Prepared in cooperation with the San Antonio Water System

Quality of Surface-Water Runoff in Selected Streams in the San Antonio Segment of the Edwards Aquifer Recharge Zone, Bexar County, Texas, 1997–2012

Data Series 740

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

Cover photographs:

U.S. Geological Survey hydrographers at Culebra Creek in Government Canyon State Natural Area near Helotes, Texas, October 23, 2000 (photographs by Michael B. Nyman).

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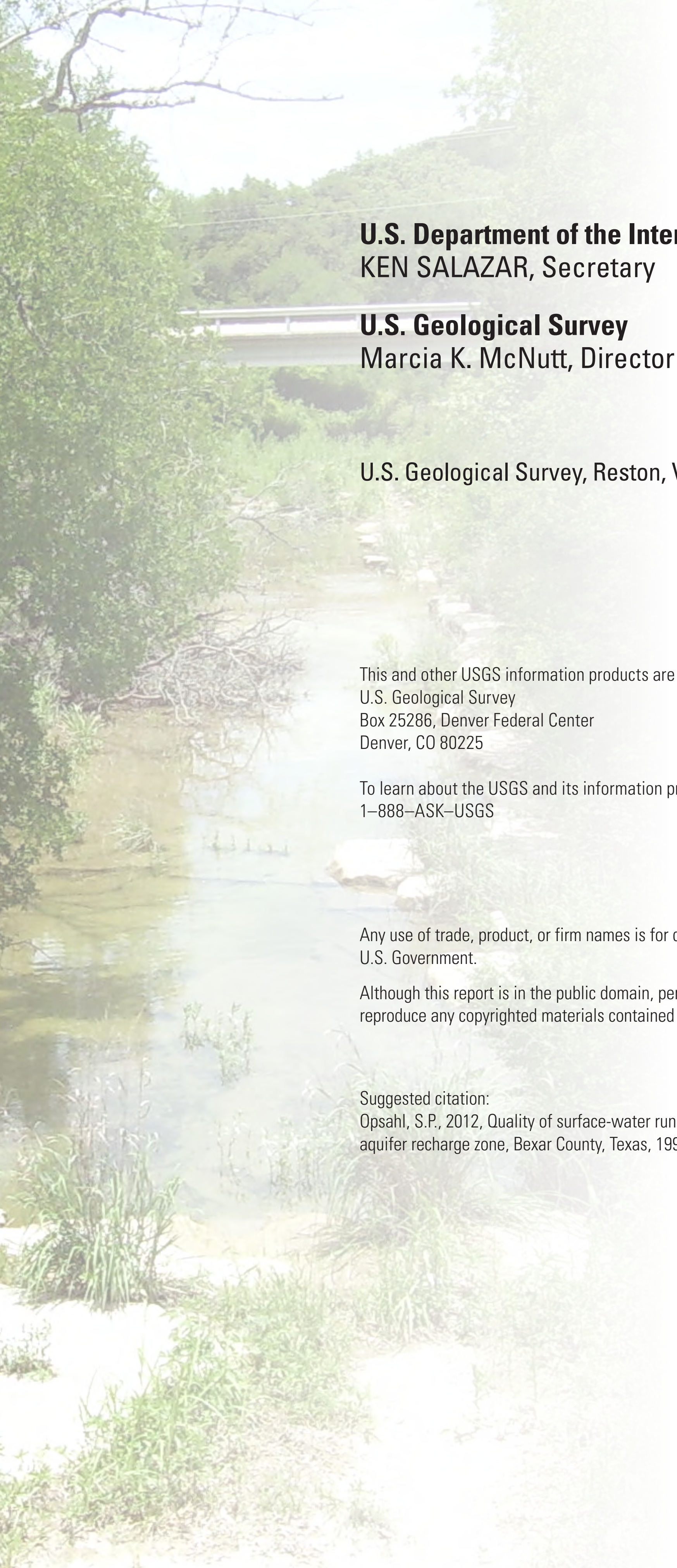

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
acre-foot (acre-ft)	1,233	cubic meter (m^3)
acre-foot (acre-ft)	0.001233	cubic hectometer (hm^3)

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).

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

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or in micrograms per liter (μg/L).

Quality of Surface-Water Runoff in Selected Streams in the San Antonio Segment of the Edwards Aquifer Recharge Zone, Bexar County, Texas, 1997–2012

By Stephen P. Opsahl

Abstract

During 1997–2012, the U.S. Geological Survey, in cooperation with the San Antonio Water System, collected and analyzed water-quality constituents in surface-water runoff from five ephemeral stream sites near San Antonio in northern Bexar County, Texas. The data were collected to assess the quality of surface water that recharges the Edwards aquifer. Samples were collected from four stream basins that had small amounts of developed land at the onset of the study but were predicted to undergo substantial development over a period of several decades. Water-quality samples also were collected from a fifth stream basin located on land protected from development to provide reference data by representing undeveloped land cover. Water-quality data included pH, specific conductance, chemical oxygen demand, dissolved solids (filtered residue on evaporation in milligrams per liter, dried at 180 degrees Celsius), suspended solids, major ions, nutrients, trace metals, and pesticides. Trace metal concentration data were compared to the Texas Commission on Environmental Quality established surface water quality standards for human health protection (water and fish). Among all constituents in all samples for which criteria were available for comparison, only one sample had one constituent which exceeded the surface water criteria on one occasion. A single lead concentration (2.76 micrograms per liter) measured in a filtered water sample exceeded the surface water criteria of 1.15 micrograms per liter. The average number of pesticide detections per sample in stream basins undergoing development ranged from 1.8 to 6.0. In contrast, the average number of pesticide detections per sample in the reference stream basin was 0.6. Among all constituents examined in this study, pesticides, dissolved orthophosphate phosphorus, and dissolved total phosphorus demonstrated the largest differences between the four stream basins undergoing development and the reference stream basin with undeveloped land cover.

Introduction

The Edwards aquifer is one of the most productive karst aquifers in the Nation and the primary public water supply for more than 1.7 million people in San Antonio and surrounding communities in Bexar County, Texas, a rapidly urbanizing region (Sharp and Banner, 1997; U.S. Environmental Protection Agency, 2006a; U.S. Census Bureau, 2012). The San Antonio segment of the Edwards aquifer system (hereinafter Edwards aquifer) in south-central Texas is characterized by numerous sinkholes, caves, and streams that supply recharge to the aquifer and by rapid interaction between surface water and groundwater (Sharp and Banner, 1997). The Edwards aquifer provides water for public water supply, agriculture, industry, military installations, recreational activities, and springs. Some springs discharging from the Edwards aquifer supply streamflow to downstream users and provide habitat for threatened and endangered species (Edwards Aquifer Research and Data Center, 2010).

Most recharge to the Edwards aquifer is from direct infiltration of precipitation and streamflow that occurs to the west of Bexar County and in northern Bexar County (Edwards Aquifer Authority, 2011). Increased residential and commercial development in Bexar County on the Edwards aquifer recharge zone has the potential to discharge substances that would impair the quality of water recharging the Edwards aquifer (Edwards Aquifer Authority, 2009; Musgrove and others, 2009). Impervious land cover associated with such development can result in increased stormwater runoff that transports contaminants from the land surface to streams or geologic features (caves, fractures) that can facilitate infiltration to the Edwards aquifer (Ockerman, 2002). The potential effects of increased land-surface development on surface-water quality in streams recharging the Edwards aquifer in northern Bexar County are not well known. To learn more about quality of surface water in streams that recharge the San Antonio segment of the Edwards aquifer, the U.S. Geological Survey (USGS), in cooperation with the San Antonio Water System (SAWS), conducted a study from 1997 through 2012 to examine the quality of surface-water runoff in streams in northern Bexar County.

Purpose and Scope

The purpose of this report is to describe water-quality data collected at five stations in the Edwards aquifer recharge zone in Bexar County, Tex., from 1997–2012. Water-quality data collected included measurements of pH, specific conductance, chemical oxygen demand (COD), and concentrations of dissolved solids (filtered residue on evaporation in milligrams per liter [mg/L], dried at 180 degrees Celsius [°C]), suspended solids, major ions, nutrients, trace metals, and pesticides. Sample-collection and analysis methods are described for each physical property or constituent, and quality-control results are summarized. Trace metal concentration data are compared to the Texas Commission on Environmental Quality (TCEQ) established surface water quality standards for human health protection (water and fish), hereinafter referred to as "TCEQ standards" (Texas Commission on Environmental Quality, 2010).

Description of Study Area

The study area is within the Edwards aquifer recharge zone and adjacent catchment area in northern Bexar County (fig. 1). For this report, catchment areas that are immediately adjacent to the Edwards aquifer recharge zone and drain to the recharge zone are considered to be in the recharge zone.

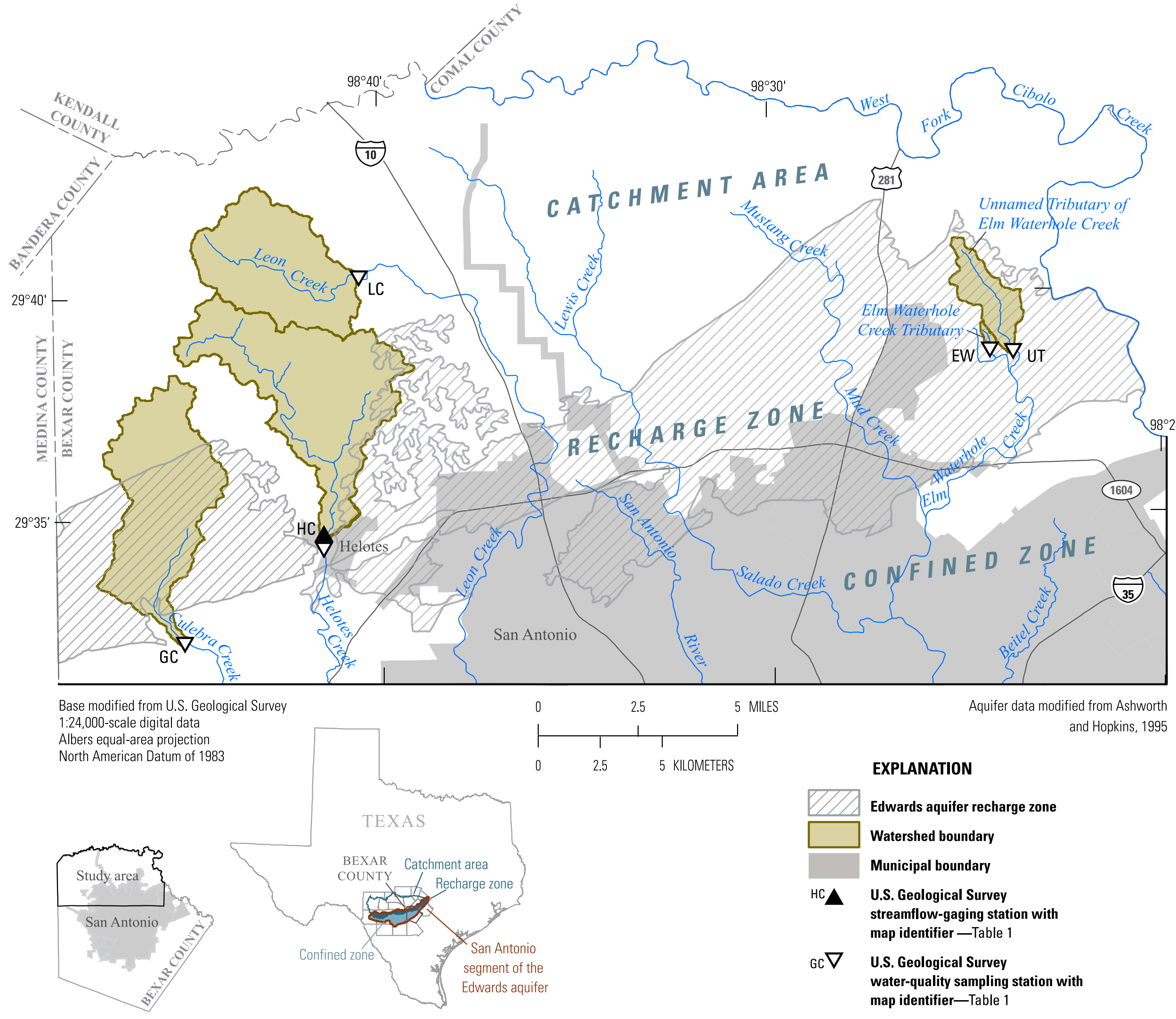


Figure 1. Location of data-collection stations in the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 1997–2012.

The catchment area and Edwards aquifer recharge zone consist of a network of stream basins and ephemeral streams that lose water to the Edwards aquifer as they cross the recharge zone. Streamflow data and runoff water-quality samples were collected from five ephemeral stream sites during 1997–2012: two small unnamed tributaries to Elm Waterhole Creek (USGS station 08178627 Elm Waterhole Creek tributary at Evans Road, near San Antonio, Tex. [hereinafter Elm Waterhole tributary 1, map identifier EW], and USGS station 08178628 Unnamed tributary of Elm Waterhole Creek at Evans Road at San Antonio, Tex. [hereinafter Elm Waterhole tributary 2, map identifier UT]); Leon Creek (USGS station 08180945 Leon Creek at Scenic Loop Road near Leon Springs, Tex. [hereinafter Leon Creek, map identifier LC]); Helotes Creek (USGS station 08181400 Helotes Creek at Helotes, Tex. [hereinafter Helotes Creek, map identifier HC]); and Culebra Creek (USGS station 08180941 Culebra Creek in Government Canyon State Natural Area near Helotes, Tex. [hereinafter Government Canyon, map identifier GC]) (table 1). Water-quality samples were collected from Government Canyon as a reference site; the land in this basin is protected from development, and data from this site represents undeveloped land cover.

The five stream basins of the study area encompass about 42.6 square miles (mi^2) of undeveloped and developed land in the Edwards aquifer recharge zone and catchment area (table 1). In this report, undeveloped land includes evergreen forest, shrub/scrub, deciduous forest, grassland/herbaceous, woody wetlands, barren land, and open water (table 2). Developed land includes developed open space, developed low intensity, and developed medium intensity. The land cover of the stream basins from which data were collected is predominantly undeveloped (table 2; fig. 2*A*, *B*; fig. 3*A*, *B*). The vegetation is primarily a mixture of oak, juniper, and shrub (University of Texas, Bureau of Economic Geology, 1985). In 2001, the undeveloped land cover ranged from 85.7 percent in Elm Waterhole tributary 1 stream basin to 99.9 percent in the Government Canyon stream basin (table 2; fig. 2*A*, *B*; fig. 3*A*, *B*). In 2006, undeveloped land cover ranged from 62.5 percent in the Elm Waterhole tributary 1 stream basin to 99.2 percent in Government Canyon stream basin. There was a large increase (23.2 percent) in the percentage of developed land cover in the Elm Waterhole tributary 1 stream basin. The decrease in the percentage of undeveloped land in the Elm Waterhole tributary 1 stream basin occurred primarily because of the conversion of evergreen forest and shrub/scrub land covers to developed open space or developed low intensity land covers. In contrast, the percentage increase in total developed land cover in four of the five stream basins (Elm Waterhole tributary 2, Leon Creek, Helotes Creek, and Government Canyon) between 2001 and 2006 was less than 2 percent.

Chemical Constituents and Selected Contaminants of Interest—Major Ions, Nutrients, Trace Metals, and Pesticides

Physical properties (pH, specific conductance, COD, dissolved solids, and suspended solids) and concentrations of water-quality constituents (major ions, nutrients, trace metals, and pesticides) were measured in water samples collected periodically at sites when runoff events occurred. Major ions make up the majority of dissolved constituents in water. Major ions are those commonly present in concentrations exceeding 1.0 mg/L (Hem, 1985). Within the study area, the constituents in water are mostly the ions calcium, magnesium, and bicarbonate because these constituents are readily weathered from carbonate minerals such as calcite and dolomite (Hem, 1985). Noncarbonate constituents such as the ions sodium, chloride, and sulfate have several possible sources in carbonate terrains, including overlying silicate soils; noncarbonate minerals incorporated in the bedrock, such as evaporite and clay minerals; and man-made compounds such as fertilizers, road salt, treated drinking water, septic tanks, and wastewater effluent (Hem, 1985).

Nutrients are chemicals that organisms need to live and grow. Excessive concentrations of nutrients such as nitrogen (N) and phosphorus (P) in aquatic environments, however, can cause eutrophication, the proliferation of algal blooms and other aquatic plants (Lopez and others, 2008; Dubrovsky and others, 2010). Common N compounds found in water include ammonium, nitrate, nitrite, and organic nitrogen. There are many sources of N compounds to water including fertilizers (manure, organic fertilizers, and synthetic fertilizers); human and animal waste (animal feces, treated wastewater effluent, and septic-system drainage); decaying plant debris; runoff from fertilized residential lawns, golf courses, and construction sites; vehicle exhaust; and precipitation (U.S. Environmental Protection Agency, 2012). National background concentrations of nitrate in streams have been estimated at 0.24 mg/L (Dubrovsky and others, 2010).

Common P compounds found in water include orthophosphate, organic P, and sorbed inorganic and organic P (Wetzel, 2001). Sources of P to water include fertilizers, sewage, detergents, livestock waste, and wildlife waste (U.S. Environmental Protection Agency, 2012). Background concentrations of orthophosphate in streams in the U.S. have been estimated at 0.010 mg/L (Dubrovsky and others, 2010). Availability of P is a critical factor controlling plant growth, as it frequently is the nutrient in most limited supply in aquatic systems (Hem, 1985).

Residential and commercial development is a potential source of trace metals to streams as impervious surfaces increase with such development and potential runoff of substances from human sources grows. Therefore, relatively large concentrations of trace metals in streams that recharge the Edwards aquifer potentially may affect groundwater quality in the aquifer. A few of the possible sources for

Table 1. U.S. Geological Survey water-quality sampling and streamflow data-collection stations in the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 1997–2012.

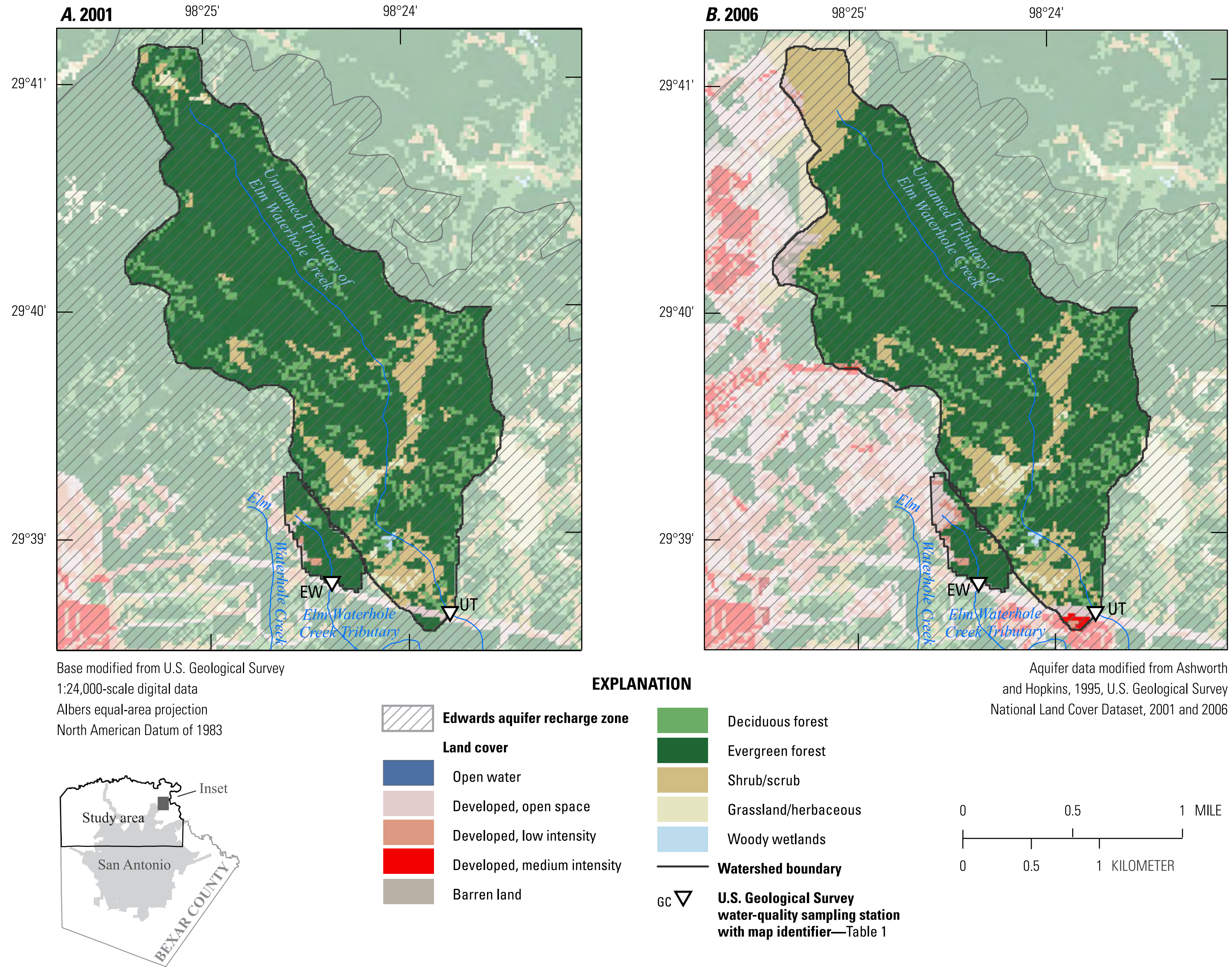
[USGS, U.S. Geological Survey; dd, degrees; mm minutes; ss seconds; mi^2, square miles; SW, continuous streamflow gaging station; QW, water quality]

Map identifier (fig. 1)	USGS station number	USGS station name	Short name	Type of data	Latitude (dd mm ss)	Longitude (dd mm ss)	Drainage area (mi^2)	Period of record used
EW	08178627	Elm Waterhole Creek Tributary at Evans Road near San Antonio, Tex.	Elm Waterhole tributary 1	QW	29 38 48	98 24 23	0.132	2001–12
UT	08178628	Unnamed Tributary of Elm Waterhole Creek at Evans Road at San Antonio, Tex.	Elm Waterhole tributary 2	QW	29 38 39.74	98 23 47.57	2.43	2009–12
LC	08180945	Leon Creek at Scenic Loop Road near Leon Springs, Tex.	Leon Creek	QW	29 40 25.43	98 40 32.04	9.97	2001–12
HC	08181400	Helotes Creek at Helotes, Tex.	Helotes Creek	SW, QW	29 34 42	98 41 29	18.0	1997–2012
GC	08180941	Culebra Creek in Government Canyon State Natural Area near Helotes, Tex.	Government Canyon	QW	29 32 21	98 45 05	12.1	1997–2012

Table 2. Summary of land-cover percentages for selected stream basins in the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, for 2001 and 2006.

[USGS, U.S. Geological Survey]

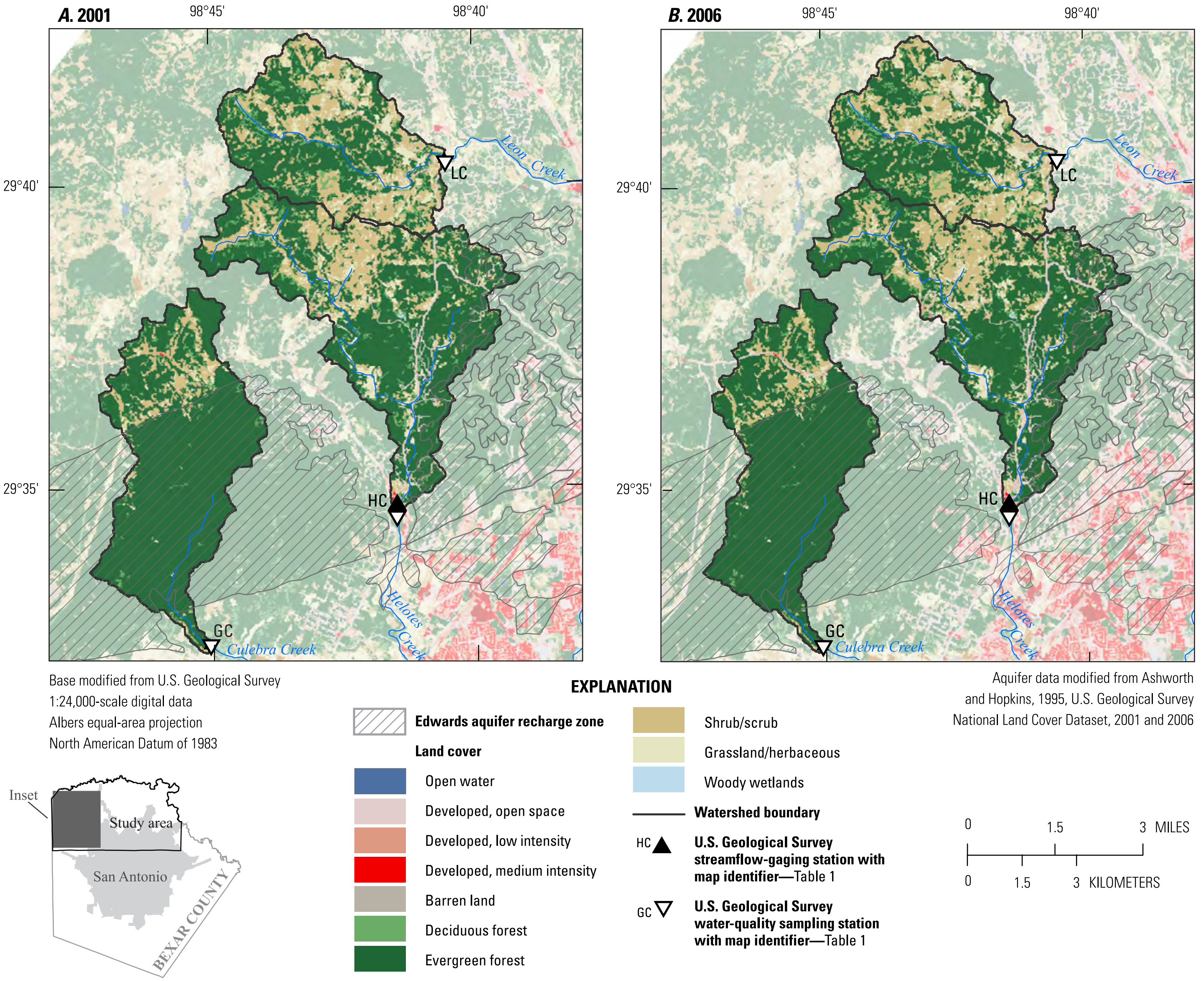
Map identifier (fig. 1)	USGS station number	Short name	Evergreen forest (percent)	Shrub/ scrub (percent)	Deciduous forest (percent)	Grassland/ herbaceous (percent)	Woody wetlands (percent)	Barren land (percent)	Open water (percent)	Developed, open space (percent)	Developed, low intensity (percent)	Developed, medium intensity (percent)
2001 National Land Cover data (Homer and others, 2004)												
EW	08178627	Elm Waterhole tributary 1	73.47	8.67	3.57	0.00	0.00	0.00	0.00	7.65	6.63	0.00
UT	08178628	Elm Waterhole tributary 2	75.40	10.80	11.50	1.80	0.13	0.00	0.00	0.37	0.00	0.00
LC	08180945	Leon Creek	47.23	33.64	7.96	9.85	0.04	0.00	0.09	1.15	0.04	0.00
HC	08181400	Helotes Creek	63.41	19.62	6.16	6.06	0.09	0.01	0.01	4.29	0.28	0.06
GC	08180941	Government Canyon	87.00	8.64	2.63	1.60	0.00	0.00	0.00	0.00	0.12	0.01
2006 National Land Cover data (Fry and others, 2011)												
EW	08178627	Elm Waterhole tributary 1	56.12	3.83	2.55	0.00	0.00	0.00	0.00	23.21	14.29	0.00
UT	08178628	Elm Waterhole tributary 2	68.19	17.12	10.40	1.47	0.13	0.46	0.00	1.67	0.33	0.23
LC	08180945	Leon Creek	46.71	33.53	7.81	9.73	0.04	0.05	0.09	2.00	0.04	0.00
HC	08181400	Helotes Creek	62.62	19.71	6.06	5.89	0.09	0.13	0.01	5.14	0.28	0.06
GC	08180941	Government Canyon	86.84	8.27	2.55	1.51	0.00	0.00	0.00	0.69	0.12	0.01



Base modified from U.S. Geological Survey
1:24,000-scale digital data
Albers equal-area projection
North American Datum of 1983

Aquifer data modified from Ashworth
and Hopkins, 1995, U.S. Geological Survey
National Land Cover Dataset, 2001 and 2006

Figure 2. Land cover for stream basins contributing flow to U.S. Geological Survey stations 08178627 Elm Waterhole Creek Tributary at Evans Road, near San Antonio, Texas (map identifier, EW), and 08178628 Unnamed Tributary of Elm Waterhole Creek at Evans Road at San Antonio, Tex. (map identifier, UT), during *A*, 2001 and *B*, 2006.



Base modified from U.S. Geological Survey
1:24,000-scale digital data
Albers equal-area projection
North American Datum of 1983

Aquifer data modified from Ashworth
and Hopkins, 1995, U.S. Geological Survey
National Land Cover Dataset, 2001 and 2006

Figure 3. Land cover for stream basins contributing flow to U.S. Geological Survey stations 08180945 Leon Creek at Scenic Loop Road near Leon Springs, Texas (map identifier LC), 08181400 Helotes Creek at Helotes, Tex. (map identifier HC), and 08180941 Culebra Creek in Government Canyon State Natural Area near Helotes, Tex. (map identifier, GC), during *A*, 2001 and *B*, 2006.

selected trace metals described in this report are as follows: barium, discharge of drilling wastes and natural erosion; beryllium, coal burning and industrial discharge; cadmium, corrosion of pipes and leaching of chemical waste; chromium, industrial discharge and natural erosion; copper, corrosion of plumbing and natural erosion; lead, corrosion of pipes and natural erosion; mercury, industrial discharge and natural erosion; antimony, fire retardants, ceramics, and electronic waste (U.S. Environmental Protection Agency, 2009). The TCEQ standard for mercury in unfiltered water samples is 2 micrograms per liter (µg/L). The TCEQ standards for barium, cadmium, lead, and antimony in filtered water samples are 2,000 µg/L, 5 µg/L, 1.15 µg/L, and 6 µg/L, respectively.

Pesticides are another group of compounds that were analyzed in this investigation; most pesticides had solely human origins. Pesticides are toxic compounds designed to kill or control plants (herbicides), insects (insecticides), fungi (fungicides), or other organisms. Many pesticides commonly used before the 1970s were relatively persistent and insoluble (for example, organochlorine pesticides). Since the 1970s, less persistent and more easily degradable pesticides have been developed. Although most recently developed pesticides degrade more quickly than organochlorine pesticides, these newer pesticides are more soluble and, therefore, frequently detected in water (Gilliom and others, 2006). Three herbicides—atrazine, prometon, and simazine, as well as the degradate of atrazine, 2-Chloro-4 isopropylamino-6-amino-s-triazine (deethylatrazine)—are among the most common compounds detected in urban streams (Ryberg and others, 2010). Other herbicides frequently detected in urban streams include benfluralin, chlorthal dimethyl, metachlor, and pendimethalin. Two of the insecticides most commonly detected in urban streams of the U.S. are carbaryl and diazinon (Gilliom and others, 2006). Other insecticides commonly found in urban streams include fipronil and four of its degradates (desulfinylfipronil amide, desulfinylfipronil, fipronil sulfide, and fipronil sulfone), disulfoton, and malathion (Ryberg and others, 2010).

Methods

Collection of Streamflow Data

Continuous streamflow data for the study period are available for one of the five stream sites, the Helotes Creek site. The streamflow data collected at the Helotes Creek site were published in the USGS National Water Information System (NWIS) (U.S. Geological Survey, 2012). At the Helotes Creek site, stage is continuously monitored by using a water-stage recorder, and streamflow is continuously recorded by a USGS-operated streamflow-gaging station. Discrete measurements of streamflow were made in accordance with USGS methods (Rantz and others, 1982; Turnipseed and Sauer, 2010). When conditions allowed (that is, when water depths were generally less than 3 feet), streams were waded, and velocity measurements were made by using rod-mounted acoustic meters (Xylem Analytics, 2012). In all other instances, boat-mounted acoustic Doppler current profilers were used to measure streamflow (Oberg and others, 2005). A stage-discharge relation (rating) was developed for the site based on the discrete discharge measurements at the site (Kennedy, 1984; Turnipseed and Sauer, 2010). Adjustments were made to the rating when discrete discharge measurements indicated changing channel conditions. From the stage-discharge relation, stage data were used to compute discharge.

Collection and Processing of Water-Quality Samples

Water-quality samples were collected during selected runoff events. Sample collection and processing techniques followed standard USGS protocols (U.S. Geological Survey, variously dated). Samples for bacteriological analyses (enterococcus, *Escherichia coli* [*E. coli*], fecal streptococcus, and total coliforms) were collected in sterile 250-milliliter (mL) glass bottles. Bottles were attached to a weighted sampling rod, which was lowered from a bridge or from the bank to collect a sample from as close to the center of the channel as possible. The remaining water-quality samples were collected by using a point-integrated sampling method. Each sample was drawn through a fixed intake mounted at the mid-point in the stream channel by using a suction-lift type automatic sampler. The automatic sampler was programmed to begin sampling at a predetermined stage that was selected to ensure streamflow was occurring. The autosampler was programmed to fill as many as four 8-liter bottles at 30-minute intervals during the runoff event. The samples were retrieved at the end of each runoff event or as soon as practical after all four bottles were filled. The samples were then chilled and transported to the USGS South Texas Program Office Laboratory for processing. The four 8-liter samples collected by the automatic sampler were composited into a single water-quality sample to represent the event mean concentration. Composited samples were mixed in a Teflon-lined stainless-steel churn, and subsamples were drawn off for analysis by the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado. On many occasions, samples representing runoff event mean concentrations could not be collected because of variations in precipitation causing flows of extended duration, occurrence of multiple discharge peaks, mechanical problems with automatic samplers, or lack of discharge data. In those instances, multiple grab samples were collected from the edge of the stream (sites Elm Waterhole tributary 1, Elm Waterhole tributary 2, and Government Canyon) or bridge (sites Helotes Creek and Leon Creek) and composited into a single water-quality sample. Constituent concentrations from multiple grab samples represent instantaneous event concentrations. For the purposes of this report, all samples should be considered to represent instantaneous event concentrations and should not be used to compute longer-term loadings of individual constituents. All data from the discrete environmental samples, including results for quality-control samples, were published in NWIS (U.S. Geological Survey, 2012).

Sample Analyses

The NWQL analyzed the water samples for pH, specific conductance, COD, and concentrations of dissolved solids, suspended solids, major ions, nutrients, metals, and pesticides (appendix 1). Dissolved solids, suspended solids, and COD were measured by using methods described by Fishman and Friedman (1989). Major ion concentrations were measured by using ion-exchange chromatography and inductively coupled plasma-atomic emissions spectrometry (ICP-AES), respectively, as described by Fishman and Friedman (1989) and Fishman (1993). Nutrient concentrations were measured by using approved methods as described by Fishman (1993), Patton and Kryskalla (2011), and Patton and Truitt (2000). Total metals were measured by using methods described by Fishman and Friedman (1989), Hoffman and others (1996), Garbarino and Damrau (2001), Garbarino and Struzeski (1998), and Garbarino and others (2006). Between 1997 and 2001, organochlorine pesticides and bulk hydrocarbons (oil and grease) were measured by using a modification of the method described in Wershaw and others (1987). Between 2002 and 2012, pesticides were measured according to Zaugg and others (1995), Lindley and others (1996), and Madsen and others (2003). Samples for bacteriological analyses were transported to the USGS South Texas Program Office Laboratory for processing and analysis. Between 2000 and 2004, *E. coli* was measured by using the mTEC MF method (U.S. Environmental Protection Agency, 2006b). After 2004, *E. coli* was measured by using defined substrate methods described by Myers and others (2007). Fecal coliform and fecal streptococci bacteria samples were analyzed by using methods described by Britton and Greeson (1987). Enterococci were measured by using U.S. Environmental Protection Agency method 1600 (U.S. Environmental Protection Agency, 2002).

The analytical quantification procedure used by the NWQL for reporting results is based on the long-term method detection level (LT–MDL) and laboratory reporting level (LRL). The LRL is defined as twice the LT–MDL and is established to limit the occurrence of false negative detections to less than or equal to 1 percent. For each constituent, the numerical values of the LT–MDL and LRL can vary over time (Childress and others, 1999).

For inorganic analyses, a constituent concentration measured prior to October 2010 was considered estimated by the laboratory when results were greater than the LT–MDL and less than the LRL; that is, a detection was considered likely, but quantification was considered questionable. The remark code of “E” (estimated) was assigned by the laboratory for these results. Beginning in October 2010, the NWQL changed the reporting convention for all inorganic analyses that use the LRL convention. For these constituents, the reporting level was set at the LT–MDL concentration. Since October 2010, concentrations that are less than the LT–MDL are reported as “less than” the LT–MDL concentration (<LT–MDL), and a remark code of “E” is no longer assigned to results greater than the LT–MDL and less than the LRL (U.S. Geological Survey, 2010). For this report, inorganic analyses are reported by using conventions in place at that time the sample was collected and analyzed.

Results for organic analyses (pesticides) were qualified as (“E”) estimated by the NWQL following laboratory reporting conventions in place at the time the sample was collected and analyzed. A remark code of “E” was used when compounds were identified, but concentrations could not be accurately quantified. Estimated pesticide values (either less than the LRL or less than the LT–MDL) were considered as detections.

Quality Assurance

The USGS protocols described in the National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated) were followed for the collection and processing of the quality-assurance samples. Sampling methods were designed to minimize potential sample contamination and preserve sample integrity. To minimize potential contamination of the environmental samples, autosamplers and collection bottles were cleaned between periods of sample collection. To clean the autosamplers, sample tubing was flushed with a soap solution, rinsed with deionized water, flushed with a 5-percent solution of hydrochloric acid, and re-rinsed with deionized water. Sample-collection bottles were washed in the laboratory following the same process.

To document possible contamination, field-equipment blank samples (hereinafter field-blank samples) were collected before and after equipment rinsing to simulate the collection of an environmental sample and to evaluate the effectiveness of the equipment-cleaning procedure (appendix 2). Field-blank samples were collected from each site before and after equipment rinsing for a total of 10 field-blank samples. These field-blank samples were collected by using inorganic and organic blank water (certified ASTM Type I deionized water) provided by the NWQL. The organic blank water was pumped through the auto-sampler tubing and into the 8-liter sample collection jars in the auto-sampler. The field-blank samples were processed following the same procedures as the environmental samples and analyzed by the NWQL for major ions, nutrients, concentrations of metals in unfiltered and filtered water samples, and pesticides. The majority of reported concentrations of these constituents were below LRLs (appendix 2). For cases in which concentrations measured in the field-blank samples were greater than the reporting levels, the concentrations were generally less than environmental-sample concentrations. For those instances, the reported concentrations of environmental samples need to be considered as potentially elevated because the sampling equipment may have introduced small amounts of the given constituent to the environmental samples.

Water-Quality Data of Stormwater Runoff in the Edwards Aquifer Recharge Zone (1997–2012)

Physical properties (pH, specific conductance, COD, dissolved solids, and suspended solids) varied among sites (table 3; appendix 1). The ranges of physical properties were as follows: pH (6.8 to 8.3), specific conductance (85 to 894 microsiemens per centimeter at 25 °C [µS/cm]), COD (<10 to 240 mg/L), dissolved solids concentration (50 to 593 mg/L), and suspended solids concentration (<1 to 1,780 mg/L). Values below the LRL were reported for 8 of the 59 COD samples and 6 of the 54 suspended solid samples. Higher COD values often correspond to wastewater discharge into streams; however, there are no wastewater discharges into any of the streams sampled in this study. Higher COD values also may result from an increase in the concentration of natural organic matter, which is common during runoff events such as those sampled in this study.

The concentration ranges of major ions (calcium, magnesium, potassium, sodium, chloride, silica, and sulfate) were as follows: calcium (12.3 to 120 mg/L), magnesium (0.573 to 14.8 mg/L), potassium (1.00 to 5.66 mg/L), sodium (0.43 to 15.4 mg/L), chloride (0.34 to 241 mg/L), silica (4.45 to 17.2 mg/L), and sulfate (0.72 to 50.2 mg/L) (table 4). The largest concentration reported for chloride (241 mg/L) was measured at the Elm Waterhole tributary 1 site and was much larger than all other environmental samples (the next highest was 32.8 mg/L at Helotes Creek site). High chloride values are sometimes associated with wastewater discharges, but there is no source of wastewater discharge to the Elm Waterhole tributary 1 site.

Concentrations of N and P constituents varied among sites (table 5). The constituents that had one or more samples below the LRLs were as follows: dissolved ammonia had 38 of 60 samples below the LRL, dissolved nitrate had 3 of 40 samples below the LRL, dissolved and total organic N had 38 of 57 samples below the LRL, orthophosphate had 9 of 46 samples below the LRL, dissolved total P had 11 of 57 samples below the LRL, total P had 3 of 57 samples below the LRL, total dissolved N had 5 of 57 samples below the LRL, and total N had 4 of 57 samples below the LRL. Among all sites, the Government Canyon site had the highest percentage of samples (39 percent [44 of 112 samples]) with nutrient concentrations that were below the LRL. The concentration ranges of nutrient samples that were above the LRLs were as follows: dissolved ammonia (0.005 to 0.450 mg/L), dissolved nitrate (0.097 to 1.89 mg/L), dissolved nitrite (0.001 to 0.233 mg/L), dissolved organic N (0.18 to 0.97 mg/L), total organic N (0.43 to 9.7 mg/L), dissolved orthophosphate (0.004 to 0.280 mg/L), dissolved total P (0.003 to 0.320 mg/L), total P (0.008 to 1.22 mg/L), total dissolved N (0.26 to 2.7 mg/L), and total N (0.42 to 10.0 mg/L). Among all nutrient constituents, dissolved orthophosphate P and dissolved total P demonstrated the largest differences between the four stream basins undergoing development and the reference stream basin with undeveloped land cover.

Trace-metal concentrations were measured in filtered water samples, unfiltered water samples, or both. Comparisons of sample concentrations to TCEQ standards (Texas Commission on Environmental Quality, 2010) are provided when available (fig. 4*A*, *C*, *F*, *G, H*). Barium concentrations in filtered water samples ranged from 2.54 µg/L to 37.6 µg/L (fig. 4*A*). All barium concentrations in filtered water samples were substantially below the TCEQ standard for filtered barium (2,000 µg/L). Beryllium concentrations in filtered water samples ranged from <0.007 µg/L to 0.085 µg/L (fig. 4*B*). Cadmium concentrations ranged from <0.016 µg/L to 0.08 µg/L in filtered water samples and from <0.018 µg/L to 0.473 µg/L in unfiltered water samples (fig. 4*C*). The largest cadmium concentration (0.08 µg/L) in filtered water samples occurred at Elm Waterhole tributary 1 and that concentration was much lower than the TCEQ criterion for filtered cadmium (5 µg/L). Chromium in filtered water samples ranged from 0.06 µg/L to 2.1 µg/L (fig. 4*D*). Concentrations of copper in filtered water samples (<0.4 µg/L to 3.9µg/L) were generally smaller compared to copper concentrations in unfiltered water samples (<1.0 µg/L to 17.6 µg/L) (fig. 4*E*). Lead concentrations in filtered water samples were relatively small, ranging from 0.025µg/L to 2.76 µg/L (fig. 4*F*). In one filtered water sample from site Helotes Creek, the lead concentration (2.76 µg/L) exceeded the TCEQ criterion for filtered lead of 1.15 µg/L. Lead concentrations in unfiltered water samples ranged from 0.33 µg/L to 122 µg/L. Mercury concentrations in unfiltered water samples ranged from 0.005 µg/L to 0.085 µg/L (fig. 4*G*), all of which were less than the TCEQ criterion for unfiltered mercury (2 µg/L). Antimony concentrations in filtered water samples ranged from 0.04 µg/L to 0.203 µg/L (fig. 4*H*), all of which were less than the TCEQ criterion for filtered antimony (6 µg/L). Among all constituents for all samples for which TCEQ criteria were available, there was only one exceedance, which was for filtered lead.

Between 1997 and 2001, 24 organochlorine pesticides were measured at four of the five sites: once at the Elm Waterhole tributary 1 site, once at the Leon Creek site, 12 times at the Helotes Creek site, and 5 times at the Government Canyon site. Among the 19 samples that were analyzed for 24 organochlorine pesticides, there was 1 constituent detected in 1 sample. The pesticide p, p’-DDD, a degradate of p, p’-DDT, was measured at an estimated

Table 3. Summary of physical properties measured in samples collected at U.S. Geological Survey stations from selected streams crossing the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 1997–2012.

[LRL, laboratory reporting level; USGS, U.S. Geological Survey; mg/L, milligrams per liter; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; values for chemical oxygen demand below the laboratory reporting levels are reported as <10 mg/L (appendix 1); values for suspended solids below the laboratory reporting levels are reported as <1 mg/L (appendix 1); —, not calculated because of the large number of values less than the laboratory reporting level]

Constituent	Number of Samples	Number of concentrations equal to or greater than the LRL	Minimum concentration (mg/L)	Maximum concentration (mg/L)	Median concentration (mg/L)
USGS station 08178627 Elm Waterhole Creek Tributary at Evans Road, near San Antonio, Tex.					
pH	9	9	7.0	8.2	8.0
Specific conductivity (µS/cm at 25 °C)	10	10	103	894	172
Chemical oxygen demand (mg/L)	11	11	30	130	50
Dissolved solids (mg/L)	10	10	65	593	129
Suspended solids (mg/L)	10	10	26	1,080	66
USGS station 08178628 Unnamed Tributary of Elm Waterhole Creek at Evans Road at San Antonio, Tex.					
pH	3	3	7.7	8.0	8.0
Specific conductivity (µS/cm at 25 °C)	3	3	127	187	186
Chemical oxygen demand (mg/L)	3	2	[1]20	30	—
Dissolved solids (mg/L)	3	3	104	136	119
Suspended solids (mg/L)	3	2	[1]31	65	—
USGS station 08180945 Leon Creek at Scenic Loop Road near Leon Springs, Tex.					
pH	9	9	7.8	8.3	8.1
Specific conductivity (µS/cm at 25 °C)	9	9	96	481	303
Chemical oxygen demand (mg/L)	9	8	[1]10	60	—
Dissolved solids (mg/L)	8	8	80	212	174
Suspended solids (mg/L)	8	8	29	400	211
USGS station 08181400 Helotes Creek at Helotes, Tex.					
pH	23	23	6.8	8.3	8.0
Specific conductivity (µS/cm at 25 °C)	23	23	85	538	221
Chemical oxygen demand (mg/L)	24	19	[1]10	240	—
Dissolved solids (mg/L)	22	22	50	344	133
Suspended solids (mg/L)	21	17	[1]1	1,780	—
USGS station 08180941 Culebra Creek in Government Canyon State Natural Area near Helotes, Tex.					
pH	11	11	7.6	8.1	8.0
Specific conductivity (µS/cm at 25 °C)	11	11	135	452	195
Chemical oxygen demand (mg/L)	12	11	[1]10	240	40
Dissolved solids (mg/L)	13	13	102	286	140
Suspended solids (mg/L)	12	11	[1]2	455	59

[1] Does not include concentrations less than the LRL.

Table 4. Summary of major-ion concentrations measured in samples collected at U.S. Geological Survey stations from selected streams crossing the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 1997–2012.

[USGS, U.S. Geological Survey; n, number of samples analyzed; Min, minimum concentration; Max, maximum concentration; Med, median concentration; mg/L, milligrams per liter]

Constituent	USGS station 08178627 Elm Waterhole Creek Tributary at Evans Road, near San Antonio, Tex. (n=10)			USGS station 08178628 Unnamed Tributary of Elm Waterhole Creek at Evans Road at San Antonio, Tex. (n=3)			USGS station 08180945 Leon Creek at Scenic Loop Road near Leon Springs, Tex. (n=8)			USGS station 08181400 Helotes Creek at Helotes, Tex. (n=22)			USGS station 08180941 Culebra Creek in Government Canyon State Natural Area near Helotes, Tex. (n=13)		
	Min (mg/L)	Max (mg/L)	Med (mg/L)	Min (mg/L)	Max (mg/L)	Med (mg/L)	Min (mg/L)	Max (mg/L)	Med (mg/L)	Min (mg/L)	Max (mg/L)	Med (mg/L)	Min (mg/L)	Max (mg/L)	Med (mg/L)
Calcium	14.0	120	25.9	20.2	30.4	29.5	14.2	59.6	51.4	12.3	91.3	31.7	20.9	89.0	36.0
Magnesium	0.573	1.70	1.31	1.04	1.74	1.69	0.779	5.28	3.50	0.668	14.8	3.86	0.932	8.56	1.88
Potassium	2.70	5.66	4.25	3.71	4.35	3.77	2.04	3.84	2.51	1.00	3.68	1.99	1.67	3.35	2.21
Sodium	1.10	4.21	2.42	1.37	2.29	2.19	0.93	5.13	2.66	0.43	15.4	2.54	0.75	4.70	1.47
Chloride	1.45	241	3.30	1.18	3.16	2.31	2.50	10.4	3.80	0.34	32.8	4.09	0.70	8.22	2.01
Silica	5.12	17.2	9.13	6.57	14.2	9.37	5.06	10.1	8.99	4.45	11.8	5.25	5.25	10.5	6.09
Sulfate	1.85	11.8	4.43	3.23	13.6	8.30	2.25	13.5	6.14	0.72	50.2	7.25	1.55	11.2	2.59

Table 5. Summary of nutrient concentrations measured in samples collected at U.S. Geological Survey stations from selected streams crossing the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 1997–2012.

[USGS, U.S. Geological Survey; mg/L, milligrams per liter; E, estimated; —, not calculated because of the large number of values less than the laboratory reporting level]

Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Minimum concentration (mg/L)	Maximum concentration (mg/L)	Median concentration (mg/L)
USGS station 08178627 Elm Waterhole Creek Tributary at Evans Road, near San Antonio, Tex.					
Dissolved ammonia nitrogen (mg/L)	11	[1]5	0.011	0.450	—
Dissolved nitrate nitrogen (mg/L)	11	11	E0.156	1.89	0.549
Dissolved nitrite nitrogen (mg/L)	11	11	E0.005	0.050	0.014
Dissolved organic nitrogen (mg/L)	11	[1]4	0.58	0.97	—
Total organic nitrogen (mg/L)	11	[1]4	1.10	3.00	—
Dissolved orthophosphate phosphorus (mg/L)	11	10	0.010	0.119	0.046
Dissolved total phosphorus (mg/L)	10	10	0.022	0.132	0.051
Total phosphorus (mg/L)	10	10	0.087	0.938	0.163
Total dissolved nitrogen (mg/L)	10	10	0.56	2.7	1.2
Total nitrogen (mg/L)	10	10	1.00	4.60	1.95
USGS station 08178628 Unnamed Tributary of Elm Waterhole Creek at Evans Road at San Antonio, Tex.					
Dissolved ammonia nitrogen (mg/L)	3	[1]1	0.076	0.076	—
Dissolved nitrate nitrogen (mg/L)	3	3	0.283	1.57	0.593
Dissolved nitrite nitrogen (mg/L)	3	3	0.007	0.017	0.010
Dissolved organic nitrogen (mg/L)	3	[1]1	0.38	0.38	—
Total organic nitrogen (mg/L)	3	[1]1	0.64	0.64	—
Dissolved orthophosphate phosphorus (mg/L)	3	3	0.014	0.074	0.031
Dissolved total phosphorus (mg/L)	3	3	0.027	0.081	0.038
Total phosphorus (mg/L)	3	3	0.074	0.146	0.111
Total dissolved nitrogen (mg/L)	3	3	0.81	2.1	1.1
Total nitrogen (mg/L)	3	3	1.20	2.26	1.30
USGS station 08180945 Leon Creek at Scenic Loop Road near Leon Springs, Tex.					
Dissolved ammonia nitrogen (mg/L)	9	[1]3	0.005	0.100	—
Dissolved nitrate nitrogen (mg/L)	9	9	0.097	1.07	0.286
Dissolved nitrite nitrogen (mg/L)	9	[1]8	0.001	0.233	—
Dissolved organic nitrogen (mg/L)	8	[1]2	0.42	0.45	—
Total organic nitrogen (mg/L)	8	[1]2	1.20	2.10	—
Dissolved orthophosphate phosphorus (mg/L)	9	9	0.005	0.160	0.016
Dissolved total phosphorus (mg/L)	8	8	0.011	0.170	0.029
Total phosphorus (mg/L)	8	8	0.050	0.460	0.200
Total dissolved nitrogen (mg/L)	8	8	0.27	1.6	0.65
Total nitrogen (mg/L)	8	8	0.83	2.7	1.7
USGS station 08181400 Helotes Creek at Helotes, Tex.					
Dissolved ammonia nitrogen (mg/L)	24	[1]9	0.015	0.130	—
Dissolved nitrate nitrogen (mg/L)	16	16	0.210	0.890	0.494

Table 5. Summary of nutrient concentrations measured in samples collected at U.S. Geological Survey stations from selected streams crossing the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 1997–2012.—Continued

[USGS, U.S. Geological Survey; mg/L, milligrams per liter; E, estimated; —, not calculated because of the large number of values less than the laboratory reporting level]

Constituent	Number of samples	Number of concentrations equal to or greater than the LRL	Minimum concentration (mg/L)	Maximum concentration (mg/L)	Median concentration (mg/L)
USGS station 08181400 Helotes Creek at Helotes, Tex.—Continued					
Dissolved nitrite nitrogen (mg/L)	16	[1]12	0.001	0.020	—
Dissolved organic nitrogen (mg/L)	22	[1]8	0.18	0.64	—
Total organic nitrogen (mg/L)	22	[1]8	0.43	9.7	—
Dissolved orthophosphate phosphorus (mg/L)	16	[1]12	0.004	0.280	—
Dissolved total phosphorus (mg/L)	22	[1]18	0.003	0.320	—
Total phosphorus (mg/L)	22	22	0.008	1.22	0.120
Total dissolved nitrogen (mg/L)	22	[1]20	0.26	1.5	0.67
Total nitrogen (mg/L)	22	[1]21	0.42	10.0	1.10
USGS station 08180941 Culebra Creek in Government Canyon State Natural Area near Helotes, Tex.					
Dissolved ammonia nitrogen (mg/L)	13	[1]4	0.016	0.084	—
Dissolved nitrate nitrogen (mg/L)	7	7	0.256	1.07	0.342
Dissolved nitrite nitrogen (mg/L)	7	[1]6	0.004	0.016	—
Dissolved organic nitrogen (mg/L)	13	[1]4	0.47	0.91	—
Total organic nitrogen (mg/L)	13	[1]4	0.71	4.50	—
Dissolved orthophosphate phosphorus (mg/L)	7	[1]3	0.005	0.020	—
Dissolved total phosphorus (mg/L)	13	[1]7	0.009	0.028	—
Total phosphorus (mg/L)	13	[1]11	0.040	0.460	—
Total dissolved nitrogen (mg/L)	13	[1]11	0.68	2.0	—
Total nitrogen (mg/L)	13	[1]11	1.00	5.60	—

[1] Does not include concentrations less than the LRL.

concentration of 0.0017 µg/L at Helotes Creek (USGS station 08181400) on November 23, 2000 (appendix 1).

Between 2002 and 2012, a different pesticide analysis that measured 52 pesticides and pesticide degradates was used (table 6). During this phase of the study, 35 of the 52 pesticide compounds were not detected in any of the 40 samples. A total of 17 of the 52 pesticides were detected one or more times over the course of the study, with a total of 102 detections in 40 samples (table 6). Among all samples, atrazine and its degradate, deethylatrazine, were the most commonly detected pesticides. For atrazine and deethylatrazine, the fewest detections occurred at the Government Canyon site. Simizine, an herbicide that is similar to atrazine in chemical composition and environmental application, was detected in 9 of the 40 samples. The insecticide fipronil and four of its degradates were also frequently detected, with most detections being measured at Elm Waterhole tributary 1 and Elm Waterhole tributary 2. Other herbicides that were detected between 2002 and 2012 included benfluralin, chlorthal dimethyl, metachlor, pendimethalin, and prometon. Other insecticides that were detected between 2002 and 2012 included carbaryl, diazinon, disulfoton, and malathion. Detections among constituents (calculated by dividing the total number of detections by the number of samples) showed that atrazine was the most frequently detected pesticide during the investigation. A comparison of the average number of detections per sample among sites (calculated by dividing the total number of detections by the number of samples collected at each site) showed that sites undergoing development had higher average number of detections per sample (1.8 to 6.0 percent) and samples collected from the Government Canyon reference site had the smallest average number of detections per sample (0.6 percent).

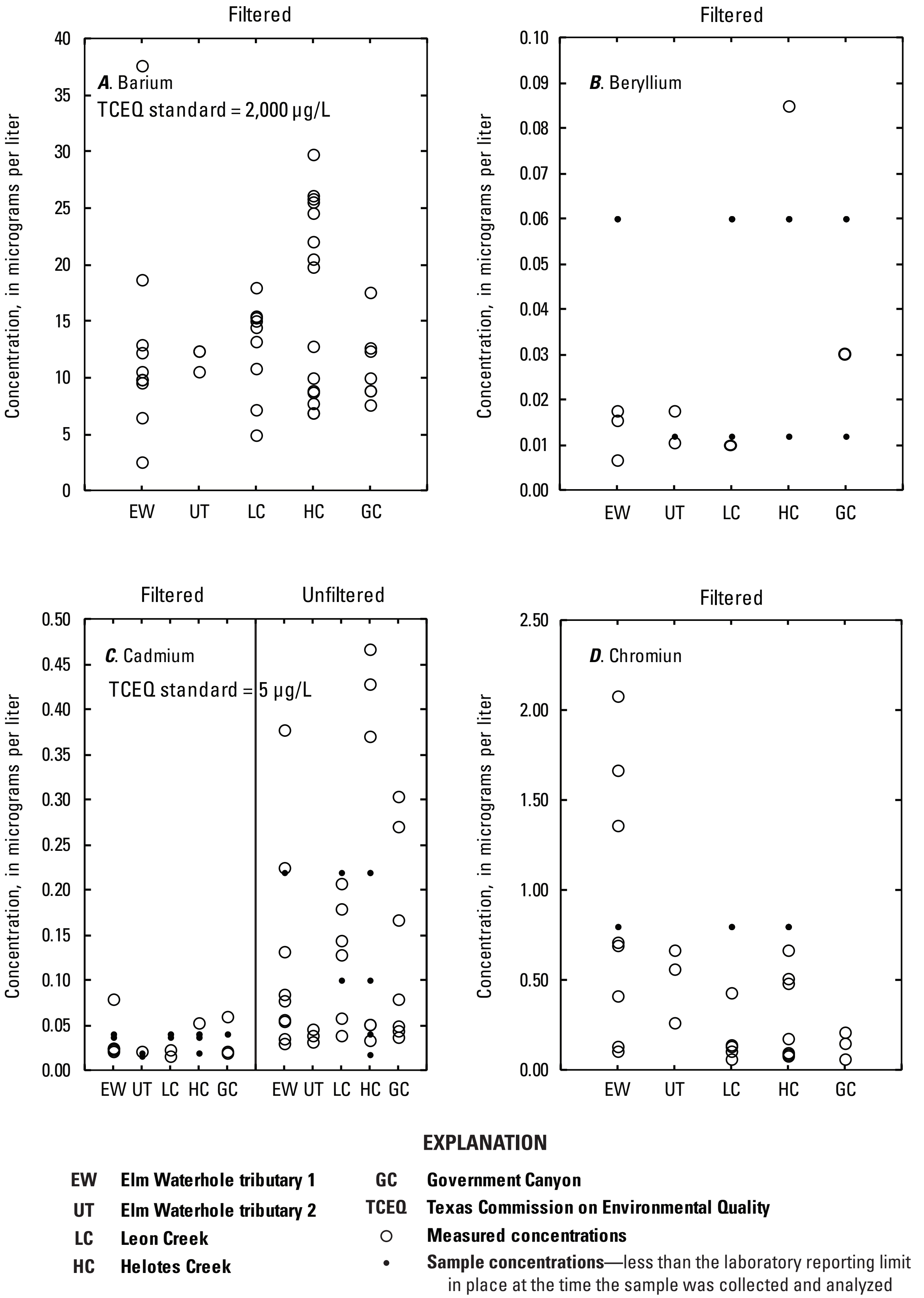
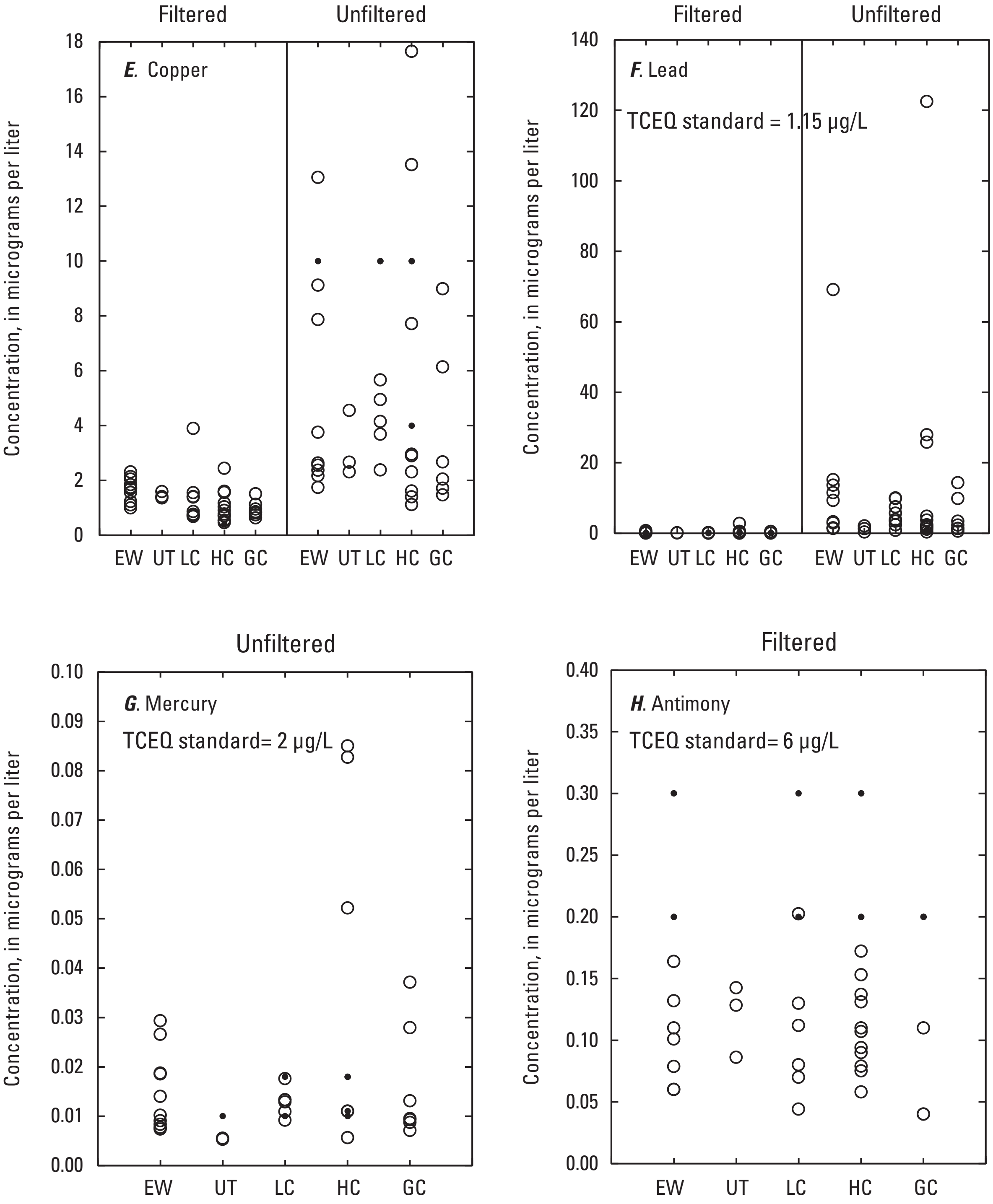


Figure 4. Graphs of selected trace-metal concentrations for selected streams in the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 1997–2012.



EXPLANATION

EW	**Elm Waterhole tributary 1**	**GC**	**Government Canyon**
UT	**Elm Waterhole tributary 2**	**TCEQ**	**Texas Commission on Environmental Quality**
LC	**Leon Creek**	○	**Measured concentrations**
HC	**Helotes Creek**	•	**Sample concentrations**—less than the laboratory reporting limit in place at the time the sample was collected and analyzed

Figure 4. Graphs of selected trace-metal concentrations for selected streams in the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 1997–2012.—Continued

Table 6. Summary of pesticide detections in samples collected at U.S. Geological Survey stations from selected streams crossing the San Antonio segment of the Edwards aquifer recharge zone, Bexar County, Texas, 2001–12.

[USGS, U.S. Geological Survey; n, number of samples analyzed; H, herbicide; I, insecticide; -, not detected[1]; —, not applicable. Constituents shown in italics are pesticide degradates]

	Type of pesticide	USGS station Elm Waterhole Creek Tributary at Evans Road near San Antonio, Tex. (n=10)	USGS station Unnamed Tributary of Elm Waterhole Creek at Evans Road at San Antonio, Tex. (n=3)	USGS station Leon Creek at Scenic Loop Road near Leon Springs, Tex. (n=8)	USGS station Helotes Creek at Helotes, Tex. (n=12)	USGS station Culebra Creek in Government Canyon State Natural Area near Helotes, Tex. (n=7)	Percentage of detections (n=40)
2-Chloro-4-isopropylamino-6-amino-s-triazine	H	4	2	2	3	1	30
Atrazine	H	8	3	7	9	2	73
Benfluralin	H	-	-	1	-	-	2.5
Carbaryl	I	2	1	-	5	-	20
Chlorthal dimethyl	H	2	1	1	1	-	13
Desulfinylfipronil amide	I	1	1	-	-	-	5.0
Desulfinylfipronil	I	4	2	-	2	-	20
Diazinon	I	1	-	1	5	-	18
Disulfoton	I	-	-	-	1	-	2.5
Fipronil sulfide	I	-	2	-	-	-	5.0
Fipronil sulfone	I	1	-	-	-	-	2.5
Fipronil	I	2	2	-	-	-	10
Malathion	I	1	1	1	3	-	15
Metachlor	H	1	-	1	-	1	7.5
Pendimethalin	H	-	-	-	1	-	2.5
Prometon	H	3	-	-	-	-	7.5
Simazine	H	3	3	-	3	-	23
Total number of detections per station[1]	—	33	18	14	33	4	—
Average number of detections per sample[1]	—	3.3	6.0	1.8	2.8	0.6	—

[1] Estimated pesticide values (either less than the laboratory reporting level or less than the long-term method dection level) were considered as detections.

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