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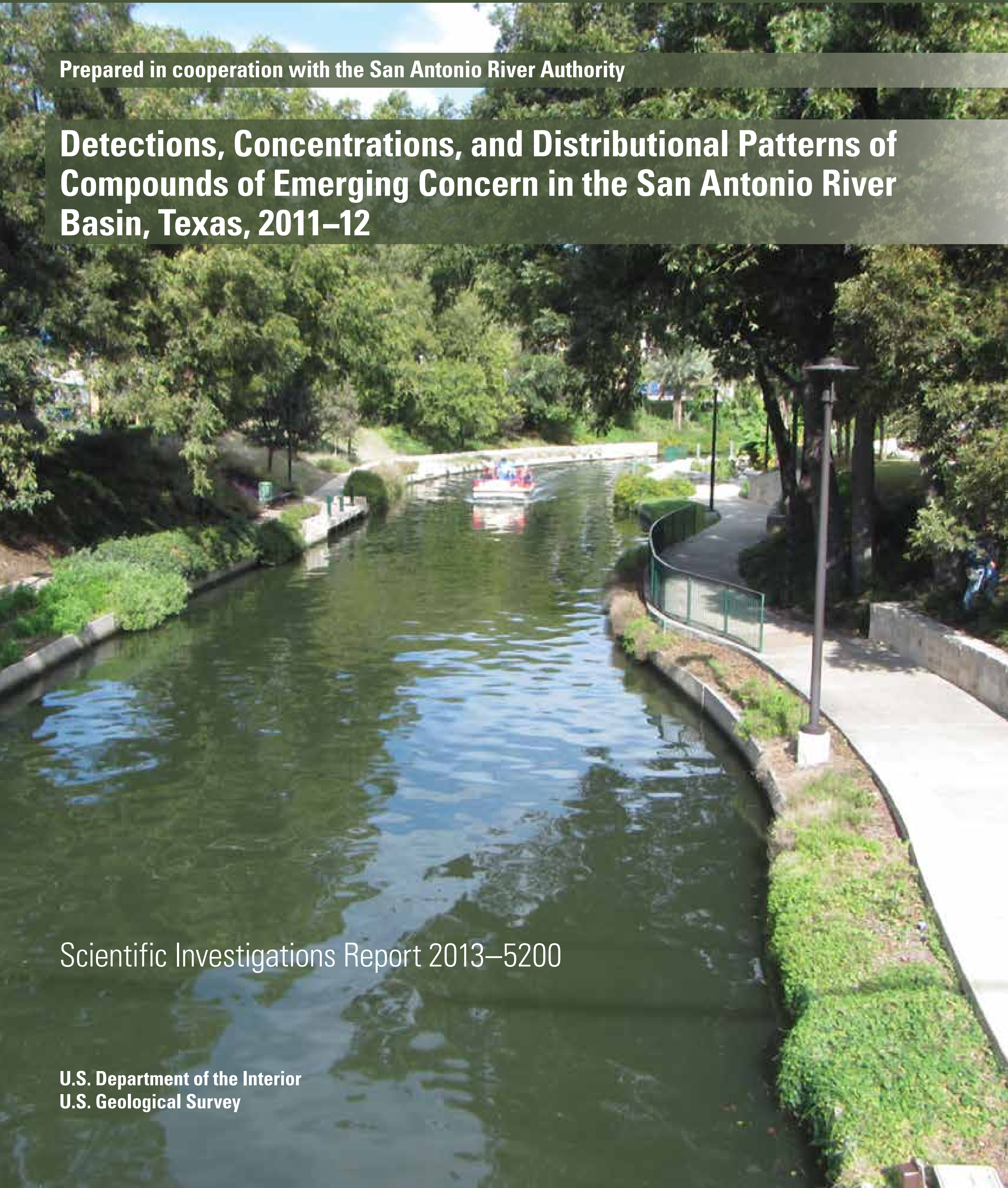

Prepared in cooperation with the San Antonio River Authority

Detections, Concentrations, and Distributional Patterns of Compounds of Emerging Concern in the San Antonio River Basin, Texas, 2011–12

Scientific Investigations Report 2013–5200

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

Front cover, View of the San Antonio River oriented upstream in San Antonio, Texas (photograph taken on November 14, 2013, by Michael B. Nyman, U.S. Geological Survey).

Back cover:

Top, View of the San Antonio River oriented upstream in San Antonio, Texas (photograph taken on November 14, 2013, by Michael B. Nyman, U.S. Geological Survey).

Bottom right, U.S. Geological Survey hydrographers collecting water sample for analysis of compounds of emerging concern (photograph taken on May 31, 2011, by Chiquita S. Lopez, U.S. Geological Survey).

Bottom left, Equipment used for measuring field properties during water sample collection (photograph taken on May 31, 2011, by Chiquita S. Lopez, U.S. Geological Survey).

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U.S. Department of the Interior
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U.S. Geological Survey
Suzette M. Kimball, Acting Director

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
acre	0.004047	square kilometer (km^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

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

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

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

Concentrations of chemical compounds in water are given in either micrograms per liter (µg/L) or nanograms per liter (ng/L).

Detections, Concentrations, and Distributional Patterns of Compounds of Emerging Concern in the San Antonio River Basin, Texas, 2011–12

By Stephen P. Opsahl and Rebecca B. Lambert

Abstract

During 2011–12, the U.S. Geological Survey, in cooperation with the San Antonio River Authority, evaluated detections, concentrations, and distributional patterns of selected compounds of emerging concern (hereinafter referred to as “CECs”) from water-quality samples (hereinafter referred to as “samples”) collected at a total of 20 sampling sites distributed throughout the San Antonio River Basin, Texas. Of the 54 wastewater compounds analyzed, 32 were detected in at least one sample collected from the San Antonio River Basin, and 22 of those compounds were not detected in any samples. The flame retardants tris (2-chloroethyl) phosphate and tris (dichloroisopropyl) phosphate, both possible endocrine disruptors, were the most frequently detected wastewater compounds with 28 of the 33 samples analyzed for wastewater compounds having measureable concentrations of those compounds. Of the 13 analyzed pharmaceuticals, 4 compounds were detected in a least one sample. Carbamazepine, an anticonvulsant, was the most frequently detected prescription pharmaceutical with 24 detections in 34 samples analyzed for pharmaceuticals. Of the 17 steroidal hormones, 4 were detected in at least one sample from the San Antonio River Basin. Estrone was detected in 9 of 34 samples analyzed for steroidal hormones, making it the most frequently detected steroidal hormone. Of the 4 sterols, all 4 were detected in at least one sample from the San Antonio River Basin. Cholesterol, detected in 19 of 34 samples analyzed for sterols, was the most frequently detected sterol.

Three synoptic sampling events were completed as part of this study. The first and second synoptic sampling events included samples collected at the same 12 sampling sites. During the first and second synoptic sampling events, the lowest number of detections (2 and 0, respectively) and the lowest total concentrations of all measured compounds (0.62 and not measureable, respectively) occurred in samples collected at the Macdona site (Medina River near Macdona, Tex.). The highest number of detections (21 and 23, respectively) and highest total concentrations of all measured compounds (7.75 and 3.97 micrograms per liter [µg/L], respectively) occurred in samples collected at the SAR Elmendorf site (San Antonio River near Elmendorf, Tex.). The third synoptic sampling event included samples collected at seven sites that were added to the study after the first two synoptic sampling events were completed. During the third synoptic sampling event, the lowest number of detections (two) and the lowest total concentration (0.14 µg/L) of compounds were measured in samples collected at the North Prong site (North Prong Medina River above confluence Wallace Creek near Medina, Tex.). The highest number of detections (21) occurred at the SAR Mitchell site (San Antonio River at Mitchell Street, San Antonio, Tex.). The Dos Rios site (the Dos Rios wastewater treatment plant outfall at San Antonio, Tex.) had the highest total concentration of all measured compounds (4.37 µg/L) in the third synoptic sampling event. Because Ecleto Creek flows only intermittently at the Ecleto site (Ecleto Creek near Runge, Tex.), samples from the Ecleto site were collected at different times than were samples from the other sites and were not included in a synoptic sampling event. The presence of wastewater compounds at the Ecleto site indicates that at least some wastewater compounds can be introduced into surface waters in rural parts of the San Antonio River Basin during runoff or because of onsite wastewater system seepage. The steroidal hormone and sterols detected at the Ecleto site, including estrone, cholesterol, *beta*-sitosterol, and *beta*-stigmastanol, likely were derived from cattle waste rather than from wastewater effluent.

The distributional patterns of detections and concentrations of individual compounds and compound classes show the influence of wastewater-treatment plant (WWTP) outfalls on the quality of water in the San Antonio River Basin. In the Medina River Subbasin, the minimal influence of wastewater is evident as far downstream as the Macdona site. Downstream from the Macdona site, the Medina River receives treated municipal wastewater from both the Medio Creek Water Recycling Center site from an unnamed tributary at the plant and the Leon Creek Water Recycling Center site from Comanche Creek at the plant, and corresponding increases in both the number of detections

and the total concentrations of all measured compounds at all downstream sampling sites were evident. Similarly, the San Antonio River receives treated municipal wastewater as far upstream as the SAR Witte site (San Antonio River at Witte Museum, San Antonio, Tex.) and additional WWTP outfalls along the Medina River upstream from the confluence of the Medina and San Antonio Rivers. Consequently, all samples collected along the main stem of the San Antonio River had higher concentrations of CECs in comparison to sites without upstream WWTPs. Sites in urbanized areas without upstream WWTPs include the Leon 35 site (Leon Creek at Interstate Highway 35, San Antonio, Tex.), the Alazan site (Alazan Creek at Tampico Street, San Antonio, Tex.), and the San Pedro site (San Pedro Creek at Probandt Street, at San Antonio, Tex.). The large number of detections at sites with no upstream wastewater source demonstrated that CECs can be detected in streams flowing through urbanized areas without a large upstream source of treated municipal wastewater. A general lack of detection of pharmaceuticals in streams without upstream outfalls of treated wastewater appears to be typical for streams throughout the San Antonio River Basin and may be a useful indicator of point-source versus nonpoint-source contributions of these compounds in urban streams. Observations of lower concentrations of compounds at the furthest downstream sampling sites in the basin indicate some natural attenuation of these compounds during transport; however, a more focused assessment is needed to make this determination.

Introduction

Advancements in laboratory analytical techniques have provided the capability to identify large numbers of previously unrecognized organic compounds derived from wastewater treatment plants (WWTPs), industrial effluent, runoff from urban and agricultural land cover, land application of human and animal waste, and onsite wastewater treatment systems (Richardson and Ternes, 2011). Such organic compounds are commonly referred to as “compounds of emerging concern” (CECs) and include wastewater compounds, pharmaceutical drugs (hereinafter referred to as “pharmaceuticals”), and natural and synthetically produced hormones (Glassmeyer and others, 2005; Focazio and others, 2008). Prior studies have demonstrated that many of these compounds are commonly detectable in surface waters (Kolpin and others, 2002; Oblinger and others, 2007; Haack, 2009; Lawrence and LaFontaine, 2010; Lee and others, 2011; Reif and others, 2012) and groundwater (Barnes and others, 2008; Katz and others, 2010). Some of these compounds are known or suspected endocrine disrupters (Lintelmann and others, 2003) that can interfere with normal endocrine system functions responsible for regulating various developmental processes in the body (U.S. Environmental Protection Agency, 2012). The potential for individual CECs or some combination of CECs to affect human health and aquatic life remains poorly understood, and most CECs remain unregulated (U.S. Environmental Protection Agency, 2012); however, data on the detection and concentration of CECs are becoming more widely available, providing managers and policy makers with more information that may be used for water treatment and water resource management.

Understanding the sources and fate of CECs at the river basin scale is important to water resource managers. Point-source discharges from WWTPs are a primary source of CECs to urban streams (Kolpin and others, 2004). Nonpoint sources such as seepage from onsite wastewater treatment systems (Katz and others, 2010), leakage from sewer lines (Lawrence and LaFontaine, 2010), urban runoff (Marklund and others, 2005), agricultural and livestock operations (Chambers and Leiker, 2006), and atmospheric deposition (Schuetzle and others, 1975; Peck and Hornbuckle, 2006; Ligocki and others, 1985a, b) also represent common pathways for CECs to enter the environment. The fate of CECs in streams is partially determined by natural attenuation processes including sorption to sediments (Tolls, 2001; Kolpin and others, 2002), microbial decomposition (Yamamoto and others, 2009), and photochemical degradation (Carlos, 2012; Klamerth and others, 2010).

San Antonio and surrounding municipalities in Bexar County, Texas, are in a rapidly urbanizing region in the San Antonio River Basin (fig. 1) (U.S. Census Bureau, 2013), and patterns of water usage have changed as a result of this rapid urbanization (Texas Instream Flow Program and San Antonio River Authority, 2009). As the San Antonio area continues to grow, increases in residential and commercial development likely will enhance runoff into streams during storm events and increase chemical loads into the drainage network (Ockerman and McNamara, 2003). Although there are multiple WWTPs in the San Antonio area, other municipalities, both upstream from and downstream from San Antonio, also represent potential sources of CECs to the San Antonio River system (fig. 1, table 1). To better understand the quality of surface water in the San Antonio River Basin, the U.S. Geological Survey (USGS), in cooperation with the San Antonio River Authority, evaluated detections, concentrations, and distributional patterns of selected compounds of emerging concern (hereinafter referred to as “CECs”) from water-quality samples (hereinafter referred to as “samples”) collected at sampling sites distributed throughout the San Antonio River Basin, Tex., during 2011–12. Each wastewater discharge site has a wastewater facility name, a National Pollutant Discharge Elimination System (NPDES) identifier, and a short name (table 1), and each sampling site has a USGS station number, USGS station name, and short name (table 2). In this report, the short names listed in tables 1 and 2 are used for referring to wastewater discharge sites and sampling sites, respectively. Map identifiers (tables 1, 2) cross referenced to the short names are provided on all of the map-based figures in the report.

Purpose and Scope

This report summarizes the number of detections, concentrations, and distributional patterns of wastewater compounds, pharmaceuticals, steroidal hormones, and sterols analyzed in samples collected from 20 sampling sites along streams throughout the San Antonio River Basin, Tex., during 2011–12. Results are presented for 54 wastewater compounds, 13 pharmaceuticals, 17 steroidal hormones, and 4 sterols. The report presents data for the number of detections and concentrations of individual compounds from all samples collectively and for the number of detections and concentrations of individual compounds and compound classes for each of three synoptic sampling events. The report also describes basin-wide distributional patterns of detections and concentrations of all compounds to provide insight into the potential sources and transport of compounds from streams in the San Antonio River Basin.

Description of Study Area

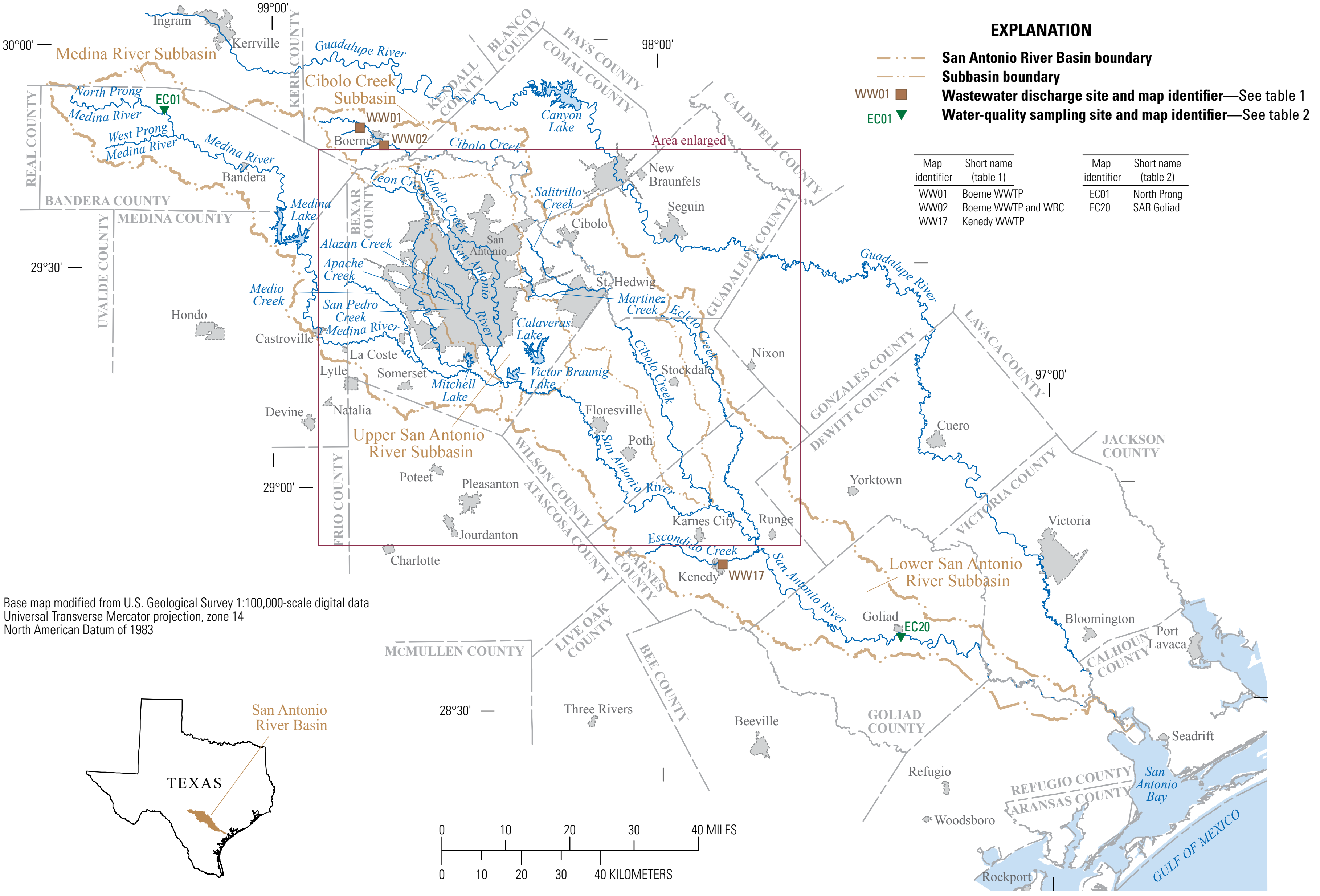
The San Antonio River drains an area of approximately 4,180 square miles and extends about 240 miles from its headwaters northwest of San Antonio to the confluence of the San Antonio and Guadalupe Rivers (San Antonio River Authority, 2013) (fig. 1). The Guadalupe River drains into the San Antonio Bay and the Gulf of Mexico downstream from where the San Antonio River flows into the Guadalupe River. The San Antonio River Basin drains parts of the following counties: Atascosa, Bandera, Bexar, Comal, DeWitt, Goliad, Guadalupe, Karnes, Kendall, Kerr, Medina, Refugio, Victoria, and Wilson. Much of the population in the study area resides in Bexar County where San Antonio is located. Major subbasins of this basin include the Medina River Subbasin, the Upper San Antonio River Subbasin, the Cibolo Creek Subbasin, and the Lower San Antonio River Subbasin (fig. 1).

Wastewater processing facilities in the San Antonio River Basin include WWTPs and water recycling centers (WRCs), both of which treat municipal wastewater and discharge it to streams. There are outfalls of treated municipal wastewater throughout Bexar County, and the majority of sampling sites were located in Bexar County (fig. 1, table 1, table 2). The San Antonio Water System manages WRCs, and estimates for discharge by WRCs were provided by the San Antonio Water System (Gregg Eckhardt, oral commun., 2013). Treated municipal wastewater discharge from Dos Rios WRC (map identifier WW07, fig. 1, table 1), the largest WRC in San Antonio, averages approximately 75–80 million gallons per day (Mgal/d), or 116–124 cubic feet per second (ft^3/s). Treated municipal wastewater discharge from Leon Creek WRC (map identifier WW13, fig. 1, table 1) averages approximately 36–38 Mgal/d (56–59 ft^3/s). Treated municipal wastewater discharge from the Medio Creek WRC (map identifier WW15, fig. 1, table 1) averages approximately 7.5 Mgal/d (12 ft^3/s).

Some of the treated municipal wastewater from Dos Rios WRC, Leon Creek WRC, and Medio Creek WRC may be discharged at the following sites along the San Antonio River, where it is used to help maintain base flows (Gregg Eckhardt, San Antonio Water System, oral commun., 2013): Dos Rios Tuleta (map identifier WW08, fig. 1, table 1), Dos Rios Flood Tunnel (map identifier WW09, fig. 1, table 1), Dos Rios Rittiman (map identifier WW10, fig. 1, table 1), Dos Rios Convention Center (map identifier WW11, fig. 1, table 1), and Dos Rios Blue Wing (map identifier WW12, fig. 1, table 1). Typical treated municipal wastewater discharges at these sites under base flow conditions are 4–5 Mgal/d (6.2–7.7 ft^3/s) at the Dos Rios Tuleta wastewater discharge site, 0.5–1.0 Mgal/d (0.8–1.5 ft^3/s) at the Dos Rios Convention Center wastewater discharge site, and 0.5 Mgal/d (0.8 ft^3/s) at the Dos Rios Rittiman wastewater discharge site. The Dos Rios Flood Tunnel wastewater discharge site typically is used as a backup, and the Dos Rios Blue Wing wastewater discharge site currently is (2013) not in operation.

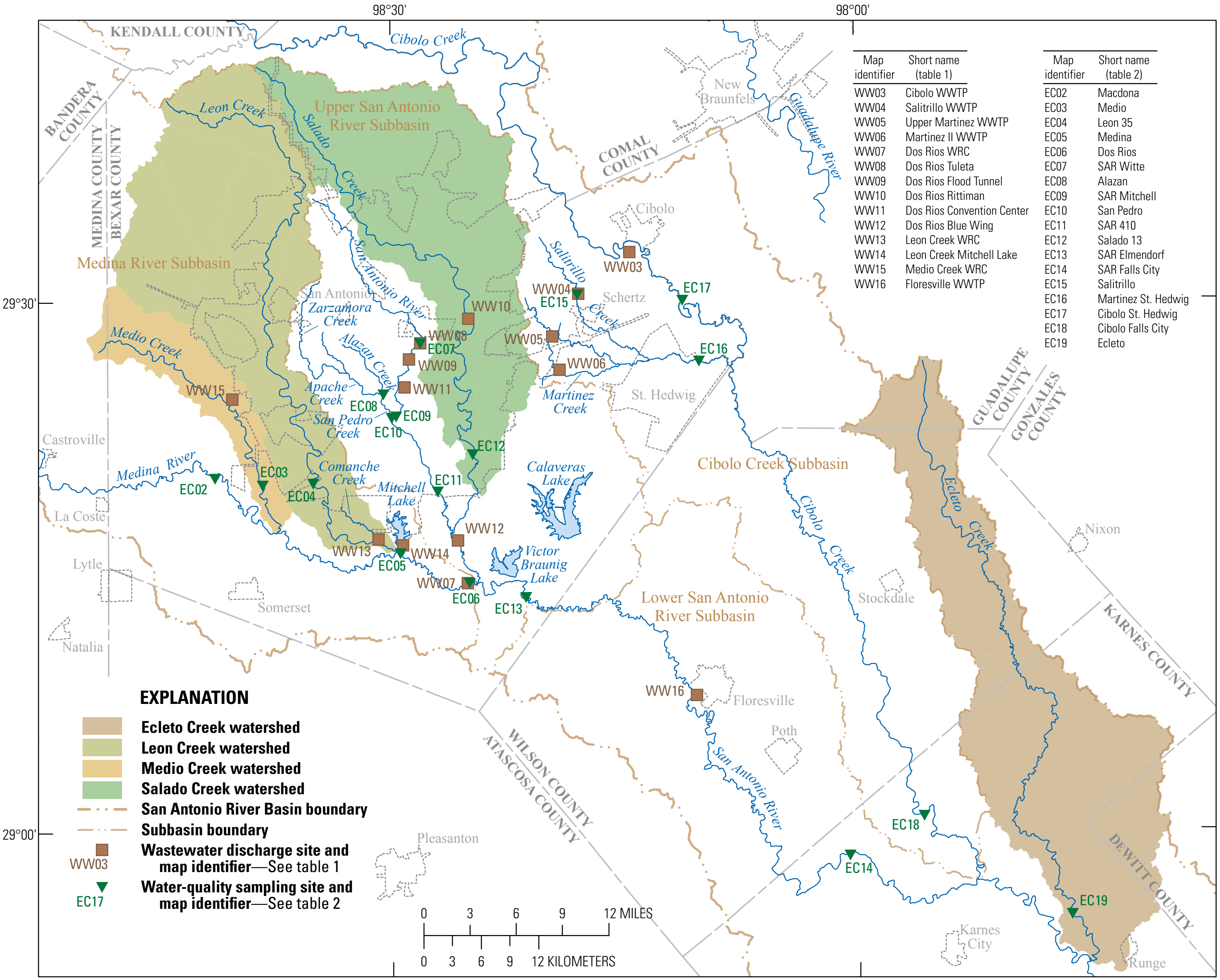
In the Cibolo Creek Subbasin, there are two wastewater discharge sites (map identifiers WW01 and WW02, fig. 1, table 1) located in Boerne, Tex. Under normal base flow conditions, the discharge from these sites infiltrates the stream channel and becomes groundwater recharge within about 3 miles downstream from Boerne where Cibolo Creek typically goes dry. Farther downstream from WW01 and WW02 in the Cibolo Creek Subbasin, there are multiple sites of treated municipal wastewater discharge that maintain base flow in Cibolo Creek until the confluence of Cibolo Creek and the San Antonio River. These sites include the Cibolo WWTP (map identifier WW03, fig. 1, table 1) on the main stem of Cibolo Creek, the Salitrillo WWTP on Salitrillo Creek (map identifier WW04, fig. 1, table 1), and the Upper Martinez WWTP (map identifier WW05, fig. 1, table 1) and the Martinez II WWTP (map identifier WW06, fig. 1, table 1) on Martinez Creek.

The upper parts of the Medina River Subbasin and the Ecleto Creek watershed are not affected by WWTPs (fig. 1). The North Prong site (map identifier EC01, fig. 1, table 2), in the upper part of the Medina River Subbasin, was included in the study as a reference site. The North Prong site is in an area composed primarily of rangeland with no large upstream municipalities and is the northernmost data collection site from which samples were collected. The Ecleto site (map identifier EC19, fig. 1, table 2), in the Ecleto Creek watershed was not part of the three synoptic sampling events; it was selected to represent rangeland conditions characteristic of much of the San Antonio River Basin.



Base map modified from U.S. Geological Survey 1:100,000-scale digital data
Universal Transverse Mercator projection, zone 14
North American Datum of 1983

Figure 1. Locations of wastewater discharge and water-quality sampling sites in the San Antonio River Basin, 2011–12.



Map identifier	Short name (table 1)
WW03	Cibolo WWTP
WW04	Salitrillo WWTP
WW05	Upper Martinez WWTP
WW06	Martinez II WWTP
WW07	Dos Rios WRC
WW08	Dos Rios Tuleta
WW09	Dos Rios Flood Tunnel
WW10	Dos Rios Rittiman
WW11	Dos Rios Convention Center
WW12	Dos Rios Blue Wing
WW13	Leon Creek WRC
WW14	Leon Creek Mitchell Lake
WW15	Medio Creek WRC
WW16	Floresville WWTP

Map identifier	Short name (table 2)
EC02	Macdona
EC03	Medio
EC04	Leon 35
EC05	Medina
EC06	Dos Rios
EC07	SAR Witte
EC08	Alazan
EC09	SAR Mitchell
EC10	San Pedro
EC11	SAR 410
EC12	Salado 13
EC13	SAR Elmendorf
EC14	SAR Falls City
EC15	Salitrillo
EC16	Martinez St. Hedwig
EC17	Cibolo St. Hedwig
EC18	Cibolo Falls City
EC19	Ecleto

Base modified from U.S. Geological Survey 1:100,000-scale digital data
Universal Transverse Mercator, zone 14
North American Datum of 1983

Figure 1. Locations of wastewater discharge and water-quality sampling sites in the San Antonio River Basin, 2011–12.—Continued

Table 1. Wastewater discharge sites in the San Antonio River Basin, Texas.

[NPDES, National Pollutant Discharge Elimination System; NAD 83, horizontal coordinate information referenced to North American Datum of 1983; dd, degrees; mm, minutes; ss, seconds; WWTP, wastewater treatment plant; WWTF, wastewater treatment facility; WRC, water recycling center; --, no NPDES identifier available. Data from U.S. Environmental Protection Agency (2013a)]

Map identifier (as shown in figs. 1, 13, 14, and 15)	Short name	County	Wastewater facility name	NPDES identifier
WW01	Boerne WWTP	Kendall	Boerne WWTP	TX0024465
WW02	Boerne WWTP and WRC	Kendall	Boerne WWTP and Recycling Center	TX0131831
WW03	Cibolo WWTP	Guadalupe	Cibolo Creek WWTP	TX0077232
WW04	Salitrillo WWTP	Bexar	Salitrillo Creek	TX0053074
WW05	Upper Martinez WWTP	Bexar	Upper Martinez Creek WWTF	TX0024082
WW06	Martinez II WWTP	Bexar	Martinez II WWTP	TX0095583
WW07	Dos Rios WRC	Bexar	Medina River at plant site	TX0077801
WW08	Dos Rios Tuleta	Bexar	San Antonio River at Tuleta Street	--
WW09[1]	Dos Rios Flood Tunnel	Bexar	San Antonio River at flood tunnel inlet	--
WW10	Dos Rios Rittiman	Bexar	Salado Creek at Rittiman Road	--
WW11	Dos Rios Convention Center	Bexar	San Antonio River at Convention Center	--
WW12[1]	Dos Rios Blue Wing	Bexar	San Antonio River near Blue Wing Road	--
WW13	Leon Creek WRC	Bexar	Comanche Creek at plant site	--
WW14	Leon Creek Mitchell Lake	Bexar	Mitchell Lake	TX0065641
WW15	Medio Creek WRC	Bexar	Unnamed tributary at plant site	TX0055689
WW16	Floresville WWTP	Wilson	Floresville WWTP	TX0056227
WW17	Kenedy WWTP	Karnes	Kenedy WWTF	TX0027774

[1] Site inactive during the time that samples were collected for all synoptics.

Table 2. Water-quality sampling sites in the San Antonio River Basin, Texas, 2011–12.

[USGS, U.S. Geological Survey; NAD 83, horizontal coordinate information referenced to North American Datum of 1983; dd, degrees; mm, minutes; ss, seconds; TCEQ, Texas Commission on Environmental Quality; IH, interstate highway; WWTP, wastewater treatment plant; SAR, San Antonio River; --, not available]

Map identifier (as shown in figs. 1, 13, 14, and 15)	Short name	County	USGS station number	USGS station name	Synoptic number	Latitude (NAD 83) (dd mm ss)	Longitude (NAD 83) (dd mm ss)	TCEQ segment number
EC01	North Prong	Bandera	08178863	North Prong Medina River above confluence Wallace Creek near Medina, Tex.	3	29° 51′ 14″	99° 16′ 50″	1905
EC02	Macdona	Bexar	08180700	Medina River near Macdona, Tex.	1,2	29° 20′ 06″	98° 41′ 23″	1903
EC03	Medio	Bexar	08180750	Medio Creek at Pearsall Road, San Antonio, Tex.	1,2	29° 19′ 41″	98° 38′ 20″	1912
EC04	Leon 35	Bexar	08181480	Leon Creek at IH 35, San Antonio, Tex.	1,2	29° 19′ 48″	98° 35′ 03″	1906
EC05	Medina	Bexar	08181500	Medina River at San Antonio, Tex.	1,2	29° 15′ 51″	98° 29′ 27″	1903
EC06	Dos Rios	Bexar	291407098243701	Dos Rios WWTP Outfall at San Antonio, Tex.	3	29° 14′ 09″	98° 24′ 58″	1903
EC07	SAR Witte	Bexar	08177825	San Antonio River at Witte Museum, San Antonio, Tex.	3	29° 27′ 42″	98° 28′ 06″	1911
EC08	Alazan	Bexar	292449098303000	Alazan Creek at Tampico Street, San Antonio, Tex.	3	29° 24′ 49″	98° 30′ 30″	1911
EC09	SAR Mitchell	Bexar	08178050	San Antonio River at Mitchell Street, San Antonio, Tex.	3	29° 23′ 35″	98° 29′ 41″	1911
EC10	San Pedro	Bexar	08178504	San Pedro Creek at Probandt Street, at San Antonio, Tex.	3	29° 23′ 30″	98° 29′ 59″	1906
EC11	SAR 410	Bexar	08178565	San Antonio River at Loop 410, San Antonio, Tex.	1,2	29° 19′ 20″	98° 27′ 01″	1911
EC12	Salado 13	Bexar	08178800	Salado Creek at Loop 13, San Antonio, Tex.	1,2	29° 21′ 26″	98° 24′ 46″	1910
EC13	SAR Elmendorf	Bexar	08181800	San Antonio River near Elmendorf, Tex.	1,2	29° 13′ 20″	98° 21′ 21″	1911
EC14	SAR Falls City	Bexar	08183550	San Antonio River at Highway 181 at Falls City, Tex.	1,2	28° 58′ 38″	98° 00′ 37″	1901
EC15	Salitrillo	Bexar	293025098175700	Salitrillo Creek downstream of Schaeffer Road in Converse, Tex.	3	29° 30′ 25″	98° 17′ 57″	1913
EC16	Martinez St. Hedwig	Bexar	08185100	Martinez Creek near Saint Hedwig, Tex.	1,2	29° 26′ 38″	98° 10′ 08″	1902
EC17	Cibolo St. Hedwig	Guadalupe	08185065	Cibolo Creek near Saint Hedwig, Tex.	1,2	29° 30′ 05″	98° 11′ 10″	1902
EC18	Cibolo Falls City	Karnes	08186000	Cibolo Creek near Falls City, Tex.	1,2	29° 00′ 51″	97° 55′ 49″	1902
EC19	Ecleto	Karnes	08186500	Ecleto Creek near Runge, Tex.	--	28° 55′ 13″	97° 46′ 20″	1901
EC20	SAR Goliad	Goliad	08188500	San Antonio River at Goliad, Tex.	1,2	28° 38′ 57″	97° 23′ 05″	1901

Previous Studies and Background Information

Wastewater Compounds

WWTPs effectively remove some wastewater compounds during treatment, although the efficiency of removal varies on the basis of the chemical properties of individual compounds and environmental conditions (Loyo-Rosales and others, 2007; Phillips and others, 2005; Baker and Kasprzyk-Hordern, 2013). For example, in a study that examined the fate of alkylphenolic compounds in three large WWTPs, the efficiency of removal of 4-*n*-octylphenol and 4-nonylphenol ethoxylates ranged from 71.5 percent to 99.1 percent (Loyo-Rosales and others, 2007). That study also reported that the removal efficiency was observed to be greater at a higher temperature, presumably the result of enhanced microbial transformations stimulated by higher temperatures (Loyo-Rosales and others, 2007). Phillips and others (2005) reported that biological treatment of wastewater removed a higher percentage of wastewater compounds than did filtration or disinfection processes, and removal efficiency was enhanced with higher sludge retention efficiencies. The number of individual compounds that may be present in treated municipal wastewater remains unknown.

Certain subclasses of wastewater compounds are commonly present in streams including detergent metabolites, personal-use compounds, pesticides, industrial compounds, disinfection compounds, polycyclic aromatic hydrocarbons (PAHs), and flame retardants and plasticizers (Kolpin and others, 2002; Lawrence and LaFontaine, 2010; Lee and others, 2011). Detergent metabolites present in environmental samples generally result from the degradation or metabolism of alkylphenol polyethoxylate detergents, widely used as cleaning agents during wastewater treatment (Loyo-Rosales and others, 2007). Seven detergent metabolites were analyzed in this study (table 3), and all are known to be endocrine disruptors because of their ability to mimic estrogenic hormones (White and others, 1994). Personal-use compounds are contained in many widely used personal-use products that enter wastewater and thus can be useful wastewater indicators (Oblinger and others, 2007). Thirteen personal-use compounds representing a broad range of chemical additives including flavorants, food preservatives, fragrances, and stimulants were analyzed in this study (table 3). Among the 9 pesticides analyzed for this study, 3 were herbicides (bromacil, metachlor, and prometon), 4 were insecticides (carbaryl, carbazole, chlorpyrifos, and diazinon), and 1 was a fungicide (metalaxyl) (table 3). A suspected carcinogen, the fumigant 1,4-dichlorobenzene is traditionally used as a moth repellent and is also classified as a pesticide, although it may be appropriately classified as a personal-use compound because of its use in urinal cakes (Montgomery and Welkom, 1990; National Institute of Environmental Health Sciences, 2011; Reif and others, 2012). Three of the pesticides (carbaryl, chlorpyrifos, and diazinon) are known endocrine disruptors, and two (1,4-dichlorobenzene and metachlor) are suspected endocrine disruptors (table 3) (Reif and others, 2012). There were 10 industrial compounds representing preservatives, antioxidants, solvents, fixatives, dyes, and other manufacturing compounds analyzed in this study (table 3). One compound, 3-*tert*-Butyl-4-hydroxyanisole (BHA), is a known endocrine disruptor. Two industrial compounds analyzed for this study, *p*-cresol and benzophenone, are compounds with suspected endocrine disrupting potential (Reif and others, 2012). Tribromomethane and phenol were the two disinfectant compounds analyzed in this study. Tribromomethane, a potential human carcinogen (table 3), is produced as a disinfection byproduct during chlorination (U.S. Environmental Protection Agency, 2007). PAHs are compounds typically associated with fossil fuels because they are constituents of natural gas, oil, and tar (table 3). PAHs also are formed during the combustion of carbon-based materials and the byproducts of fossil fuel combustion represent one of the largest pathways for PAHs into the environment (Nagpal, 1993). Recent studies have found that coal-tar sealants are another major source of PAHs to the environment (Van Metre and Mahler, 2010; Mahler and others, 2012). One pathway for coal-tar sealants into water and air includes weathering of road surfaces followed by aeolian transport or stormwater runoff of fine particles containing PAHs. Volatilization is another pathway by which PAHs from coal-tar sealants may enter the atmosphere (Van Metre and others, 2012). Among the nine PAHs analyzed in this study (table 3), benzo[a]-pyrene is a potential human carcinogen and a known endocrine disruptor that is highly bioaccumulative (U.S. Environmental Protection Agency, 2011). Flame retardants and plasticizers are used in the manufacture of flame retardants, plastics, resins, wax, and other products (Reif and others, 2012) (table 3). Of the six flame retardants and plasticizers analyzed in this study, tris (2-chloroethyl) phosphate and tris (dichloroisopropyl) phosphate are suspected endocrine disruptors.

Table 3. Wastewater compounds, pharmaceuticals, steroidal hormones, and sterols analyzed in water-quality samples collected from the San Antonio River Basin, Texas, 2011–12.

[LRL, laboratory reporting level; CASRN, Chemical Abstracts Service Registry Number; USGS, U.S. Geological Survey; NWIS, USGS National Water Information System; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available; PAH, polycyclic aromatic hydrocarbon]

Compound name	LRL	CASRN	Description of use or sources	Source reference	USGS NWIS parameter code
Wastewater compounds - detergent metabolites					
4-Cumylphenol[1]	0.060 µg/L	599-64-4	Nonionic detergent metabolite	(9)	62060
4-*n*-Octylphenol[1]	0.06 µg/L	1806-26-4	Nonionic detergent metabolite	(9)	62061
4-Nonylphenol (sum of all isomers)[1]	2 µg/L	84852-15-3	Nonionic detergent metabolite	(9)	62085
4-Nonylphenol diethoxylate (sum of all isomers) (NP2EO/NPE02)[1]	5 µg/L	--	Nonionic detergent metabolite	(9)	62083
4-*tert*-Octylphenol diethoxylate (OPE02)[1]	1 µg/L	2315-61-9	Nonionic detergent metabolite	(9)	61705
4-*tert*-Octylphenol monoethoxylate (OPE01)[1]	1 µg/L	2315-67-5	Nonionic detergent metabolite	(9)	61706
4-*tert*-Octylphenol[1]	0.14 µg/L	140-66-9	Nonionic detergent metabolite	(9)	62062
Wastewater compounds - personal-use compounds					
Camphor	0.044 µg/L	76-22-2	Flavor, odorant, ointments	(9)	62070
3-Methyl-1H-indole (Skatole)	0.036 µg/L	83-34-1	Fragrance, stench in feces, and coal tar	(9)	62058
Acetophenone	0.40 µg/L	98-86-2	Fragrance in detergent and tobacco, flavor in beverages	(9)	62064
Acetyl hexamethyl tetrahydronaphthalene (AHTN)[2]	0.028 µg/L	21145-77-7	Musk fragrance, persistent and widespread in groundwater	(9)	62065
Caffeine	0.06 µg/L	58-08-2	Stimulant	(9)	50305
N, N-diethyl-*meta*-toluamide (DEET)	0.06 µg/L	134-62-3	Insecticide, urban uses, mosquito repellent	(9)	62082
Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	0.052 µg/L	1222-05-5	Musk fragrance, persistent and widespread in groundwater	(9)	62075
Indole	0.08 µg/L	120-72-9	Inert pesticide ingredient, fragrance, in coffee	(9)	62076
Isoborneol	0.08 µg/L	124-76-5	Fragrance in perfumery, in disinfectants	(9)	62077
Isoquinoline	0.046 µg/L	119-65-3	Flavors and fragrances	(9)	62079
d-Limonene	0.08 µg/L	5989-27-5	Fragrance in aerosols, antimicrobial, antiviral, and fungicide	(9)	62073
Menthol	0.32 µg/L	89-78-1	Cigarettes, cough drops, liniment, mouthwash	(9)	62080
Triclosan[3]	0.20 µg/L	3380-34-5	Disinfectant, antimicrobial (concern for acquired microbial resistance)	(9)	62090

Table 3. Wastewater compounds, pharmaceuticals, steroidal hormones, and sterols analyzed in water-quality samples collected from the San Antonio River Basin, Texas, 2011–12.—Continued

[LRL, laboratory reporting level; CASRN, Chemical Abstracts Service Registry Number; USGS, U.S. Geological Survey; NWIS, USGS National Water Information System; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available; PAH, polycyclic aromatic hydrocarbon]

Compound name	LRL	CASRN	Description of use or sources	Source reference	USGS NWIS parameter code
Wastewater compounds - pesticides					
1,4-Dichlorobenzene[3]	0.040 µg/L	106-46-7	Used as an ingredient in urinal cakes, deodorant, disinfectant and chemical intermediate in addition to uses as a general insecticide, moth repellent, fumigant, and germicide	(5, 9, 11)	34572
Bromacil	0.36 µg/L	314-40-9	Uracil compound used as a herbicide for brush control on noncropland areas such as road shoulders. Greater than 80 percent noncrop usage on grass	(6, 9, 12)	4029
Carbaryl (1-naphthylmethylcarbamate)[1]	0.16 µg/L	63.25-2	Broad-spectrum carbamate insecticide used to control over 100 species of insects on citrus trees, fruit trees, nut trees, cotton, vegetables, forests, lawns, ornamentals, shade trees, and other crops, as well as poultry, livestock, and pets	(6, 7)	82680
Carbazole	0.03 µg/L	86-74-8	Insecticide, manufacturing of dyes, explosives, and lubricants	(9)	62071
Chlorpyrifos[1]	0.16 µg/L	2921-88-2	Broad-spectrum, chlorinated organophosphate (OP) insecticide, acaricide, and nematicide used on grain, cotton, field, fruit, nut, and vegetable crops, as well as on lawns, ornamental plants, and golf course turf. Also registered for direct use on sheep and turkeys, for horse site treatment, dog kennels, domestic dwellings, farm buildings, storage bins, and commercial establishments as well as nonstructural wood treatments including processed wood products, fence posts, and utility poles. Can lead to neurotoxicity	(6, 7)	38933
Diazinon	0.16 µg/L	333-41-5	Nonsystemic organophosphate Restricted Use Pesticide (RUP) for professional pest control operator use only. Greater than 40 percent nonagricultural usage on a wide variety of trees, fruit, row crops, and vegetables. No longer used on golf courses and sod farms because of die-offs of birds that often congregated in these areas. Classified as moderately toxic	(6, 9)	39572
Metalaxyl	0.12 µg/L	57837-19-1	Systemic benzenoid compound used as a pesticide, herbicide, and fungicide. Applied as either a foliar spray, soil treatment, or a seed treatment to control downy mildews. Used on many different food crops, including tobacoo, ornamentals, conifer, and golf course/turf applications	(6, 9)	50359
Metolachlor[3]	0.028 µg/L	51218-45-2	Preemergent herbicide used to control certain broadleaf and annual grassy weeds in row crops, fruit and nut trees, highway rights-of-way, and woody ornamentals. General use pesticide that is an indicator of agricultural drainage	(6, 9)	39415
Prometon	0.12 µg/L	1610-18-0	Herbicide, noncrop only, applied prior to blacktop	(9)	4037
Wastewater compounds - industrial compounds					
p-Cresol (*para*-Cresol)[3]	0.08 µg/L	106-44-5	Wood preservative	(9)	62084
3-*tert*-Butyl-4-hydroxyanisole (BHA)[1]	0.6 µg/L	121-00-6	Antioxidant and general preservative	(9)	62059
5-Methyl-1H-benzotriazole	1.2 µg/L	136-85-6	Antioxidant in antifreeze and deicers	(9)	62063
9,10-Anthraquinone	0.16 µg/L	84-65-1	Manufacturing of dye/textiles, seed treatment, bird repellent	(9)	62066
Benzophenone[3]	0.08 µg/L	119-61-9	Fixative for perfumes and soap	(9)	62067
Isophorone	0.032 µg/L	78-59-1	Used as solvent for paints, tin coatings, agricultural chemicals, and synthetic resins; excellent solvent for vinyl resins, cellulose esters, ethers, pesticides, storing lacquers; pesticide manufacturing Solvent for lacquer, plastic, oil, silicon, resin	(1, 5, 9, 13)	34409

Table 3. Wastewater compounds, pharmaceuticals, steroidal hormones, and sterols analyzed in water-quality samples collected from the San Antonio River Basin, Texas, 2011–12.—Continued

[LRL, laboratory reporting level; CASRN, Chemical Abstracts Service Registry Number; USGS, U.S. Geological Survey; NWIS, USGS National Water Information System; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available; PAH, polycyclic aromatic hydrocarbon]

Compound name	LRL	CASRN	Description of use or sources	Source reference	USGS NWIS parameter code
Wastewater compounds - industrial compounds—Continued					
Isopropylbenzene (cumene)	0.30 µg/L	98-82-8	Manufacturing phenol/acetone, fuels and paint thinner	(9)	62078
Methyl salicylate	0.044 µg/L	119-36-8	Liniment, food, beverage, UV-absorbing lotion	(9)	62081
Tetrachloroethene (Tetrachloroethylene)[4]	0.12 µg/L	127-18-4	Solvent and degreaser. Used in drycleaning fluids, degreasing and drying metals and other solids; solvent for waxes, greases, fats, oils, gums; manufacturing printing inks and paint removers; preparation of fluorocarbons and trichloroacetic acid; vermifuge; organic synthesis	(5, 9)	34476
Triethyl citrate (ethyl citrate)	0.16 µg/L	77-93-0	Cosmetics, pharmaceuticals	(9)	62091
Wastewater compounds - disinfection compounds					
Phenol	0.16 mg/L	108-95-2	Antiseptic and disinfectant. Used in pharmaceuticals, germicidal paints, dyes, indicators, slimicide, laboratory reagents; phenolic resins; epoxy resins (bisphenol-A), nylon-6, 2,4-D. Also used as a solvent for refining lubricating oils, preparation of acids and other compounds	(5, 9)	34466
Tribromomethane (Bromoform)[4]	0.10 mg/L	75-25-2	Wastewater ozination byproduct. Also used as solvent for waxes, greases, and oils; separating solids with lower densities, component of fire-resistant chemicals, geological assaying, medicine (sedative), intermediate in organic synthesis, military/explosives	(5, 9, 13)	34288
Wastewater compounds - polycyclic aromatic hydrocarbons					
1-Methylnaphthalene	0.022 µg/L	90-12-0	2–5 percent of gasoline, diesel fuel, or crude oil	(9, 14)	62054
2,6-Dimethylnaphthalene	0.06 µg/L	581-42-0	Present in diesel/kerosene (trace in gasoline)	(9, 14)	62055
2-Methylnaphthalene	0.036 µg/L	91-57-6	2–5 percent of gasoline, diesel fuel, and crude oil. Used in organic synthesis and insecticides	(5, 9, 14)	62056
Anthracene[4]	0.01 µg/L	120-12-7	Wood preservative, component of coal tar pitch volatiles, diesel, or crude oil; used in dyes, preparation of phenanthrene, carbazole, anthraquinone, and insecticides, organic semiconductor research	(5, 9, 13, 14)	34221
Benzo[a]-pyrene[1,4]	0.06 µg/L	50-32-8	Regulated PAH and byproduct of incompleted combustion, component of coal tar pitch volatiles and used in cancer research	(5, 9, 14)	34248
Fluoranthene[4]	0.024 µg/L	206-44-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuels); used as a research chemical. Combustion product	(5, 9, 14)	34377
Naphthalene[3,4]	0.04 µg/L	91-20-3	PAH also known as “camphor tar” and derived from coal tar or crude oil. Used as a fumigant and moth repellent, in preparation of pesticides, fungicides, dyes, detergents, wetting agents, synthetic resins, celluloids, preservatives, and lubricants. Major component (about 10 percent) of gasoline	(5, 7, 9, 14)	34443
Phenanthrene[4]	0.016 µg/L	85-01-8	Used in explosives, dyes, biochemical research, synthesis of drugs, and organic synthesis; combustion product	(5, 9, 14)	34462
Pyrene[4]	0.042 µg/L	129-00-0	Research chemical derived from industrial and experimental coal gasification operations. Component of coal tar and asphalt (only traces in gasoline or diesel fuel)	(5, 9, 14)	34470

Table 3. Wastewater compounds, pharmaceuticals, steroidal hormones, and sterols analyzed in water-quality samples collected from the San Antonio River Basin, Texas, 2011–12.—Continued

[LRL, laboratory reporting level; CASRN, Chemical Abstracts Service Registry Number; USGS, U.S. Geological Survey; NWIS, USGS National Water Information System; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available; PAH, polycyclic aromatic hydrocarbon]

Compound name	LRL	CASRN	Description of use or sources	Source reference	USGS NWIS parameter code
Wastewater compounds - flame retardants and plasticizers					
Tributyl phosphate	0.16 µg/L	126-73-8	Antifoaming agent, flame retardant	(9)	62089
Triphenyl phosphate	0.12 µg/L	115-86-6	Plasticizer, resin, wax, finish roofing paper	(9)	62092
Tris (2-butoxyethyl) phosphate	0.8 µg/L	78-51-3	Flame retardant	(9)	62093
Tris (2-chloroethyl) phosphate[3]	0.10 µg/L	115-96-8	Plasticizer, flame retardant	(9)	62087
Tris (dichloroisopropyl) phosphate[3]	0.16 µg/L	13674-87-8	Flame retardant	(9)	62088
Bisphenol A (BPA)	100 ng/L	80-05-7	Plasticizer	(10)	67304
Pharmaceuticals - nonprescription and metabolites					
1,7-Dimethylxanthine (*para*-Xanthine)	0.10 µg/L	611-59-6	Caffeine metabolite	(9)	62030
Acetaminophen	0.12 µg/L	103-90-2	Analgesic	(9)	62000
Codeine	0.046 µg/L	76-57-3	Analgesic	(9)	62003
Cotinine	0.038 µg/L	486-56-6	Nicotine metabolite	(9)	62005
Diphenhydramine	0.058 µg/L	147-24-0	Antihistamine, antiemetic (antinausea), sleep aid and sedative	(8, 9)	62796
Pharmaceuticals - prescription					
Thiabendazole	0.06 µg/L	148-79-8	Anthelmintics (used to treat worm infections)	(9)	62801
Albuterol (Salbutamol)	0.08 µg/L	18559-94-9	Antiasthmatic	(9)	62020
Carbamazepine	0.06 µg/L	298-46-4	Anticonvulsant and antimanic	(9)	62793
Dehydronifedipine	0.08 µg/L	67035-22-7	Antianginal	(9)	62004
Diltiazem	0.06 µg/L	42399-41-7	Antihypertensive	(9)	62008
Sulfamethoxazole	0.091 µg/L	723-46-6	Human antibiotic often used in combination with trimethoprim	(9)	62021
Trimethoprim	0.034 µg/L	738-70-5	Human antibiotic often used in combination with sulfamethoxazole	(9)	62023
Warfarin	0.08 µg/L	81-81-2	Anticoagulant. In large concentrations used as a rodenticide for controlling rats and house mice in and around homes, animal and agricultural premises, and commercial and industrial sites	(6, 9)	62023
Steroidal hormones - natural androgens					
11-Ketotestosterone	2 ng/L	564-35-2	Very strong androgen	(9)	64507
4-Androstene-3,17-dione	0.8 ng/L	63-05-8	Testosterone precursor, illicit steroid	(9)	64513
cis-Androsterone	0.8 ng/L	53-41-8	Testosterone metabolite, commonly used in deer repellent	(9)	64515
Dihydrotestosterone (DHT)	4 ng/L	521-18-6	Also known as Stanolone. Testosterone metabolites; very strong androgen	(9)	64524
Epitestosterone	2 ng/L	481-30-1	Human androgen	(9)	64517
Testosterone	1.6 ng/L	58-22-0	Principal human androgen, strong androgen	(9)	64525

Table 3. Wastewater compounds, pharmaceuticals, steroidal hormones, and sterols analyzed in water-quality samples collected from the San Antonio River Basin, Texas, 2011–12.—Continued

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Compound name	LRL	CASRN	Description of use or sources	Source reference	USGS NWIS parameter code
Steroidal hormones - natural estrogens					
17-*alpha*-Estradiol	0.8 ng/L	57-91-0	Low occurrence in humans, common in other species	(9)	64508
17-*beta*-Estradiol[1]	0.8 ng/L	50-28-2	Principal estrogen in humans, strong estrogen	(9)	64510
Equilenin	2 ng/L	517-09-9	Equine estrogen used in hormone replacement therapy	(9)	64518
Equilin	8 ng/L	474-86-2	Equine estrogen used in hormone replacement therapy	(9)	64519
Estriol	2 ng/L	50-27-1	Metabolite of 17-*beta*-estradiol	(9)	64520
Estrone	0.8 ng/L	53-16-7	Metabolite of 17-*beta*-estradiol	(9)	64521
Steroidal hormones - synthetic estrogens					
17-*alpha*-Ethynyl estradiol[1]	0.8 ng/L	57-63-6	Used in oral contraceptives, very strong estrogen	(9)	64509
Mestranol	0.8 ng/L	72-33-3	Used in oral contraceptives, metabolized to ethylnyl estradiol prior to excretion	(9)	64522
trans-Diethylstilbestrol	0.8 ng/L	56-53-1	Used in pharmaceuticals	(9)	64516
Steroidal hormones - natural progestin					
Progesterone	8 ng/L	57-83-0	Principal human progestational hormone	(9)	64523
Steroidal hormones - synthetic progestin					
Norethindrone (19-Norethisterone)	0.8 ng/L	68-22-4	Used in oral contraceptives	(9)	64511
Sterols - animal					
3-*beta*-Coprostanol	200 ng/L	360-68-9	Animal fecal indicator, useful sewage tracer	(9)	64512
Cholesterol	200 ng/L	57-88-5	Ubiquitous, produced by animals and plants	(9)	64514
Sterols - plant					
beta-Sitosterol	4 µg/L	83-46-5	Plant sterol	(9)	62068
beta-Stigmastanol	2.6 µg/L	19466-47-8	Plant sterol	(9)	62086

[1] Known endocrine disrupting potential (see source reference for more information).

[2] Concern for bioaccumulation and toxicity (see source reference for more information).

[3] Suspected endocrine disrupting potential (see source reference for more information).

[4] Potential human carcinogen (see source reference for more information).

[5] Montgomery and Welkom (1990).

[6] Extension Toxicology Network (EXTOXNET) (1996).

[7] National Pesticide Information Center (2011).

[8] Couper and Logan (2004).

[9] Reif and others (2012).

[10] National Institute of Environmental Health Sciences (2013).

[11] National Institute of Environmental Health Sciences (2011).

[12] Washington State Department of Transportation (2006).

[13] U.S. Environmental Protection Agency (2007).

[14] Nagpal (1993).

Pharmaceuticals

Pharmaceuticals are chemical substances that are manufactured and administered to humans or animals to prevent, treat, or cure a variety of physical and mental afflictions. Pharmaceuticals are introduced into the environment through disposal practices such as flushing unused medication, direct excretion, or discharge of effluent from pharmaceutical manufacturing facilities (Phillips and others, 2010). Pharmaceuticals have been detected in both surface water and groundwater and often are associated with wastewater (Kolpin and others, 2002, 2004; Barnes and others, 2008; Rounds and others, 2009). Rounds and others (2009) reported a wide range of removal rates of different pharmaceuticals during wastewater treatment, ranging from 18 percent for carbamazepine to greater than 99 percent for acetaminophen, indicating the efficiency of removal during wastewater treatment is an important factor in determining the concentrations of different pharmaceuticals introduced into streams. Many pharmaceuticals are known endocrine disruptors and some have been shown to have adverse effects on aquatic biota (Lintelmann and others, 2003). A total of 13 pharmaceuticals were analyzed for this study (table 3). Five of the compounds were nonprescription pharmaceuticals or metabolites, and eight were prescription pharmaceuticals.

Steroidal Hormones and Sterols

Steroidal hormones are biologically produced chemicals that serve a variety of functions in animal and plant metabolism. Synthetic hormone derivatives such as anabolic steroids and birth-control compounds also are widely used by humans (Reif and others, 2012). As with pharmaceuticals, both natural and synthetic hormones may be introduced into the environment through direct excretion or disposal into wastewater systems. Both natural and synthetic hormones have been detected in aquatic systems, promoting concerns about negative effects on freshwater biota (National Academy of Sciences, 1999). For example, feminization of male fish, based on increased vitellogen production and production of early stage eggs in the testes of male fish, has been observed in conjunction with the presence of 17-*alpha*-ethynyl-estradiol, a form of synthetic estrogen (Kidd and others, 2007). For this study, 21 natural androgens, natural and synthetic estrogens, natural and synthetic progestin, animal sterols, and plant sterols were analyzed (table 3).

Methods

Collection of Streamflow Data

Continuous streamflow was measured at USGS streamflow-gaging stations by using USGS methods described by Rantz and others (1982a, b) and Turnipseed and Sauer (2010). A stage-discharge relation (rating) was developed on the basis of the discrete discharge measurements at each site (Kennedy, 1984; Turnipseed and Sauer, 2010). Adjustments were made to site ratings when discrete discharge measurements indicated changing channel conditions. From the rating, stage data were used to compute discharge (Kennedy, 1983). Discrete discharge measurements were made in accordance with USGS methods (Rantz and others, 1982a, b; Turnipseed and Sauer, 2010) preceding water-quality-sample collection. Streams were waded, and velocity measurements were made by using rod-mounted acoustic velocity meters (Xylem Analytics, 2012). The instantaneous discharges at the time the samples were collected are listed in appendixes 1–3 and were obtained from stage-discharge relations or by making discrete discharge measurements. Streamflow data were not used in the analyses but are included in appendixes 1–3.

Collection and Processing of Water-Quality Samples

Samples were collected at 20 sites in the San Antonio River Basin during March 2011–May 2012 (fig. 1, table 2). All of the samples were collected and processed by following the methods and guidelines described in the “National Field Manual for the Collection of Water-Quality Data” (U.S. Geological Survey, variously dated). The specific sites where wastewater compounds, pharmaceuticals, and steroidal hormones and sterols were collected during each synoptic sampling event and the dates when samples were collected are shown in appendixes 1–3, respectively. With the exception of the samples collected at the Ecleto site, all samples were collected during base flow or low-flow conditions. At the Ecleto site, samples were collected during January–March 2012 and in July 2012 in response to storm events when streamflow sufficient for sampling was generated. Compared to the samples collected at the other sites, the samples collected at the Ecleto site have different sample collection dates for wastewater compounds, pharmaceuticals, steroidal hormones, and sterols (apps. 1–3). Multiple samples were collected during January–March 2012 at the Ecleto site because of processing difficulties associated with sediment-laden storm samples; the large amounts of suspended sediment in the samples sometimes clogged the sample-extraction cartridges used to process the samples at the National Water Quality Laboratory (NWQL) in Denver, Colorado, resulting in an insufficient sample volume to analyze for wastewater compounds.

Sample Analyses

Samples were analyzed for selected wastewater compounds, pharmaceuticals, steroidal hormones, and sterols at the NWQL. Physicochemical properties including dissolved oxygen (DO), pH, specific conductance (SC), water temperature, and turbidity (apps. 1–3) also were measured in the field prior to sample collection by following standard USGS protocols (U.S. Geological Survey, variously dated).

Selected wastewater compounds were analyzed by using solid-phase extraction and gas chromatography/mass spectrometry techniques described in Zaugg and others (2002) (app. 1). These compounds include detergent metabolites, personal-use compounds, pesticides, industrial compounds, disinfection compounds, polycyclic aromatic hydrocarbons, flame retardants and plasticizers, and plant sterols (table 3). Although the plant sterols *beta*-sitosterol and *beta*-stigmastanol were analyzed with the wastewater-compound method, they are discussed in this report along with steroidal hormones and related compounds because they more closely match natural hormones in terms of function and source. The animal sterols 3-*beta*-coprostanol and cholesterol were analyzed by using both the wastewater-compound method and the hormones method, but the hormone method was chosen for the analysis in this study because of superior detection levels (Zaugg and others, 2002; Foreman and others, 2012).

All of the analytical methods used for this study can detect low-level concentrations of wastewater compounds, pharmaceuticals, steroidal hormones, and sterols in environmental samples such as the samples collected during the study. The analytical results from each of these methods are described as to whether or not they exceed the long-term method detection limits (LT-MDLs) and LRLs. The LT-MDLs and LRLs are guidelines that can be used in interpretation of data, determining whether or not data will need to be censored to minimize the number of false positive detections, and to quantify false negative detections within a particular set of data (Childress and others, 1999). The LT-MDL is a modification of the method detection limit (MDL) analysis used by the U.S. Environmental Protection Agency (USEPA) (Childress and others, 1999, p. 6). The LT-MDL establishes the minimum concentration of a compound that can be measured and reported with a 99 percent confidence level when the analyte concentration in the sample is greater than zero. The LT-MDL is designed to minimize the chance of a false positive result (detecting the compound when it is not present in the sample), but does not imply accuracy or precision of the quantitative measurement (Childress and others, 1999). The LT-MDL limits the risk of false positive values in a sample, but does not adequately address the possibility of false negatives in a sample when the compound may be present in the sample but is not detected. The LRL is a laboratory quantification limit that generally is two times the LT-MDL and is designed to minimize the number of false negatives in a dataset (Childress and others, 1999). Because information-rich mass spectrometry methods were used to augment the identification of the compounds described in this report, estimated concentrations less than the LT-MDL were considered valid chemical detections (U.S. Geological Survey, 2010). Detections are reported when the concentration of the compound equaled or exceeded the LT-MDL, for qualified concentrations less than the LT-MDL, and when the presence of the compound was verified but not quantified. In this report, compound concentrations are qualified with an “E” remark code to indicate that the sample value is estimated if the quantification of the analyte is considered by the NWQL to be highly variable, if the compound concentration was extrapolated below the calibration curve, or if the compound concentration was less than the LT-MDL (U.S. Geological Survey, 2010). Compounds that were verified, but not quantified, are qualified with an “M” remark code. When a compound was analyzed and the criteria for a detection were not met, the concentration is reported as “not measureable.”

Prescription and nonprescription pharmaceuticals and metabolites (table 3) were analyzed by using solid-phase extraction and high-performance liquid chromatography/mass spectrometry methods and techniques described in Furlong and others (2008) (app. 2). The pharmaceutical cotinine was analyzed by using both the wastewater-compound method and the pharmaceutical method, but the pharmaceutical method was chosen for the analysis in this study to be consistent with the pharmaceuticals analysis.

Steroidal hormones and sterols (table 3) were analyzed by using the solid-phase extraction, derivatization, and gas chromatography with tandem mass spectrometry methods described in Foreman and others (2012) (app. 3). Bisphenol A also was analyzed by using the hormone analysis, but is categorized in this report as a flame retardant and plasticizer compound. At the start of the study, the hormone analysis was considered a research analytical method, but the method was approved by the NWQL for general use on June 21, 2012, and documented in Foreman and others (2012). Concentrations of steroidal hormones are reported by the NWQL in units of nanograms per liter, whereas all other compounds are reported in units of micrograms per liter. For use in selected figures (bar graphs and pie charts depicting concentrations for different compound classes), concentrations of steroidal hormones were converted from nanograms per liter to micrograms per liter by dividing nanograms per liter by 1,000. Converting all of the concentration values to a single unit of measure facilitated comparison of results from different compound classes, and was necessary when concentrations were summed to compute total concentrations.

Quality Assurance

For quality-assurance purposes, several quality-control samples, including an equipment blank, two field blanks, and two split replicates, were collected to qualify the precision and accuracy of the environmental samples collected. The equipment blank was collected to determine the extent of contamination that might be introduced during sample processing in the laboratory and laboratory analysis. The field blank samples were collected to determine the extent of contamination that might have been introduced during sample collection, sample processing, and laboratory analysis. Equipment blank and field blank samples were collected and processed by using organic-free, deionized water obtained from the NWQL and certified to contain nondetectable concentrations of the compounds that were analyzed. Split replicate samples were collected along with environmental samples to determine the amount, or degree, of variability that might have resulted from the procedures used to collect, process, and analyze the samples. The quality-control samples were analyzed for the same wastewater compound, pharmaceutical, and hormone analytical schedules as were the environmental samples. Results of the quality-assurance analyses are shown in appendix 4.

Prior to collecting the first environmental sample, an equipment blank was collected on March 29, 2011, and analyzed for concentrations and surrogate recoveries for selected wastewater compounds, pharmaceuticals, steroidal hormones, and sterols (app. 4). No pharmaceuticals, steroidal hormones, or sterols were detected in the equipment blank; four wastewater compounds were detected. The four wastewater compounds detected were 4-nonylphenol (all isomers) (the presence of 4-nonylphenol was verified but not quantified), benzophenone, isophorone, and tetrachloroethene. Where quantified, concentrations of these detected compounds ranged from an estimated 0.03 micrograms per liter (µg/L) for tetrachloroethene to 0.17 µg/L for isophorone (app. 4). The laboratory reagent blank data provided by the NWQL confirmed no contamination during analysis at the NWQL, indicating sample processing in the field was likely the source of contamination for these compounds.

Field blank samples were collected on November 1, 2011, and April 26, 2012, during the second and third synoptic sampling events (app. 4). There were detectable concentrations of four wastewater compounds in the two field blank samples. The four compounds detected in the field blank collected on November 1, 2011, at the Leon 35 site (map identifier EC04, fig. 1, table 2) were *N,N*-diethyl-*meta*-toluamide (DEET) (0.01µg/L), 4-nonylphenol (all isomers) (estimated concentration of 2 µg/L), benzophenone (0.04 µg/L), and isophorone (0.16 µg/L) (app. 4). The only wastewater compound detected in the field blank collected on April 26, 2012, at the North Prong site was isophorone (0.062 µg/L) (app. 4). The laboratory reagent blank data provided by the NWQL confirmed no contamination during analysis at the NWQL, indicating that when these compounds were detected in the field blank samples they likely were introduced during sample processing in the field. Similar to the results from the equipment blank sample, pharmaceuticals, steroidal hormones, or sterols were not detected in either of the field blanks.

The equipment blank and field blank results were analyzed to determine if any results needed to be rejected and not reported because the concentrations in the blank samples were greater than the concentrations in the environmental samples. For two of the compounds, 4-nonylphenol (all isomers) and isophorone, all environmental sample values and 2 replicate sample values for these compounds were rejected and not reported because the concentrations of these compounds in the blank samples were close to or exceeded the concentrations measured in the environmental samples (app. 1, app. 4). For the remaining compounds detected in the blank samples, including benzophenone, DEET, and tetrachloroethene, a threshold value of three times the concentration measured in the blank samples was used to determine whether or not to reject data for an individual compound in each field sample because of potential contamination as a result of sample handling or analytical procedures. The threshold value for benzophenone was 0.12 µg/L, and environmental sample concentrations less than or equal to 0.12 µg/L were rejected and not reported (app. 1). Likewise for DEET and tetrachloroethene, with threshold values of 0.03 µg/L and 0.09 µg/L, respectively, environmental sample concentrations of DEET less than or equal to 0.03 µg/L and environmental sample concentrations of tetrachloroethene less than or equal to 0.09 µg/L were rejected and not reported (app. 1).

Split replicate samples were collected along with paired environmental samples from the Medina site (map identifier EC05, fig. 1, table 2, app. 1, app. 4) on November 1, 2011, and from the SAR Mitchell site (map identifier EC09, fig. 1, table 2, app. 1, app. 4) on April 25, 2012. The split replicate sample results were compared to the environmental sample results by calculating the relative percent difference (RPD) for each detected concentration pair by using the equation

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

where

C_1 is the detected concentration in the environmental sample, and

C_2 is the detected concentration in the split replicate sample.

RPDs were calculated for only those compound pairs with detectable concentrations greater than or equal to the LRL in both the environmental and the split replicate sample (app. 4). RPDs were not computed for sample pair compound concentrations that had one or more nondetected or estimated values. RPDs calculated for 11 paired concentrations from the sample collected at the Medina site on November 1, 2011, ranged from 0.00 to 35.05 percent (app. 4). RPDs of less than or equal to 15 percent were used to indicate good agreement between the environmental and split replicate sample results when concentrations were sufficiently large compared to the LRL. Only 4 of the 11 paired concentrations from the Medina site exceeded the 15 percent threshold, and most of the values exceeding the 15 percent threshold were associated with concentrations that were low and close to the LRL. RPDs were calculated for 19 paired concentrations from the samples collected on April 25, 2012, at the SAR Mitchell site. RPDs for these samples ranged from 0.00 to 66.67 percent (app. 4). Four of the 19 paired concentrations exceeded the 15 percent threshold, and many of these paired concentrations were close to the LRL.

Detections and Concentrations of Compounds of Emerging Concern

Detections and Concentrations of Individual Compounds

Of the 60 wastewater compounds analyzed by the NWQL, 2 compounds (4-nonylphenol and isophorone) were rejected and not reported or discussed because of contamination of the equipment blank and field blank quality-control samples. Four compounds (*beta*-sitosterol, *beta*-stigmastanol, 3-*beta*-coprostanol, and cholesterol) included in USGS wastewater compound analysis used in this study were reclassified as sterols and discussed in association with sterols, and cotinine was reclassified and discussed as a pharmaceutical (table 3). The compound bisphenol A, a plasticizer analyzed in the hormone analysis, was reclassified and included in the discussion on wastewater compounds; a total of 54 compounds were therefore classified as wastewater compounds for the purposes of this report (app. 1). Of these 54 compounds, 32 were detected in at least 1 sample, and 22 were not detected in any samples collected during this study (fig. 2, table 4). Of the detected compounds, 18 were measured at concentrations greater than or equal to the LRL, and 14 compounds only were detected at concentrations less than the LRL. There were 302 detections in the 33 samples analyzed for wastewater compounds in the study (app. 1).

Two of six detergent metabolites, 4-*n*-octylphenol and 4-nonylphenol diethoxylate, both known endocrine-disrupting compounds (Reif and others, 2012), each were detected in at least one sample, yielding a total of nine detections for detergent metabolites (fig. 2, table 4). The most commonly detected detergent metabolite, 4-nonylphenol diethoxylate, was detected in 8 of 33 samples at concentrations ranging from an estimated 0.4 µg/L to an estimated 0.8 µg/L. The other detergent metabolite, 4-*n*-octylphenol, was detected in one sample on the basis of its mass spectra; however, the concentration could not be quantified and it was coded with an "M" (app. 1).

There were 88 detections of personal-use compounds, and 9 of the 13 personal-use compounds were detected in at least one sample (fig. 2, table 4). The most commonly detected personal-use compound, DEET (the active ingredient in many insect repellents), was detected in 23 of 33 samples at concentrations ranging from 0.04 µg/L to 0.34 µg/L.

There were 19 detections of pesticides, and 3 of 9 pesticides were detected in at least one sample (fig. 2, table 4). The most commonly detected pesticide, 1,4-dichlorobenzene, was detected in 8 of 33 samples at concentrations ranging from an estimated 0.014 µg/L to 0.065 µg/L.

There were 62 detections of industrial compounds, and 6 of 10 individual industrial compounds were detected in at least one sample (fig. 2). The most frequently detected industrial compound, 5-methyl-1H-benzotriazole (a common component of antifreeze), was detected in 19 of the 33 samples at concentrations ranging from an estimated 0.1 µg/L to 1.4 µg/L (table 4).

There were 13 detections of two different disinfection compounds, both of which were detected in at least one sample (fig. 2, table 4). Tribromomethane, a disinfection byproduct of water treatment (U.S. Environmental Protection Agency, 2004, 2007), was detected in 8 of 33 samples at concentrations ranging from an estimated 0.01 µg/L to 0.67 µg/L (table 4). Phenol, a widely used disinfectant, was detected in 5 of 33 samples at concentrations ranging from 0.12 µg/L to 0.25 µg/L.

There were 11 detections of PAHs, and 5 of 9 PAHs were detected in at least one sample (fig. 2, table 4). Phenanthrene and fluoranthene, both components of tar and petroleum products, were detected more frequently than the other PAHs. These compounds were detected in 4 of 33 samples at concentrations ranging from an estimated 0.003 µg/L to an estimated 0.008 µg/L for phenanthrene and an estimated 0.003 µg/L to 0.012 µg/L for fluoranthene.

There were 100 detections of flame retardants and plasticizers, and 5 of 6 compounds in this subclass were detected in at least one sample (fig. 2, table 4). Bisphenol A was the only compound in this subclass that was not detected in any of the samples. Detected in 28 of the 33 samples, tris (2-chloroethyl) phosphate and tris (dichloroisopropyl) phosphate were the most commonly detected compounds in the study and had concentrations ranging from an estimated 0.02 µg/L to 0.52 µg/L and an estimated 0.02 µg/L to 0.82 µg/L, respectively. Tris (2-chloroethyl) phosphate and tris (dichloroisopropyl) phosphate are suspected endocrine disruptors (Reif and others, 2012).

Of the wastewater compounds that were detected, the lowest measured concentrations were an estimated 0.003 µg/L for 3-methyl-1H-indole, fluoranthene, and phenanthrene, all of which were less than their respective LRLs (table 4). The highest concentration of a wastewater compound was measured in the personal-use compound hexahydrohexamethyl-cyclopentabenzopyran (HHCB), with a concentration measured at 1.90 µg/L. The second highest concentration of a wastewater compound in the study was 1.4 µg/L of the industrial compound 5-methyl-1H-benzotriazole, a common component of antifreeze. All of the remaining wastewater compounds were measured at concentrations less than 1.0 µg/L.

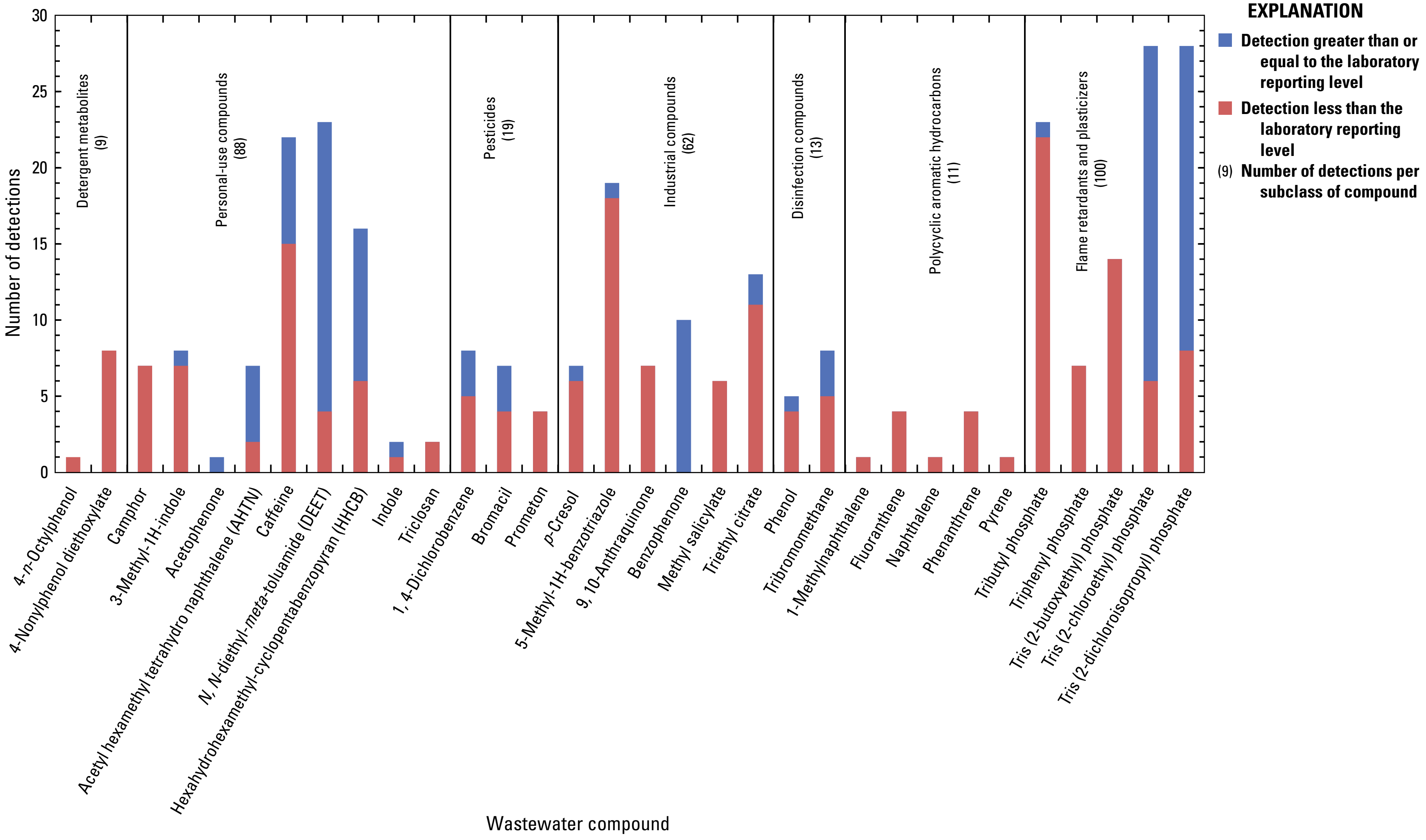


Figure 2. The number of detections of wastewater compounds in 33 water-quality samples collected from the San Antonio River Basin, 2011–12. Laboratory reporting levels (LRLs) for each compound are listed in table 4.

Table 4. Laboratory reporting levels, total number of detections, and concentration ranges for wastewater compounds in 33 water-quality samples collected from the San Antonio River Basin, Texas, 2011–12.

[Wastewater compounds and water-quality data listed in appendix 1. LRL, laboratory reporting level; µg/L, micrograms per liter; M, presence verified but not quantified; E, estimated]

Compound	LRL (µg/L)	Total number of detections	Range in detected compounds (µg/L)
Detergent metabolites			
4-*n*-Octylphenol[1]	0.06	1	M
4-Nonylphenol diethoxylate[1]	5.0	8	E0.4–E0.8
Personal-use products			
Camphor	0.044	7	E0.011–0.040
3-Methyl-1H-indole	0.036	8	E0.003–0.540
Acetophenone	0.4	1	0.4
Acetyl hexamethyl tetrahydro naphthalene (AHTN)	0.028	7	E0.007–0.130
Caffeine	0.06	22	E0.02–0.46
N, N-diethyl-meta-toluamide (DEET)	0.06	23	0.04–0.34
Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	0.052	16	E0.006–1.90
Indole	0.08	2	E0.01–0.09
Triclosan[2]	0.20	2	E0.02–E0.09
Pesticides			
1,4-Dichlorobenzene[2]	0.040	8	E0.014–0.065
Bromacil	0.36	7	E0.06–0.74
Prometon	0.12	4	E0.02–0.10
Industrial compounds			
p-Cresol[2]	0.08	7	E0.02–0.89
5-Methyl-1H-benzotriazole	1.2	19	E0.1–1.4
9,10-Anthraquinone	0.16	7	E0.02–E0.04
Benzophenone[2]	0.08	10	0.13–0.26
Methyl salicylate	0.044	6	E0.007–E0.015
Triethyl citrate	0.16	13	E0.02–0.23
Disinfection compounds			
Phenol	0.16	5	0.12–0.25
Tribromomethane (Bromoform)[3]	0.10	8	E0.01–0.67
Polycyclic aromatic hydrocarbons			
1-Methylnaphthalene	0.022	1	E0.009
Fluoranthene	0.024	4	E0.003–0.012
Naphthalene	0.040	1	E0.017
Phenanthrene	0.016	4	E0.003–E0.008
Pyrene	0.042	1	E0.006
Flame retardants and plasticizers			
Tributyl phosphate	0.16	23	E0.01–0.62
Triphenyl phosphate	0.12	7	E0.01–E0.04
Tris(2-butoxyethyl) phosphate	0.8	14	E0.1–0.7
Tris(2-chloroethyl) phosphate[2]	0.10	28	E0.02–0.52
Tris(dichloroisopropyl) phosphate[2]	0.16	28	E0.02–0.82

[1] Known endocrine disrupter (Reif and others, 2012).

[2] Suspected endocrine disrupter (Reif and others, 2012).

[3] Potential human carcinogen (U.S. Environmental Protection Agency, 2007).

Fourteen nonprescription and prescription pharmaceuticals were included in the USGS pharmaceutical analysis used in this study. One of the compounds, caffeine, was reclassified for this report as a wastewater compound (personal-use compound); the remaining 13 pharmaceuticals were considered pharmaceuticals for the purposes of this report (table 3). Of the 13 pharmaceuticals, only 4 compounds, 1 nonprescription pharmaceutical (diphenhydramine) and 3 prescription pharmaceuticals (carbamazepine, dehydronifedipine, and sulfamethoxazole), were detected in at least one sample collected from the San Antonio River Basin (fig. 3, table 5). There were a total of 58 detections of pharmaceuticals in the 34 samples analyzed for pharmaceuticals in the study.

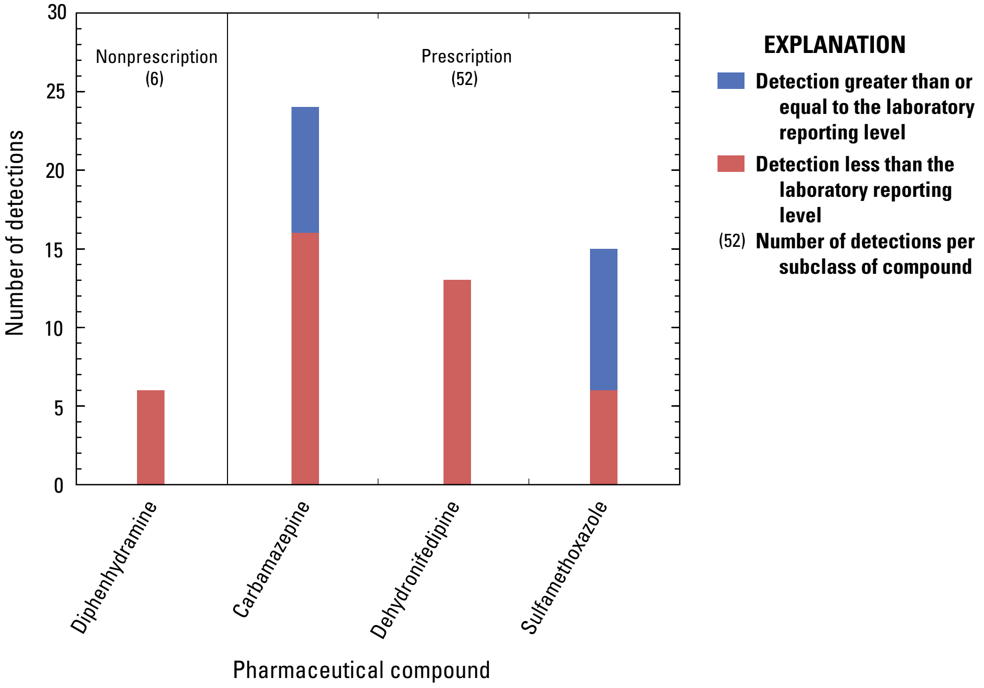


Figure 3. The number of detections of pharmaceuticals in 34 water-quality samples collected from the San Antonio River Basin, 2011–12. Laboratory reporting levels (LRLs) for each compound are listed in table 5.

Table 5. Laboratory reporting levels, total number of detections, and concentration ranges for pharmaceuticals in 34 water-quality samples collected from the San Antonio River Basin, Texas, 2011–12.

[Pharmaceuticals and water-quality data listed in appendix 2. LRL, laboratory reporting level; µg/L, micrograms per liter; E, estimated]

Compound	LRL (µg/L)	Total number of detections	Range in detected compounds (µg/L)
Nonprescription			
Diphenhydramine	0.058	6	E0.005–E0.015
Prescription			
Carbamazepine	0.060	24	E0.005–E0.121
Dehydronifedipine	0.080	13	E0.003–E0.013
Sulfamethoxazole	0.091	15	E0.014–0.267

Diphenhydramine, primarily used as an antihistamine (O'Neil, 2001) and the only detected nonprescription pharmaceutical, was detected in 6 of 34 samples at concentrations ranging from an estimated 0.005 µg/L to an estimated 0.015 µg/L (fig. 3, table 5). Carbamazepine, an anticonvulsant and antimanic (mood stabilizing) compound (O'Neil, 2001) and the most frequently detected prescription pharmaceutical, was detected in 24 of 34 samples at concentrations ranging from an estimated 0.005 µg/L to an estimated 0.121 µg/L. Sulfamethoxazole, a prescription antibiotic (O'Neil, 2001), was detected in 15 of 34 samples at concentrations ranging from an estimated 0.014 µg/L to 0.267 µg/L. Dehydronifedipine, an antianginal pharmaceutical (O'Neil, 2001), was detected in 13 of 34 samples at concentrations ranging from an estimated 0.003 µg/L to an estimated 0.013 µg/L. Both carbamazepine and sulfamethoxazole were detected at concentrations greater than or equal to the LRL in some samples, whereas diphenhydramine and dehydronifedipine only were detected at concentrations less than the LRL. The lowest reported concentration of a pharmaceutical was an estimated 0.003 µg/L for dehydronifedipine, and the highest concentration was 0.267 µg/L for sulfamethoxazole.

There were 20 measured compounds in the USGS analysis of steroidal hormones and sterols used for this study. Bisphenol A was analyzed as part of the steroidal hormones and sterols method but was classified in this report with the wastewater compounds because it is also a plasticizer and an endocrine disrupter (U.S. Environmental Protection Agency, 2013b). Two plant sterols (*beta*-sitosterol and *beta*-stigmastanol) analyzed as part of the wastewater compounds method were reclassified as sterols, resulting in a total of 17 steroidal hormones and 4 sterols being analyzed for this report (table 3, app 3). Of the 17 steroidal hormones, 4 were detected in at least one sample from the San Antonio River Basin (fig. 4, table 6). Of the 4 detected steroidal hormones, 2 were measured at concentrations greater than or equal to the LRL, and 2 only were detected at concentrations less than the LRL. Of the 4 sterols, all 4 were detected in at least one sample from the San Antonio River Basin. Both animal sterols were measured at concentrations greater than or equal to the LRL, and both plant sterols only were detected at concentrations less than the LRL. There were a total of 16 detections of steroidal hormones and 41 detections of sterols in the 34 samples analyzed for steroidal hormones in the study. Steroidal hormones had lower LRLs than wastewater compounds, pharmaceuticals, and sterols. A lower LRL indicates greater analytical sensitivity and the ability to detect compounds at lower concentrations.

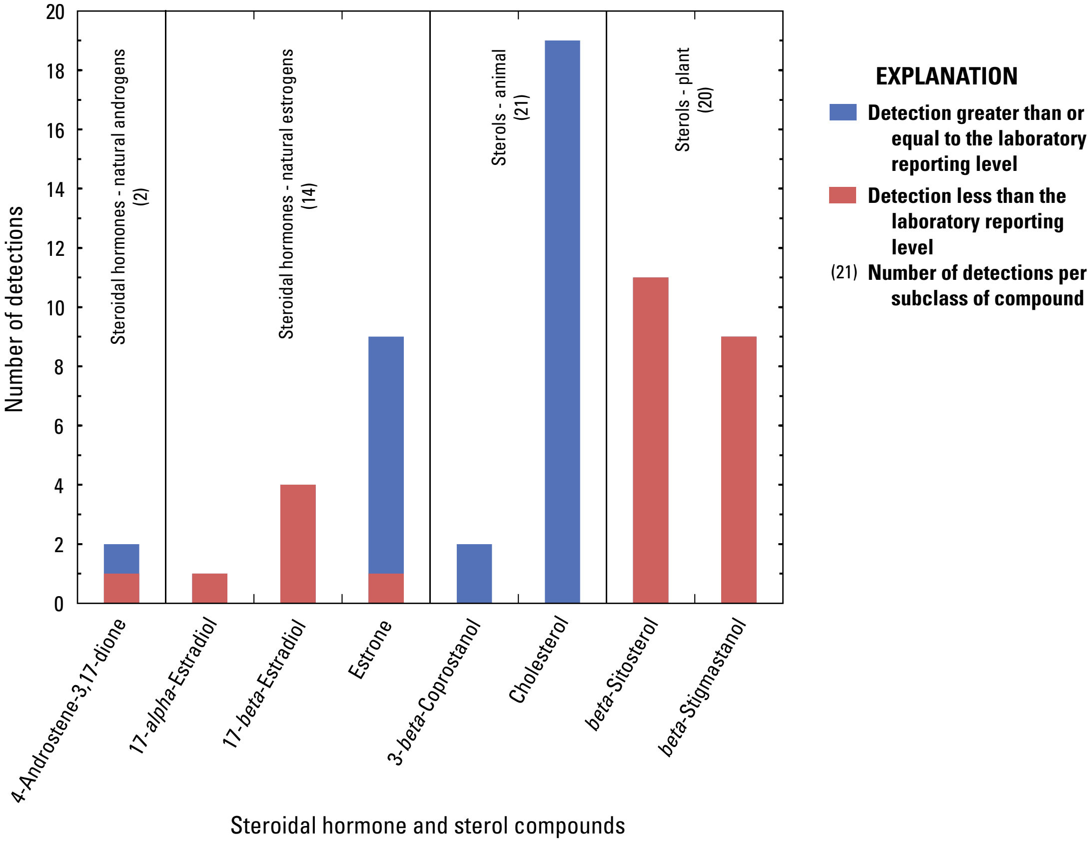


Figure 4. The number of detections of steroidal hormones and sterols in 34 water-quality samples collected from the San Antonio River Basin, 2011–12. Laboratory reporting levels (LRLs) for each compound are listed in table 6.

Table 6. Laboratory reporting levels, total number of detections, and concentration ranges for steroidal hormones and sterols in 34 water-quality samples collected from the San Antonio River Basin, Texas, 2011–12.

[Steroidal hormones, sterols, and water-quality data listed in appendix 3. LRL, laboratory reporting level; ng/L, nanograms per liter; µg/L, micrograms per liter; M, presence verified but not quantified; E, estimated]

Compound	LRL (ng/L)	Total number of detections	Range in detected compounds (ng/L)
Steroidal hormones - natural androgens			
4-Androstene-3,17-dione	0.80	2	E0.21–2.58
Steroidal hormones - natural estrogens			
17-*alpha*-Estradiol	0.80	1	E0.31
17-*beta*-Estradiol	0.80	4	E0.09–0.43
Estrone	0.80	9	0.68–4.50
Sterols - animal			
3-*beta*-Coprostanol	200	2	252–422
Cholesterol	200	19	200–1,740

Compound	LRL (µg/L)	Total number of detections	Range in detected compounds (µg/L)
Sterols - plant			
beta-Sitosterol	4	11	M–E1
beta-Stigmastanol	2.6	9	E0.1–E0.8

Concentrations of steroidal hormones were much lower in comparison to sterols (table 6). The steroidal hormone 4-androstene-3,17-dione occurs naturally and as a synthetic steroid and was measured at concentrations ranging from an estimated 0.21 nanograms per liter (ng/L) to 2.58 ng/L (table 6). The concentration of 17-*alpha*-estradiol was an estimated 0.31 ng/L, and the concentration of 17-*beta*-estradiol ranged from an estimated 0.09 ng/L to 0.43 ng/L. Estrone, a metabolite of 17-*beta*-estradiol, was the most commonly detected compound related to estrogen and was detected in 9 of 34 samples at concentrations ranging from 0.68 ng/L to 4.50 ng/L. The animal sterol, 3-*beta*-coprostanol, was detected in 2 of 34 samples, and concentrations ranged from 252 ng/L to 422 ng/L. Cholesterol was detected in 19 of 34 samples at concentrations ranging from 200 ng/L to 1,740 ng/L (fig. 4, table 6). The two natural plant sterols, *beta*-sitosterol and *beta*-stigmastanol, were detected in 11 and 9 of the 34 samples, respectively. The concentrations of *beta*-sitosterol ranged from "M" (presence verified but not quantified) to an estimated 1 µg/L, and the concentrations of *beta*-stigmastanol ranged from an estimated 0.1 µg/L to an estimated 0.8 µg/L.

Detections and Concentrations for Each Synoptic Sampling Event

The number of detections for all compound classes from the first synoptic sampling event (March–May 2011) is shown in figure 5. The number of detections of wastewater compounds ranged from 2 in samples collected at multiple sites to 13 in the sample collected at the Medina site (figs. 1, 5*A*). Of the 91 detections of wastewater compounds in the first synoptic sampling event, approximately 47 percent were greater than or equal to the LRL. The number of detections for pharmaceuticals ranged from 0 at multiple sites to 3 at multiple sites (fig. 5*B*). Of the 22 detections of pharmaceuticals, concentrations greater than or equal to the LRL were measured in approximately 36 percent of the samples. The number of detections of steroidal hormones ranged from 0 at multiple sites to 2 at multiple sites (fig. 5*C*). Of the 11 detections of steroidal hormones, approximately 55 percent were greater than or equal to the LRL. The number of detections of sterols ranged from 0 at the Macdona site (map identifier EC02, fig. 1, table 2) to 4 at the SAR Elmendorf site (map identifier EC13, fig. 1, table 2) (fig. 5*D*). Of the 28 detections of sterols, approximately 43 percent were greater than or equal to the LRL.

Total concentrations for the different compound classes from the first synoptic sampling event are shown in figure 6. Total concentrations of wastewater compounds ranged from 0.22 µg/L at the Cibolo Falls City site (map identifier EC18, fig. 1, table 2) to 5.86 µg/L at the SAR Elmendorf site (fig. 6*A*). Total concentrations of pharmaceuticals ranged from not measureable at multiple sites to 0.37 µg/L at the Medio site (map identifier EC03, fig. 1, table 2) (fig. 6*B*). Total concentrations of steroidal hormones ranged from not measureable at multiple sites to 0.00493 µg/L at the SAR Elmendorf site (fig. 6*C*). Total concentrations of sterols ranged from not measureable at the Macdona site to 1.74 µg/L at the SAR Goliad site (map identifier EC20, fig. 1, table 2) (fig. 6*D*). The high concentration of sterols at the SAR Goliad site was related to detection only of the animal sterol cholesterol. The plant sterol *beta*-sitosterol was detected in this sample, but it was not measurable. When measurement data for wastewater, pharmaceutical, steroidal hormone, and sterol compounds were grouped together, the Macdona site had both the lowest number of total detections (2) and the lowest total concentrations (0.62 µg/L), and the SAR Elmendorf site had the highest number of detections (21) and highest total concentrations (7.75 µg/L).

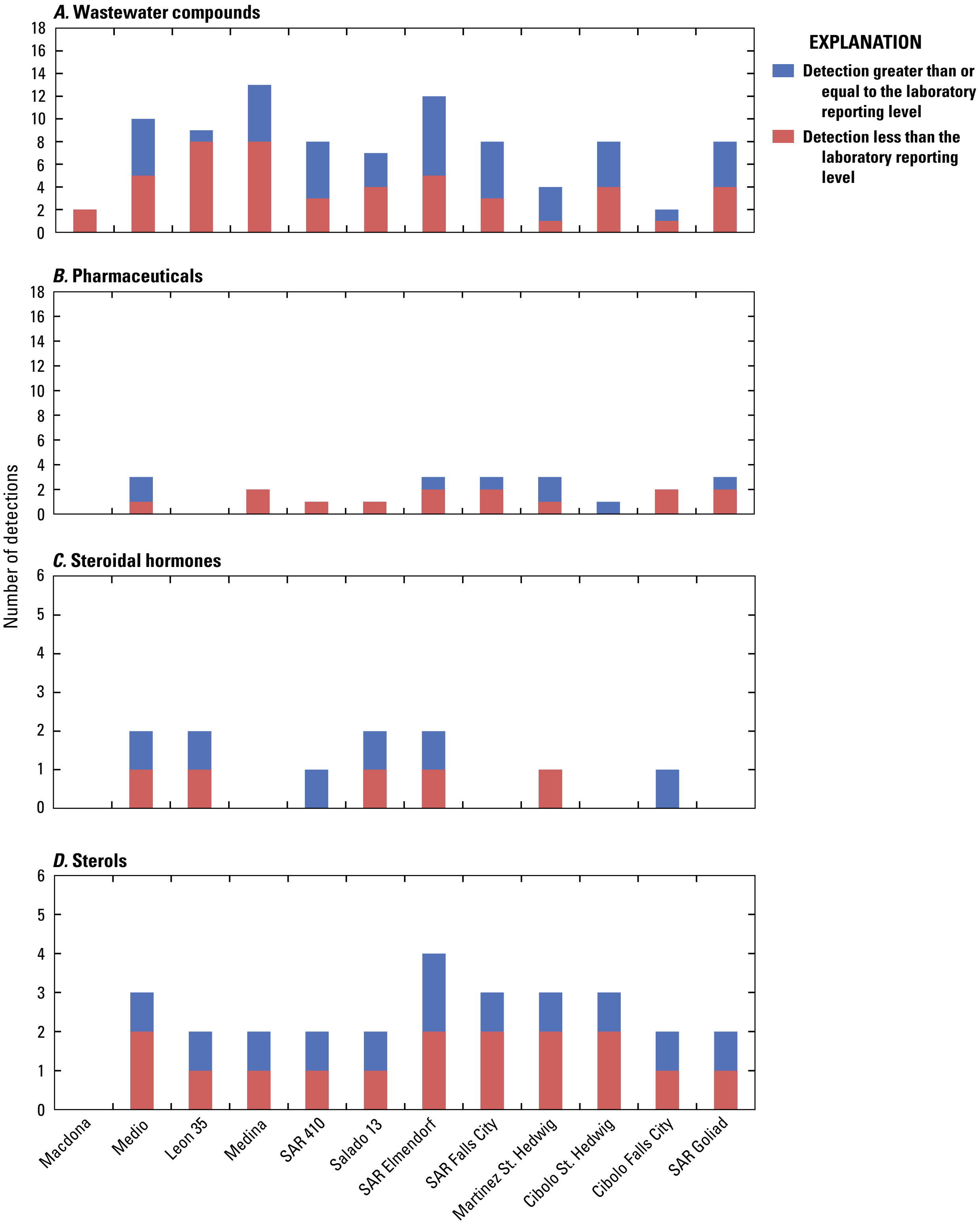


Figure 5. The number of detections in water-quality samples collected from the San Antonio River Basin during synoptic sampling event 1, March–May 2011, of *A*, wastewater compounds, *B*, pharmaceuticals, *C*, steroidal hormones, and *D*, sterols.

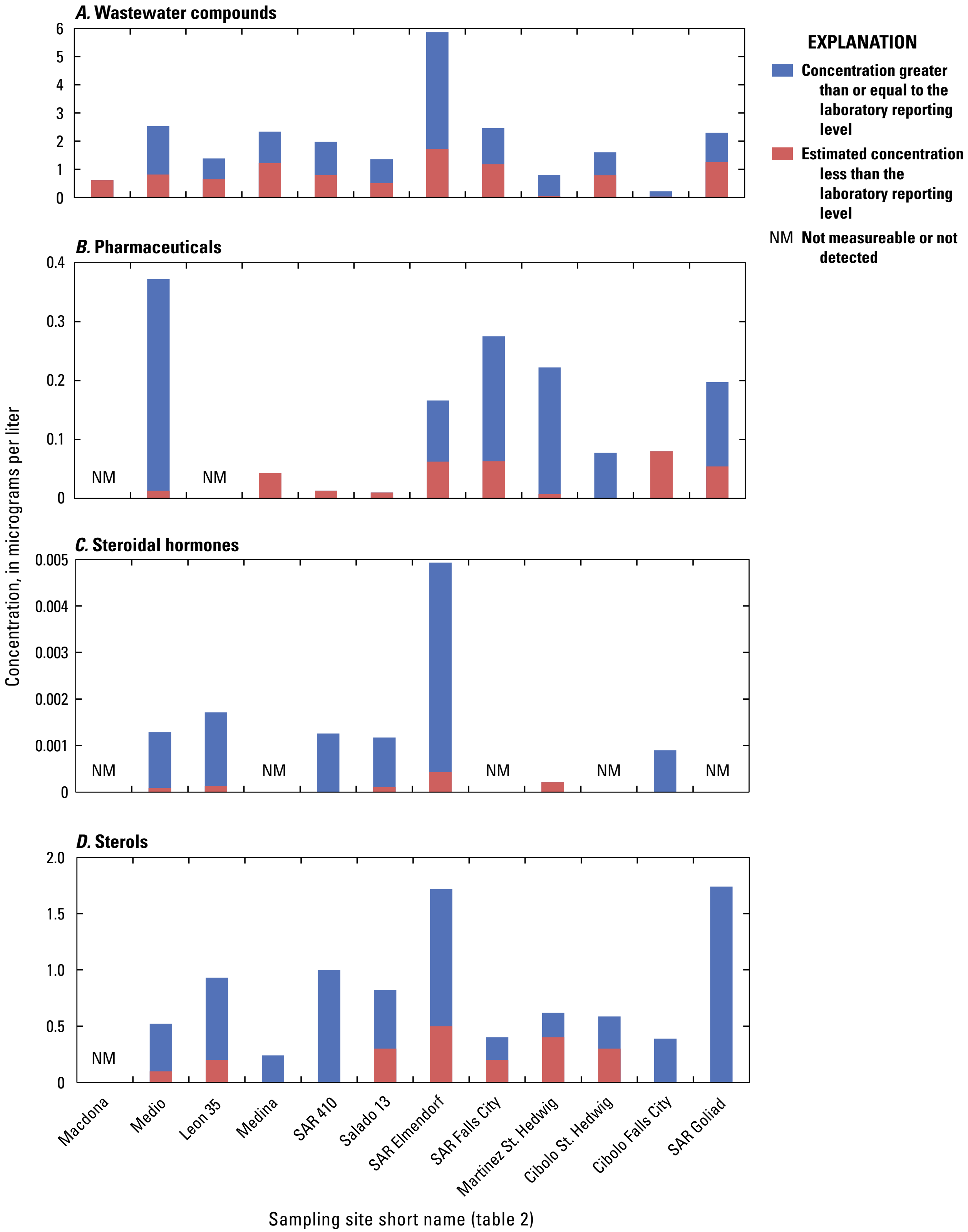


Figure 6. The concentrations in water-quality samples collected from the San Antonio River Basin during synoptic sampling event 1, March–May 2011, of *A*, wastewater compounds, *B*, pharmaceuticals, *C*, steroidal hormones, and *D*, sterols.

The number of detections for all compound classes for the second synoptic sampling event (October–November 2011) is shown in figure 7. The number of detections of wastewater compounds ranged from 0 in samples collected at the Macdona site to 17 in the sample collected at the SAR Elmendorf site (figs. 1, 7*A*). Of the 121 detections of wastewater compounds in the second synoptic sampling event, approximately 31 percent were greater than or equal to the LRL. The number of detections of pharmaceuticals ranged from 0 at multiple sites to 4 in the sample collected at the Medio site (fig. 7*B*). Of the 23 detections of pharmaceuticals, concentrations greater than or equal to the LRL were measured in approximately 22 percent of the samples. The number of detections of steroidal hormones was 0 at all sites with the exception of the SAR Elmendorf site, where there was 1 detection of a steroidal hormone (estrone) at a concentration greater than or equal to the LRL (fig. 7*C*). The number of detections of sterols ranged from 0 at multiple sites to 2 at multiple sites (fig. 7*D*). Of the 8 detections of sterols, 75 percent were for concentrations greater than or equal to the LRL.

The total concentrations for the different compound classes from the second synoptic sampling event are shown in figure 8. Total concentrations of wastewater compounds ranged from not measureable at the Macdona site to 3.29 µg/L at the SAR Elmendorf site (figs. 1, 8*A*). Total concentrations of pharmaceuticals ranged from not measureable at multiple sites to 0.25 µg/L at the Martinez St. Hedwig site (map identifier EC16, fig. 1, table 2) (fig. 8*B*). Total concentrations of steroidal hormones were not measureable at all sites with the exception of the SAR Elmendorf site (fig. 8*C*), which had a concentration of 0.00215 µg/L. Total concentrations of sterols ranged from not measureable at multiple sites to 0.59 µg/L at the SAR Elmendorf site (fig. 8*D*). When measurement data for wastewater compounds, pharmaceuticals, steroidal hormones, and sterols were grouped together, the Macdona site had the lowest number of detections (zero), and total concentrations were not measureable. The SAR Elmendorf site had the highest number of detections (23) and the highest total concentrations (3.97 µg/L).

The third synoptic sampling event (April–May 2012) included collection of samples at seven sites that were added to the study after the first 2 synoptic sampling events were completed to better characterize CECs in certain areas in the San Antonio River Basin (fig. 9). During the third synoptic sampling event, the number of detections of wastewater compounds ranged from 2 at the North Prong site to 18 at the SAR Mitchell site (figs. 1, 9*A*). Of the 84 detections of wastewater compounds during this sampling event, approximately 32 percent were detected at concentrations greater than or equal to the LRL. The number of pharmaceutical detections ranged from 0 at multiple sites to 4 at multiple sites (fig. 9*B*). Of the 13 detections of pharmaceuticals, approximately 31 percent were detected at concentrations greater than or equal to the LRL. The number of detections of steroidal hormones ranged from 0 at multiple sites to 2 at the Salitrillo site (map identifier EC15, fig. 1, table 2) (fig. 9*C*). Of the 3 detections of steroidal hormones, approximately 33 percent were greater than or equal to the LRL. The number of detections of sterols was zero at all sites with the exception of the Alazan site (map identifier EC08, fig. 1, table 2) which had 1 detection greater than or equal to the LRL (fig. 9*D*).

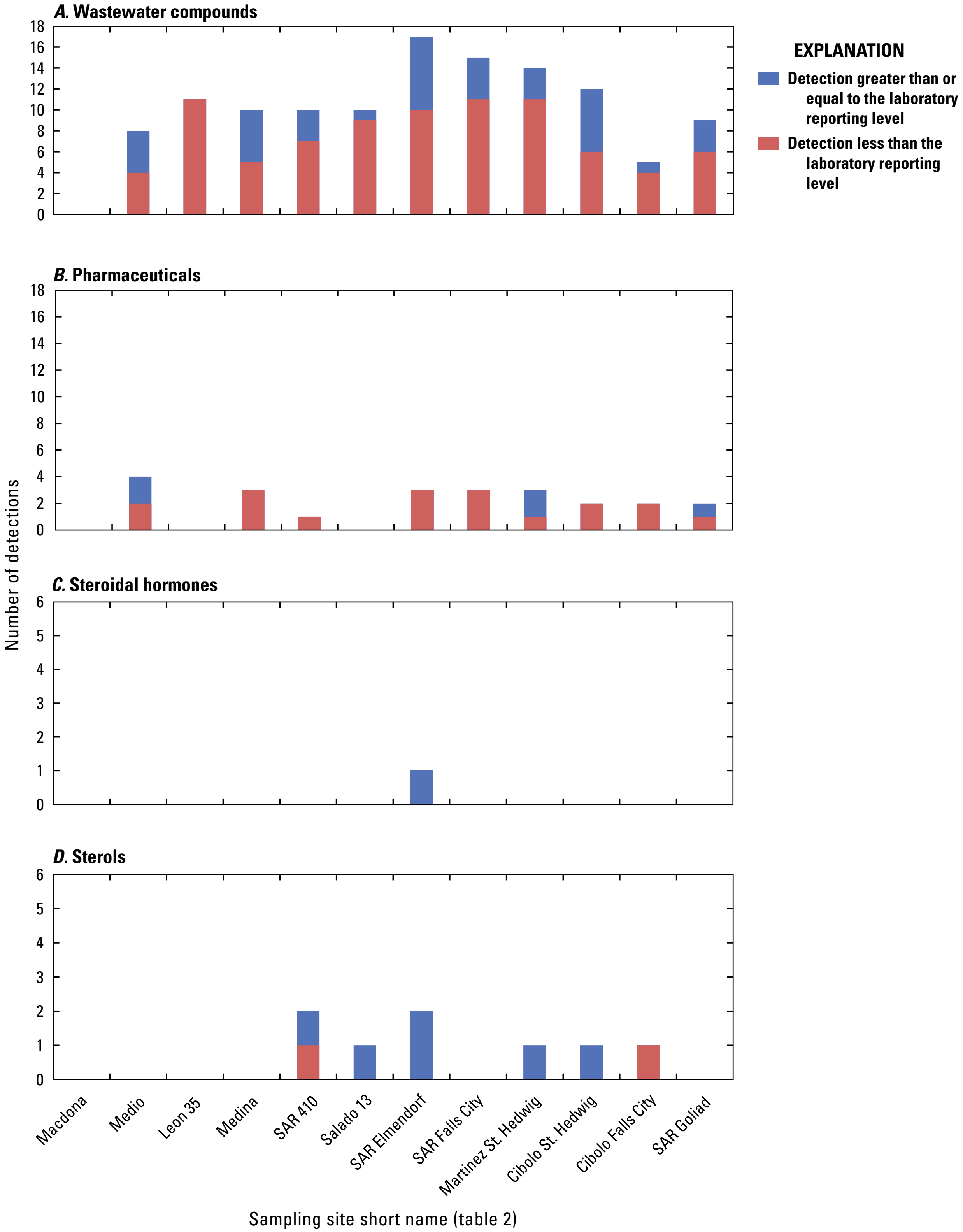


Figure 7. The number of detections in water-quality samples collected from the San Antonio River Basin during synoptic sampling event 2, October–November 2011, of *A*, wastewater compounds, *B*, pharmaceuticals, *C*, steroidal hormones, and *D*, sterols.

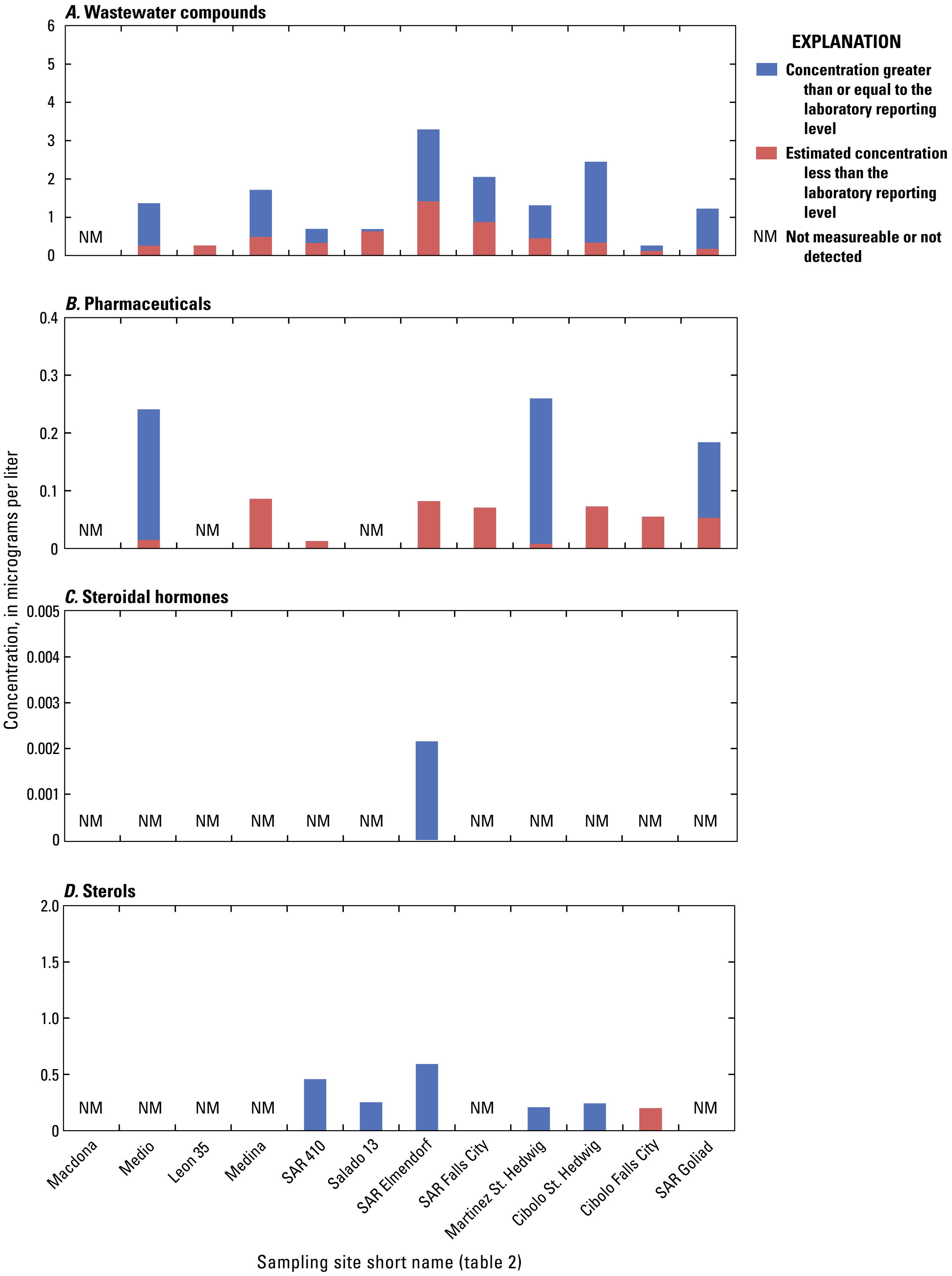


Figure 8. The concentrations in water-quality samples collected from the San Antonio River Basin during synoptic sampling event 2, October–November 2011, of *A*, wastewater compounds, *B*, pharmaceuticals, *C*, steroidal hormones, and *D*, sterols.

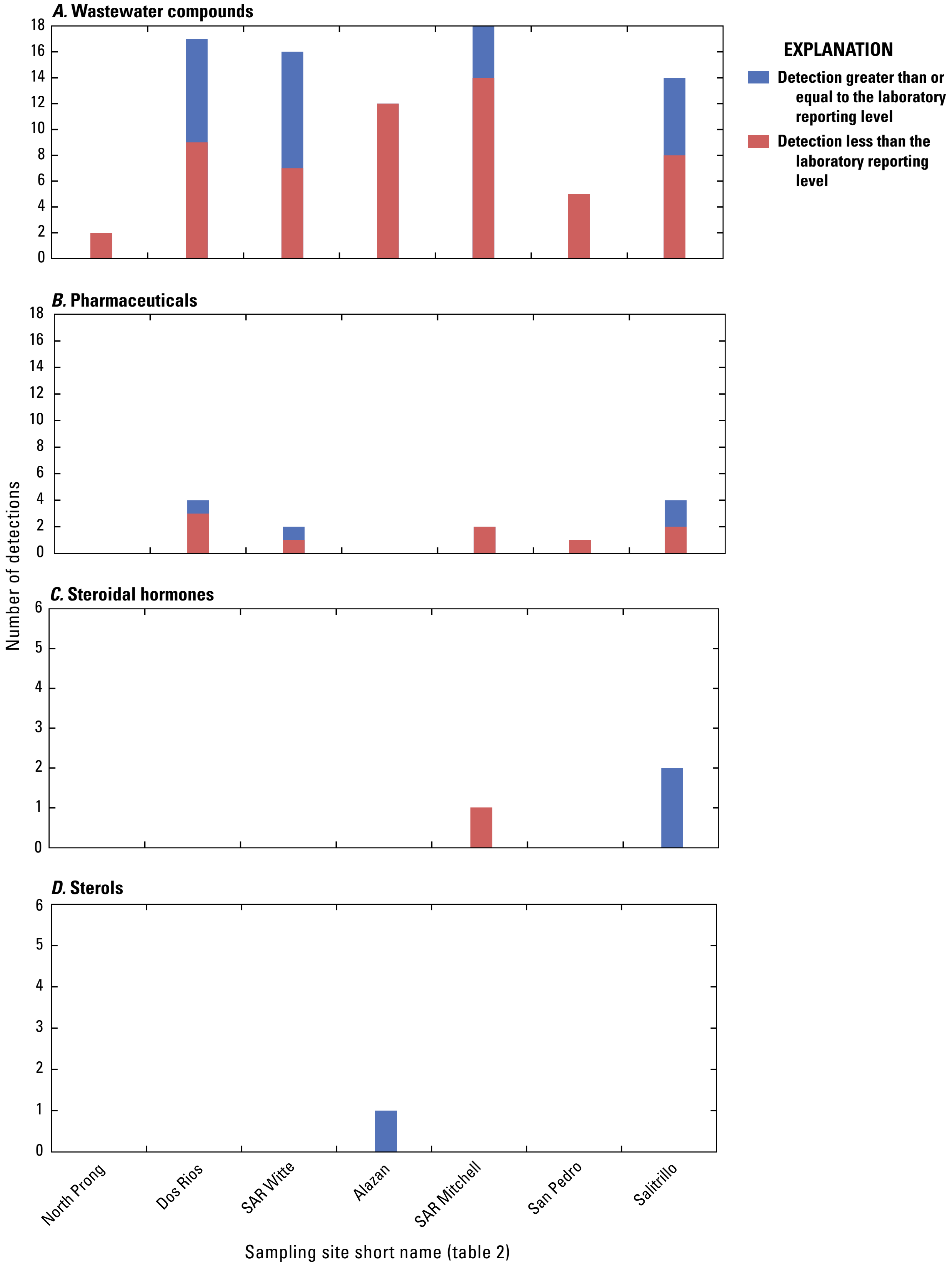


Figure 9. The number of detections in water-quality samples collected from the San Antonio River Basin during synoptic sampling event 3, April–May 2012, of *A*, wastewater compounds, *B*, pharmaceuticals, *C*, steroidal hormones, and *D*, sterols.

The total concentrations for the different compound classes from the third synoptic sampling event are shown in figure 10. Total concentrations of wastewater compounds measured during the third synoptic sampling ranged from 0.14 µg/L at the North Prong site to 4.15 µg/L at the Dos Rios site (fig. 1, 10*A*). Total concentrations of pharmaceuticals ranged from no detections at multiple sites to 0.24 µg/L at the Salitrillo site (fig. 10*B*). Total concentrations of steroidal hormones ranged from not measureable at multiple sites to 0.00491 µg/L at the Salitrillo site (fig. 10*C*). Total concentrations of sterols were not measureable at all sites with the exception of the Alazan site (fig. 10*D*), which had a concentration of 0.33 µg/L. When wastewater compounds, pharmaceuticals, steroidal hormones, and sterols were grouped together, the North Prong site had both the lowest number of total detections (two) and lowest total concentrations (0.14 µg/L). The highest number of detections (21) occurred at the SAR Mitchell site, and the highest total concentration (4.37 µg/L) occurred at the Dos Rios site.

A total of 4 samples were collected at the Ecleto site (fig. 1), and 2 of these samples were analyzed for wastewater compounds (figs. 11*A* and 12*A*). At the Ecleto site, 2 wastewater compounds were detected in the first sample collected, and 4 compounds were detected in the second sample collected. Although there were detections of wastewater compounds in both samples, concentrations were relatively low in samples from the Ecleto site in comparison to most other sites (figs. 6*A*, 8*A*, and 10*A*). Three of four samples collected at the Ecleto site were analyzed for pharmaceuticals, steroidal hormones, and sterols. There were no detections of pharmaceuticals in any of the samples collected at the Ecleto site. The steroidal hormone estrone, a metabolite of the human hormone 17-*beta*-estradiol, and three sterols were detected in the first sample collected at the Ecleto site on January 26, 2012 (figs. 11*B* and 11*C*). The concentration of 17-*beta*-estradiol in this sample was 0.68 ng/L (0.00068 µg/L), which is less than the LRL (fig. 12*B*). There were no steroidal hormones and one sterol detected in the second sample and no detections of steroidal hormones or sterols in the third sample from the Ecleto site. Concentrations of sterols generally were higher in samples collected at the Ecleto site (fig. 12*C*) compared to concentrations for these compounds at most other sites (figs. 6*C*, 8*C*, and 10*C*). The high concentrations of steroidal hormones and sterols at the Ecleto site primarily were a result of the presence of natural sterols (cholesterol, *beta*-sitosterol, and *beta*-stigmastanol).

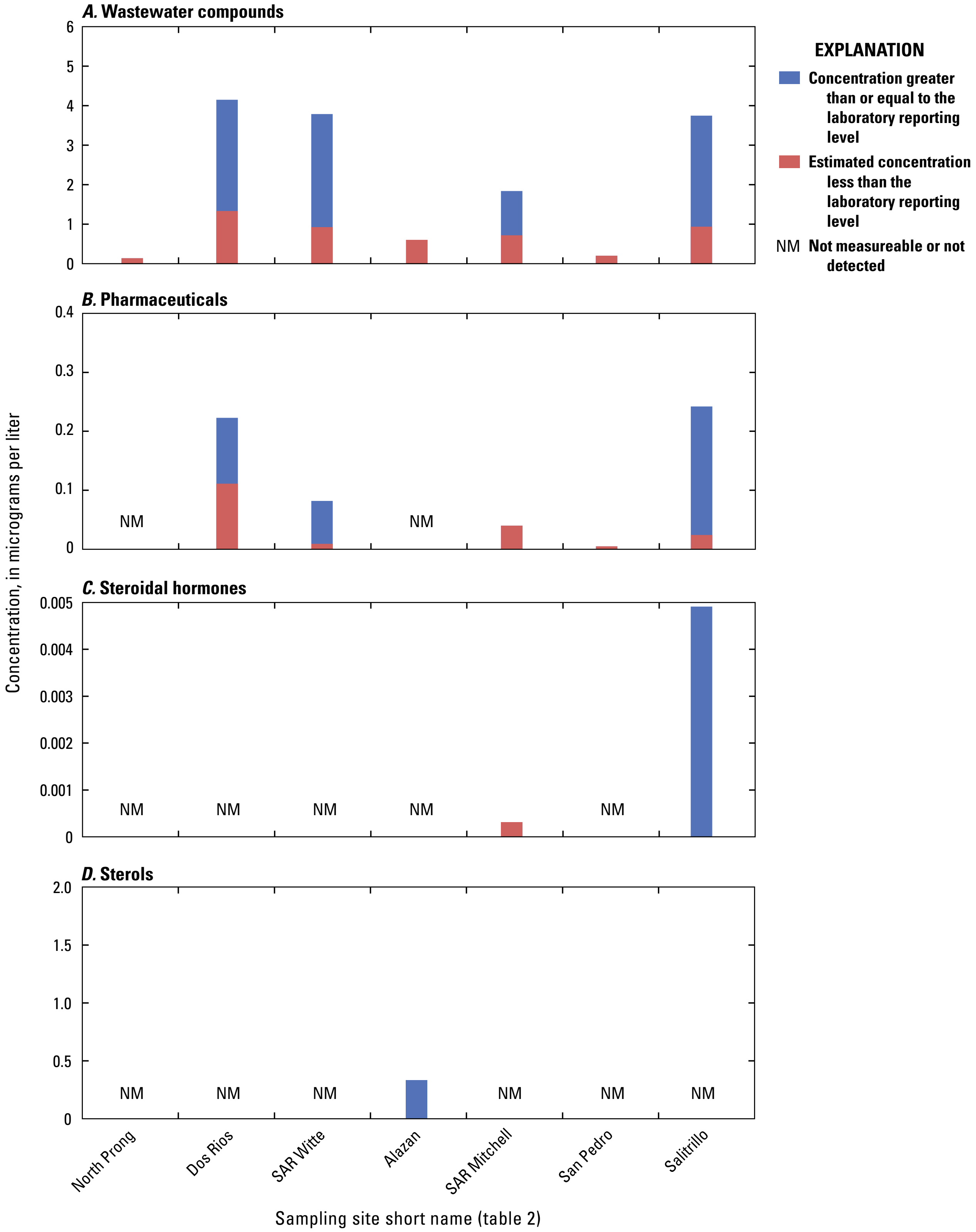


Figure 10. The concentrations in water-quality samples collected from the San Antonio River Basin during synoptic sampling event 3, April–May 2012, of *A*, wastewater compounds, *B*, pharmaceuticals, *C*, steroidal hormones, and *D*, sterols.

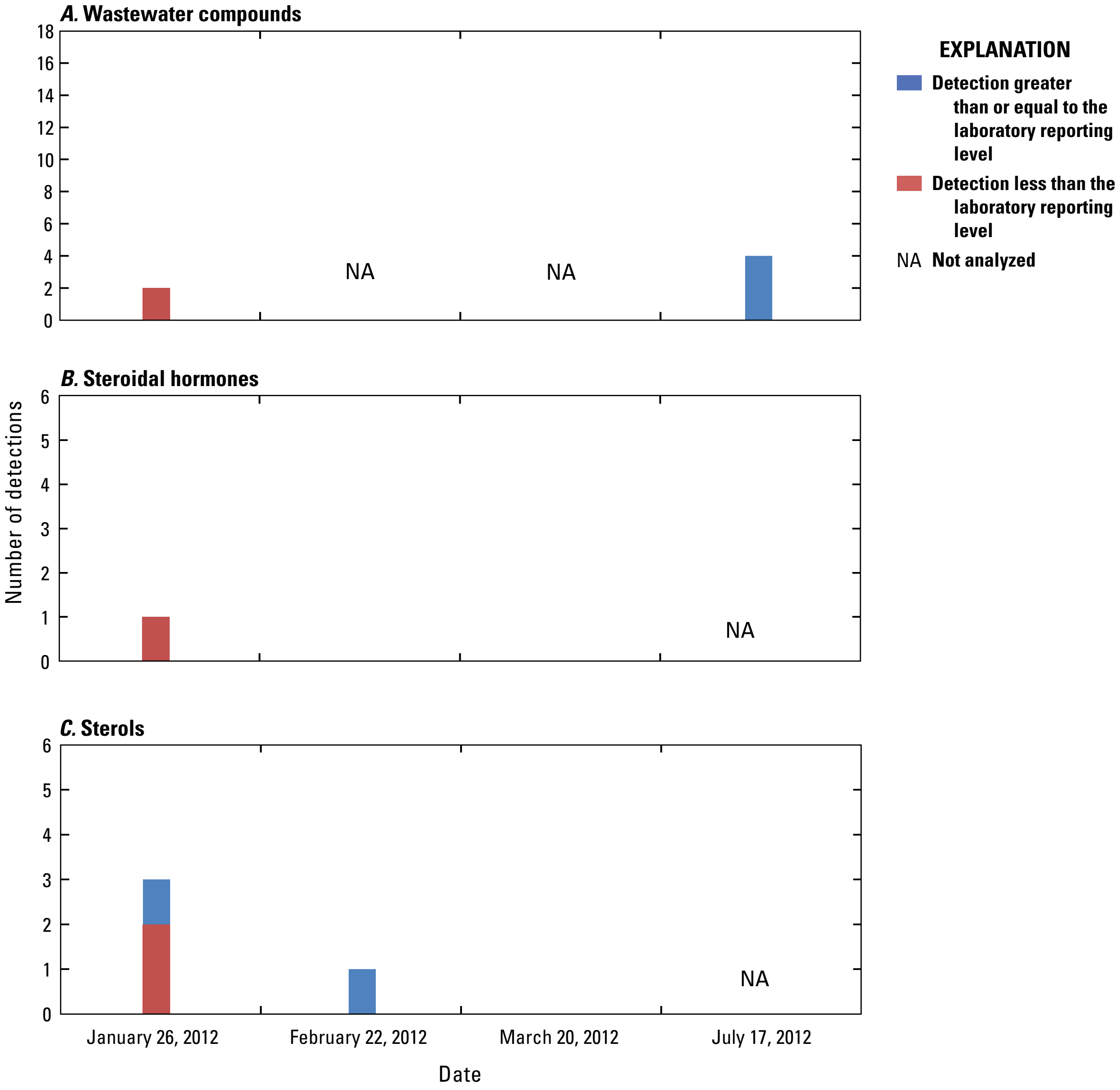


Figure 11. The number of detections in water-quality samples collected from Ecleto Creek at the Ecleto site (table 2) in the San Antonio River Basin, January–July 2012, of *A*, wastewater compounds, *B*, steroidal hormones, and *C*, sterols.

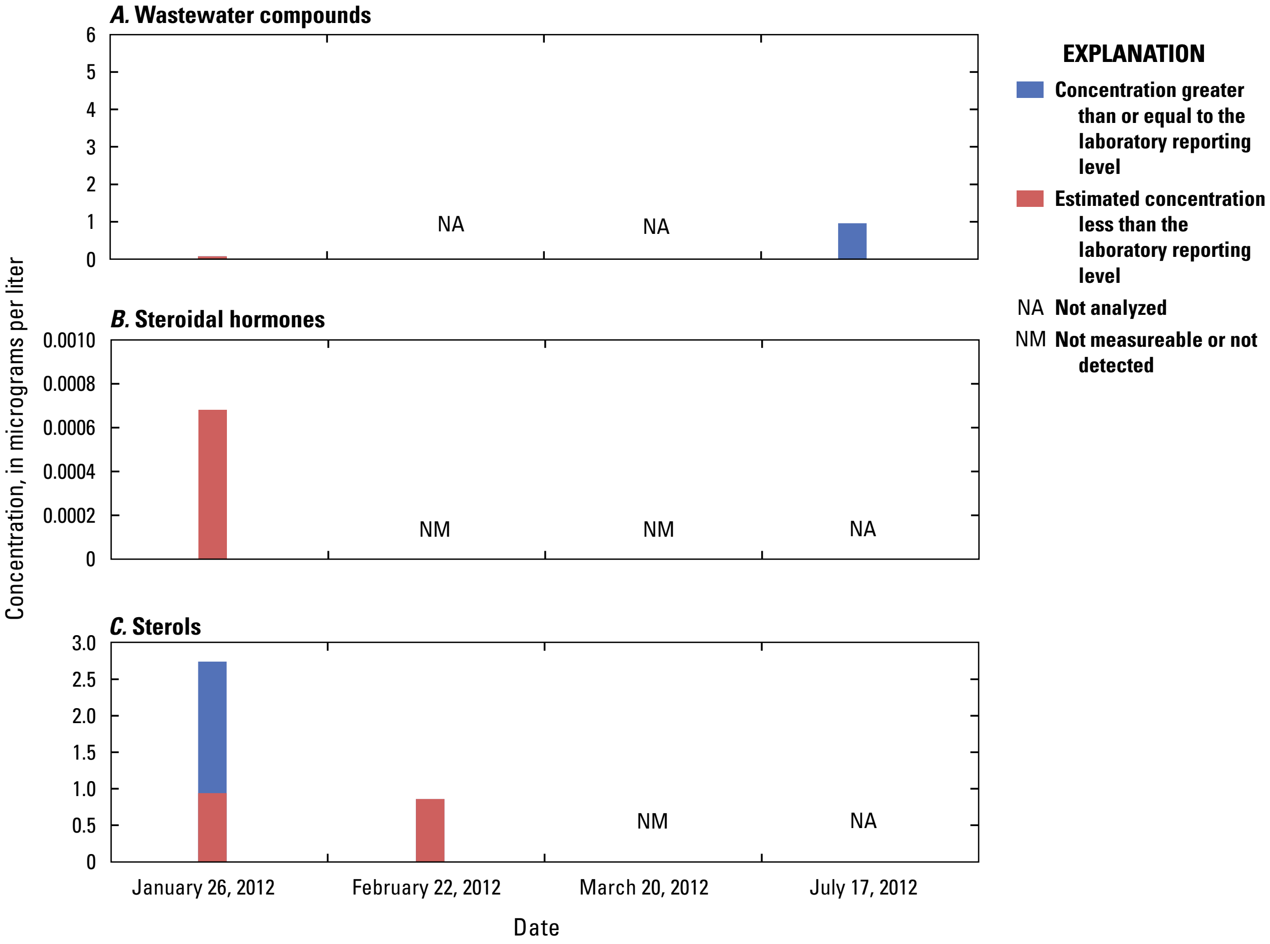


Figure 12. The concentrations in water-quality samples collected at the Ecleto site (table 2) on Ecleto Creek in the San Antonio River Basin, January–July 2012, of *A*, wastewater compounds, *B*, steroidal hormones, and *C*, sterols.

Distributional Patterns of Compounds of Emerging Concern

Distributional Patterns of Wastewater Compounds

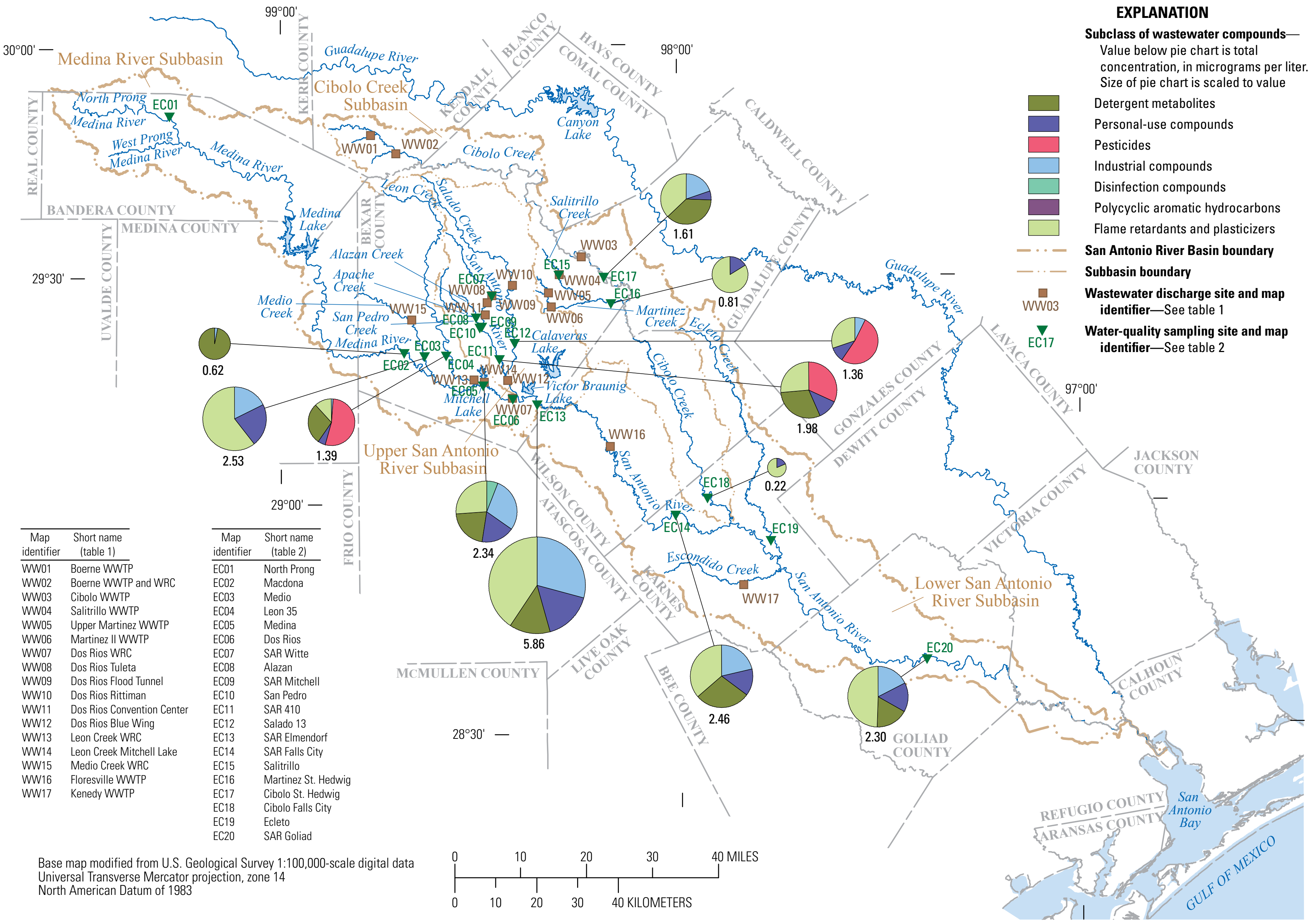
Wastewater compounds were classified as detergent metabolites, personal-use compounds, pesticides, industrial compounds, disinfection compounds, polycyclic aromatic hydrocarbons, and flame retardants and plasticizers. To qualitatively evaluate the distribution of different subclasses of wastewater compounds, the relative proportions of each subclass were estimated by summing the concentrations of individual wastewater compounds in each subclass and comparing them to total concentrations of wastewater compounds measured in samples (app. 5). To estimate concentrations, all values that met the criteria for a detected analyte as explained in the Sample Analysis section were included. When there were no reported concentrations for any of the individual compounds, the total concentration was reported as “not measureable.” The distributional patterns of wastewater compound subclasses are qualitatively depicted by using pie charts scaled to represent differences in total concentrations of wastewater subclasses among the sampling sites (figs. 13, 14, and 15).

During the first and second synoptic sampling events, concentrations of PAHs were low compared to some of the other subclasses (figs. 13 and 14). Disinfection compounds were detected only in samples collected at the Medina site during the first synoptic sampling event and in samples collected at four sites during the second synoptic sampling event (tribromomethane was detected at SAR Falls City, but the concentration was too low to be visible on the pie chart). Personal-use compounds and flame retardants and plasticizers frequently composed substantial proportions of total wastewater compound concentrations measured in samples collected from the San Antonio River Basin. Personal-use compounds and flame retardants and plasticizers were not detected in the samples collected at the Macdona site, a site which is not downstream from a WWTP discharge location. Personal-use compounds and flame retardants and plasticizers were present, however, in both samples collected at the Leon 35 site, another site that is not downstream from WWTP discharge sites.

During the first synoptic sampling event, a higher proportion of pesticides was measured in samples collected at three sites, Leon 35, SAR 410 (map identifier EC11, fig. 1, table 2), and Salado 13 (map identifier EC12, fig. 1, table 2), compared to the proportion of pesticides measured in samples collected at all other sites in the basin (fig. 13). During the second synoptic sampling event, samples collected at two of the same sites, Leon 35 and Salado 13, again contained a higher proportion of pesticides in comparison to samples collected from all of the other sites in the basin (fig. 14). Bromacil, a herbicide commonly used to control weeds along roadsides (Washington State Department of Transportation, 2006; Reif and others, 2012), was the predominant compound contributing to the high proportions of pesticides in samples collected at the Leon 35, SAR 410, and Salado 13 sites.

Downstream from San Antonio, there were similarities in the distributional patterns of wastewater compounds along the main stem of the San Antonio River (fig. 13). The SAR Elmendorf site receives the combined discharge from all of the WWTPs in the western part of the basin. During the first synoptic sampling event, the concentration of wastewater compounds at the SAR Elmendorf site was dominated by flame retardants and plasticizers, industrial compounds, personal-use compounds, and detergent metabolites. This pattern also was observed at the SAR Falls City site (map identifier EC14, fig. 1, table 2) and farther downstream at the SAR Goliad site although the total concentrations were lower at those two downstream sites. During the second synoptic sampling event, there was an absence of detergent metabolites in the sample collected at the SAR Elmendorf site, but disinfectant compounds were present (fig. 14). As with the first synoptic sampling event, concentrations were lower at the SAR Falls City and SAR Goliad sites, and no industrial compounds were measured in the sample collected at the SAR Goliad site.

In the Cibolo Creek Subbasin there were both similarities and differences in the distributional patterns and concentrations of wastewater compounds in comparison to sites along the main stem of the San Antonio River. Both the Cibolo St. Hedwig site (map identifier EC17, fig. 1, table 2) and the Martinez St. Hedwig site are downstream from WWTPs (fig. 1). During the first synoptic sampling event, the total concentrations of wastewater compounds in samples collected at those sites were not as high as those in the samples collected at sites along the main stem of the San Antonio River including the SAR Elmendorf, SAR Falls City, and SAR Goliad sites (fig. 13). During the second synoptic sampling event, concentrations at the Cibolo St. Hedwig and Martinez St. Hedwig sites were higher than during the first synoptic sampling event and closer in concentration to those in the samples collected during the second synoptic sampling event along the main stem of the San Antonio River including the SAR Elmendorf, SAR Falls City, and SAR Goliad sites. During both the first and second synoptic sampling events, concentrations at the Cibolo Falls City site were lower than water-quality samples collected upstream at the Cibolo St. Hedwig and Martinez St. Hedwig sites.

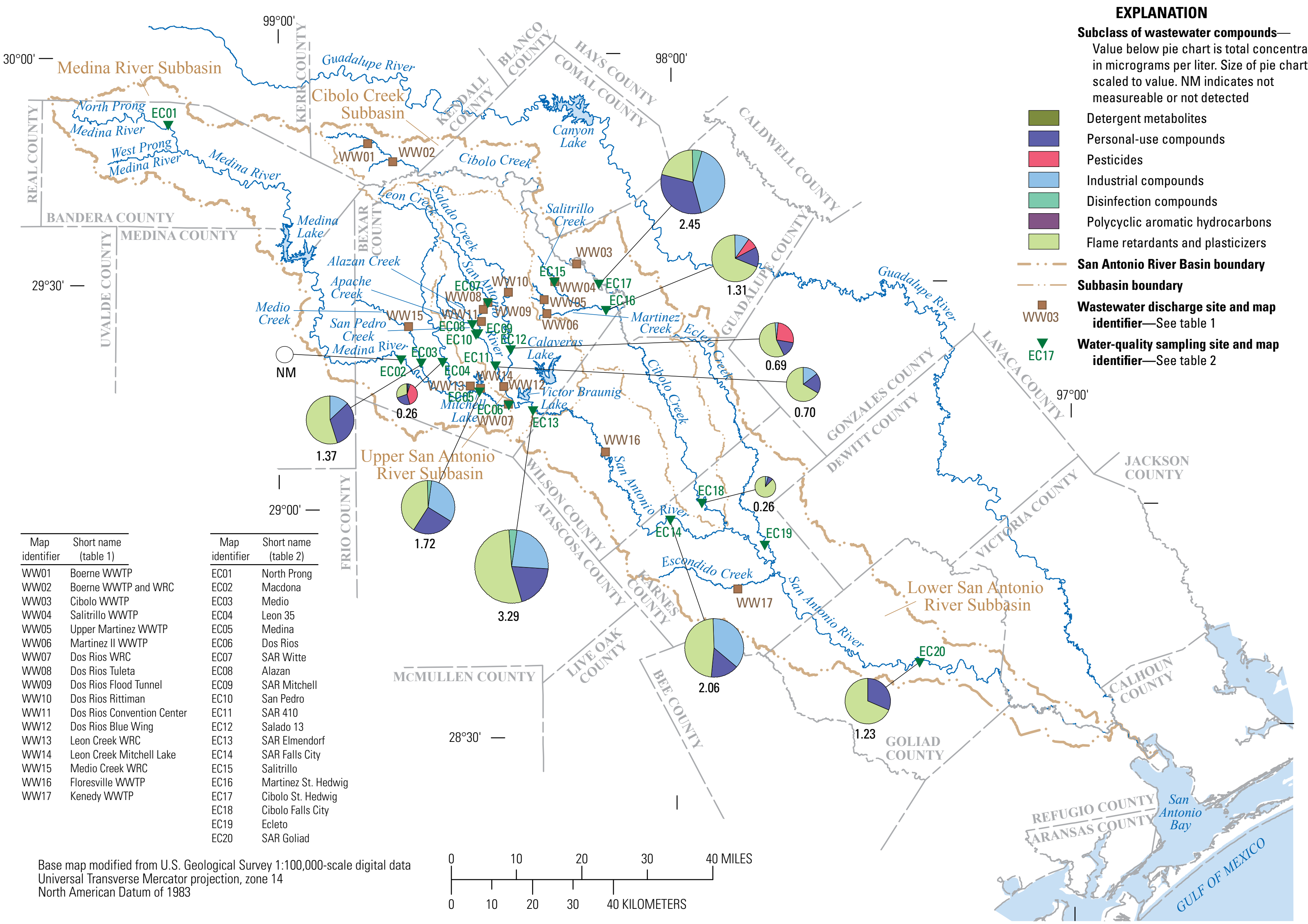


Map identifier	Short name (table 1)
WW01	Boerne WWTP
WW02	Boerne WWTP and WRC
WW03	Cibolo WWTP
WW04	Salitrillo WWTP
WW05	Upper Martinez WWTP
WW06	Martinez II WWTP
WW07	Dos Rios WRC
WW08	Dos Rios Tuleta
WW09	Dos Rios Flood Tunnel
WW10	Dos Rios Rittiman
WW11	Dos Rios Convention Center
WW12	Dos Rios Blue Wing
WW13	Leon Creek WRC
WW14	Leon Creek Mitchell Lake
WW15	Medio Creek WRC
WW16	Floresville WWTP
WW17	Kenedy WWTP

Map identifier	Short name (table 2)
EC01	North Prong
EC02	Macdona
EC03	Medio
EC04	Leon 35
EC05	Medina
EC06	Dos Rios
EC07	SAR Witte
EC08	Alazan
EC09	SAR Mitchell
EC10	San Pedro
EC11	SAR 410
EC12	Salado 13
EC13	SAR Elmendorf
EC14	SAR Falls City
EC15	Salitrillo
EC16	Martinez St. Hedwig
EC17	Cibolo St. Hedwig
EC18	Cibolo Falls City
EC19	Ecleto
EC20	SAR Goliad

Base map modified from U.S. Geological Survey 1:100,000-scale digital data
Universal Transverse Mercator projection, zone 14
North American Datum of 1983

Figure 13. Relative concentrations and proportions of individual subclasses of wastewater compounds in water-quality samples collected during synoptic sampling event 1 from the San Antonio River Basin, March–May 2011.



EXPLANATION

Subclass of wastewater compounds—Value below pie chart is total concentration, in micrograms per liter. Size of pie chart is scaled to value. NM indicates not measureable or not detected

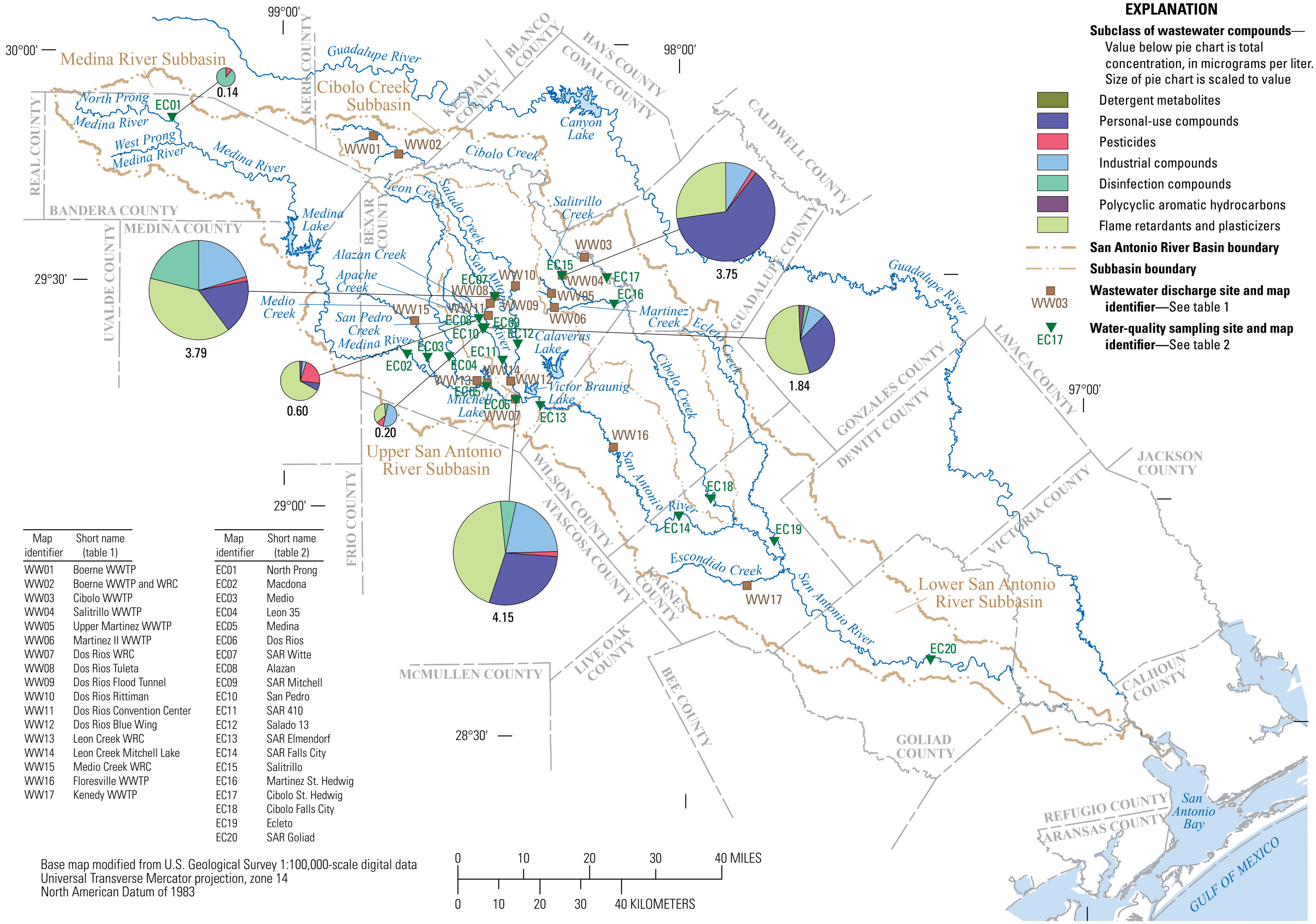
■	Detergent metabolites
■	Personal-use compounds
■	Pesticides
■	Industrial compounds
■	Disinfection compounds
■	Polycyclic aromatic hydrocarbons
■	Flame retardants and plasticizers
— · —	**San Antonio River Basin boundary**
— · —	**Subbasin boundary**
■ WW03	**Wastewater discharge site and map identifier**—See table 1
▼ EC17	**Water-quality sampling site and map identifier**—See table 2

Map identifier	Short name (table 1)
WW01	Boerne WWTP
WW02	Boerne WWTP and WRC
WW03	Cibolo WWTP
WW04	Salitrillo WWTP
WW05	Upper Martinez WWTP
WW06	Martinez II WWTP
WW07	Dos Rios WRC
WW08	Dos Rios Tuleta
WW09	Dos Rios Flood Tunnel
WW10	Dos Rios Rittiman
WW11	Dos Rios Convention Center
WW12	Dos Rios Blue Wing
WW13	Leon Creek WRC
WW14	Leon Creek Mitchell Lake
WW15	Medio Creek WRC
WW16	Floresville WWTP
WW17	Kenedy WWTP

Map identifier	Short name (table 2)
EC01	North Prong
EC02	Macdona
EC03	Medio
EC04	Leon 35
EC05	Medina
EC06	Dos Rios
EC07	SAR Witte
EC08	Alazan
EC09	SAR Mitchell
EC10	San Pedro
EC11	SAR 410
EC12	Salado 13
EC13	SAR Elmendorf
EC14	SAR Falls City
EC15	Salitrillo
EC16	Martinez St. Hedwig
EC17	Cibolo St. Hedwig
EC18	Cibolo Falls City
EC19	Ecleto
EC20	SAR Goliad

Base map modified from U.S. Geological Survey 1:100,000-scale digital data
Universal Transverse Mercator projection, zone 14
North American Datum of 1983

Figure 14. Relative concentrations and proportions of individual subclasses of wastewater compounds in water-quality samples collected during synoptic sampling event 2 from the San Antonio River Basin, October–November 2011.



Map identifier	Short name (table 1)
WW01	Boerne WWTP
WW02	Boerne WWTP and WRC
WW03	Cibolo WWTP
WW04	Salitrillo WWTP
WW05	Upper Martinez WWTP
WW06	Martinez II WWTP
WW07	Dos Rios WRC
WW08	Dos Rios Tuleta
WW09	Dos Rios Flood Tunnel
WW10	Dos Rios Rittiman
WW11	Dos Rios Convention Center
WW12	Dos Rios Blue Wing
WW13	Leon Creek WRC
WW14	Leon Creek Mitchell Lake
WW15	Medio Creek WRC
WW16	Floresville WWTP
WW17	Kenedy WWTP

Map identifier	Short name (table 2)
EC01	North Prong
EC02	Macdona
EC03	Medio
EC04	Leon 35
EC05	Medina
EC06	Dos Rios
EC07	SAR Witte
EC08	Alazan
EC09	SAR Mitchell
EC10	San Pedro
EC11	SAR 410
EC12	Salado 13
EC13	SAR Elmendorf
EC14	SAR Falls City
EC15	Salitrillo
EC16	Martinez St. Hedwig
EC17	Cibolo St. Hedwig
EC18	Cibolo Falls City
EC19	Ecleto
EC20	SAR Goliad

Base map modified from U.S. Geological Survey 1:100,000-scale digital data
Universal Transverse Mercator projection, zone 14
North American Datum of 1983

Figure 15. Relative concentrations and proportions of individual subclasses of wastewater compounds in water-quality samples collected during synoptic sampling event 3 from the San Antonio River Basin, April–May 2012.

During the third synoptic sampling event, differences in wastewater compound concentrations resulted from the presence or absence of an upstream wastewater discharge location and land use. During this sampling event, concentrations of wastewater compounds at three sites (North Prong, Alazan, and San Pedro; map identifiers EC01, EC08, and EC10, respectively, fig. 1, table 2) that did not have large wastewater discharge sites upstream (fig. 15) typically were lower compared to the concentrations of wastewater compounds at three sites (Dos Rios, SAR Witte, and Salitrillo; map identifiers EC06, EC07, and EC15, respectively, fig. 1, table 2) that are located downstream from wastewater discharge sites. In the sample collected at the North Prong site, which is in a largely undeveloped area, pesticides and disinfection compounds were detected, but the total concentrations of wastewater compounds in the sample collected at this site were lower than those measured in the samples collected at the Alazan and San Pedro sites, which are in a highly urbanized area of San Antonio. Concentrations of wastewater compounds in samples collected at the SAR Mitchell site were less than the concentrations of wastewater compounds measured in samples collected at the SAR Witte site, which is upstream from the Mitchell site.

Basin-Wide Distributional Patterns

The North Prong site is in the uppermost reaches of the Medina River Subbasin and is upstream from any municipalities. The disinfectant phenol and 1,4-dichlorobenzene were detected during the third synoptic sampling event, although concentrations were low (figs. 9*A*, 10*A*). Detection of CECs at a reference site such as the North Prong site is consistent with the report by Barber and others (2003), and the source of these compounds at reference sites without upstream WWTPs remains uncertain. These compounds might be associated with household use and could be introduced through nonpoint-source pathways such as surface runoff, onsite wastewater treatment systems, or aerosols rather than by discharge from WWTPs.

Minimal concentrations of wastewater compounds were measured as far downstream as the Macdona site. The detergent metabolite 4-nonylphenol diethoxylate and the industrial compound *p*-cresol were the only wastewater compounds detected at the Macdona site in the first synoptic sampling event, and none were detected in the second synoptic sampling event (app. 1). Because the detergent metabolite 4-nonylphenol diethoxylate is used in a variety of products including deicing agents, detergents, and antiseptic cleaners (O'Neil, 2001, p. 1196), sources other than treated municipal wastewater may introduce 4-nonylphenol diethoxylate into the San Antonio River Basin. The compound *p*-cresol commonly is used as a preservative for treated wood (Zaugg and others, 2002); *p*-cresol might have been released to the environment by the weathering of preserved wood such as the wood used to build docks and piers upstream at Medina Lake.

The highest concentrations of wastewater compounds and pharmaceuticals were measured in samples collected during the first and second synoptic sampling events from the Medio site (fig. 1, table 2), which is about 5 miles downstream from the Medio WRC. The confluence of Medio Creek with the Medina River downstream from the Macdona site represents a substantial input of wastewater compounds to the Medina River. The Leon Creek WRC, downstream from the Leon 35 site, is one of the largest wastewater treatment facilities in San Antonio. Leon Creek WRC source water was not sampled in this study, but its treated municipal wastewater is discharged just upstream from the confluence of Leon Creek with the Medina River, representing another source of wastewater compounds into the Medina River. The contributions of compounds from these two wastewater sources are evident in samples collected downstream at the Medina site (figs. 5*A–B*, 6*A–B*, 7*A–B*, 8*A–B*).

The Dos Rios WRC (map identifier WW07) is the largest wastewater discharger in San Antonio; some of its effluent is pumped to the Dos Rios Tuleta wastewater discharge site (map identifier WW08), the same location as the SAR Witte site (map identifier EC07, fig. 1, table 2), and some of the effluent from the Dos Rios WRC is pumped to the Dos Rios Convention Center wastewater discharge site (map identifier WW11, fig. 1, table 2). The Dos Rios site (map identifier EC06, fig. 1, table 2) and the SAR Witte site were sampled during the third synoptic sampling event; the number of detections and concentrations of wastewater compounds at both sites were similar, and pharmaceuticals were present in samples collected at both sites (figs. 9*A–B*, 10*A–B*). The large number of detections and concentrations of wastewater compounds at the SAR Mitchell site probably are related to treated municipal wastewater contributions from these upstream sources (figs. 9*A–B*, 10*A–B*); however, concentrations of wastewater compounds were lower at the SAR Mitchell site than at the Dos Rios or Witte sites, possibly because of dilution from San Pedro Creek or natural attenuation processes.

There were nine wastewater compounds from five compound classes detected in the sample collected at the Leon 35 site (fig. 1) during the first synoptic sampling event (fig. 5*A*), even though there is no WWTP upstream from this site. There were 11 wastewater compounds representing 5 compound classes measured in the sample collected at that site during the second synoptic sampling event (fig. 7*A*), demonstrating that wastewater compounds can be detected in streams flowing through a highly urbanized area without a large upstream source of treated municipal wastewater. Bromacil was the only pesticide and the most abundant compound measured in samples collected at the Leon 35 site during the first and second synoptic sampling events (figs. 13 and 14).

The Alazan and San Pedro sites are two urbanized sites with no large upstream wastewater sources that were sampled during the third synoptic sampling event (fig. 1).

At the Alazan site, 12 wastewater compounds were detected, and at the San Pedro site, 5 wastewater compounds were detected (fig. 9*A*). The pharmaceutical carbamazepine was also detected at the San Pedro site (fig. 9*B*, app. 2). Total concentrations of wastewater compounds and pharmaceuticals were substantially lower at the Alazan and San Pedro sites than at either the Dos Rios site or the SAR Witte site (fig. 15); upstream from the Dos Rios and SAR Witte sites there are discharges of treated municipal wastewater whereas there are no WWTPs above the Alazon and San Pedro sites. Similar to the Leon 35 site, the large number of detections of wastewater compounds measured in samples collected at the Alazan and San Pedro sites demonstrate that wastewater compounds can be detected in surface water in a highly urbanized area without a known source of treated municipal wastewater. The presence of carbamazepine is difficult to explain without an upstream source of treated wastewater. It is possible that carbamazepine is associated with groundwater seepage from onsite wastewater treatment systems or leaky sewer lines. Alazan Creek flows into San Pedro Creek, which in turn flows into the San Antonio River downstream from the SAR Mitchell site (map identifier EC09, fig. 1, table 2), and the San Antonio River in turn flows past the SAR 410 site (map identifier EC11, fig. 1, table 2). Numerous wastewater compounds were detected in samples collected at both the SAR Mitchell and SAR 410 sites. Depending on streamflow conditions, concentrations may vary for wastewater compounds measured in samples collected at sites on the San Antonio River downstream from Alazan and San Pedro Creeks, such as the SAR Mitchell and SAR 410 sites. For example, during relatively wet periods, inflows from Alazan and San Pedro Creeks will be larger compared to relatively dry periods, and wastewater compounds in the San Antonio River at the SAR 410 site likely will be diluted by these inflows.

Part of the base flow in Salado Creek is supplied by treated municipal wastewater discharged at the Dos Rios Rittiman wastewater discharge site. The number of detections of wastewater compounds at the Salado 13 site during the first and second synoptic sampling events indicates a large treated wastewater component (figs. 5*A–D*, 7*A–D*). The concentrations of both wastewater compounds and pharmaceuticals at the Salado 13 site, however, were less than the concentrations measured in samples collected at the same time from other sites (Medio, SAR 410, and SAR Elmendorf) that receive the same treated municipal wastewater. The low streamflow and the long distance from the treated municipal wastewater discharge location at the Dos Rios Rittiman wastewater discharge site to the Salado 13 site might facilitate removal through natural attenuation processes.

The Dos Rios WRC (site WW07) discharges a large volume of treated municipal wastewater into the Medina River just upstream from the confluence of the Medina and San Antonio Rivers, and streamflow from this entire drainage network flows past the SAR Elmendorf site (fig. 1). Samples collected at the SAR Elmendorf site during the first and second synoptic sampling events had more detections and higher concentrations of wastewater compounds than did all sites upstream from the SAR Elmendorf site sampled at the same time. The higher concentrations of wastewater compounds at the SAR Elmendorf site during the first and second synoptic sampling events indicate that the Dos Rios WRC likely was discharging wastewater compounds at higher concentrations than were the other upstream sources. Unaccounted variations in the quantity and quality of wastewater discharge and streamflow during the first and second synoptic sampling events, however, limit the ability to compare the distribution and concentration of wastewater compounds among sites.

The distribution of wastewater compounds, pharmaceuticals, steroidal hormones, and sterols in the Cibolo Creek Subbasin is influenced by a combination of hydrologic factors and source inputs. In the city of Boerne, there are two WWTPs (fig. 1); however, under normal base flow conditions, the discharge from these sites goes into groundwater storage approximately 3 miles downstream from the Boerne city limits rather than being transported farther downstream. In the Cibolo Creek Subbasin near San Antonio, there are four large wastewater discharge points including Cibolo WWTP, Salitrillo WWTP, Upper Martinez WWTP, and Martinez II WWTP (map identifiers WW03, WW04, WW05, and WW06, respectively) upstream from the Martinez St. Hedwig and Cibolo St. Hedwig sites. The number of detections and concentrations of wastewater compounds, pharmaceuticals, steroidal hormones, and sterols at the Martinez St. Hedwig and Cibolo St. Hedwig sites generally were similar to those in samples collected from other sites downstream from known wastewater discharge (figs. 5*A–D*, 6*A–D*, 7*A–D*, and 8*A–D*).

An examination of the number of detections and total concentrations of CECs measured in samples collected from Cibolo Creek and the San Antonio River indicates there was a pattern of lower total concentrations and fewer detections at downstream sites. Total concentrations of all CECs were lower at Cibolo Falls City than at the Cibolo St. Hedwig and Martinez St. Hedwig sites (figs. 1, 6, and 8). Because this reach of Cibolo Creek is known to increase in flow because of groundwater discharge, particularly immediately upstream from the Cibolo Falls City site (Lizárraga and Wehmeyer, 2012), dilution by groundwater might be part of the cause of lower concentrations of wastewater compounds measured at the Cibolo Falls City site. Concentrations of wastewater compounds decreased between the SAR Elmendorf site and the SAR Falls City site during the first and second synoptic sampling events (figs. 13 and 14). Concentrations of wastewater compounds from samples collected during the first and second synoptic sampling events also further decreased between the SAR Falls City site and the SAR Goliad site (figs. 13 and 14). These decreases in concentrations may be the result of dilution caused by increased flow from Cibolo Creek discharging into the San Antonio River between the SAR Falls City and SAR Goliad sites (fig. 1).

The general pattern of downstream decreases in wastewater compounds in both the San Antonio River and Cibolo Creek indicates that natural attenuation processes may be reducing concentrations of wastewater compounds; however, a more comprehensive assessment would be needed to quantify the effects of such processes on wastewater compound concentrations in local streams.

The Ecleto site on Ecleto Creek (fig. 1) was included in the study because it drains rangeland with no major population centers and provides a representation of a substantial proportion of the land cover in the San Antonio River Basin. There were two detections of wastewater compounds in the first sample collected at the Ecleto site (fig. 11*A*) including the flame retardant tris (dichloroisopropyl) phosphate and the herbicide bromacil commonly used to control roadside weeds. It is possible that these compounds were introduced into Ecleto Creek by runoff during the time of sample collection. Four wastewater compounds were detected in the second sample collected at the Ecleto site including two personal-use compounds, the fragrance acetophenone and the insect repellent DEET. Also, the industrial compound benzophenone (a fixative for soaps and perfumes) and the disinfectant compound phenol were detected in the second sample collected at the Ecleto site. The presence of these CECs indicates that at least some wastewater compounds can be introduced into surface waters in rural parts of the San Antonio River Basin during runoff or can result from onsite wastewater system seepage. The presence of a natural source of phenol, however, cannot be excluded (National Pollutant Inventory, 2013). Although detection of estrone often indicates human source, estrone has other sources such as female cattle, a likely source to Ecleto Creek. Furthermore, the high concentrations of steroidal hormones and sterols at the Ecleto site were primarily a result of the presence of natural sterols (cholesterol, *beta*-sitosterol, and *beta*-stigmastanol) in the stream that likely were derived from cattle waste rather than wastewater effluent.

A general lack of pharmaceuticals at stream sites without large known sources of treated wastewater appears to be a typical pattern for streams throughout the San Antonio River Basin. This finding is supported by the observation that the Leon 35, Macdona, North Prong, and Alazan sites (figs. 5*B*, 7*B*, and 9*B*) had no detectable concentrations of pharmaceuticals. One site with no large upstream wastewater treatment facility, San Pedro, only had one detection of carbamazepine, the most common pharmaceutical measured in the study (fig. 9*B*, app. 2). Carbamazepine is resistant to breakdown during water treatment (Walker and others, 2012), and it is possible that an onsite wastewater treatment system may be the source of carbamazepine at this site. Although the source of carbamazepine at one urban site remains uncertain, a general lack of detectable pharmaceuticals may be a useful indicator for identifying point- and nonpoint-source wastewater contributions to urban streams.

Summary

Advancements in laboratory analytical techniques have provided the capability to identify large numbers of previously unrecognized compounds of emerging concern (CECs) in streams. Some of these compounds are known or suspected endocrine disrupters. Point-source discharges from WWTPs are a primary source of CECs to urban streams. Nonpoint sources such as seepage from on-site wastewater treatment systems, leakage from sewer lines, urban runoff, agricultural and livestock operations, and atmospheric deposition also represent common pathways for organic compounds to enter surface waters. To better understand the quality of surface water in the San Antonio River Basin, the U.S. Geological Survey (USGS), in cooperation with the San Antonio River Authority, evaluated detections, concentrations, and distributional patterns of selected compounds of emerging concern (hereinafter referred to as "CECs") from water-quality samples (hereinafter referred to as "samples") collected at sampling sites along streams throughout the San Antonio River Basin, Texas, during 2011–12.

Results are presented for 54 wastewater compounds, 13 pharmaceuticals, 17 steroidal hormones, and 4 sterols analyzed in samples. Of the 54 wastewater compounds, 32 were detected in at least 1 sample collected at a site in the San Antonio River Basin and 22 compounds were not detected in any samples. Detected in 28 of the 33 samples analyzed for wastewater compounds, tris (2-chloroethyl) phosphate and tris (dichloroisopropyl) phosphate were the most commonly detected compounds in the study. Tris (2-chloroethyl) phosphate and tris (dichloroisopropyl) phosphate are suspected endocrine disruptors. The highest concentration of a wastewater compound (1.90 µg/L) was measured from the fragrance hexahydrohexamethyl-cyclopentabenzopyran (HHCB). The second highest concentration of a wastewater compound in the study was 1.4 µg/L of the industrial compound 5-methyl-1H-benzotriazole, a common component of antifreeze. All of the remaining wastewater compounds were measured at concentrations less than 1.0 µg/L. Of the 13 pharmaceuticals, only 4 compounds, 1 non-prescription pharmaceutical (diphenhydramine) and 3 prescription pharmaceuticals (carbamazepine, dehydronifedipine, and sulfamethoxazole), were detected in at least one sample collected from the San Antonio River Basin. Carbamazepine, an anti-convulsant and the most frequently detected prescription pharmaceutical, was detected in 24 of 34 samples analyzed for pharmaceuticals. Of the 17 steroidal hormones, 4 were detected in at least one sample from the San Antonio River Basin. Of the 4 sterols, all 4 were detected in at least one sample from the San Antonio River Basin. Estrone, a metabolite of 17-*beta*-estradiol, was the most commonly detected compound related to estrogen and was detected in 9 of 34 samples analyzed for steroidal hormones and sterols. Cholesterol was detected in 19 of 34 samples.

Three synoptic sampling events were completed as part of this study. When measurement data for wastewater, pharmaceutical, steroidal hormone, and sterol compounds from the first synoptic sampling event were grouped together, the Macdona site (Medina River near Macdona, Tex.) had both the lowest number of total detections (2) and the lowest total concentrations (0.62 µg/L), and the SAR Elmendorf site (San Antonio River near Elmendorf, Tex.) had the highest number of detections (21) and highest total concentrations (7.75 µg/L). When measurement data for wastewater compounds, pharmaceuticals, steroidal hormones, and sterols from the second synoptic sampling event were grouped together, the Macdona site had the lowest number of detections (zero), and total concentrations were not measureable. The SAR Elmendorf site had the highest number of detections (23) and highest total concentrations (3.97 µg/L). When wastewater compounds, pharmaceuticals, steroidal hormones, and sterols from the third synoptic sampling event were grouped together, the North Prong site (North Prong Medina River above confluence Wallace Creek near Medina, Tex.) had both the lowest number of total detections (two) and lowest total concentrations (0.14 µg/L). The highest number of detections (21) occurred at the SAR Mitchell site (San Antonio River at Mitchell Street, San Antonio, Tex.), and the highest total concentration (4.37 µg/L) occurred at the Dos Rios site (Dos Rios WWTP Outfall at San Antonio, Tex.).

The North Prong site is in the uppermost reaches of the Medina River Subbasin and is upstream from any municipalities. The disinfectant phenol and 1,4-dichlorobenzene were detected at the North Prong site during the third synoptic sampling event, although concentrations were low. These compounds might be associated with household use and could be introduced through nonpoint-source pathways such as surface runoff, onsite wastewater treatment systems, or aerosols rather than by discharge from WWTPs. Minimal concentrations of wastewater compounds were measured as far downstream as the Macdona site where only the detergent metabolite 4-nonylphenol diethoxylate (a compound used in deicing agents, detergents, and antiseptic cleaners) and the industrial compound *p*-cresol were detected in the first synoptic sampling; these results indicate sources other than treated wastewater might also be introducing 4-nonylphenol diethoxylate into the San Antonio River Basin. The compound *p*-cresol commonly is used as a preservative for treated wood; *p*-cresol might have been released to the environment by the weathering of preserved wood such as the wood used to build docks and piers upstream at Medina Lake.

The confluence of Medio Creek with the Medina River downstream from the Macdona site represents a substantial input of wastewater compounds to the Medina River. Source water from the Leon Creek WRC site on Comanche Creek at the plant was not sampled in this study, but its treated municipal wastewater is discharged just upstream from the confluence of Leon Creek with the Medina River, representing another source of wastewater compounds into the Medina River. The contributions of compounds from these two wastewater sources are evident in samples collected downstream at the Medina site (Medina River at San Antonio, Tex.). The Dos Rios WRC site on the Medina River at the plant is the largest wastewater discharger in San Antonio; some of its effluent is pumped to the Dos Rios Tuleta wastewater discharge site, the same location as the SAR Witte site (San Antonio River at Witte Museum, San Antonio, Tex.), and some of the effluent from the Dos Rios WRC is pumped to the Dos Rios Convention Center site (San Antonio River at the Convention Center). The large number of detections and concentrations of wastewater compounds at the SAR Mitchell site (San Antonio River at Mitchell Street, San Antonio, Tex.) probably are related to treated municipal wastewater contributions from these upstream sources.

The Leon 35 site (Leon Creek at Interstate Highway 35, San Antonio, Tex.), the Alazan site (Alazan Creek at Tampico Street, San Antonio, Tex.), and the San Pedro site (San Pedro Creek at Probandt Street, at San Antonio, Tex.) are urbanized sampling sites with no large upstream wastewater sources. There were multiple detections of wastewater compounds at all three sites. The pharmaceutical carbamazepine also was detected at the San Pedro site. The large number of detections at sites with no upstream wastewater source demonstrated that wastewater compounds and pharmaceuticals can be detected in streams flowing through a highly urbanized area without a large upstream source of treated municipal wastewater. Part of the base flow in Salado Creek is supplied by treated municipal wastewater discharged at the Dos Rios Rittiman wastewater discharge site on Salado Creek at Rittiman Road that also receives treated municipal wastewater from WRCs. The low streamflow and the long distance from the treated municipal wastewater discharge location at the Dos Rios Rittiman site to the Salado 13 site (Salado Creek at Loop 13, San Antonio, Tex.) might facilitate removal through natural attenuation processes.

Samples collected at the SAR Elmendorf site during the first and second synoptic sampling events had more detections and higher concentrations of wastewater compounds than did all sites upstream from the SAR Elmendorf site sampled at the same time. The higher concentrations of wastewater compounds at the SAR Elmendorf site during the first and second synoptic sampling events indicate that the Dos Rios WRC likely was discharging wastewater compounds at higher concentrations than were the other upstream sources. An examination of the number of detections and total concentrations of CECs occurring in Cibolo Creek and the San Antonio River indicates there was a pattern of lower total concentrations and fewer detections at downstream sites. Dilution by groundwater might be part of the cause of lower concentrations of wastewater compounds measured at the Cibolo Falls City site (Cibolo Creek near Falls City, Tex.). Decreases in the San Antonio River may be the result of dilution cause by increased flow from Cibolo Creek discharging into the San Antonio River between the SAR Falls City site (San Antonio River at Highway 181 at Falls

City, Tex.) and the SAR Goliad site (San Antonio River at Goliad, Tex.). The general pattern of downstream decreases in wastewater compounds in both the San Antonio River and Cibolo Creek indicates that natural attenuation processes may be reducing concentrations of wastewater compounds.

The Ecleto site (Ecleto Creek near Runge, Tex.) was not part of the three synoptic sampling events; it was included in the study because it drains rangeland with no major population centers and provides a representation of a substantial proportion of the land cover in the San Antonio River Basin. The presence of CECs indicates that at least some wastewater compounds can be introduced into surface waters in rural parts of the San Antonio River Basin during runoff or can result from onsite wastewater system seepage. The high concentrations of steroidal hormones and sterols at the Ecleto site were primarily a result of the presence of natural sterols (cholesterol, *beta*-sitosterol, and *beta*-stigmastanol) in the stream that likely were derived from cattle waste rather than wastewater effluent.

One site with no large upstream wastewater treatment facility, San Pedro, had only one detection of carbamazepine, the most commonly occurring pharmaceutical measured in the study. Carbamazepine is resistant to breakdown during water treatment, and it is possible that an onsite wastewater treatment system may be the source of carbamazepine at this site. Although the source of carbamazepine at one urban site remains uncertain, a general lack of detectable pharmaceuticals may be a useful indicator for identifying point- and nonpoint-source wastewater contributions to urban streams.

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