounted for by the increase in well pads changed from 0.022 percent in 2008 to 0.663 percent in 2015, which is an increase of approximately thirtyfold.

Oil and Natural-Gas Production-Related Features

Oil and natural-gas production-related features accounted for the second largest change (in surface area acres) in land cover associated with oil and natural-gas production activities (table 12). The total number of oil and natural-gas production-related features increased from 12 to 247 between 2008 and 2015. The areal coverage associated with oil and natural-gas production-related features increased from 35 acres to 897 acres. The average size of an oil and natural-gas production-related feature was 2.90 acres in 2008 and 3.63 acres in 2015, both of which were larger than the corresponding average well-pad sizes in 2008 (1.71 acres) and 2015 (2.93 acres). The total percentage of the study area accounted for by oil and natural-gas production-related features increased from 0.006 percent in 2008 to 0.152 percent in 2015.



Base modified from U.S. Geological Survey digital data 1:24,000 quadrangles
Universal Transverse Mercator projection,
North American Datum of 1983, Zone 14

Figure 6. Comparison of well-pad locations for *A*, the 2008 imagery from the National Agricultural Imagery Program (U.S. Department of Agriculture, Natural Resources Conservation Service, 2011) and *B*, the 2015 imagery from the Texas Natural Resources Information System (Texas Natural Resources Information System, 2018) within the image analysis area of the lower San Antonio River watershed oil and natural-gas production.

Roads

Roads associated with oil and natural-gas production activities also accounted for a substantial change in land cover (surface area) during the study period (table 12). The number of individual roads associated with oil and natural-gas production activities increased from 67 to 1,182 between 2008 and 2015. The areal coverage from roads associated with oil and natural-gas production activities increased from 38 acres in 2008 to 573 acres in 2015, a net increase of 535 acres. The average land-surface area represented by delineated roads associated with an individual oil and natural-gas production activity was 0.56 acres in 2008 and 0.48 acres in 2015, indicating little difference between years. The total percentage of the study area accounted for by roads associated with oil and natural-gas production activities increased more than sixteenfold from 0.006 percent in 2008 to 0.097 percent in 2015.

Storage Ponds

Patterns of change observed for ponds varied based on pond type (table 12). The number of storage ponds changed from 1 in 2008 to 127 in 2015. Storage ponds can be used to provide water for wells and thus are expected to remain on the landscape as long as there is a demand for the water, which can be indefinite because of ongoing drilling in the region. The average surface area of storage ponds in 2015 was 3.09 acres, and storage ponds covered 393 acres, or 0.066 percent of the study area.

Runoff Ponds

The number of runoff ponds changed from 5 in 2008 to 112 in 2015 (table 12). Runoff ponds are used to capture runoff associated with drilling activities; once drilling is completed, the runoff pond is typically removed from the well-pad area. Therefore, runoff ponds are likely to be largely absent except in areas of active drilling operations.

Impervious Surface

Impervious surface in this study is defined as land cover consisting of well pads, oil- and gas-related features, or roads (table 12). The areal coverage associated with impervious surface increased from 201 acres to 5,390 acres (net increase of 5,189) between 2008 and 2015. The total percentage of the study area accounted for by impervious surface resulting from oil and natural-gas production activities increased from 0.034 percent to 0.912 percent, which is an increase of approximately 27-fold. Collectively, 0.878 percent of the study area was converted to new impervious surface between 2008 and 2015. If the area associated with new storage ponds (0.066 percent) is added to the estimate of total land-cover changes as a result of oil and natural-gas production, then 0.944 percent of the study area was altered between 2008 and 2015.

Continued Changes Since 2015

Oil and natural-gas production activities in the study area have continued to increase since 2015, and the resulting land-cover changes are likely to continue to increase proportionally. In 2015, there were 7,574 permitted oil wells and 3,886 permitted gas wells in the Eagle Ford Group throughout Texas, for a total of 11,460 wells at the time the 2015 imagery was produced (Railroad Commission of Texas, 2018). As of April 2018, there were 12,219 permitted oil wells, 5,866 permitted gas wells, and 2,482 pending permits for wells completed in the Eagle Ford Group throughout Texas (Railroad Commission of Texas, 2018). If all pending permits are completed, then the number of oil and natural-gas wells within the Eagle Ford Group as a whole could increase to 20,567 wells, representing a 1.8-fold increase as compared to 2015. Assuming that changes in impervious cover within the study area will increase proportionally to the Eagle Ford Group as a whole, then impervious cover is estimated to increase from 0.912 percent (table 12) to 1.64 percent of the total study area.

Concentrations of Selected Constituents

For this report, parts of Wilson, Karnes, and DeWitt Counties are considered the area of active oil and natural-gas production in the study area (fig. 1). The following sites were considered upstream from most active oil and natural-gas production: (1) SAR Elmendorf, SAR Trib 220, and SAR 541 sites in the San Antonio River watershed; (2) Cibolo St. Hedwig, Cibolo Trib 332, and Cibolo 537 sites in the Cibolo Creek watershed, and (3) the Ecleto 3335 site in the Ecleto Creek watershed. The remaining 10 sampling sites (fig. 1; table 1) were considered to be within the area of active oil and natural-gas production.

Constituents in Surface-Water Samples

Surface-water samples collected from five of the sites were analyzed for concentrations of a broad range of major and trace elements and organic constituents that might be associated with oil and natural-gas production. To help put concentrations of select major and trace elements and organic constituents in the surface-water samples in context, detected concentrations were compared to the EPA's drinking water standards and health advisories (EPA, 2018b) and national recommended aquatic life criteria for freshwater (EPA, 2018c) (table 13). EPA bases aquatic life criteria on how much of a chemical can be present in surface water before it is likely to harm plant and animal life.

Table 13. Drinking water standards and health advisories (U.S. Environmental Protection Agency, 2018b) and national recommended aquatic life criteria (U.S. Environmental Protection Agency, 2018c) that were used to evaluate the contaminant concentrations in surface-water samples collected from five sites in the lower San Antonio River watershed, Texas, 2015–17.

[MCL, maximum contaminant level; DWEL, drinking water equivalent level; µg/L, micrograms per liter; --, no data; <, less than; E, estimated]

Constituent	Drinking water standards	Health advisories		Aquatic life criteria		Concentrations in surface-water samples	
	MCL (µg/L)	DWEL (µg/L)	Lifetime (µg/L)	Chronic (µg/L)	Acute (µg/L)	Minumum (µg/L)	Maximum[1] (µg/L)
Major and trace elements							
Calcium	--	--	--	--	--	16,600	37,400
Sodium	--	--	--	--	--	13,200	49,900
Bromide	--	--	--	--	--	37	170
Chloride	--	--	--	230,000	860,000	9,700	57,100
Sulfate	--	--	--	--	--	11,600	50,800
Sulfide	--	--	--	--	--	49	190
Aluminum	--	--	--	--	--	<20	130
Barium	2,000	7,000	--	--	--	24,500	51,600
Cadmium	5	20	5	0.72	1.8	<0.6	<0.6
Chromium	--	--	--	--	--	<0.6	<0.6
Iron	--	--	--	1,000	--	31.2	135
Lead	15	--	--	2.5	65	0.078	0.263
Lithium	--	--	--	--	--	3.56	16.4
Manganese	--	1,600	300	--	--	0.86	6.38
Molybdenum	--	200	40	--	--	<2.2	1.53
Nickel	--	700	100	52	470	<1.2	2.3
Strontium	--	20,000	4,000	--	--	88.1	266
Zinc	--	10,000	2,000	120	120	<2.0	3.1
Arsenic	10	10	--	150	340	1.4	2.7
Boron	--	7,000	6,000	--	--	51	153
Semivolatile organic compounds							
2,4,6-Trichlorophenol	--	10	--	--	--	<0.34	0.03
2,4-Dichlorophenol	--	100	20	--	--	<0.36	0.05
4-Nitrophenol	--	300	60	--	--	<0.52	0.36
Pentachlorophenol	1	200	40	15	19	<0.6	0.8
9H-Fluorene	--	1,000	--	--	--	<0.034	0.02
Acenaphthene	--	2,000	--	--	--	<0.28	0.02
Benzo[a]pyrene	0.2	--	--	--	--	<0.32	0.08
Benzo[b]fluoranthene	--	--	--	--	--	<0.30	E0.12
Benzo[ghi]perylene	--	--	--	--	--	<0.38	E0.13
Benzo[k]fluoranthene	--	--	--	--	--	<0.30	E0.07
Chrysene	--	--	--	--	--	<0.32	E0.08
Diethyl phthalate	--	30,000	--	--	--	<0.62	E0.11
Di-n-butyl phthalate	--	4,000	--	--	--	<2.80	E0.27
Di-n-octyl phthalate	6	700	--	--	--	<0.6	0.1
Fluoranthene	--	--	--	--	--	<0.30	0.14
Indeno[1,2,3-cd]pyrene	--	--	--	--	--	<0.38	E0.13
Isophorone	--	7,000	100	--	--	<0.26	0.07

Table 13. Drinking water standards and health advisories (U.S. Environmental Protection Agency, 2018b) and national recommended aquatic life criteria (U.S. Environmental Protection Agency, 2018c) that were used to evaluate the contaminant concentrations in surface-water samples collected from five sites in the lower San Antonio River watershed, Texas, 2015–17.—Continued

[MCL, maximum contaminant level; DWEL, drinking water equivalent level; µg/L, micrograms per liter; --, no data; <, less than; E, estimated]

Constituent	Drinking water standards	Health advisories		Aquatic life criteria		Concentrations in surface-water samples	
	MCL (µg/L)	DWEL (µg/L)	Lifetime (µg/L)	Chronic (µg/L)	Acute (µg/L)	Minumum (µg/L)	Maximum[1] (µg/L)
Semivolatile organic compounds—Continued							
Naphthalene	--	700	100	--	--	<0.26	0.03
Phenanthrene	--	--	--	--	--	<0.32	0.08
Pyrene	--	--	--	--	--	<0.36	0.11
Volatile organic compounds							
Carbon disulfide	--	--	--	--	--	<0.1	E0.1
1,2,4-Trimethylbenzene	--	--	--	--	--	<0.032	0.033
Benzene	5	100	3	--	--	<0.026	0.048
Bromodichloromethane	80	100	--	--	--	<0.034	0.050
Ethylbenzene	700	3,000	700	--	--	<0.036	0.022
Hexane	--	--	--	--	--	<0.024	E0.011
m-Xylene plus p-xylene	10,000	7,000	--	--	--	<0.08	0.03
Naphthalene	--	700	100	--	--	<0.26	0.03
n-Pentane	--	--	--	--	--	<0.022	0.031
o-Xylene	10,000	7,000	--	--	--	<0.032	0.014
Toluene	1,000	3,000	--	--	--	<0.02	0.16
Trichloromethane	80	350	70	--	--	<0.03	0.21

[1] Dynamic reporting levels in some constituents can result in a maximum concentration value that appears to be less than the minimum concentration value.

Major and Trace Elements

Eighteen of the 20 major and trace elements measured in surface-water samples were detected in the samples collected from the 5 sites (Crow and others, 2018). Cadmium and chromium were not detected in any of the surface-water samples. All major and trace element concentrations were less than any of the EPA’s water-quality standards (table 13).

Sulfide was selected for analysis because of its common occurrence in produced waters (Tibbetts and others, 1992). Small concentrations of sulfide ranging from verified values less than the LRL to values slightly greater than the LRL were detected in all five surface-water samples (Crow and others, 2018). The LRL for sulfide provided by RTI was 0.10 milligram per liter (mg/L), and reported concentrations ranged from 0.049 mg/L at the Cibolo St. Hedwig site to 0.190 mg/L at the Ecleto 326 site (Crow and others, 2018). The presence of sulfide was verified but not quantified at the SAR Elmendorf site. Sulfide was not detected in samples collected in the previous study in this area (Opsahl and Crow, 2015); however, because of improved analytical methods, the LRL for sulfide used during the previous study (0.79 mg/L) was greater than the LRL used in this study, and sulfide concentrations less than 0.79 mg/L may have been present in samples collected in the previous study. The observed distribution of small sulfide concentrations, including those at sites located upstream from the area of active oil and natural-gas production, is consistent with little or no enhanced inputs of sulfide from sites within the area of active oil and natural-gas production.

Organic Constituents

Glycols are commonly used in hydraulic fracturing fluids as scale inhibitors (FracFocus Chemical Disclosure Registry, 2018). Four glycols—diethylene glycol, ethylene glycol, propylene glycol, and triethylene glycol—were analyzed for in surface-water samples collected for this study. The MDLs provided by RTI were 1 mg/L for diethylene glycol, propylene glycol, and triethylene glycol and 2 mg/L for ethylene glycol. Diethylene glycol, ethylene glycol, and triethylene glycol were detected in a water sample collected from the Ecleto 326 site at concentrations of 3.1, 11, and 3.8 mg/L, respectively (table 14). Glycols were not detected in the other four water samples collected for this study. Glycols were not detected in samples collected for the previous study

Table 14. Glycol concentrations in surface-water samples collected from five sites in the lower San Antonio River watershed, Texas, 2015–17.

[USGS, U.S. Geological Survey; mg/L, milligrams per liter; SAR, San Antonio River; St., Saint; <, less than. Dates are formatted as month-day-year]

Map identifier (fig. 1)	Short name	USGS station number	USGS station name	Date	Diethylene glycol (mg/L)	Ethylene glycol (mg/L)	Propylene glycol (mg/L)	Triethylene glycol (mg/L)
1	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	08-07-2017	<1	<2	<1	<1
4	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	10-25-2015	<1	<2	<1	<1
5	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	10-25-2015	<1	<2	<1	<1
8	Ecleto 326	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	05-20-2016	3.1	11	<1	3.8
10	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	08-03-2017	<1	<2	<1	<1

in this area (Opsahl and Crow, 2015). Because of improved analytical methods, however, the LRLs available during the previous study (1.9 to 18.7 mg/L) were greater than those used in this study, so it cannot be determined whether the increased number of glycol detections indicate a change in the environmental concentrations between studies. Although concentrations of glycols were greater than the MDLs and indicate the presence glycol in the surface water at the Ecleto 326 site, the presence of glycols does not necessarily indicate that the source is from hydraulic fracturing fluid because diethylene glycol, ethylene glycol, and triethylene glycol also have other sources including the use of diethylene and ethylene glycols in antifreeze used in vehicles (Dow Chemical Company, 2018) and the use of triethylene glycol in antibacterial air sanitizers (EPA, 2005).

Surface-water samples were analyzed for SVOCs and VOCs during this study because of their common occurrence as petroleum hydrocarbons in oil and associated produced waters (Tibbetts and others, 1992). Of the 56 SVOCs and 49 VOCs analyzed for during this study, there were 30 low-level detections of 20 different SVOCs and 23 low-level detections of 12 different VOCs in the 5 water samples (table 15). None of the detected SVOCs and VOCs exceeded any of the EPA's water-quality standards (table 13), including drinking water maximum contaminant levels (MCLs). The benzene concentrations in the surface-water samples also were less than the EPA's health advisory criteria for lifetime exposure for benzene (3 µg/L), which is less than the MCL for benzene (5 µg/L).

Seventeen SVOCs were detected in the sample collected from the SAR Elmendorf site, 4 were detected in the water sample collected from the SAR 72 site, and 3 each were detected in the water samples collected from the Cibolo St. Hedwig, Cibolo Falls City, and Ecleto 326 sites (table 15). The concentrations of SVOCs detected in the SAR Elmendorf sample were generally greater that those detected in the other four water samples and ranged from 0.02 µg/L for 9H-fluorene and acenaphthene to 0.36 µg/L for 4-nitrophenol, with a median detected concentration of 0.11 µg/L. The SVOC concentrations detected in the other four samples ranged from an estimated 0.01 µg/L for 2,4-dichlorophenol in the Cibolo Falls City sample to 0.8 µg/L for pentachlorophenol in the Cibolo St. Hedwig sample, with a median detected concentration of 0.03 µg/L.

The majority of VOCs were detected in samples from the main stem of the San Antonio River (table 15). Eleven VOCs were detected in the water sample collected from the SAR Elmendorf site (upstream from the area of oil and natural-gas production), and 9 were detected in the sample collected from the SAR 72 site (downstream from the area of oil and natural-gas production) (fig. 1). The VOC concentrations detected in the samples collected from SAR Elmendorf and SAR 72 were similar. VOC concentrations in the SAR Elmendorf sample ranged from 0.012 µg/L for n-pentane to 0.16 µg/L for toluene, with a median of 0.03 µg/L. VOC concentrations in the SAR 72 sample ranged from 0.01 µg/L for trichloromethane to an estimated 0.1 µg/L for carbon disulfide, with a median of 0.03 µg/L.

Table 15. Summary of semivolatile organic compound and volatile organic compound detections in surface-water samples collected at five sites in the lower San Antonio River watershed, Texas, 2015–17.

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; SAR, San Antonio River; St., Saint; --, not detected; E, estimated; M, presence verified but not quantified. Dates are formatted as month-day-year]

Map identifier (fig. 1)	Short name	USGS station number	USGS station name	Date	Sample start time	Semivolatile organic compounds					
						2,4,6-Trichlorophenol, unfiltered (µg/L)	2,4-Dichlorophenol, unfiltered (µg/L)	4-Nitrophenol, unfiltered (µg/L)	Pentachlorophenol, unfiltered (µg/L)	9H-Fluorene, unfiltered (µg/L)	Acenaphthene, unfiltered (µg/L)
Sites upstream from the area of active oil and natural-gas production											
1	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	08-07-2017	1605	--	--	0.36	0.2	0.02	0.02
4	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	10-25-2015	1700	0.02	--	--	0.8	--	--
Sites within the area of active oil and natural-gas production											
5	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	10-25-2015	1400	--	E0.01	--	E0.8	--	--
8	Ecleto 326	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	05-20-2016	1030	0.03	0.05	--	--	--	--
10	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	08-03-2017	1530	--	--	--	0.1	--	--

Map identifier (fig. 1)	Short name	USGS station number	USGS station name	Date	Sample start time	Semivolatile organic compounds						
						Benzo[a]pyrene, unfiltered (µg/L)	Benzo[b]fluoranthene, unfiltered (µg/L)	Benzo[ghi]perylene, unfiltered (µg/L)	Benzo[k]fluoranthene, unfiltered (µg/L)	Chrysene, unfiltered (µg/L)	Diethyl phthalate, unfiltered (µg/L)	Di-n-butyl phthalate, unfiltered (µg/L)
Sites upstream from the area of active oil and natural-gas production												
1	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	08-07-2017	1605	0.08	E0.12	E0.13	E0.07	E0.08	E0.11	E0.27
4	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	10-25-2015	1700	--	--	--	--	--	--	--
Sites within the area of active oil and natural-gas production												
5	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	10-25-2015	1400	--	--	--	--	--	--	--
8	Ecleto 326	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	05-20-2016	1030	--	--	--	--	--	--	--
10	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	08-03-2017	1530	--	E0.02	--	--	--	--	--

Table 15. Summary of semivolatile organic compound and volatile organic compound detections in surface-water samples collected at five sites in the lower San Antonio River watershed, Texas, 2015–17.—Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; SAR, San Antonio River; St., Saint; --, not detected; E, estimated; M, presence verified but not quantified. Dates are formatted as month-day-year]

Map identifier (fig. 1)	Short name	USGS station number	USGS station name	Date	Sample start time	Semivolatile organic compounds						
						Di-n-octyl phthalate, unfiltered (µg/L)	Fluoranthene, unfiltered (µg/L)	Indeno[1,2,3-cd]pyrene, unfiltered (µg/L)	Isophorone, unfiltered (µg/L)	Naphthalene, unfiltered (µg/L)	Phenanthrene, unfiltered (µg/L)	Pyrene, unfiltered (µg/L)
Sites upstream from the area of active oil and natural-gas production												
1	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	08-07-2017	1605	0.1	0.14	E0.13	--	0.03	0.08	0.11
4	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	10-25-2015	1700	--	--	--	0.03	--	--	--
Sites within the area of active oil and natural-gas production												
5	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	10-25-2015	1400	--	--	--	E0.04	--	--	--
8	Ecleto 326	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	05-20-2016	1030	--	--	--	0.07	--	--	--
10	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	08-03-2017	1530	--	0.02	--	--	--	--	0.02

Map identifier (fig. 1)	Short name	USGS station number	USGS station name	Date	Sample start time	Volatile organic compounds					
						Carbon disulfide, unfiltered (µg/L)	1,2,4-Trimethylbenzene, unfiltered (µg/L)	Benzene, unfiltered (µg/L)	Bromodichloromethane, unfiltered (µg/L)	Ethylbenzene, unfiltered (µg/L)	Hexane, unfiltered (µg/L)
Sites upstream from the area of active oil and natural-gas production											
1	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	08-07-2017	1605	M	0.033	E0.016	0.032	0.013	--
4	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	10-25-2015	1700	--	--	--	0.05	--	--
Sites within the area of active oil and natural-gas production											
5	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	10-25-2015	1400	--	--	--	--	--	--
8	Ecleto 326	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	05-20-2016	1030	M	--	--	--	--	--
10	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	08-03-2017	1530	E0.1	--	0.048	--	0.022	E0.011

Table 15. Summary of semivolatile organic compound and volatile organic compound detections in surface-water samples collected at five sites in the lower San Antonio River watershed, Texas, 2015–17.—Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; SAR, San Antonio River; St., Saint; --, not detected; E, estimated; M, presence verified but not quantified. Dates are formatted as month-day-year]

Map identifier (fig. 1)	Short name	USGS station number	USGS station name	Date	Sample start time	Volatile organic compounds					
						m-Xylene plus p-xylene, unfiltered (µg/L)	Naphthalene, unfiltered (µg/L)	n-Pentane, unfiltered (µg/L)	o-Xylene, unfiltered (µg/L)	Toluene, unfiltered (µg/L)	Trichloromethane, unfiltered (µg/L)
Sites upstream from the area of active oil and natural-gas production											
1	SAR Elmendorf	08181800	San Antonio River near Elmendorf, Tex.	08-07-2017	1605	0.03	0.03	0.012	0.014	0.16	0.05
4	Cibolo St. Hedwig	08185065	Cibolo Creek near Saint Hedwig, Tex.	10-25-2015	1700	--	--	--	--	--	0.21
Sites within the area of active oil and natural-gas production											
5	Cibolo Falls City	08186000	Cibolo Creek near Falls City, Tex.	10-25-2015	1400	--	--	--	--	--	--
8	Ecleto 326	08186550	Ecleto Creek at County Road 326 near Runge, Tex.	05-20-2016	1030	--	--	--	--	--	--
10	SAR 72	08188060	San Antonio River at State Highway 72 near Runge, Tex.	08-03-2017	1530	0.03	--	0.031	0.012	0.09	0.01

The SAR Elmendorf site is the site from which the water sample with the greatest number of detections and, generally, the greatest concentrations of SVOCs and VOCs was collected (table 15). Compared with samples collected for the previous study in this area (Opsahl and Crow, 2015), in general, a greater number of SVOCs and VOCs were detected in samples collected for this study, but at smaller concentrations. The greatest SVOC and VOC concentrations from the previous study also were observed in samples collected from sites upstream from the area of active oil and natural-gas production and just downstream from urban areas. Many SVOCs and VOCs are commonly found in urban settings (Lopes and Dionne, 1998; Bender and others, 2009), and previous studies (Ging, 1999; Bush and others, 2000) confirm that SVOCs and VOCs have been detected in streams in the San Antonio, Tex., area at concentrations similar to those detected in this study. The SAR Elmendorf site is upstream from the area of active oil and natural-gas production and just downstream from San Antonio (fig. 1). The SAR 72 site is further downstream from San Antonio and is within the area of active oil and natural-gas production. The SVOCs and VOCs that were detected at the SAR 72 site also were detected upstream at the SAR Elmendorf site, indicating that the likely source of most SVOCs and VOCs in the study area is the upstream urbanized part of the lower San Antonio River watershed.

Benzene, toluene, ethylbenzene, and all isomers of xylene (hereinafter referred to as BTEX) are a subset of VOC compounds that often are useful for tracing petroleum hydrocarbon sources in aquatic environments (Khan and others, 2016). In this study, all BTEX compounds were measured in the SAR Elmendorf and SAR 72 samples at small concentrations, and no BTEX compounds were measured in samples collected from the other three sites, including Cibolo Falls City and Ecleto 326 within the area of active oil and natural-gas production. The SAR 72 site is within the area of active oil and natural-gas production, which raises the possibility of a local source of BTEX compounds in this section of the San Antonio River. However, BTEX concentrations were small and generally similar to those at the SAR Elmendorf site, indicating that BTEX compounds detected at the SAR 72 site likely originated upstream. Although only five surface-water samples were collected and analyzed for BTEX compounds, the lack of BTEX compounds for most sites within the area of active oil and natural-gas production indicates that little, if any, local runoff associated with the area of active oil and natural-gas production has contaminated the surface water with BTEX compounds.

Constituents in Streambed-Sediment Samples

Some constituents that could be indicators of the presence of hydraulic fracturing fluids or produced waters, such as certain trace elements and PAHs, are hydrophobic and preferentially sorb to sediment (Harwell and others, 2003). Sediment-associated contaminants can affect the health of aquatic organisms that ingest particulate matter when bioaccumulation of trace elements and organic compounds occurs (Förstner and Wittmann, 1979; Luoma, 1983). The accumulation of some inorganic and organic compounds can cause various physiological issues and can ultimately result in death of aquatic organisms. Subsequent ingestion of aquatic organisms by consumers (organisms that eat other organisms) can transfer accumulated fat-soluble (lipophilic) contaminants upward through the food chain, resulting in biomagnification (Neely, 1980; Borgå and others, 2004).

Concentrations of the contaminants in the streambed-sediment samples were compared to the consensus-based sediment quality guidelines (SQGs) of MacDonald and others (2000) (table 16). The SQGs evaluate the potential toxicity of bed sediments to sediment-dwelling organisms. Two SQG concentration levels are used: (1) a lower level, called the threshold effect concentration (TEC), below which harmful effects to benthic biota are not expected, and (2) a higher level, the probable effect concentration (PEC), above which harmful effects are expected to occur frequently. In samples with concentrations between the TEC and PEC, additional environmental conditions often factor into the toxicity to different biota, so samples are not predicted to be toxic or nontoxic to benthic biota. The sediment screening levels used by the Texas Commission on Environmental Quality's Ecological Assessment Program (Texas Commission on Environmental Quality, 2015) are identical to the PECs of MacDonald and others (2000).

Major and Trace Elements

Many of the major and trace elements measured for this study are naturally occurring and typically found in sediment samples; they also can be derived from anthropogenic sources (Levings and others, 1998; Kimball and others, 2008). All 15 of the major and trace elements analyzed in streambed-sediment samples were detected in at least 1 sample (Crow and others, 2018). The concentrations of arsenic, cadmium, chromium, lead, nickel, and zinc in the streambed-sediment samples collected in 2016 were compared to their SQGs (table 16). Chromium, lead, nickel, and zinc concentrations in all samples were less than their respective TEC concentrations. The arsenic and cadmium concentrations in the sample collected from the Cibolo Trib 332 site were greater than their TECs (fig. 7). The PEC for arsenic was exceeded in the sample collected from the Ecleto 3335 site. The origins of the elevated arsenic and cadmium concentrations are unknown, but the Cibolo Trib 332 and the Ecleto 3335 sites are upstream from the area of active oil and natural-gas production; therefore, the elevated arsenic and cadmium concentrations at these sites are likely not related to oil and natural-gas production. Major and trace element concentrations from streambed-sediment samples collected from six sites for this study (SAR Elmendorf, SAR Falls City, SAR 72, Cibolo St. Hedwig, Cibolo Falls City, and Ecleto Runge) were compared with samples collected from the same sites during 2011–13

Table 16. Consensus-based sediment quality guidelines of MacDonald and others (2000) that were used to evaluate the contaminant concentrations in streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

[mg/kg, milligrams per kilogram; <, less than; µg/kg, micrograms per kilogram; PAHs, polycyclic aromatic hydrocarbons]

Constituent	Threshold effect concentration	Probable effect concentration	Concentrations in streambed-sediment samples	
			Minumum	Maximum
Trace elements (mg/kg)				
Arsenic	9.79	33.0	3.0	43.6
Cadmium	0.99	4.98	<0.1	1.1
Chromium	43.4	111	3.4	22
Lead	35.8	128	9.1	32
Nickel	22.7	48.6	3.0	16.7
Zinc	121	459	19	120
Polycyclic aromatic hydrocarbons (µg/kg)				
Anthracene	57.2	845	<0.79	12
Benzo[a]anthracene	108	1,050	<0.79	53
Benzo[a]pyrene	150	1,450	<0.79	98
Chrysene	166	1,290	<0.79	67
Dibenzo[a,h]anthracene	33.0	none	<0.79	12
Fluoranthene	423	2,230	<0.79	110
Fluorene	77.4	536	<0.79	<21
Naphthalene	176	561	<0.79	3.9
Phenanthrene	204	1,170	<0.79	24
Pyrene	195	1,520	<0.79	88
Total PAHs	1,610	22,800	<0.79	423

for the study done by Opsahl and Crow (2015). All arsenic, cadmium, chromium, lead, nickel, and zinc concentrations detected in the previous study were less than their respective TECs (fig. 7). No evidence was found in the major and trace element data to indicate changes related to oil and natural-gas production.

Organic Constituents

Selected PAHs were analyzed for in streambed-sediment samples for this study because of their potential usefulness as indicators of petroleum hydrocarbons associated with produced waters resulting from oil and natural-gas production (Hostettler and others, 2013). Other common sources of PAHs include coal-tar-based sealcoat; automobile exhaust; used motor oil; automobile tire particles; and burning wood, oil, coal, or other combustibles for cooking, heating, or energy production (Mahler and others, 2005; Van Metre and Mahler, 2010). PAH concentrations were analyzed in each streambed-sediment sample for two different size fractions to determine if these organic constituents are more likely to sorb to the exclusively silt- and clay-sized particles that compose the <63-µm size fraction than to the mixture of silt and clay and larger sized particles that compose the <2-mm size fraction.

Total PAH concentrations in all samples, regardless of size fraction, were less than the TEC for total PAHs of 1,610 µg/kg (table 16). Total PAH concentrations in the <2-mm size-fraction samples ranged from less than the LRL in samples collected from multiple sites in 2015 and 2016 to 221 µg/kg in the 2016 sample collected from the Cibolo St. Hedwig site (fig. 8). Total PAH concentrations in the <63-µm size-fraction samples ranged from less than the LRL in samples collected from multiple sites in 2015 and 2016 to 424 µg/kg in the 2015 sample collected from the SAR Elmendorf site (fig. 9). Total PAH concentrations generally were greater in the <63-µm size-fraction samples than in the <2-mm size-fraction samples, indicating that PAHs could potentially sorb to the silt- and clay-sized particles that compose the <63-µm size-fraction samples more readily than to the mixture of silt-, clay-, and sand-sized particles that compose the <2-mm size-fraction samples. Based on these findings, it might be anticipated that the greater the percentage of silt- and clay-sized particles in a sample, the greater the total PAH concentration in that sample. However, a comparison of the total PAH concentrations in the <2-mm size-fraction samples to the percentage of silt- and clay-sized particles (<63-µm size fraction) derived from the particle size distribution data showed no correlation (r-squared value

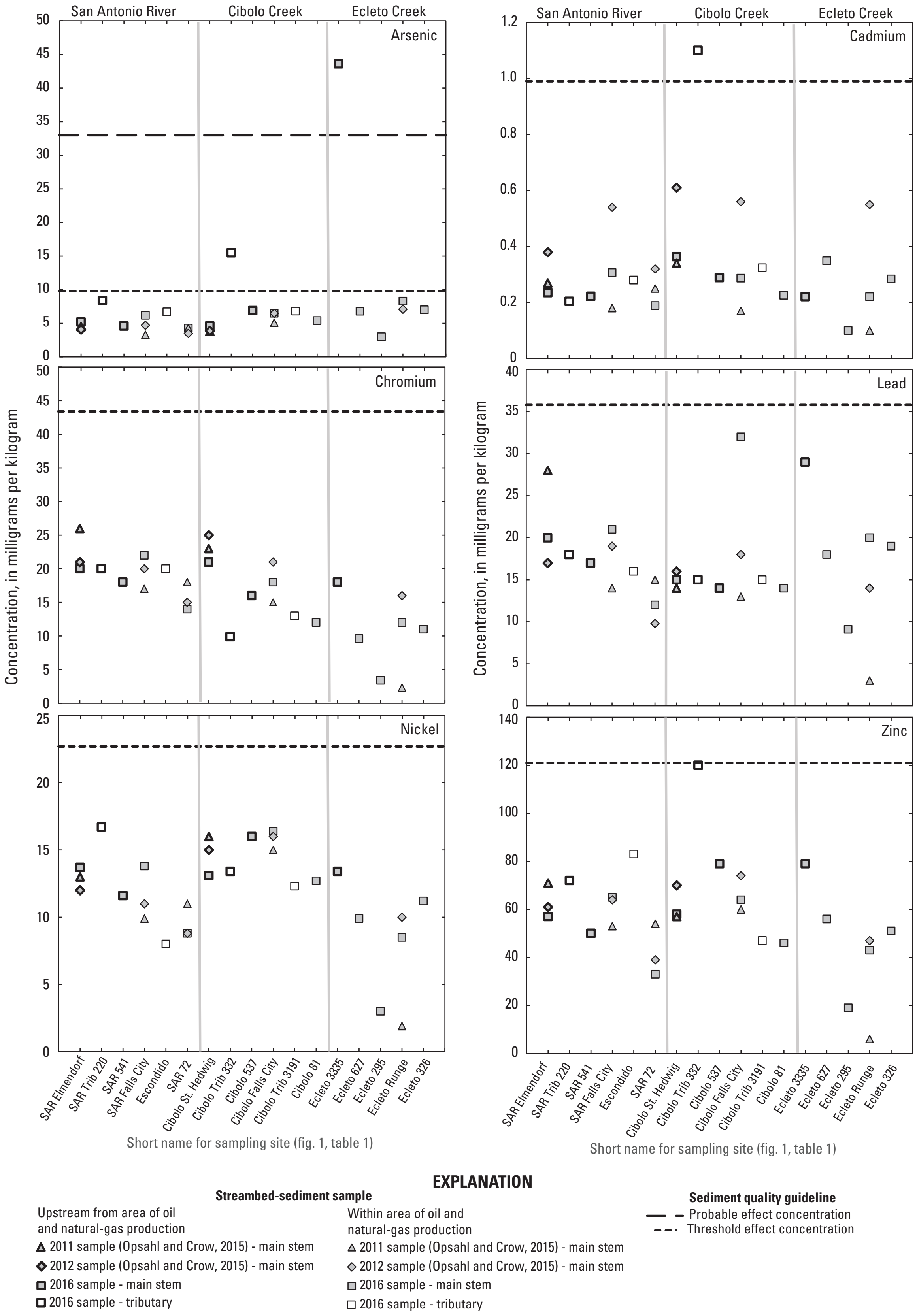


Figure 7. Concentrations of trace elements in streambed-sediment samples in relation to sediment quality guidelines (MacDonald and others, 2000), lower San Antonio River watershed, 2011 and 2012 (from Opsahl and Crow, 2015) and 2016.

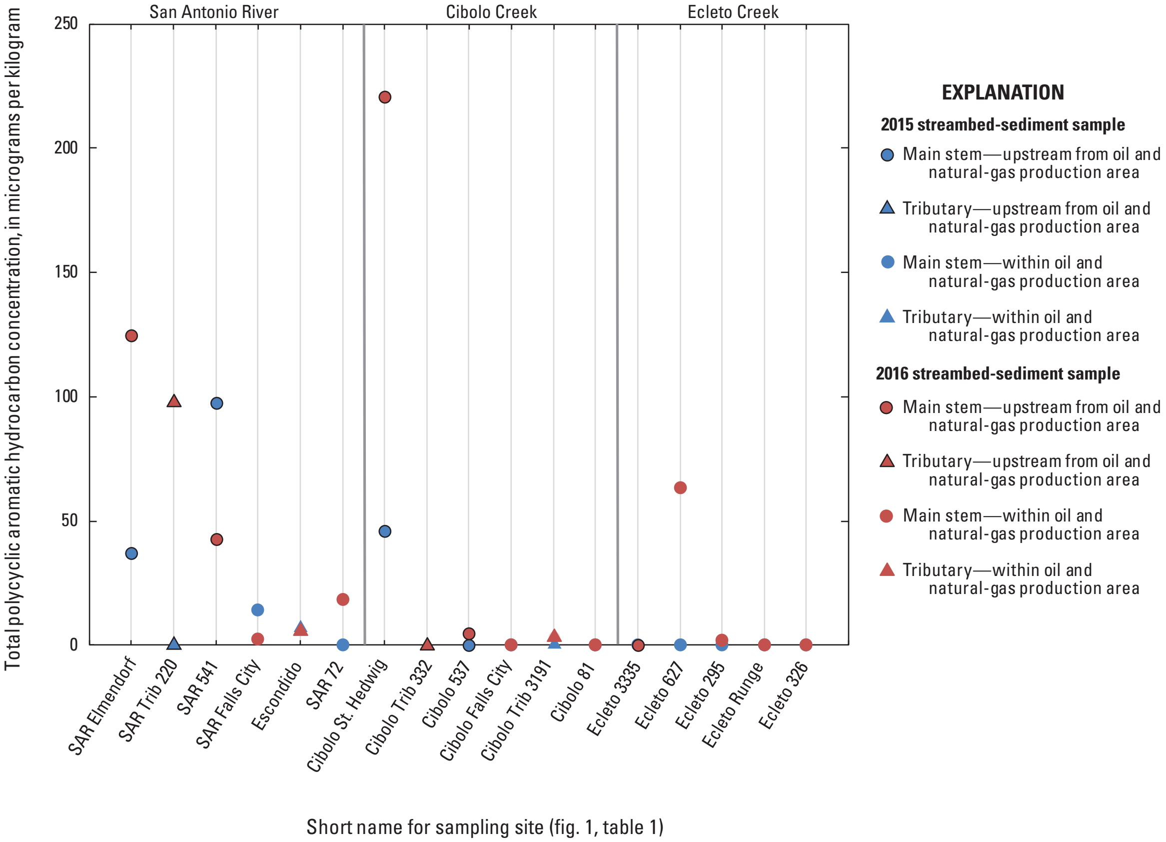


Figure 8. Total polycyclic aromatic hydrocarbon concentrations in less than 2-millimeter size-fraction streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

of 0.16) (fig. 10). At a given site, the concentration of PAHs is likely to be greater in the silt- and clay-sized particles in comparison to sand particles; however, the concentration of PAHs is primarily determined by the presence or absence of a local source.

In the <63-µm and <2-mm size fractions, total PAH concentrations typically were greater in the samples collected from the sites upstream from the area of active oil and natural-gas production compared to those collected from sites within the area (figs. 8 and 9). Because of improved analytical methods, the LRLs for individual PAHs available during the previous study (13–250 µg/kg) were greater than those used in this study (0.80–6.3 µg/kg); therefore, PAHs in the previous study could have been present at concentrations that were less than the LRLs used in this study. The observed distribution of small PAH concentrations and the observations of often greater concentrations at sites located upstream from the area of active oil and natural-gas production are consistent with little or no enhanced inputs of PAHs from sites within the area of active oil and natural-gas production.

Total PAH concentrations were computed by using a different method than was used in the Opsahl and Crow (2015) study, so direct comparison between the results of the two studies was not possible. The total PAH concentrations observed in the previous study display a similar pattern to those in the current study in which the greater concentrations are observed near urban areas upstream from the area of active oil and natural-gas production. PAHs are commonly found in urban settings (Moring and Rose, 1997; Van Metre and Mahler, 2005), and previous studies (Ging and others, 1999; Wilson, 2011; Crow and others, 2016) confirm that PAHs have been detected in streams in the San Antonio area at concentrations that are similar to or greater than the concentrations detected in this study. Ging and others (1999) examined sediment cores from a lake in a rapidly urbanizing area of Bexar County and found that concentrations of PAHs were increasing with increasing urbanization. Wilson (2011) examined sediments throughout Bexar County where total PAH concentrations ranged from not detected to 4,000 µg/kg. In a study that assessed possible contamination in streams flowing through some of San Antonio’s oldest neighborhoods (Crow and others, 2016), total PAH concentrations ranged from 750 to 99,000 µg/kg. The smaller PAH concentrations measured in samples collected from within the area of active oil and natural-gas production in comparison to the upstream urbanized areas indicate relatively minor additional local contributions of PAHs of uncertain origin to the watershed.

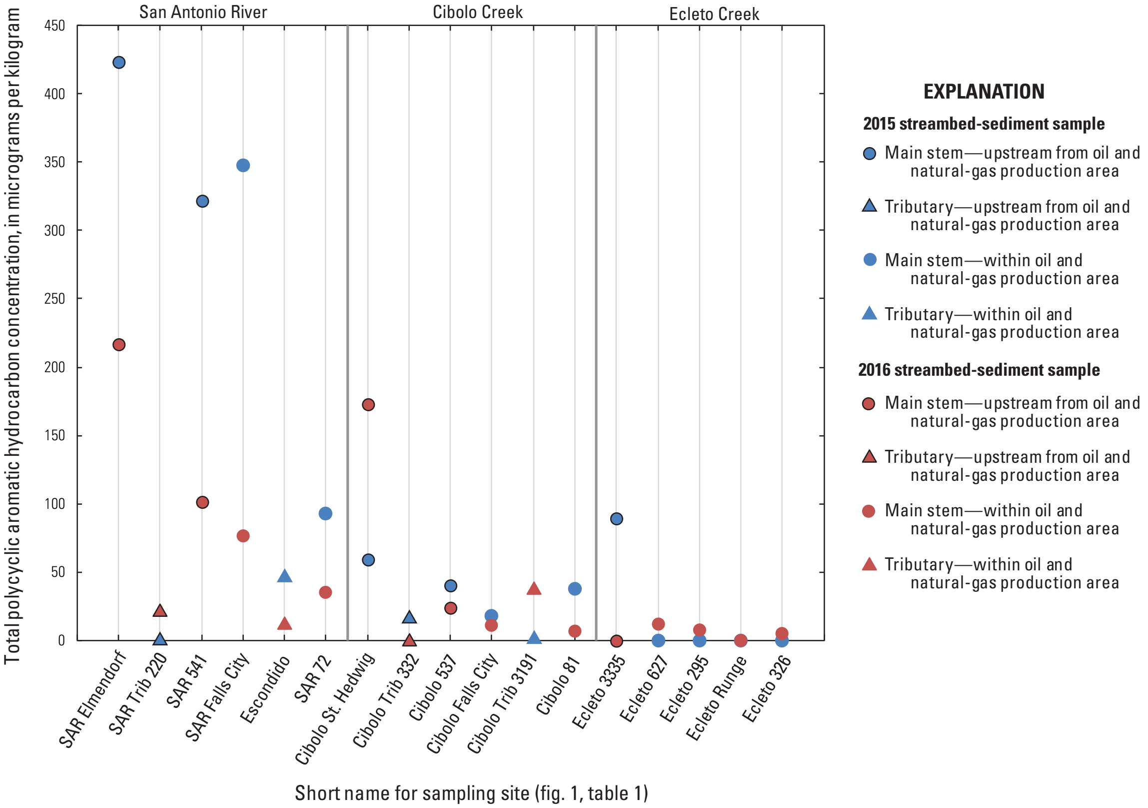


Figure 9. Total polycyclic aromatic hydrocarbon concentrations in less than 63-micrometer size-fraction streambed-sediment samples collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

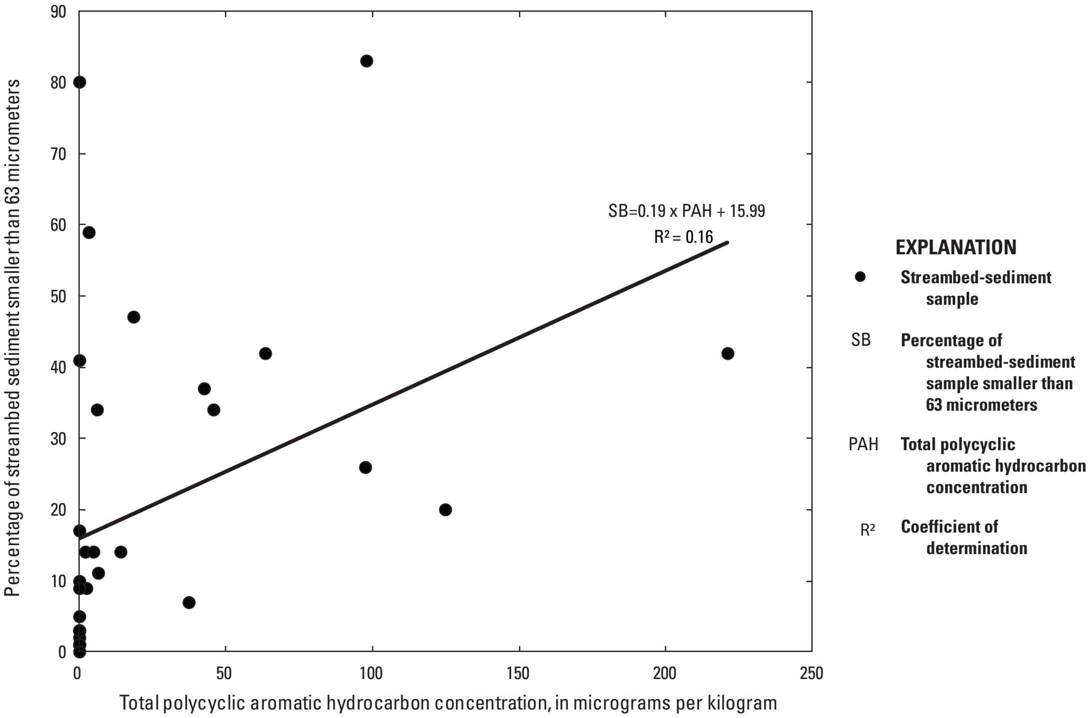


Figure 10. Relation of total polycyclic aromatic hydrocarbon concentrations in less than 2-millimeter size-fraction samples to percentage of streambed-sediment samples smaller than 63 micrometers collected from selected sites in the lower San Antonio River watershed, Texas, 2015–16.

Summary

Oil and natural-gas production from shale formations such as those present in the Eagle Ford Group in south Texas represented about 50 percent of U.S. crude oil production in 2017. The extensive development of oil and natural-gas resources in south Texas during the past 10 years has led to questions regarding possible environmental effects of processes associated with oil and natural-gas production, in particular the process of hydraulic fracturing, on water and other natural resources.

Part of the lower San Antonio River watershed intersects an area of oil and natural-gas production from the sedimentary rocks that compose the Eagle Ford Group. The rapid expansion of infrastructure associated with oil and natural-gas production increases potential pathways for inorganic and organic contaminants to enter surface-water systems. The U.S. Geological Survey, in cooperation with the San Antonio River Authority, analyzed geospatial data from different years (2008 and 2015) to evaluate changes in land cover associated with oil and natural-gas production activities in the lower San Antonio River watershed. Additionally, surface-water samples collected from 5 sites and streambed-sediment samples collected from 17 sites in the lower San Antonio River watershed during 2015–17 were analyzed for a broad range of constituents that might be associated with oil and natural-gas production.

Land-cover changes associated with oil and natural-gas production activities were quantified by comparing aerial imagery data collected during 2008 and 2015. Oil and natural-gas features were identified on the aerial imagery so that total area covered by each feature could be calculated to provide an estimate of change in each feature between 2008 and 2015. Well pads accounted for the largest land-cover change among the categories defined and delineated within the study area. The total percentage of the study area accounted for by well pads increased from 0.022 percent in 2008 to 0.663 percent in 2015, which is an increase of approximately thirtyfold. Oil and natural-gas production-related features accounted for the second largest change in land cover associated with oil and natural-gas production activities; the total percentage of the study area accounted for by oil and natural-gas production-related features increased from 0.006 percent in 2008 to 0.152 percent in 2015. Roads associated with oil and natural-gas production activities also accounted for a substantial change in land cover during the study period; the total percentage of the study area accounted for by roads associated with oil and natural-gas production increased from 0.006 percent in 2008 to 0.097 percent in 2015. Patterns of change observed for ponds varied based on pond type. The number of storage ponds increased from 1 in 2008 to 127 in 2015. The average surface area of storage ponds in 2015 was 3.09 acres, and storage ponds covered 393 acres, or 0.066 percent of the study area. The number of runoff ponds increased from 5 in 2008 to 112 in 2015. Impervious surface in this study is defined as land cover consisting of well pads, oil- and gas-related features, or roads. The areal coverage associated with impervious surface increased from 201 acres to 5,390 acres (net increase of 5,189 acres) between 2008 and 2015. The total percentage of the study area accounted for by impervious surface resulting from oil and natural-gas production activities increased from 0.034 percent to 0.912 percent, which is an increase of approximately 27-fold. Collectively, 0.878 percent of the study area was converted to new impervious surface between 2008 and 2015. If the area associated with new storage ponds (0.066 percent) is added to the estimate of total land-cover changes as a result of oil and natural-gas production, then 0.944 percent of the study area was altered between 2008 and 2015.

Five surface-water samples and 34 streambed-sediment samples were collected from 17 sites in the lower San Antonio River watershed during 2015–17. Surface-water samples were analyzed for total suspended solids, dissolved solids, major and trace elements, glycols, methylene blue active substances, semivolatile organic compounds (SVOCs), and volatile organic compounds (VOCs). Streambed-sediment samples were composited and put through a stainless steel 2-millimeter (mm) sieve in preparation for the analyses of polycyclic aromatic hydrocarbons (PAHs), total organic carbon (TOC), radium-226, and radium-228; instead of the 2-mm sieve, a 63-micrometer (µm) plastic sieve fabric was used in preparation for the analyses of major and trace elements and for additional analyses of PAHs and TOC.

The surface-water samples collected from five of the sites were analyzed for concentrations of a broad range of major and trace elements and organic constituents that might be associated with oil and natural-gas production. To help put concentrations of select trace elements and organic constituents in the surface-water samples in context, detected concentrations were compared to the U.S. Environmental Protection Agency's (EPA) drinking water standards and health advisories and national recommended aquatic life criteria for freshwater. Eighteen of the 20 major and trace elements measured in surface-water samples were detected in the samples. Cadmium and chromium were not detected in any of the surface-water samples. All major and trace element concentrations were less than any of the EPA's water-quality standards. Glycols, which are commonly used in hydraulic fracturing fluids as scale inhibitors, were detected in the sample collected from Ecleto Creek within the area of oil and natural-gas production. The presence of glycols does not necessarily indicate that the source is from hydraulic fracturing fluid because the glycols detected in this sample also have other potential sources, including the use of diethylene and ethylene glycols in antifreeze used in vehicles and the use of triethylene glycol in antibacterial air sanitizers.

Surface-water samples also were analyzed for SVOCs and VOCs during this study because of their common occurrence as petroleum hydrocarbons in oil and associated produced waters. Of the 56 SVOCs and 49 VOCs analyzed for during this study, there were 30 low-level detections of 20 different SVOCs and 23 low-level detections of 12 different VOCs in the 5 water samples. None of the detected SVOCs and VOCs exceeded any of the EPA's water-quality standards, including drinking water maximum contaminant levels (MCLs). The benzene concentrations in the surface-water samples also were less than the EPA's health advisory criteria for lifetime exposure for benzene (3 micrograms per liter [µg/L]), which is less than the MCL for benzene (5 µg/L). The surface-water sample from the SAR Elmendorf site had the greatest number of SVOC and VOC detections and, generally, the greatest concentrations. The greatest SVOC and VOC concentrations were observed in samples collected from sites upstream from the area of active oil and natural-gas production and just downstream from urban areas. Benzene, toluene, ethylbenzene, and all isomers of xylene (hereinafter BTEX) are a subset of VOC compounds that often are useful for tracing petroleum hydrocarbon sources in aquatic environments. Although only five surface-water samples were collected and analyzed for BTEX compounds, the lack of BTEX compounds for most sites within the area of active oil and natural-gas production indicates that little, if any, local runoff associated with the area of active oil and natural-gas production has contaminated the surface water with BTEX compounds.

Some constituents that could be indicators of the presence of hydraulic fracturing fluids or produced waters, such as certain trace elements and PAHs, are hydrophobic and preferentially sorb to sediment. Concentrations of the contaminants in the streambed-sediment samples were compared to the consensus-based sediment quality guidelines (SQGs). The SQGs evaluate the potential toxicity of bed sediments to sediment-dwelling organisms. Two SQG concentration levels are used: (1) a lower level, called the threshold effect concentration (TEC), below which harmful effects to benthic biota are not expected, and (2) a higher level, the probable effect concentration (PEC), above which harmful effects are expected to occur frequently.

Many of the major and trace elements measured for this study are naturally occurring and typically found in sediment samples; they also can be derived from anthropogenic sources. All 15 of the major and trace elements analyzed in streambed-sediment samples were detected in at least 1 sample. The concentrations of arsenic, cadmium, chromium, lead, nickel, and zinc in the streambed-sediment samples collected in 2016 were compared to their SQGs. Chromium, lead, nickel, and zinc concentrations in all samples were less than their respective TEC concentrations. The arsenic and cadmium concentrations in the sample collected from the Cibolo Trib 332 site were greater than their TECs. The PEC for arsenic was exceeded in the sample collected from the Ecleto 3335 site. The origins of the elevated arsenic and cadmium concentrations are unknown, but the Cibolo Trib 332 and the Ecleto 3335 sites are upstream from the area of active oil and natural-gas production; therefore, the elevated arsenic and cadmium concentrations at these sites are likely not related to oil and natural-gas production.

Streambed-sediment samples were analyzed for selected PAHs during this study because of their potential usefulness as indicators of petroleum hydrocarbons associated with produced waters resulting from oil and natural-gas production. PAH concentrations were analyzed in each streambed-sediment sample for two different size fractions to determine if these organic constituents are more likely to sorb to the exclusively silt- and clay-sized particles that compose the <63-µm size fraction than to the mixture of silt and clay and larger sized particles that compose the <2-mm size fraction. Total PAH concentrations in all samples, regardless of size fraction, were less than the TEC for total PAHs of 1,610 micrograms per kilogram. Total PAH concentrations generally were greater in the <63-µm size-fraction samples than in the <2-mm size-fraction samples, indicating that PAHs could potentially sorb to the silt- and clay-sized particles that compose the <63-µm size-fraction samples more readily than to the mixture of silt-, clay-, and sand-sized particles that compose <2-mm size-fraction samples. Based on these findings, it might be anticipated that the greater the percentage of silt- and clay-sized particles in a sample, the greater the total PAH concentration in that sample. However, a comparison of the total PAH concentrations in the <2-mm size-fraction samples to the percentage of silt- and clay-sized particles (<63-µm size fraction) derived from the particle size distribution data showed no correlation (r-squared value of 0.16). At a given site, the concentration of PAHs is likely to be greater in the silt- and clay-sized particles than in sand particles; however, the concentration of PAHs is primarily determined by the presence or absence of a local source. In both size fractions, total PAH concentrations typically were greater in the samples collected from the sites upstream from the area of active oil and natural-gas production compared to those collected from sites within the area. The smaller PAH concentrations measured in samples collected from within the area of active oil and natural-gas production in comparison to the upstream urbanized areas indicate relatively minor additional local contributions of PAHs of uncertain origin to the watershed.

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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

Crow and others—**Land-Cover Changes Associated With Oil and Natural-Gas Production, South Texas, 2008–17**—SIR 2018–5119

ISBN 978-1-4113-4261-3

ISSN 2328-031X (print)
ISSN 2328-0328 (online)
https://doi.org/10.3133/sir20185119