



900 E. Quincy
San Antonio, TX 78215
edwardsaquifer.org

JULY 2014
2014 UPDATE



WATER QUALITY TRENDS ANALYSIS

OF THE SAN ANTONIO SEGMENT, BALCONES FAULT ZONE EDWARDS AQUIFER, TEXAS

Prepared by:

Steven Johnson, P.G., Hydrogeology Manager
Geary Schindel, P.G., Director/Chief Technical Officer



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EXECUTIVE SUMMARY

The Edwards Aquifer Authority (EAA) and other public agencies have collected and analyzed thousands of groundwater, surface water, and springwater samples to evaluate water quality in the San Antonio segment of the Balcones Fault Zone Edwards Aquifer of south central Texas. Samples were collected for a wide range of purposes, including evaluation of background conditions, basic and applied research, and site-specific investigations related to spills. The purpose of this report is to examine this body of water quality data to characterize historical water quality, existing conditions, and water quality trends, as well as to identify specific constituents of concern (COCs) within the aquifer. Emphasis is placed on evaluating the presence of COCs that may have resulted from human activity in the study area. This report was originally published in July 2009 and included all data available through August 2006. This update includes analytical data collected through June 2013.

The current study utilized available water quality data collected by the EAA, its predecessor agency, the Edwards Underground Water District (EUWD); the United States Geological Survey (USGS); and the Texas Water Development Board (TWDB) between 1913 and 2013. More than 13,000 samples totaling more than 700,000 individual parameters were compiled for this report. Most (approximately 70 %) of the historical data consist of five or fewer samples from approximately 1,700 groundwater, surface water, or spring locations. The largest group of samples was collected approximately monthly from saline water-line transect water wells from July 1985 through September 2000 in support of research on the interaction between saline water and freshwater in the downdip part of the aquifer. However, monthly samples from Comal and San Marcos springs since 2006 have substantially increased the number and frequency of freshwater samples over saline water samples.

Parameters detected in the water quality data consist of volatile organic compounds (VOCs), nutrients, herbicides and pesticides, metals, and semivolatile organic compounds (SVOCs). Concentrations were

compared with protective concentration levels (PCLs) established by the Texas Commission on Environmental Quality (TCEQ), which include federal drinking-water standards. Detections were not widespread; organic compounds (of all kinds) were detected in 1.2% (2,075 out of 177,254 samples) of groundwater analyses, 0.3% (332 out of 113,787 samples) of springwater analyses, and 1.7% (497 out of 40,991 samples) of surface water analyses. Tetrachloroethene concentrations exceeded PCLs in 46 samples, which was the highest exceedance rate for any organic compound. No other organic compound exceeded PCLs in more than seven samples. Nitrate concentrations exceeded the PCL (10 mg/L as nitrogen) in approximately 0.4% (31 out of 8,943 samples) of the samples. Regulated metals exceeded PCLs in 1.2% (620 out of 53,209 samples) of the samples, although arsenic, cadmium, selenium, and lithium were detected mainly above PCLs in samples of water from the saline zone (>1,000 mg/L total dissolved solids), which has not been considered drinking water for the purposes of this report. Of the 60 locations sampled for pharmaceutical and personal care products (PPCPs), one or more compounds were detected at 19 locations PPCP. The most commonly detected PPCP compounds were caffeine, DEET (insecticide), and lincomycin (antibiotic).

Analytical data evaluated for the update of this report since 2006 have not changed the conclusions of the original report. Seven samples of groundwater (not saline) and four spring samples contained metals concentrations above their PCLs, and only three additional detections of organic compounds were above their PCLs. Historical data are characterized by occasional detections of a small number of organic compounds, a small fraction of which occur in concentrations that exceed PCLs. This report contains many more detections of nutrients because of sewage spills that EAA investigated in 2010 and 2012.

These results are consistent with the low detection rates of potential contaminants from multiple sources indicated by historical data. Despite the additional data,

infrequent detections and low concentrations render the data insufficient to determine whether concentrations are increasing or decreasing.

Given all of the historical analyses through June 2013, concentrations of 28 parameters exceeded PCLs in one or more samples, which include one additional parameter (nitrite) from the post-2006 analyses. Parameters were selected as COCs because their concentrations

exceeded the assimilative capacity of the aquifer, which is the ability of the aquifer to attenuate concentrations of contaminants to acceptable levels before they reach a well or spring (EPA, 1987). Vulnerability of the aquifer to contamination has been demonstrated by the detection of parameters that do not occur naturally in the aquifer. Organic compounds were detected mainly in urban areas, whereas nitrate was detected throughout the aquifer.

INTRODUCTION

The Edwards Aquifer Authority (EAA) was created by the Texas Legislature in 1993 to manage the southern segment of the Balcones Fault Zone Edwards Aquifer (the aquifer), the water supply for more than 1.7 million people. One of the EAA's statutory responsibilities is to prevent waste and pollution of water in the aquifer. To monitor the aquifer for pollution, the EAA monitors the quality of groundwater within the aquifer, surface water recharging the aquifer, and springs discharging water from the aquifer. EAA and its predecessor agency, the Edwards Underground Water District (EUWD); the U.S. Geological Survey (USGS); and the Texas Water Development Board (TWDB) have collected and analyzed thousands of samples of groundwater, surface water, and springs for a wide range of purposes, including evaluation of background and ambient conditions, basic and applied research, and site-specific investigations related to spills. The purpose of this report is to examine this body of water quality data to characterize historical water quality, existing conditions, and water quality trends, as well as to identify specific constituents of concern (COCs) within the aquifer. Emphasis is placed on evaluating the presence of COCs that may have resulted from human activity in the study area. Originally published in 2009 (Johnson et al., 2009) using analytical data through 2006, this report has been updated using analytical results collected through June 2013.

Like the original report, this report consists of an examination of available analytical results of groundwater, surface water, and spring samples associated with the aquifer. Historical results are grouped as volatile organic compounds (VOCs), herbicides and pesticides, nitrogen, metals, and semivolatile organic compounds (SVOCs). In addition, this report describes results of analyses for pharmaceuticals and personal care products (PPCPs) that EAA has analyzed since 2011 and the USGS since 2001. The analytical results were added to the original database, which categorized them according to sample locations, sampling frequency, chemical types and concentrations, number of detections, and other attributes.

Concentrations of detectable parameters were compared with protective concentration levels (PCLs) established by the Texas Commission on Environmental Quality (TCEQ) under the Texas Risk Reduction Program (TRRP), which include maximum contaminant levels (MCLs) and secondary drinking-water standards (SDWS) established by the U.S. Environmental Protection Agency. PCLs are based on residential exposure to the parameters through ingestion of water. Statistical parameters such as maximums, minimums, and means were calculated to describe the distributions of parameter concentrations. In this report, parameters whose concentrations were observed above PCLs were selected as COCs.

Results of the original study were used to refine the EAA's water quality monitoring program. For example, PPCPs and passive sampling techniques, which will be the subject of a separate report, were added to the program. EAA may change other sampling strategies and techniques in the future to increase efficiency or effectiveness of monitoring.

Additional (post-2006) analytical results also reinforced EAA's understanding of the vulnerability of the aquifer to activities that involve potential contaminants. The recharge zone, where the Edwards Limestone crops out, is particularly vulnerable because attenuation of released contaminants may be negligible. Potential threats to water quality in the artesian and transition zones include abandoned or poorly completed water wells. Detection of parameters that do not occur naturally is evidence that activities on the surface are impacting water quality in the aquifer. Types of parameters, detection frequencies, concentrations, and other information will help in identifying activities that may impact the aquifer and routes that pollutants follow into the aquifer.

This analysis will identify contaminants whose concentrations have locally exceeded the assimilative capacity of the aquifer, which is the ability of the aquifer to attenuate concentrations of contaminants to acceptable levels before they reach a well or spring (EPA, 1987). Chemicals that exceeded the assimilative capacity will be identified as COCs.

EDWARDS AQUIFER

The physical characteristics that make the Edwards Aquifer a prolific source of water also make it vulnerable to contamination and affect its ability to attenuate potential pollutants. The Edwards is a karst aquifer, meaning that it is part of a unique system formed by the dissolution of soluble rocks, such as limestone, dolomite, and gypsum. Where the Edwards Limestone is exposed at the surface, the karst terrain is manifested by the presence of sinkholes, sinking streams, and caves. In the subsurface, groundwater, through dissolutional processes, has created highly permeable flowpaths, resulting in prolific wells, but it may also carry potential contaminants with little or no filtration.

Hydrogeology of the Edwards Aquifer

The Edwards Aquifer system extends from a western groundwater divide located near Brackettville in Kinney County, east to San Antonio, and then northeast through San Marcos to the eastern groundwater divide near Kyle in Hays County—a distance of more than 290 km (180 mi). The aquifer, ranging from eight to 100 km (five to 60 mi) in width, is the primary water supply for more than two million people.

The aquifer system is divided into three zones: the drainage area, the recharge zone, and the artesian zone. The drainage area, which lies to the north and

west of the recharge zone, is generally composed of the less permeable Upper and Lower Glen Rose limestones. Water that discharges from springs along the edge of the Edwards Plateau—and also falls as rain in the Texas Hill Country—is collected in surface streams and rivers and is conveyed toward the Gulf of Mexico.

The recharge zone occurs where the Balcones Fault System has created a series of normal faults that are downthrown to the south toward the Gulf of Mexico, exposing the Edwards Limestone at the surface. When surface streams from the drainage area cross the recharge zone, they become sinking streams that recharge the aquifer. Recharge also occurs from precipitation falling directly onto the exposed Edwards Limestone. Water is conveyed through solution-enlarged fractures, faults, bedding-plane partings, caves, and conduits. Groundwater generally occurs under unconfined conditions within the recharge zone. The intersection of the drainage area and the recharge zone is considered the upgradient limit of the Edwards Aquifer.

Water from the recharge zone moves laterally (generally south and/or east) to enter the artesian zone, where the Edwards Limestone is fully saturated and confined by the Del Rio Clay. The downgradient limit of potable water within the aquifer is generally considered the 1,000-mg/L total dissolved solids (TDS) isoconcentration line.

WATER QUALITY DATA OVERVIEW

Water quality data compiled for this analysis came from EAA databases and from databases of the USGS and TWDB. Data from more than 13,000 samples consisting of over 700,000 individual parameter analyses were reviewed; the samples are from approximately 1,700 locations. Although the sampling locations are well distributed over the study area, thousands of wells and numerous springs and recharging streams were not sampled and are, therefore, not represented in the historical data.

Data Sources

Data in this report were acquired from the EAA, the USGS, and the TWDB, which have historically collected most analyses of Edwards Aquifer water (Table 1). Table 1 lists the number of samples and the number of individual chemical parameters analyzed. The USGS collected and analyzed Edwards Aquifer samples as early as 1930. The EUWD was established in 1959 and contracted with the USGS to conduct its sampling and analytical program. The EUWD largely took over the

Table 1. Sources of Analytical Data for This Report Update

Agency	Number of Samples through August 2006	Number of Samples after August 2006	Number of Individual Parameters Analyzed through August 2006	Post 2009 Number of Individual Parameters Analyzed after August 2006	Earliest Sample Year
Edwards Aquifer Authority and Edwards Underground Water District	1,342	1,673	104,802	230,011	1993
U.S. Geological Survey	5,731	623	219,867	56,671	1930
Texas Water Development Board	4,227	199	79,137	34,330	1913
Total	11,300	2,495	403,806	321,012	

program in 1993, although the USGS has continued to collect groundwater and surface water samples for its own projects, as well as for other cooperators, such as the EAA and the San Antonio Water System (SAWS). In 1996 the EUWD was replaced by the EAA, which has incorporated and expanded the EUWD's water quality sampling and analysis program. The TWDB maintains a database of Texas groundwater analyses that contains results of its own sampling programs, plus results submitted by others, such as the EAA and the USGS. The earliest aquifer sample in the database was collected by the TWDB in 1913. The original report (Johnson et al., 2009) contains samples collected through August 10, 2006, and the current, updated report includes samples collected through June 30, 2013.

Construction and Update of the Database

Water quality analyses from the Edwards Aquifer have been generated by many researchers and laboratories. The EAA and the EUWD submitted water samples to the following laboratories: Pollution Control Services (PCS) in San Antonio, Texas (1993–2001); Severn-Trent Laboratories in Corpus Christi and Austin, Texas, and Tallahassee, Florida (2000–2004); Anacon, Inc., in Houston, Texas (2004–2010); and TestAmerica, Inc. (2010–present). The USGS submits water samples to its internal laboratories, and the TWDB uses subcontract laboratories that may change from year to year. Consequently, results represent a wide variety of laboratory operations and analytical methods. Data

have been managed by several agencies for many years, and sample collection and analytical techniques have changed. Variability in detection limits, significant figures, target analytes, and other analytical details is wide. In addition, for samples where documentation of water well and surface water sampling protocols are not unavailable, this report has been prepared on the assumption that analyses are representative of the ground- and surface water that was sampled. Differences in sampling protocols and analytical techniques are significant on a sample-by-sample basis but probably do not substantively affect the presence or absence of trends in the results.

The database was constructed with all results being gathered into a consistent format on the basis of sample location, analyte, collection date, and concentration. First, Edwards Aquifer samples were identified in the databases. Because many historical USGS and EAA analyses were in the TWDB database, all duplicate data were eliminated. Uniform analyte names were developed from the U.S. Environmental Protection Agency's storage and retrieval system for water quality data (STORET) codes used in USGS and TWDB databases and Chemical Abstract Service (CAS) codes in the EAA database. Finally, quality-control flags for nondetectable, estimated, and nonquantifiable concentrations were reconciled among the three data sources. The resulting database contains more than 13,000 samples and more than 700,000 individual chemical analyses of groundwater, surface water, and springs.

Table 2. Frequency of Sampling

Number of Samples at Each Location	Number of Locations	Percent of Locations
1	975	46.0%
2 to 5	587	27.7%
5 to 10	226	10.7%
10 to 15	102	4.8%
15 to 20	80	3.8%
20 to 50	34	1.6%
25 to 50	76	3.6%
50 to 100	17	0.8%
100 to 200	13	0.6%
200 to 226	8	0.4%

Summary of Analytical Data

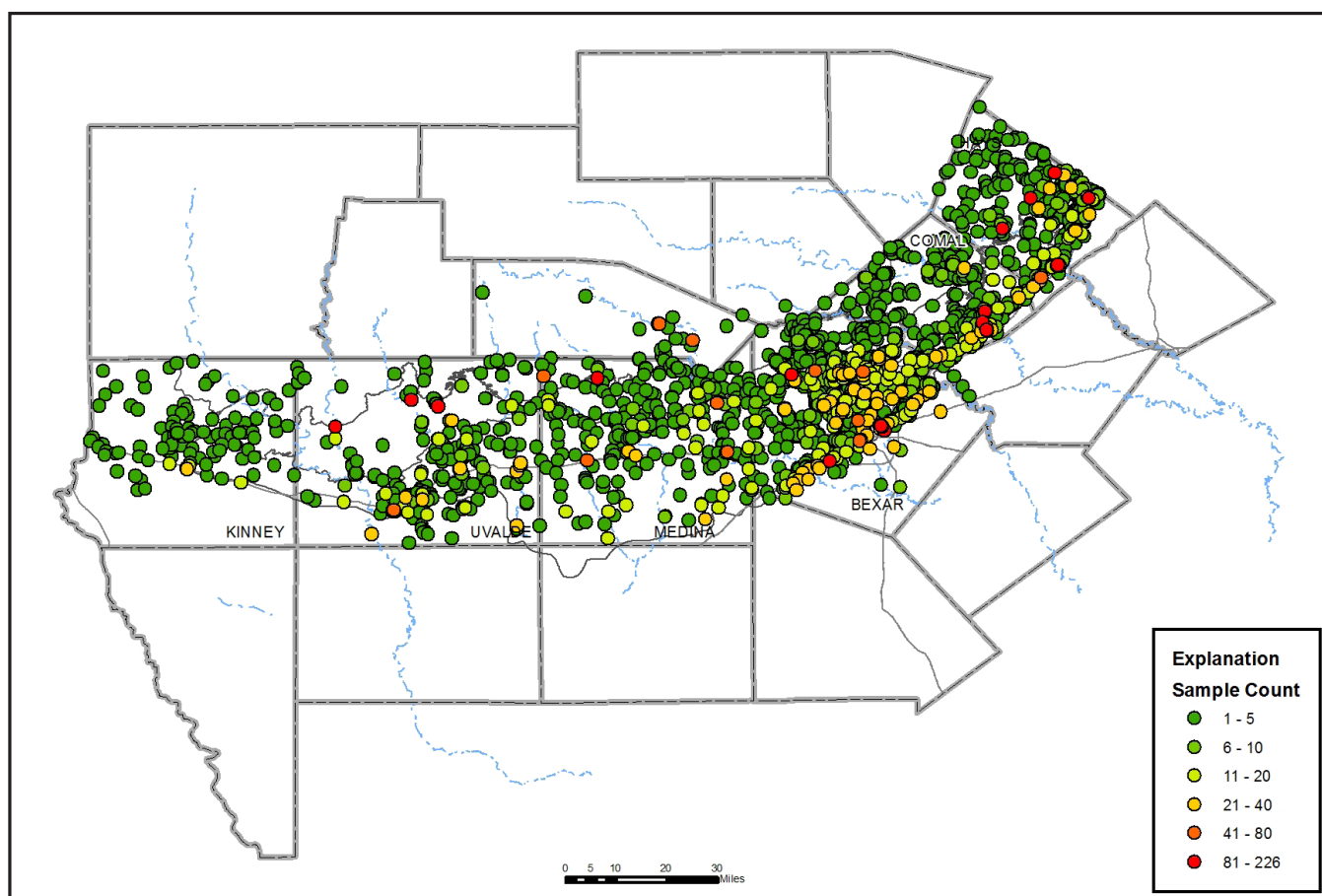
The analytical data are from water samples collected from groundwater, surface water, and springs throughout the EAA's jurisdictional area. Groundwater samples are from many public and private wells that were collected by the EAA, EUWD, USGS, TWDB, or other agencies. Surface water sampling locations of streams are on or near the recharge zone, such as the Nueces, Frio, Dry Frio, Sabinal, Medina, and Blanco rivers, and Seco, Hondo, and Helotes creeks. The Guadalupe River is not included because it provides little or no recharge to the Edwards Aquifer. The USGS also collected stormwater from ephemeral streams in the region, but only data from streams on the recharge zone or the drainage area are considered in this report. Spring locations include primarily one or more orifices at Comal, San Marcos, Hueco, San Antonio, San Pedro, Pinto, and Las Moras springs.

Water wells, streams, and springs in the database have been sampled between one and 200+ times (Table 2). Distributions of all sampling locations and numbers of samples collected are shown in Figure 1. Slightly fewer than half the locations were sampled once, whereas approximately one-third of the locations were sampled

up to five times. Fewer than 10% of the remaining locations were sampled more than five times. Highest sample densities are in Bexar, Comal, and Hays counties and at water supply wells in Medina and Uvalde counties (Figure 1). Most locations with the highest number of samples are freshwater/saline water interface-transect monitoring wells (transect wells) in Bexar and Comal counties (frequent samples from 1993 through 2002), wells summarized by Wells (1985), and several streams on the recharge zone.

The top 25 sample locations (all sources) compose approximately 24% of the samples in the updated database, as compared with approximately 32% in the original database (Table 3). The top 25 sample locations still reflect the intensive sampling of transect water wells prior to 2006, although Comal Spring #1 at Landa Park is now the most frequently sampled location. The EAA reduced the frequency of sampling transect water wells after December 2000. Other locations such as Deep and Hotel springs at San Marcos and monitoring well AY-68-28-608 have been sampled frequently in the last few years. The EAA has been sampling the springs in its jurisdictional area monthly since June 2009, when the drought in south central Texas intensified.

Figure 1. Distribution of Sampling Locations.



Data include principally analyses of metals, nutrients, major anions and cations, VOCs, SVOCs, herbicides, and pesticides. Most parameters in the analyses are major anions and cations, which have been collected for many years. Since the mid-1980s, organic compounds and metals have been added to analyses. Nutrients, such as nitrate, nitrite, ammonia, and phosphorus, were also commonly included in many historical analyses. Analyses of other organic compounds, isotopes, radioactive constituents, and bacteria are relatively few and thus will not be considered in this report. PPCPs will be covered in more detail in this report because the EAA started analyses of PPCPs in 2011, although the USGS had run analyses for some PPCPs as early as 2005.

Data Limitations

Although thousands of samples related to the aquifer have been collected from groundwater, surface water,

and springs over the years, the data have limitations for characterizing water quality trends. Before 1999, the EAA's water quality monitoring program concentrated on collecting samples from transect wells. In 2000, the data collection program was modified to emphasize collection of samples from wells within freshwater parts of the aquifer, as well as from streams and springs. In addition, the 1999 list of analytes was expanded to include VOCs, herbicides, pesticides, nutrients, and bacteria. Consequently, the number of samples from freshwater wells, streams, and springs increased relative to the number of transect well samples. As of 2009, approximately 60% (1,892 out of 3,000) of samples from the top 25 locations were from transect wells. Currently transect well samples make up approximately 48% (1,905 out of 3,939 samples) of samples from the top 25 locations. Consequently, a limited number of sample locations have an extensive range of analytes or a time series sufficient to provide insight into water quality trends.

Table 3. Top 25 Sample Locations

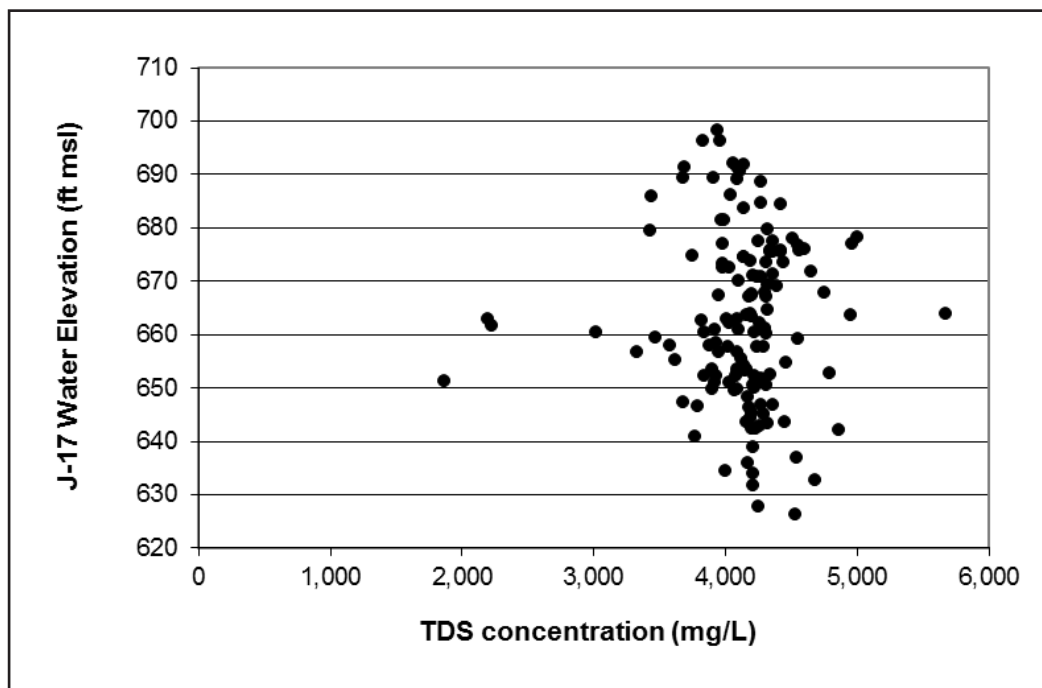
Location Name	Type	County	Number of Samples	Samples in Original Report
Comal Springs #1	Spring adjacent to Landa Park Drive	Comal	221	133
AY-68-37-521	Transect well (saline)	Bexar	220	219
AY-68-37-524	Transect well (fresh)	Bexar	219	218
AY-68-37-526	Transect well (fresh)	Bexar	217	217
AY-68-37-522	Transect well (saline)	Bexar	209	209
AY-68-37-525	Transect well (saline)	Bexar	208	207
AY-68-37-523	Transect well (saline)	Bexar	207	206
Frio River at Concan	Stream on recharge zone	Uvalde	197	178
AY-68-37-527	Transect well (fresh)	Bexar	203	202
Onion Creek near Driftwood	Stream on contributing zone	Hays	188	Not included
Hueco Springs A	Spring	Comal	172	88
LR-67-01-801	Hotel Spring at San Marcos	Hays	150	87
Blanco River at Wimberley	Stream on contributing zone	Hays	150	135
Nueces River at Laguna	Stream on contributing zone	Uvalde	138	123
Hondo Creek near Tarpley	Stream on recharge zone	Medina	137	124
Dry Frio River near Reagan Wells	Stream on recharge zone	Uvalde	130	117
DX-68-23-617	Transect well (fresh)	Comal	118	114
Bear Creek below FM 1826 near Driftwood	Stream on contributing zone	Hays	117	Not included
LR-67-01-819	Deep Spring at San Marcos	Hays	115	Not in top 25
DX-68-23-618	Transect well (fresh)	Comal	111	108
DX-68-23-619	Transect well (fresh)	Comal	101	101
Helotes Creek at Helotes	Stream on contributing zone	Bexar	98	89
LR-58-58-403	Municipal well	Hays	98	97
DX-68-23-616	Transect well (saline)	Comal	91	91
DX-68-28-624	Well on artesian zone	Comal	85	Not in top 25

Most historical data consist of six or fewer samples from approximately 2,200 groundwater, spring, or surface water locations, which is a small fraction of the total number of possible sampling points in the region. Although the number is not precisely known, it is estimated that approximately 15,000 Edwards Aquifer wells exist within the EAA's jurisdictional area. Therefore, existing data from wells represent a small subset of all the wells. Such widely spaced data are useful as a snapshot

of water quality at the time of sampling. Also, statistical techniques can be used to create general profiles and trends of water quality in the aquifer from these analyses.

In addition, yearly or even monthly sampling frequencies may be insufficient to determine water quality changes related to storm events or chemical releases in some parts of the aquifer. For example, results from the EAA's tracer testing program indicate that groundwater

Figure 2. Total Dissolved Solids Concentrations at AY-68-37-521



velocities in some parts of the aquifer can exceed 12,000 ft per day and that sampling frequencies ranging from hours to a day are sometimes required to detect and characterize dye breakthrough curves (Schindel et al., 2007). Consequently, after a precipitation event, the pulse of rainwater that enters the aquifer may pass by a monitoring point in a matter of hours or days, and it would not be detected if a well's sampling frequency were once per year. This aliasing of data, wherein groundwater movement is too fast for the sampling rate, is an inherent and well-recognized problem in monitoring water quality in karst aquifers.

Of the 25 locations with the greatest number of samples, 11 are transect wells. The purpose of the frequent analyses of groundwater from the transect wells was to detect encroachment of the saline zone toward the freshwater zone when water levels declined. The transect wells were sampled almost monthly from July 1985 until September 2000 to track any movement of the saline water line, which is defined by a TDS concentration of 1,000 mg/L or higher. The last round of samples in the EAA database was collected in December 2006 by the USGS.

Transect wells are AY-68-37-521, AY-68-37-524, AY-68-37-526, AY-68-37-522, AY-68-37-525, AY-68-37-523, AY-68-37-527, DX-68-23-617, DX-68-23-618, DX-68-23-619, and DX-68-23-616. The relationship between TDS and water level elevation at Bexar County index well J-17 (AY-68-37-203) between 1985 and 2000 can be shown as a way of detecting movement of the saline water line in the aquifer (Figure 2). Water levels were occasionally measured at the transect wells, and they correlate strongly with J-17 water levels. Although J-17 water levels fluctuated more than 30 ft between 1985 and 2000, which is virtually its entire historical range, no statistically significant trend in the TDS concentrations related to aquifer levels was found. If saline water were to encroach on the freshwater part of the aquifer during drought conditions, TDS would be expected to increase as J-17 water level elevations decrease. This expectation suggests that the saline water line is not sensitive to water levels in the artesian zone of the aquifer over the range of historically observed water levels. Other transect wells showed similar behavior. Several freshwater/saline water interface monitoring well transects are in place in the region so that changes in the position of the interface can be observed. The EAA and other agencies continue to monitor these wells.

Previous Water Quality Assessment Reports

A few other reports have examined large sets of water quality data from the aquifer. The USGS, for example, has summarized large sets of water analyses in two studies: an open file report by F.C. Wells (1985) and various National Water Quality Assessment (NAWQA) studies of the south central Texas unit (e.g., Ging et al., 1997; Bush et al., 2000; Fahlquist and Ardis, 2004). Early reports on the aquifer, such as Sayre (1936) and Bennett and Sayre (1962), typically do not address water quality or groundwater contamination and have not been considered in this report.

Wells (1985) presented statistical summaries of water quality analyses from 90 wells and three springs located throughout the EAA's jurisdiction that had been sampled between 1968 and 1982. Statistics include maximum, minimum, mean, standard deviation, and 95-, 75-, 50-, 25-, and five-percent quintiles for each constituent. The constituents consist of major anions and cations, nutrients, metals, selected herbicides and pesticides, and bacteria. Not all samples were analyzed for all constituents.

Ging et al. (1997) evaluated analyses from 89 Edwards Aquifer wells located throughout the region as part of an NAWQA study. The most commonly detected VOCs were tetrachloroethene (PCE), trichloroethene (TCE), bromoform, chloroform, and dibromochloromethane. The report identifies three known sources of VOCs: West Avenue Landfill, a leaking underground storage tank on Thousand Oaks Drive in San Antonio, and an industrial laundry facility in the City of Uvalde that was destroyed by fire in 1979. However, other unidentified sources may have also resulted in VOC contamination of groundwater.

Bush et al. (2000) summarized findings from samples collected between 1996 and 1998 under the NAWQA program. Results indicate that the quality of water in Edwards and Trinity aquifers reflects some evidence of "human activities," such as urban development and agricultural land uses as indicated by numerous organic chemicals detected at extremely low concentrations in the aquifer. The greatest frequencies of detection

of pesticides and VOCs in the Edwards Aquifer were in urban (northern San Antonio) recharge-zone samples, and they were also detected in many surface water samples.

Buszka (1987) investigated the vulnerability of groundwater to contamination originating from human activities using nearly 1,500 chemical analyses from 280 wells and three springs from the Edwards Aquifer that were collected between 1976 and 1985. He classified five land uses in four major subareas of the aquifer and statistically compared them with groundwater chemistry and hydrogeology. He concluded that highest nitrite-plus-nitrate concentrations were associated with cropland over the unconfined zone throughout the aquifer and may have originated from streamflow recharge. Fecal coliform bacteria also were detected mainly in wells located in the recharge zone of the aquifer. Several organic compounds were detected in wells in the unconfined zone, although metals concentrations were similar in the unconfined and confined zones of the aquifer. Two sites were described in which contaminant concentrations exceeded drinking-water standards: (1) northeast of Garner Field in Uvalde, Texas, where PCE was detected in groundwater samples, and (2) north-central Bexar County, where PCE and benzene were detected in groundwater samples.

Fahlquist and Ardis (2004) investigated the presence of nitrate and organic compounds, such as solvents, herbicides, and pesticides, in the Trinity and Edwards aquifers, on the basis of 125 water samples from 119 wells and six springs in south central Texas collected between 1996 and 1998. Some nitrate nitrogen (N) concentrations in the Edwards Aquifer were elevated, ranging as high as 8.23 mg/L as N, although none of the samples exceeded the U.S. Environmental Protection Agency (EPA) and Texas public drinking-water standard (10 mg/L as N). Pesticides and VOCs were generally detected at low concentrations (<1 µg/L) and were detected most frequently in developed areas on the aquifer recharge zone. The herbicide atrazine and its breakdown product deethylatrazine were the most frequently detected pesticides, and trihalomethanes (i.e., chloroform, chlorodibromomethane, bromodichloromethane) were the most frequently detected VOCs. Simazine and

diazinon also were detected in six out of 30 samples from developed areas on the recharge zone. The authors concluded that detections of these compounds even at low concentrations over a large area indicate that urban development affects groundwater quality.

Green et al. (2006) used existing groundwater quality analyses as part of their investigation of the groundwater conditions in Kinney and Uvalde counties. The chemical characteristics of groundwater supported the location of the Knippa Gap east of Uvalde. This high-capacity flowpath contains calcium bicarbonate waters, whereas slower moving and saline waters are more concentrated in magnesium, sulfate, and chloride.

Musgrove et al. (2010) analyzed data from groundwater samples collected for the NAWQA program between 1996 and 2006 from the San Antonio segment of the Edwards Aquifer to assess geochemical evolution processes and investigate relationships between water quality, potential groundwater contaminants, and groundwater age. The report uses geochemical and isotopic data to trace groundwater recharge, flow, mixing, and water-rock interactions. For example, groundwater age may be inferred by molar magnesium:calcium ratios that increase with residence time in the aquifer. Surface water recharging the Edwards Aquifer may be recognized through water quality changes. A small number of contaminants were detected frequently, including atrazine, deethylatrazine, simazine, chloroform from water disinfectants, and tetrachloroethene. These contaminants were detected in both shallow/urban unconfined and deep, confined parts of the aquifer, indicating that the entire aquifer is vulnerable to anthropogenic (human-made) activities. Geochemical age tracers suggest that apparent groundwater ages in the Edwards Aquifer are largely either less than 50 years old or less than 10 years old with extensive mixing. Finally, the report concludes that current models underestimate groundwater velocities related to flow through conduits.

Musgrove and Crow (2012) investigated the sources of discharge from San Marcos Springs between November 2008 and December 2010, which included drought and wetter than normal weather conditions. The investigation consisted of periodic and stormwater samples from streams, wells, and springs that were analyzed for major

ions, trace elements, nutrient, and selected stable and radiogenic isotopes. The report concludes that discharge from San Marcos Springs is composed primarily of regional groundwater, even under wet conditions. Local recharge from sources such as the Blanco River ranged from 0 to less than 30%.

Data Analysis

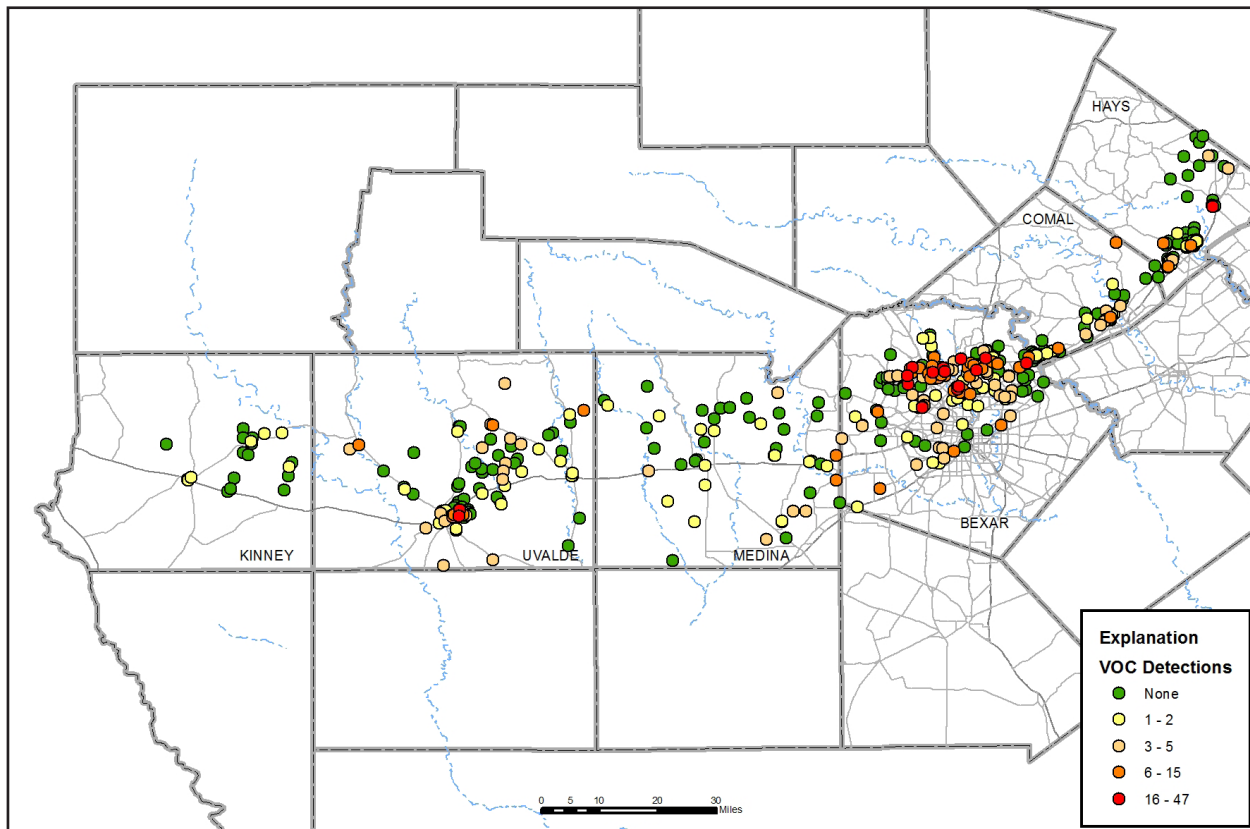
The data analysis section focuses on the occurrence and distribution of constituents of concern (COCs) that were identified in historical water quality data. COCs are anthropogenic contaminants, such as volatile organic compounds, herbicides and pesticides, and SVOCs. In addition, naturally occurring chemicals such as metals and nutrients, especially nitrate, may be COCs when their concentrations are elevated above drinking-water standards.

The presence or absence of a particular chemical is defined by the laboratory method detection limit, whereas the usability or value of the water represented by the sample is determined by appropriate health-based standards. Detection of a potential contaminant signals the need for caution and investigation, but it does not necessarily render the water unusable. As discussed next, many samples contained detectable concentrations of one or more potential contaminants, but the PCLs will be used as a point of reference to assess whether the concentrations affect the usability of the water.

Detection of Volatile Organic Compounds

VOCs are compounds that have a high vapor pressure and generally have lower water solubility than do other groups of compounds. Many VOCs are human-made chemicals that are used and produced in the manufacture of paints, pharmaceuticals, refrigerants, fuels, and industrial solvents. Most VOCs do not generally occur naturally in groundwater or the environment and indicate human-induced contamination. Several common VOCs (e.g., benzene, TCE, and PCE) are known carcinogens, although they were commonly handled and disposed of with little caution before the development of regulatory programs in the mid-1970s. Many samples of groundwater, surface water, and springs have been analyzed for VOCs to monitor for this common

Figure 3. Locations of Wells with VOC Detections.



contaminant type. Distribution and concentration trends of various VOCs may reveal locations and strength of potential sources of contaminants.

VOCs have been detected in groundwater, surface water, and springs in the study area (Figure 3). A total of 679 sites were sampled and analyzed for VOCs, which constituted more than 65,000 analytes. Two or fewer VOCs were detected at 268 out of 541 sites (50%) (Figure 3). Approximately 0.1% (66 out of 65,733 samples) of individual VOCs in groundwater exceeded PCLs, whereas one sample of springwater contained VOCs above PCLs. Most locations are wells in Bexar and Uvalde counties associated with known releases, although 19 VOCs were detected at various springs.

VOCs in Groundwater

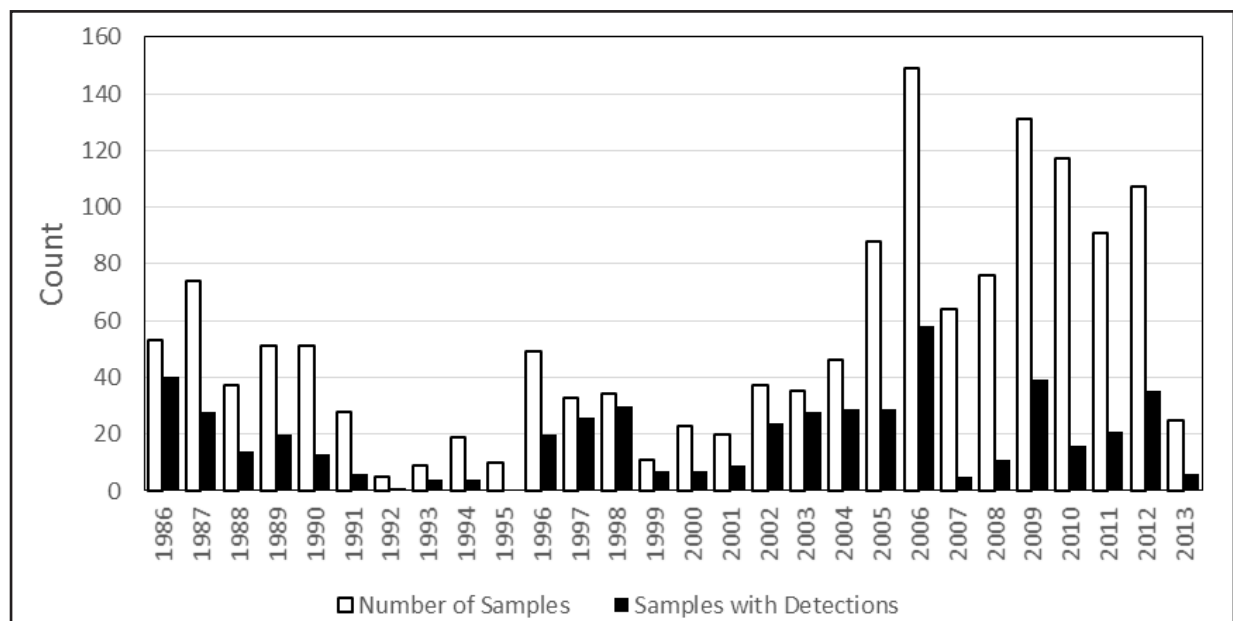
VOCs have been detected in some groundwater samples almost every year since 1983 at a variety of locations (Figure 3 and Table 4). Samples were collected for annual routine analyses and for specific investigations. The frequency of detection for VOCs is shown in

Figure 4. Although the number of groundwater samples has increased in recent years, the number of samples that contained one or more VOCs was inconsistent from year to year.

Table 5 lists VOCs and their ranges of concentrations. Most commonly detected VOCs were PCE, trans-1, 2-dichloroethene, 1,2-dichloroethane, TCE, toluene, carbon tetrachloride, and chloroform, and PCE concentrations exceeded PCLs in seven of the samples. Although methylene chloride, carbon disulfide, and acetone were reported in 62 groundwater sample analyses, they are suspected of being laboratory analytical artifacts and are not listed.

Since 2000, VOCs have been analyzed routinely as part of the EAA's water quality sampling program. However, VOC analyses, especially analyses performed before 1992, were collected primarily for specific investigations related to VOC spills; therefore, the database includes a bias toward a higher number of VOC detections. Two investigations involved VOCs. First, many samples were analyzed for VOCs beginning in the 1980s as part of an

Figure 4. Frequency of Detection of VOCs in Edwards Aquifer Wells, 1986–2013.



investigation of VOCs in the aquifer on the east side of the City of Uvalde. Of the 51 samples that were collected from wells near the source of the spill through 2013, 38 samples contained PCE above the PCL of five µg/L. The second investigation of VOCs in the aquifer was near West Avenue Landfill in north-central San Antonio, involving 72 samples for VOC analyses between 1983 and 1991. PCE or TCE concentrations in seven of those samples exceeded the PCL.

Releases from former dry-cleaning facilities in Leon Valley contaminated groundwater in the Austin Chalk and the Edwards Aquifer. PCE and TCE were detected in wells along and east of Bandera Road and Poss Road, south along Bandera Road, and west along Grissom Road (EPA, 2010b). The TCEQ identified the presence of PCE and TCE in wells located near the intersection of Bandera Road and Poss Road in 2004. The discovery occurred during an investigation under the Voluntary Cleanup Program at the Savings Square Shopping Center. In March 2007, the site was placed on EPA's National Priorities List, which qualified it for federal funds for investigation and remediation under the Superfund program (EPA, 2010a). In 2010, EPA (EA Engineering, Science, and Technology, Inc., 2011) completed a remedial investigation at the site identified as the Bandera Road Ground Water Plume Superfund Site in Leon Valley. EAA staff assisted EPA by conducting a

tracer test involving some of the contaminated wells. The site is defined by groundwater contaminated by PCE and TCE. Concentrations of PCE and TCE detected in several private wells completed in the Austin Chalk and Edwards aquifers exceed the Safe Drinking Water Act, Maximum Contaminant Level (MCL) of 5.0 mg/L (µg/L). In addition, two City of Leon Valley public water supply wells are within one mile of the center of the contaminated groundwater plume (EPA, 2010b). On the basis of results of several subsurface investigations, EPA determined that relatively high concentrations of PCE and TCE remained in the soil and Austin Chalk Aquifer near properties currently occupied by Savings Square and Pilgrims Dry Cleaners (EPA, 2010a). Results of groundwater analyses suggest that contaminants were moving within the Austin Chalk Aquifer and downward into the Edwards Aquifer. Of the 14 samples collected by EAA or the USGS, PCE concentrations exceeded MCL in one sample, a well owned by a business. Much higher PCE concentrations were detected in samples collected by EPA in other wells.

PCE and other solvents were also detected in wells in northern Bexar County near Highway 281 and Thousand Oaks Drive. Samples from AY-68-29-418 have contained PCE concentrations as high as 4.87 µg/L since sampling began in 1998. PCE was also detected in other wells in the area, such as AY-68-

29-109, AY-68-29-112, AY-68-29-113, AY-68-29-114, AY-68-29-406, AY-68-29-410, AY-68-29-412, and AY-68-29-415 (Table 6). The source of these contaminants is suspected to be dry-cleaning fluid, although neither the location nor the timing of the leakage is known. EAA has turned over its analytical results to the TCEQ Superfund Group to investigate the extent and magnitude of the contamination.

The remaining detections were in Bexar County, with fewer samples from Uvalde and Hays counties. Table 6 lists the range of concentrations of PCE and TCE—the most commonly detected VOCs—in Bexar County wells completed in either the Edwards or the Trinity Aquifer.

Table 4. Summary of Sample Types Analyzed for VOCs

Year	Groundwater Samples	Detections	Springs Samples	Detections	Surface Water Samples	Detections
1983	12	9	0	0	0	0
1984	52	23	1	0	0	0
1985	40	18	0	0	3	0
1986	80	143	2	0	0	0
1987	94	49	4	1	0	0
1988	43	42	3	0	0	0
1989	61	52	3	0	0	0
1990	58	30	0	0	0	0
1991	34	19	1	0	0	0
1992	6	1	0	0	0	0
1993	12	9	1	0	2	1
1994	22	4	2	0	0	0
1995	9	0	2	0	0	0
1996	67	55	0	0	2	0
1997	61	81	4	5	4	1
1998	64	75	2	0	8	4
1999	18	13	1	0	0	0
2000	28	21	6	1	4	0
2001	28	15	4	0	7	2
2002	55	38	16	19	4	4
2003	61	49	17	32	4	7
2004	72	65	16	20	3	3
2005	113	73	11	5	1	0
2006	185	93	10	0	1	1
2007	65	12	14	6	1	0
2008	75	29	10	0	1	0
2009	106	82	9	0	9	1
2010	107	25	16	8	12	1
2011	92	27	14	4	1	0
2012	90	69	10	2	3	0
2013	23	8	8	1	14	1

Table 5. Range of VOC Concentrations Detected in Edwards Aquifer Wells

Parameter Analyzed	Total Number of Samples Analyzed	Number of Samples with Detectable Volatile Organic Compounds	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	PCL (µg/L)
1,1,1-Trichloroethane	1567	12	0.01E	0.4	200
1,1,2,2-Tetrachloroethane	1571	1	1.0	1.0	4.56
1,1,2-Trichloro-1,2,2-trifluoroethane	630	14	0.02E	0.49	73,3258.91
1,1-Dichloroethane	1569	10	0.01E	1.8	2444.2
1,1-Dichloroethene	1566	4	0.3E	0.64	7
1,2,4-Trichlorobenzene	1105	1	0.3E	0.3	70
1,2,4-Trimethylbenzene	1061	2	0.01E	0.01	244.42
1,2-Dibromoethane	1307	1	0.7	0.7	0.05
1,2-Dibromoethene	134	6	0.2	0.3	NE
1,2-Dichlorobenzene	1446	2	0.3	0.7	600
1,2-Dichloroethane	1564	18	0.2	0.6	5
1,2-Dichloroethene	206	1	0.8	0.8	NE
1,2-Dichloropropane	1570	16	0.01E	3	5
1,3-Dichlorobenzene	1449	2	4.0	4.0	733.26
1,3-Dichloropropene	867	1	3	3	9.12
1,4-Dichlorobenzene	1451	16	0.006E	9.5	75
2-Butanone	1151	8	0.1E	6	14,665.18
2-Chlorotoluene	1038	1	0.428	0.428	488.84
3,4-Dichloroaniline	170	6	0.0039E	0.014	NE
Benzene	1572	7	0.01E	15.0	5
Bromobenzene	1058	1	M		488.84
Bromodichloromethane	1571	76	0.01E	8.8	14.72
Bromoform	1576	63	0.01E	8.1	115.51
Bromomethane	1567	4	0.4E	0.7	34.22
Carbon tetrachloride	1575	4	0.010E	4	5
Chlorine	4	4	0.02	0.07	4000
Chlorobenzene	1572	5	0.2	2.4	100
Chlorodifluoromethane	1	1	1.9	1.9	999,000
Chloroethane	1567	2	0.2	11	9776.79
Chloroform	1568	300	0.01E	8.6	244.42
Chloromethane	1477	29	0.1E	5.05	70.19
cis-1,2-Dichloroethene	1154	2	0.01E	0.02	70
Cyclohexane	180	2	2.2	2.36	12,2209.82
Cyclohexane	77	1	4	4	12,2209.82
Dibromochlorobenzene	46	1	0.5	0.5	NE
Dibromochloromethane	1554	52	0.05E	5.6	10.86
Dibromomethane	962	1	0.01E	0.01	121.67
Dichlorodifluoromethane	1558	17	0.02E	4.0	4888.39
Ethylbenzene	1571	12	0.02E	5	700
Hexane	180	1	2.26	2.26	1466.52
Iodomethane	1046	5	M		34.22
Isopropylbenzene	1112	3	0.01E	0.284	2444.2
m,p-Xylenes	1580	9	0.02E	4.1	10,000
Methyl tertiary-butyl ether	1140	5	0.05E	0.991	244.42
n-Butylbenzene	1030	1	0.746	0.746	977.68
n-Propylbenzene	1030	1	1.02	1.02	977.68
o-Xylene	1020	2	0.01E	0.922	10,000
Styrene	1469	2	0.013E	0.013	100
Sulfur hexafluoride	4	4	0.06	0.23	NE
t-Butyl ethyl ether	322	2	0.01E	0.02	24.44
Tetrachloroethene	1576	290	0.006	9.9	5
Tetrahydrofuran	326	3	1E	42	120.07
Toluene	1569	45	0.01E	7	1000
trans-1,2-Dichloroethene	1543	19	0.2	4.6	100
trans-1,3-Dichloropropene	1459	1	2	2	9.12
Trichloroethene	1570	56	0.01E	7.4	5
Trichlorofluoromethane	1558	20	0.01E	5	7332.59
Vinyl chloride	1565	3	0.2	3	2

PCL = Protective concentration level

E = Estimated concentration

NE = Not established

M = Parameter present at a concentration too low to quantify

Table 6. Summary of PCE and TCE Concentrations Detected in Bexar County Wells

Well	Owner/Operator	Date	PCE Concentration (µg/L)	TCE Concentration (µg/L)
Eastern Bexar County				
AY-68-29-920	Windcrest	4/19/1988	2.2	<0.2
AY-68-29-920	Windcrest	6/12/1997	0.01E	<0.04
AY-68-29-924	Vapa Butane Co.	8/22/1986	<0.2	130
AY-68-30-109	SAWS	6/23/1997	0.16	0.03E
Helotes and northwestern Bexar County				
AY-68-27-307	EAA	10/23/1998	0.02E	<0.04
AY-68-27-517	EAA	11/10/1998	0.01E	<0.04
AY-68-27-517	EAA	9/1/2006	0.03E	<0.038
AY-68-27-517	EAA	4/10/2009	0.063E	<0.02
AY-68-27-609	EAA	11/10/1998	0.07E	<0.04
AY-68-27-609	EAA	9/5/2006	0.015E	<0.038
AY-68-27-610	EAA	12/10/1998	0.06E	<0.04
AY-68-27-611	EAA	11/12/1998	0.02E	<0.04
AY-68-27-611	EAA	9/6/2006	0.039E	<0.038
AY-68-27-612	EAA	12/10/1998	0.05E	<0.04
AY-68-27-612	EAA	5/25/1999	0.07E	<0.04
AY-68-27-612	EAA	6/7/2000	0.05E	<0.04
AY-68-27-612	EAA	6/4/2001	0.05E	<0.04
AY-68-27-612	EAA	12/3/2002	0.02E	<0.04
AY-68-27-612	EAA	12/3/2004	0.02E	<0.04
AY-68-27-612	EAA	9/5/2006	0.034E	<0.038
AY-68-27-612	EAA	12/18/2006	0.037E	<0.02
AY-68-27-612	EAA	10/24/2008	0.025E	<0.02
AY-68-27-612	EAA	12/15/2010	0.029	<0.022
AY-68-27-910	Barren Van Delden	8/20/1986	0.3	<0.2
Leon Valley area				
AY-68-36-133	USGS	10/31/2007	0.365	<0.02
AY-68-36-133	USGS	4/8/2009	0.383	<0.02
AY-68-36-133	USGS	10/5/2009	0.634	<0.022
AY-68-36-133	USGS	10/7/2009	0.68	<0.022
AY-68-36-133	USGS	10/17/2009	0.681	<0.022
AY-68-36-133	USGS	10/28/2009	0.706	<0.022
AY-68-36-133	USGS	11/18/2009	0.574	<0.022
AY-68-36-134	USGS	10/30/2007	0.479	<0.02
AY-68-36-134	USGS	4/9/2009	0.587	<0.02
AY-68-36-134	USGS	10/5/2009	0.727	<0.022
AY-68-36-134	USGS	10/8/2009	0.81	<0.022
AY-68-36-134	USGS	10/18/2009	0.814	<0.022
AY-68-36-134	USGS	10/29/2009	0.733	<0.022
AY-68-36-134	USGS	11/18/2009	0.733	<0.022
AY-68-36-132	USGS	11/1/2007	0.174	<0.02
AY-68-36-132	USGS	4/9/2009	0.257	<0.02
AY-68-36-132	USGS	10/5/2009	0.277	<0.022
AY-68-36-132	USGS	10/8/2009	0.306	<0.022
AY-68-36-132	USGS	10/18/2009	0.288	<0.022
AY-68-36-132	USGS	10/29/2009	0.306	<0.022
AY-68-36-132	USGS	11/18/2009	0.265	<0.022
AY-68-28-702	Leon Valley	4/16/2004	0.2E	<1
AY-68-28-702	Leon Valley	4/26/2005	0.1E	<0.04
AY-68-28-807	SAWS	5/26/2005	0.05E	<0.04
AY-68-36-102	SAWS	4/24/1987	0.2	<0.2
AY-68-36-102	SAWS	6/25/1990	0.2	<0.2
AY-68-36-104	SAWS	12/13/2004	0.1E	<0.04
AY-68-36-104	SAWS	8/31/2005	0.14	<0.04
AY-68-36-107	Leon Valley	4/16/2004	0.3E	<1
AY-68-36-131	SAWS	10/6/2009	0.292	<0.022
AY-68-36-131	SAWS	10/9/2009	0.29	<0.022
AY-68-36-131	SAWS	10/19/2009	0.408	<0.022

(Table 6. continued)

Well	Owner/Operator	Date	PCE Concentration (µg/L)	TCE Concentration (µg/L)
AY-68-36-131	SAWS	10/30/2009	0.295	<0.022
AY-68-36-131	SAWS	11/19/2009	0.247	<0.022
AY-68-36-1DR	Private	12/6/2005	30.5	<1.3
AY-68-36-206	SAWS	12/13/2004	M	<0.04
AY-68-36-206	SAWS	8/31/2005	0.02E	<0.04
North central Bexar County				
AY-68-28-113	EAA	11/12/1998	0.04E	<0.04
AY-68-28-113	EAA	9/7/2006	0.033E	<0.038
AY-68-28-203	Shavano Park	8/17/1989	<0.2	0.3
AY-68-28-203	Shavano Park	4/19/2005	0.06E	<0.04
AY-68-28-203	Shavano Park	5/16/2006	0.073E	<0.038
AY-68-28-205	Shavano Park	8/16/1989	<0.2	2.6
AY-68-28-205	Shavano Park	8/6/1996	0.01E	<0.05
AY-68-28-210	EAA	10/26/1998	0.01E	<0.04
AY-68-28-211	EAA	11/14/1998	0.03E	<0.04
AY-68-28-211	EAA	5/27/1999	0.03E	0.02E
AY-68-28-211	EAA	6/29/2000	0.04E	<0.04
AY-68-28-211	EAA	6/5/2001	0.01E	<0.04
AY-68-28-211	EAA	11/20/2002	0.02E	0.08E
AY-68-28-211	EAA	12/9/2004	0.02E	<0.04
AY-68-28-211	EAA	8/24/2006	0.028E	<0.038
AY-68-28-211	EAA	12/19/2006	0.03E	<0.02
AY-68-28-211	EAA	10/29/2008	0.027E	<0.02
AY-68-28-211	EAA	12/17/2010	0.025	<0.022
AY-68-28-313	EAA	11/4/1998	0.04E	<0.04
AY-68-28-313	EAA	9/8/2006	0.091E	<0.038
AY-68-28-314	EAA	6/8/2000	0.03E	<0.04
AY-68-28-315	EAA	11/11/1998	0.09E	<0.04
AY-68-28-406	EAA	11/6/1998	0.04E	<0.04
AY-68-28-406	EAA	9/6/2006	0.073E	<0.038
AY-68-28-407	EAA	9/11/2006	0.031E	<0.038
AY-68-28-514	Shavano Park	4/18/1989	0.4	<0.2
AY-68-28-514	Shavano Park	5/15/1990	0.2	<0.2
AY-68-28-515	EAA	11/6/1998	0.02E	<0.04
AY-68-28-515	EAA	8/30/2006	0.032E	<0.038
AY-68-28-516	EAA	12/8/1998	0.02E	<0.04
AY-68-28-516	EAA	5/1/2003	0.2E	<1
AY-68-28-516	EAA	4/7/2004	0.2E	<1
AY-68-28-516	EAA	8/30/2006	0.074E	<0.038
AY-68-28-517	EAA	12/8/1998	0.06E	<0.04
AY-68-28-517	EAA	5/26/1999	0.08E	<0.04
AY-68-28-517	EAA	6/28/2000	0.08E	<0.04
AY-68-28-517	EAA	6/5/2001	0.07E	<0.04
AY-68-28-517	EAA	11/19/2002	0.06E	<0.04
AY-68-28-517	EAA	12/9/2004	0.04E	<0.04
AY-68-28-517	EAA	8/31/2006	<	<
AY-68-28-517	EAA	8/31/2006	<	<
AY-68-28-517	EAA	12/19/2006	0.052E	<0.02
AY-68-28-517	EAA	10/27/2008	0.044E	<0.02
AY-68-28-517	EAA	12/13/2010	0.048	<0.022
AY-68-28-518	EAA	12/11/1998	0.07E	0.01E
AY-68-28-518	EAA	8/24/2006	<	<
AY-68-28-518	EAA	8/24/2006	<	<
AY-68-28-519	EAA	11/14/1998	0.02E	0.01E
AY-68-28-519	EAA	8/29/2006	0.015E	<0.038
AY-68-28-601	Cadillac Water Co.	5/17/2005	<0.5	0.02E
AY-68-28-609	EAA	11/11/1998	0.01E	<0.04
AY-68-28-609	EAA	8/29/2006	0.019E	<0.038

(Table 6. continued)

Well	Owner/Operator	Date	PCE Concentration (µg/L)	TCE Concentration (µg/L)
AY-68-29-109	SAWS	8/6/1996	0.03E	<0.05
AY-68-29-109	SAWS	4/20/2005	0.04E	<0.04
AY-68-29-109	SAWS	5/18/2006	0.035E	<0.038
AY-68-29-112	EAA	12/9/1998	0.03E	0.01E
AY-68-29-112	EAA	8/23/2006	0.089E	<0.038
AY-68-29-113	EAA	8/23/2006	0.015E	<0.038
AY-68-29-114	EAA	11/3/1998	0.06E	<0.04
AY-68-29-114	EAA	8/21/2006	0.141	<0.038
AY-68-29-406	Simmang	5/29/2002	0.4E	<1
AY-68-29-406	Simmang	8/6/2003	0.3E	<1
AY-68-29-410	SAWS	8/16/1989	<0.2	0.7
AY-68-29-414	SAWS	4/19/2002	0.53E	<1
AY-68-29-414	SAWS	6/25/2002	0.8E	<1
AY-68-29-414	SAWS	7/30/2003	0.6E	<1
AY-68-29-414	SAWS	12/6/2004	0.3E	<0.04
AY-68-29-414	SAWS	9/1/2005	0.83	<0.04
AY-68-29-415	SAWS	6/25/2002	0.5E	<1
AY-68-29-418	EAA	12/9/1998	0.16	<0.04
AY-68-29-418	EAA	8/21/2006	0.953	<0.038
AY-68-29-418	EAA	1/25/2011	1.68	<
AY-68-29-418	EAA	4/4/2011	2.02	<
AY-68-29-418	EAA	1/17/2012	4.55	<
AY-68-29-418	EAA	2/10/2012	4.45	<
AY-68-29-418	EAA	5/31/2012	3.43	<
AY-68-29-418	EAA	9/25/2012	3.84	<
AY-68-29-418	EAA	12/19/2012	4.34	<
AY-68-29-418	EAA	2/21/2013	4.87	<
AY-68-29-418	EAA	5/22/2013	4.33	<
AY-68-29-505	Capitol Cement	8/21/1986	0.3	1.4
AY-68-29-505	Capitol Cement	8/19/1987	<0.2	2.3
AY-68-29-506	USGS	5/20/1989	0.2	<0.2
AY-68-29-506	USGS	9/13/2012	4.39	NA
Northeastern Bexar County				
AY-68-29-210	USGS	6/11/1986	0.2	0.6
AY-68-29-213	EAA	11/5/1998	0.07E	<0.04
AY-68-29-213	EAA	8/18/2006	0.061E	<0.038
AY-68-29-216	EAA	11/9/1998	0.02E	<0.04
AY-68-29-216	EAA	5/27/1999	0.03E	<0.04
AY-68-29-216	EAA	6/29/2000	0.03E	<0.04
AY-68-29-216	EAA	12/4/2002	0.02E	<0.04
AY-68-29-216	EAA	10/29/2008	0.021E	<0.02
AY-68-29-5AZ	Autozone	9/14/2012	0.845	NA
AY-68-29-610	SAWS	12/15/2004	0.1E	0.02E
AY-68-29-610	SAWS	8/29/2005	0.1E	<0.04
AY-68-29-912	Bexar County WC&ID#10	8/28/1986	0.7	0.2
AY-68-29-929	SAWS	12/15/2004	M	<0.04
San Antonio Airport area				
AY-68-28-902	SAWS	7/17/1986	2.1	0.5
AY-68-28-903	SAWS	6/24/1983	3	<3
AY-68-28-903	SAWS	6/14/1984	4	<3
AY-68-28-903	SAWS	8/16/1984	3	<3
AY-68-28-903	SAWS	8/25/1984	3	<3
AY-68-28-903	SAWS	2/13/1985	3	<3
AY-68-28-903	SAWS	8/6/1986	5.0	1.0
AY-68-28-903	SAWS	7/17/1987	3.1	<0.2
AY-68-28-903	SAWS	6/27/1988	2.0	0.8
AY-68-28-903	SAWS	8/8/1989	0.2	1.2
AY-68-28-903	SAWS	5/16/1990	1.0	0.3

(Table 6. continued)

Well	Owner/Operator	Date	PCE Concentration (µg/L)	TCE Concentration (µg/L)
AY-68-28-903	SAWS	8/15/1991	2.0	0.9
AY-68-28-904	SAWS	4/22/1987	0.6	<0.2
AY-68-28-904	SAWS	8/8/1989	0.5	<0.2
AY-68-28-904	SAWS	7/7/1997	0.402	0.04E
AY-68-28-905	SAWS	8/10/1989	0.3	<0.2
AY-68-28-907	SAWS	8/9/1989	0.2	<0.2
AY-68-28-909	SAWS	8/22/1989	0.2	<0.2
AY-68-28-909	SAWS	6/25/1990	0.2	<0.2
AY-68-28-913	SAWS	6/30/2005	0.20	<0.04
AY-68-28-917	A DeLosSantos	12/8/1989	<0.2	0.6
AY-68-28-918	Otis Sale	8/12/1986	9.9	3.2
AY-68-28-919	SAWS	4/22/1987	0.2	<0.2
AY-68-28-919	SAWS	8/9/1989	0.3	<0.2
AY-68-28-919	SAWS	5/16/1990	0.2	<0.2
AY-68-28-920	EAA	10/18/1983	8	1
AY-68-28-920	EAA	6/13/1984	9	<3
AY-68-28-920	EAA	7/15/1986	4.0	0.9
AY-68-28-920	EAA	4/12/1988	6.3	3.9
AY-68-28-920	EAA	6/7/1989	9.0	1.5
AY-68-28-920	EAA	6/11/1991	4.1	2.3
AY-68-29-419	SAWS	8/16/2011	0.284	<
AY-68-29-702	SAWS	8/22/1989	0.3	<0.2
AY-68-29-703	SAWS	8/14/1990	0.2	<0.2
AY-68-29-714	SAWS	12/14/2004	0.1E	0.02E
AY-68-29-714	SAWS	8/30/2005	0.24	0.02E
AY-68-29-804	SAWS	4/21/1987	0.3	1.2
AY-68-29-810	Green Light	4/21/1987	0.3	<0.2
AY-68-37-105	SAWS	12/14/2004	M	<0.04
AY-68-37-105	SAWS	8/31/2005	M	NA
South of downtown				
AY-68-36-908	SAWS	6/16/1986	0.3	0.6
Southwestern Bexar County				
AY-68-36-613	San Pedro Spring	7/9/1997	0.03E	<0.04
AY-68-36-613	San Pedro Spring	3/10/2003	0.2E	<1
AY-68-36-803	SAWS	6/16/1986	<0.2	0.2
AY-68-44-203	SAWS	6/16/1986	<0.2	0.3
AY-68-44-212	SAWS	6/16/1986	<0.2	0.2
Western Bexar County				
AY-68-35-404	Zedler	6/6/1986	0.5	<0.2

E = Estimated concentration

M = Parameter present at a concentration too low to quantify

NA = Not analyzed

TWDB records:

BM = Bexar Metropolitan Water District

SAWS = San Antonio Water System

COSA = City of San Antonio

WCID = Bexar County Water Control and Improvement District No. 16

EAA = EAA

Table 7. VOC Compounds that Exceeded PCLs in Edwards Aquifer Wells

Parameter	Total Analyses	Number above PCL	PCL (µg/L)
PCE	987	46	5
TCE	976	3	5
Benzene	977	2	5
Vinyl chloride	969	1	2

Table 7 lists the total number of analyses and the number that exceeded PCLs for PCE, TCE, benzene, and vinyl chloride in groundwater. PCE is by far the most commonly detected VOC and exceeds its PCL more frequently than the other VOCs. Although approximately 135 more analyses were run for VOCs, only one additional exceedance occurred since the original report, which was PCE in a sample from YP-69-51-114 on July 22, 2008.

VOCs in Surface Water

EAA generally does not analyze surface water samples for VOCs because this class of chemicals usually volatilizes quickly from surface water. Between 1995 and 1998, the USGS analyzed five surface water samples from recharge zone locations for VOCs and detected ethylbenzene, toluene, and m,p-xylenes. The samples were from Salado Creek at Wilderness Road, Stone Mountain Drainage Channel at Granite Path in the Stone Oak area, and Cedar Elm outfall on a Huebner Creek tributary—all in Bexar County. The purpose of the samples was to characterize stormwater quality. More recently, EAA collected surface water samples under quiescent and stormwater conditions in Landa Lake, Dry Comal Creek, San Marcos River, Sink Creek, Spring Lake, and Sessoms Creek for the Edwards Aquifer Habitat Conservation Plan. Other surface water locations included occasional samples from San Geronimo Creek, Lorence Creek, Bear Creek, Onion Creek, and Las Moras Creek. Fewer than five analytes were detected from these locations, and all were below the surface water standards for VOCs.

VOCs in Springwater

Since 2002 the EAA has routinely analyzed springwater samples for VOCs. Samples are collected from San Antonio, San Pedro, and Hueco springs, as well as multiple orifices at Comal and San Marcos springs. Table 8 lists VOCs that were detected and the range of concentrations, with the exception of methylene chloride, carbon disulfide, and acetone, which are considered laboratory analytical artifacts. Figure 5 shows the annual number of samples and the frequency of VOC detections. The detections are indicated by the vertical column for each year, whereas the total number of samples is below the column. The annual number of samples increased beginning in 2002, when the EAA began routinely collecting quarterly samples at the springs with additional samples during critical periods (drought conditions). Table 8 lists the VOC compounds that exceeded PCLs in the samples from the springs between 1986 and 2013. Table 9 lists the VOCs that were detected at each spring location, except for laboratory artifacts. The relatively large number of detections in 2002 through 2004 were laboratory artifacts such as acetone and carbon disulfide.

VOCs that were detected in spring samples since the original report consisted of 1,3,5-trimethylbenzene for the first time and 1,2,4-trimethylbenzene, benzene, chloroform, chloromethane, and toluene. Since the original report, only one VOC exceeded its PCL: benzene at a concentration of 11.8 µg/L in a sample from Hueco B springs on May 4, 2010 (Table 10).

Table 8. Range of VOC Concentrations Detected in Edwards Aquifer Springwater

Parameter Analyzed	Total Number of Samples Analyzed	Number of Samples with Detectable Analytes	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)
1,1,1-Trichloroethane	593	1	0.2	0.2
1,1-Dichloroethene	595	2	0.2	0.3
1,2,4-Trimethylbenzene	573	3	0.87	4.54
1,2-Dichloroethane	595	2	0.3	13.4
1,2-Dichloropropane	595	1	69.8	69.8
Benzene	597	6	0.4	11.8
Bromomethane	597	6	0.4E	0.8
Chloroform	596	3	0.04E	0.04E
Chloromethane	594	14	0.2E	0.944
Dichlorodifluoromethane	596	1	0.01E	0.01E
o-Xylene	420	1	1.68	1.68
Tetrachloroethene	595	5	0.003	0.04E
Toluene	594	2	0.3	2.49
Trichloroethene	595	1	0.01E	0.01E
Trichlorofluoromethane	594	1	0.02E	0.02E

E = Estimated concentration

Table 9. VOC Detections by Spring

Spring Name	Detections	Number of Samples Analyzed	Parameter
Comal Springs #1	1	85	Benzene
Comal Springs #1	1	85	Bromomethane
Comal Springs #1	1	84	Chloroform
Comal Springs #1	3	84	Chloromethane
Comal Springs #1	1	84	Dichlorodifluoromethane
Comal Springs #1	1	83	Trichloroethene
Comal Springs #1	1	83	Trichlorofluoromethane
Comal Springs #3	1	62	Chloromethane
Comal Springs #7	1	77	Benzene

(Table 9. continued)

Spring Name	Detections	Number of Samples Analyzed	Parameter
Comal Springs #7	2	77	Chloromethane
Comal Springs #7	1	77	Tetrachloroethene
Hueco Springs A	1	77	1,1,1-Trichloroethane
Hueco Springs A	1	74	1,2,4-Trichlorobenzene
Hueco Springs A	1	64	1,2,4-Trimethylbenzene
Hueco Springs A	1	64	1,3,5-Trimethylbenzene
Hueco Springs A	1	64	2,2-Dichloropropane
Hueco Springs A	1	78	Benzene
Hueco Springs A	1	78	Bromomethane
Hueco Springs A	1	56	m,p-Xylene
Hueco Springs A	1	78	Toluene
Hueco Springs B	1	36	1,1-Dichloroethene
Hueco Springs B	1	36	Benzene
LR-67-01-801	1	67	1,2,4-Trimethylbenzene
LR-67-01-801	1	86	1,2-Dichloroethane
LR-67-01-801	1	86	1,2-Dichloropropane
LR-67-01-801	1	86	Benzene
LR-67-01-801	1	86	Bromomethane
LR-67-01-801	3	84	Chloromethane
LR-67-01-801	1	56	m,p-Xylene
LR-67-01-801	1	58	o-Xylene
LR-67-01-819	1	66	1,2,4-Trimethylbenzene
LR-67-01-819	2	76	Bromomethane
LR-67-01-819	2	76	Chloromethane
LR-67-01-819	1	76	Tetrachloroethene
San Antonio Springs	1	33	Benzene
San Antonio Springs	1	33	Bromomethane
San Antonio Springs	2	33	Chloromethane
San Antonio Springs	1	33	Tetrachloroethene
San Antonio Springs	1	33	Toluene
San Pedro Springs	1	52	1,1-Dichloroethene
San Pedro Springs	1	52	1,2-Dichloroethane
San Pedro Springs	2	52	Chloroform
San Pedro Springs	1	52	Chloromethane
San Pedro Springs	2	52	Tetrachloroethene

Figure 5. Frequency of Detection of VOCs in Edwards Aquifer Springs, 1986–2013.

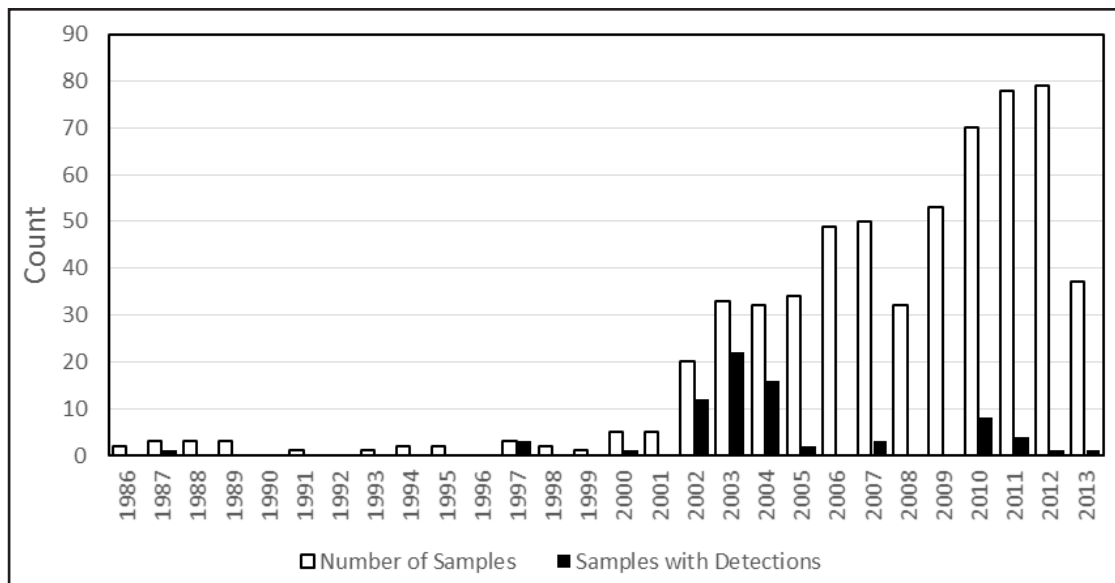


Table 10. VOC Compounds that Exceeded PCLs in Springwater

Parameter	Total Analyses	Number above PCL	PCL (µg/L)
1,2-Dichloroethane	595	1	5
1,2-Dichloropropane	595	1	5
Benzene	597	1	5

Detection of Semivolatile Organic Compounds

Because SVOCs are less mobile in the environment than VOCs, they are less likely to be detected far from a spill area. Therefore, they tend to be analyzed for site-specific investigations more than regional aquifer monitoring. For these reasons, fewer SVOCs than those in other analyses in the data sets have been reviewed for this study. Some SVOCs (aromatic hydrocarbons) are related to fuels and have been detected in aquifer samples, whereas other SVOCs are used as sealants for asphalt parking lots (Van Metre et al., 2006).

Figure 6 shows locations at which more than two SVOCs were detected. Locations at which a single SVOC was detected were ignored because it was likely a laboratory contaminant or other false positive. Most detections occur at stormwater sites in Bexar County sampled by the USGS.

SVOCs in Groundwater

SVOCs are occasionally detected in aquifer groundwater samples. Figure 7 shows the frequency of detection, percentage of samples in which SVOCs were detected, and the total number of samples that were analyzed from 1986 through 2006 from Edwards Aquifer wells. Table 11 lists the SVOCs and ranges of concentrations that have been detected. Most detections in 2004 were bis (2ethylhexyl) phthalate, which is generally considered a contaminant from sampling equipment, well construction material (PVC casing), or the laboratory. Phenol was the other analyte detected most frequently in 2004 and the principal analyte detected in 2005. Only bis (2-ethylhexyl) phthalate (which is considered a sampling artifact) was detected above PCLs in groundwater samples (Table 12). No new SVOCs have been detected since the original report.

Figure 6. Locations with More than Two Detections of SVOCs.

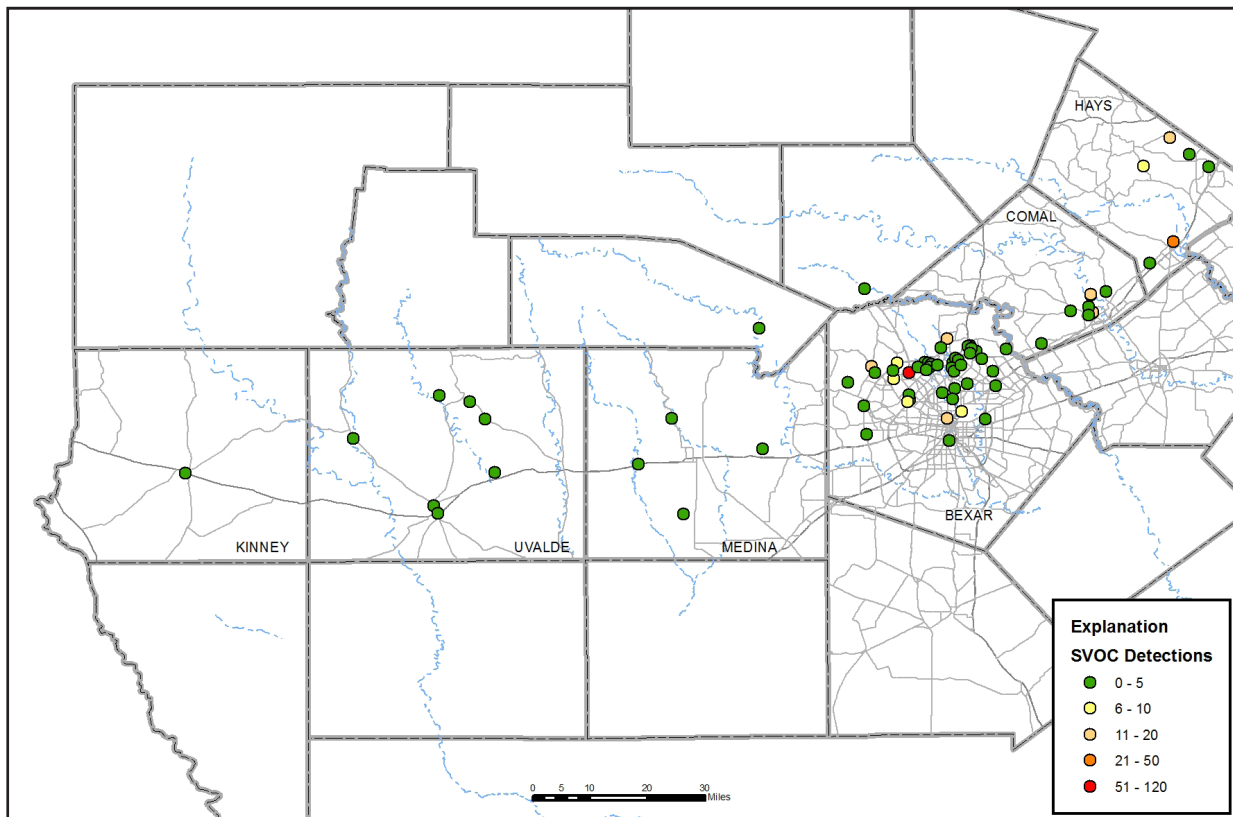


Figure 7. Frequency of Detection of SVOCs in Edwards Aquifer Wells, 1986–2013.

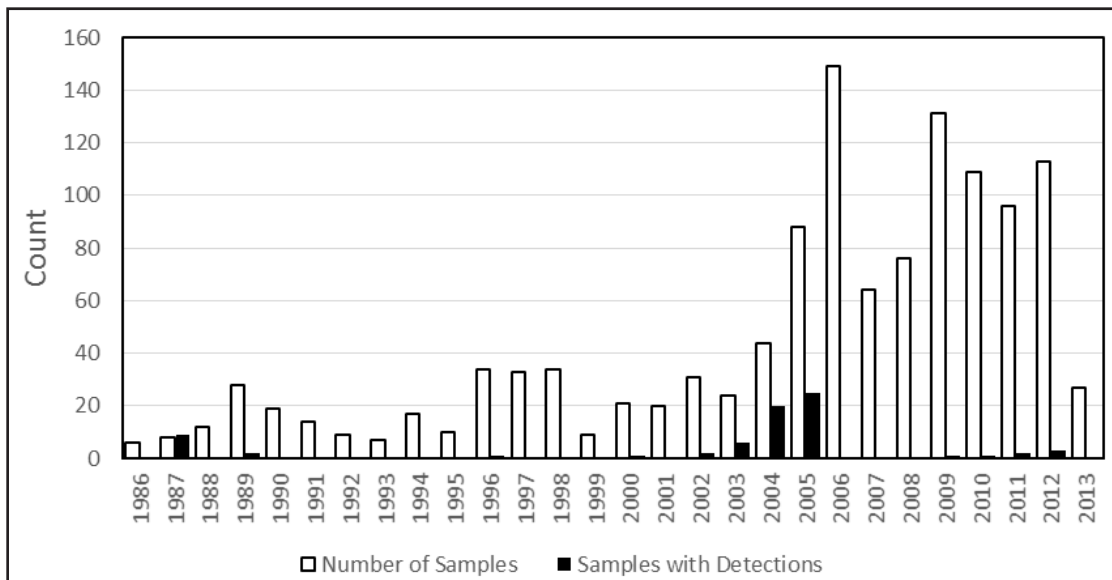


Table 11. Range of SVOC Concentrations Detected in Edwards Aquifer Wells

Parameter	Number of Samples Analyzed	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	Number of Samples with Detections	PCL (µg/L)
4-nonylphenol	58	1E	3	15	2444
Benzophenone	42	0.03E	0.2	13	164
bis (2-Ethylhexyl) phthalate	136	0.5E	8700	19	6
Caffeine	75	0.005E	53	9	None
Cotinine	58	1.7	1.7	1	None
DRO hydrocarbons	85	1.13	1.13	1	None
Ethanol, 2-butoxy-, phosphate	42	0.1E	0.3	2	None
Hexachloroethane	459	0.05	0.05	1	24.44
Isophorone	178	0.009E	0.009	1	960
MBAS	337	0.01	20.0	85	None
Naphthalene	1105	0.0358	1.73	4	489
ORO hydrocarbons	85	0.877	0.877	1	None
Phenol	178	0.1E	4.0	32	7332
Total petroleum hydrocarbons	85	0.877	1.13	2	
Tributyl phosphate	42	0.14E	0.14	1	

E = Estimated

Table 12. SVOC Compounds that Exceeded PCLs in Edwards Aquifer Wells

Parameter	Total Analyses	Number above PCL	PCL (µg/L)
bis (2-Ethylhexyl) phthalate	539	5	6

SVOCs in Surface Water

Figure 8 shows the frequency of detection, percentage of samples in which SVOCs were detected, and total number of samples that were analyzed from 1986 through 2006 in surface water. SVOCs are occasionally detected in Edwards Aquifer-related surface water, although they have been included in analytical suites only since 1995.

Table 13 lists the SVOCs and ranges of concentrations that have been detected in surface water. SVOCs were detected primarily in samples from Olmos Creek and a tributary to Huebner Creek in 1997 and 1998 and in

occasional samples from streams on the recharge zone or drainage area. Bis (2-ethylhexyl) phthalate is generally considered a contaminant from either the sampling equipment or the laboratory and not a COC. Other than bis (2ethylhexyl) phthalate, only benzo(a)pyrene (seven samples) and pentachlorophenol (three samples) were detected at concentrations above PCLs.

Samples collected since the original report contained 11 new SVOCs, although the frequency of detection was consistently low (Table 13).

Figure 8. Frequency of Detection of SVOCs Detected in Surface Water Recharging the Edwards Aquifer, 1986-2013.

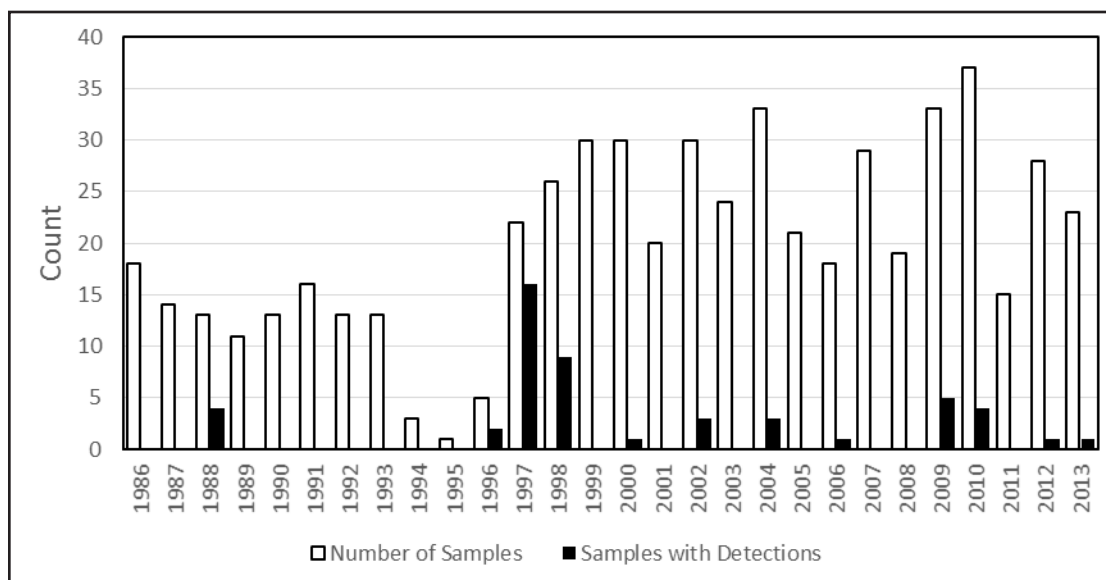


Table 13. Range of SVOC Concentrations Detected in Surface Water Recharging the Edwards Aquifer

Parameter	Number of Samples Analyzed	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	Number of Samples with Detectable SVOCs	PCL (µg/L)
1-Methylnaphthalene*	107	0.003E	0.003	1	1711
2,4-Dimethylphenol	136	0.1E	0.1	1	489
2-Methyl-4,6-dinitrophenol*	197	2E	2	1	49
Acenaphthene*	207	M	M	6	1466
Acenaphthylene*	207	M	M	4	1466
Anthracene*	249	M	M	6	7332
Benzo(a)anthracene	207	1E	4	8	1.25
Benzo(a)pyrene	249	1E	5	11	0.2
Benzo(b)fluoranthene	207	1E	8	8	1.25
Benzo(ghi)perylene	207	1E	4	10	733
Benzo(k)fluoranthene	207	1E	3	8	12.5
Benzophenone*	42	0.02E	0.05	2	164
bis (2-Ethylhexyl) phthalate	136	15	2	6	6
Chrysene	207	1E	6	8	125
Di-n-butyl phthalate*	136	0.91	0.91	1	2444
Di-n-octyl phthalate*	136	1.67	1.67	1	489

(Table 13. continued)

Parameter	Number of Samples Analyzed	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	Number of Samples with Detectable SVOCs	PCL (µg/L)
Fluoranthene	249	2E	9	10	978
Fluorene*	207	M		6	978
Indeno(1,2,3-cd) pyrene	207	2E	3	9	1.25
Isophorone*	178	0.007E	0.031	5	960
MBAS	337	0.01	0.48	42	NE
Methyl salicylate*	42	0.046E	0.046	1	NE
Naphthalene	1105	0.013E	2	6	489
Pentachlorophenol	629	0.25	1.3	4	1
Phenanthrene	249	1E	4	9	733
Phenol	178	0.15E	3.0	9	7332
Pyrene	249	2E	7	10	733
Tributyl phosphate*	42	0.01E	0.07	3	NE

E = Estimated

NE = None established

* = New analyte detected since the original report

SVOCs in Springwater

Prior to 2002, springwater samples were rarely analyzed for SVOCs. Since 2002, however, the EAA has routinely analyzed springwater samples for SVOCs.

Figure 9 shows the frequency of detection, percentage of samples in which SVOCs were detected, and total number of samples analyzed from 1986 through 2006 in springwater. Table 14 lists SVOCs and ranges of concentrations that have been detected. SVOCs were detected primarily at Hueco Springs B and San Marcos,

San Antonio, and San Pedro springs. Bis (2-ethylhexyl) phthalate is generally considered a contaminant from either the sampling equipment or the laboratory and not a COC.

Since the original report, five new SVOCs have been detected in spring samples (Table 14). All but one of the detections in 2011, 2012, and 2013 are bis (2-ethylhexyl) phthalate or another phthalate, which are considered sampling artifacts from the tubing used to collect spring samples.

Figure 9. Frequency of Detection of SVOCs in Edwards Aquifer Springwater, 1986–2013.

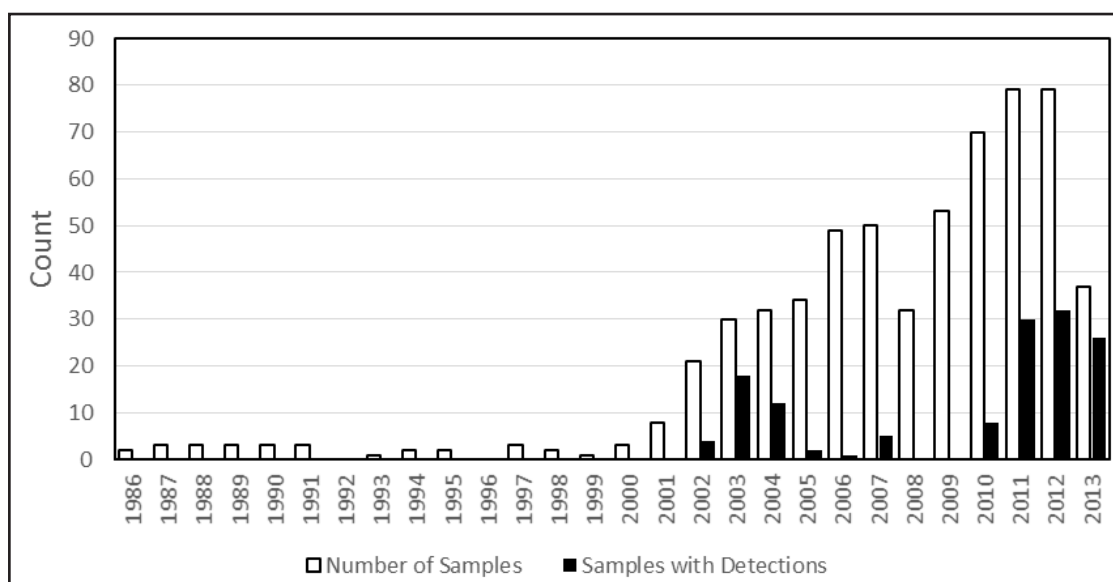


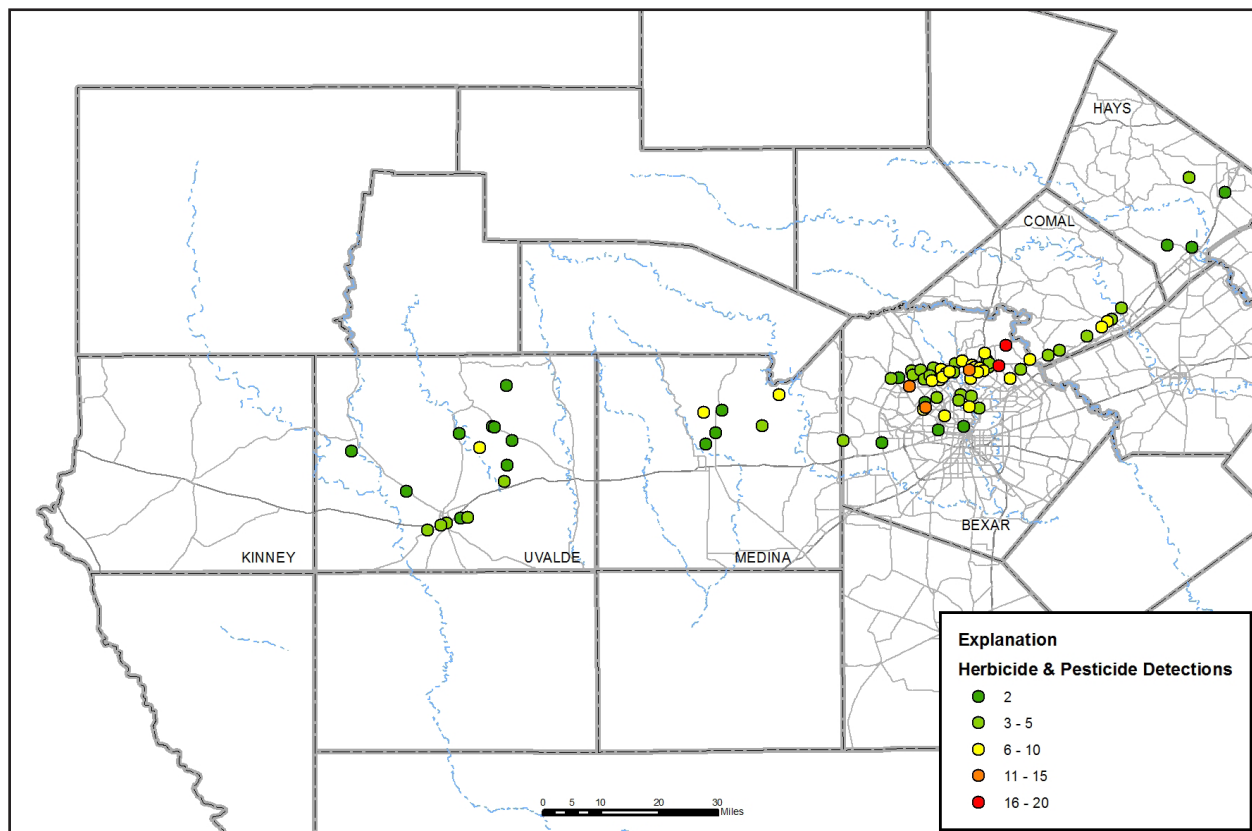
Table 14. Range of SVOC Concentrations Detected in Edwards Aquifer Springwater

Parameter	Number of Samples Analyzed	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	Number of Samples with Detectable SVOCs	PCL (µg/L)
2-Methyl-naphthalene*	235	1.02	1.29	3	97.8
Benzoic acid*	79	12	12	1	97,768
bis (2-Ethylhexyl) phthalate	136	0.5E	9.66	122	6
bis (2-ethylhexyl) Adipate*	79	4.44	4.44	1	400
Butyl benzyl phthalate*	136	0.8E	2.24	4	4888
Diethyl phthalate	136	0.543	2.64	16	19554
Di-n-butyl phthalate	136	2E	2	1	2444
Di-n-octyl phthalate*	136	2.95	3.04	2	489
MBAS	337	0.10	0.10	2	NE
Naphthalene	1,105	1E	1	1	489
Phenol*	178	0.4	4.47	8	7332
Pyridine*	93	0.63	0.63	1	24.4

E = Estimated

* = New analyte detected since the original report

Figure 10. Locations of Wells with More than Two Detections of Herbicides or Pesticides.



Detection of Herbicides and Pesticides

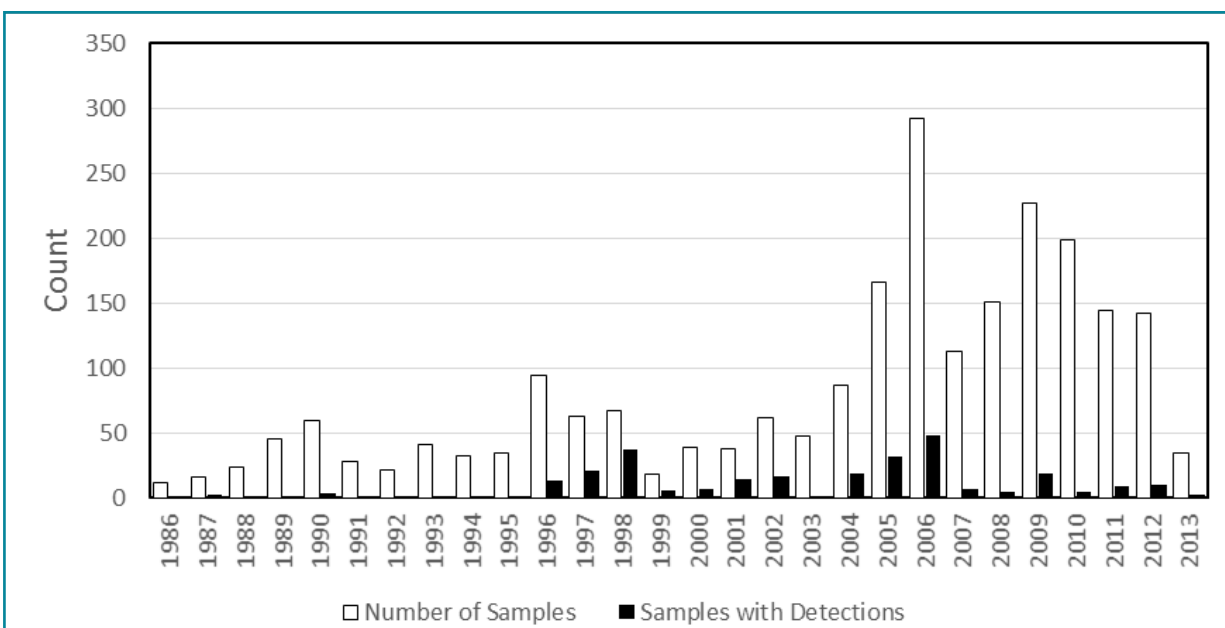
Herbicides and pesticides consist of a variety of chemicals used for controlling weeds and insects and do not occur naturally in the environment. Specific chemicals included in the analyses for herbicides and pesticides also vary from laboratory to laboratory. However, the frequency of detection provides some insight into the presence of these types of chemicals in the aquifer. Although herbicides and pesticides are used throughout the study area, they are not widely detected. Figure 10 shows the locations of samples with two or more detections of herbicides or pesticides. Single detections are not compelling evidence of persistent sources of herbicides or pesticides. Most of the samples were collected in urban areas of Bexar County during routine sampling by EAA or under the NAWQA program by USGS. In these areas, a potential for contaminants to reach the aquifer exists through the recharge zone. In contrast, agricultural applications occur largely on the artesian zone rather than the recharge zone, where the

aquifer is at depth below confining units and groundwater gradients are generally vertically upward, thus limiting infiltration of contaminants from the surface.

Herbicides or Pesticides in Groundwater

Herbicides or pesticides have been detected sporadically in Edwards Aquifer groundwater samples since 1986 (Figure 11). Table 15 lists all detected herbicides or pesticides, which include two new compounds detected in groundwater samples since the original report—EPN and heptachlor. Most herbicides and pesticides were detected in samples collected by the USGS and EAA from wells in Bexar, Medina, Comal, and Uvalde counties. Atrazine (herbicide), simazine (herbicide), and diazinon (insecticide) were detected in Bexar, Medina, and Comal counties, whereas 4,4'-DDE and 4,4'-DDT were detected in Uvalde County. As of December 31, 2004, the sale of diazinon for outdoor, nonagricultural applications has been unlawful in the United States, although simazine and atrazine remain in use as pre-

Figure 11. Frequency of Detection of Herbicides and Pesticides in Edwards Aquifer Wells, 1986–2013.



and postemergence grass and broadleaf herbicides. Diazanone detections are due to residual concentrations leaching from soil or illegal use. Barbash et al. (1999) found that atrazine and simazine are among the most commonly used herbicides in the U.S. and that 4,4'-DDT was a pesticide widely used on crops and as an insect vector control. Introduced during the 1940s, in 1972 it was banned for use in the U.S.; 4,4'-DDE is a breakdown product or contaminant of 4,4'-DDT that was never produced for commercial use.

Table 16 lists well locations at which two or more herbicides or pesticides were detected, along with a range of sample collection dates and number of detections for each compound. Only ethion, an organophosphate pesticide, was above PCLs in one sample (AY-68-38-111

in southern Bexar County) collected by the USGS in 1985, and it was not resampled.

Figure 12 contains time-series charts for four wells, and Figure 13 shows their locations in Bexar County. In these charts, zero concentrations indicate no detection. Results indicate that a persistent source of herbicides exists, especially in Bexar County, but the variability of sample frequencies and locations, attenuation of the compound, and other factors affect the actual concentrations detected. This herbicide persistence may reflect a number of causes, including broad application and use of herbicides in urban landscaping activities, bias from sampling frequency, and physical characteristics of the aquifer. Consequently, results are insufficient to determine whether a trend exists.

Table 15. Range of Herbicide and Pesticide Concentrations Detected in Edwards Aquifer Wells

Parameter	Number of Samples Analyzed	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	Number of Samples with Detectable SVOCs	PCL (µg/L)
2,4,5-TP (Silvex)	933	0.01E	0.061	3	50
2,4-D	969	0.01E	0.184	19	70
4,4'-DDE	1033	0.001E	0.040	13	2.7
4,4'-DDT	894	0.017	1.00	3	2.7
Alpha-Endosulfan	981	0.03	0.03	1	49
Atrazine	800	0.0018E	0.132	162	3
Benfluralin	315	0.004E	0.004	1	7332
Bromacil	121	0.14	0.14	1	2444
Carbaryl	329	0.006E	0.036	6	2444
CEAT	34	0.01E	0.01	6	NE
DCPA	318	0.001E	0.001	1	244
Deethyl-atrazine	317	0.0014E	0.066	210	NE
delta-BHC	578	0.00276	0.00314	2	0.51
Diazinon	1177	0.002E	1.20	18	22
Dicamba	218	0.02E	0.09	2	733
Dichloroprop	399	0.01	0.01	1	244
Dieldrin	1207	0.001E	0.003	3	0.06
Diuron	95	0.20	0.20	1	49
EPN*	546	0.0858	0.0898	2	0.24
Ethion	501	40	40	1	12
Ethoprop	820	0.077	0.077	1	2.4
Fipronil	194	0.008E	0.008	1	NE
Fipronil sulfide	194	0.008E	0.008	1	NE
Fipronil sulfone	194	0.009E	0.009	1	NE
gamma-BHC (Lindane)	1035	0.00116	0.01	7	0.2
gamma-Chlordane	522	0.05E	0.05	1	NE
Hydroxyatrazine	30	4	0.003	0.007	NE
Heptachlor*	894	0.00219	0.00219	1	0.4
Malathion	1174	0.01	0.7	2	488.84
Metolachlor	318	0.001E	0.003	3	3666
Metribuzin	316	0.004	6.7	2	611
Metsulfuron	34	0.03E	0.03	1	NE
Oryzalin	95	0.08	0.08	1	NE
Parathion	990	2.80	2.80	1	147
Parathion Methyl	1174	1.60	1.60	1	6.11
Prometon	322	0.0043E	0.07	55	367
Simazine	785	0.001E	0.052	117	4
Tebuthiuron	317	0.01E	0.042	3	1711
Terbacil	164	0.003E	0.035	12	NE
Trifluralin	315	0.003E	0.003	1	118

E = Estimated

NE = None established

* = New analyte detected since the original report

Table 16. Summary of Herbicide and Pesticide Concentrations Detected in Edwards Aquifer Wells

Location	County	Earliest Date	Most Recent Date	Number of Detections	Compound
AY-68-21-806	Bexar	12/7/1998	8/22/2006	2	Atrazine
AY-68-21-806	Bexar	12/7/1998	8/22/2006	2	Deethyl-atrazine
AY-68-21-806	Bexar	12/7/1998	8/22/2006	2	Prometon
AY-68-21-806	Bexar	12/7/1998	8/22/2006	2	Simazine
AY-68-21-903	Bexar	12/2/2011	1/11/2013	7	Deethyl-atrazine
AY-68-21-903	Bexar	1/25/2012	1/30/2012	3	Atrazine
AY-68-21-903	Bexar	1/25/2012	1/30/2012	3	Carbaryl
AY-68-21-903	Bexar	1/25/2012	1/30/2012	3	Simazine
AY-68-27-307	Bexar	10/23/1998	9/7/2006	2	Deethyl-atrazine
AY-68-27-517	Bexar	11/10/1998	9/1/2006	2	Deethyl-atrazine
AY-68-27-610	Bexar	12/10/1998	11/17/2009	5	Atrazine
AY-68-27-610	Bexar	12/10/1998	11/17/2009	5	Deethyl-atrazine
AY-68-27-610	Bexar	9/11/2006	11/17/2009	4	Simazine
AY-68-27-611	Bexar	11/12/1998	9/6/2006	2	Deethyl-atrazine
AY-68-27-612	Bexar	12/10/1998	12/15/2010	10	Atrazine
AY-68-27-612	Bexar	12/10/1998	12/15/2010	10	Deethyl-atrazine
AY-68-27-612	Bexar	5/25/1999	12/3/2004	3	Prometon
AY-68-27-612	Bexar	5/25/1999	12/15/2010	6	Simazine
AY-68-28-113	Bexar	11/12/1998	9/7/2006	2	Deethyl-atrazine
AY-68-28-113	Bexar	11/12/1998	9/7/2006	2	Simazine
AY-68-28-203	Bexar	4/19/2005	5/16/2006	2	Atrazine
AY-68-28-203	Bexar	4/19/2005	5/16/2006	2	Deethyl-atrazine
AY-68-28-203	Bexar	4/19/2005	5/16/2006	2	Prometon
AY-68-28-203	Bexar	4/19/2005	5/16/2006	2	Simazine
AY-68-28-210	Bexar	10/26/1998	9/12/2006	2	Deethyl-atrazine
AY-68-28-211	Bexar	11/14/1998	12/17/2010	8	Atrazine
AY-68-28-211	Bexar	11/14/1998	12/17/2010	9	Deethyl-atrazine
AY-68-28-211	Bexar	11/20/2002	10/29/2008	3	Prometon
AY-68-28-211	Bexar	8/24/2006	12/17/2010	3	Simazine
AY-68-28-313	Bexar	11/4/1998	9/8/2006	2	Atrazine
AY-68-28-313	Bexar	11/4/1998	9/8/2006	2	Deethyl-atrazine
AY-68-28-313	Bexar	11/4/1998	7/8/2002	2	Diazinon
AY-68-28-313	Bexar	11/4/1998	9/8/2006	2	Simazine
AY-68-28-314	Bexar	12/7/1998	12/15/2010	9	Atrazine
AY-68-28-314	Bexar	12/7/1998	12/15/2010	9	Deethyl-atrazine
AY-68-28-314	Bexar	6/6/2001	12/15/2010	7	Simazine
AY-68-28-314	Bexar	6/6/2001	12/5/2002	2	Terbacil
AY-68-28-315	Bexar	11/11/1998	8/28/2006	2	Atrazine
AY-68-28-315	Bexar	11/11/1998	8/28/2006	2	Deethyl-atrazine
AY-68-28-315	Bexar	11/11/1998	8/28/2006	2	Simazine
AY-68-28-406	Bexar	11/6/1998	9/6/2006	2	Atrazine
AY-68-28-406	Bexar	11/6/1998	9/6/2006	2	Deethyl-atrazine
AY-68-28-407	Bexar	11/13/1998	9/11/2006	2	Atrazine
AY-68-28-407	Bexar	11/13/1998	9/11/2006	2	Deethyl-atrazine
AY-68-28-515	Bexar	11/6/1998	8/30/2006	2	Atrazine
AY-68-28-515	Bexar	11/6/1998	8/30/2006	2	Deethyl-atrazine
AY-68-28-515	Bexar	11/6/1998	8/30/2006	2	Simazine
AY-68-28-516	Bexar	12/8/1998	8/30/2006	2	Atrazine

(Table 16. continued)

Location	County	Earliest Date	Most Recent Date	Number of Detections	Compound
AY-68-28-516	Bexar	12/8/1998	8/30/2006	2	Deethyl-atrazine
AY-68-28-516	Bexar	12/8/1998	8/30/2006	2	Simazine
AY-68-28-516	Bexar	12/8/1998	8/30/2006	2	Tebuthiuron
AY-68-28-517	Bexar	12/8/1998	12/13/2010	8	Atrazine
AY-68-28-517	Bexar	12/8/1998	12/13/2010	8	Deethyl-atrazine
AY-68-28-517	Bexar	12/8/1998	12/13/2010	7	Prometon
AY-68-28-517	Bexar	12/8/1998	12/13/2010	7	Simazine
AY-68-28-518	Bexar	12/11/1998	8/24/2006	2	Deethyl-atrazine
AY-68-28-519	Bexar	11/14/1998	8/29/2006	2	Atrazine
AY-68-28-519	Bexar	11/14/1998	8/29/2006	2	Deethyl-atrazine
AY-68-28-519	Bexar	11/14/1998	8/29/2006	2	Simazine
AY-68-28-608	Bexar	3/12/2012	3/23/2012	2	2,4-D
AY-68-28-609	Bexar	11/11/1998	8/29/2006	2	Atrazine
AY-68-28-609	Bexar	11/11/1998	8/29/2006	2	Deethyl-atrazine
AY-68-28-609	Bexar	11/11/1998	8/29/2006	2	Simazine
AY-68-29-109	Bexar	8/6/1996	5/18/2006	3	Atrazine
AY-68-29-109	Bexar	8/6/1996	5/18/2006	3	Deethyl-atrazine
AY-68-29-109	Bexar	8/6/1996	5/18/2006	3	Prometon
AY-68-29-109	Bexar	4/20/2005	5/18/2006	2	Simazine
AY-68-29-112	Bexar	12/9/1998	8/23/2006	2	Atrazine
AY-68-29-112	Bexar	12/9/1998	8/23/2006	2	Deethyl-atrazine
AY-68-29-112	Bexar	12/9/1998	8/23/2006	2	Simazine
AY-68-29-113	Bexar	11/7/1998	8/23/2006	2	Atrazine
AY-68-29-113	Bexar	11/7/1998	8/23/2006	2	Deethyl-atrazine
AY-68-29-113	Bexar	11/7/1998	8/23/2006	2	Prometon
AY-68-29-114	Bexar	11/3/1998	8/21/2006	2	Atrazine
AY-68-29-114	Bexar	11/3/1998	8/21/2006	2	Deethyl-atrazine
AY-68-29-114	Bexar	11/3/1998	8/21/2006	2	Simazine
AY-68-29-213	Bexar	11/5/1998	8/18/2006	2	Atrazine
AY-68-29-213	Bexar	11/5/1998	8/18/2006	2	Deethyl-atrazine
AY-68-29-213	Bexar	11/5/1998	8/18/2006	2	Simazine
AY-68-29-214	Bexar	11/8/1998	8/16/2006	2	Atrazine
AY-68-29-214	Bexar	11/8/1998	8/16/2006	2	Deethyl-atrazine
AY-68-29-214	Bexar	11/8/1998	8/16/2006	2	Simazine
AY-68-29-215	Bexar	11/5/1998	8/17/2006	2	Atrazine
AY-68-29-215	Bexar	11/5/1998	8/17/2006	2	Deethyl-atrazine
AY-68-29-216	Bexar	11/9/1998	12/16/2010	9	Atrazine
AY-68-29-216	Bexar	11/9/1998	12/16/2010	10	Deethyl-atrazine
AY-68-29-216	Bexar	11/9/1998	12/16/2010	9	Simazine
AY-68-29-216	Bexar	6/6/2001	12/4/2002	2	Terbacil
AY-68-29-217	Bexar	11/9/1998	8/17/2006	2	Deethyl-atrazine
AY-68-29-306	Bexar	8/19/1996	6/29/2011	7	Atrazine
AY-68-29-306	Bexar	8/19/1996	6/29/2011	7	Deethyl-atrazine
AY-68-29-306	Bexar	8/15/2005	6/29/2011	5	Simazine
AY-68-29-414	Bexar	12/6/2004	9/1/2005	2	Atrazine
AY-68-29-414	Bexar	12/6/2004	9/1/2005	2	Deethyl-atrazine
AY-68-29-414	Bexar	12/6/2004	9/1/2005	2	Prometon
AY-68-29-414	Bexar	12/6/2004	9/1/2005	2	Simazine

(Table 16. continued)

Location	County	Earliest Date	Most Recent Date	Number of Detections	Compound
AY-68-29-418	Bexar	12/9/1998	8/21/2006	2	Atrazine
AY-68-29-418	Bexar	12/9/1998	8/21/2006	2	Deethyl-atrazine
AY-68-29-418	Bexar	12/9/1998	8/21/2006	2	Simazine
AY-68-29-610	Bexar	12/15/2004	8/29/2005	2	Atrazine
AY-68-29-610	Bexar	12/15/2004	8/29/2005	2	CEAT
AY-68-29-610	Bexar	12/15/2004	8/29/2005	2	Deethyl-atrazine
AY-68-29-610	Bexar	12/15/2004	8/29/2005	2	Prometon
AY-68-29-714	Bexar	12/14/2004	8/30/2005	2	Deethyl-atrazine
AY-68-36-104	Bexar	12/13/2004	8/31/2005	2	Atrazine
AY-68-36-104	Bexar	12/13/2004	8/31/2005	2	Deethyl-atrazine
AY-68-36-131	Bexar	10/19/2009	11/19/2009	3	Atrazine
AY-68-36-131	Bexar	10/19/2009	11/19/2009	3	Deethyl-atrazine
AY-68-36-132	Bexar	11/1/2007	11/18/2009	4	Deethyl-atrazine
AY-68-36-132	Bexar	10/18/2009	11/18/2009	3	Atrazine
AY-68-36-133	Bexar	10/31/2007	11/18/2009	4	Atrazine
AY-68-36-133	Bexar	10/31/2007	11/18/2009	4	Deethyl-atrazine
AY-68-36-133	Bexar	10/31/2007	11/18/2009	3	Simazine
AY-68-36-134	Bexar	10/30/2007	11/18/2009	4	Atrazine
AY-68-36-134	Bexar	10/30/2007	11/18/2009	4	Deethyl-atrazine
AY-68-36-134	Bexar	10/29/2009	11/18/2009	2	Simazine
AY-68-36-206	Bexar	12/13/2004	8/31/2005	2	Atrazine
AY-68-36-206	Bexar	12/13/2004	8/31/2005	2	Deethyl-atrazine
AY-68-37-105	Bexar	12/14/2004	8/31/2005	2	Atrazine
AY-68-37-105	Bexar	12/14/2004	8/31/2005	2	Deethyl-atrazine
DX-68-23-601	Comal	12/8/2004	9/1/2005	2	Atrazine
DX-68-23-601	Comal	12/8/2004	9/1/2005	2	Deethyl-atrazine
DX-68-23-601	Comal	12/8/2004	9/1/2005	2	Simazine
DX-68-23-620	Comal	6/20/1996	6/20/2006	2	Atrazine
DX-68-23-620	Comal	6/20/1996	6/20/2006	2	Prometon
DX-68-24-122	Comal	6/11/1996	6/20/2006	2	Deethyl-atrazine
TD-68-25-703	Medina	7/23/1996	5/17/2006	5	Deethyl-atrazine
TD-69-39-301	Medina	7/24/1996	5/18/2009	4	Deethyl-atrazine
TD-69-39-301	Medina	7/24/1996	5/18/2009	5	Simazine
TD-69-39-301	Medina	8/16/2005	5/18/2009	2	Dieldrin
TD-69-40-605	Medina	8/16/2005	5/19/2009	3	Deethyl-atrazine
YP-69-35-602	Uvalde	6/7/1988	6/12/2001	2	Diazinon
YP-69-35-602	Uvalde	6/12/2001	12/5/2002	2	Terbacil
YP-69-35-804	Uvalde	5/21/1968	8/10/1968	3	4,4'-DDE
YP-69-35-804	Uvalde	5/21/1968	8/10/1968	3	4,4'-DDT
YP-69-43-606	Uvalde	8/18/1997	5/11/2005	2	Atrazine
YP-69-43-606	Uvalde	8/18/1997	5/11/2005	2	Deethyl-atrazine
YP-69-51-114	Uvalde	8/23/1984	7/12/2011	2	2,4-D

Figure 12. Time-Series Charts of Herbicides at Three Edwards Aquifer Wells.

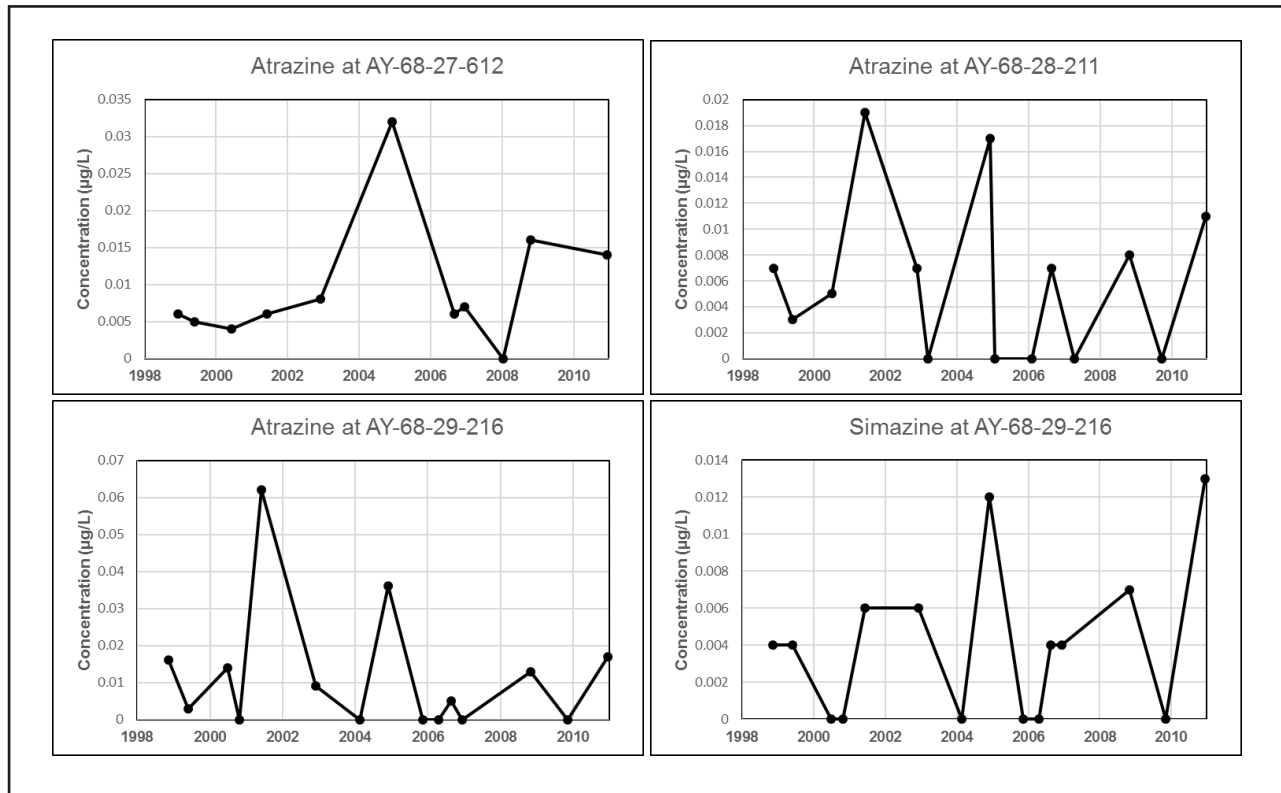


Figure 13. Locations of Wells Presented in Figure 12.

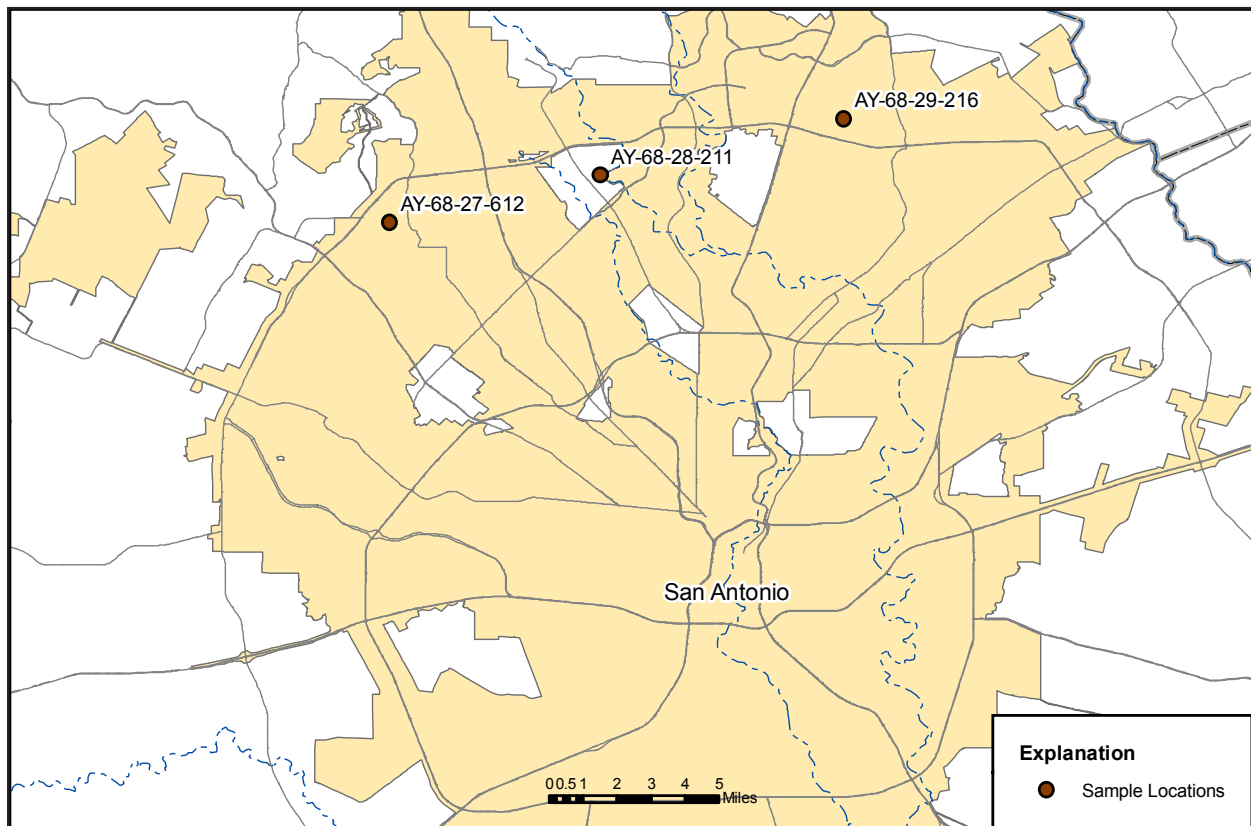
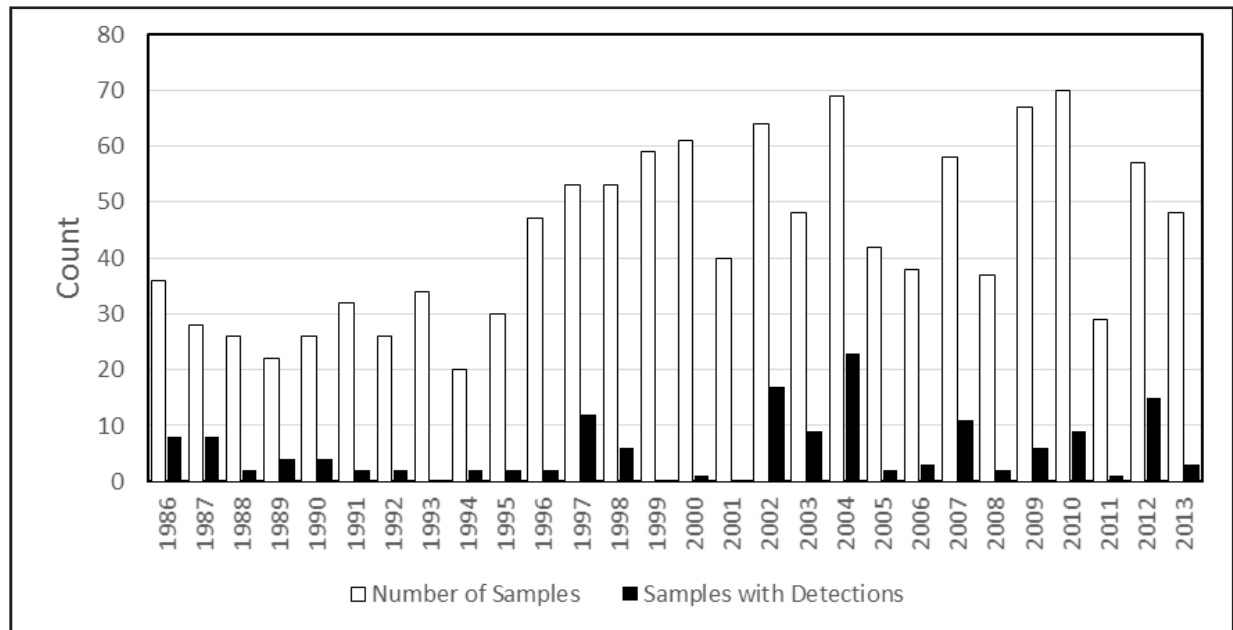


Figure 14. Frequency of Detection of Herbicides and Pesticides in Surface Water Recharging the Edwards Aquifer, 1986–2013.



Herbicides or Pesticides in Surface Water

Herbicides or pesticides have been detected in as many as 46% (16 out of 35 samples) of surface water samples collected in the study area each year since 1986 (Figure 14). The relatively high numbers of detections in 2003 and 2004 were in stormwater samples collected by the USGS in Leon Creek, San Marcos River, Elm Waterhole, and other sites. Table 17 lists all detected herbicides or pesticides and the range of concentrations detected. Sample counts are lower than listed in the original report because some stormwater samples were inadvertently included that would not affect the Edwards Aquifer. Principal herbicides and pesticides detected in surface water are 2,4,5-T; 2,4,5TP (Silvex); 2,4-D; 4,4'-DDD; 4,4'-DDE; 4,4'-DDT; atrazine; diazinon; dieldrin; gamma-BHC (Lindane); heptachlor epoxide; malathion; and simazine. For comparison, the table also lists PCLs. Diazinon (insecticide) and 2,4,5-T and 2,4-D (both herbicides) were the most commonly detected compounds. Since December 31, 2004, sale of diazinon for outdoor, nonagricultural applications in the U.S. has been unlawful, and use of 2,4,5-T was canceled in

1985 in the U.S., although 2,4-D (e.g., Weed-B-Gon®) remains in use.

Table 18 lists surface water locations at which at least two herbicides or pesticides were detected, along with the range of dates and concentrations of samples. Most herbicides and pesticides were detected in samples collected by the USGS during stormwater sampling from ephemeral streams on or near the recharge zone in Bexar County, such as Helotes, Leon, Olmos, Lorence, and West Elm creeks. Other perennial streams (e.g., Frio, Dry Frio, Sabinal, Nueces rivers) yielded only infrequent detections of herbicides or pesticides. Diazinon (insecticide) and 2,4-D and 2,4,5-T (both herbicides) were the most commonly detected compounds. Figure 15 contains time-series charts for selected locations. Samples were collected during storm events, and detections occurred intermittently. Results indicate that a persistent source of herbicides exists, but the variability of amount of precipitation, sample times, antecedent soil conditions, herbicide application rates and locations, and other factors affect the actual concentrations that were detected. No herbicide or pesticide was detected above a PCL in surface water.

Table 17. Range of Herbicide and Pesticide Concentrations Detected in Surface Water Recharging the Edwards Aquifer

Parameter	Number of Samples Analyzed	Number of Samples with Detectable Herbicides and Pesticides	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	PCL (µg/L)
2,4,5-T	753	34	0.01	2.2	244
2,4,5-TP (Silvex)	752	3	0.01	1.6	50
2,4-D	754	48	0.01	1.9	70
4,4'-DDD	823	4	0.002E	0.050	3.8
4,4'-DDE	904	10	0.0015	0.020	2.68
4,4'-DDT	824	9	0.001E	0.110	2.68
4-Nitrophenol	57	8	10E	8	48.88
Aldrin	823	1	0.003	0.003	0.05
alpha-BHC	332	1	0.0033	0.0033	0.14
Alpha-Endosulfan	704	1	0.003	0.003	48.88
Atrazine	331	55	0.003E	5.01	3
Benfluralin	82	1	0.005E	0.005	7332
Bentazon	159	6	1.8	2.2	NE
Carbaryl	110	23	0.004E	0.898	2444
Chlordane	612	8	0.1	0.2	2.61
Chlorpyrifos	349	1	0.02	0.02	73.3
DCPA	82	9	0.0012	0.0055	244
Deethyl-atrazine	83	32	0.003E	0.172	NE
Diazinon	856	92	0.003E	3.17	22
Dichloroprop	258	2	0.03	0.03	244
Dieldrin	906	18	0.001E	0.020	0.06
Dinoseb	290	3	0.81	1.0	7
Disulfoton	358	1	0.005E	0.005	0.98
Endrin	826	1	0.003	0.003	2
Endrin ketone	207	1	0.00164	0.00164	7.33
Fipronil	74	4	0.006E	0.033	NE
Fipronil sulfide	74	2	0.002E	0.026	NE
Fipronil sulfone	74	1	0.005E	0.005	NE
gamma-BHC (Lindane)	902	13	0.00124	0.0300	0.2
Heptachlor	823	1	0.003	0.003	0.4
Heptachlor epoxide	824	5	0.003	0.010	0.2
Malathion	820	21	0.007E	0.61	489
Methoxychlor	524	1	0.004E	0.004	40
Metolachlor	92	6	0.005E	0.077	3666
Mirex	525	2	0.003	0.010	4.89
Parathion	819	1	0.04	0.04	147
Parathion Methyl	822	3	0.01	0.19	6.11
Pendimethalin	82	1	0.004E	0.004	978
Picloram	233	4	1.2	1.4	500
Prometon	112	12	0.004	0.2	367
Simazine	331	23	0.002E	0.843	4
Tebuthiuron	82	1	0.025	0.025	1711

PCL = Protective concentration level

E = Estimated

NE = None established

**Table 18. Summary of Locations for Herbicides and Pesticides in
Surface Water Recharging the Edwards Aquifer**

Location	Earliest Date	Most Recent Date	Number of Detections	Compound
Bear Ck bl FM 1826 nr Driftwood	7/26/1982	5/8/2008	3	Prometon
Bear Ck bl FM 1826 nr Driftwood	7/11/2007	5/8/2008	2	Atrazine
Bear Ck bl FM 1826 nr Driftwood	7/11/2007	5/8/2008	2	Deethyl-atrazine
Bear Ck bl FM 1826 nr Driftwood	7/11/2007	5/8/2008	2	Simazine
Cedar Elm Off at Huebner Ck Tr	2/12/1997	2/14/1998	6	4-Nitrophenol
Devine Springs	3/10/2009	5/22/2013	3	Atrazine
Elm Waterhole Ck Trib at Evans Rd	3/26/2007	1/25/2012	5	Atrazine
Elm Waterhole Ck Trib at Evans Rd	3/26/2007	10/9/2009	3	Deethyl-atrazine
Elm Waterhole Ck Trib at Evans Rd	3/26/2007	1/25/2012	3	Simazine
Elm Waterhole Ck Trib at Evans Rd	10/9/2009	1/25/2012	2	DCPA
Elm Waterhole Ck Trib at Evans Rd	10/9/2009	1/25/2012	2	Fipronil
Elm Waterhole Trib at Evans Rd	7/8/2003	8/10/2005	3	Atrazine
Elm Waterhole Trib at Evans Rd	7/8/2003	8/10/2005	2	Carbaryl
Elm Waterhole Trib at Evans Rd	11/17/2004	8/10/2005	2	Prometon
Frio Rv at Concan	7/30/1980	5/5/2004	2	2,4,5-T
Frio Rv at Concan	9/2/1987	1/11/1989	2	Diazinon
Helotes Ck at Helotes	5/12/1969	8/8/1974	7	2,4,5-T
Helotes Ck at Helotes	5/12/1969	4/5/1991	11	2,4-D
Helotes Ck at Helotes	4/17/1973	6/28/2007	19	Diazinon
Helotes Ck at Helotes	6/12/1973	8/8/1974	3	Dieldrin
Helotes Ck at Helotes	7/18/1979	4/28/1994	2	Parathion Methyl
Helotes Ck at Helotes	4/5/1991	10/9/2009	6	Malathion
Helotes Ck at Helotes	7/1/2002	5/25/2013	11	Atrazine
Helotes Ck at Helotes	7/1/2002	5/25/2013	7	Carbaryl
Helotes Ck at Helotes	7/2/2002	1/15/2010	3	Simazine
Helotes Ck at Helotes	7/5/2003	3/20/2012	4	Deethyl-atrazine
Helotes Ck at Helotes	10/9/2009	9/28/2012	3	DCPA
Helotes Ck at Helotes	3/20/2012	9/28/2012	2	Prometon
Hondo Ck nr Tarpley	8/27/1971	9/1/1987	2	2,4-D
Leon Ck at Hausman Rd	6/30/2002	6/30/2004	4	Atrazine
Leon Ck at Hausman Rd	6/30/2002	6/30/2004	4	Carbaryl
Leon Ck at Hausman Rd	6/30/2002	6/30/2004	3	Deethyl-atrazine
Leon Ck at Hausman Rd	6/30/2002	2/20/2003	3	Diazinon
Leon Ck at Hausman Rd	10/24/2002	2/20/2003	2	Simazine
Leon Ck at Prue Rd	6/30/2002	8/16/2007	8	Atrazine
Leon Ck at Prue Rd	6/30/2002	8/16/2007	8	Carbaryl
Leon Ck at Prue Rd	6/30/2002	6/28/2007	7	Deethyl-atrazine
Leon Ck at Prue Rd	6/30/2002	6/28/2007	5	Diazinon
Leon Ck at Prue Rd	6/30/2002	10/24/2002	2	Prometon
Leon Ck at Prue Rd	6/30/2002	8/16/2007	6	Simazine
Leon Ck at Prue Rd	10/24/2002	11/16/2004	2	Malathion

(Table 18. continued)

Location	Earliest Date	Most Recent Date	Number of Detections	Compound
Leon Ck at Scenic Loop Rd	10/24/2002	5/14/2012	8	Atrazine
Leon Ck at Scenic Loop Rd	10/24/2002	5/14/2012	2	Malathion
Leon Ck at Scenic Loop Rd	3/30/2007	5/14/2012	4	Deethyl-atrazine
Leon Ck at Scenic Loop Rd	10/9/2011	5/14/2012	2	DCPA
Leon Ck Trib at FM 1604	5/26/1970	8/8/1974	2	4,4'-DDE
Leon Ck Trib at FM 1604	5/26/1970	8/8/1974	2	4,4'-DDT
Leon Ck Trib at FM 1604	6/25/1973	4/29/1979	4	Diazinon
Little Bear Ck at FM 1626	11/6/1978	4/25/1980	2	Diazinon
Lorence Ck at Thousand Oaks	5/15/1980	5/20/1983	3	Chlordane
Lorence Ck at Thousand Oaks	5/15/1980	5/27/1986	11	Diazinon
Lorence Ck at Thousand Oaks	10/18/1980	6/6/1985	3	2,4,5-T
Lorence Ck at Thousand Oaks	10/18/1980	10/21/1985	8	2,4-D
Lorence Ck at Thousand Oaks	10/18/1980	5/21/1983	2	gamma-BHC (Lindane)
Lorence Ck at Thousand Oaks	5/21/1983	7/3/1985	3	Dieldrin
Lorence Ck at Thousand Oaks	5/21/1983	5/26/1986	4	Malathion
Medina Rv at Bandera	8/4/1986	8/31/1987	2	2,4-D
Medina Rv nr Pipe Creek	3/21/1977	8/8/1978	2	2,4-D
Olmos Ck Trib at FM 1535	5/26/1970	6/13/1981	13	2,4,5-T
Olmos Ck Trib at FM 1535	5/26/1970	9/13/1978	8	Dieldrin
Olmos Ck Trib at FM 1535	5/26/1970	3/21/1979	2	gamma-BHC (Lindane)
Olmos Ck Trib at FM 1535	5/7/1972	10/17/1998	15	Diazinon
Olmos Ck Trib at FM 1535	9/16/1973	9/13/1978	3	Heptachlor epoxide
Olmos Ck Trib at FM 1535	11/1/1977	6/13/1981	2	2,4-D
San Marcos Rv Trib at Sessoms	9/12/2003	5/1/2004	2	4,4'-DDE
San Marcos Rv Trib at Sessoms	9/12/2003	3/4/2004	2	Dieldrin
San Marcos Rv Trib at Sessoms	3/4/2004	5/1/2004	2	4,4'-DDT
Stone Mtn Drn Chan at Granite	11/24/1996	1/6/1998	9	Diazinon
Stone Mtn Drn Chan at Granite	2/12/1997	1/6/1998	2	4-Nitrophenol
Unnamed Trib Elm Wtrhole Ck at Evans	10/9/2009	1/25/2012	3	Atrazine
Unnamed Trib Elm Waterhole Ck at Evans	10/9/2009	1/25/2012	3	Simazine
Unnamed Trib Elm Wtrhole Ck at Evans	1/15/2010	1/25/2012	2	Carbaryl
Unnamed Trib Elm Wtrhole Ck at Evans	1/15/2010	1/25/2012	2	Deethyl-atrazine
Unnamed Trib Elm Wtrhole Ck at Evans	1/15/2010	1/25/2012	2	Fipronil
Unnamed Trib Elm Wtrhole Ck at Evans	1/15/2010	1/25/2012	2	Fipronil sulfide
W Elm Ck at San Antonio	8/30/1976	5/20/1988	15	Diazinon
W Elm Ck at San Antonio	4/19/1977	3/21/1979	2	4,4'-DDE
W Elm Ck at San Antonio	4/19/1977	5/15/1980	3	4,4'-DDT
W Elm Ck at San Antonio	3/21/1979	5/20/1988	3	gamma-BHC (Lindane)
W Elm Ck at San Antonio	10/18/1980	5/20/1988	11	2,4-D
W Elm Ck at San Antonio	10/18/1980	5/20/1983	2	Chlordane
W Elm Ck at San Antonio	6/22/1985	5/20/1988	3	Malathion

Herbicides or Pesticides in Springwater

Herbicides and pesticides are occasionally detected in Edwards Aquifer spring samples. Figure 16 shows the frequency of detection and percentage of samples containing herbicides or pesticides and the total number of samples that were analyzed from 1986 through 2006. The EAA has been collecting 20 to 30 spring samples annually since 2002, and herbicides or pesticides were

detected in fewer than two percent of the samples (up to 11 detections out of approximately 600 samples for most compounds). Table 19 lists herbicides or pesticides and ranges of concentrations that have been detected. Principal herbicides and pesticides detected in springs are 2,4-D; 4,4'DDE; atrazine; deltaBHC; gamma-BHC (Lindane); gamma-chlordane; mononcrotophos; and heptachlor, with most detections occurring at Comal

(continued on page 42)

Figure 15. Time-Series Charts of Herbicides at Four Surface Water Locations.

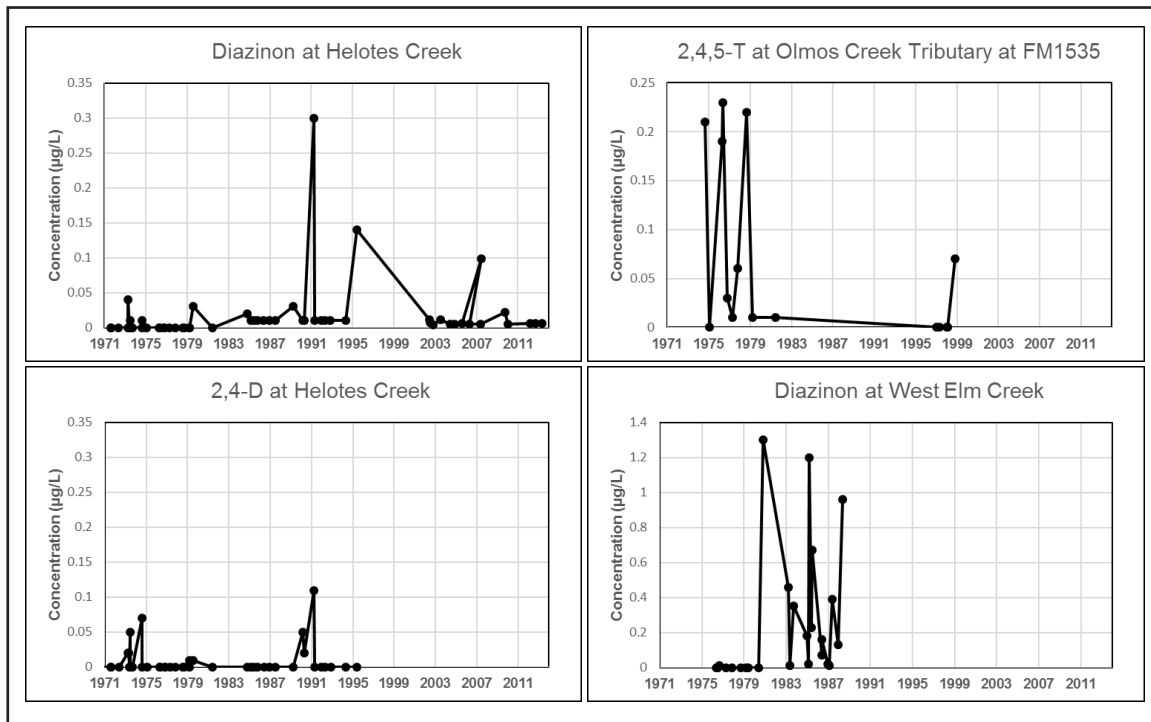


Figure 16. Frequency of Detection of Herbicides and Pesticides in Edwards Aquifer Springwater, 1986–2013.

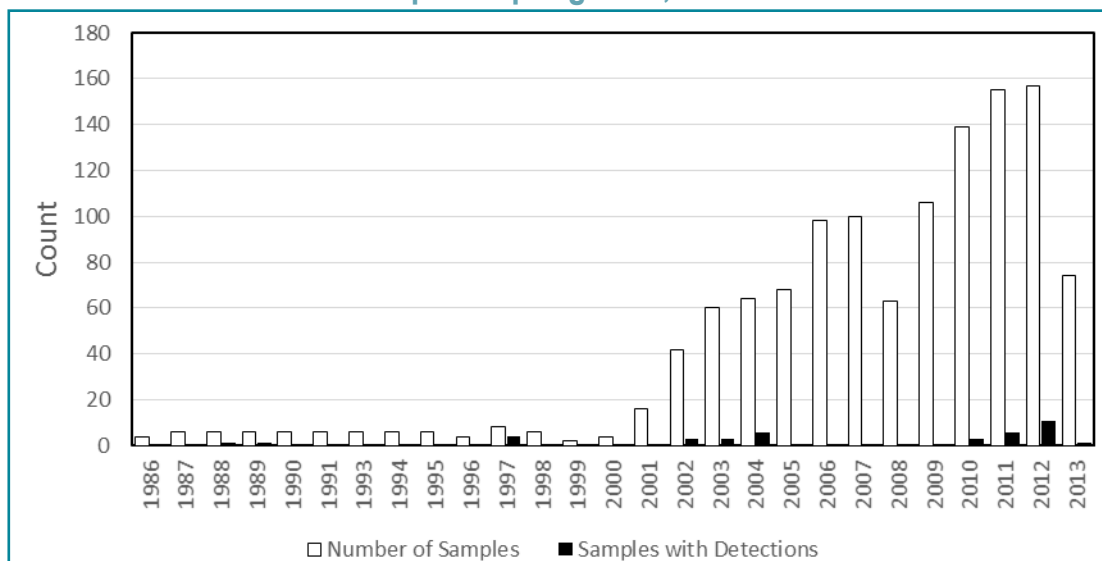


Table 19. Range of Herbicide and Pesticide Concentrations Detected in Edwards Aquifer Springwater

Parameter	Number of Samples Analyzed	Number of Samples with Detectable Herbicides and Pesticides	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	PCL (µg/L)
2,4-D	620	6	0.04	10.4	70
4,4'-DDD	622	1	0.00854	0.00854	3.8
4,4'-DDE	624	4	0.00197	0.00511	2.68
4,4'-DDT	621	1	0.00796	0.00796	2.68
Aldrin	621	2	0.00404	0.0151	0.05
alpha-BHC	569	1	0.02E	0.02	0.14
alpha-Chlordane	563	1	0.00726	0.00726	2.61
Atrazine	353	3	0.0028E	0.003	3
beta-BHC	566	1	0.0132	0.0132	0.51
Beta-Endosulfan	587	1	0.0083	0.0083	147
Deethyl-atrazine	3	3	0.0038E	0.0038	NE
delta-BHC	566	8	0.00329	0.01	0.51
Diazinon	618	2	0.01	0.010	22
Dinoseb	570	1	0.76E	0.76	7
Endosulfan sulfate	566	1	0.00953	0.00953	147
Endrin	621	1	0.00712	0.00712	2
Endrin aldehyde	566	1	0.0125	0.0125	7.33
Endrin ketone	564	1	0.00784	0.00784	7.33
gamma-BHC (Lindane)	624	11	0.00118	0.03	0.2
gamma-Chlordane	538	3	0.005E	0.0157	NE
Heptachlor	622	3	0.00232	0.006	0.4
Heptachlor epoxide	621	2	0.00659	0.0441	0.2
Mononocrotophos	551	4	6.12	8.2	NE
Prometon	4	1	0.0065E	0.0065	367
Toxaphene	618	1	1.91	1.91	3

PCL = Protective concentration level

NE = None established

E = Estimated

Table 20. Range of Concentrations of Nutrients Detected in Wells, Surface Water, and Springwater

Nutrient	Type	Number of Samples Analyzed	Minimum (mg/L as N)	Maximum (mg/L as N)	Mean (mg/L as N)	PCL (mg/L as N)	Number of Analyses Exceeding PCL	
							Original	Total
Ammonia	Groundwater	2,671	<0.01	5.94	0.12	1.5*	11	18
Nitrate-N	Groundwater	6,351	<0.01	47.9	1.78	10	18	27
Nitrite-N	Groundwater	1,987	<0.005	1.82	2.6	1	2	2
Phosphorus	Groundwater	3,038	<0.001	3.04	0.034	NE	0	0
Ammonia	Springs	148	<0.01	0.44	0.044	1.5*	0	0
Nitrate-N	Springs	800	<0.15	5.55	1.63	10	0	0
Nitrite-N	Springs	180	<0.005	0.004	0.0098	1	0	0
Phosphorus	Springs	534	<0.004	4.71	0.056	NE	0	0
Ammonia	Surface water	1,332	<0.002	0.95	0.053	1.5*	0	0
Nitrate-N	Surface water	1,792	<0.001	10.6	0.65	10	0	1
Nitrite-N	Surface water	1,405	<0.005	0.47	0.02	1	0	0
Phosphorus	Surface water	1,602	<0.001	14.0	0.11	NE	0	0
Total		21,840					31	48

All concentrations in mg/L as N

* = Secondary drinking-water standard

NE = Not established

PCL = Protective concentration level established by TCEQ TRRP

(continued from page 40)

Springs #1 and San Marcos Deep Springs. All maximum concentrations are well below the corresponding PCL.

Detection of Nutrients

Nutrients that are commonly detected in groundwater, surface water, and spring samples are nitrite, ammonia, and phosphorus. Nitrate ($\text{NO}_3\text{-N}$) is the most frequently detected nutrient; it was detected in 5,149 out of 6,351 samples. Nitrite ($\text{NO}_2\text{-N}$) and ammonia (NH_3) are rarely detected because they readily convert to nitrate in the oxygen-rich groundwater in the aquifer. Consequently, high ammonia concentrations are associated only with saline water samples, which contain little or no free oxygen. Phosphorus was detected in 49% of approximately

5,200 groundwater, surface water, and springwater samples, and only 36 concentrations exceeded 1 mg/L spanning the period of the database. Given that phosphorus concentrations are not regulated by PCLs and the concentrations are relatively low, phosphorus is not considered a significant contaminant. Nitrate concentrations (as nitrogen, N) will be compared with the PCL of 10 mg/L as N, and ammonia concentrations will be compared with a PCL of 1.5 mg/L as N. Nitrate concentrations above the PCL have been shown to cause methemoglobinemia (blue baby syndrome), which interferes with the ability of newborn babies and some elderly persons to transmit oxygen in the blood. Table 20 lists minimum and maximum concentrations of nutrients in Edwards Aquifer waters.

Figure 17. Maximum Nitrate Concentrations Detected at Edwards Aquifer Groundwater, Surface Water, and Springwater Sample Locations.

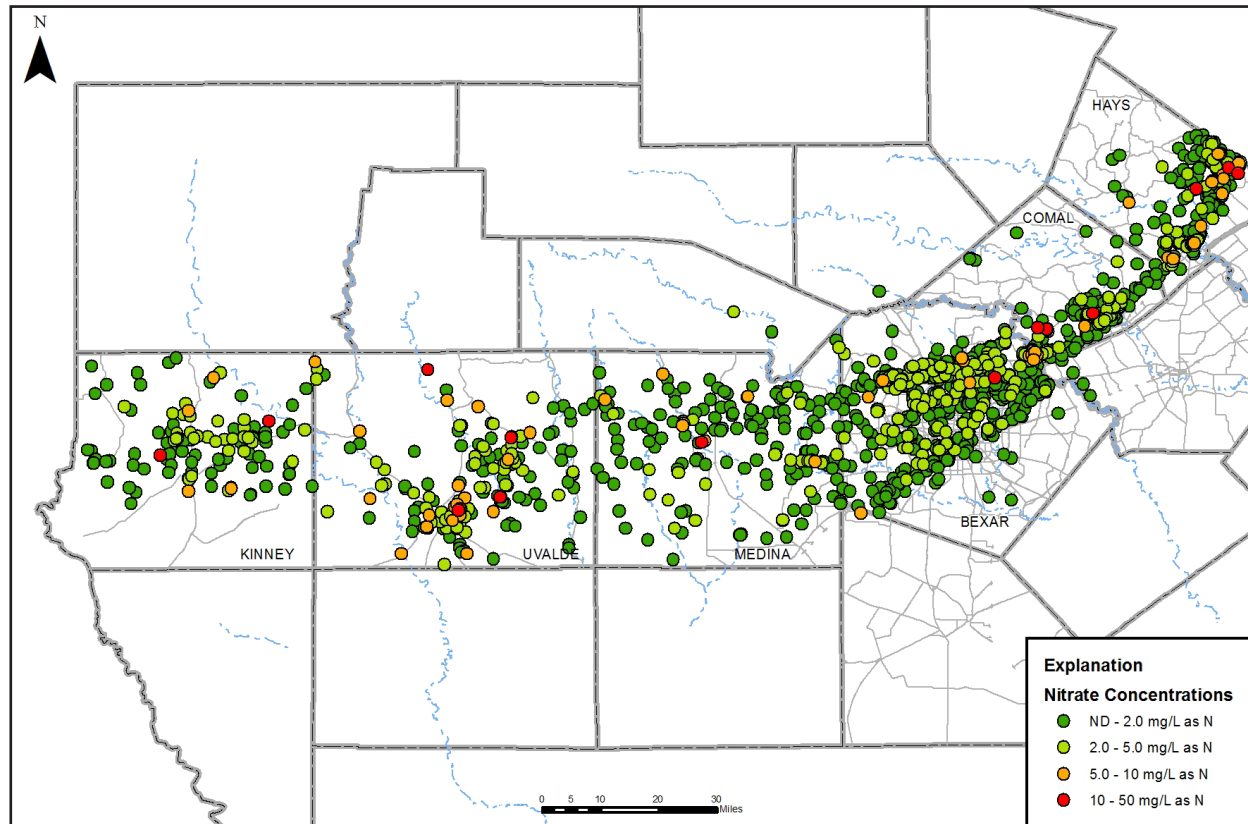


Table 20 also lists the number of nutrient analyses that exceeded PCLs. In the original report, which included analyses through 2006, ammonia or nitrate-N exceeded its PCL in 29 analyses. The current total, which includes analyses through early 2013, is 46 analyses. The total number of analyses was 15,602 in the original report and 18,268 in this report.

Nutrients in Groundwater

Although groundwater samples are analyzed frequently for nutrients, their concentrations rarely exceed the drinking-water standard. Of the analytical data reviewed,

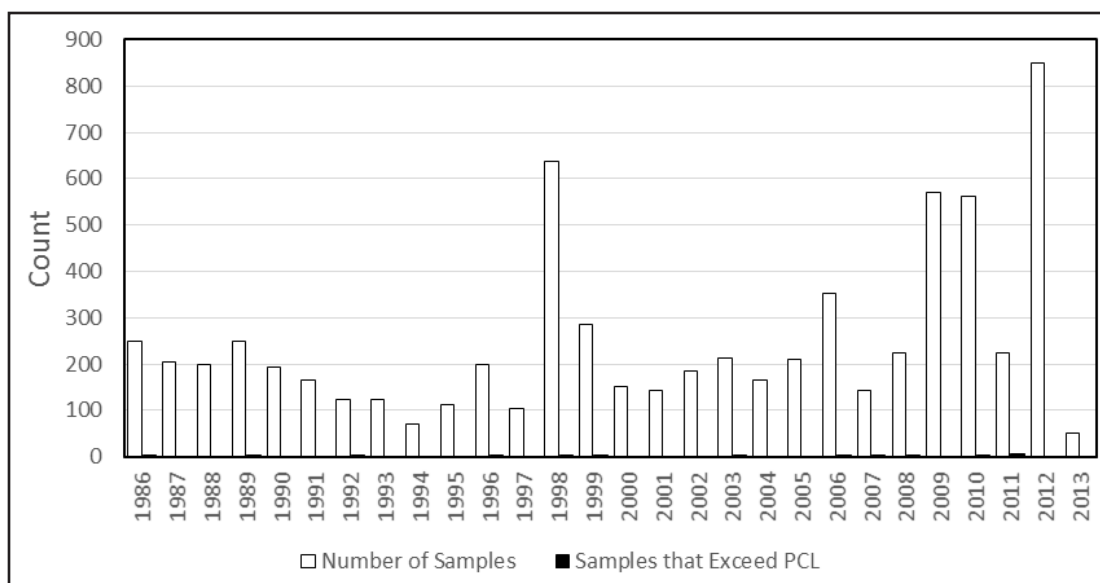
which had been collected between 1913 and 2013, approximately 0.4% (27 out of 6,351 samples) of nitrate analyses exceeded the PCL. Table 21 shows the percentage of groundwater samples in which nutrient concentrations have exceeded PCLs. Of all the samples in the database, only 0.7% (18 out of 2,671 samples) of ammonia analyses and 0.4% (18 out of 6,494 samples) of nitrate analyses exceeded PCLs (Table 21). This exceedance rate is similar to that of results from the original report (Johnson et al., 2009). Figure 17 shows maximum nitrogen concentrations detected at each groundwater, surface water, and spring sample location in the analyses evaluated for this report.

Table 21. Frequency of Nutrient Concentrations that Exceeded PCLs in Edwards Aquifer Wells.

Nutrient	Total Analyses	Analyses Exceeding PCL	Percent Analyses Exceeding PCL*	PCL (mg/L)
Ammonia	2,671	18	0.75 (0.5)	1.5
Nitrate-Nitrite as N	6,351	24	0.4 (0.3)	10
Phosphorus	3,038	0	0 (0)	None

* = Percentages in parentheses from 2009 report

Figure 18. Frequency of Nutrient Concentrations that Exceeded PCLs in Edwards Aquifer Wells, 1986–2013.



With the exception of a few localized areas, current nitrogen concentrations in the aquifer are below the PCL. Figure 18 indicates that nutrient concentrations have rarely exceeded their PCLs in historical analyses. Nutrient concentrations that exceed their PCLs generally reflect a site-specific problem (point source), rather than aquiferwide contamination (nonpoint source). Table 22 lists specific wells in which nutrient concentrations exceeded their PCLs.

An exception is the high ammonia concentrations that occur naturally in Bexar County saline water monitoring wells and two wells in the “Hot Wells” area (saline zone) in Bexar County. High ammonia concentrations are characteristic of saline water in the Edwards Aquifer, which is down dip of the freshwater zone. Ammonia is compatible with the anaerobic nature of saline

groundwater, and little nitrate is formed that would reduce the amount of ammonia.

A localized area represented by wells YP69-51-114 and YP-69-51-104, just northeast of Uvalde, has consistently yielded samples having nitrate concentrations of between 3.1 and 7.34 mg/L as N (Figure 19). Wells AY-68-28-313 and AY-68-21-804 in the recharge zone in Bexar County also periodically contain elevated nitrate concentrations (one to six mg/L). The highest concentration, 47.9 mg/L as N, is from Woodard Cave (YP6929903) in Uvalde County, which at the time of sampling contained a large bat colony and sizable guano deposits.

EAA is investigating an area of relatively high nitrate concentrations in groundwater near Cibolo Creek and Evans Road in eastern Bexar County and southwestern

Comal County. Samples from public and commercial wells have contained concentrations of nitrate as high as 11.9 mg/L as N since the earliest sample in 1998. For example, DX-68-30-221 in Comal County yielded

higher than average concentrations of nitrate, ranging from four to seven mg/L as N. To date only one nitrate concentration in any of the wells has exceeded its PCL.

Figure 19. Nitrate Concentrations Detected in YP-69-51-114 (left) and YP-69-51-104 (right).

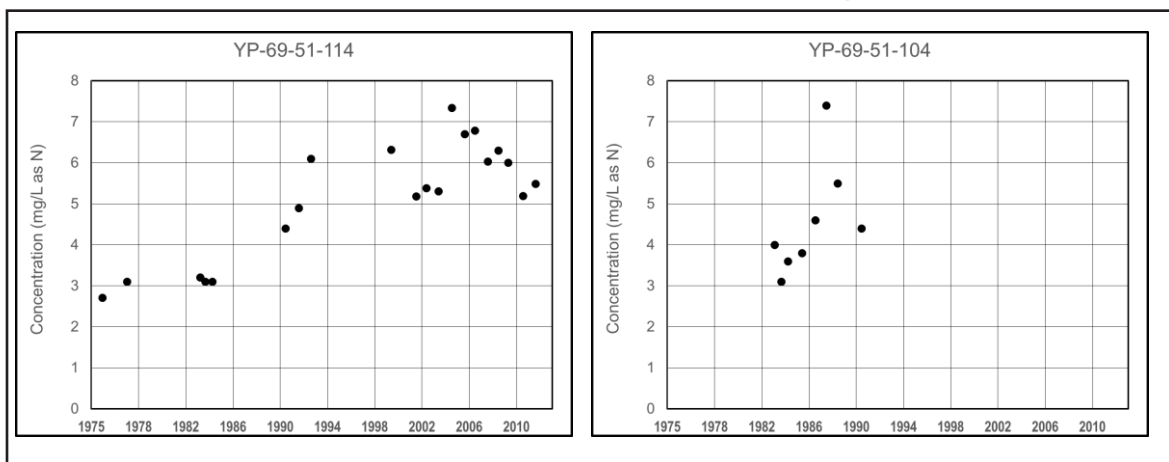


Table 22. Nutrient Concentrations that Exceeded the PCLs in Edwards Aquifer Wells

Sample Location	Sample Date	Concentration (mg/L as N)	Nutrient
TD-69-29-903	6/1/1952	47.89	Nitrate
TD-69-39-907	6/12/1950	23.94	Nitrate
DX-68-22-505	7/8/1982	21.92	Nitrate
DX-68-22-503	5/10/1945	18.7	Nitrate
LR-58-58-403	8/11/1992	18.1	Nitrate
AY-68-29-510	3/6/1992	17.0	Nitrate
DX-68-23-209	9/15/1944	16.4	Nitrate
YP-69-43-309	8/13/1996	16.09	Nitrate
RP-70-39-401	6/14/1938	15.0	Nitrate
YP-69-43-908	4/26/1972	12.65	Nitrate
DX-68-30-225 ²	6/22/2011	12.35	Nitrate
LR-58-57-805	7/15/1985	12.31	Nitrate
LR-58-58-505	8/10/1992	12.2	Nitrate
AY-68-30-211 ²	11/19/1998	11.9	Nitrate
TD-69-55-604	6/21/2011	11.33	Nitrate
TD-69-39-506	8/23/1978	11.29	Nitrate
YP-69-26-501	11/7/1956	11.0	Nitrate
LR-67-09-1SM	11/13/2007	10.5	Nitrate
YP-69-50-207	7/13/2011	10.36	Nitrate

(Table 22. continued)

Sample Location	Sample Date	Concentration (mg/L as N)	Nutrient
DX-68-30-1GV ²	7/6/2010	10.2	Nitrate
TD-68-49-201	6/23/2011	10.14	Nitrate
YP-69-50-306	2/25/1986	10.09	Nitrate
AY-68-34-803	5/29/2003	10.09	Nitrate
DX-68-23-203	6/20/2011	10.05	Nitrate
LR-67-01-812 ¹	5/17/2007	5.94	Ammonia
AY-68-37-525 ¹	8/7/1998	2.64	Ammonia
AY-68-45-301	7/16/1970	2.4	Ammonia
AY-68-37-521 ¹	8/7/1998	2.31	Ammonia
AY-68-37-525 ¹	7/20/1989	2.3	Ammonia
AY-68-37-523 ¹	8/7/1998	2.24	Ammonia
AY-68-37-521 ¹	7/20/1989	2.2	Ammonia
AY-68-37-525 ¹	12/19/2006	2.16	Ammonia
AY-68-44-2AJ	11/15/2010	2.1	Ammonia
AY-68-45-101	3/4/1985	2.1	Ammonia
AY-68-37-523 ¹	7/20/1989	2.1	Ammonia
AY-68-37-525 ¹	5/26/1999	1.92	Ammonia
AY-68-44-505	11/14/2006	1.88	Ammonia
AY-68-37-523 ¹	12/18/2006	1.84	Ammonia
AY-68-37-521 ¹	12/18/2006	1.81	Ammonia
YP-69-59-302	6/2/2008	1.67	Ammonia
AY-68-37-523 ¹	5/26/1999	1.64	Ammonia
AY-68-37-521 ¹	5/26/1999	1.64	Ammonia

¹Well located in saline zone²Well located in Evans Road/Cibolo Creek area

Nutrients in Surface Water

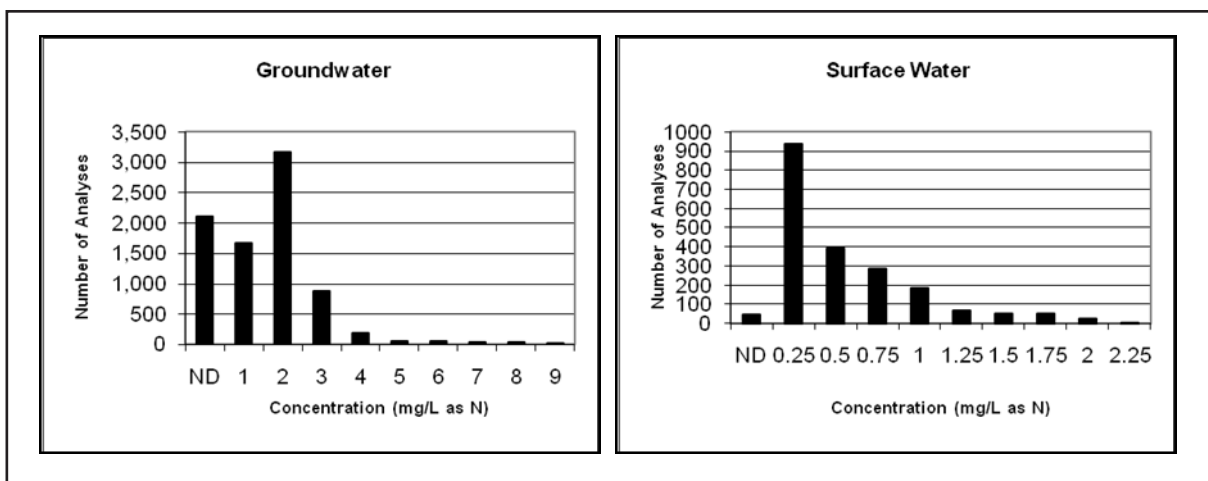
Average nitrate concentration in streams that cross the Edwards Aquifer recharge zone is 0.65 mg/L as N, which represents the nitrate concentration that is recharging the aquifer. Figure 20 indicates that nitrate concentrations in surface water form a smoothly decreasing distribution.

For comparison, groundwater concentrations are tightly distributed around the mean of 1.68 mg/L as N. Only one nitrate concentration in surface water exceeded its PCL, which was a sample collected from Pinto Creek (Kinney County) (at CR2804) on June 16, 2010 (Table 23).

Table 23. Frequency of Nutrient Concentrations that Exceeded PCLs in Surface Water Recharging the Edwards Aquifer

Nutrient	Total Analyses	Analyses Exceeding PCL	Percent Analyses Exceeding PCL	PCL (mg/L)
Ammonia	1,315	0	0%	1.5
Nitrate-nitrite as N	1,792	1	0%	10
Phosphorus	1,602	0	0%	None

Figure 20. Frequency Distributions of Nitrate Concentrations Detected in Groundwater and Surface Water in the Recharge Zone.



Nutrients in Springwater

Table 24 lists the frequency of nutrient concentrations that exceed PCLs in Edwards Aquifer springwater. Frequency distributions of Comal, San Marcos, and Hueco springs are shown in Figure 21. Nitrate concentrations are generally highest in Comal Springs, ranging to 2.5 mg/L as N, whereas other springs average approximately 1.5 mg/L as N. Figure 22 shows time-series charts for San Antonio, San Pedro, Hueco A, San Marcos (Hotel and Deep springs), and Comal springs. Although concentrations are variable, San Antonio and San

Pedro springs concentrations appear to be declining. Hueco A Springs concentrations are currently lower than in the 1940s and 1950s, whereas Comal Springs concentrations have increased since the 1940s and have been decreasing since about 2000. More study will be necessary to interpret the cause(s) of these results. None of the nitrate concentrations in the spring samples exceeded the PCL. However, the level and increase in concentrations of nitrates do indicate anthropogenic loading from the recharge area of the aquifer.

Table 24. Frequency of Nutrient Concentrations that Exceed PCLs in Edwards Aquifer Springwater

Nutrient	Total Analyses	Analyses Exceeding PCL	Percent Analyses Exceeding PCL	PCL (mg/L)
Ammonia	148	0	0%	1.5
Nitrate-nitrite as N	800	0	0%	10
Phosphorus	534	0	0%	None

Figure 21. Frequency Distributions of Nitrate Concentrations Detected in Comal, San Marcos, and Hueco Springs.

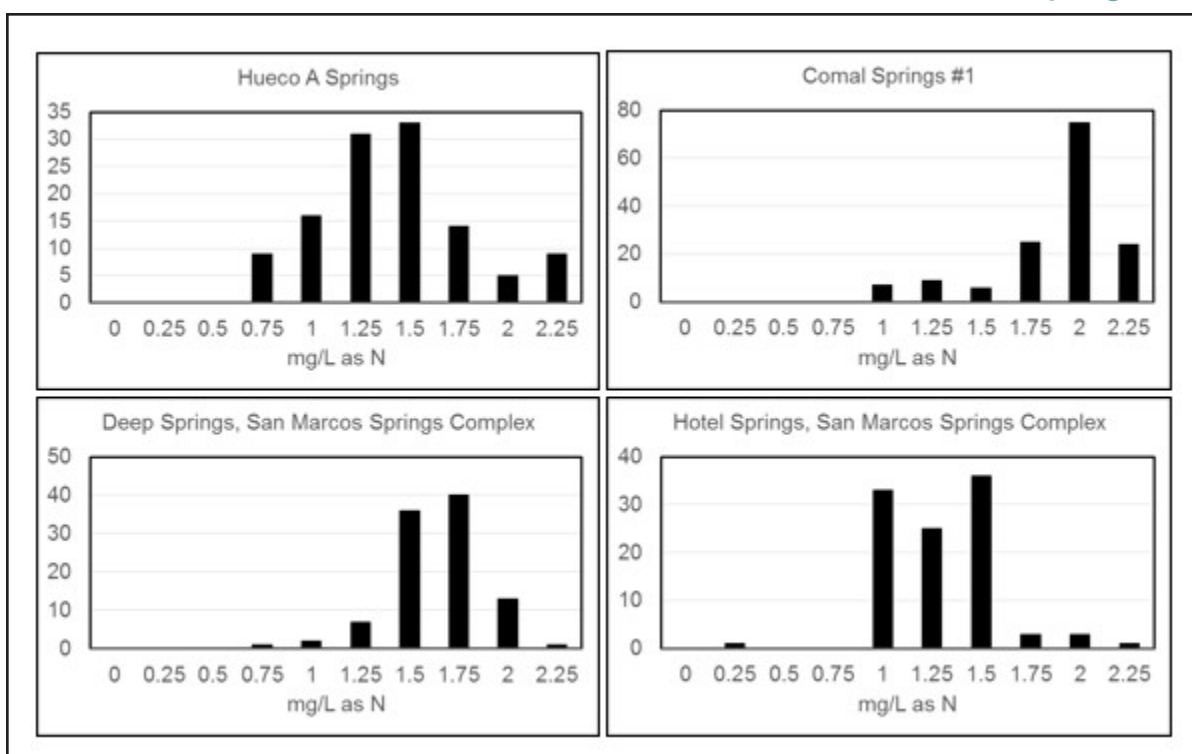


Figure 22. Nitrate Concentrations in Springwater.

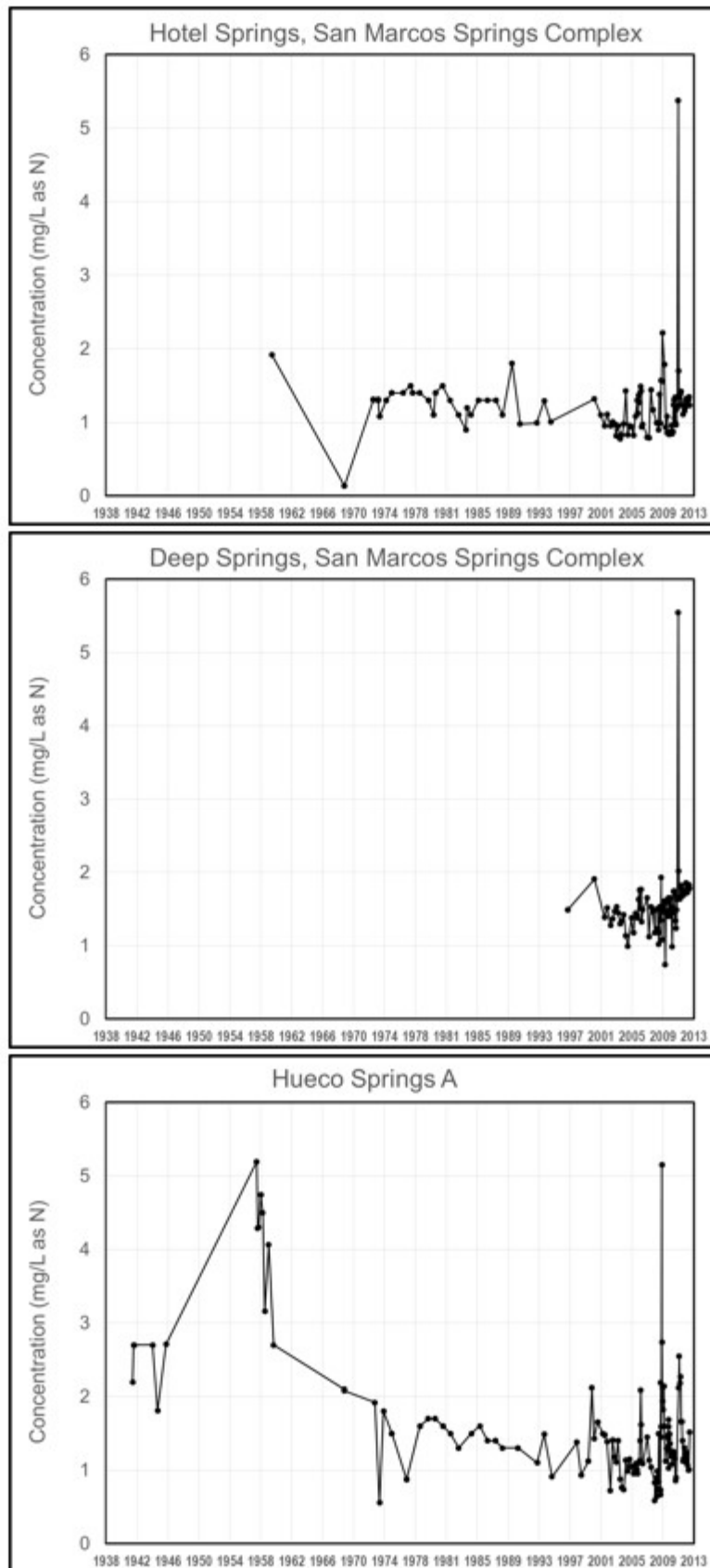


Figure 22 (cont'd). Nitrate Concentrations in Springwater.

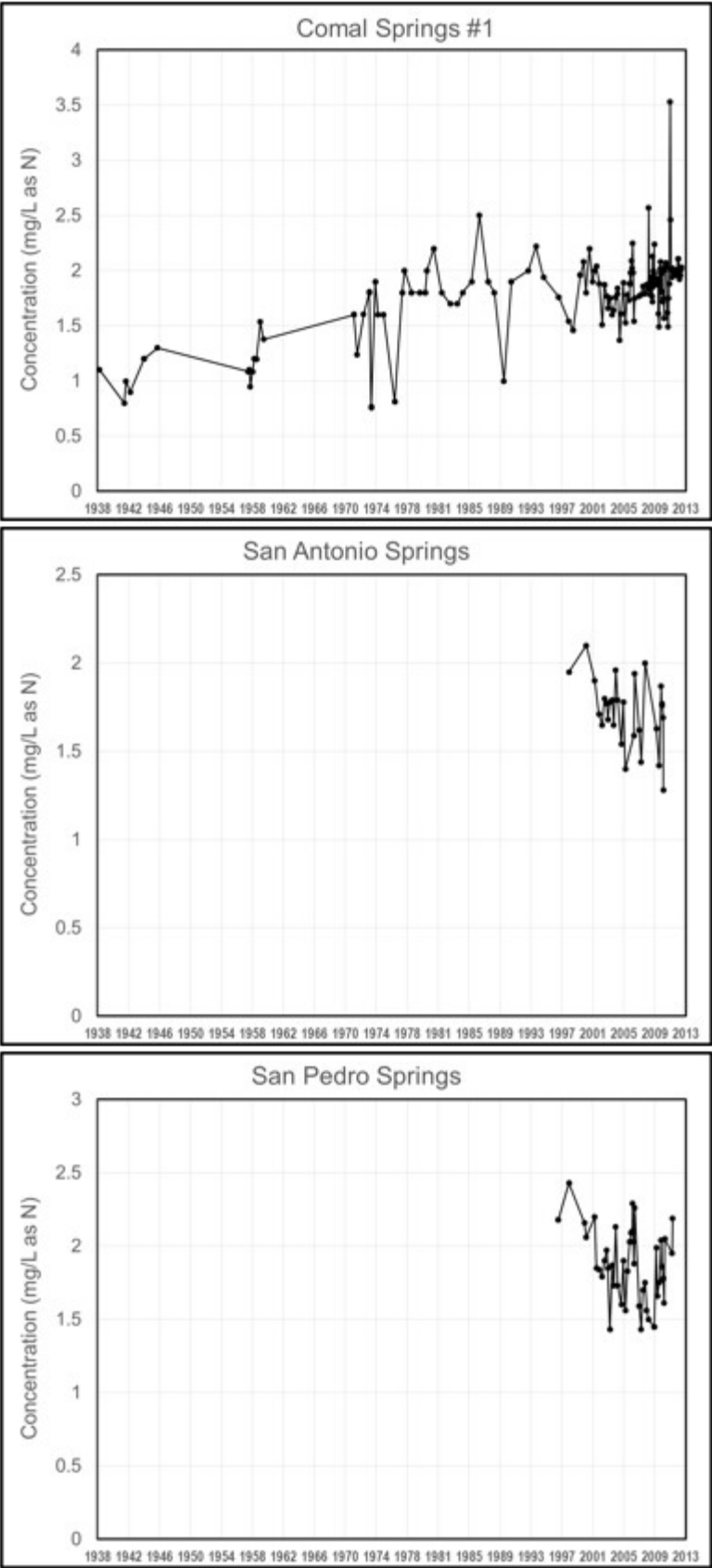


Table 25. Range of Concentrations of Metals Detected in Wells, Surface Water, and Springwater

Metal	Groundwater Maximum (mg/L)	Surface Water Maximum (mg/L)	Springs Maximum (mg/L)	PCL (mg/L)
Aluminum	1.1	0.29	0.612	24.4
Antimony	0.0374	0.0138	0.0305	0.006
Arsenic	0.588	2.62	0.0270	0.01
Barium	0.90	37.6	0.30	2
Beryllium	0.0033	0.0023	0.00268	0.004
Boron	75	0.114	1.20	4.9
Bromide	67.8	0.876	0.470	NE
Cadmium	0.026	0.202	0.00266	0.005
Chromium	0.20	7.29	0.01	NE
Cobalt	0.0158	0.0042	0.00143	1.5
Copper	0.40	0.0283	0.364	1.3
Iron	129	3	1.29	0.3
Lead	1.30	11.7	0.0161	0.015
Lithium	5.66	0.02	0.02	0.049
Manganese	1.35	2.0	0.137	1.15
Mercury	0.0096	0.0039	0.00353	0.002
Molybdenum	0.23	0.0033	0.0021	0.12
Nickel	0.123	0.0297	0.028	0.49
Selenium	0.243	0.28	0.0245	0.05
Silver	5.0	2.0	0.0034	0.1222098
Strontium	425	3.85	1.5	14.7
Thallium	0.0348	0.0087	0.0308	NE
Vanadium	0.067	0.01	0.0045	0.17
Zinc	4.5	47.3	0.17	7.3

PCL = Protective concentration level

NE = Not established

Detection of Metals

Metals dissolve from rock and soil and are carried into the aquifer by stormwater runoff. Most analyses indicate dissolved concentrations of metals. Before analysis, EAA, USGS, and TWDB sampling protocols specify filtering of a sample for metals, leaving only the dissolved fraction for analysis.

Most metals occur in nondeleterious concentrations in Edwards Aquifer waters (Table 25), although maximum concentrations of several metals exceed PCLs for antimony, arsenic, boron, cadmium, iron, lead, lithium, manganese, molybdenum, selenium, and strontium. Frequency of exceedances is discussed in subsequent sections on metals in groundwater, surface water, and springs.

Metals in Groundwater

Metals are commonly detected in groundwater from the Edwards Aquifer, especially in samples from the saline zone. Table 26 shows the frequency of detection and percentage of groundwater samples in which metals concentrations exceeded PCLs since 1986. The percentage of samples with one or more metals concentrations that exceed one or more PCLs has ranged from less than five percent to approximately 30% each year since 1986, which means that as many as 28 of 100 to 200 samples have contained metals concentrations above PCLs each year (Figure 23). Few concentrations of individual metals exceed PCLs (Table 26). Exceedance frequencies of all metals are approximately three percent or less each year, except for iron, strontium, and

Figure 23. Frequency of Metals Concentrations Detected in

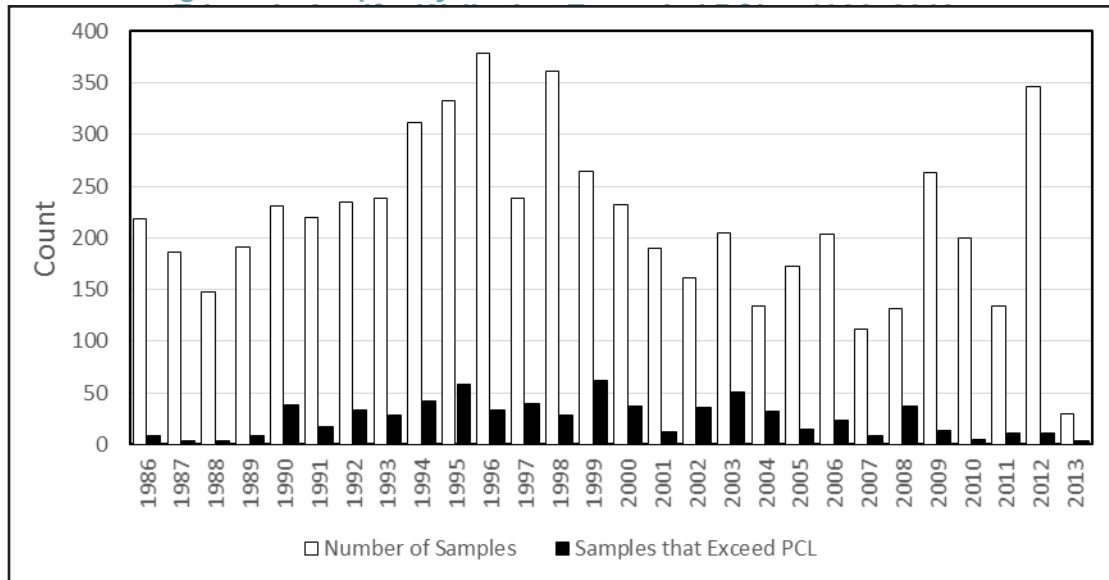


Table 26. Frequency of Metals Concentrations that Exceeded PCLs in Edwards Aquifer Wells

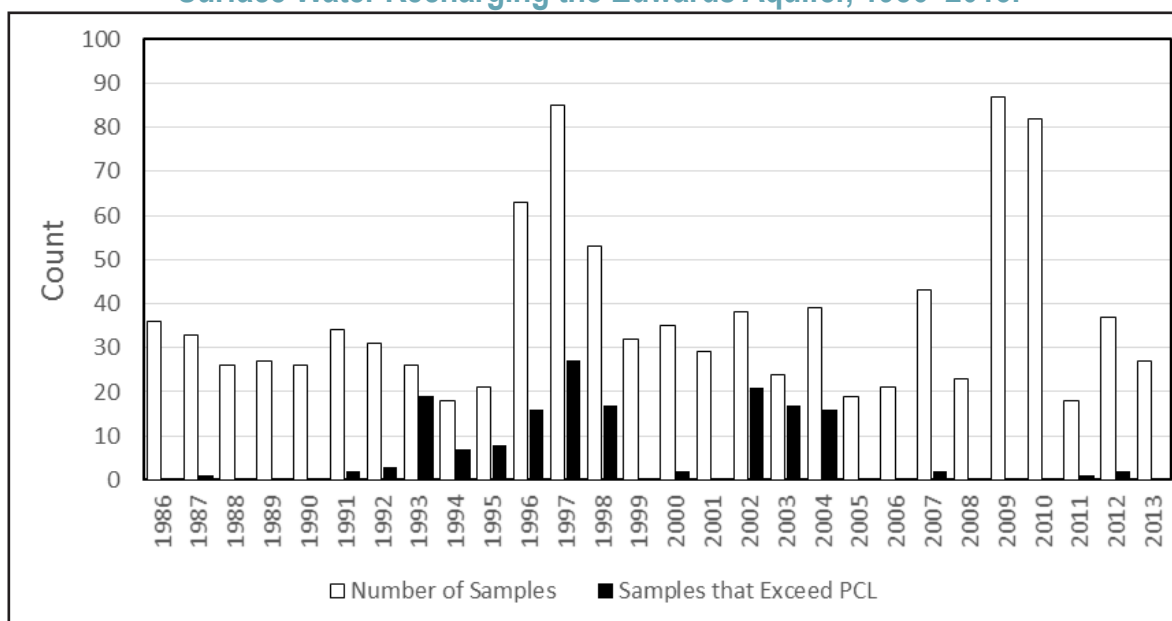
Metal	Total Analyses	Analyses Exceeding PCL	Percent Analyses Exceeding PCL	PCL (mg/L)
Antimony	2,405	15 (0)	0.6	0.006
Arsenic	3,928	9 (4)	0.2	0.01
Boron	1,735	2 (1)	0.1	4.9
Cadmium	3,752	7 (3)	0.2	0.005
Iron	5,167	209 (56)	4.0	0.3
Lead	3,872	19 (2)	0.5	0.015
Lithium	1,522	77 (44)	5.1	0.049
Manganese	4,982	1 (0)	0.02	1.15
Mercury	2,502	9 (2)	0.4	0.002
Molybdenum	1,721	1 (0)	0.06	0.12
Selenium	3,740	8 (7)	0.2	0.05
Silver	2,774	3 (0)	0.1	0.12
Strontium	2,993	201 (96)	6.7	14.7

Number of total exceedances detected in saline zone samples shown in parentheses

lithium concentrations, which exceed PCLs in as high as four percent of total samples collected. In most samples, iron, strontium, or lithium was the parameter that exceeded the PCL. Of a total of 388 exceedances for iron, strontium,

and lithium, 125 are from groundwater samples from the saline water zone, in which TDS exceeds 1,000 mg/L, and the water is generally not used as a drinking-water source.

Figure 24. Frequency of Metals Concentrations that Exceeded PCLs in Surface Water Recharging the Edwards Aquifer, 1986–2013.



Metals in Surface Water

Metals are commonly detected in surface waters recharging the Edwards Aquifer. Figure 24 shows the frequency of detection and percentage of surface water samples in which metals concentrations have exceeded PCLs since 1986. The exceedance frequency is fairly consistent, with the exception of that in 2002, when 25% (eight out of 32 samples) of surface water samples contained one or more metals concentrations that exceeded PCLs. The 2002 analyses included samples collected during a storm event in October at a tributary to Elm Waterhole, Helotes Creek, two locations on Leon Creek in Bexar County, and Panther Canyon Creek in New Braunfels, Comal County. The stormwater samples contained higher concentrations of metals such as lead and zinc than the nonstormwater samples routinely collected from Edwards Aquifer-related streams. All exceedances for individual metals were two percent or less (Table 27).

Lead concentrations can often be interpreted as indicators of urban pollutants. Between 2000 and 2004, the USGS sampled stormwater in a tributary to the San Marcos River at Sessoms Road. Lead concentrations ranged from 0.0001 to 0.0358 mg/L, and seven of the nine samples exceeded a PCL of 0.015 mg/L.

Metals in Springwater

Metals are rarely detected in aquifer springs. Figure 25 shows the frequency of detection, percentage of spring samples, and number of samples analyzed in which metals concentrations exceeded PCLs from 1986 through 2006. Only samples from 2002 through 2004 and 2006 contained at least one metal concentration that exceeded its PCL. Antimony concentrations in spring samples exceeded its PCL in 1.8% of the samples (12 out of 670 samples) (Table 28). Samples from Deep Springs at San Marcos Springs and San Pedro Springs in San Antonio yielded the most exceedances of antimony concentrations of all springs. The most likely source of antimony is naturally occurring sources from the Edwards Limestone because of its ubiquity.

Detection of Pharmaceuticals and Personal Care Products

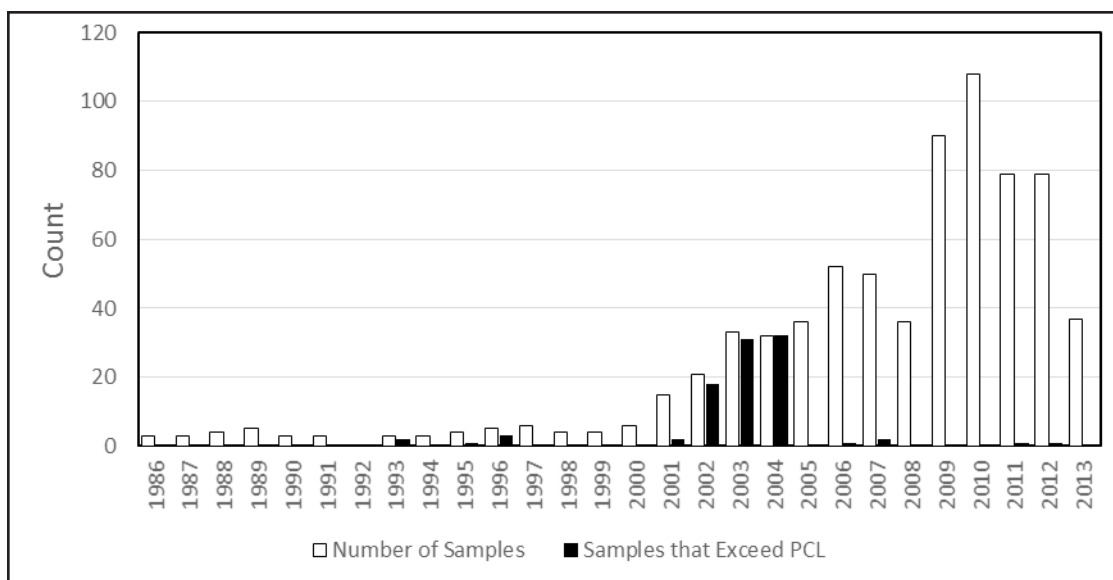
Since 2011, EAA has analyzed groundwater, surface water, and springwater for pharmaceuticals and personal care products (PPCPs). PPCPs generally refer to products used for personal health or cosmetic reasons or used by agribusiness to enhance growth or health of livestock. They include thousands of prescription and over-the-counter therapeutic drugs, veterinary drugs, fragrances,

Table 27. Frequency of Metals Concentrations that Exceeded PCLs in Surface Water that Recharges the Edwards Aquifer

Metal	Total Analyses	Analyses Exceeding PCL	Percent Analyses Exceeding PCL	PCL (mg/L)
Antimony	415	5 (3)	1.2	0.006
Arsenic	986	8 (8)	0.8	0.01
Cadmium	988	2 (2)	0.2	0.005
Iron	1,079	4 (4)	0.4	0.3
Lead	1,034	14 (12)	1.4	0.015
Manganese	1,110	1 (1)	0.09	1.15
Mercury	964	2 (3)	0.2	0.002
Silver	898	1 (1)	0.1	0.12
Zinc	1,058	1 (0)	0.09	7.3

Number of total exceedances from original report shown in parentheses

Figure 25. Frequency of Metals Concentrations that Exceeded PCLs in Edwards Aquifer Springwater, 1986–2013.



lotions, and cosmetics. The purpose of EAA's sampling program has been to determine whether PPCPs are present in the Edwards Aquifer. USGS has also analyzed PPCPs and organic wastewater contaminants (OWCs) in the Edwards Aquifer region since 1999. EAA's analytical program has consisted of compounds for which methods are commercially available under Method 1694 and

others, whereas USGS developed its own methods for PPCP compounds. All compounds detected by EAA or USGS are listed in Table 29.

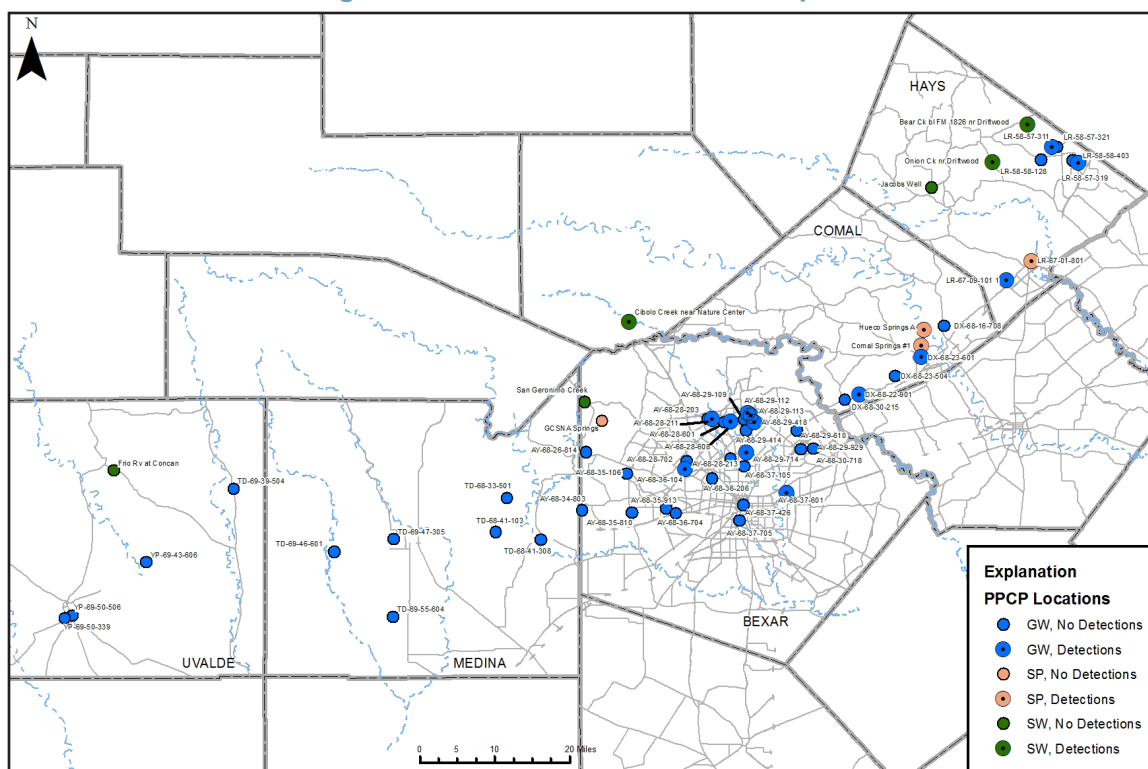
Initially, EAA sampled wells in unsewered areas in northern Bexar County where septic tanks are a potential source. More recently, samples have been collected

Table 28. Frequency of Metals Concentrations that Exceeded PCLs in Edwards Aquifer Springwater

Metal	Total Analyses	Analyses Exceeding PCL	Percent Analyses Exceeding PCL	PCL (mg/L)
Antimony	670	12 (12)	1.8	0.006
Arsenic	748	2 (0)	0.3	0.01
Iron	770	4 (3)	0.5	0.3
Lead	747	1 (1)	0.1	0.015
Mercury	649	2 (0)	0.3	0.002

Number of total exceedances from original report shown in parentheses

Figure 26. Locations of PPCP Samples.



from selected surface waters and springs throughout EAA's jurisdictional area. USGS sampled groundwater and surface water locations throughout the country in 1999–2001 (Barnes et al., 2008), local wells in 2003–2010, and Barton Springs area locations in 2009–2010 (Mahler et al., 2011). None of these samples came from drinking-water supplies. Figure 26 shows locations of the samples. EAA collected a background sample from TD-69-39-504 in Medina County as a quality control sample under the assumption that it would contain no detectable PPCPs (and it did not). Table 30 lists the sample sites and results of PPCP analyses to date.

Out of the 60 sample locations, one or more PPCP compounds were detected at 19. The most commonly detected compound was caffeine (13 samples), followed by DEET (six samples) and lincomycin (six samples). Other compounds detected at four locations were estrone, cotinine, and 17 α -estradiol. USGS (Barnes et al., 2008) most frequently detected these compounds: N,N-diethyltoluamide (DEET), bisphenol-A, cholesterol, metolachlor (herbicide), carbamazepine, and others in groundwater and surface water. Mahler et al. (2011) detected DEET, caffeine, camphor, and isophorone most frequently in stream, spring, and groundwater samples.

Table 29. Pharmaceuticals and Personal Care Products Analytes

Compound	Application
17a-Estradiol	Estrogen
17a-Ethynyl Estradiol	Estrogen
17b-Estradiol	Estrogen
Acetaminophen	Analgesic/anti-inflammatory
Bisphenol-A	Plastic additive
Caffeine	Stimulant
Camphor	Pharmaceutical
Carbamazepine	Anti-epileptic medication
Cholesterol	Sterol
Cotinine	Nicotine metabolite
N,N-diethyltoluamide (DEET)	Insect repellent
Diltiazem	Blood-pressure medication
Equilenin	Estrogen
Estriol	Estrogen
Estrone	Estrogen
Fluoxetine	Antidepressant
Galaxolide	Musk ketone
Gemfibrozil	Lipid regulator
Ibuprofen	Analgesic/anti-inflammatory
Iopromide	X-ray contrast media
Isophorone	Solvent
Lincomycin	Antibiotic
Naproxen	Analgesic/anti-inflammatory
Nonylphenol Diethoxylate (Tech.)	Additive in plastics and surfactants
Nonylphenol Monoethoxylate (Tech.)	Additive in plastics and surfactants
p-Nonylphenol (Tech.)	Additive in plastics and surfactants
Progesterone	Steroid
p-tert-Octylphenol	Surfactant
Sulfamethoxazole	Antibiotic
Testosterone	Hormone
Thiabendazole	Parasite medication
Triclocarban	Antibacterial soap
Triclosan	Antibiotic
Trimethoprim	Antibiotic
Tylosin	Veterinary antibiotic

Although PPCPs occur at concentrations measured in nanograms per liter (ng/L) or parts per trillion, their presence is an unmistakable indicator of anthropogenic impacts on the Edwards Aquifer. Results suggest that PPCPs are fairly ubiquitous in urban areas in Bexar, Comal, and Hays counties. Although unsewered areas are potential sources, analyses are insufficient to identify specific sources.

At present no regulatory standards have been established for PPCPs in drinking water. Consequently, no point of comparison exists to determine whether PPCPs in groundwater, surface water, or springwater pose a potential health risk. In addition, little is known regarding the health effects of exposure to a mixture of one or more PPCPs.

Table 30. Results of Pharmaceuticals and Personal Care Products Analyses

Location	Sample Date	PPCP Compound	Concentration (ng/L)
Wells			
AY-68-28-211	8/22/2011	17a-Estradiol	1.2
AY-68-28-211	8/22/2011	Equilenin	3.8
AY-68-28-211	8/22/2011	Estrone	6.9
AY-68-28-211	8/22/2011	Triclocarban	2.9
AY-68-28-211	8/22/2011	Tylosin	2.3
AY-68-28-211	7/2/2012	P-Nonylphenol (Tech.)	3.1
AY-68-28-608	8/18/2011	Cotinine	1.7
AY-68-28-608	8/18/2011	Lincomycin	0.51
AY-68-28-608	9/19/2012	Diltiazem	7.9
AY-68-29-112	8/18/2011	Lincomycin	0.42
AY-68-29-112	1/11/2012	Caffeine	53
AY-68-29-112	1/11/2012	Estrone	1.6
AY-68-29-112	1/11/2012	Lincomycin	0.27
AY-68-29-113	8/18/2011	Lincomycin	0.31
AY-68-29-113	1/10/2012	17a-Estradiol	1.4
AY-68-29-113	1/10/2012	17b-Estradiol	1.5
AY-68-29-113	1/10/2012	Caffeine	320
AY-68-29-113	1/10/2012	Diltiazem	0.48
AY-68-29-113	1/10/2012	Estrone	1.3
AY-68-29-113	1/10/2012	Lincomycin	0.69
AY-68-29-113	1/10/2012	Triclosan	17
AY-68-29-418	1/17/2012	Lincomycin	0.38
AY-68-29-714	12/14/2004	Caffeine	E0.006
AY-68-36-104	12/13/2004	Caffeine	E0.009
AY-68-37-601	12/15/2004	Caffeine	E0.005
DX-68-22-901	5/18/2005	Bisphenol-A	M
DX-68-23-601	12/8/2004	Caffeine	E0.009
LR-58-57-311	5/20/2003	Caffeine	E0.005
LR-58-57-311	7/13/2004	Caffeine	E0.006
LR-58-58-403	2/26/2009	DEET	E0.01
LR-58-58-403	3/2/2010	DEET	E0.03
LR-67-09-101 1	2/14/2012	Caffeine	250
LR-67-09-101 1	2/14/2012	Carbamazepine	19
LR-67-09-101 1	2/14/2012	Sulfamethoxazole	12
Springs			
Comal Springs #1	8/23/2011	17a-Estradiol	4.3
Comal Springs #1	8/23/2011	17b-Estradiol	7.0
Comal Springs #1	8/23/2011	Equilenin	0.72
Comal Springs #1	8/23/2011	Estrone	5.8
Hueco Springs A	12/3/2012	17a-Estradiol	1.6
Hueco Springs A	12/3/2012	Cotinine	4.85
Hueco Springs A	12/3/2012	Diltiazem	0.705
LR-67-01-801	12/3/2012	Cotinine	4.73
LR-67-01-801	12/3/2012	Diltiazem	0.451
Surface Water			
Bear Ck bl FM 1826 nr Driftwood	3/13/2009	Caffeine	E0.09
Bear Ck bl FM 1826 nr Driftwood	3/13/2009	DEET	E0.02
Bear Ck bl FM 1826 nr Driftwood	9/12/2009	Caffeine	E0.23

(Table 30. continued)

Location	Sample Date	PPCP Compound	Concentration (ng/L)
Bear Ck bl FM 1826 nr Driftwood	9/12/2009	DEET	E0.18
Bear Ck bl FM 1826 nr Driftwood	9/12/2009	Galaxolide	E0.014
Bear Ck bl FM 1826 nr Driftwood	11/8/2009	DEET	E0.03
Bear Ck bl FM 1826 nr Driftwood	1/15/2010	Cholesterol	E0.2
Bear Ck bl FM 1826 nr Driftwood	1/15/2010	DEET	E0.03
Cibolo Creek near Nature Center	8/16/2012	Caffeine	64
Cibolo Creek near Nature Center	8/16/2012	Carbamazepine	160
Cibolo Creek near Nature Center	8/16/2012	Cotinine	19
Cibolo Creek near Nature Center	8/16/2012	Diltiazem	8.1
Cibolo Creek near Nature Center	8/16/2012	p-Nonylphenol (Tech.)	4.5
Cibolo Creek near Nature Center	8/16/2012	Sulfamethoxazole	1200
Cibolo Creek near Nature Center	8/16/2012	Thiabendazole	24
Onion Ck nr Driftwood	11/8/2009	DEET	0.16
Onion Ck nr Driftwood	1/14/2010	Caffeine	E0.02
Onion Ck nr Driftwood	1/14/2010	Cholesterol	E0.4
Onion Ck nr Driftwood	1/14/2010	DEET	E0.1

E = Estimated

DISCUSSION OF FINDINGS

This report is an update of a detailed review of water quality data for the Edwards Aquifer that was originally published in 2009 (Johnson et al., 2009). It covers chemical analyses of groundwater within the aquifer, surface water recharging the Edwards Aquifer, and springwater discharging from the aquifer. The original report includes historical analytical data through August 2006, and this report adds analytical data through June 2013. After the large volume of historical water quality data was examined, some areas of water quality concern were noted; however, the extent of contamination within the Edwards Aquifer is relatively small, and given the PCL as an indicator, a vast majority of the aquifer appears to be unimpaired. The absence of long-term water quality records from specific sampling locations in much of the freshwater part of the aquifer, coupled with a complex hydrology, makes determining clear trends for most COCs difficult. Detection of anthropogenic compounds, some above PCLs, indicates that specific locations within the aquifer have been impacted by human activities. The presence of these compounds also indicates the vulnerability of the aquifer, and the addition of post-2006 analytical data confirms these conclusions.

Vulnerability of the Edwards Aquifer

The U.S. EPA has recognized that karst aquifers are one of the aquifer types most vulnerable to contamination from anthropogenic sources (Schindel et al., 1996; Federal Register, 2000). Potential threats to Edwards Aquifer water quality may include transport and use of hazardous materials and other chemicals in the recharge zone, abandoned or poorly completed water wells, improperly installed or maintained septic systems and sewer lines, and urban nonpoint source runoff. Some cases of contamination involving organic compounds have been noted in the recharge and artesian parts of the Edwards Aquifer. Contaminants are generally detected in urbanized areas in Bexar and Uvalde counties, as observed by Buszka (1987) and Fahlquist and Ardis (2004). Although the Edwards Aquifer has a relatively large capacity to attenuate contamination, primarily through dilution, this capability can be exceeded, resulting in degradation of water quality and exceedance of PCLs.

Assimilative Capacity of the Edwards Aquifer

The assimilative capacity of the Edwards Aquifer is its capacity to attenuate, largely through dilution, concentrations of contaminants to acceptable levels before they reach a well or spring (EPA, 1987). According to Rubin (1991), assimilative capacity is the answer to the question “How much is too much?” For freshwater parts of the aquifer, the assimilative capacity has been exceeded when contaminant concentrations exceed a PCL. The assimilative capacity of the Edwards Aquifer is based primarily on its ability to dilute contaminant concentrations below PCLs, although chemical degradation and biological processes are factors as well.

The assimilative capacity of the aquifer depends on many factors, including physical properties of the contaminant, such as its solubility, reactivity, and susceptibility to chemical and biologic degradation, which influences its fate in groundwater. For example, VOCs may be attenuated primarily by dilution, whereas nutrient concentrations may be reduced through biological processes. Hydraulic characteristics of the aquifer, such as gradients, porosity, and permeability, affect residence time in the aquifer for contaminants. The nature of the release, such as distance to a receptor, soil thickness, and physical properties of the contaminant, also affects how the aquifer can attenuate contaminants.

Assimilative capacity is also defined at different scales. Regionally the aquifer has a large assimilative capacity for attenuating contaminants. Containing billions of gallons of water, it has an enormous capacity for dilution, which is reflected by the relatively high quality of springwater. However, when contaminants are detectable in springs or other areas, the source must be large enough to overcome the assimilative capacity of the aquifer, even on a regional scale. Locally the assimilative capacity for tetrachloroethene has been exceeded near the Bandera Road Plume Superfund Site in Bexar County and in the eastern part of the City of Uvalde because several wells (approximately four in Bexar County and approximately 14 in Uvalde County) have had consistent detections above the PCL. Other examples are nitrate concentrations near Cibolo Creek and Evans Road and PCE contamination in the eastern Hollywood Park area

in Bexar County. Continuing detections indicate that some sources of COCs are persistent in the aquifer.

Nitrogen Loading of the Aquifer

Although nitrogen compounds occur naturally in the aquifer, high concentrations contributed by anthropogenic sources may exceed the aquifer's assimilative capacity. Water quality analyses indicate that nitrogen concentrations increase as water recharged into the aquifer flows to the springs (Comal and San Marcos springs). Nitrogen concentrations in streams that cross the recharge zone range from 0.25 to 2.25 mg/L as N, with an average of 0.65 mg/L as N, whereas average concentrations at the springs are higher, averaging 1.5 to 2 mg/L as N, suggesting that a substantial amount of nitrogen in the form of nitrate is added to aquifer flowpaths between activities in recharging areas and the springs. These concentrations are well below the regional assimilative capacity using the PCL as a measure. However, nitrate as N levels may be higher than desired for aquatic communities that rely on the Edwards Aquifer springs for flow. In contrast, nitrate concentrations in samples from 30 wells were higher than 10 mg/L as N, indicating that the assimilative capacity was locally exceeded at the time of sampling. Potential sources of nitrates within the Edwards Aquifer region include fertilizers, precipitation, blasting agents, and human and animal waste.

Constituents of Concern

Parameters detected at least once in the aquifer at concentrations exceeding their PCLs are considered COCs. Table 31 lists the 28 parameters that were identified as COCs in previous sections of this report and the media in which they were detected. Nitrite was added because it has an MCL (1.0 mg/L as N). Numbers in parentheses are the number of detections presented in the original report (Johnson et al., 2009). Not listed are iron and manganese, which have only secondary drinking-water standards, and methylene chloride and bis (2-ethyl hexyl) phthalate, which are considered artifacts from sampling or analytical equipment. PPCPs are not listed because they have no PCLs, although their presence indicates that they have exceeded the

assimilative capacity of the aquifer. Among anthropogenic parameters, tetrachloroethene was detected most often, whereas, among naturally occurring parameters, nitrate, lithium, and strontium were detected most often. Selenium and lithium were detected mainly in samples of water from the saline zone (>1,000 mg/L TDS), which is not considered a drinking-water source for the purposes of this report, and occasionally in freshwater samples. Approximately half of the exceedances of arsenic and cadmium were from saline water samples. Concentrations of semivolatile organic compounds and herbicides and pesticides rarely exceeded PCLs.

Table 31 shows detections above PCLs with the addition of analytical results since 2006. Arsenic and mercury were detected in two samples of springwater, and lead was detected in one additional groundwater sample and two springwater samples. The increase in lithium detections is from samples from saline wells collected in late 2006. The large increase in nitrate detections is due to groundwater samples that EAA collected in response to sewage spills on the recharge zone in 2010 and 2012. Of the organic compounds detected above their PCLs, the additional data contained only one more detection of PCE in groundwater, one more detection of benzene in springwater, and one more detection of atrazine.

Table 31. Constituents of Concern

Parameter	Maximum Concentration (mg/L)	PCL (mg/L)	Type	Number of Detections above PCL		
				GW	SP	SW
1,2-Dibromoethane	0.0007	0.00005	VOC	1		
1,2-Dichloroethane	0.0134	0.005	VOC		1	
1,2-Dichloropropane	0.0698	0.005	VOC		1	
Antimony	0.0374	0.006	Metal	15 (14)	12	2 (3)
Arsenic	0.588	0.01	Metal	10	2 (0)	8
Atrazine	0.003	0.003	Herbicide			2 (1)
Benzene	0.043	0.005	VOC	2	1 (0)	
Benzo(a)anthracene	0.004	0.00125	SVOC			4
Benzo(a)pyrene	0.005	0.0002	SVOC			6
Benzo(b)fluoranthene	0.008	0.00125	SVOC			7
Boron	75	4.9	Metal	2		
Cadmium	0.026	0.005	Metal	7		3
Ethion	0.04	0.012	Herbicide	1		
Indeno(1,2,3-cd)pyrene	0.003	0.00125	SVOC			5
Lead	1.3	0.015	Metal	19 (18)	1	14 (12)
Lithium	5.66	0.049	Metal	76 (62)		
Mercury	0.0096	0.002	Metal	10 (8)	2 (0)	3
Metribuzin	6.7	0.61	Herbicide	1		
Molybdenum	0.23	0.12	Metal	1		
Nitrate	47.9	10	Nutrient	30 (19)		1 (0)
Nitrite	1.82	1.0	Nutrient			3 (0)
Pentachlorophenol	0.0013	0.001	SVOC			3
Selenium	0.243	0.05	Metal	8		
Silver	5.0	0.12	Metal	3		1
Strontium	54.7	14.7	Metal	201 (138)		
Tetrachloroethene	0.12	0.005	VOC	46 (45)		
Trichloroethene	0.13	0.005	VOC	3		
Vinyl chloride	0.003	0.002	VOC	1		

GW = Groundwater

SW = Surface water

SP = Springs

Numbers in parentheses are totals from 2009 report (Johnson et al., 2009)

Detections of organic compounds were not widespread. With the exception of sampling points close to known contaminant sources, historical data are characterized

by occasional detections of a small number of organic compounds, a small fraction of which occur in concentrations that exceed PCLs.

Table 32. Breakdown of Detected Organic Compounds

Type	Detected	Herbicides	Pesticides	SVOCs	VOCs	All Organic Compounds
Groundwater	No	32,273	27,661	16,334	100,986	177,254
	Yes	610 (1.9%)	62 (0.2%)	178 (1.1%)	1,225 (1.2%)	2,075 (1.2%)
Springs	No	19,255	17,160	34,900	42,472	113,787
	Yes	18 (0.1%)	46 (0.3%)	162 (0.5%)	106 (0.2%)	332 (0.3%)
Surface water	No	14,151	17,598	4,655	4,587	40,991
	Yes	281 (1.9%)	192 (1.1%)	219 (4.5%)	26 (0.6%)	497 (1.7%)

CONCLUSIONS

- More than 13,000 water samples from the Edwards Aquifer area have been collected since 1913 by the EAA and its predecessor, the EUWD, as well as the USGS and the TWDB. These samples include surface water recharging the aquifer, groundwater samples from wells, and springwater discharging from the aquifer. Samples were collected for annual monitoring programs, specific investigations, or a variety of other purposes. Most historical data (approximately 70%) consist of five or fewer total samples from approximately 1,700 groundwater, surface water, or spring locations.
- Historical water sample data are valuable because they provide a snapshot of groundwater quality at the time of sampling and identify contaminants that may be present in the aquifer at any particular time.
- The largest number of samples was collected from transect wells between 1985 and 2000 so that the nature and occurrence of the freshwater/saline water interface line could be better understood. With the exception of transect well monitoring, few long-term records of water quality exist for any particular well, surface water location, or spring. Consequently, data are insufficient to draw statistically valid conclusions regarding long-term trends of contaminant concentrations.
- Potential contaminants detected consist of VOCs, SVOCs, nutrients, herbicides, and pesticides. Concentrations of 28 parameters exceeded PCLs in one or more samples. They were selected as COCs because their concentrations exceeded the assimilative capacity of the aquifer at least near the sample locations. Metals occur naturally in the aquifer but rarely exceed PCLs in the freshwater parts of the aquifer. Concentrations of metals such as arsenic, cadmium, iron, lithium, selenium, and strontium exceeded PCLs mostly in samples of saline water (>1,000 mg/L TDS), which has not been considered a drinking-water source for the purposes of this report. Most organic chemicals do not occur naturally and are the result of anthropogenic (human-made) sources such as leaks or spills related to urban, agricultural, or industrial activities, especially on the recharge zone or near abandoned or poorly constructed wells. Of the anthropogenic parameters, tetrachloroethene was detected most often, whereas, of the naturally occurring parameters, nitrate was detected most often in the freshwater part of the aquifer.
- Table 32 summarizes the classes of organic compounds detected, along with percentages of analyses that reported detectable concentrations. Quantities refer to individual analytes. Although quantities have increased with additional analytes since 2006, detection percentages are generally a few tenths of a percent lower. Organic compounds were detected in approximately two percent (1,392 out of 79,911 samples) of groundwater analyses, 0.5% (126 out of 26,155 samples) of springwater analyses, and two percent (497 out of 25,008 samples) of surface water analyses.
- Detections of organic compounds were not widespread. With the exception of sampling points close to known contaminant sources, historical data are characterized by occasional detections of a small number of organic compounds, a small fraction of which occur in concentrations that exceed PCLs.

- The nitrogen balance shows that nitrogen in the form of nitrate is added to the aquifer as water makes its way from surface streams in the recharge zone to the springs. Although the Edwards Aquifer has a large regional assimilative capacity, detections indicate that its assimilative capacity has been at times locally exceeded.
- Results demonstrate that the Edwards Aquifer is vulnerable to contamination by organic compounds and elevated concentrations of naturally occurring metals or nutrients.

Although data are insufficient to confirm whether concentrations are increasing or decreasing, detections indicate that a variety of organic compounds have reached the aquifer from multiple sources. This observation is consistent with the nature of karst aquifers in general: rapid infiltration with little filtration of potential contaminants and vulnerability to abandoned or poorly completed water wells, improperly installed or maintained septic systems and sewer lines, and urban nonpoint source runoff.

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APPENDIX A. Analytical Data Included in This Report

(database available in electronic form upon request)