

**Edwards Aquifer Habitat Conservation Plan
Expanded Water Quality Monitoring Report**

December 2014

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1.0 INTRODUCTION

The Edwards Aquifer Authority (EAA) and its predecessor agency, the Edwards Underground Water District (EUWD), in cooperation with the U.S. Geological Survey (USGS) and the Texas Water Development Board (TWDB) have maintained a water quality sampling program since 1968. Analyses of these data have been used by the EAA to assess aquifer water quality. This routine or historical sampling program involves the analyses of a broad spectrum of parameters in wells, springs, and streams across the region. Generally, the routine sampling program includes sampling a minimum of 80 wells, eight streams, and major springs across the region (at frequencies ranging from annually to monthly). The EAA's existing sampling program was expanded with the adoption of the Edwards Aquifer Habitat Conservation Program (EAHCP) to include collection of additional samples and sample types in the immediate vicinity of Comal and San Marcos Springs. The expanded water quality sampling program was developed in accordance with the directives of the EAHCP to identify and assess potential impairments to water quality within the Comal River and headwaters of the San Marcos River systems. The expanded EAHCP sampling requirements are described in the *Water Quality Monitoring Program Strategy for Comal Springs and San Marcos Springs in Support of the Edwards Aquifer Habitat Conservation Plan* (EAHCP Workplan) (EAA 2012) which is included in Appendix A of this document.

Based on the requirements of the EAHCP Workplan, the expanded sampling program requires the collection of the following sample types:

1. Surface water (base flow) samples
2. Sediment samples
3. Real time instrument (RTI) water quality monitoring
4. Stormwater sampling
5. Passive Diffusion Samplers (PDS)

SWCA Environmental Consultants, Inc. (SWCA) was contracted by the EAA to execute the expanded sampling program in 2014 and 2015, with the exception of RTI water quality monitoring, which is still conducted by the EAA. Surface water quality monitoring was enhanced for 2014 and 2015 by the addition of passive diffusion samplers (PDS) for trace organic compounds analyses, which was conducted by SWCA. A groundwater sampling element was also included in the sampling program, which was to be conducted during periods of extremely low spring flow from Comal and San Marcos springs. The groundwater sampling element of the sampling program was only to be conducted if spring flow rates dropped below 30 cubic feet per second (cfs) at Comal Springs or below 50 cfs at San Marcos Springs. Spring flow rates remained above 30 cfs at Comal Springs and above 50 cfs at San Marcos Springs during 2014 and; therefore, the groundwater sampling element was not conducted. Hydrographs of spring flow are presented in Appendix B.

Prior to the implementation of the EAHCP, the historical sampling program had not specifically addressed surface water quality, sediment quality, real time changes for basic water quality parameters, or stormwater impacts along the Comal River or headwaters of the San Marcos River. Therefore, this expanded sampling program was designed to gather data specific to all of the new parameters. This report presents the surface water, sediment, stormwater and PDS data collected by SWCA in 2014. The data set

represents the second year of the program and is not sufficient to establish any long-term trends or patterns.

For purposes of this report, the Comal River may also be referred to as Comal Springs or Comal Springs complex, and the San Marcos River headwaters may also be referred to as San Marcos Springs or San Marcos springs complex. An overview of surface water, sediment, and stormwater sample locations for Comal and San Marcos springs are shown in Figures 1 and 2. Figures 3–6 provide detailed location data for sample points at the Comal Springs complex. Figures 7–10 provide detailed locations for the sample points at the San Marcos Springs complex.

1.1 Surface Water (Base Flow) Samples

Surface water (base flow) samples are collected twice annually at each spring complex. The Comal Springs complex has five sample locations along the Comal system from the upstream end of Landa Lake (where Blieders Creek empties into the headwaters of Landa Lake) to the south end of the Comal River, upstream of the confluence with the Guadalupe River. In the San Marcos system, surface water samples are collected at seven locations. Sample sites begin at Sink Creek upstream of the headwaters of Spring Lake on the north end of the system and end downstream of Capes Dam on the south end of the system.

Surface water sample locations are designed to provide water quality data for the majority of the surface waters of each spring system and river reach of concern. Samples are collected both above and below where each system's surface waters are influenced by springflow as well as other potential surface water inputs (such as Dry Comal Creek or Purgatory Creek). Surface water samples are analyzed for a broad spectrum of parameters as outlined in Table 1. Surface water samples were collected in the April and September 2014.

Regulatory standards for surface water quality vary dependent upon type of use. For this report, surface water results are compared to drinking water quality standards (30 TAC, Chapter 290, Subchapter F) for detected constituents of concern. These guidelines were selected for use since in general they provide the most stringent quality standards. For detections of interest that do not have an established maximum contaminant level (MCL) under 30 TAC 290, the Texas Risk Reduction Program (TRRP) from 30 TAC 350 was substituted. The TRRP standards used are the Tier I, residential standards and are referred to as protective concentration levels (PCL). Pharmaceutical and Personal Care Products (PPCP) including caffeine can be chemicals of concern because they can indicate the presence of contamination from anthropogenic sources including wastewater discharge (EPA 2012). There are not currently regulatory standards to compare caffeine detections against, but results are listed in this report to provide an indication of potential anthropogenic impacts. Additionally, bacteriological results were compared with Texas Surface Water Quality Standards for primary recreational waters (30 TAC, Chapter 307, Rule 307.7). The 30 TAC 307.7 standards are typically applied to waters affected by anthropogenic sources and are used here solely to provide a reference level for bacterial counts. Other guidelines may be more useful or appropriate for particular research; however, for the scope of this report these standards provide an appropriate and applicable guideline with regard to water quality.

Sample Name Convention

Cornal Springs

HCS110

HCP Sample Location

Sample Type

(1 = Surface Water, 2 = Storm, 3 = Sediment, 4 = PDS)

Sampling Locations:

- HCS120 (Surface Water)**
HCS320 (Sediment)
HCS420 (PDS)
- HCS110 (Surfacewater)**
HCS210 (Stormwater)
HCS310 (Sediment)
HCS410 (PDS)
- HCS140 (Surface Water)**
HCS240 (Stormwater)
HCS340 (Sediment)
HCS440 (PDS)
- HCS130 (Surface Water)**
HCS330 (Sediment)
HCS430 (PDS)
- HCS250 (Stormwater)**
- HCS160 (Surface Water)**
HCS360 (Sediment)
HCS460 (PDS)
- HCS260 (Stormwater)**
- HCS270 (Stormwater)**

Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, I-cubed, USDA, USGS, AEX, Getmapping, SWCA PN. 27122, Production: December 30, 2014. SMH

SWCA
ENVIRONMENTAL CONSULTANTS

Figure 2. EAHCP expanded water quality monitoring program, San Marcos Springs and River.

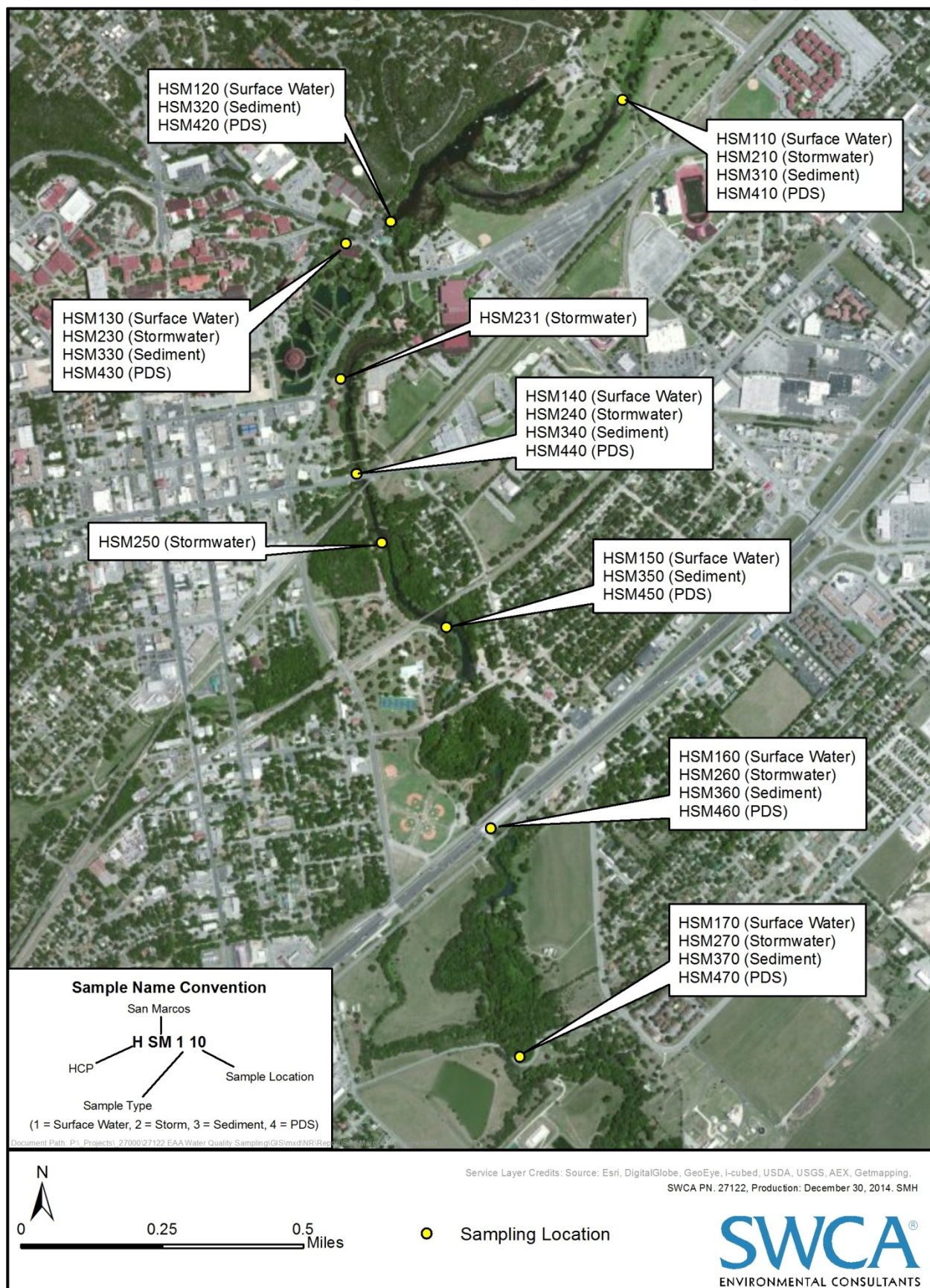


Table 1. Listing of Analytical Parameters by Sample Type

Analytical Parameter	Surface Water (Base Flow) Samples	Stormwater Samples	Sediment Samples	PDS
Volatile Organic Compounds (VOCs)	Yes	Yes	Yes	Yes*
Semi-volatile Organic Compounds (SVOCs)	Yes	Yes	Yes	Yes*
Organochlorine Pesticides	Yes	Yes	Yes	Yes*
Polychlorinated Biphenyls (PCBs)	Yes	Yes	Yes	No
Organophosphorous Pesticides	Yes	Yes	Yes	No
Herbicides	Yes	Yes	Yes	No
Metals (Al, Sb, As, Ba, Be, Cd, Cr (total), Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Tl, and Zn)	Yes	Yes	Yes	No
General Water Quality Parameters (GWQP), Total Alkalinity (as CaCO ₃), Bicarbonate Alkalinity (as CaCO ₃), Carbonate Alkalinity (as CaCO ₃); Cl, Br, NO ₃ , SO ₄ , F, pH, TDS, TSS, Ca, Mg, Na, K, Si, Sr, CO ₃ ,	Yes	Yes	No TDS, TSS, or TKN	No
Phosphorus (total)	Yes	Yes	Yes	No
Total Organic Carbon (TOC),	Yes	Yes	Yes	No
Dissolved Organic Carbon (DOC)	Yes	Yes	Yes	No
Total Kjeldahl Nitrogen (TKN)	Yes	Yes	Yes	No
Bacteria (<i>E. coli</i>)	Yes	Yes	No	No
Field Parameters (DO, pH, Conductivity, Turbidity, Temperature)	Yes	Yes	No	No
Caffeine	Yes	Yes	No	No

*PDS samplers are analyzed for a modified set of VOCs, SVOCs, and organochlorine pesticides

1.2 Sediment Samples

Collection of sediment samples within each spring system was included in the program to help ascertain potential effects on listed species via direct or indirect exposure to sediments. Designated sediment sample locations were coincident with surface water (base flow) sample locations at each spring complex. Specifically, five sediment samples were collected from the Comal Springs area, and seven locations are sampled within the San Marcos area. As in year one, all sediment samples in year two were collected from the sediment surface to approximately 18 inches below the surface. Samples were then homogenized at the laboratory and analyzed for the parameters listed in Table 1. Sediment for volatile organic compound (VOC) analyses was removed from the sample prior to homogenization by the contract laboratory staff. In years 2013 and 2014, sediment samples were collected on the basis of investigating general sediment quality in the uppermost 18 inches of sediment. Future sediment sample collection may be tailored to focus on more discrete intervals in order to further refine the understanding of sediment quality at each spring group.

Sediment samples were collected as close to each associated surface water sample location as possible. However, for many of the samples, collection points were moved slightly to find adequate sediment, or to avoid rocky substrates that prevented collection of adequate sample volume. Appendix C of this report discusses sample locations where any significant deviations from this approach occurred.

Analytical results for sediment samples are compared to the sediment quality guidelines published in *Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems* (MacDonald et al. 2000). These guidelines are based on determination of probable sediment toxicity in freshwater ecosystems and provide a numerical sediment quality guideline for 28 chemicals of concern. The guidance provides two basic standards for comparison: 1) threshold effect concentration (TEC), and 2) probable effect concentration (PEC). PEC values for additional chemicals of concern that were not included in MacDonald et al. (2000) were taken from the 2012 Guidance for Assessing and Reporting Surface Water Quality in Texas developed by the Texas Commission on Environmental Quality (TCEQ 2012). Analytical results with a concentration below the TEC are predicted to be non-toxic (on sediment-dwelling organisms), while results with a concentration above the PEC are indicated as having a probable toxic effect on sediment-dwelling organisms. Detected compounds with concentrations between the TEC and PEC are considered equally likely to be toxic or non-toxic. While numerous other guidelines for sediment quality exist, these guidelines provide a good reference for the scope of the current investigation. Future researchers may find other guidelines more specific to particular concerns or interest.

1.3 Stormwater Samples

Stormwater sampling was performed at five Comal Springs locations and at seven San Marcos Springs locations. Stormwater sample collection was adopted as part of the expanded water quality monitoring effort to assess potential contaminants that may be present in surface water runoff generated by storm events. The stormwater sampling effort was designed to assess what changes in water quality occur within each surface water system during a storm event. Storm samples were collected in association with various surface water inputs along each spring complex within the study area. Appendix C of this report discusses details of each stormwater sample location and any deviations from the workplan. Stormwater samples were analyzed for the same parameters as surface water (base flow) samples as outlined in Table 1.

Stormwater samples were collected at three points across the storm hydrograph for each stormwater sampling site. Sample collection was targeted for the rising limb, peak, and receding limb of the storm hydrograph. Timing for sample collection was generally determined using the RTI system's conductivity and turbidity parameters rather than the flow measurements from the USGS streamflow gauges. The USGS gauges are only updated on an hourly basis whereas the RTIs were available on 15-minute intervals and provided more timely data. Automated sample collection equipment was not utilized for stormwater sample collection due to sample volume, preservation, and analysis limitations. Therefore, sampling was conducted manually. Each spring group was sampled twice for stormwater events during calendar year 2014 per the EAHCP Workplan.

As previously mentioned, standards for surface water quality vary dependent upon type of use. For this report, stormwater results are compared to drinking water quality standards (30 TAC, Chapter 290, Subchapter F) for detected chemicals of concern. These guidelines were selected for use since, in general, they provide the most stringent quality standards. For detections of interest that do not have an established MCL under 30 TAC 290, the TRRP from 30 TAC 350 was substituted. The TRRP standards used are the Tier I, residential standards and are referred to as PCLs. There are not currently regulatory standards to compare caffeine detections against, but results are listed in this report to provide an indication of anthropogenic contamination. Bacterial counts were compared with Texas Surface Water Quality Standards (30 TAC 307). Other guidelines may be more useful or appropriate for particular research; however, for the scope of this report these standards provide an appropriate and applicable guideline with regard to water quality.

1.4 Surface Water Passive Sampling

Amplified Geochemical Imaging (AGI) LLC, PDSs were deployed in both spring complexes to measure trace organic constituents. Samplers consist of a sorbent solid phase material that concentrates compounds from the environment. Following collection, the analytes of interest were eluted and analyzed by gas chromatography coupled with a mass spectrometry detector (GC-MS). The increased contact time associated with long-term deployment of the collection material allows the analytes to be greatly concentrated beyond what is typically found in water samples. Therefore, the PDS provides greater sensitivity to trace level constituents. Analyzed parameters can be found in Table 1.

PDS samplers were deployed to each of the twelve sample sites for two-week periods in March, April, June, August, October and December 2014. Sample points coincided with surface water collection points unless prevented by field conditions, and any alterations are discussed in Appendix C.

2.0 SAMPLE LOCATION DETAIL

Details of individual sample locations are provided in the following figures. Figures 3–6 show sample location details for the Comal Springs area. Figures 7–10 provide sample location details for the San Marcos Springs area.

Figure 3. EAHCP Comal Springs detailed map indicating sample locations 110, 210, 310, 120, and 320.

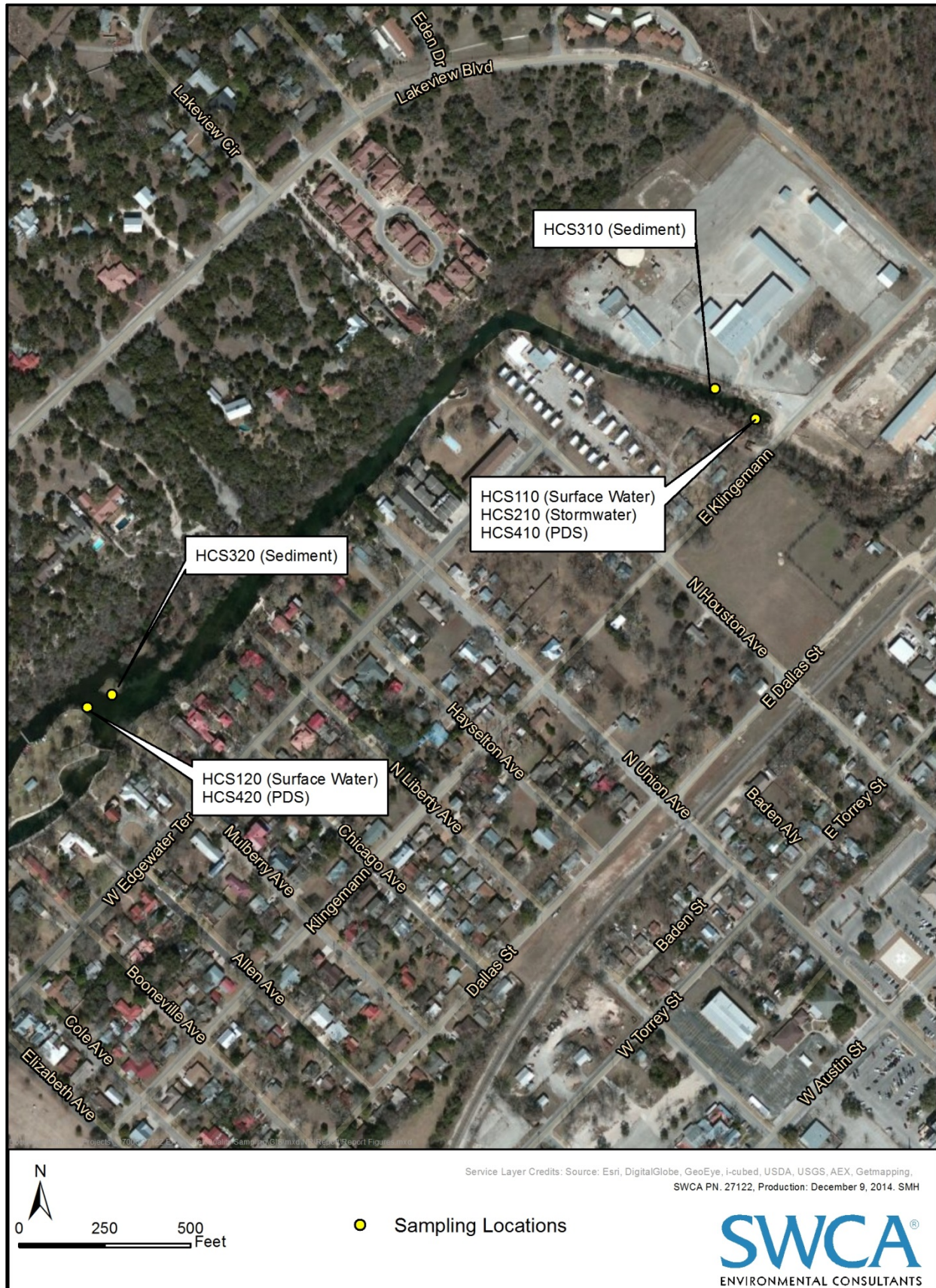


Figure 4. EAHCP Comal Springs detailed map indicating sample locations 130 and 330.



Figure 5. EAHCP Comal Springs detailed map indicating sample locations 140, 240, 340, 250, 160, 260, and 360.

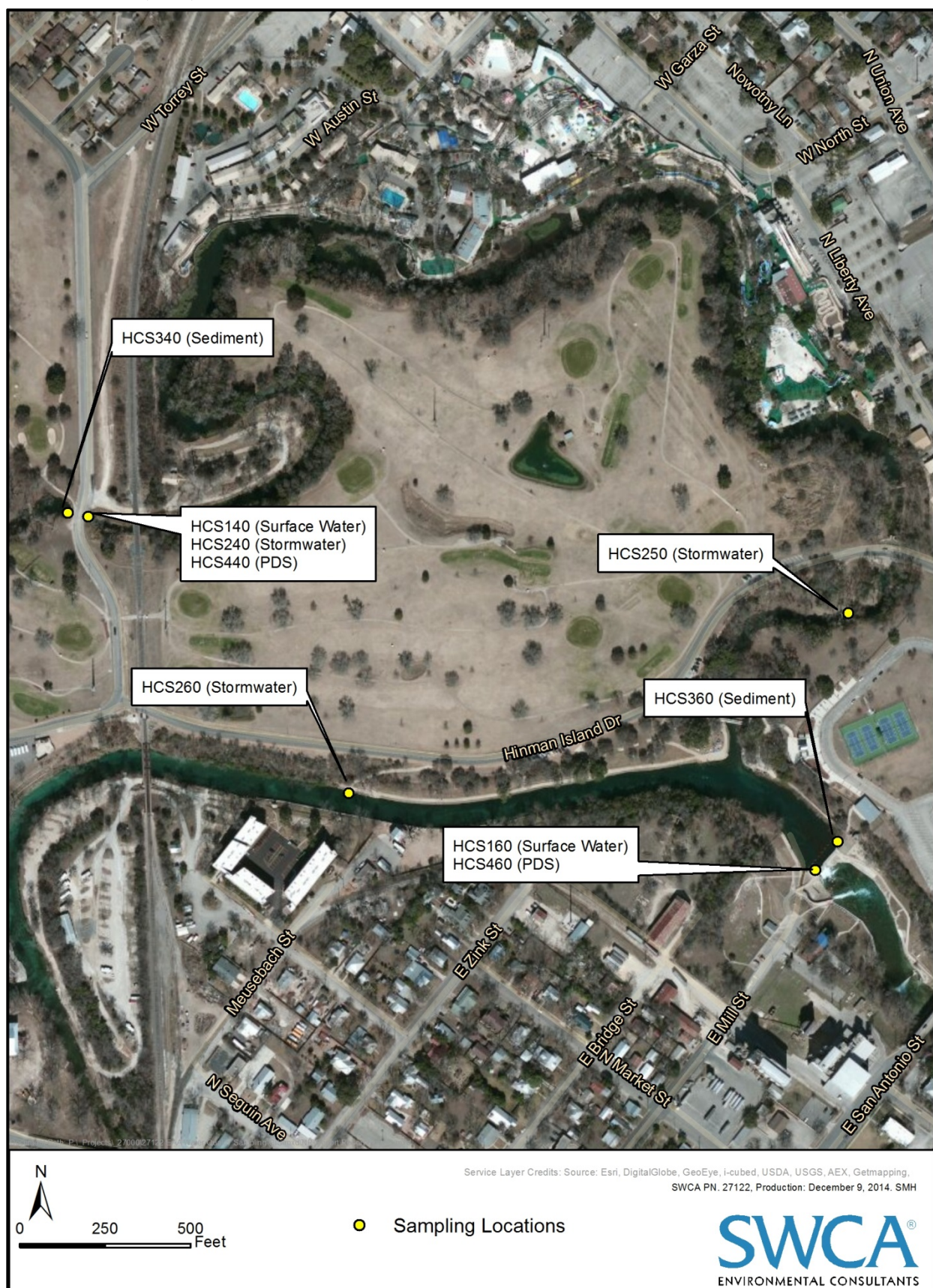


Figure 6. EAHCP Comal Springs detailed map indicating sample location 270.

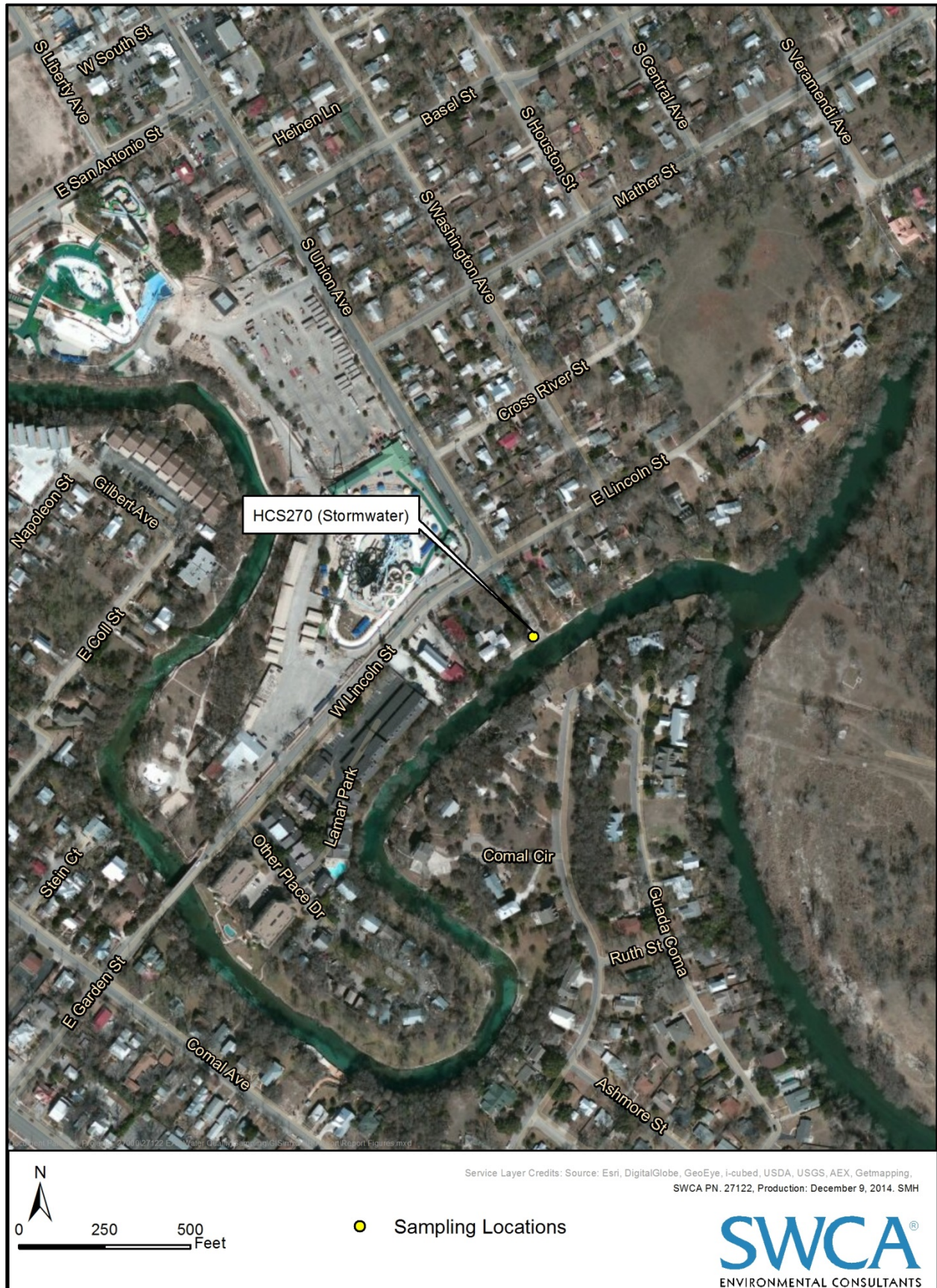


Figure 7. EAHCP San Marcos Springs detailed map indicating sample locations 110, 210, 310, 120, and 320.

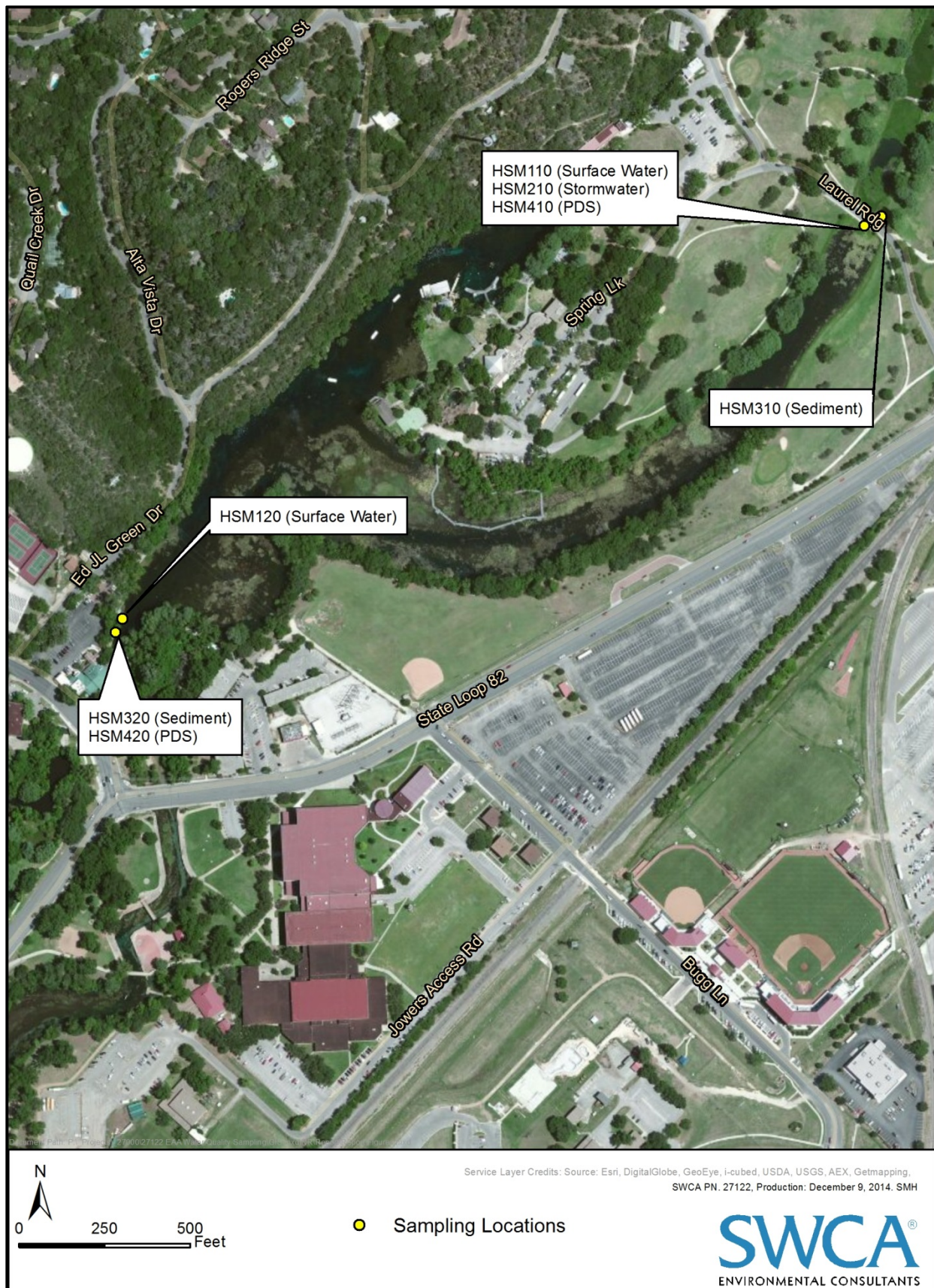


Figure 8. EAHCP San Marcos Springs detailed map indicating sample locations 130, 230, 330, 231, 140, 240, and 340.

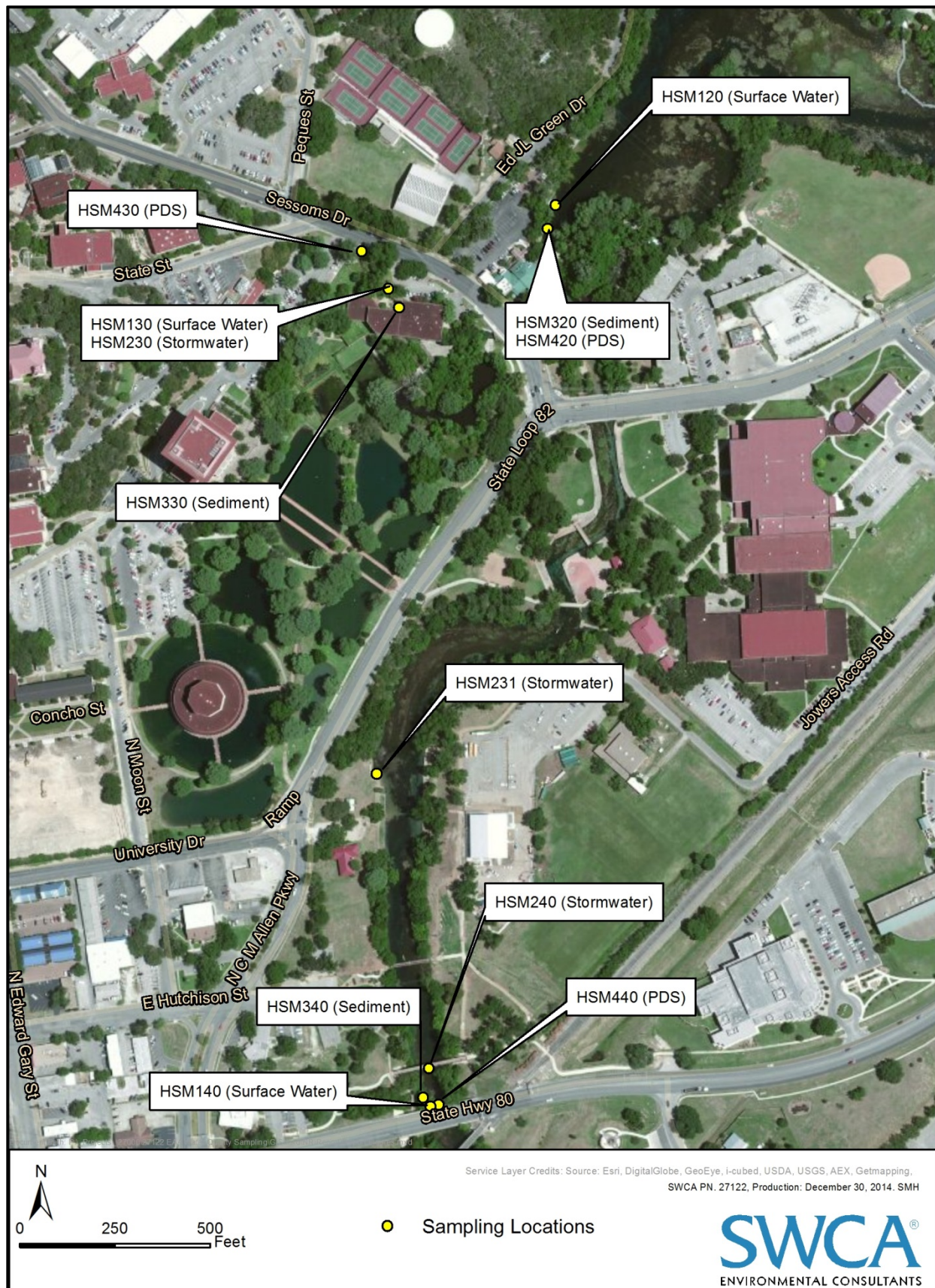


Figure 9. EAHCP San Marcos Springs detailed map indicating sample locations 150, 250, and 350.



Figure 10. EAHCP San Marcos Springs detailed indicating map sample locations 160, 260, 360, 170, 270, and 370.



3.0 MODIFICATIONS OF ACTIVITIES DUE TO DROUGHT

Sampling activities were affected by the ongoing drought conditions in the area. Since flow rates did not drop below 30 cfs at Comal Springs, or below 50 cfs at San Marcos Springs, no extreme low-flow sampling was initiated at water wells (Sections 6.4.3.3 and 6.4.4.3 of the Edwards Aquifer Habitat Conservation Plan). However, the ongoing drought made stormwater sampling exceedingly difficult to perform. Rain events were generally scattered in nature and often too small in magnitude to generate sufficient runoff to sample.

4.0 AFFECT ON COVERED SPECIES

The implementation of the EAHCP water quality and sediment sampling program provided baseline data along the Comal River and upper reaches of the San Marcos River system. Water quality grab samples were collected twice from each river during base flow conditions and during two storm events. Sediment samples were also collected from both systems. PDSs were used to evaluate trace organic compounds six times throughout the year.

The collection and analysis of water quality and sediment samples aids evaluation of the habitat of species by providing base flow, storm flow, and sediment quality data. The data included water quality discharging directly from the springs and water discharging into the Comal and San Marcos Rivers below the springs.

In Section 7, analytical results are compared to various water quality and sediment standards as guidelines to identify any existing problems and create a body of baseline data to ascertain any long-term sediment and water quality trends.

5.0 LOGISTICS

In order to accommodate the needs of the EAHCP's expanded water quality monitoring program, a significant number of person hours were required to obtain necessary equipment, construct deployment devices for the PDSs, and develop sampling strategies. Below is a short synopsis of events and tasks undertaken to accomplish the necessary logistics for the EAHCP sampling program.

5.1 Surface Water Sampling Program

On January 22, 2014, SWCA and EAA staff visited all sample locations at Comal and San Marcos Springs complexes to develop strategies for sample collection and identify appropriate parties to notify prior to sample events. In March and April 2014, SWCA staff purchased water quality sampling supplies for stormwater and surface water sample collection.

5.2 Sediment Sampling Program

In May 2014, SWCA staff purchased a Hand Core Sampler and other supplies necessary for collection of sediment samples.

5.3 Stormwater Program

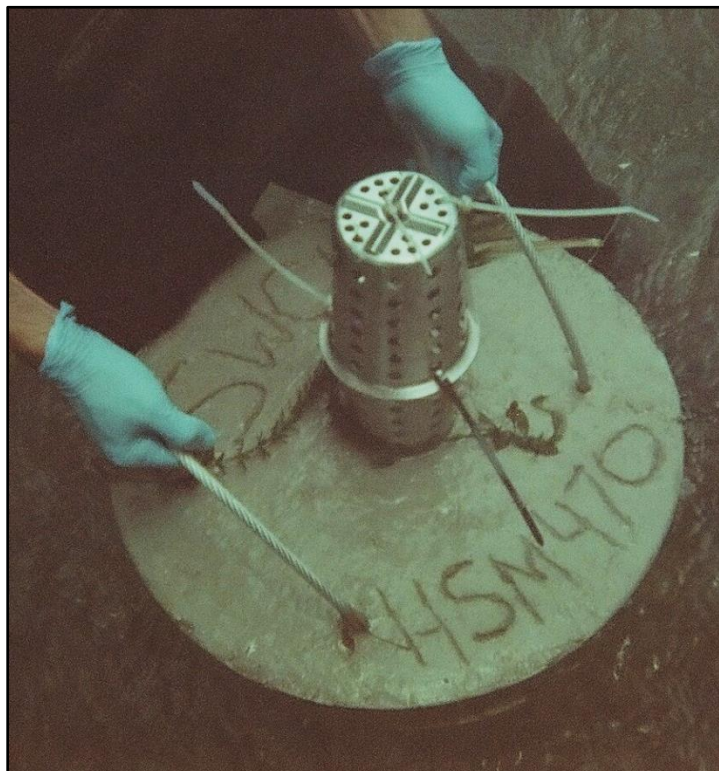
In March and April 2014, EAA field staff completed the procurement process for stormwater sampling equipment (such as life vests, rain suits, head lamps, throw ropes, strobe lights, first aid kits, and 24-foot telescopic retractable poles).

In May and June 2014, disposable bailers and dippers were acquired to eliminate the need for decontamination of reusable equipment. Subsequent stormwater sampling events used only new, disposable sampling equipment or samples were collected directly within bottles as opposed to using equipment.

5.4 Surface Water Passive Sampling Program

In June 2014, SWCA staff fabricated deployment devices for the PDSs. The majority of PDSs deployed in March and April were lost due to vandalism and/or being washed downstream. Therefore, prior to the June 2014 event, a more secure method of deployment was designed and constructed. The deployment device is pictured in Figure 11 and additional photographs are included in Appendix E. Each PDS deployment device consists of two stainless steel cups set within a 2-inch thick, 18-inch diameter, steel mesh reinforced, concrete slab. The PDS is attached to the top of one stainless steel cup with a plastic cable tie. The cup is then inverted and attached to the second stainless steel cup using plastic cable ties. The stainless steel cups have holes to allow water flow. Therefore, each PDS is enclosed within two cups, and one of the cups is set within the concrete slab. The concrete slab is equipped with steel cable handles that are used to set and retrieve the slabs within the stream at the sample locations.

Figure 11. PDS deployment device being retrieved from site HSM70.



6.0 SAMPLE COLLECTION METHODOLOGY

6.1 Surface Water / Base Flow Sampling Program

Surface water quality base flow grab samples were collected from five sites throughout the Comal Springs complex and seven sites throughout the San Marcos Springs complex biannually. According to the EAHCP workplan, the sample dates were to be six months apart. The preferred method for obtaining a surface water sample is to reach the sampling location from the shoreline or wade to the sample location, obtain field parameters (pH, specific conductivity, dissolved oxygen, and temperature) and then insert the sample bottle directly into the water or use a sample bottle and pole assembly. SWCA collected samples directly within sample bottles as opposed to using a pole assembly. Samples collected while wading were collected on the upstream side of the sampler. Samples were collected in accordance with the criteria set forth in the *EAA Groundwater Quality Monitoring Plan*.

Filtration for methods 6010B (metals), 6020 (metals), 7470A (mercury) and field alkalinity were performed at the sample location by using a 0.45-micron high capacity cartridge filter inserted into a weighted, pressurizable, single-sample disposable bailer. Preservatives were placed in the bottles (as appropriate) by the contracted laboratory. Ice was placed into the cooler prior to or immediately after sampling and later shipped to the contract laboratory. When not in use or after collection, sampling equipment and/or coolers containing samples were secured inside the SWCA vehicles to maintain appropriate sample custody and security.

The *EAA Groundwater Quality Monitoring Plan* required the collection of one field duplicate sample for each spring complex per sampling event. The field duplicate was sampled after the parent water quality sample and in the same manner as the parent water quality sample.

Analyses for field alkalinity for the fall sampling event were conducted at SWCA's San Antonio office or in a secure location in the field. Except where described in Appendix C, the method used for field alkalinity is discussed in detail in the *EAA Groundwater Quality Monitoring Plan* (Appendix D). Representative photographs of field activities are included in Appendix E.

6.2 Sediment Sampling Program

Sediment samples were collected once annually from the first 18 inches of sediment below the streambed surface at each of the twelve sampling locations. Sediment sample collection points generally coincided with the surface water collection points at each of the 12 sample locations in the spring complexes but varied slightly based on field conditions. Based on the amount of available sediment at each site, the location and area sampled varied. Sample collection location variations are discussed in Appendix C. Sediment sample collection methods were consistent with the guidelines established in the *EAA Groundwater Quality Monitoring Plan*. Samples were collected with a Hand Core Sampler consisting of a 2-inch-diameter, 20-inch-long stainless steel barrel with a plastic tube liner. Laboratory analytical requirements dictated that a total of approximately 150 grams of sediment were needed to have adequate volume for all analyses. After collection of adequate sample volume, tube ends were wrapped with Parafilm laboratory film and closed with end caps. Samples for VOC analyses were collected from the sample tubes at the contract laboratory, and the remaining samples were individually homogenized prior to remaining analyses.

In compliance with the *EAA Groundwater Quality Monitoring Plan* and consistent with the EAA practices of 2013, two field duplicates and one equipment blank were collected. One field duplicate sample is required for each spring complex. The field duplicates were collected at the same locations as two of the field samples using the same methods as the field samples. The equipment blank was collected in the laboratory of the SWCA San Antonio office. To collect the blank, ASTM Type II Reagent Grade water was poured through a new plastic sampling tube into sample collection containers. The sample was containerized in the same manner as a surface water sample using the same types of containers and preservatives. Sample portions for metals analyses requiring field filtration were filtered using a 0.45-micron high capacity cartridge filter and disposable bailer. The equipment blank was not analyzed for the following analytes: field parameters, turbidity, field alkalinity, and bacteria.

All samples were labeled and put on ice immediately upon collection for later shipment to the contract laboratory. Samples were secured inside locked SWCA vehicles during field operations and appropriate custody maintained at all times. Representative photographs of field activities are included in Appendix E.

6.3 Stormwater Sampling Program

Stormwater samples are designated by the EAHCP Workplan (Appendix A) for collection twice annually from each spring complex. Stormwater samples were collected when rainfall amounts were adequate to initiate at least a 5 percent rise at the respective USGS gauging locations for each spring complex. Samples were collected across the storm-affected stream hydrograph at the rise, peak, and recession limb of the associated stream hydrograph. As with the other sample types, five locations at Comal Springs and seven locations at San Marcos Springs were sampled. In general, the turbidity and conductivity data from the RTIs at each site were used as a surrogate for the stream hydrograph due to immediate availability of the data. Graphs showing water quality parameters during each storm event are included in Appendix B.

Stormwater sample collection was affected by the ongoing drought conditions across the region. Often, storms that materialized were insufficient to create adequate runoff for sample collection. As a result, members of the stormwater sampling team spent many more hours on-call than were expected. In general, when rainfall probabilities exceeded 20 percent for a given time period, the team was placed on-call for sample collection. The team was mobilized when rainfall probabilities exceeded 50 percent. Multiple scenarios involved a mobilization that was later cancelled due to insufficient rainfall or storms that dissipated prior to reaching the sample area. Storm team duty is summarized and documented in Appendix F of this document.

Due to the inherently unsafe conditions associated with stormwater flow, SWCA field staff used a retractable pole, beta sampler, or disposable single-use bailers when needed in order to safely obtain water samples during stormwater sampling events. Field parameters were collected first by inserting the sonde probe as close to the sample location as possible. At HSM230 during the May storm event debris blocked access to the sample site, SWCA field staff used the telescopic retractable pole to retrieve the sample for the Lead and Peak sample points. A 500 mL Teflon® beaker attached to a stainless steel swivel at the end of the sampling pole was inserted into the water to collect the sample. After collecting each sample, water was transferred from the beaker into the appropriate sample bottle. In May 2014, HSM240 was accessed using a beta sampler lowered from a bridge for the Lead and Peak samples. The

beta sampler consists of an acrylic tube lowered into the water to collect samples. After retrieval, the water was transferred to the sample containers. In July 2014, HSM240 was sampled using disposable bailers. Bailers were lowered from the bridge above the sample location. A rope affixed to the bailer was used for retrieval. New bailers and rope were used for each sample point. After retrieval the water was transferred to the sample containers. Only new disposable equipment was used for sampling during the July 2014 storm event in San Marcos Springs and the September and November sampling events in Comal Springs.

Stormwater sampling efforts conformed to the protocols outlined in the *EAA Groundwater Quality Monitoring Plan* for sample collection, handling, and decontamination. Filtration for methods 6010B (metals), 6020 (metals), and field alkalinity were performed using a 0.45-micron high capacity cartridge filter and peristaltic pump. Preservatives were placed in the bottles (as needed) by the contract laboratory prior to sample collection. All samples were immediately placed into coolers with ice after sampling and later shipped to the contract laboratory. When not in use or after collection, sampling equipment and/or coolers containing samples were secured inside locked SWCA vehicles to maintain appropriate sample custody and security.

According to the *EAA Groundwater Quality Monitoring Plan*, two field duplicates were collected for the Comal Springs complex and three field duplicates for the San Marcos Springs complex per rain event. Field duplicates were sampled after collection of the parent sample and in the same manner as the field sample. However, due to a field oversight, no field duplicates were collected during the first storm event on May 12, 2014, in the San Marcos Springs complex.

According to the *EAA Groundwater Quality Monitoring Plan*, one equipment blank was sampled for each piece of reusable equipment used per rain event. The equipment blanks were sampled after the lead parent samples were collected. Equipment blanks were collected from the collection pole and beta sampler on May 13, 2014, at the San Marcos Nature Center, for the associated San Marcos Springs rain event. An additional sample of the distilled water used for decontamination was also collected for this event. Equipment blanks were obtained by filling the collection equipment with distilled water which was then carefully poured into sample bottles in the same manner as a field sample. Equipment blanks were not performed for the following analytes: field parameters, turbidity, field alkalinity, and bacteria. For all subsequent stormwater sampling events, only single-use disposable equipment was utilized making decontamination and equipment blanks unnecessary. Analyses for field alkalinity were performed at the field staging area or at the SWCA San Antonio office. The method used for field alkalinity is discussed in detail in the *EAA Groundwater Quality Monitoring Plan*. Representative photographs of field activities are included in Appendix E.

6.4 Surface Water Passive Samplers

The PDSs were deployed at each of the twelve sample locations during the months of March, April, June, August, October, and December 2014. In general, PDS locations corresponded to surface water sampling points unless prevented by field conditions. The majority of PDSs deployed in March and April 2014 were lost due to vandalism and/or being washed downstream. Therefore, prior to the June event, a more secure method of deployment was designed and constructed. Lost PDSs, human tampering and any variations in deployment locations are discussed in Appendix C.

Deployment devices were constructed by SWCA staff at the SWCA San Antonio office in June 2014. Two-inch thick, 18-inch diameter, concrete disks were poured and a stainless steel silverware cup was set approximately one inch deep in the center of the disk. Handles were formed by inserting both ends of an 18-inch length of vinyl-coated stainless steel cable into each side of the disk. Site numbers were marked in the wet concrete to dedicate each device to a sample location. The concrete was allowed to cure, and each device was decontaminated following the *EAA Groundwater Quality Monitoring Plan* guidelines and placed in a clean plastic bag prior to the first deployment. The same decontamination procedures were followed for subsequent sampling events.

Upon arrival at the sample location, the PDS was removed from a dedicated vial and affixed inside of a second stainless steel silverware cup with a plastic cable tie. This cup was inverted and placed on top of the cup set in the concrete sampling device enclosing the PDS inside the two cups. The two cups were secured to one another with additional plastic cable ties. The device was then gently lowered into the water. Installation date and time and PDS identification numbers were noted in the field notebook and on the PDS vial. To retrieve the PDS, the devices were simply removed from the water and the cable ties cut. The PDS was then immediately placed back in the vial dedicated for that PDS and retrieval date and time were notated. Deployment devices were secured at SWCA offices when PDSs were not deployed.

Field duplicates were collected as directed by the *EAA Groundwater Quality Monitoring Plan*. To collect field duplicates, a second PDS was installed inside selected deployment devices. Field PDSs were always accompanied by test blank samplers to monitor for VOC contamination. Deployment devices were dedicated to each sample location to avoid cross contamination and were decontaminated following the *EAA Groundwater Quality Monitoring Plan* guidelines prior to each use. Representative photographs of field activities are included in Appendix E.

7.0 SAMPLE RESULTS

Results from the sampling efforts related to the EAHCP sampling program are discussed in the paragraphs that follow. Results are discussed by sample type for Comal Springs, followed by a separate discussion by sample type for San Marcos Springs. Sample events are listed in the order of surface water (base flow) samples, sediment samples, stormwater samples, and PDS. A complete record of laboratory analyses and field parameters is provided in Appendix G of this document. The laboratory data were reviewed by SWCA staff with the results of that review provided as Appendix H (data validation discussion) of this document. Each sample location (latitude/longitude), name, and other location information is also summarized in Appendix I of this document.

7.1 Comal Springs Sample Results

The Comal Springs complex was sampled for water quality during surface water base flow conditions in March and September 2014. In general, few detections were noted. As discussed previously, surface water base flow samples are compared to the drinking water standards for water quality in this report.

Sediments at the Comal Springs complex were sampled in June 2014. Sediment results are compared to the standards developed by McDonald et al. (2000) and TCEQ (2012). These standards are based on the probability of a detected compound having a toxic effect on sediment-dwelling organisms and are referred to as the TEC and PEC. Detections below the TEC are not considered to be toxic, while detections above

the PEC are considered to be toxic to sediment dwelling organisms. Detections above the TEC but less than the PEC are considered to be equally likely to be toxic or non-toxic.

Stormwater events were sampled at the Comal Springs complex in September and November 2014. Stormwater results did not indicate a significant number of detections of concern.

7.1.1 Comal Springs Surface Water / Base Flow Sampling

The Comal Springs complex was sampled on March 25 and September 25–26, 2014, for surface water (base flow) events. Resampling for metals and nitrate analyses also occurred on April 29, 2014, due to a problem with the filtration and preservation of metals and nitrate samples; the decision was made to completely resample for these analyses to ensure the validity of the data.

7.1.1.1 Surface Water / Base Flow - Bacteria

Bacteria results for surface water (base flow) associated with the Comal Springs complex ranged from 25.9 MPN/100 mL (most probable number of colony-forming units per 100 milliliters of water) through 579 MPN/100 mL for *E. coli*. Because of the presence of various fauna in surface water collection sites, positive detections are not uncommon. The 2014 Texas Surface Water Quality Standard for *E. coli* in primary recreation waters is a geometric mean of 126 MPN/100 mL with no individual sample exceeding 399 MPN/100 mL (30 TAC 307.7). The geometric mean for surface water samples collected from the Comal Springs complex during 2014 was 139 MPN/100 mL. Two samples exceeded the maximum limit of 399 MPN/100 mL. HCS110, sampled in March 2014, had a concentration of 579 MPN/mL and HCS120, sampled in September 2014, had a concentration of 470 MPN/mL. Surface water (base flow) bacteria counts are summarized in Table 2. A field duplicate was not collected in the Comal Springs complex during sampling on March 25, 2014, as discussed in Appendix C.

Table 2. Surface Water Samples – Bacteria Counts – Comal Springs Complex

Location	Date	Count (MPN/100 mL)
HCS110	3/25/2014	579H
	9/25/2014	46
HCS120	3/25/2014	25.9
	9/25/2014	470
HCS130	3/25/2014	40.2
	9/26/2014	270
HCS140	3/25/2014	56.5
	9/25/2014	260
FDHCS140	3/25/2014	NA
	9/25/2014	290
HCS160	3/25/2014	74.3
	9/26/2014	330

H – Analyzed outside hold time, result included for comparison but not considered valid

MPN/100 mL – Most probable number per 100 milliliters of water.

NA – Not analyzed

7.1.1.2 Surface Water / Base Flow - Volatile Organic Compounds (VOCs)

No VOCs were detected at any of the five sampling sites from the Comal Springs complex during the March or September 2014 sampling events. However, there was a detection of VOCs in the VOC Trip Blank during the September sampling event. The Trip Blank tested positive for 0.65 micrograms per liter (µg/L) 1,2-dichloroethane and 1.6 µg/L toluene, which were not detected in any field samples.

7.1.1.3 Surface Water / Base Flow - Semi-volatile Organic Compounds (SVOCs)

Generally, Semi-volatile Organic Compounds (SVOCs) were analyzed because their detection can indicate the presence of chemicals originating from anthropogenic sources, and therefore, be used to evaluate potential impacts on water quality. There were no SVOC detections at any of the five sampling sites in the Comal Springs complex during the March or September 2014 sampling events.

7.1.1.4 Surface Water / Base Flow - Pesticides

Surface water samples were analyzed for pesticides because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, be used to evaluate potential impacts on

water quality. No pesticides were detected in any of the samples collected for either the March or September 2014 sampling events at all five sites for the Comal Springs complex.

7.1.1.5 Surface Water / Base Flow - Herbicides

Surface water samples were analyzed for herbicides because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, be used to evaluate potential impacts on water quality. Herbicide analyses indicated no detections for both the March and September 2014 sampling events at all five sites for the Comal Springs complex.

7.1.1.6 Surface Water / Base Flow - Polychlorinated Biphenyls (PCBs)

Surface water samples were analyzed for the various Aroclor compounds that are collectively referred to as Polychlorinated Biphenyls (PCBs) because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, be used to evaluate potential impacts on water quality. PCB analyses were non-detect for both the March and September 2014 sampling events at all five sites for the Comal Springs complex.

7.1.1.7 Surface Water / Base flow - Metals

Surface water samples were analyzed for metals because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, be used to evaluate potential impacts on water quality. Although metals were detected for the April and September 2014 sampling events at all five sites for the Comal Springs complex, no metals of concern at a concentration in excess of the drinking water standards were noted. The metals aluminum, arsenic, barium, chromium, copper, iron, lead, manganese, nickel, selenium, and zinc were the detected metals of concern; however, none of the concentrations approached the MCL. These detections are listed below in Table 3, note many detections are “J” flagged, indicating the detected concentration is below the laboratory reporting limit, but above the method detection limit. Also note that some metals are naturally occurring in rock, soil, groundwater, and surface water and may not indicate an anthropogenic source. Samples from April 2014 were not analyzed for manganese due to an oversight in the field as discussed in Appendix C.

Table 3. Surface Water Samples – Metal detections - Comal Springs Complex

Location	Date Collected	Arsenic (mg/L)	Barium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Lead (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Zinc (mg/L)	Aluminum (mg/L)	Iron (mg/L)	Manganese (mg/L)
HCS110	4/29/2014	<0.000386	0.0720	<0.000402	<0.000140	<0.0000898	0.00135	<0.000168	0.0977	<0.00331	0.0543	NA
	9/25/2014	0.000395J	0.0526	0.000585J	0.000323J	<0.0000898	0.00300	0.000189J	0.0340	0.00611J	0.0746	0.00140
HCS120	4/29/2014	<0.000386	0.0536	0.00110	<0.000140	<0.0000898	0.00153	<0.000168	0.00852	<0.00331	<0.00926	NA
	9/25/2014	<0.000386	0.0508	0.00125	0.000965J	<0.0000898	0.00360	0.000390J	0.00809	0.00577J	0.0750	0.000615J
HCS130	4/29/2014	<0.000386	0.0569	<0.000402	<0.000140	<0.0000898	0.00125	<0.000168	0.0370	<0.00331	0.0585	NA
	9/26/2014	0.000530J	0.0550	0.000698J	0.000522J	<0.0000898	0.00336	0.000432J	0.0131	0.00810J	0.0829	0.00159
HCS140	4/29/2014	<0.000386	0.0556	<0.000402	<0.000140	<0.0000898	0.00125	<0.000168	0.0357	<0.00331	<0.00926	NA
	9/25/2014	<0.000386	0.0565	0.000474J	0.000510J	<0.0000898	0.00332	0.000438J	0.0117	0.00601J	0.0889	0.00140
FDHCS140	9/25/2014	<0.000386	0.0562	0.000491J	0.000482J	0.000103J	0.00327	0.000339J	0.0124	0.00567J	0.0649	0.000975J
HCS160	4/29/2014	<0.000386	0.0560	<0.000402	<0.000140	<0.0000898	0.00132	<0.000168	0.0372	<0.00331	<0.00926	NA
	9/26/2014	0.000406J	0.059200	0.000794J	0.0008202J	<0.0000898	0.00358	0.000458J	0.00413J	0.00813J	0.0988	0.00224
MCL		0.010	2	0.1	NE	NE	NE	0.05	NE	NE	NE	NE
PCL		--	--	--	1.3	0.015	0.49	--	7.3	24	NE	1.1

J – Detection is above the method detection limit, but below the reporting limit

mg/L – milligrams per Liter

NA – Not analyzed

NE – Not established

-- – Not applicable

7.1.1.8 Surface Water / Base Flow - Nitrates

Surface water samples were analyzed for nitrate-nitrite as nitrogen. Laboratory analyses indicated a limited range of nitrate-nitrite as nitrogen in surface water samples. Of the 11 surface water samples (ten environmental samples and one field duplicate) collected for the two sample events, concentrations ranged from 0.11 milligrams per liter (mg/L) to 1.7 mg/L. None of the nitrate concentrations detected exceeded the MCL of 10 mg/L for drinking water. The highest nitrate concentration in surface water at the Comal Springs complex was 1.7 mg/L from HCS130 sampled on September 26, 2014; however, this sample did exceed the laboratory hold time. The laboratory hold time was exceeded for two samples for nitrate because samples were collected on a Friday afternoon at the same time a storm was approaching. The samples were held at the SWCA office until Monday morning due to limited shipping options and laboratory receiving hours available on the weekend. The samples contained the proper preservatives and were kept on ice during this time. This issue is discussed further in Appendix C. Nitrate-nitrogen results are summarized in Table 4.

**Table 4. Surface Water Samples – Nitrate Detections
- Comal Springs Complex**

Location	Date	Concentration (mg/L)
HCS110	4/29/2014	0.11
	9/25/2014	0.43
HCS120	4/29/2014	1.6
	9/25/2014	1.6
HCS130	4/29/2014	1.6
	9/26/2014	1.7H
HCS140	4/29/2014	1.5
	9/25/2014	1.6
FDHCS140	9/25/2014	1.6
HCS160	4/29/2014	1.6
	9/26/2014	1.6H

H – Analyzed outside hold time, result included for comparison but not considered valid
mg/L – milligrams per liter

7.1.1.9 Surface Water / Base Flow – Caffeine

Surface water base flows were analyzed for caffeine. PPCPs like caffeine can indicate an anthropogenic source of impacts. Caffeine may enter the system directly into surface water or it may be present in the aquifer from sources in the recharge zone (EPA 2012). Potential ecological effects are currently unknown but could include reduced reproductive success (EPA 2012). Caffeine detections in surface water samples from Comal Springs in 2014 ranged from 2.5 nanograms per liter (ng/L) to 66 ng/L. There is no regulatory standard or expected value for comparison. Results are shown in Table 5. A field duplicate was collected at site HCS130 in March 2014 and at HCS140 in September 2014.

Table 5. Surface Water Samples – Caffeine Detections - Comal Springs Complex

Location	Date Collected	Caffeine (ng/L)
HCS110	3/25/2014	2.5
	9/25/2014	30
HCS130	3/25/2014	66
	9/26/2014	31
HCS160	3/25/2014	< 2.0
	9/26/2014	33

ng/L – nanograms per liter

7.1.2 Comal Springs Sediment Sampling

7.1.2.1 Sediment - Volatile Organic Compounds (VOCs)

No VOCs were detected in any of the sediment samples collected at Comal Springs during 2014.

7.1.2.2 Sediment - Semi-volatile Organic Compounds (SVOCs)

All SVOC detections in the Comal system were polycyclic aromatic hydrocarbons (PAH) compounds found at two locations. These detections are listed in Table 6 comparing the individual and total PAH concentrations to the TEC and PEC values of MacDonald et al. (2000) and TCEQ (2012). PAH detections are shown below in Figure 12, where the total PAH concentrations are compared to the total TEC and PEC values.

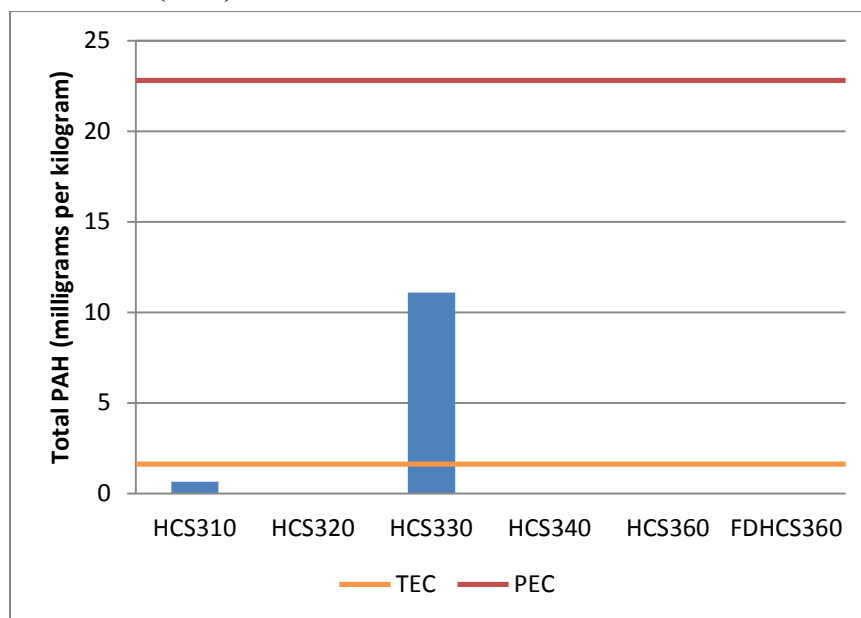
Table 6. Sediment Samples - Semi-volatile Organic Compounds Detections - Comal Springs Complex

Location	Date Collected	Benzo (a) Anthracene (mg/kg)	Benzo (a) Pyrene (mg/kg)	Benzo (b) Fluoranthene (mg/kg)	Benzo (k) Fluoranthene (mg/kg)	Chrysene (mg/kg)	Fluoranthene (mg/kg)	Phenanthrene (mg/kg)	Pyrene (mg/kg)	Total PAH (mg/kg)
HCS310	6/26/2014	<0.19	<0.085	<0.084	<0.11	<0.094	0.65	<0.12	<0.10	0.65
HCS330	6/25/2014	1.1	1.0	1.1	0.88	1.1	3.0	1.1	1.8	11.08
TEC		0.108	0.15	NE	NE	0.166	0.423	0.204	0.195	1.61
PEC		1.05	1.45	NE	NE	1.29	2.23	1.17	1.52	22.8

mg/kg – milligrams per kilogram

NE – Not established

Figure 12. Comal Springs Sediment Polycyclic Aromatic Hydrocarbons Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values



7.1.2.3 Sediment - Pesticides

Sediment samples were analyzed for both organochlorine and organophosphorous pesticides. Due to the persistence of certain pesticide compounds, their detection in sediment is not unusual. However, there were no pesticide detections in any of the sediment samples collected in the Comal Springs complex.

7.1.2.4 Sediment - Herbicides

Sediments were analyzed for herbicide compounds to further assess sediment quality at the Comal Springs complex. No herbicides were detected in any of the sediment samples collected from the Comal Springs complex using analysis method SW 8151A.

7.1.2.5 Sediment - Polychlorinated Biphenyls

Sediments were analyzed for PCB compounds to further assess sediment quality at the Comal Springs complex. No PCB compounds were detected in any of the sediment samples collected from the Comal Springs complex.

7.1.2.6 Sediment - Metals

Sediment samples are generally expected to exhibit higher concentrations of metals (and other compounds) than water samples. Many metals are naturally occurring within soil, rock, and sediment. Sediment sample results for metals at the Comal Springs complex tested positive for several metals, generally at low concentrations. Metals detected above the method detection limit and subsequently evaluated in this report for potential toxic effects using the TEC and/or PEC standards are: arsenic, chromium, copper, iron, lead, manganese nickel, silver, and zinc. Other metals detected that do not have a TEC or PEC value available are: aluminum, barium, and beryllium. These metals (aluminum, barium, and beryllium) were compared to Texas-specific background concentrations (TSBC) (TSBC 2014) for soil. None of these exceeded the listed background concentration.

Lead exceeded the TEC for the field duplicate collected at FDHCS360, and zinc exceeded the TEC at HCS310. Metal detections are listed in Table 7 below. Metals with detections above an established TEC value are displayed graphically in Figures 12 and 13 for lead and zinc, respectively. No metals were detected above a PEC.

Table 7. Sediment Samples – Metal Detections - Comal Springs Complex

Location	Date Collected	Arsenic (mg/kg)	Barium (mg/kg)	Beryllium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Nickel (mg/kg)	Silver (mg/kg)	Zinc (mg/kg)	Aluminum (mg/kg)	Iron (mg/kg)	Manganese (mg/kg)
HCS310	6/26/2014	<0.259	20.5	<0.137	4.12	9.21	6.43	3.07	0.328	228	1940	2120	22.3
HCS320	6/26/2014	<0.259	46.3	<0.137	11.4	10.1	13.3	9.29	0.704	50.5	5750	5720	44.4
HCS330	6/25/2014	<0.259	43.4	0.558	11.1	8.89	11.5	7.99	<0.0857	21.8	7800	7940	121
HCS340	6/25/2014	1.54	36.5	<0.137	8.24	11.8	9.57	6.30	0.531	19.3	3190	6190	63.0
HCS360	6/25/2014	<0.259	54.0	0.570	11.7	14.2	23.7	8.47	<0.0857	60.4	6620	6290	120
FDHCS360	6/25/2014	<0.259	68.2	0.715	14.5	14.8	38.3	10.7	0.630	71.6	7890	8040	148
TEC		9.79	NE	NE	43.4	31.6	35.8	22.7	NE	121	NE	NE	NE
PEC		33	NE	NE	111	149	128	48.6	2.2	459	NE	40000	1100
Soil background level		5.9	300	1.5	30	15	15	10	NE	30	30000	15000	300

mg/kg – milligram per kilogram

NE – Not established

Figure 13. Lead in Comal Springs Complex Sediments Compared to the Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values

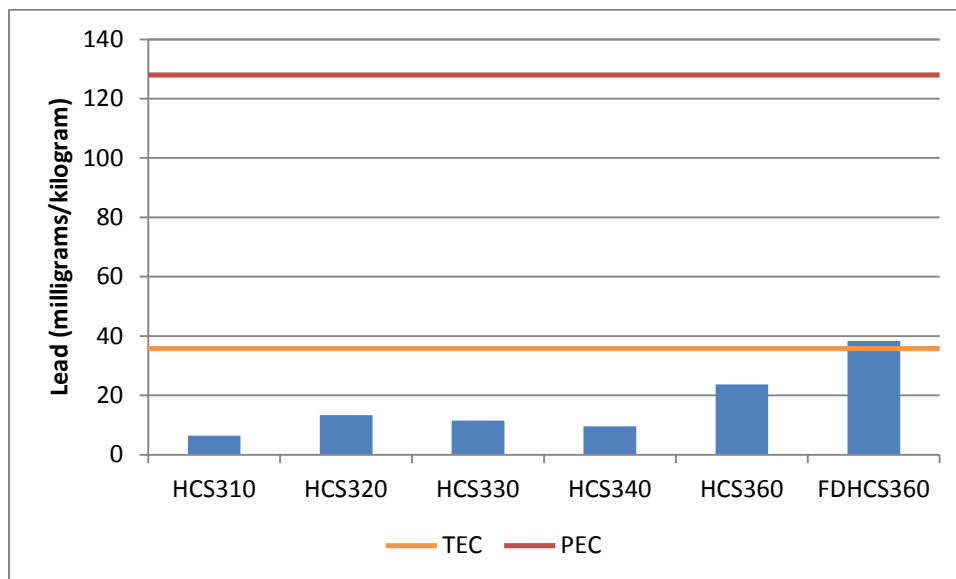
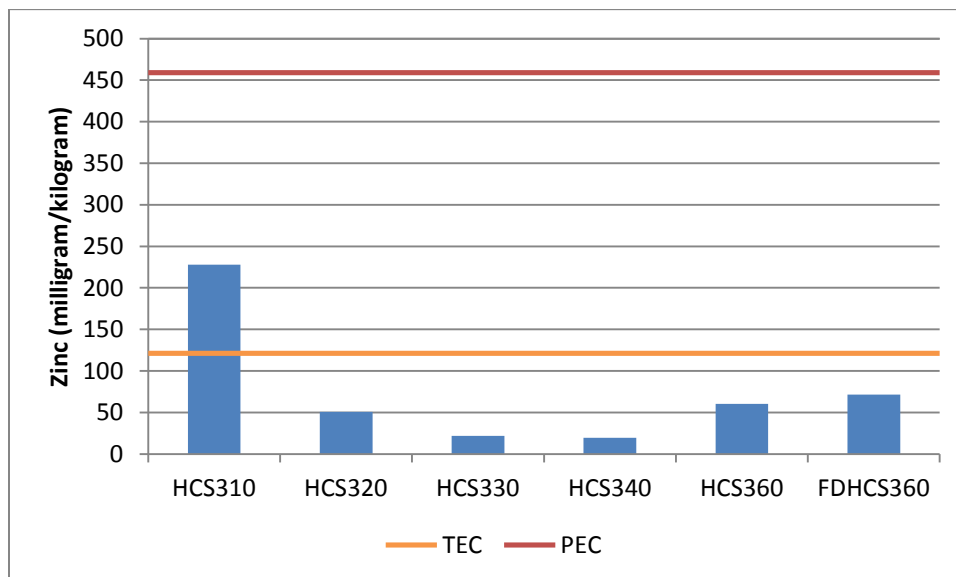


Figure 14. Zinc in Comal Springs Complex Sediments Compared to the Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values



7.1.3 Comal Springs Stormwater Sampling

Stormwater samples were collected during two storm events at the Comal Springs complex. The events were sampled according to the guidelines in the EAHCP workplan. The events occurred on September 26, 2014, and November 4, 2014. Total rainfall for the September 2014 event was approximately 0.75 to 1.0 inches (NOAA 2014) causing streamflow measured at USGS Gauge 08169000 to increase from approximately 84 cfs to a peak of 101 cfs (USGS 2014). The second event occurred on November 4, 2014, with approximately 2–3 inches of rainfall (NOAA 2014) and increase in streamflow from 91 cfs to 151 cfs (USGS 2014).

7.1.3.1 Stormwater - Bacteria Detections

Stormwater samples collected and analyzed for bacteria analyses generally tested positive for high levels of bacteria. Bacterial analyses were performed for *E. coli*, using a most probable number method. The 2014 Texas Surface Water Quality Standard for *E. coli* in primary recreation waters is a geometric mean of 126 MPN/100 mL with no individual sample exceeding 399 MPN/100 mL (30 TAC 307.7). The geometric mean for stormwater samples collected from the Comal Springs complex during 2014 was 1396 MPN/100 mL. Bacteria counts ranged from 150 MPN/100 mL to 5500 MPN/100 mL with several samples exceeding the individual sample limit. Individual detections are listed below in Table 8. Due to the timing of storm events and laboratory working hours, it was not possible to deliver all samples to the laboratory within sample holding times, as discussed in Appendix C. These samples were included in the range and geometric mean calculations. However, the standards were still exceeded even if samples exceeding hold times were not included in calculation of mean values.

Table 8. Stormwater Samples – Bacteria Counts - Comal Springs Complex

Location	Date	Count (MPN/100 mL)
HCS210 Lead	9/26/2014	1600H
	11/4/2014	730H
HCS210 Peak	9/26/2014	570H
	11/5/2014	1100H
HCS210 Trail	9/27/2014	150
	11/5/2014	2400
HCS240 Lead	9/26/2014	1200H
	11/4/2014	1200H
HCS240 Peak	9/26/2014	750H
	11/5/2014	1200H
HCS240 Trail	9/27/2014	490
	11/5/2014	1300

Location	Date	Count (MPN/100 mL)
HCS250 Lead	9/26/2014	2000H
	11/4/2014	2400H
HCS250 Peak	9/26/2014	1500H
	11/5/2014	1000H
HCS250 Trail	9/27/2014	640
	11/5/2014	1100
HCS260 Lead	9/26/2014	710H
	11/4/2014	1400H
HCS260 Peak	9/26/2014	4600H
	11/5/2014	870H
HCS260 Trail	9/27/2014	3300
	11/5/2014	510
FDHCS260 Trail	9/27/2014	3700
	11/5/2014	1100
HCS270 Lead	9/26/2014	1000H
	11/4/2014	1700H
HCS270 Peak	9/26/2014	3700H
	11/5/2014	610H
HCS270 Trail	9/27/2014	3100
	11/5/2014	980
FDHCS270 Trail	9/27/2014	5500
	11/5/2014	650

H – Analyzed outside hold time, result included for comparison but not considered valid

MPN/100 mL – Most probable number per 100 milliliters of water

7.1.3.2 Stormwater - Volatile Organic Compounds (VOCs)

There were no VOC detections in the field samples for the September 2014 rain event in Comal Springs. There were, however, two positive detections in the Trip Blank: 0.34 µg/L 1,2-dichloroethane and 0.38 µg/L toluene. These detections were well below the established MCLs for drinking water and were not detected in the associated field samples.

Four compounds were detected during the November sampling event. All detections but one were below the reporting limit for the analysis method and all were well below the established MCLs. Results are shown in Table 9.

Table 9. Stormwater Samples – Volatile Organic Compound Detections - Comal Springs Complex

Location	Date Collected	Acetone (µg/L)	1,2-Dichloroethane (µg/L)	Toluene (µg/L)	Vinyl Chloride (µg/L)
HCS210 Lead	11/4/2014	17J	<0.24	<0.24	<0.30
HCS210 Peak	11/5/2014	10J	<0.24	<0.24	<0.30
HCS240 Lead	11/4/2014	<10	<0.24	<0.24	0.40J
HCS240 Peak	11/5/2014	<10	<0.24	<0.24	<0.30
HCS250 Lead	11/4/2014	<10	<0.24	<0.24	0.36J
HCS250 Peak	11/5/2014	10J	<0.24	<0.24	<0.30
HCS270 Trail	11/5/2014	<10	0.84	0.77J	<0.30
MCL		NE	5	1000	2
PCL		27997.8	5	--	--

J – Detection is above the method detection limit, but below the reporting limit

µg/L – milligrams per Liter

NE – Not established

-- – Not applicable

7.1.3.3 Stormwater - Semi-volatile Organic Compounds (SVOCs)

Stormwater samples collected during September and November 2014 were analyzed for SVOCs and were generally non-detect for these compounds, with the exception of one sample which tested positive for three SVOC compounds. These detections are all below the laboratory reporting limit and the established drinking water PCL for each compound. The results are shown in Table 10.

Table 10. Stormwater Samples – Semi-volatile Organic Compound Detections - Comal Springs Complex

Location	Date Collected	2-Methylnaphthalene (µg/L)	1-Methylnaphthalene (µg/L)	Naphthalene (µg/L)
HCS260 Peak	9/26/2014	8.3J	4.9J	8.7J
MCL		NE	NE	NE
PCL		97.8	1710.9	488.8

J – Detection is above the method detection limit, but below the reporting limit

µg/L – milligrams per Liter

NE – Not established

7.1.3.4 Stormwater - Herbicides and Pesticides

There were no herbicide or organophosphorous pesticide detections for the storm events in the Comal Springs Complex sampled during September and November 2014. There were two positive detections of the organochlorine pesticide, Beta-BHC, during the November event. The compound was detected at HCS270 in the Trail and Trail Field Duplicate samples at 0.1 µg/L and 0.039J µg/L respectively. These detections are both below the established PCL of 0.5 µg/L. Beta-BHC was not detected during the September 2014 storm event at any of the five locations in the Comal Springs complex.

7.1.3.5 Stormwater - Polychlorinated Biphenyls (PCBs)

Stormwater samples were analyzed for the various Aroclor compounds that are generally referred to collectively as PCBs. None of the stormwater samples from the Comal Springs complex indicated positive detections of PCBs compounds during the September and November sampling events.

7.1.3.6 Stormwater - Metals

Stormwater samples were analyzed for metals in accordance with the EAHCP workplan. Several positive metal detections were noted in the sample set; however, no samples contained a metal at a concentration in excess of the drinking water MCL and most detections were below laboratory reporting limits.

7.1.3.7 Stormwater - Nitrates

Stormwater samples were analyzed for nitrate-nitrite as nitrogen in accordance with the EAHCP workplan. All nitrate results were below the MCL of 10 mg/L. The range of nitrate results was 0.36 mg/L to 1.9 mg/L in the sample set. The nitrate values in stormwater for both sample events averaged 1.4 mg/L, whereas the average nitrate in spring water samples at Comal Springs for calendar 2013 was 1.92 mg/L (EAA 2014). Nitrate analysis was unavailable for HCS210 Peak on September 26, 2014, because the sample was lost by the courier during shipment to the laboratory. Due to the timing of the September 26, 2014, storm event it was not possible to ship the samples to the laboratory immediately and the hold time was exceeded for nitrate samples. These deviations to the workplan are discussed in Appendix C. Nitrate results are summarized in Table 11.

Table 11. Stormwater Samples – Nitrate Detections - Comal Springs Complex

Location	Date	Concentration (mg/L)
HCS210 Lead	9/26/2014	0.58H
	11/4/2014	1.1
HCS210 Peak	9/26/2014	NA
	11/5/2014	0.36
HCS210 Trail	9/27/2014	0.46H
	11/5/2014	0.45
HCS240 Lead	9/26/2014	1.7H
	11/4/2014	1.9
HCS240 Peak	9/26/2014	1.7H
	11/5/2014	1.9
HCS240 Trail	9/27/2014	1.7H
	11/5/2014	1.8
HCS250 Lead	9/26/2014	1.4H
	11/4/2014	1.5
HCS250 Peak	9/26/2014	1.6H
	11/5/2014	1.6
HCS250 Trail	9/27/2014	1.7H
	11/5/2014	1.8
HCS260 Lead	9/26/2014	1.6H
	11/4/2014	1.7

Location	Date	Concentration (mg/L)
HCS260 Peak	9/26/2014	1.2H
	11/5/2014	1.2
HCS260 Trail	9/27/2014	1.4H
	11/5/2014	1.5
FDHCS260 Trail	9/27/2014	1.4H
	11/5/2014	1.4
HCS270 Lead	9/26/2014	1.6H
	11/4/2014	1.6
HCS270 Peak	9/26/2014	1.5H
	11/5/2014	1.5
HCS270 Trail	9/27/2014	1.4H
	11/5/2014	1.2
FDHCS270 Trail	9/27/2014	1.4H
	11/5/2014	1.2

H – Analyzed outside hold time, result included for comparison but not considered valid

mg/L – milligrams per liter

NA – Not Analyzed

7.1.3.8 Stormwater – Caffeine

Stormwater was analyzed for caffeine. PPCPs like caffeine can indicate an anthropogenic source of impacts. Caffeine may enter the system directly into surface water or it may be present in the aquifer from sources in the recharge zone (EPA 2012). Potential ecological effects are currently unknown but could include reduced reproductive success (EPA 2012). Caffeine detections in stormwater samples from Comal Springs in 2014 ranged from 13 ng/L to 600 ng/L. There is no regulatory standard or expected value for comparison. These results are shown in Table 12. The stormwater sample collected from HCS210 Peak was not analyzed for caffeine as it was lost in transit to the laboratory as discussed in Appendix C.

**Table 12. Stormwater Samples – Caffeine Detections
- Comal Springs Complex**

Location	Date Collected	Caffeine (ng/L)
HCS210 Lead	9/26/2014	140
	11/4/2014	510
HCS210 Peak	9/26/2014	NA
	11/5/2014	77
HCS210 Trail	9/27/2014	51
	11/5/2014	89
HCS240 Lead	9/26/2014	40
	11/4/2014	45
HCS240 Peak	9/26/2014	28
	11/5/2014	13
HCS240 Trail	9/27/2014	13
	11/5/2014	14
HCS250 Lead	9/26/2014	310
	11/4/2014	230
HCS250 Peak	9/26/2014	160
	11/5/2014	56
HCS250 Trail	9/27/2014	13
	11/5/2014	38
HCS260 Lead	9/26/2014	75
	11/4/2014	85
HCS260 Peak	9/26/2014	240
	11/5/2014	290
HCS260 Trail	9/27/2014	120
	11/5/2014	98
FDHCS260 Trail	9/27/2014	130
	11/5/2014	81
HCS270 Lead	9/26/2014	30

Location	Date Collected	Caffeine (ng/L)
	11/4/2014	25
HCS270 Peak	9/26/2014	220
	11/5/2014	95
HCS270 Trail	9/27/2014	120
	11/5/2014	130
FDHCS270 Trail	9/27/2014	600
	11/5/2014	95

NA – Not analyzed

ng/L – nanograms per liter

7.1.4 Comal Springs Surface Water Passive Sampling

Passive Diffusion Samplers were installed in the Comal Springs system in March, April, June, August, October, and December 2014. The PDSs at sites HCS 420, 440 and 460 were not recovered in March 2014. PDSs were not analyzed from the April 2014 deployment due to low PDS retrieval. In August 2014, HCS430 was removed from the river by a construction crew and was not analyzed. These issues are discussed in Appendix C. There is not a suitable set of regulatory standards to compare PDS results to, but rather the data is a qualitative tool for evaluating the presence of trace concentrations of organic compounds. PDSs were analyzed for SVOCs, VOCs, and organochlorine pesticides. Positive detections are shown in Tables 13 and 14.

Table 13. Passive Diffusion – Volatile Organic Compounds (VOCs) – Comal Springs Complex

Location	Month 2014	BTEX (µg)	Chloroform (µg)	Ethylbenzene (µg)	Pentadecane (µg)	Tetrachloroethene (µg)	Toluene (µg)	1,2,4-Trimethylbenzene (µg)	p/m-Xylene (µg)	o-Xylene (µg)	TPH (µg)
HCS410	March	<0.02	0.06	<0.02	0.22	0.08	<0.02	<0.02	<0.02	<0.02	1.85
	April	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	June	0.03	<0.02	<0.02	<0.05	0.11	<0.02	<0.02	0.03	<0.02	2.64
	August	<0.02	0.04	<0.02	<0.05	0.04	<0.02	<0.02	<0.02	<0.02	2.01
	October	<0.02	0.1	<0.02	<0.05	0.03	<0.02	<0.02	<0.02	<0.02	1.60
	December	<0.02	0.08	<0.02	<0.05	0.07	<0.02	<0.02	<0.02	<0.02	<0.50
HCS420	March	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	April	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.02	<0.02	<0.05	0.23	<0.02	<0.02	<0.02	<0.02	1.03
	August	<0.02	<0.02	<0.02	<0.05	0.14	<0.02	<0.02	<0.02	<0.02	1.16
	October	<0.02	<0.02	<0.02	<0.05	0.16	<0.02	<0.02	<0.02	<0.02	2.19
	December	<0.02	<0.02	<0.02	<0.05	0.23	<0.02	<0.02	<0.02	<0.02	<0.50
HCS430	March	0.02	<0.02	<0.02	0.15	0.57	0.02	<0.02	<0.02	<0.02	5.07
	April	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.02	<0.02	<0.05	0.21	<0.02	<0.02	<0.02	<0.02	1.00
	August	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	October	<0.02	<0.02	<0.02	<0.05	0.26	<0.02	<0.02	<0.02	<0.02	1.64
	December	<0.02	<0.02	<0.02	<0.05	0.38	<0.02	<0.02	<0.02	<0.02	0.50
HCS440	March	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	April	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.02	<0.02	<0.05	0.45	<0.02	0.03	<0.02	<0.02	1.81

Location	Month 2014	(µg) BTEX	(µg) Chloroform	(µg) Ethylbenzene	(µg) Pentadecane	(µg) Tetrachloroethene	(µg) Toluene	(µg) 1,2,4-Trimethylbenzene	(µg) p/m-Xylene	(µg) o-Xylene	(µg) TPH
	August	0.02	<0.02	<0.02	<0.05	0.41	0.02	<0.02	<0.02	<0.02	1.48
	October	<0.02	<0.02	<0.02	<0.05	0.33	<0.02	<0.02	<0.02	<0.02	1.13
	December	<0.02	<0.02	<0.02	<0.05	0.53	<0.02	<0.02	<0.02	<0.02	<0.50
FDHCS440	March	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	April	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.02	<0.02	<0.05	0.45	<0.02	0.03	<0.02	<0.02	1.62
	August	0.03	<0.02	<0.02	<0.05	0.42	0.03	<0.02	<0.02	<0.02	1.50
	October	<0.02	<0.02	<0.02	<0.05	0.30	<0.02	<0.02	<0.02	<0.02	1.51
	December	<0.02	<0.02	<0.02	<0.05	0.47	<0.02	<0.02	<0.02	<0.02	<0.50
HCS460	March	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	April	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	June	0.23	<0.02	0.02	<0.05	0.19	<0.02	0.03	0.14	0.07	3.09
	August	0.29	<0.02	0.03	<0.05	0.17	<0.02	<0.02	0.18	0.08	3.37
	October	<0.02	<0.02	<0.02	<0.05	0.18	<0.02	<0.02	<0.02	<0.02	1.86
	December	<0.02	<0.02	<0.02	<0.05	0.31	<0.02	<0.02	<0.02	<0.02	<0.50
Trip Blank	March	0.03	<0.02	<0.02	<0.05	<0.02	0.03	<0.02	<0.02	<0.02	0.89
	April	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.02	<0.02	0.83
	August	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.02	<0.02	1.50
	October	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.02	<0.02	1.14
	December	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.02	<0.02	<0.50

NA – Not analyzed

µg – micrograms

Table 14. Passive Diffusion – Semi-Volatile Organic Compounds (SVOCs) – Comal Springs Complex

Location	Month 2014	Fluoranthene (µg)	Fluorene (µg)	Phenanthrene (µg)
HCS410	March	<0.05	<0.05	<0.05
	April	NA	NA	NA
	June	<0.05	<0.05	2.72
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05
HCS440	March	NA	NA	NA
	April	NA	NA	NA
	June	<0.05	<0.05	1.44
	August	<0.05	0.06	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05
HCS460	March	NA	NA	NA
	April	NA	NA	NA
	June	<0.05	<0.05	3.72
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05

NA – Not analyzed

µg – micrograms

7.2 San Marcos Springs Sample Results

The surface waters associated with the San Marcos Springs complex were sampled for surface water base flow conditions in March and September 2014. In general, few detections were noted. As discussed previously, surface water samples are compared to the drinking water standards for water quality in this report.

Sediments at the San Marcos Springs complex were sampled in June 2014. Sediment results were compared to the standards developed by McDonald et al. (2000) and TCEQ (2012). These standards are based on the probability of a detected compound having a toxic effect on sediment dwelling organisms and are referred to as the TEC and PEC. Detections below the TEC are not considered to be toxic, while detections above the PEC are considered to be toxic to sediment dwelling organisms. Detections above the TEC but less than the PEC are considered to be equally likely to be toxic or non-toxic.

Stormwater events were sampled at the San Marcos Springs complex in May and July 2014. Stormwater results did not indicate a significant number of detections of concern.

7.2.1 San Marcos Springs Surface Water / Base Flow Sampling

The San Marcos Springs complex was sampled on March 25 and September 26, 2014, for surface water (base flow) events. An additional sample date of April 29, 2014, was due to a problem with the filtration and preservation of metals and nitrate samples. The decision was made to resample for these analyses to ensure the validity of the data.

7.2.1.1 Surface Water / Base flow - Bacteria

Bacteria results for surface water (base flow) associated with the San Marcos Springs complex ranged from 1 MPN/100 mL through 460 MPN/100 mL for *E. coli*. Because of the presence of various fauna in surface water collection sites, positive detections are not uncommon. The 2014 Texas Surface Water Quality Standard for *E. coli* in primary recreation waters is a geometric mean of 126 MPN/100 mL with no individual sample exceeding 399 MPN/100 mL (30 TAC 307.7). The geometric mean for surface water samples collected from the San Marcos Springs complex during 2014 was 39 MPN/100 mL. However, the sample from HSM130 collected on September 26, 2014, exceeded the maximum individual sample limit with a result of 460 MPN/100 mL. Surface water (base flow) bacteria counts are summarized in Table 15. A field duplicate was not collected in the San Marcos Springs complex during sampling on March 25, 2014, as discussed in Appendix C.

Table 15. Surface Water Samples – Bacteria Counts - San Marcos Springs Complex

Location	Date	Count (MPN/100 mL)
HSM110	3/25/2014	1
	9/26/2014	18
HSM120	3/25/2014	16.9
	9/26/2014	39
HSM130	3/25/2014	47.1
	9/26/2014	460
HSM140	3/25/2014	30.9
	9/26/2014	91
HSM150	3/25/2014	35.9
	9/26/2014	44
HSM160	3/25/2014	32.7
	9/26/2014	96
FDHSM160	3/25/2014	NA
	9/26/2014	72
HSM170	3/25/2014	34.1
	9/26/2014	78

MPN/100 mL – most probable number per 100 milliliters

NA – Not analyzed

7.2.1.2 Surface Water / Base Flow - Volatile Organic Compounds (VOCs)

The majority of samples did not contain detectable VOCs during the surface water sampling events. However, for the March 25, 2014, event, sample site HSM150 contained toluene at 0.37 J µg/L. This detection is well below the MCL of 1,000 µg/L. No additional VOC detections were noted in field samples for the San Marcos surface water sampling events. There were however two VOCs detected in the VOC Trip Blank for the September 26, 2014, sampling event. The Trip Blank tested positive for 1,2-dichloroethane (0.65 µg/L) and toluene (1.6 µg/L), but neither constituent was detected in any associated field samples.

7.2.1.3 Surface Water / Base Flow - Semi-volatile Organic Compounds (SVOCs)

Surface water samples were analyzed for SVOCs because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, be used to evaluate potential impacts on water quality. There were no SVOC detections in any of the surface water samples from the San Marcos Springs complex during March and September 2014.

7.2.1.4 Surface Water / Base Flow - Pesticides

Surface water samples were analyzed for pesticides because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, be used to evaluate potential impacts on water quality. There were no pesticide detections in any of the San Marcos Springs complex surface water samples during March and September 2014.

7.2.1.5 Surface Water / Base flow - Herbicides

Surface water samples were analyzed for herbicides because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, be used to evaluate potential impacts on water quality. Herbicides were not detected for the March and September 2014 sampling events at all seven sites for the San Marcos Springs complex.

7.2.1.6 Surface Water / Base Flow - Polychlorinated Biphenyls (PCBs)

Surface water samples were analyzed for the various Aroclor compounds that are generally referred to collectively as PCBs. PCBs are sampled because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, help in the evaluation of potential impacts on water quality. PCBs were not detected for the March and September 2014 sampling events at all seven sites for the San Marcos Springs complex.

7.2.1.7 Surface Water / Base Flow - Metals

Surface water samples were analyzed for metals because their detection can indicate the presence of chemicals originating from anthropogenic sources and therefore, be used to evaluate potential impacts on water quality. Although metals were detected for the April and September 2014 sampling events at all seven sites for the San Marcos Springs complex, no metals of concern were noted at a concentration in excess of the drinking water standards. Aluminum, antimony, arsenic, barium, chromium, copper, iron, lead, manganese, nickel, selenium, thallium and zinc were detected; however, none of the concentrations exceeded a regulatory standard. These detections are listed in Table 16. Note many detections are “J” flagged, indicating the detected concentration is below the laboratory reporting limit, but above the method detection limit. Samples from April 2014 were not analyzed for manganese due to an oversight in the field as discussed in Appendix C.

Table 16. Surface Water Samples – Metal Detections - San Marcos Springs Complex

Location	Date Collected	Antimony (mg/L)	Arsenic (mg/L)	Barium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Lead (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Thallium (mg/L)	Zinc (mg/L)	Aluminum (mg/L)	Iron (mg/L)	Manganese (mg/L)
HSM110	4/29/2014	<0.0000995	<0.000386	0.0357	<0.000402	<0.000140	<0.0000898	0.00142	<0.000168	<0.000101	0.0447	<0.00331	0.0616	NA
	9/26/2014	0.000187J	0.000639J	0.0331	0.000556J	0.00121	0.000194J	0.00386	0.000232J	<0.000101	0.0433	0.0364J	0.116	0.0251
HSM120	4/29/2014	<0.0000995	<0.000386	0.0383	<0.000402	<0.000140	<0.0000898	0.00145	<0.000168	<0.000101	0.00716	<0.00331	<0.00926	NA
	9/26/2014	<0.0000995	<0.000386	0.0395	0.000539J	0.000651J	<0.0000898	0.00364	0.000332J	<0.000101	0.00632	0.00433J	0.0937	0.000991J
HSM130	4/29/2014	<0.0000995	<0.000386	0.0401	<0.000402	<0.000140	<0.0000898	0.00153	<0.000168	<0.000101	0.0369	<0.00331	0.0635	NA
	9/26/2014	<0.0000995	0.000422J	0.0413	<0.000402	0.000415J	<0.0000898	0.00377	0.000402J	<0.000101	0.0163	0.0105J	0.0901	0.00635
HSM140	4/29/2014	<0.0000995	<0.000386	0.0379	<0.000402	<0.000140	<0.0000898	0.00146	<0.000168	<0.000101	0.0261	<0.00331	0.0596	NA
	9/26/2014	0.000125J	<0.000386	0.0396	0.000599J	0.00106	0.000199J	0.00385	0.000350J	0.000135J	0.00482J	0.00681J	0.104	0.00255
HSM150	4/29/2014	<0.0000995	<0.000386	0.0388	<0.000402	<0.000140	<0.0000898	0.00157	<0.000168	<0.000101	0.0184	<0.00331	<0.00926	NA
	9/26/2014	<0.0000995	<0.000386	0.0368	0.000531J	0.00062J	<0.0000898	0.00351	0.000360J	<0.000101	0.00499J	0.0215J	0.0858	0.00154
HSM160	4/29/2014	<0.0000995	<0.000386	0.0385	<0.000402	<0.000140	<0.0000898	0.00152	<0.000168	<0.000101	0.0456	<0.00331	<0.00926	NA
	9/26/2014	<0.0000995	<0.000386	0.0380	0.000530J	0.000879J	<0.0000898	0.00378	0.000263J	<0.000101	0.00418J	0.00566J	0.0755	0.00215
FDHSM160	9/26/2014	<0.0000995	<0.000386	0.0393	0.000544J	0.000444J	<0.0000898	0.00349	0.000309J	<0.000101	0.00393J	0.00676J	0.0991	0.00200
HSM170	4/29/2014	<0.0000995	<0.000386	0.0388	<0.000402	<0.000140	<0.0000898	0.00157	<0.000168	<0.000101	0.0376	<0.00331	0.0504	NA
	9/26/2014	<0.0000995	<0.000386	0.0381	0.000520J	0.000648J	<0.0000898	0.00365	0.000400J	<0.000101	0.00363J	0.00552J	0.0895	0.00221
FDHSM170	4/29/2014	<0.0000995	<0.000386	0.0379	<0.000402	<0.000140	<0.0000898	0.00142	<0.000168	<0.000101	0.0404	<0.00331	0.0502	NA
MCL		0.006	0.010	2	0.1	NE	NE	NE	0.05	0.002	NE	NE	NE	NE
PCL		--	--	--	--	1.3	0.015	0.49	--	--	7.3	24	NE	1.1

J – Detection is above the method detection limit, but below the reporting limit.
mg/L – milligrams per liter
NA – Not Analyzed
NE – None Established
-- -- Not applicable

7.2.1.8 Surface Water / Base Flow - Nitrates

Surface water samples were analyzed for nitrate-nitrite as nitrogen. Laboratory analyses indicated a limited range of nitrate-nitrite as nitrogen in surface water samples. Of the 16 surface water samples (14 environmental samples and two field duplicates) collected for the two sample events, concentrations ranged from 0.18 mg/L to 1.6 mg/L. None of the nitrate concentrations exceeded the MCL of 10 mg/L for drinking water. The highest nitrate concentration in surface water at the San Marcos Springs complex was 1.6 mg/L from HSM130 sampled on September 26, 2014, although this sample was analyzed beyond the recommended hold time. Nitrate-nitrogen results are summarized in Table 17.

**Table 17. Surface Water Samples – Nitrate
Detections - San Marcos Springs Complex**

Location	Date	Concentration (mg/L)
HSM110	4/29/2014	0.18
	9/26/2014	0.19H
HSM120	4/29/2014	1.1
	9/26/2014	1.4H
HSM130	4/29/2014	1.4
	9/26/2014	1.6H
HSM140	4/29/2014	1.1
	9/26/2014	1.2H
HSM150	4/29/2014	1.1
	9/26/2014	1.3H
HSM160	4/29/2014	1.1
	9/26/2014	1.3H
FDHSM160	9/26/2014	1.3H
HSM170	4/29/2014	1.1
	9/26/2014	1.3H
FDHSM170	4/29/2014	1.1

H – Analyzed outside hold time, result included for comparison but not considered valid
mg/L – milligrams per liter

7.2.1.9 Surface water / base flow – Caffeine

Surface water base flows were analyzed for caffeine. PPCPs like caffeine can indicate the presence of human wastewater discharge. Caffeine may enter the system directly into surface water or it may be present in the aquifer from sources in the recharge zone (EPA 2012). Potential ecological effects are currently unknown but could include reduced reproductive success (EPA 2012). Caffeine detections in surface water samples from Comal Springs in 2014 ranged from 2.7 ng/L to 70 ng/L. There is no regulatory standard or expected value for comparison. Results are shown in Table 18. A field duplicate was not collected for the San Marcos system in March 2014 as discussed in Appendix C.

Table 18. Surface Water Samples – Caffeine Detections - San Marcos Springs Complex

Location	Date Collected	Caffeine (ng/L)
HCS110	3/25/2014	< 1.9
	9/26/2014	19
HCS120	3/25/2014	< 1.9
	9/26/2014	70
HCS130	3/25/2014	5.3
	9/26/2014	20
HSM140	3/25/2014	15
	9/26/2014	17
HSM160	3/25/2014	2.7
	9/26/2014	49
FDHSM160	3/25/2014	NA
	9/26/2014	48

NA – not analyzed

ng/L – nanograms per liter

7.2.2 San Marcos Springs Sediment Sampling

7.2.2.1 Sediment - Volatile Organic Compounds (VOCs)

No VOCs were detected in sediment samples collected at any of the seven sample sites in the San Marcos Springs complex in 2014.

7.2.2.2 Sediment - Semi-volatile Organic Compounds (SVOCs)

Generally, sediments would be expected to contain some SVOCs if the sediments have been exposed to these compounds. In summarizing the sediment SVOC detections, any compounds suspected as false positives are listed here in the text. Compounds of interest (primarily polycyclic aromatic hydrocarbons) are discussed in detail.

Based on analysis of 2013 laboratory data, the EAA concluded that three compounds may have been laboratory artifacts. The compounds were bis(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate, and di-n-butyl phthalate. The EAA noted in the 2013 Edwards Aquifer Habitat Conservation Plan Expanded Water Quality Report (EAA 2013) that as the data set grows, additional conclusions could be drawn. The 2014 laboratory analyses of sediment samples did not detect di-n-octyl phthalate or di-n-butyl phthalate. However, DEHP was detected in three of the sediment samples (HSM320, HSM330, and HSM350). DEHP was not detected in the laboratory method blank or trip blank. Therefore, it appears DEHP may be present within sediment samples. Future analyses may assist in better understanding the possible presence of DEHP within sediments in both Comal and San Marcos Spring complexes. The concentrations of DEHP ranged from 2.1 mg/kg to 9.2 mg/kg. One other non-PAH compound, butyl benzyl phthalate, was detected at a concentration of 59 mg/kg at HSM340. No TECs or PECs have been established for either of the non-PAH SVOCs detected.

The remaining SVOC detections are all PAH compounds. These detections are listed in Table 19 and further displayed as a graphic comparing the total PAH concentrations to the TEC and PEC values of MacDonald et al. (2000) and Texas Commission on Environmental Quality (2012). A total of 11 different PAH compounds were detected in the San Marcos Springs complex sediments.

Table 19. Sediment Samples – Semi-volatile Organic Compound Detections - San Marcos Springs Complex

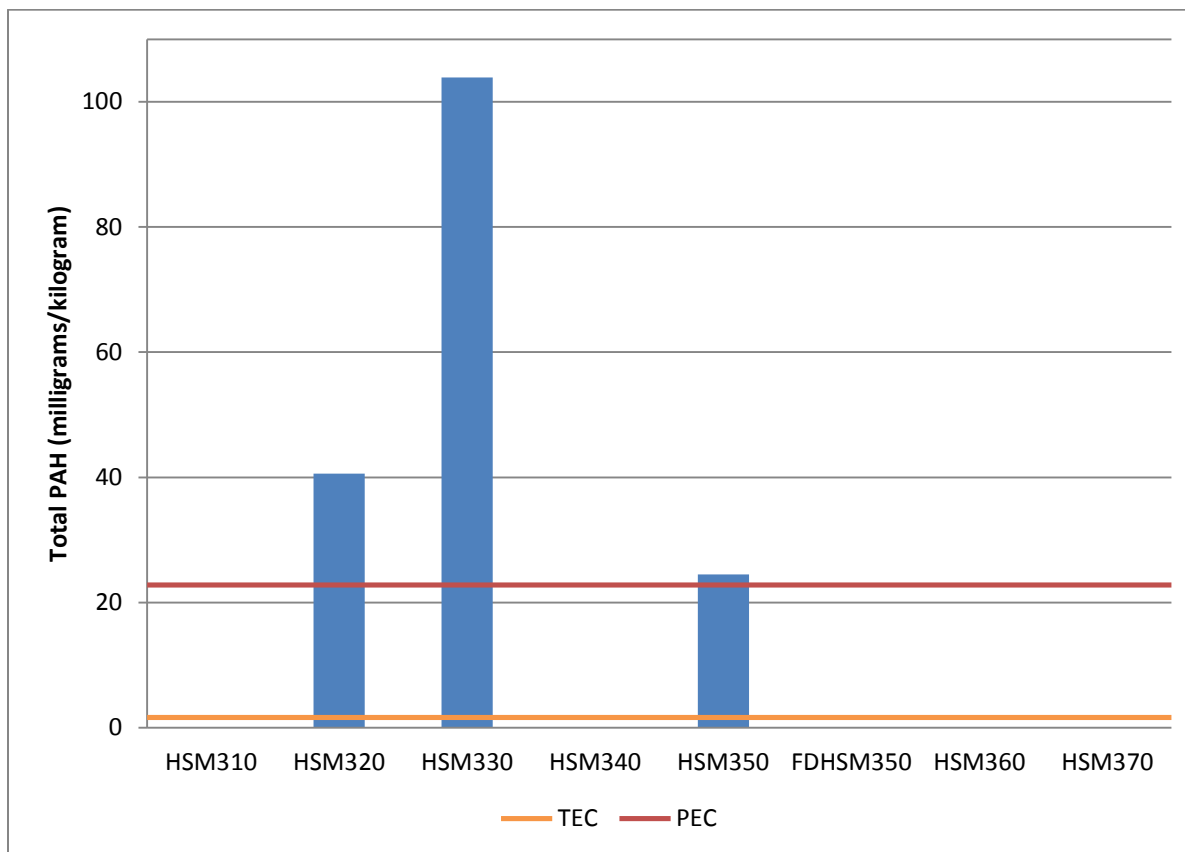
Location	Date Collected	Anthracene (mg/kg)	Benzo (a) Anthracene (mg/kg)	Benzo (a) Pyrene (mg/kg)	Benzo (b) Fluoranthene (mg/kg)	Benzo (g,h,i) Perylene (mg/kg)	Benzo (k) Fluoranthene (mg/kg)	Chrysene (mg/kg)	Fluoranthene (mg/kg)	Indeno(1,2,3-c,d) Pyrene (mg/kg)	Phenanthrene (mg/kg)	Pyrene (mg/kg)	Total PAH (mg/kg)	Bis(2-Ethylhexyl) Phthalate (mg/kg)	Butyl Benzyl Phthalate (mg/kg)
HSM320	6/30/2014	<0.11	3.4	4.6	5.5	3.6	3.6	5.2	6.3	3.5	<0.12	4.9	40.6	<0.096	<0.10
HSM330	6/30/2014	2.1	7.9	8.1	8.6	5.1	6.9	10	22	5.2	12	16	103.9	<0.096	<0.10
HSM340	6/26/2014	<0.11	<0.19	<0.085	<0.084	<0.090	<0.11	<0.094	<0.11	<0.099	<0.12	<0.10	0	9.2	59
HSM350	6/30/2014	<0.11	2.0	2.5	2.4	1.9	2.0	2.5	4.3	<0.099	2.1	4.8	24.5	2.1	<0.10
FDHSM350	6/30/2014	<0.11	<0.19	<0.085	<0.084	<0.090	<0.11	<0.094	<0.11	<0.099	<0.12	<0.10	0	2.2	<0.10
TEC		0.0572	0.108	0.15	NE	NE	NE	0.166	0.423	NE	0.204	0.195	1.61	NE	NE
PEC		0.845	1.05	1.45	NE	NE	NE	1.29	2.23	NE	1.17	1.52	22.8	NE	NE

mg/kg – milligrams per kilogram

NE – Not established

PAH detections are shown in Figure 15, where the total PAH concentrations (sum of all detected concentrations for each sample point) are compared to the total TEC and PEC values for PAH concentration. Sample locations HSM320, HSM330, and HSM350 exceed the allowable total for PAH concentrations, based on the PEC value established by MacDonald et al. (2000).

Figure 15. San Marcos Springs Sediment Polycyclic Aromatic Hydrocarbons Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) values



7.2.2.3 Sediment - Pesticides

Sediment samples were analyzed for both organochlorine and organophosphorous pesticides. Due to the persistence of certain pesticide compounds, their detection in sediment is not unusual. Pesticides were only detected in one of the seven sample locations, HSM340, which is one of the sample locations that exhibited pesticide detections in 2013. Only three pesticides were detected in the sample HSM340, but all three detected compound concentrations exceeded both the TEC and PEC values. Detected compounds are listed in Table 20 and as graphs in Figures 15, 16 and 17.

Table 20. Sediment Samples – Pesticide Detections - San Marcos Springs Complex

Location	Date Collected	Chlordane ($\mu\text{g}/\text{kg}$)	4,4-DDE ($\mu\text{g}/\text{kg}$)	4,4-DDT ($\mu\text{g}/\text{kg}$)
HSM340	6/26/2014	110	21	13
TEC		3.24	3.16	4.16
PEC		17.6	31.3	62.9

$\mu\text{g}/\text{kg}$ – micrograms per kilogram

Figure 16. San Marcos Springs Sediment Chlordane Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) values

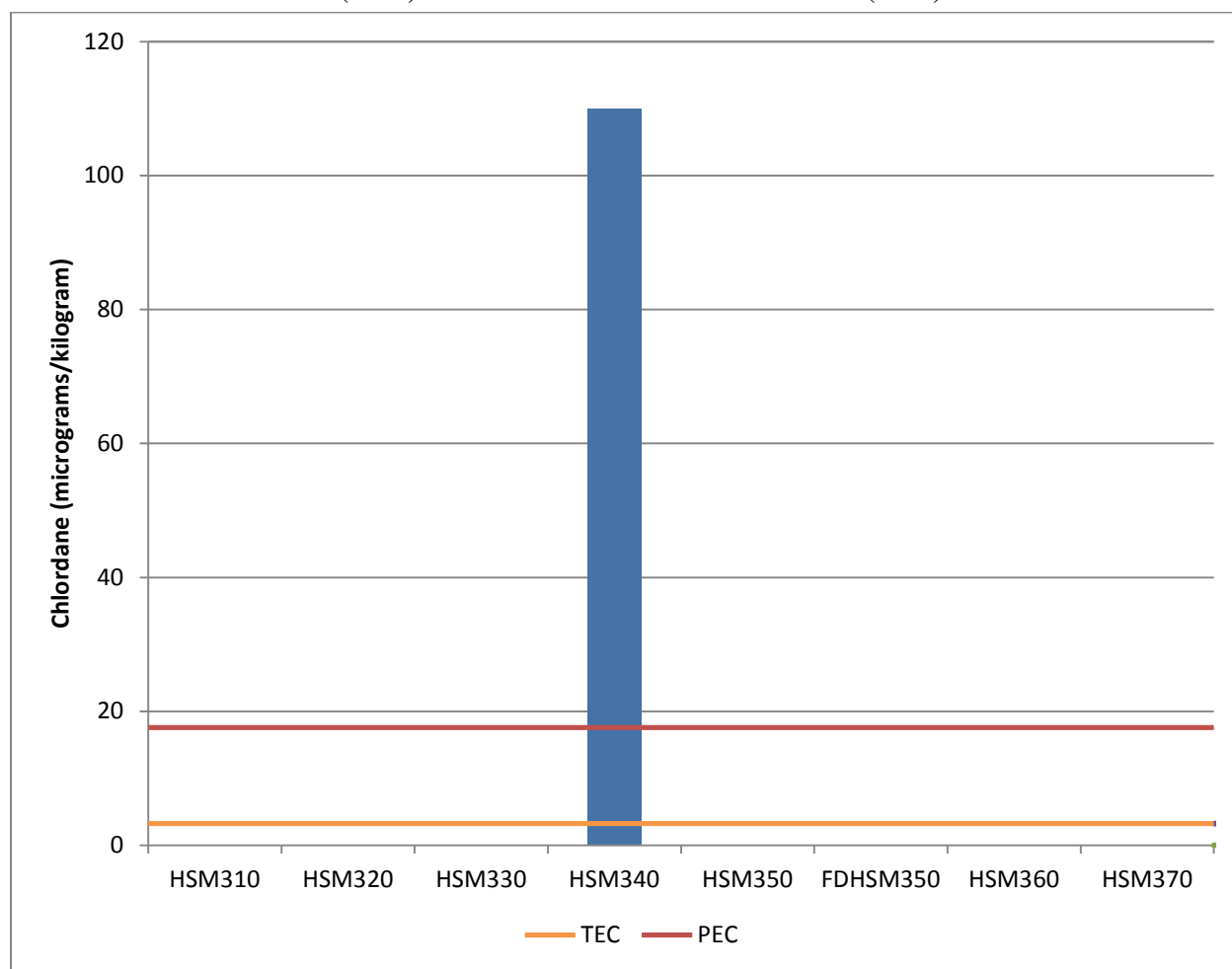


Figure 17. San Marcos Springs Sediment 4,4-DDD Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) values

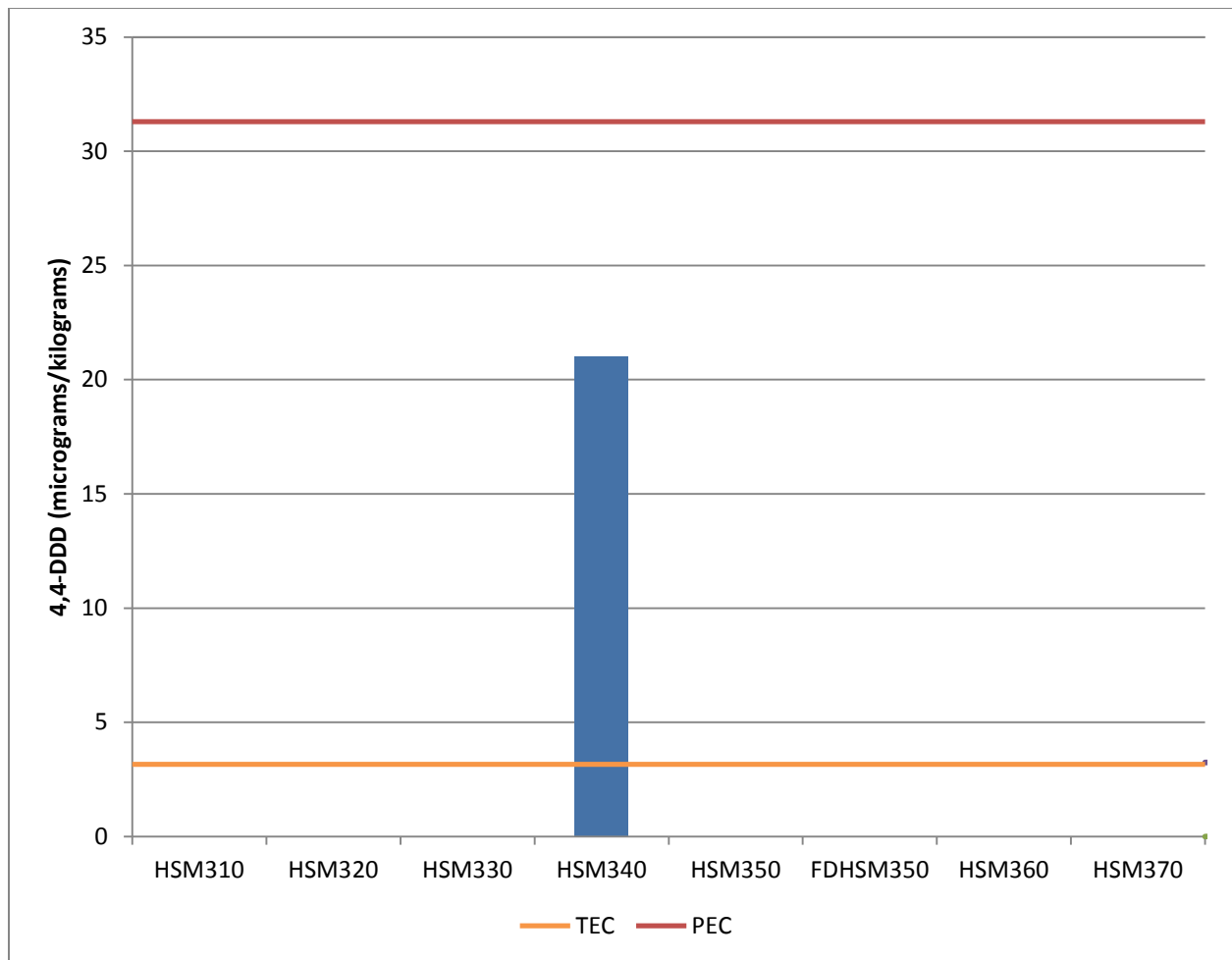
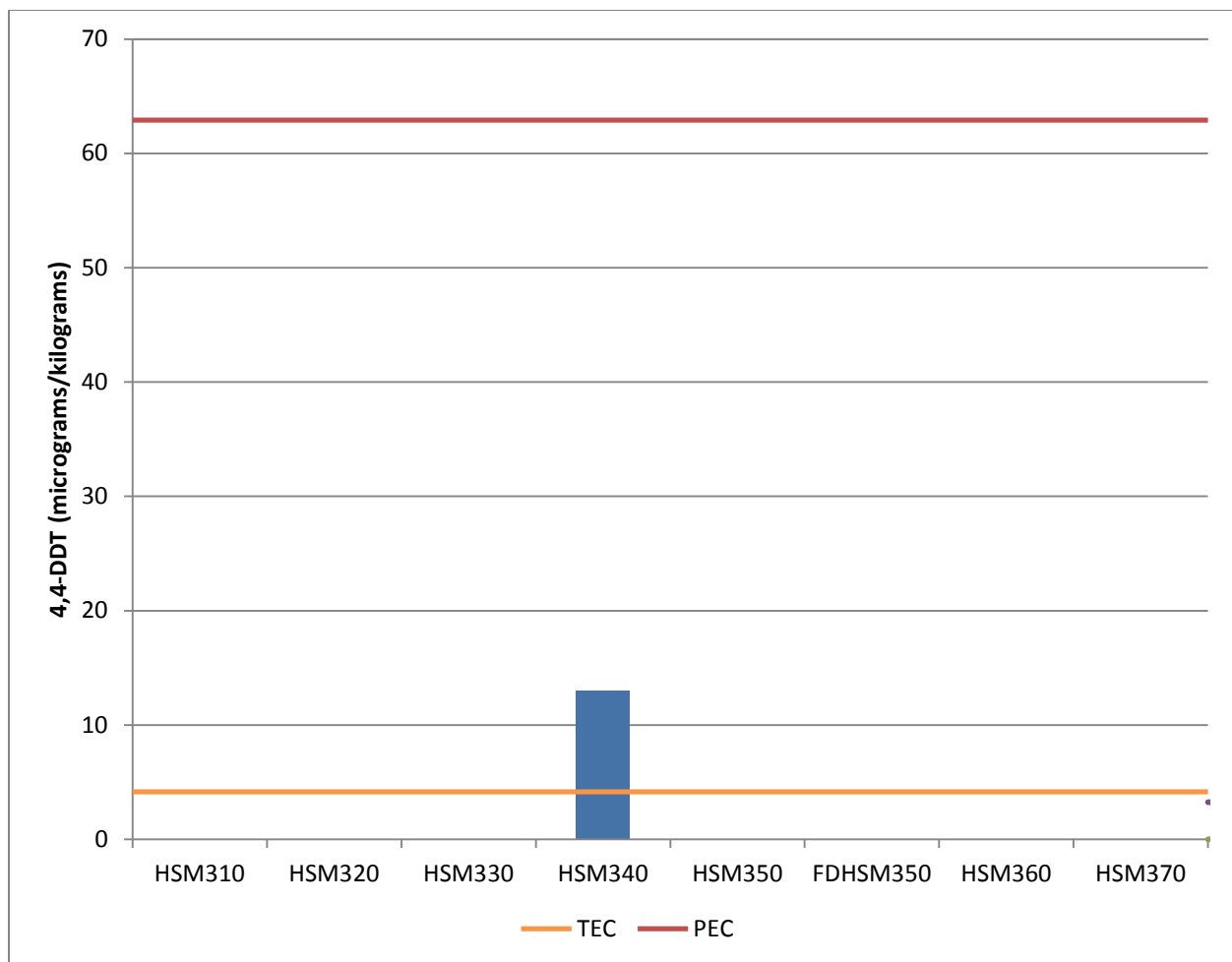


Figure 18. San Marcos Springs Sediment 4,4-DDT Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) value



7.2.2.4 Sediment - Herbicides

Sediments were analyzed for herbicide compounds to further assess sediment quality at the San Marcos Springs complex. No herbicides were detected in any of the sediment samples from the seven sites in the San Marcos Springs complex, using method SW 8151A.

7.2.2.5 Sediment - Polychlorinated Biphenyls

Sediments were analyzed for PCB compounds to further assess sediment quality at the San Marcos Springs complex. No PCB compounds were detected in any of the sediment samples collected from the seven sites in the San Marcos Springs complex.

7.2.2.6 Sediment - Metals

Sediment samples are generally expected to exhibit higher concentrations of metals (and other compounds) than water samples. Sediment sample results for metals at the San Marcos Springs complex tested positive for several metals, generally at low concentrations. Metals detected above the method detection limit and subsequently evaluated in this report for potential toxic effects using the TEC and PEC standards are: arsenic, chromium, copper, lead, mercury, nickel, and zinc. Other metals detected that do not have a TEC or PEC value available are aluminum, barium, beryllium, and iron. Of these metals, aluminum, barium, and beryllium, were compared to TSBC (TSBC 2014). None of these metals exceeded the listed background concentration. Lead in sample HSM340 exceeded the TEC and PEC values. Metal detections are listed in Table 21.

Metals with detections above an established TEC or PEC value are displayed graphically in Figures 18–22, for arsenic, chromium, copper, lead, and zinc, respectively.

Table 21. Sediment Samples – Metal Detections - San Marcos Springs Complex

Location	Date Collected	Arsenic (mg/kg)	Barium (mg/kg)	Beryllium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Nickel (mg/kg)	Silver (mg/kg)	Zinc (mg/kg)	Aluminum (mg/kg)	Iron (mg/kg)	Manganese (mg/kg)	Mercury (mg/kg)
HSM310	6/30/2014	11.5	118	1.19	25.8	14.2	16.5	21.2	<0.0857	47.3	14300	16400	539	<0.00587
HSM320	6/30/2014	<0.259	66.0	0.845	63.4	89.3	78.7	9.47	<0.0857	246	7070	15300	190	<0.00587
HSM330	6/30/2014	1.67	28.2	<0.137	25.2	6.04	90.7	6.20	0.664	76.1	2570	5620	137	0.156
HSM340	6/26/2014	2.27	60.5	0.896	63.8	14.9	235	9.41	0.657	113	6910	12600	194	<0.00587
HSM350	6/30/2014	<0.259	42.5	0.517	14.2	13.5	35.6	11.7	0.758	65.7	5620	9210	189	<0.00587
FDHSM350	6/30/2014	8.47	55.4	0.814	20.1	21.5	25.0	16.4	0.749	43.0	9690	15400	351	<0.00587
HSM360	6/30/2014	<0.259	32.2	0.548	11.8	5.39	8.40	5.55	0.703	19.8	7640	5050	159	<0.00587
HSM370	6/26/2014	1.62	80.1	0.900	17.8	10.4	12.5	12.7	<0.0857	32.1	14400	12500	411	<0.00587
TEC		9.79	NE	NE	43.4	31.6	35.8	22.7	NE	121	NE	NE	NE	0.18
PEC		33	NE	NE	111	149	128	48.6	2.2	459	NE	40000	1100	1.06
Soil background level		5.9	300	1.5	30	15	15	10	NE	30	30000	15000	300	0.04

mg/kg – milligrams per kilograms

NE – Not established

Figure 19. San Marcos Springs Sediment Arsenic Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values

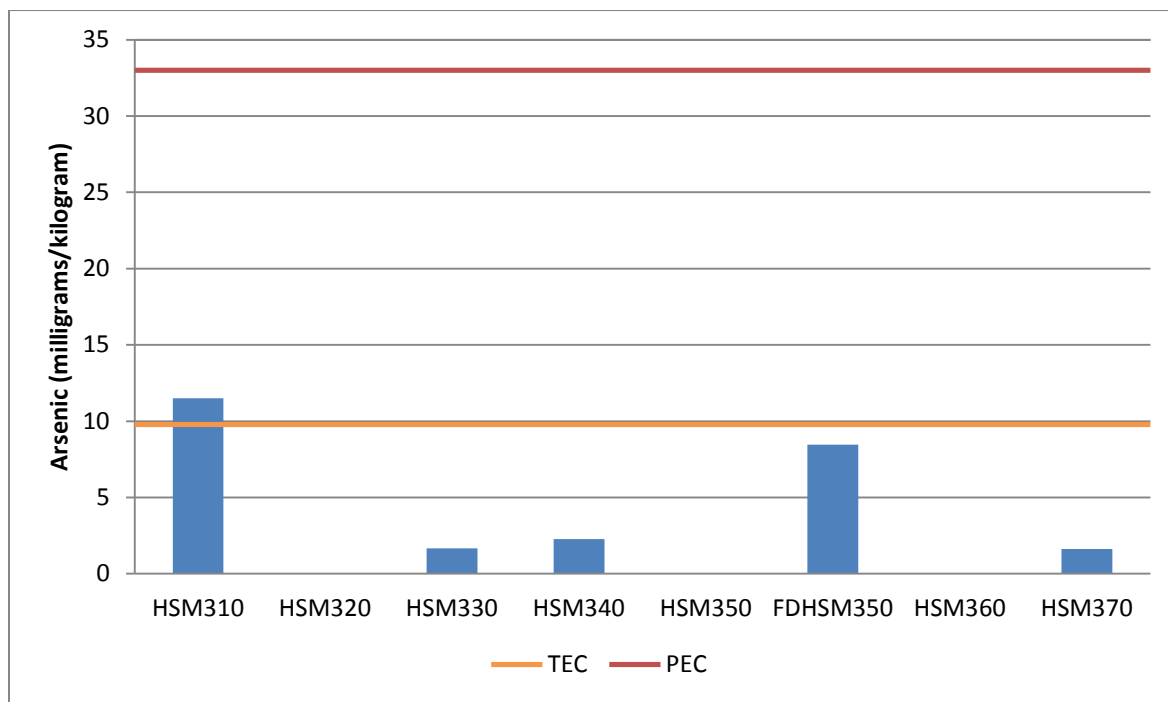


Figure 20. San Marcos Springs Sediment Chromium Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values

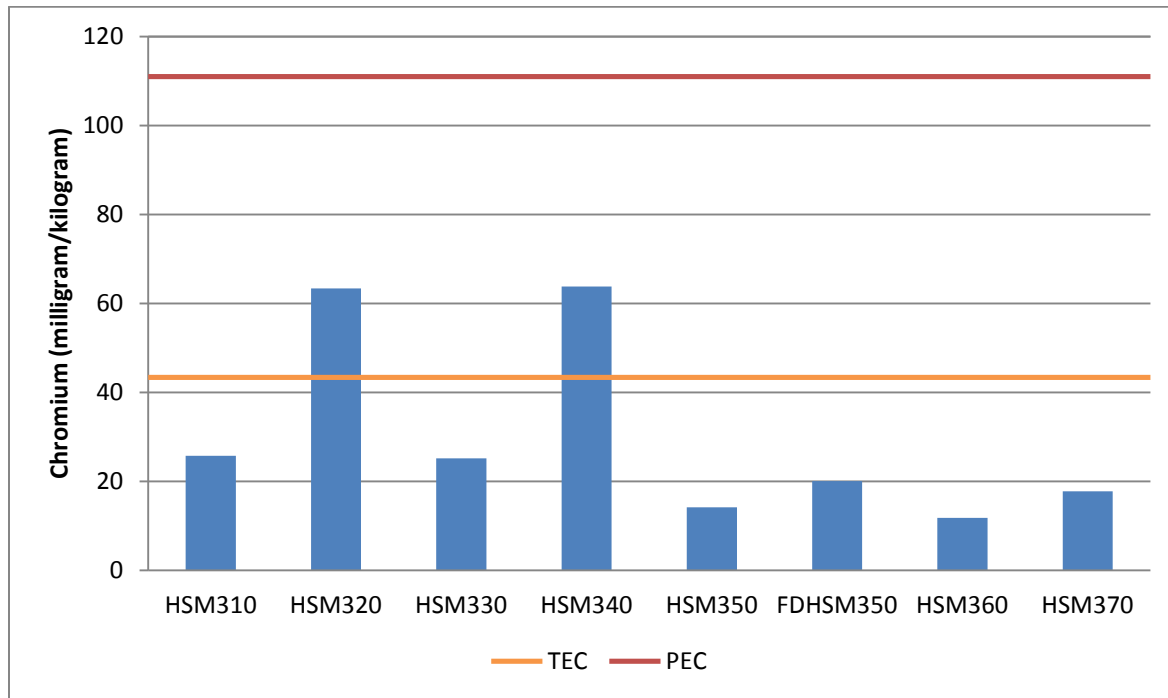


Figure 21. San Marcos Springs Sediment Copper Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values

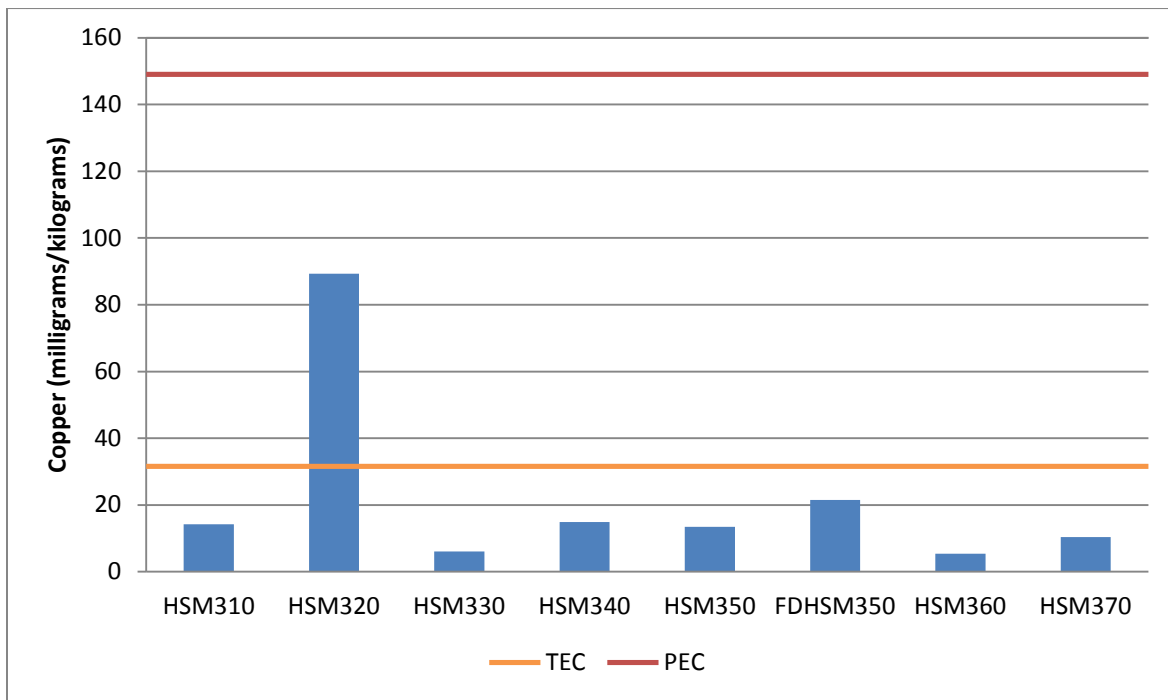


Figure 22. San Marcos Springs Sediment Lead Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values

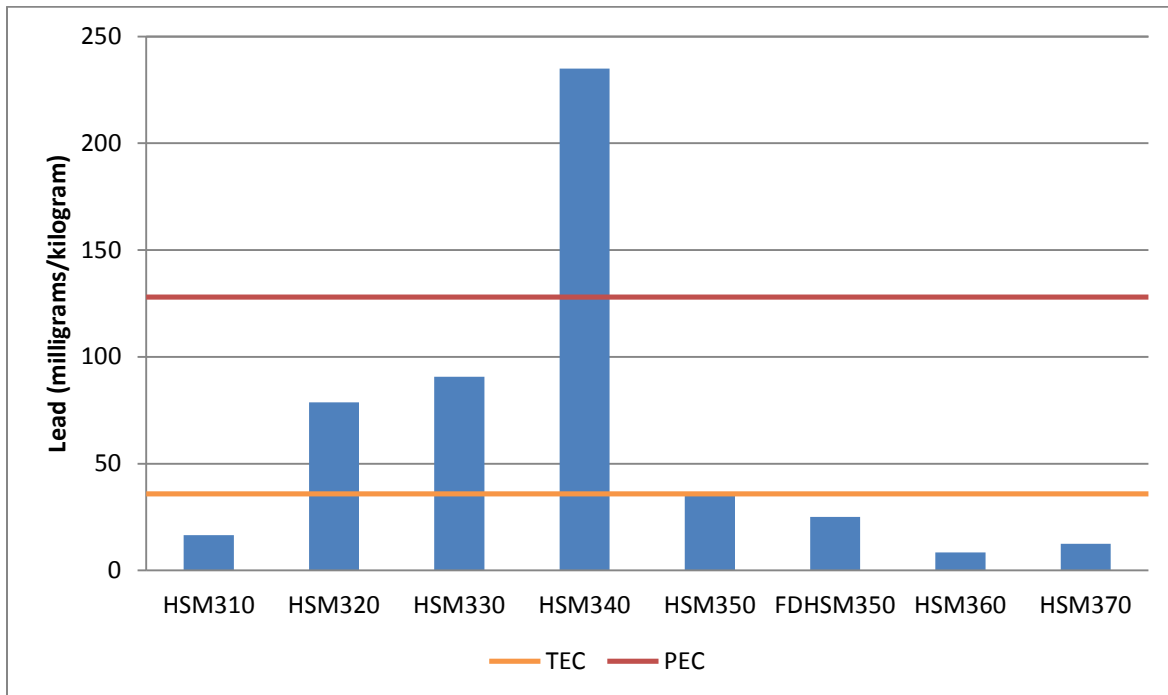
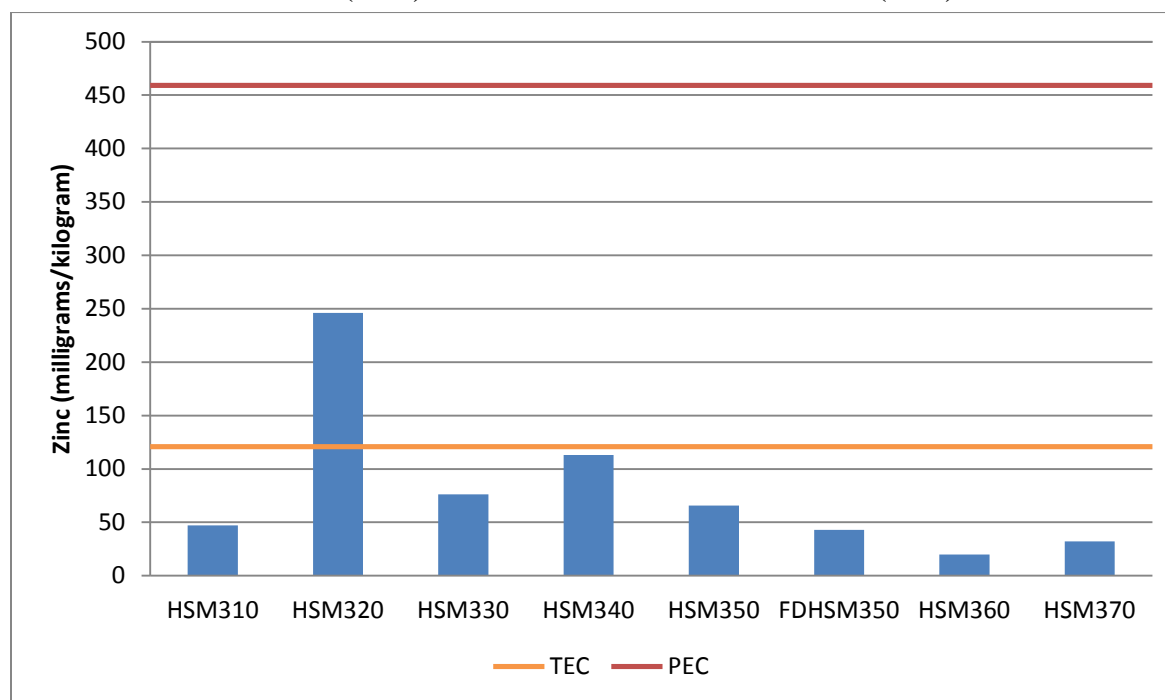


Figure 23. San Marcos Springs Sediment Zinc Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values



7.2.3 San Marcos Springs Stormwater Sampling

Stormwater samples were collected during two storm events at the San Marcos Springs complex. Each event was sampled according to the guidelines in the EAHCP workplan. Event 1 occurred on May 12, 2014. Total rainfall for the first event was approximately 3–4 inches (NOAA 2014) causing streamflow measured at USGS Gauge 08170500 to increase from approximately 107 cfs to a peak of 286 cfs during the event. The second event occurred on July 15, 2014, with approximately 0.5–1 inch of rainfall (NOAA 2014) and increase in streamflow from 138 cfs to 361 cfs.

7.2.3.1 Stormwater - Bacteria Detections

Stormwater samples collected and analyzed for bacteria analyses generally tested positive for high levels of bacteria. The 2014 Texas Surface Water Quality Standard for *E. coli* in primary recreation waters is a geometric mean of 126 MPN/100 mL with no individual sample exceeding 399 MPN/100 mL (30 TAC 307.7). The geometric mean for stormwater samples collected from the San Marcos Springs complex during 2014 was 7,679 MPN/100 mL. Bacteria counts ranged from 310 MPN/100 mL to 120,000 MPN/100 mL with several samples exceeding the individual sample limit. Individual detections are listed below in Table 22. Due to the timing of storm events and laboratory working hours, it was not possible to deliver all samples to the laboratory within sample holding times, as discussed in Appendix C. Samples exceeding hold times were included in the range and geometric mean calculations. However, the standards were still exceeded even when samples exceeding hold times were not included in the mean calculations.

**Table 22. Stormwater Samples – Bacteria Counts -
San Marcos Springs Complex**

Location	Date	Concentration (MPN/100 mL)
HSM210 Lead	5/12/2014	NA
	7/15/2014	680H
HSM210 Peak	5/13/2014	NA
	7/15/2014	310H
HSM210 Trail	5/13/2014	5700H
	7/16/2014	17000H
FDHSM210 Trail	5/13/2014	NA
	7/16/2014	10000H
HSM230 Lead	5/12/2014	9200H
	7/15/2014	10000H
HSM230 Peak	5/13/2014	NA
	7/15/2014	9800H
HSM230 Trail	5/13/2014	120000
	7/16/2014	8700H
FDHSM230 Trail	5/13/2014	NA
	7/16/2014	9800H
HSM231 Lead	5/13/2014	20000H
	7/15/2014	10000H
HSM231 Peak	5/13/2014	7300H
	7/15/2014	9800H
HSM231 Trail	5/13/2014	5200
	7/16/2014	8700H
FDHSM231 Trail	5/13/2014	NA
	7/16/2014	10000H
HSM240 Lead	5/13/2014	NA
	7/15/2014	5500H

Location	Date	Concentration (MPN/100 mL)
HSM240 Peak	5/13/2014	3700H
	7/15/2014	1700H
HSM240 Trail	5/13/2014	820
	7/16/2014	8700H
HSM250 Lead	5/12/2014	NA
	7/15/2014	24000H
HSM250 Peak	5/13/2014	44000H
	7/15/2014	17000H
HSM250 Trail	5/13/2014	1700
	7/16/2014	20000H
HSM260 Lead	5/12/2014	2100H
	7/15/2014	12000H
HSM260 Peak	5/13/2014	17000H
	7/15/2014	9100H
HSM260 Trail	5/13/2014	4100
	7/16/2014	16000H
HSM270 Lead	5/12/2014	6500H
	7/15/2014	6100H
HSM270 Peak	5/13/2014	15000H
	7/15/2014	12000H
HSM270 Trail	5/13/2014	5500
	7/16/2014	14000H

H – Analyzed outside hold time, result included for comparison but not considered valid

MPN/100 mL – Most probable number per 100 milliliters of water

NA – Not Analyzed

7.2.3.2 Stormwater - Volatile Organic Compounds (VOCs)

Stormwater samples collected in May and July 2014 were analyzed for VOCs and were generally non-detect for these compounds. A total of three VOC analytes were detected during the 2014 events, all at levels below the laboratory reporting limit and well below established MCLs and PCLs. These particular detections are summarized in Table 23.

Table 23. Stormwater Samples – Volatile Organic Compound Detections - San Marcos Springs Complex

Location	Date Collected	Time Collected	Acetone (µg/L)	1,4-Dichlorobenzene (µg/L)	Toluene (µg/L)
HSM230 Lead	7/15/2014	21:49	18J	<0.43	<0.24
HSM230 Peak	7/15/2014	23:13	11J	<0.43	<0.24
HSM231 Lead	7/15/2014	21:05	18J	<0.43	0.60J
HSM240 Trail	7/16/2014	4:51	<10	0.57J	<0.24
HSM250 Lead	5/12/2014	22:48	<10	<0.43	0.56J
	7/15/2014	21:22	17J	<0.43	0.60J
HSM250 Peak	7/15/2014	23:30	16J	<0.43	<0.24
HSM260 Peak	7/15/2014	23:35	14J	<0.43	<0.24
HSM270 Lead	7/15/2014	21:55	11J	<0.43	<0.24
HSM270 Peak	7/15/2014	23:40	15J	<0.43	<0.24
MCL			NE	NE	1000
PCL			27997.8	75	1000

J – Detection is above the method detection limit, but below the reporting limit

NE – Not established

µg/L – micrograms per liter

7.2.3.3 Stormwater - Semi-volatile Organic Compounds (SVOCs)

Stormwater samples were collected and analyzed for SVOCs. There were no detections of SVOCs in any of the samples collected from the San Marcos Springs complex during the May 12, 2014, or July 15, 2014, sampling events.

7.2.3.4 Stormwater - Herbicides and Pesticides

Stormwater samples were collected and analyzed for organochlorine pesticides, organophosphorous pesticides, and herbicides. There were no detections of pesticides or herbicides in any of the stormwater samples collected from the San Marcos Springs complex during the May 12, 2014, or July 15, 2014, events.

7.2.3.5 Stormwater - Polychlorinated Biphenyls

Stormwater samples were analyzed for the various Aroclor compounds that are generally referred to collectively as PCBs. None of the stormwater samples from the San Marcos Springs complex indicated positive detections of PCB compounds during the May or July 2014 sampling events.

7.2.3.6 Stormwater - Metals

Stormwater samples were analyzed for metals in accordance with the EAHCP workplan. Several positive metal detections were noted in the sample set; however, no samples detected a metal at a concentration in excess of the drinking water MCL, and most detections were below laboratory reporting limits during the 2014 sampling events.

7.2.3.7 Stormwater - Nitrates

Stormwater samples were analyzed for nitrate-nitrite as nitrogen in accordance with the EAHCP workplan. All samples contained nitrate results below the MCL of 10 mg/L. The range of nitrate results was 0.18–1.4 mg/L in the sample set. The nitrate values in stormwater for both sample events averaged 0.84 mg/L whereas the average nitrate in spring water samples at San Marcos Springs for calendar year 2013 was 1.44 mg/L (EAA 2014). Nitrate detections are summarized in Table 24. Due to a field oversight, duplicate samples were not collected during the May 2014 event as discussed in Appendix C.

Table 24. Stormwater Samples – Nitrate Detections - San Marcos Springs Complex

Location	Date	Concentration (mg/L)
HSM210 Lead	5/12/2014	0.18
	7/15/2014	0.25
HSM210 Peak	5/13/2014	0.59
	7/15/2014	0.24
HSM210 Trail	5/13/2014	0.50
	7/16/2014	0.27
FDHSM210 Trail	5/13/2014	NA
	7/16/2014	1.3
HSM230 Lead	5/12/2014	0.47
	7/15/2014	0.89
HSM230 Peak	5/13/2014	0.28
	7/15/2014	0.79
HSM230 Trail	5/13/2014	1.1
	7/16/2014	1.3
FDHSM230 Trail	5/13/2014	NA
	7/16/2014	0.24
HSM231 Lead	5/13/2014	0.68
	7/15/2014	0.78
HSM231 Peak	5/13/2014	0.79
	7/15/2014	1.2
HSM231 Trail	5/13/2014	1.4
	7/16/2014	1.2
FDHSM231 Trail	5/13/2014	NA
	7/16/2014	1.2
HSM240 Lead	5/13/2014	0.82
	7/15/2014	0.91
HSM240 Peak	5/13/2014	1.1
	7/15/2014	1.1

Location	Date	Concentration (mg/L)
HSM240 Trail	5/13/2014	1.1
	7/16/2014	1.1
HSM250 Lead	5/12/2014	1.0
	7/15/2014	0.48
HSM250 Peak	5/13/2014	0.65
	7/15/2014	0.82
HSM250 Trail	5/13/2014	1.1
	7/16/2014	1.2
HSM260 Lead	5/12/2014	0.94
	7/15/2014	0.86
HSM260 Peak	5/13/2014	0.65
	7/15/2014	0.70
HSM260 Trail	5/13/2014	1.0
	7/16/2014	1.2
HSM270 Lead	5/12/2014	1.1
	7/15/2014	0.96
HSM270 Peak	5/13/2014	0.64
	7/15/2014	0.70
HSM270 Trail	5/13/2014	0.94
	7/16/2014	1.1

mg/L – milligrams per liter

NA – Not analyzed

7.2.3.8 Stormwater – Caffeine

Stormwater was analyzed for caffeine. PPCPs like caffeine can indicate an anthropogenic source of impacts. Caffeine may enter the system directly into surface water or it may be present in the aquifer from sources in the recharge zone (EPA 2012). Potential ecological effects are currently unknown but could include reduced reproductive success (EPA 2012). Caffeine detections in stormwater samples from San Marcos Springs in 2014 ranged from 6.9 ng/L to 2800 ng/L. There is no regulatory standard or expected value for comparison. Results are shown in Table 25. Due to a field oversight, no field duplicates were collected for the May 2014 event as discussed in Appendix C.

**Table 25. Stormwater Samples – Caffeine Detections
- San Marcos Springs Complex**

Location	Date Collected	Caffeine (ng/L)
HCS210 Lead	5/12/2014	6.9
	7/15/2014	27
HCS210 Peak	5/13/2014	580
	7/16/2014	34
HCS210 Trail	5/13/2014	150
	7/16/2014	100
FDHSM210 Trail	5/13/2014	NA
	7/16/2014	660
HSM230 Lead	5/12/2014	260
	7/15/2014	1000
HSM230 Peak	5/13/2014	18
	7/16/2014	1000
HSM230 Trail	5/13/2014	1500
	7/16/2014	990
FDHSM230 Trail	5/13/2014	NA
	7/16/2014	23
HSM231 Lead	5/13/2014	440
	7/15/2014	210
HSM231 Peak	5/13/2014	320
	7/16/2014	290
HSM231 Trail	5/13/2014	620
	7/16/2014	32
FDHSM231 Trail	5/13/2014	NA
	7/16/2014	21
HCS240 Lead	5/13/2014	260

Location	Date Collected	Caffeine (ng/L)
	7/15/2014	200
HCS240 Peak	5/13/2014	72
	7/16/2014	62
HCS240 Trail	5/13/2014	39
	7/16/2014	69
HCS250 Lead	5/13/2014	500
	7/15/2014	2800
HCS250 Peak	5/12/2014	390
	7/16/2014	860
HCS250 Trail	5/13/2014	28
	7/16/2014	59
HCS260 Lead	5/12/2014	450
	7/15/2014	1300
HCS260 Peak	5/13/2014	330
	7/16/2014	1200
HCS260 Trail	5/13/2014	48
	7/16/2014	37
HCS270 Lead	5/12/2014	20
	7/15/2014	230
HCS270 Peak	5/13/2014	420
	7/16/2014	1100
HCS270 Trail	5/13/2014	89
	7/16/2014	160

NA – Not analyzed

ng/L – nanograms per liter

7.2.4 San Marcos Springs Surface Water Passive Sampling

PDSs were installed in the San Marcos Springs system in March, April, June, August, October, and December. In March 2014, PDSs were only recovered from sites HSM410, HSM420, HSM450 and HSM460. PDSs were not analyzed from the April deployment due to low PDS retrieval. These issues are discussed in Appendix C (Deviations). There is not a suitable set of regulatory standards for comparison to PDS results. PDSs were analyzed for VOCs, SVOCs and organochlorine pesticides. Positive detections are shown below in Tables 26 and 27.

Table 26. Passive Diffusion Sampler – Volatile Organic Compounds (VOCs) – San Marcos Springs Complex

Location	Month 2014	BTEX (µg)	Pentadecane (µg)	Tetrachloroethene (µg)	Toluene (µg)	TPH (µg)	Undecane (µg)
HSM410	March	0.05	0.07	<0.02	0.05	3.19	<0.05
	April	NA	NA	NA	NA	NA	NA
	June	0.05	<0.05	<0.02	0.05	2.56	<0.05
	August	<0.02	<0.05	<0.02	<0.02	1.31	<0.05
	October	<0.02	<0.05	<0.02	<0.02	1.38	<0.05
	December	<0.02	<0.05	<0.02	<0.02	0.65	<0.05
HSM420	March	<0.02	0.05	0.24	<0.02	1.13	<0.05
	April	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.05	0.06	0.05	1.49	<0.05
	August	<0.02	<0.05	0.08	<0.02	1.52	<0.05
	October	<0.02	<0.05	0.07	<0.02	1.40	<0.05
	December	<0.02	<0.05	0.09	<0.02	0.63	<0.05
HSM430	March	NA	NA	NA	NA	NA	NA
	April	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.05	0.47	<0.02	2.57	<0.05
	August	<0.02	<0.05	0.49	<0.02	1.06	<0.05
	October	<0.02	<0.05	0.38	<0.02	2.15	<0.05
	December	<0.02	<0.05	0.43	<0.02	<0.50	<0.05
FDHSM430	March	NA	NA	NA	NA	NA	NA
	April	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.05	0.47	<0.02	2.02	0.08
	August	<0.02	<0.05	0.44	<0.02	1.13	<0.05
	October	<0.02	<0.05	0.40	<0.02	1.29	<0.05
	December	<0.02	<0.05	0.43	<0.02	0.52	<0.05

Location	Month 2014	BTEX (µg)	Pentadecane (µg)	Tetrachloroethene (µg)	Toluene (µg)	TPH (µg)	Undecane (µg)
HSM440	March	NA	NA	NA	NA	NA	NA
	April	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.05	0.16	<0.02	1.81	<0.05
	August	<0.02	<0.05	0.13	<0.02	1.40	<0.05
	October	<0.02	<0.05	0.15	<0.02	1.51	<0.05
	December	<0.02	<0.05	0.16	<0.02	<0.50	<0.05
HSM450	March	0.04	0.23	0.19	0.04	4.24	<0.05
	April	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.05	0.06	<0.02	1.17	<0.05
	August	<0.02	<0.05	0.08	<0.02	1.41	<0.05
	October	<0.02	<0.05	0.05	<0.02	1.40	<0.05
	December	<0.02	<0.05	0.05	<0.02	0.58	<0.05
HSM460	March	<0.02	<0.05	0.16	<0.02	0.63	<0.05
	April	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.05	0.09	<0.02	1.34	<0.05
	August	<0.02	<0.05	0.10	<0.02	1.52	<0.05
	October	<0.02	<0.05	0.10	<0.02	1.24	<0.05
	December	<0.02	<0.05	0.12	<0.02	<0.50	<0.05
HSM470	March	NA	NA	NA	NA	NA	NA
	April	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.05	0.10	<0.02	2.14	<0.05
	August	<0.02	<0.05	0.12	<0.02	1.67	<0.05
	October	<0.02	<0.05	0.11	<0.02	1.44	<0.05
	December	<0.02	<0.05	0.10	<0.02	<0.50	<0.05
Trip Blank	March	0.03	<0.05	<0.02	0.03	0.89	<0.05
	April	NA	NA	NA	NA	NA	NA
	June	<0.02	<0.05	<0.02	<0.02	0.83	<0.05
	August	<0.02	<0.05	<0.02	<0.02	1.50	<0.05
	October	<0.02	<0.05	<0.02	<0.02	1.14	<0.05
	December	<0.02	<0.05	<0.02	<0.02	<0.50	<0.05

NA – Not analyzed

µg - micrograms

Table 27. Passive Diffusion – Semi-Volatile Organic Compounds (SVOCs) – San Marcos Springs Complex

Location	Month 2014	Fluoranthene (µg)	Phenanthrene (µg)	Pyrene (µg)
HSM410	March	<0.05	<0.05	<0.05
	April	NA	NA	NA
	June	<0.05	1.73	<0.05
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05
HSM430	March	NA	NA	NA
	April	NA	NA	NA
	June	4.74	8.70	2.21
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05
FDHSM430	March	NA	NA	NA
	April	NA	NA	NA
	June	4.21	7.49	1.85
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05
HSM440	March	NA	NA	NA
	April	NA	NA	NA
	June	<0.05	2.02	<0.05
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05
HSM450	March	<0.05	<0.05	<0.05
	April	NA	NA	NA
	June	1.38	2.52	0.86
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05
HSM460	March	<0.05	<0.05	<0.05

Location	Month 2014	Fluoranthene (µg)	Phenanthrene (µg)	Pyrene (µg)
	April	NA	NA	NA
	June	1.79	2.76	1.10
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05
HSM470	March	NA	NA	NA
	April	NA	NA	NA
	June	1.68	3.01	1.06
	August	<0.05	<0.05	<0.05
	October	<0.05	<0.05	<0.05
	December	<0.05	<0.05	<0.05

NA – Not analyzed

µg - micrograms

8.0 SUMMARY OF RESULTS

SWCA staff collected surface water (base flow), stormwater, sediment, and passive diffusion samples from Comal Springs and River and San Marcos Springs and the headwaters of the San Marcos River. The sampling events meet the requirements of the EAHCP and provide background data for these two systems. The limited number of detections above any of the comparative standards is indicative of generally high water quality. However, the results of a few analyses were of concern. Continued sampling will be helpful in assessing if these detected compounds are repeated and have the potential for any long-term impact on listed species. Specific detections of interest, such as compounds detected above an MCL (for water) or PEC (for sediment), are listed below.

San Marcos Sediment

HSM320	June 30	Total PAH	40.6 mg/kg (PEC = 22.8)
HSM330	June 30	Total PAH	103.9 mg/kg (PEC = 22.8)
HSM340	June 26	Chlordane	110 µg/kg (PEC = 17.6)
		Lead	235 mg/kg (PEC = 128)
HSM350	June 30	Total PAH	24.5 mg/kg (PEC = 22.8)

This data is fairly consistent with the initial sampling program of 2013. However, the 2013 sampling program detected cadmium above the PEC in a sediment sample (HCS340) from the Comal Spring complex. That exceedance was not duplicated in 2014. Two samples of Comal and San Marcos spring stormwater exceeded MCLs for arsenic and antimony. Those exceedances did not occur in 2014 stormwater sampling. PAHs were detected above MCLs in some sediment samples from the San Marcos

Spring complex in both 2013 and 2014; however, chlordane and lead were also detected above PECs in San Marcos Springs sediment in 2014.

DEHP was detected in the majority of sediment samples from the Comal and San Marcos spring complexes in 2013, but was considered to likely be a laboratory or sampling equipment artifact. The presence of DEHP in some San Marcos sediment samples collected in 2014, although other plasticizers were not present and different laboratories and sampling equipment were used, suggests DEHP may be present in San Marcos sediments. Additional data is needed to further evaluate this possibility.

Other detections were noted for particular anthropogenic compounds, but at concentrations below a comparative standard. Those detections are detailed in the body of the report, and listed in Appendix G, with the full set of laboratory results.

Based on the data collected for this report combined with completion of several sample events, a few points worth consideration in future years are suggested. Although this data set adds to an initial baseline established by the 2013 sampling program, currently the data set is not adequate to make significant assessments regarding water or sediment quality. The current data set is extremely important for use in developing a baseline such that in the future, additional information can be added to it, allowing interested parties to better understand the surface water quality, stormwater impacts, and sediment quality trends of each system. In addition, the RTIs are very valuable for gathering basic water quality data and tracking any changes to basic water quality over time.

Based on this second year of work, a few minor changes should be considered for the 2015 EAHCP Workplan. Specific changes include the following.

- Sediment samples should be collected at a more discreet interval. Rather than the long interval of zero to 18 inches below the surface, consideration should be given to collecting the uppermost 3 inches of sediment in 2015, with future sampling years (beyond 2015) having another modified interval based on the additional sample results.
- Consideration should be given to using sediment sampling equipment that lacks plasticizers to further evaluate the possible presence of DEHP in San Marcos Springs complex sediments.

9.0 DATA QUALITY OBJECTIVES

SWCA evaluated each sampling event to determine if procedures should be modified to improve data collection to ensure data quality objectives were met. A discussion of problems encountered, deviations to the workplan, and resolutions to these circumstances are provided in Appendix C. The following is a brief summary of field conditions and circumstances which are discussed in greater detail in Appendix C:

- Surface water grab samples (base flow) from the April event that were collected without filtering and exceeded hold times were resampled to provide reliable sample results.
- Problems with equipment decontamination procedures and equipment blank sample collection were resolved after the first stormwater sampling event by use of only single-use, disposable equipment and direct sample collection into sample bottles.
- Failure to collect field duplicates during the first stormwater sampling event was corrected during subsequent sampling events through use of specially labeled sample kits.
- Hold times of *E. coli* samples were exceeded for some samples when stormwater samples were collected during laboratory non-working hours. Special runners were utilized to deliver samples to the laboratory as early as possible to minimize hold time exceedances.
- PDS deployment devices were constructed to house PDSs, which significantly improved retrieval rates.
- Based on procedures implemented to correct or improve data collection methods and the relatively low significance of the deviations, the circumstances experienced do not compromise the integrity of the study or this report.

10.0 DEFINITIONS

Alkalinity	The capacity of water to neutralize acids, a property imparted by the water's content of carbonate, bicarbonate, hydroxide, and on occasion borate, silicate, and phosphate. It is expressed in milligrams per liter of equivalent calcium carbonate (mg/l CaCO ₃).
Aquifer	Underground geological formation or group of formations containing water; source of groundwater for wells and springs.
ASTM	Abbreviation for American Society for Testing and Materials. A nonprofit organization that develops and publishes approximately 12,000 technical standards, covering the procedures for testing and classification of materials of every sort.
Bacteria	Microscopic living organisms that can aid in pollution control by metabolizing organic matter in sewage, oil spills, or other pollutants. However, certain bacteria in soil, water, or air can also cause human, animal, and plant health problems.
Basin	Any area draining to a point of interest.
Baseline data	Initial data generated by consistent monitoring of the same sites over time.
Caffeine	A stimulant drug found naturally in coffee, tea, and chocolate, and also within soft drinks and other foods. If detected, it might indicate an anthropogenic source of water impacts.
Channel	A long, narrow excavation or surface feature that conveys surface water and is open to the air.
Deionized water	Water with all ions removed.
Detection limit	The lowest concentration of a given pollutant that an analytical method or equipment can detect and still report as greater than zero. Generally, as readings approach the detection limit, they become less and less reliable quantitatively.
Digital titrator	A titrator unit having a counter that displays numbers. As the reagent is dispensed, the counter changes in proportion to the amount of reagent used.
Dissolved solids	The total amount of dissolved material, organic, and inorganic, contained in water or wastewater. Measurements are expressed as ppm or mg/L.
DO	Abbreviation for dissolved oxygen. Oxygen molecules that are dissolved in water and available for living organisms to use for respiration. Usually expressed in milligrams per liter or percent of saturation. The concentration of DO is an important environmental parameter contributing to water quality.

DOC	Abbreviation for dissolved organic carbon, a broad classification of organic molecules of varied origin and composition within aquatic systems. Organic carbon compounds are a result of decomposition processes from dead organic matter, such as plants.
DQO	Abbreviation for data quality objectives, a process used to develop performance and acceptance criteria or data quality objectives that clarify study objectives, define the appropriate type of data, and specify tolerable levels of data needed to support decisions.
Drainage	The collection, conveyance, containment, and/or discharge of surface and stormwater runoff.
EARIPHCP	Abbreviation for Edwards Aquifer Recovery Implementation Program Habitat Conservation Plan.
Endpoint	That state in titration at which an effect, such as a color change, occurs, indicating that a desired point in the titration has been reached.
Equipment blank	Sample used to assess the effectiveness of the decontamination process on sampling equipment. The equipment blank is prepared by pouring reagent-grade water over/through sampling equipment and analyzing for parameters of concern (to match the sampling routine applicable to the site).
Field duplicate	Second sample collected simultaneously from the same source as the parent sample, but which is submitted and analyzed as a separate sample. This sample should generally be identified such that the laboratory is unaware that it is a field duplicate.
Filtration	The process of separating solids from a liquid by means of a porous substance (filter) through which only the liquid can pass.
Groundwater	Water found beneath Earth's surface that fills pores between materials, such as sand, soil, or gravel.
Habitat	The specific area of environment in which a particular type of plant or animal lives and grows.
HCP	Abbreviation for Habitat Conservation Plan. A planning document that is required by the United States Fish and Wildlife Service as part of their enforcement of the Endangered Species Act.
LCS/LCSD	Abbreviation for Laboratory control samples and laboratory control sample duplicate. LCS/LCSD are evaluated to assess overall method performance and are the primary indicators of laboratory performance. In general, laboratory control samples are similar in composition as the environmental samples, contain known concentrations of all the analytes of interest, and undergo the same

preparatory and determinative procedures as the environmental samples. A LCS/LCSD may be analyzed to provide information on the precision of the analytical method.

MS/MSD	Abbreviation for matrix spike/matrix spike duplicate. MS/MSD results are examined to evaluate the impact of matrix effects on overall analytical performance and potential usability of the data. A matrix spike is a representative environmental sample that is spiked with target analytes of interest prior to being taken through the entire analytical process in order to evaluate analytical bias for an actual matrix. A matrix duplicate is a collected (e.g., a VOC soil sample) or a homogenized sample that is processed through the entire analytical procedure in order to evaluate overall precision for an actual matrix.
MDL	Abbreviation for method detection limit, minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero, as determined from analysis of a sample containing the analyte in a given matrix.
MPN	Abbreviation for most probable number. An analytical method used to detect the presence of coliforms in a water sample and estimate their numbers.
PCBs	Abbreviation for polychlorinated biphenyls. Group of more than 200 chlorinated toxic hydrocarbon compounds that can be biomagnified.
PCL	Abbreviation for protective concentration levels which is established to protect human health.
Peak	Maximum instantaneous flow at a specific location resulting from a given storm condition.
pH	A measure of the alkalinity or acidity of a substance. Also defined as “the negative logarithm of the hydrogen ion concentration ($-\log_{10}[\text{H}^+]$) where H^+ is the hydrogen ion concentration in moles per liter. The pH of a substance is neutral at 7.0, acidic below 7.0, and alkaline above 7.0.
PQL	Abbreviation for practical quantitation limit, which is the smallest concentration of the analyte that can be reported with a specific degree of confidence.
Precipitation	The discharge of water, in liquid or solid state, out of the atmosphere, generally upon a land or water surface. Precipitation includes rainfall, snow, hail, and sleet.
Precision	The ability of a measurement to be consistently reproduced.
QA/QC	Abbreviation for quality assurance/quality control. The total integrated program for assuring reliability of monitoring and measurement data.

Recession	End of runoff event, which is defined as the point in time when the recession limb of the hydrograph is <2 percent of the peak or is within 10 percent of the prestorm base flow, whichever is greater.
RPD	Abbreviation for relative percent difference. The RPD provide a measure of precision.
Representative	Said of samples collected that are similar to those of groundwater in its in situ condition.
RL	Abbreviation for reporting limit, the smallest concentration of an analyte reported by the laboratory to a customer. The RL is never less than the PQL and is generally twice the MDL.
Runoff	Precipitation, snow melt, or irrigation water that runs off the land into surface water. Runoff can carry pollutants from the air and land into the receiving waters.
Sediment	Fragmental material that originates from weathering of rocks and is transported by, suspended in, or deposited by water or air.
Shelby Sampler	A thin-walled tube with a cutting edge at the toe. A sampler head attaches the tube to the drill rod and pressure vents. Generally used in cohesive soils. Soil or sediment sampled from this sampler is considered undisturbed.
Spring	Water coming naturally out of the ground.
Stormwater	Stormwater is the water that runs off surfaces such as rooftops, paved streets, highways, and parking lots. It can also come from hard, grassy surfaces such as lawns, play fields, graveled roads, and parking lots.
Surface water	That which forms and remains above ground, such as lakes, ponds, rivers, (Base flow) streams, bays, and oceans.
SVOC	Abbreviation for semi-volatile organic compounds, which is a group of chemicals composed primarily of carbon and hydrogen that have a relatively low tendency to evaporate (volatilize) into the air from water or soil. Some of the compounds that make up asphalt are examples of SVOCs.
TDS	Abbreviation for total dissolved solids, or the total amount of all inorganic and organic substances, including minerals, salts, metal, cations, or anions that are dispersed within a volume of water.
Temporal	Over a period of time.
TKN	Abbreviation for total kjeldahl nitrogen, which is the total concentration of organic and ammonia nitrogen in wastewater.

TOC	Abbreviation for total organic carbon, which is the gross amount of organic matter found in natural water. Suspended-particulate, colloidal, and dissolved organic matter are part of the TOC measurement. Settable solids consisting of inorganic sediments and some organic particulate are not transferred from the sample by the lab analyst and are not part of the TOC measurement.
TSCB	Texas-specific Background Concentrations as established by the Texas Commission on Environmental Quality
Turbidimeter	An instrument for measuring turbidity in which a standard suspension is used for reference.
Turbidity	A measure of how clear the water is; how much the suspended material in water results in the scattering and absorption of light rays. An analytical quantity is usually reported in turbidity units and determined by measurements of light diffraction. Material that can increase turbidity (reduce clarity of water) are suspended clay, silt, sand, algae, plankton, microbes, and other substances.
Trip blank	Sample known to be free of contamination (for target analytes) that is prepared in the laboratory and treated as an environmental sample after receipt by the sampler. Trip blank samples are applicable to VOC analysis only.
TSS	Abbreviation for total suspended solids, which are the nonfilterable residue retained on a glass-fiber disk filter mesh measuring 1.2 micrometers after filtration of a sample of water or wastewater.
USGS	Abbreviation for United States Geological Services. USGS is a federal research organization which provides impartial information on health of ecosystems and environment, natural hazards which may threaten us, natural resources, impacts of climate and land use change, and core science systems which provide timely, relevant, and useable information.
VOC	Abbreviation for volatile organic compounds, which are often used as solvents in industrial processes and are either known or suspected carcinogens or mutagens. The five most toxic are vinyl chloride, tetrachloroethene, trichloroethene, 1,2-dichloroethane, and carbon tetrachloride.
Whirl-Pak®	Sterilized, clear polyethylene bag used to collect water samples for analysis.
WQAL	Abbreviation for a list of parameters defined as the following: pH, conductivity, temperature, dissolved oxygen, turbidity, and alkalinity in the field. Other parameters submitted for laboratory analysis include cations, anions, nutrients, metals, VOCs, SVOCs, herbicides and pesticides, bacteria, TOC, PCBs and phosphorous.

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12.0 REFERENCES

- Edwards Aquifer Authority. 2012. Water Quality Monitoring Program Strategy for Comal Springs and San Marcos Springs in Support of the Edwards Aquifer Habitat Conservation Plan, 19 p.
- . 2013. Edwards Aquifer Habitat Conservation Plan Expanded Water Quality Report 2013, 33 p.
- . 2014. *Hydrologic Data Report for 2013*, Edwards Aquifer Authority Report 13-01, 371 p.
- Environet. 2014. RTI Water Quality Data. Available online at: <https://ienvironet.com>. Accessed October 2014.
- MacDonald, D.D., C.G. Ingersoll, T.A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology*, 31 p.
- National Oceanic and Atmospheric Administration (NOAA). 2014. Precipitation Data. Available online at: http://www.srh.noaa.gov/ridge2/RFC_Precip/. Accessed October 2014.
- Office of the Secretary of State. 2014. MCL information and tables. Available online at: [http://info.sos.state.tx.us/pls/pub/readtac\\$ext.ViewTAC?tac_view=5&ti=30&pt=1&ch=290&sch=F&rl=Y](http://info.sos.state.tx.us/pls/pub/readtac$ext.ViewTAC?tac_view=5&ti=30&pt=1&ch=290&sch=F&rl=Y). Accessed October 2014.
- . 2014. Texas specific soil background metals concentrations. Available online at: <http://info.sos.state.tx.us/fids/200700768-1.html>. Accessed October 2014.
- Texas Commission on Environmental Quality (TCEQ). 2012. Table 3.5 Screening Levels for Sediments. In *2012 Guidance for Assessing and Reporting Surface Water Quality in Texas*, p. 3-16.
- . 2014. Texas risk reduction program rules and protective concentration levels (PCL) tables. Available online at: http://www.tceq.state.tx.us/assets/public/remediation/trrp/trrptbls1_5_042308.xls. Accessed October 2014.
- U.S. Environmental Protection Agency (EPA). 2012. Pharmaceutical and personal care products. Available online at: <http://www.epa.gov/ppcp/>. Accessed October 2014.
- U.S. Geological Survey (USGS). 2014. Water resources streamflow data. Available online at: <http://www.usgs.gov/water/>. Accessed October 2014.

APPENDIX A

**EDWARDS AQUIFER HABITAT CONSERVATION PLAN
(EAHCP) WORKPLAN**

2014 Water Quality Monitoring Program Strategy for Comal Springs and San Marcos Springs in Support of the Edwards Aquifer Habitat Conservation Plan

June 11, 2013

Prepared by

Edwards Aquifer Authority

INTRODUCTION

This Work Plan details the sampling strategy and protocols for water quality monitoring in 2014 for the Edwards Aquifer Habitat Conservation Plan (EAHCP) (Section 5.7.2) to be implemented by the Edwards Aquifer Authority (EAA), utilizing a third party contractor. The goal of the Water Quality Monitoring Program, first implemented in 2013, is to detect water quality impairments that may negatively impact the listed species by allowing the investigation and adoption of any necessary measures through the aquifer management planning process. In the event that certain constituents of concern are detected at levels indicating the potential for adverse effects, the Implementing Committee member with jurisdictional authority will be consulted to identify sources and consider Best Management Practices (BMPs) to reduce and/or eliminate the constituents of concern. If necessary, additional testing could be included in the current or following year to assist in determining the source of contamination and the Science Committee could be consulted to assist with BMP identification and source determination.

SCOPE OF WORK

In accordance with the EAHCP, in 2013 the EAA expanded its Water Quality Monitoring Program to include additional surface water (and storm water), groundwater, and sediment sampling within Comal Springs and San Marcos Springs and associated river systems. All contractors who will be collecting water quality data and samples as part of the EAHCP process will conduct sampling per this Water Quality Monitoring Program for Comal and San Marcos springs. Sampling locations for 2014 are shown in the attached figures and will utilize the exact sampling locations used in 2013. However, changes in springflow, surface water runoff, land use, site security and access may dictate minor modification to sample collection locations and schedules as sampling efforts progress. Any minor changes resulting from these factors that are necessary as a result of safety or equipment concerns will be noted in the field sample sheets and dedicated field books. Should logistics or safety issues require any significant changes through the course of the year, they will be presented to the Science Committee for review prior to implementation.

COMAL SPRINGS

Comal Springs discharges an average of 291 cubic feet second (cfs) into Landa Lake, located within the city of New Braunfels, Texas. Comal Springs is considered a spring complex with multiple discharge points along the 4,500 foot reach of Landa Lake. Comal Springs issue from the Edwards Group limestone along the 4,500-foot section of the northeast-southwest trending

escarpment formed by the Comal Springs Fault. Landa Lake forms the headwaters of the Comal River which flows approximately two miles before entering the Guadalupe River.

Discharge measurements have been collected from Comal Springs since 1933 and the EAA has been collecting water quality samples for more than ten years. In recent years, the EAA has been collecting samples from Spring 1, Spring 3, and Spring 7 on a quarterly basis during normal flow conditions and on a monthly basis when the San Antonio Pool critical period triggers have been reached. Spring 1, Spring 3, and Spring 7 discharge into Landa Lake and make up part of the Comal Springs complex. Figure 1 indicates these historical groundwater sampling locations. Water quality samples are generally collected and analyzed for: dissolved oxygen (DO), pH, conductivity, and temperature, in the field and alkalinity¹. Samples are also submitted to the EAA contract laboratory for analysis of cations, anions, nutrients, metals, VOCs, SVOCs, herbicides and pesticides, bacteria, TOC, PCBs, and phosphorous. This list of parameters is defined as the water quality analytical list (WQAL).

Surface Water Sampling Locations

To comply with sampling requirements outlined in the EAHCP, five additional surface water sampling locations (Figure 2) were identified in the 2013 EAHCP Water Quality Work Plan for intensive monitoring in the Landa Lake and Comal River area as listed below:

- Upper Springs (near Bleiders Creek);
- Upper Landa Lake - (near Spring Island);
- Lower Landa Lake - (above outfalls);
- Upper Old Channel - (Elizabeth Street); and,
- USGS Gauge - (above San Antonio Street Bridge).

Surface Water Sampling Frequency

In 2014, water samples will be collected bi-annually (twice a year) from each of the five surface water locations listed above. The interval between sampling events will be approximately six months. Water samples will be analyzed for the WQAL parameters using a National Environmental Laboratory Accreditation Program (NELAP) laboratory. A listing of analytical parameters is provided in Appendix A. The Edwards Aquifer Authority will consult with the Science Committee regarding the addition of caffeine testing to this program. Following input from the Science Committee, the EAA will consult with the Implementing Committee to determine the appropriateness of including additional caffeine sampling. Regarding caffeine sampling, the executed contract between the EAA and the selected contractor will reflect the decision of the Implementing Committee.

Sampling Methods

All samples will be collected following the EAA's *Field Sampling Plan* or contractor established and approved methods. Samples will be analyzed by a NELAP accredited contract laboratory.

Sediment Sampling

One sediment sample will be collected during 2014 from each of the surface water sampling locations (Figure 2). Three samples will be collected from each sample site and composited into

¹ Alkalinity analysis will be conducted within eight hours of sample collection.

one sample for analysis. Sediment samples will be analyzed for the analytical parameters provided in Appendix B. Results of sediment sampling analysis will be used to formulate future sediment sampling at Landa Lake and the Comal River.

Storm Water Sampling Program for Comal Springs

Two storm water sampling events will be performed in 2014 to evaluate storm water quality from the urban landscape. A storm water sampling event will be triggered when a local rainfall event causes a significant increase in spring flow at the historic Comal Springs gauging station. Three water quality samples will be collected and analyzed from each surface water sampling location during the sampling event. Sample times will be spaced to reflect changes in the stream hydrograph (initial rise or first flush, peak flow, and recession limb). Water samples will be analyzed for the WQAL parameters. A listing of analytical parameters is provided in Appendix A, for storm water samples.

The following locations will be sampled for storm water as indicated on Figure 3:

- Upper Springs (near Blieders Creek);
- New Channel – (below confluence with Dry Comal Creek);
- Upper Old Channel - (at Elizabeth Street);
- Lower Old Channel - (above Hinman Island); and,
- Comal River - (above confluence with Guadalupe River).

Groundwater Sample Collection for Extreme Low Flow Scenarios for Comal Springs

In the event flow at Comal Springs drops below 30 cfs, the EAHCP (6.4.3.3) calls for weekly monitoring of three wells in the vicinity of the spring complex for DO, conductivity, pH, and temperature. Should springflow drop below 20 cfs, then additional weekly sampling to include nutrients, TDS, and TOC are to be added to the sample regimen. Analytical costs per sample point for the second set of parameters (flows below 20 cfs) is included in Appendix A. Based on conditions during the drought of record (circa 1950s), sampling for a lower flow scenario could last for up to 21 weeks. The three specific wells to be used will be determined at the time of sampling based on well conditions and aquifer levels.

Water Quality Data Logging Program for Comal Springs

Continuous water quality monitoring stations were established in 2013 and will continue in 2014 at the following locations indicated on Figure 4:

- Spring Run #3;
- Spring # 7; and,
- New Channel (below confluence with Dry Comal Creek).

Monitoring will be performed using a data logging sonde capable of collecting data on 15 minute intervals. The parameters measured will include temperature, dissolved oxygen, pH, turbidity, and specific conductance. These data will be evaluated to identify short-term and long-term water quality variations of the spring system as well as changes in water quality related to storm water runoff.

Continuous water quality monitoring stations will be operated and maintained by EAA.

SAN MARCOS SPRINGS

San Marcos Springs, located in San Marcos, Texas discharges an averages of 176 cfs into Spring Lake. San Marcos Springs is located on the campus of Texas State University. The springs issue from the Edwards Group limestone along the northeast-southwest trending escarpment formed by the San Marcos Springs Fault. Spring Lake forms the headwaters of the San Marcos River.

Discharge measurements have been collected from San Marcos Springs since 1957 and the EAA has been collecting water quality samples for more than ten years.

In recent years, the EAA has been collecting samples from Deep Spring and Hotel Spring on a quarterly basis during normal flow conditions and on a monthly basis when the San Antonio pool critical period triggers have been reached. Both Deep and Hotel springs are located in the bed of Spring Lake and make up part of the San Marcos Springs complex. Figure 5 indicates these historical groundwater sample locations at San Marcos Springs. Water quality samples are generally collected and analyzed for: dissolved oxygen (DO), pH, conductivity, and temperature, in the field and alkalinity². Samples are also submitted to the EAA contract laboratory for analysis of cations, anions, nutrients, metals, VOCs, SVOCs, herbicides and pesticides, bacteria, TOC, PCBs, and phosphorous. This list of parameters is defined as the water quality analytical list (WQAL) and is an identical list of parameters analyzed for Comal Springs.

Surface Water Sampling Locations

To comply with sampling requirements outlined in the EAHCP, seven additional surface water sampling locations (Figure 6) were identified in the 2013 EAHCP Water Quality Work Plan for intensive monitoring as listed below:

- Sink Creek;
- Spring Lake;
- Sessoms Creek;
- City Park;
- Rio Vista Dam;
- I-35 reach; and,
- Capes Dam.

Surface Water Sampling Frequency

In 2014, water samples will be collected bi-annually (twice a year) from each of the seven surface water locations listed above. The interval between sampling events will be approximately six months. Water samples will be analyzed for the WQAL parameters using a National Environmental Laboratory Accreditation Program (NELAP) laboratory. A listing of analytical parameters is provided in Appendix A. The Edwards Aquifer Authority will consult with the Science Committee regarding the addition of caffeine testing to this program. Following input from the Science Committee, the EAA will consult with the Implementing Committee to

² Alkalinity analysis will be conducted within eight hours of sample collection.

determine the appropriateness of including additional caffeine sampling. Regarding caffeine sampling, the executed contract between the EAA and the selected contractor will reflect the decision of the Implementing Committee.

Sampling Methods

All samples will be collected following the EAA's *Field Sampling Plan* or contractor established and approved methods. Samples will be analyzed by a NELAP accredited contract laboratory.

Sediment Sampling

One sediment sample will be collected during 2014 from each of the surface water sampling locations (Figure 6). Three samples will be collected from each sample site and composited into one sample for analysis. Sediment samples will be analyzed for the analytical parameters provided in Appendix B. Results of sediment sampling analysis will be used to formulate future sediment sampling at Spring Lake and the San Marcos River.

Storm Water Sampling Program for San Marcos Springs

Two storm water sampling events will be performed in 2014 to evaluate storm water runoff from the urban landscape. A storm water sampling event will be triggered when a local rainfall event causes a significant increase in spring flow at the San Marcos Springs gauging station. Three water quality samples will be collected from each surface water sampling location during the sampling event. Sampling times will be spaced to reflect changes in the stream hydrograph (initial rise or first flush, peak flow, and recession limb). Water samples will be analyzed for the WQAL parameters. A listing of analytical parameters is provided in Appendix A, for storm water samples.

The following locations will be sampled for storm water as indicated on Figure 7:

- Sink Creek;
- Sessoms Creek;
- Dog Beach Outflow;
- Hopkins Street Outflow;
- Purgatory Creek (above San Marcos River);
- I-35 Reach; and
- Willow Creek (above San Marcos River).

Groundwater Sample Collection for Extreme Low Flow Scenarios for San Marcos Springs

In the event flow at San Marcos Springs drops below 50 cfs, the EAHCP (6.4.4.3) calls for weekly monitoring of three wells in the vicinity of the spring complex for DO, conductivity, pH, and temperature. Should springflow drop below 30 cfs, then additional weekly sampling to include Nutrients, TDS, and TOC are to be added to the sample regimen. Analytical costs per sample point for the second set of parameters (flows below 30 cfs) is included in Appendix A. Based on conditions during the drought of record (circa 1950s), sampling for a low flow scenario could last for up to 21 weeks. The three specific wells to be used will be determined at the time of sampling based on well conditions and aquifer levels.

Water Quality Data Logging Program for San Marcos Springs

Continuous water quality monitoring stations were established in 2013 and will continue in 2014 at the following locations indicated on Figure 8:

USGS gauging station; and,
Rio Vista Dam.

Monitoring will be performed using a data logging sonde capable of collecting data on 15 minute intervals. The parameters measured will include temperature, dissolved oxygen, pH, turbidity, and specific conductance. These data will be evaluated to identify short-term and long-term water quality variations of the spring system as well as changes in water quality related to storm water runoff.

Continuous water quality monitoring stations will be operated and maintained by EAA.

WATER QUALITY MONITORING RESULTS

Sampling results will be presented in an annual report by the Edwards Aquifer Authority. The report will include an evaluation of analytical data, graphs of water quality laboratory and field data sheets, photographs, sampling locations and rationale, description of sampling methods, and a description and rationale for any minor deviations from the Water Quality Sampling Plan due to logistics or safety issues. The Water Quality Sampling Plan will be reviewed internally by EAA and updated on an annual basis as needed to evaluate and refine sampling locations, parameter list, sampling and analysis methods, and any potential issues that arise, based on the analytical results.

DATA COMPILATION, ANALYSES AND REPORTING

All of the data collected as a result of the 2014 EAHCP Water Quality Monitoring Plan will be compiled, analyzed, and the results will be presented to the Implementing Committee by February 15, 2015; prior to inclusion in the EAHCP Annual Report that is required by Sections 6.2.4 and 9.3 of the EAHCP and Section 11.1c of the Implementing Agreement. The report will include an evaluation of all analytical data, including graphs, key photographs and general summary of results.

SCIENCE COMMITTEE REVIEW

This 2014 Water Quality Work Plan was reviewed by the EAHCP Science Committee on April 3, 2013. The Science Committee recommended the following additions or changes to the Water Quality Work Plan:

- Utilize automated samplers for storm water events rather than single grab sampling conducted by EAA Staff.
- Consider the feasibility of utilizing Gore Samplers.
- Utilize field method for determination of alkalinity rather than transporting samples to the lab for analysis.

After consultation with EAA water quality and technical staff, it was determined that the decision to include automated samplers would be made after proposals to perform the water quality monitoring are received from third party contractors, Gore Samplers would be included if

funding allowed, and alkalinity tests would be conducted in a manner to prevent degassing. The following reasoning was provided by the EAA water quality and technical staff:

- **Automated Samplers** – Each storm water sample requires approximately nine liters of liquid. Most automatic water samplers (auto samplers) can collect up to 24 liters of liquid which would allow for two samples to be collected per auto sampler. Considering that five to eight, or more, samples may be collected per sample site per storm water event, this would require 3 to 4 auto samplers per site to meet the sampling requirements³. In addition, many analytical parameters require preservatives or other sample collection requirements such as refrigeration and/or no head space in the container. These requirements greatly complicate or invalidate some sample analytical parameters collected using auto samplers. To properly sample each of the 12 sampling sites would require approximately 52 auto samplers to cover all parameters required by the EAHCP (plus additional replacement samplers as backup). This would increase the cost of this work plan by approximately \$312,000, not including staff time or miscellaneous installation materials, which are estimated to be an additional \$60,000. Additionally, auto samplers may not be utilized for VOC analysis⁴, which is required by the EAHCP. The benefit of auto samplers is to help ensure collection of the first flush samples of storm water events. However, auto samplers have high maintenance requirements and have a moderate failure rate. However, RFP's for the 2014 Water Quality Monitoring Program will allow the proposer to address how stormwater samples are to be collected. Upon receiving proposals, EAA staff will evaluate the varying approaches and rationale proposed, and make a decision at that time about how to sample for stormwater.
- **Gore Samplers** – EAA staff agreed that Gore Samplers could be utilized and could provide useful data. However, installation of Gore Samplers at all 12 sampling sites would increase the cost of this work plan by approximately \$125,000; not including staff time or miscellaneous installation equipment. However, installation of four Gore Samplers (one at the upstream and one at the downstream sampling point of each river), replaced monthly, could provide some very beneficial and useful baseline data for approximately \$35,000. Four Gore Samplers and analysis will be included in the RFP for 2014 Water Quality Monitoring.
- **Alkalinity** – EAA will require the contractor selected for Water Quality Monitoring to analyze alkalinity samples within eight hours of collection to minimize degassing.

BUDGET

Table 7.1 Budget: \$200,000

2014 Work Plan cost: \$550,000⁵

Stormwater Sampling: \$200,000

Low Flow Well Sampling: \$100,000

Sediment Sampling/grab samples: \$100,000

Auto-Samplers: \$150,000

Justification for Budget Adjustment

³ Of the total number of samples collected from each site, three samples will be selected based on analysis of the hydrograph.

⁴ Due to degassing of the collected sample.

⁵ Please Note: \$400,000 for sampling; \$150,000 for potential inclusion of automated samplers

The EAA will go out for competitive bids for the 2014 Water Quality Monitoring Program in the fall of 2013. The proposal will include bids for surface grab sampling, sediment sampling, well sampling, storm sampling, and Gore sampling. Real-time stations will be operated and maintained by EAA. As to storm water, the RFP will allow the bidder to propose methodology and equipment to be utilized; allowing EAA to select from bids considering methodology, product and pricing.

While the previously submitted work plan contemplated that EAA would utilize existing staff to carry out the prescribed duties and requirements of the water quality monitoring plan in both the Comal and San Marcos Springs systems, EAA has determined that such an approach is not practical in that the requirements of the work plan significantly exceed the scope of work EAA has historically conducted in this area. Although EAA has historically conducted some water quality monitoring activities in and around the spring systems, it has concluded that the highly prescriptive and time sensitive requirements of the EAHCP will be more effectively and efficiently satisfied through the contracting of a third party with the applicable expertise and germane experience necessary to meet those specific needs. EAA, therefore, would like to solicit proposals from qualified vendors to implement the water quality monitoring plan and to then manage the awarded contract accordingly. Transferring the burden of the water quality monitoring plan work from EAA staff to a contracted vendor, however, will result in an increase in budget for the combined labor and analytical costs.







Figure 5
San Marcos Springs Groundwater Sample Locations



Most of the historical EAA sampling records for San Marcos Springs pertains to the locations known as Hotel and Deep (spring vents). Other locations at San Marcos Springs may have a limited sample record.

Samples are collected monthly during low flow conditions (critical period), and quarterly during normal conditions.

Explanation

- ★ Historical Groundwater (Spring) Sample Location

Prepared by:









Appendix A

Analytical Parameters for Assessing Water Quality from Storm Water and Surface Water Locations, Comal and San Marcos Springs

Analyses
Volatile Organic Compounds (VOCs)
Semi-volatile Organic Compounds (SVOCs)
Organochlorine Pesticides
Polychlorinated Biphenyls (PCBs)
Organophosphorous Pesticides
Herbicides
Metals (Al, Sb, As, Ba, Be, Cd, Cr (total), Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Tl, and Zn)
General Chemistry (GWQP) Total Alkalinity (as CaCO ₃), Bicarbonate Alkalinity (as CaCO ₃), Carbonate Alkalinity (as CaCO ₃); (Cl, Br, NO ₃ , SO ₄ , F, pH, TDS, TSS, Ca, Mg, Na, K, Si, Sr, CO ₃), and Total Suspended Solids (TSS).
Phosphorus (total)
Total Organic Carbon (TOC),
Dissolved Organic Carbon (DOC)
Kjeldahl Nitrogen
Bacteria Testing (<i>E coli</i>)

Method	Method Description	Protocol
8260B	Volatile Organic Compounds	(GC/MS) SW846
8270C	Semivolatile Organic Compounds	(GC/MS) SW846
8081B	Organochlorine Pesticides	(GC) SW846
8082A	Polychlorinated Biphenyls (PCBs)	by Gas Chromatography SW846
8141A	Organophosphorous Pesticides	(GC) SW846
8151A	Herbicides	(GC) SW846
6010B	Metals	(ICP) SW846
6020	Metals	(ICP/MS) SW846
7470A	Mercury	(CVAA) SW846
300.0	Anions,	Ion Chromatography
340.2	Fluoride	MCAWW
365.4	Phosphorus,	Total EPA
9040C	pH	SW846
9060	Organic Carbon,	Total (TOC) SW846
SM 2320B	Alkalinity	SM
SM 2540C	Solids,	Total Dissolved (TDS) SM
SM 2540D	Solids, Total Suspended (TSS)	SM
351.2	Nitrogen, Total Kjeldahl	MCAWW

Protocol References:

EPA = US Environmental Protection Agency

MCAWW = "Methods For Chemical Analysis Of Water And Wastes", EPA-600/4-79-020, March 1983 And Subsequent Revisions.

SM = "Standard Methods For The Examination Of Water And Wastewater",

SW846 = "Test Methods For Evaluating Solid Waste, Physical/Chemical Methods", Third Edition, November 1986 And Its Updates.

Analytical Parameters for Critical Period Related (Low Flow) Sampling of Water Wells, Comal and San Marcos Springs

Analyses
General Chemistry (GWQP) Total Alkalinity (as CaCO ₃), Bicarbonate Alkalinity (as CaCO ₃), Carbonate Alkalinity (as CaCO ₃); (Cl, Br, NO ₃ , SO ₄ , F, pH, TDS, TSS, Ca, Mg, Na, K, Si, Sr, CO ₃ ,)
Total Organic Carbon (TOC)
Total Dissolved Solids (TDS)
<i>Total Cost per Sample for Potential Critical Period Sampling (Per Sample Point)</i>

QA/QC Sample Costs (Dupes / EQ Blanks)				
Comal Surface Water=	\$815.00	2		0
San Marcos Surface Water=	\$815.00	2		0
Comal Storm Water=	\$815.00	2		0
San Marcos Storm Water=	\$815.00	2		0
Comal Sediments=	\$815.00	1		0
San Marcos Sediments=	\$815.00	1		0
Total Costs QA/QC Samples				

Appendix B

Analytical Parameters for Assessing Water Quality from Sediment Sample Locations, Comal and San Marcos Springs

Analyses
Volatile Organic Compounds (VOCs)
Semi-volatile Organic Compounds (SVOCs)
Organochlorine Pesticides
Polychlorinated Biphenyls (PCBs)
Organophosphorous Pesticides
Herbicides
Metals (Al, Sb, As, Ba, Be, Cd, Cr (total), Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Tl, and Zn)
General Chemistry Total Alkalinity (as CaCO ₃), Bicarbonate Alkalinity (as CaCO ₃), Carbonate Alkalinity (as CaCO ₃); Ca, Mg, Na,
Phosphorus (total)
Total Organic Carbon (TOC),
Dissolved Organic Carbon (DOC)
Total Cost Per Sample Point (Sediment Samples)

Method	Method Description	Protocol
8260B	Volatile Organic Compounds	(GC/MS) SW846
8270C	Semivolatile Organic Compounds	(GC/MS) SW846
8081B	Organochlorine Pesticides	(GC) SW846
8082A	Polychlorinated Biphenyls (PCBs)	by Gas Chromatography SW846
8141A	Organophosphorous Pesticides	(GC) SW846
8151A	Herbicides	(GC) SW846
6010B	Metals	(ICP) SW846
6020	Metals	(ICP/MS) SW846
7470A	Mercury	(CVAA) SW846
300.0	Anions,	Ion Chromatography
340.2	Fluoride	MCAWW
365.4	Phosphorus,	Total EPA
9040C	pH	SW846
9060	Organic Carbon,	Total (TOC) SW846
SM 2320B	Alkalinity	SM
SM 2540C	Solids,	Total Dissolved (TDS) SM
SM 2540D	Solids, Total Suspended (TSS)	SM

Protocol References:

EPA = US Environmental Protection Agency

MCAWW = "Methods For Chemical Analysis Of Water And Wastes", EPA-600/4-79-020, March 1983 And Subsequent Revisions.

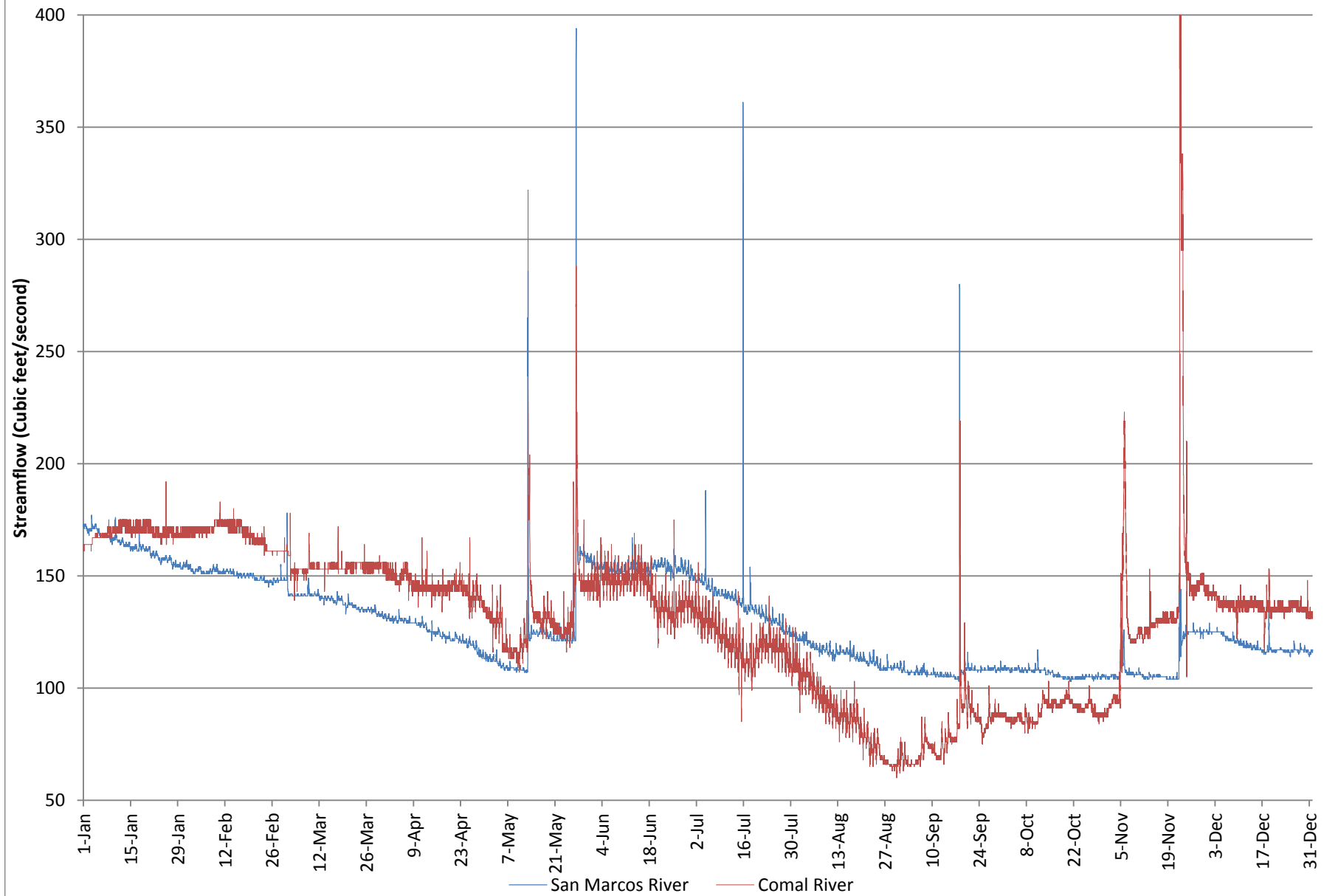
SM = "Standard Methods For The Examination Of Water And Wastewater",

SW846 = "Test Methods For Evaluating Solid Waste, Physical/Chemical Methods", Third Edition, November 1986 And Its Updates.

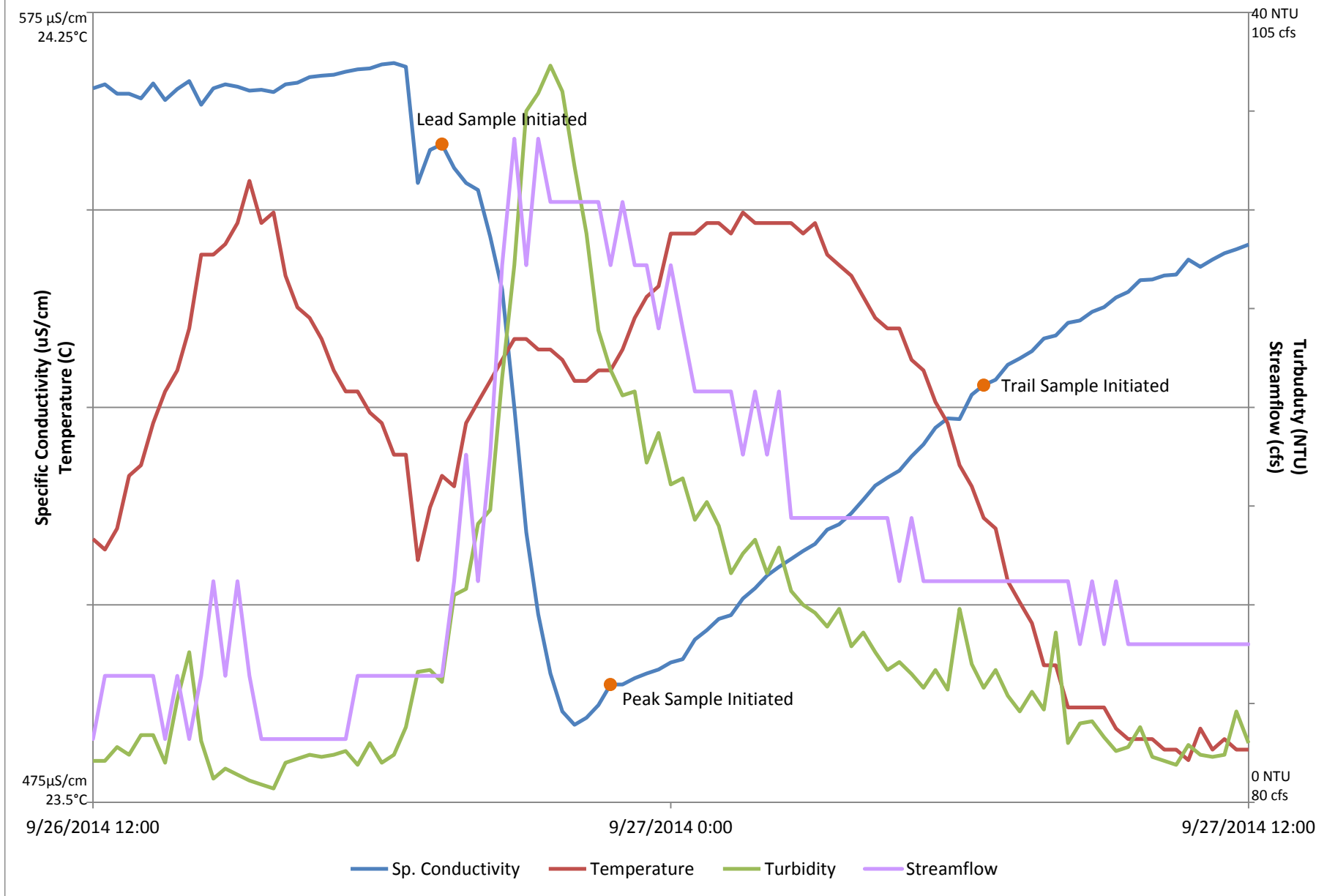
APPENDIX B

**SPRING HYDROGRAPHS AND
STORM WATER QUALITY GRAPHS**

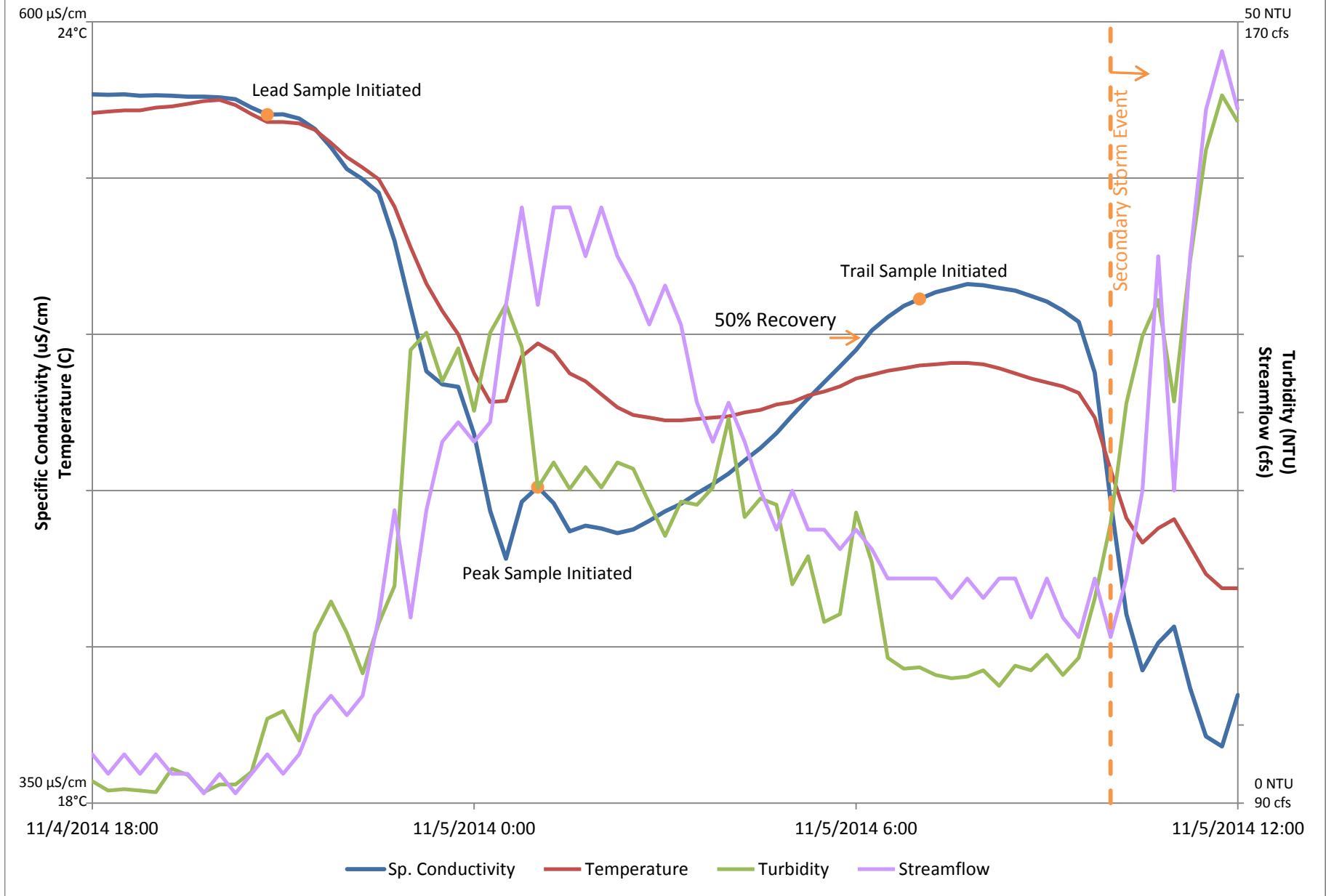
Streamflow (cfs) Raw Data Plot 2014



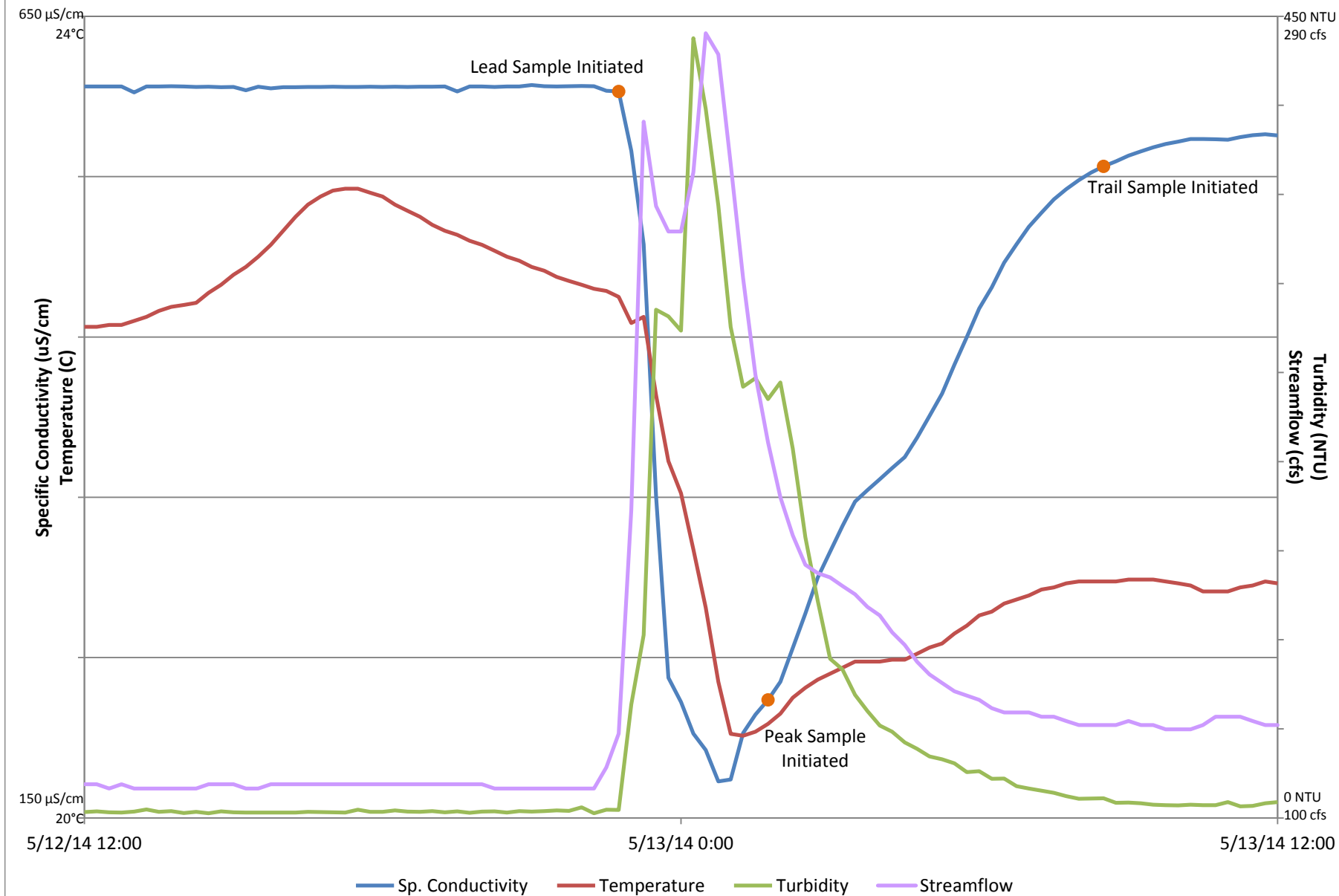
Comal River Storm Water Quality Graph September 26-27, 2014



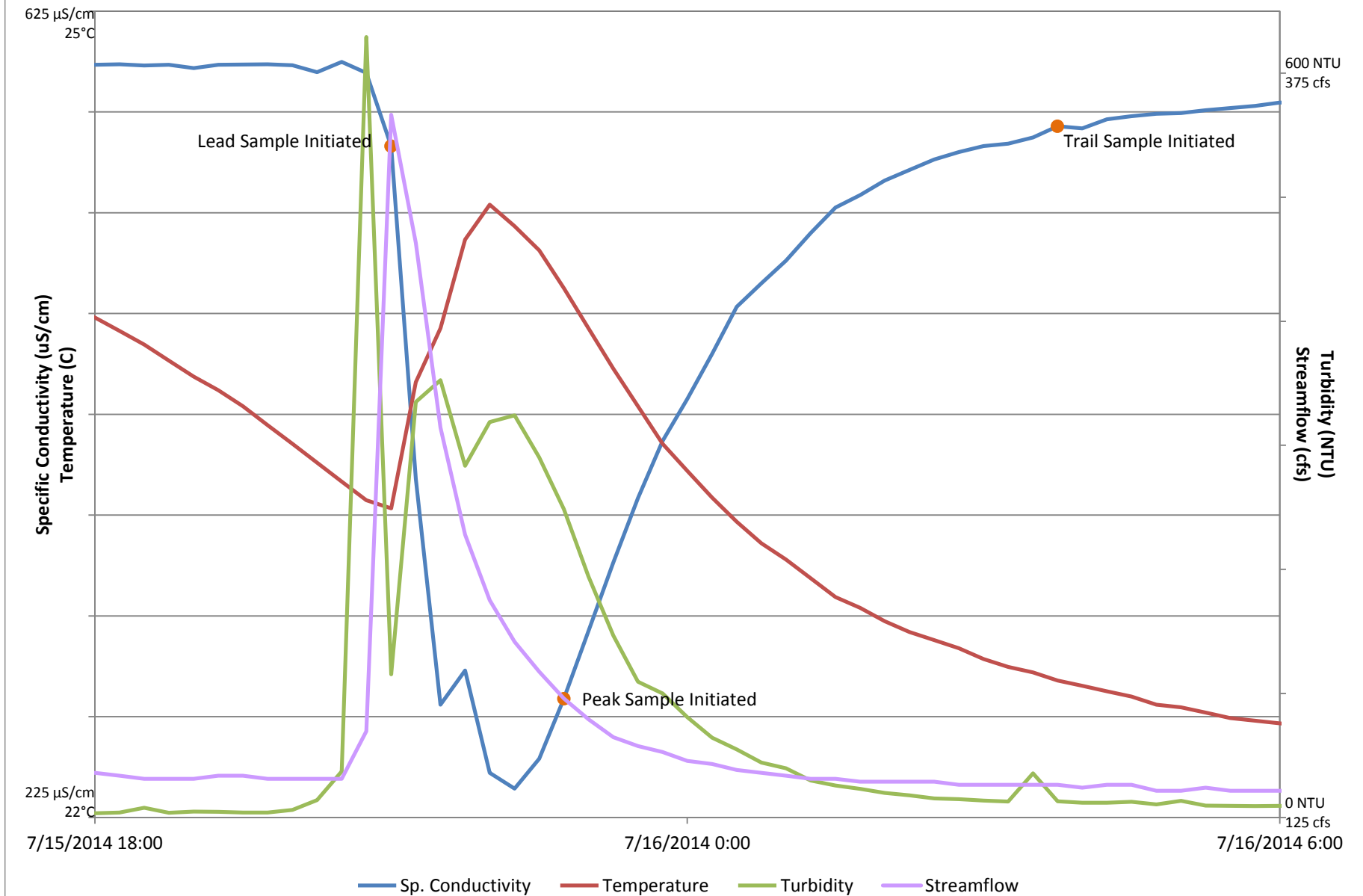
Comal River Storm Water Quality Graph November 4-5, 2014



San Marcos Storm Water Quality Graph May 12-13, 2014



San Marcos Storm Water Quality Graph July 15-16, 2014



APPENDIX C

DISCUSSION OF DEVIATIONS

Appendix C Discussion of Deviations

Comal Springs

Surface Water

Surface water was collected in the Comal Springs complex in March and September 2014. Surface water sampling locations did not deviate from the EAHCP Workplan.

March 25, 2014, Collection

Surface water grab samples were collected on March 25, 2014, by Richard Howard. The sample bottles for metals were collected without filtration, and the laboratory was asked to conduct the filtration prior to analysis. At the request of the EAA, re-sampling was conducted, and samples were filtered in the field on April 29, 2014. The results from the analyses of the samples collected on April 29, 2014, are used in the data evaluation. Samples for nitrates analyses were also collected on April 29, 2014, because holding times had been exceeded during the March 25, 2014 sampling event. Neither the original March 2014 samples nor the April 2014 resample were analyzed for manganese due to a field oversight. Field staff did not know manganese analysis was not included in the standard metals analysis and needed to be specifically requested from the contract laboratory on the chain of custody forms. A miscommunication to field staff also occurred with field duplicate collection resulting in collection of one duplicate per sampling event as oppose to one per every ten samples.

September 25 and 26, 2014, Collection

The September 2014 surface water collection was difficult to obtain due to several small rain events that occurred during the month, which affected base flow water quality conditions as monitored by the real time instruments (RTIs). Sampling was scheduled for September 29 and 30, 2014, on days EAA staff were available to observe sampling. However, a large rain event was forecasted for the evening of September 26 and 27, 2014. Therefore, in order to avoid having base flow conditions affected by a storm prior to collecting samples on September 29 and 30, 2014, SWCA staff consulted with EAA staff and decided surface water samples should be collected prior to the storm. This resulted in samples being collected on a Friday, September 26, 2014. SWCA sampling staff had to immediately mobilize to collect stormwater samples during the evening of September 26, 2014 and were therefore unable to package and ship samples to the laboratory for overnight delivery on Saturday, September 27, 2014. Samples were held on ice at the SWCA San Antonio office before being shipped to the laboratory on Monday, September 29, 2014. This delay caused the nitrate samples to exceed the recommended 48-hour hold time. The samples also exceeded the 15-minute hold time for pH analysis, however pH was measured in the field at the time of sample collection.

Stormwater

Stormwater events were sampled September 26-27 and November 4-5, 2014, in the Comal Springs complex. SWCA staff were prepared to sample storm events beginning in May 2014 however, both Comal Springs storm events were collected late in the year. The ongoing drought made storm water sampling exceedingly difficult to perform. Rain events were generally scattered in nature and often too small in magnitude to generate sufficient runoff to sample. Storm water sampling locations did not deviate from those proposed in the EAHCP Workplan.

September 26-27, 2014, Event

The rain event began at approximately 7:00PM making it impossible for *E. coli* samples from the lead and peak sampling sets to reach the laboratory within the 6-hour hold time. All samples were submitted when the San Antonio River Authority (SARA) laboratory opened on the morning of September 27, 2014.

Samples, other than *E. coli*, are normally shipped to the Calscience laboratory via overnight courier immediately after collection. However, this event occurred on a Friday evening when overnight delivery was not available. The samples were kept on ice at the SWCA San Antonio office until shipping was available Monday, September 29, 2014. Staff continued to monitor samples and replace ice throughout the weekend ensuring the samples stayed at ideal temperatures. This delay did lead to the nitrate samples exceeding the 48 hour laboratory hold time. pH samples also exceeded the recommended 15-minute hold times but pH data was also collected in the field. All other samples were delivered within hold times.

Due to the timing of the stormwater event, samples from HCS210 Peak, HCS240 Peak, HCS250 Peak, HCS270 Peak were analyzed for alkalinity outside of the 8-hour hold time. All were analyzed within 1.5 hours of hold time.

The cooler containing the samples for HCS210 Peak was lost during shipment to the laboratory. The cooler was never recovered by Fedex, and the sample was not analyzed. Field parameters, field alkalinity, and *E. coli* are the only data available for this sample.

November 4-5, 2014, Event

Due to overnight collection of samples it was not possible to submit Lead and Peak samples to the lab within hold times for *E. coli* analysis. The samples were submitted when the laboratory opened on the morning of November 5, 2014.

At the stormwater base camp when alkalinity analysis were being conducted by SWCA staff a very low pH value of 2.32 was discovered in the water within a cubitainer for sample FDHCS 270 Trail. The pH measured in the stream at the time of sample collection was 7.22. The cubitainer was used to collect and filter water for metals and field alkalinity analyses. The cubitainer and bottle for metals analyses were shipped with the rest of the sample bottles to Calscience for analyses. Measurement of alkalinity was not possible because of the low pH value.

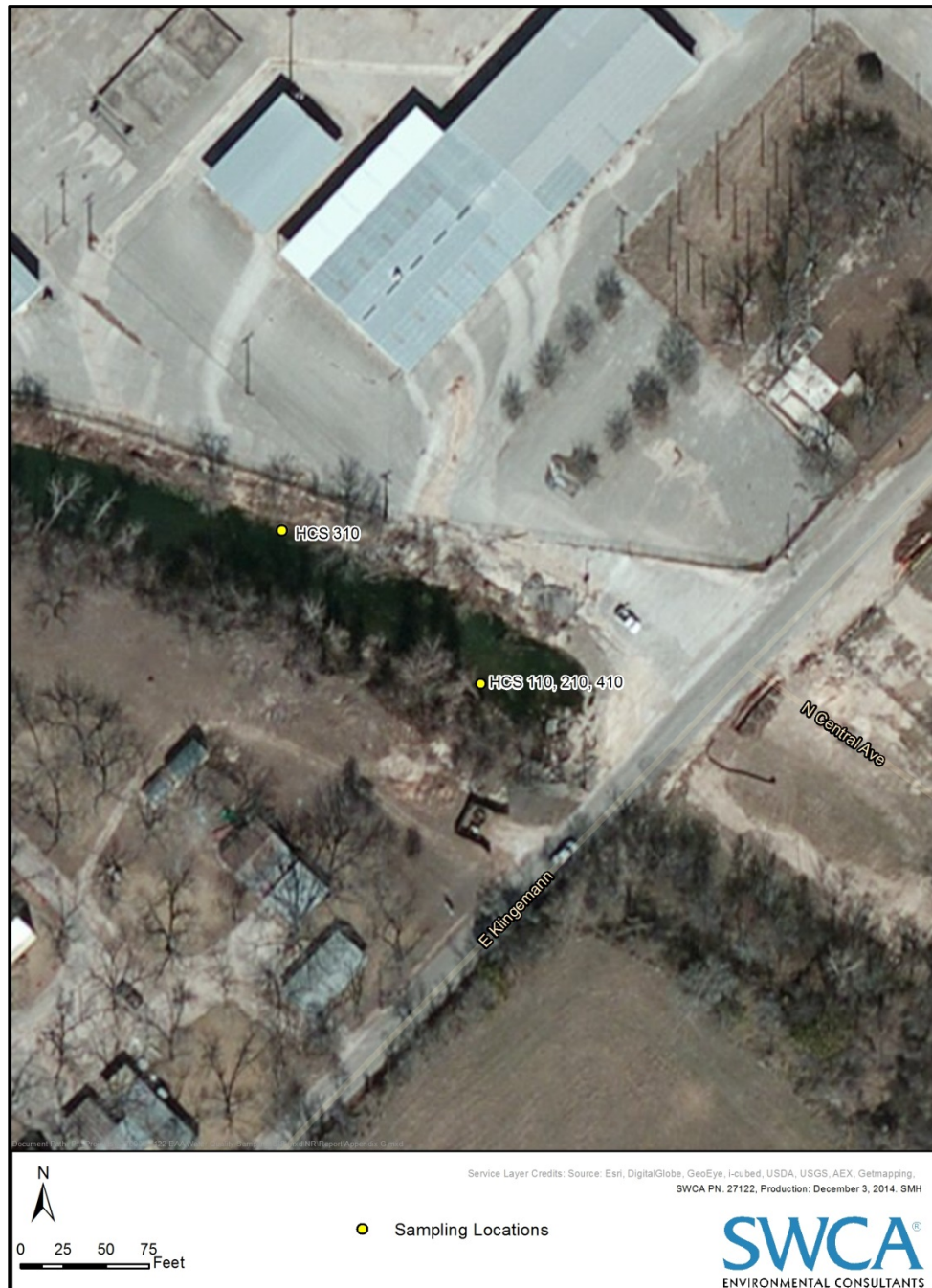
The cubitainer pH value measured by SWCA was 2.32. Calscience measured a pH value of 2.4 in the cubitainer. The pH measured with a sonde in the stream at the time of sample collection was 7.22. It appears acid was somehow introduced into the cubitainer prior to or during filling of the cubitainer. The source of acid is unknown. The cubitainer has a volume of approximately 2.5 gallons. Therefore preservative acid from one of the 1-liter bottles does not seem sufficient to have lowered the pH in the larger cubitainer to as low as 2.32 or 2.4, but it is the most likely source of acid that could have been emptied into the cubitainer during sample collection. A bottle filled with preservative acid could have mistakenly been used to fill the cubitainer. Because the sample was a field duplicate, the parent sample was not affected, and those results are still valid. In addition, water for VOC, SVOC, pesticide, herbicide, and PCB analyses was not taken from the cubitainer; and therefore, would not be affected. The only analyses potentially affected by acid within the cubitainer would be pH, metals, alkalinity, and other general water quality parameters. While the TDS and sulfates appear elevated in the field duplicate above the parent sample, the water quality parameters appear relatively consistent with the parent sample. The parent sample is valid and all results from the field duplicate appear valid with the exception of pH, alkalinity, TDS, and sulfates. Trail sampling was initiated when the data from the RTI indicated the system reached 50% recovery from the peak. A second storm moved into the area during trail sample collection and caused parameters to change again. It was determined in the field this new change in parameters indicated the beginning of a secondary storm event. The samples collected are considered a valid sampling set as the trail was collected before the beginning of the secondary event.

Sediments

Sediment samples were collected from the Comal Springs complex on June 25 and 26, 2014. The EAHCP Workplan designated sediment collection sites to coincide with surface water collection points but allowed for some deviation from these locations as field conditions dictated. Sediment samples were frequently collected more than 30 feet from surface water collection points due to limited amounts of available sediment and river depth. Sediment collection location deviations are discussed below.

HCS310

Surface water samples were collected near the center of the stream near East Klingemann Street but limited amounts of sediment and rocky substrate in this area made sample collection difficult. A sample was collected approximately 100 feet downstream, approximately 15 feet from the northern bank where more sediment appeared available. As a result of limited sediment at this site, the remaining sample was collected approximately 20 feet back upstream toward the surface water location. This sample yielded adequate sediment and was collected near the edge of the water on the northern bank. The figure below demonstrates the approximate sediment sample location.



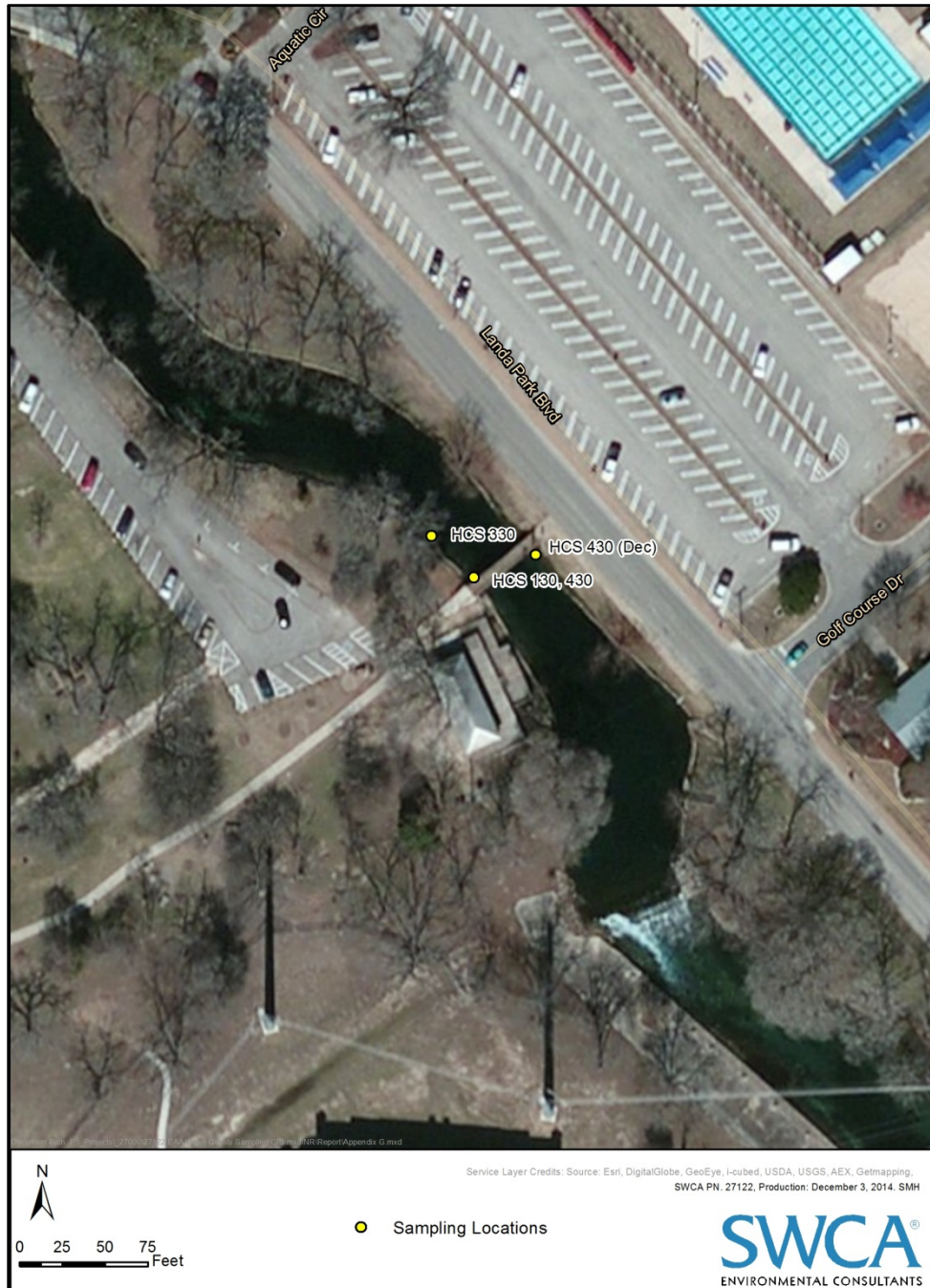
HCS320

Surface water samples at this location are collected off the northeast side of Spring Island. This area is characterized by large rocks and gravel substrate. The sediment samples were collected near the smaller island northeast of Spring Island, approximately 15 feet southeast of the smaller island. The figure below shows the approximate sample locations.



HCS330

Due to river depth and limited sediment available, the sediment samples were collected upstream of the surface water collection point. The samples were collected approximately 50 feet upstream along the west bank of the river.



HCS340

Surface water samples are collected from the eastern side of Elizabeth Avenue at this sample site, however the substrate in this area is very rocky with a strong current and little to no sediment. Sediment samples were collected upstream on the western side of Elizabeth Avenue, approximately 30 feet from the road. Sediment was collected approximately 10 feet from shore but yielded only a small sample. The remaining sample was collected approximately 25 feet from shore in the center of the stream channel.



HCS360

Surface water collection occurred on the upstream side of the bridge near the western bank at this location. Sediment was collected on the upstream side of the bridge approximately 12 feet from the eastern bank due to high river depth in the majority of the stream channel. A field duplicate was also collected in the same location.



Passive Diffusion Samplers

Passive diffusion samplers (PDS) were deployed at each of the surface water sample collection sites. When at all possible deployment locations coincided with the surface water locations, some adjustment had to be made to account for river depth, accessibility by SWCA staff for installation and retrieval, and interference by the public. PDS were deployed for two-week periods during the months of March, April, June, August, October, and December 2014. In March 2014, the PDS were deployed with a fishing weight to anchor them but had no protective housing. This resulted in retrieval of only approximately half of the deployed PDS. The missing PDS are presumed to have been removed by vandals, washed away to a point where they could not be located, or lost in vegetation. In April 2014, the PDS were deployed inside of a plastic tube held by a larger fishing weight but the retrieval rate was worse. To resolve this issue, SWCA staff designed and constructed a concrete and stainless steel deployment device to hold the PDS. The device was put into use beginning with the June 2014 deployment, this resulted in much higher PDS recovery rates. . All PDS were recovered in July, October and December 2014 except HCS430 in October. HCS 430 was removed from the Comal River by a construction company working an ongoing bank stabilization project. Despite a tag stating “Do Not Disturb,” which also provided SWCA contact information, the PDS was still removed and SWCA was not contacted. The PDS was recovered from the construction company, but it had been out of the river for an unknown period of time. Therefore the PDS was not analyzed.

The March 2014 PDSs were installed one month later than called for in the scope of work. The April 2014 PDS were deployed for a period of five weeks instead of two weeks.

Any alterations to sample locations or lost PDS are discussed below.

HCS420

March 2014 – PDS not recovered.

April 2014 – PDS not recovered.

June 2014 – Deployment device was moved 150 to 200 yards upstream by vandals. The plastic cable ties were intact between the stainless steel cups and the PDS did not appear to have been tampered with. The PDS was analyzed.

August 2014 – Deployment device was upturned but was found in the original location with the plastic cable ties intact. The PDS was analyzed.

HCS430

August 2014 – Deployment device was removed from water shortly after deployment by a bank stabilization crew working in the area. This PDS was discarded without analysis due to device being left outside of construction office along nearby road for unspecified amount of time.

October 2014 – PDS recovered successfully but the bank stabilization crew was still working on opposite bank adjacent to the sampling site.

December 2014 – Bank stabilization crew still working at site. Device deployed from opposite bank of river, directly across from normal deployment location. Alterations to the river channel by the bank stabilization construction changed the depth of the channel in this location from approximately 4 feet with a sloping entrance point to a depth of 7 feet with a large retaining wall. To account for this change, the deployment device had to be lowered from the retaining wall with a length of rope instead of placed by wading into the river. The rope was removed and not left in the water with the device. During the deployment period SWCA staff constructed two PVC poles that were used to retrieve the device. Each pole consisted of a 10 foot length of PVC with a shorter length of PVC attached at the end using PVC elbows forming a hook shape. The hooked end was used to lift the device by its handles to the surface. It is likely this device will be used in future deployments and retrievals.

HCS440

March 2014 – PDS not recovered. April 2014 – PDS not recovered.

HCS460

March 2014 – PDS not recovered.

April 2014 – PDS not recovered.

October 2014 – Deployment device opened by vandal but PDS was intact and fixed within device and within the water. The PDS was analyzed.

December 2014 – Upon retrieval the device was found approximately 20 feet from where it was deployed. It had moved outside of the chained-off life guard area into the main channel of the tube chute. One zip-tie closing the metal cups had been cut but three remained intact. The PDS was intact and did not show evidence of tampering.

San Marcos

Surface water

Surface water was collected in the San Marcos Springs complex in March and September 2014. Surface water sampling locations did not deviate from the EAHCP Workplan.

March 25, 2014, Collection

Surface water grab samples were collected on March 25, 2014, by Richard Howard. The sample bottles for metals were collected without filtration, and the laboratory was asked to conduct the filtration prior to analysis. At the request of the EAA, re-sampling was conducted and samples were filtered in the field on April 29, 2014. The results from the analyses of the samples collected on April 29, 2014, are used in the data evaluation. Sample for nitrates analysis were also collected on April 29, 2014, because hold times

had been exceeded during the March 25, 2014 sampling event. Neither the original March 2014 samples nor the April 2014 resample were analyzed for manganese due to a field oversight. Field staff did not know manganese analysis was not included in standard metals analysis and needed to be specifically requested from the contract laboratory on the chain of custody forms. A miscommunication to field staff also occurred with field duplicate collection resulting in collection of one duplicate per sampling event as oppose to one per every ten samples.

September 25 and 26, 2014, Collection

The September 2014 surface water collection was difficult to obtain due to several small rain events that occurred during the month, which affected base flow water quality conditions as monitored by the RTIs. Sampling was scheduled for September 29 and 30, 2014, on days EAA staff were available to observe sampling. However, a large rain event was forecasted for the evening of September 26 and 27, 2014. Therefore, in order to avoid having base flow conditions affected by a storm prior to collecting samples on the 29 and 30, 2014, SWCA staff consulted with EAA staff and decided surface water samples should be collected prior to the storm. This resulted in samples being collected on a Friday, September 26, 2014. SWCA sampling staff had to immediately mobilize to collect stormwater samples at Comal Springs during the evening of September 26, 2014 and were therefore, unable to package and ship samples to the laboratory for overnight delivery on Saturday. Samples were held on ice at the SWCA San Antonio office before being shipped to the laboratory on Monday, September 29, 2014. This delay caused the nitrate samples to exceed the recommended 48-hour hold time. The samples also exceeded the 15-minute hold time for pH analysis, however pH field data is available.

Stormwater

Stormwater events were sampled May 12 and July 15, 2014, in the San Marcos Springs complex. Stormwater sampling locations did not deviate from those proposed in the EAHCP Workplan.

May 12, 2014, Event

Water parameters were not able to be collected for all samples due to malfunction of one sonde probe used by sampling teams. Parameters were not collected for the following samples: HSM230 Lead, HSM210 Peak, HSM230 Peak, and HSM240 Peak. SWCA procured an additional sonde device for all following storm events in case of malfunction.

E. coli samples were not collected from sites HSM 210 Lead, 210 Peak, 230 Peak, 240 Lead, or 250 Lead. This resulted from a field oversight. The field crew was unclear on whether *E. coli* samples were to be collected when the sample collection times would not allow for delivery to the laboratory within holding times. One sampling team collected samples regardless of time and the second team did not collect samples because the event occurred overnight when it was not possible to deliver samples to the laboratory. Samples collected did exceed hold times but were analyzed.

Decontamination procedures for reusable equipment were not put in place during this event due to SWCA staff miscommunication. A sampling pole was used at HSM230 (lead and peak) and a Beta sampler was used at HSM240 (lead and peak). An equipment blank was collected using distilled water for each piece of equipment between lead and peak samples. The distilled water was used to rinse the equipment prior to collection of the equipment blank samples and reuse. Neither piece of equipment was used for the trail samples. Seventeen of the 21 samples collected did not use reusable sampling equipment.

July 15, 2014, Event

Due to time and material constraints, the alkalinity samples for the final sample set (trail) were analyzed by the San Antonio River Authority Laboratory instead of by SWCA staff in the field. Samples did exceed the 8-hour hold time specified in the EAHCP Work Plan. They were processed within the hold time specified by Standard Method 2320B used by the laboratory.

The storm event occurred during overnight hours making it impossible to deliver *E. coli* samples within the 6 hour hold time.

Sediment

Sediment samples were collected from the Comal Springs complex June 26 and 30, 2014. The EAHCP Workplan designated sediment collection sites to coincide with surface water collection points but allowed for some deviation from these locations as field conditions dictated. Sediment samples were frequently collected more than 30 feet from surface water collection points due to limited amounts of available sediment and river depth. Sediment collection location deviations are discussed below.

HSM310

Surface water samples were collected from the center of the downstream side of the West Laurel Street bridge. The bottom of this area has many large rocks and little exposed sediment. Sediment samples were collected approximately 6 feet upstream of the bridge, approximately 5 feet from the eastern bank.



HSM320

The river bottom at the location of surface water collection is littered with concrete pieces and other construction debris. Sediment samples were collected approximately 75 feet downstream where river depth and substrate were better suited to sediment collection. Sediments were collected along the western bank of the river.



HSM330

This stream bed has a rocky gravel substrate with little sediment. The sediment samples were collected approximately 40 feet downstream of surface water collection point near aquatic vegetation with ample sediment. The samples were collected along the western edge of the water.



HSM340

Surface water is collected near the middle of the river channel at this site. Sediment samples were collected along the western bank and approximately 30 feet upstream of the surface collection point due to high river depth in this location. The samples were collected in a vegetated area approximately 10 feet from the western bank.



HSM350

Water depth and access along the Rio Vista Park foot bridge limited the possibilities for sediment collection. Sediment samples were collected on the east side of the island approximately 15 feet to the east of the island. A field duplicate was collected at the same location.



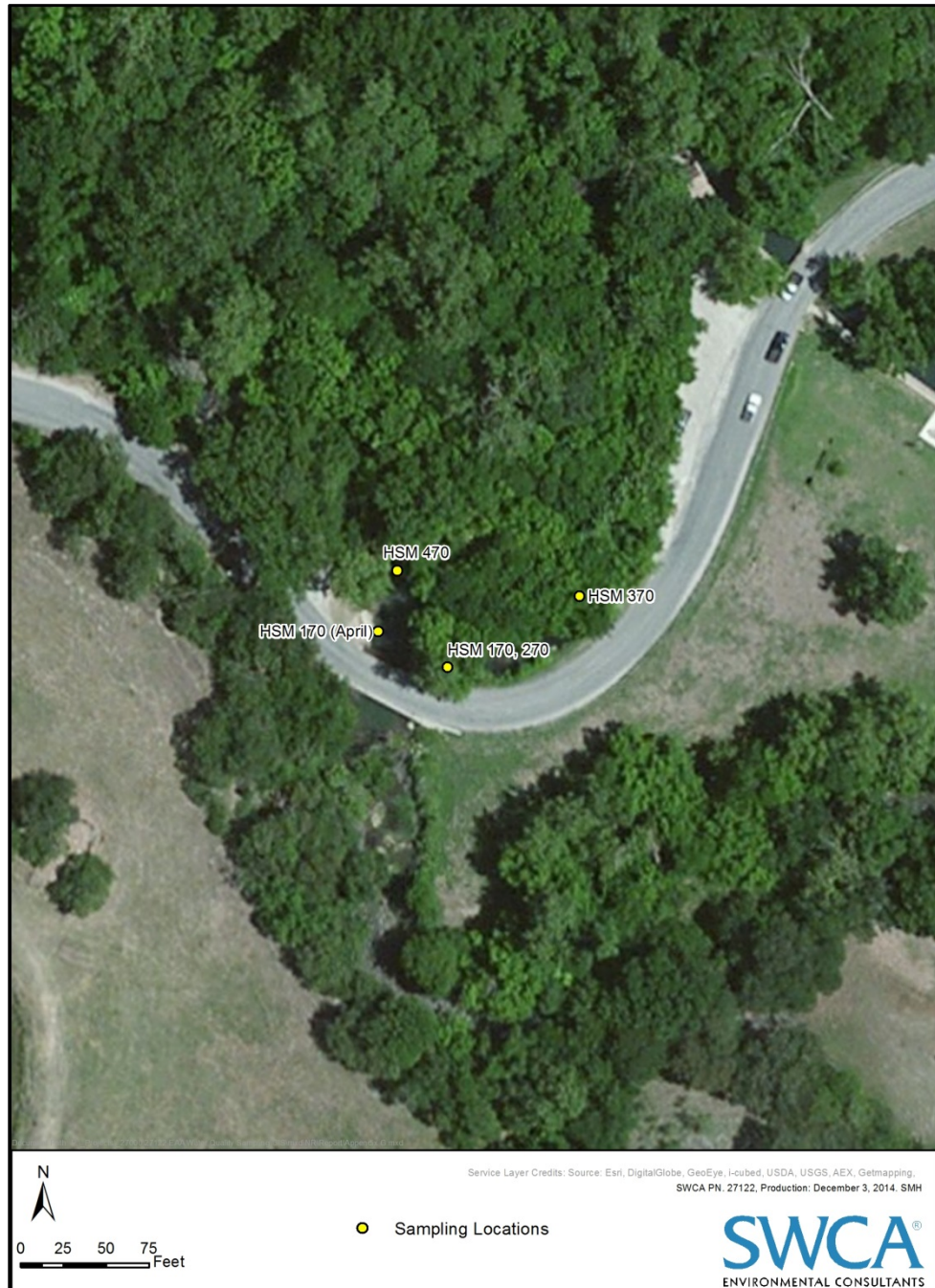
HSM360

Sediment samples were collected approximately 75 feet downstream of surface water samples due to limited sediments and high river depth at this site. Sediments were collected along the south bank of the river within 2 feet of the bank.



HSM370

Surface water samples are collected near the middle of the channel on the upstream side of the Cape Street Bridge. High water depth, strong current, and rocky bottom made sediment collection more favorable further upstream. Sediment samples were collected approximately 100 feet upstream of the bridge along the western bank of the eastern fork of the river. In this location there was vegetation with adequate amounts of sediment for sampling.



Passive Diffusion Sampling

Passive diffusion samplers were deployed at each of the surface water sample collection sites. When at all possible, deployment locations coincided with the surface water locations, some adjustment had to be made to account for river depth, accessibility by SWCA staff for installation and retrieval, and interference by the public. PDS were deployed for two-week periods during the months of March, April, June, August, October, and December 2014. In March 2014, the PDS were deployed with a fishing weight to anchor them but had no protective housing. This resulted in recovery of only approximately half of the deployed PDS. The missing PDS are presumed to have been removed by vandals, washed away to a point where they could not be located, or lost in vegetation. In April 2014, the PDS were deployed inside of a plastic tube held by a larger fishing weight but the retrieval rate was worse. To resolve this issue, SWCA staff designed and constructed a concrete and stainless steel deployment device to hold the PDS. The device was put into use beginning with the June 2014 deployment, this resulted in recovery of all PDS in San Marcos.

The March 2014 PDS were installed one month later than called for in the scope of work. The April 2014 PDS were deployed for a period of five weeks instead of two weeks.

Any alterations to sample locations or lost PDS are discussed below.

HSM420

April 2014 – PDS not recovered.

August 2014 – Location moved 75 feet downstream to same location as sediment sample collection due to water depth at the original deployment location. The water was too deep to place the PDS in an area with water flow at the original position used in previous months. All PDS after August 2014 were deployed to this location.

HSM430

March 2014 – PDS not recovered.

April 2014 – PDS not recovered.

June 2014 – SWCA staff was informed that children's camps associated with Texas State University utilize this area for creek exploration activities throughout the year. The location of the PDS was moved approximately 150 feet upstream near the road crossing beginning with the June 2014 deployment to avoid interference from the camp activities. All PDS after June 2014 were deployed to the new location.

HSM440

March 2014 – PDS not recovered.

April 2014 – PDS not recovered.

June 2014 – SWCA staff returned to the site for sediment sampling during the deployment period. The deployment device had been pulled into shallower water and opened. The PDS was still intact and fixed

inside the device. Staff closed the device with another plastic cable tie and placed it in deeper water approximately 15 feet downstream near a bridge pillar to deter tampering. All deployments after June 2014 were deployed to the new deeper water location.

HSM450

April 2014 – PDS not recovered.

HSM470

March 2014 – PDS not recovered.

April 2014 – PDS not recovered.

June 2014 – When SWCA staff visited the site to collect sediment samples the deployment device had been pulled into shallower water and opened. The PDS was still intact and fixed inside the device. The device was closed and secured with another plastic cable tie.

August 2014 – Deployment device was pulled into shallower water by vandals, but was not opened.

APPENDIX D

**EDWARDS AQUIFER AUTHORITY
GROUNDWATER QUALITY MONITORING PLAN**

Groundwater Quality Monitoring Plan

EDWARDS AQUIFER AUTHORITY

900 E. Quincy Street
San Antonio, Texas, 78215

Version 1.3
Revised July 2013



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ACRONYMS AND ABBREVIATIONS

ASTM	American Society of Testing and Materials
bgs	below ground surface
COC	chain of custody
DQO	data quality objective
EAA	Edwards Aquifer Authority
EAHCP	Edwards Aquifer Habitat Conservation Plan
e-line	electronic water level measurement device
GW	groundwater
MSL	mean sea level
NAWQA	national water quality assessment
PPCP	pharmaceutical and personal care products
psi	pounds per square inch
QA	quality assurance
QC	quality control
SOP	standard operating procedure
TWDB	Texas Water Development Board
USGS	United States Geological Survey
U.S. EPA	United States Environmental Protection Agency
VOA	volatile organic analysis
VOC	volatile organic compound

SECTION 1

PURPOSE AND OBJECTIVES

1.1 PURPOSE AND OBJECTIVES OF THE PLAN

Data derived from water quality sampling and analysis provide the primary indicator of the state of water quality in the Edwards Aquifer. These data are also a key component of assessing water quality changes over time. Water quality data also compose the primary source of information for our understanding and monitoring of contaminant loading and migration in the Edwards Aquifer. As such, analytical samples collected for assessing water quality must be collected under a set of standard operating procedures (SOPs), which are outlined in this plan. Included herein are sections on data quality objectives (DQOs), sampling programs, analytical methods, field procedures, and guidelines for plan review.

The purpose of this plan is to provide an SOP document ensuring that useful, consistent, and defensible water quality data are produced by implementation of appropriate procedures and methods when water quality samples are being collected and analyzed. Water quality samples are currently collected under various sampling programs at the Edwards Aquifer Authority (EAA). Data quality requirements vary by program and are discussed in Sections 2 and 3.

Section 2 of this plan provides a description of DQOs in general, as well as DQOs for this program. Section 3 provides detailed information for each of the sampling programs. Section 4 provides a listing of analytical methods used by the EAA, as well as data-flagging requirements, information for sample containers, hold times, and sample preservation. Section 5 outlines field procedures; Section 6 discusses staff training and field audits. Section 7 provides information regarding annual plan review, and Section 8 provides a list of references cited in the document. The appendices (A–G) provide maps of sample locations, a glossary of terms, instrument operation and calibration information, field forms, information on regulatory limits for various compounds, stormwater sample-collection details, and equipment-decontamination procedures.

The purpose of this plan can be achieved by implementation of the objectives listed below and discussed in detail in Sections 2–7 of the plan. Each EAA staff member charged with the responsibility of collecting water quality or other analytical samples is required to be familiar with this plan, along with the objectives and procedures outlined in it. The objectives of this plan are to

- Obtain quality data that are defensible for their intended purpose,

- Analyze field samples in an appropriate and consistent manner such that the results are accurate and repeatable (see calibration procedures in Appendix C),
- Collect samples for laboratory analysis in an appropriate and consistent manner that will ensure accurate and reliable analytical results with a minimal number of anomalous data,
- Select sample sites and time periods that will provide representative water quality data for a range of aquifer conditions, and
- Review the plan annually and revise as needed.

SECTION 2

DATA QUALITY OBJECTIVES

The U.S. Environmental Protection Agency (U.S. EPA) has developed criteria for data quality objectives utilizing a seven-step process that optimizes sample collection and analysis on the basis of data uses, fiscal budget, sample quantity, and other parameters (U.S. EPA, 2000). The process is iterative and may be modified by the planning team to incorporate changes as required:

- 1. State the Problem**
Define the problem, identify the planning team, and examine the budget and schedule.
- 2. Identify the Decision**
State the decision, identify study questions, and define alternative actions.
- 3. Identify Inputs to the Decision**
Identify information needed for the decision, such as information sources, bases for action level, and sampling and analysis methods.
- 4. Define the Boundaries of Study**
Specify sample characteristics, and define spatial/temporal limits and units of decision making.
- 5. Develop a Decision Rule**
Define parameters for decision rules, specify action levels, and develop logic for action.
- 6. Specify Tolerable Limits on Decision Errors**
Set acceptable limits for decision errors relative to consequences (health effects, costs, other impacts).
- 7. Optimize the Design for Obtaining Data**
Select a resource-effective sampling and analysis plan that meets performance criteria.

2.1 U.S. EPA DQO Process as Applied to EAA Analytical Programs

2.1.1 DQO—State the Problem

Collect and analyze groundwater, spring water, and surface water samples that are contained in, issue from, or provide recharge to the Edwards Aquifer. In addition, collect stormwater and sediment samples as needed to satisfy program requirements. Sampling activities are to be conducted such that sufficient funding is held in reserve to collect confirmation samples if needed. In addition, the program must be flexible enough to collect samples in the event of a contingency (spill or other event) that affects or could potentially affect water quality of the Edwards Aquifer. The planning team includes the

Chief Technical Officer (CTO) and supervisory staff of the Aquifer Science Team of the EAA. Budget is proposed by the team and presented for board approval annually. The schedule is annual, with a general goal of collecting a minimum of 80 samples from wells, sampling all major springs (monthly or quarterly, depending on hydrologic conditions), and sampling surface waters twice annually while maintaining a budget reserve sufficient to address other needs (confirmation and contingency sampling).

Under a separate budget, the same team is charged with collecting surface water, stormwater, and sediment samples in support of the Edwards Aquifer Habitat Conservation Plan (EAHCP). Surface water, stormwater, and sediment samples are collected upstream, within, and downstream of Comal and San Marcos springs. Comal Springs has five designated sample locations, whereas San Marcos Springs has seven. Surface water and stormwater samples are to be collected twice annually, whereas sediment samples are collected once annually for the first year (to obtain baseline sediment quality information). Subsequent years may vary depending on results. See *Water Quality Monitoring Program Strategy for Comal Springs and San Marcos Springs in Support of the Edwards Aquifer Habitat Conservation Plan* (EAHCP Workplan).

2.1.2 DQO—Identify the Decision

The decision is to collect the samples as described earlier under the sampling programs and protocols outlined in detail in this document. Study questions are:

- Can the quality of water entering into, residing in, and issuing forth from the Edwards Aquifer be representatively monitored?
- For the allowed budget, how many analytical parameters can be collected?
- What analytical parameters are the most informative with regard to water quality?
- Can a relevant data set that provides historical and current water quality information as relates to the Edwards Aquifer, be developed and maintained?
- Can the data indicate trends in water quality over time?
- Can contingency sampling functionally define contaminant flowpaths and ultimately help in the prevention of public exposure to contaminants in the event of a spill?
- How does the EAA functionally share the information collected with stakeholders and the public?

Alternative actions are to

- Modify the analytical parameter list to accommodate budget constraints,
- Reduce the number of sample points and sample frequency if needed to accommodate budget constraints, and

- Continually review results to assess the need for, and feasibility of, modifying the parameter list such that analytical parameters collected provide the most information for the program, as well as cost-effective information.

2.1.3 DQO—Identify Inputs to the Decision

Sample frequency, sample type, and analytical program are all based on many inputs. The EAA strategic plan dictates minimum sample numbers, for example. Other inputs of importance include findings from karst researchers worldwide regarding the varying nuances of sampling in karst environments (i.e., multiple samples from a single location are generally more valuable than single samples from multiple locations). Assimilating and incorporating information gleaned from EAA sample results annually provide significant inputs to the process as well.

Action levels as defined for this study are not directly comparable to action levels for hazardous waste cleanup. In this program, action levels generally depend on sample type and program: for example, stormwater samples are triggered by specific stormwater events. Action levels may also be related to contingencies. If a contaminant of concern is detected in relation to a contingency, then additional sampling may be triggered. In other cases, an action level may be reached if an anthropogenic compound is detected above a regulatory limit. The resulting action will generally be to utilize additional sampling so as to delineate a possible source if a “contaminant” is the trigger.

Sampling and analysis methods are specific to each sampling program and are designed to provide data on water quality and changes to water quality that may occur over time. Results of each program are reviewed regularly, and changes to the parameters for each program may be made on the basis of these reviews or other needs. All programs are generally analyzed for field parameters (conductivity, dissolved oxygen [DO], turbidity, pH, and temperature) at the time the sample is collected. Other laboratory analytical parameters are then designated on the basis of the program.

2.1.4 DQO—Define Boundaries of the Study

Spatially the study is limited to the Edwards Aquifer Region, which includes contributing area, recharge zone, and artesian zone of the aquifer, as well as contiguous areas that may be pertinent to data collection. Temporal limits are defined by sample program and hydrologic condition. Temporal parameters are described in more detail under sample programs.

2.1.5 DQO—Develop a Decision Rule

Decision rules are defined by multiple factors:

- Strategic plan,
- Board directives,
- Approved budget,

- Data analyses and results,
- Historical data for a particular site, and
- EAHCP requirements.

2.1.6 DQO—Specify Tolerable Limits on Decision Errors

Decision-error limits are dictated by sample program. Whereas all results are considered important, contingency samples have an elevated priority because of the potential to provide a warning to the public in the event water quality is impacted. As such, in the event of a major contingency that requires long-term sampling and analysis, the budget impact would be significant. In some scenarios, additional laboratory funding would be requested from the board to cover these costs. Other sample programs are expected to be well planned and orchestrated such that no budget overruns occur.

The goal of the program in general is to collect a number of samples adequate to monitor the health of the Edwards Aquifer with high confidence that results are representative and accurate. These samples are collected through various sampling programs, as outlined in the next section.

2.1.7 DQO—Optimize the Design for Obtaining Data

The sampling plan as designed provides a resource-effective plan that meets performance criteria through data review, data assessment, and program requirements. The design is optimized by the data needs of each sample program, in which analytical parameters are specific to a program and designed to provide a maximum number of data cost-effectively.

2.2 Additional Inputs for DQO Process

Another definition of DQOs is provided by the Air Force Center for Environmental Excellence (AFCEE) in its *Quality Assurance Project Plan* (QAPP), which states that “DQOs specify the data type, quality, quantity, and uses needed to make decisions and are the basis for designing data collection activities” (AFCEE, 2001). The U.S. EPA and the AFCEE both generally utilize DQOs for hazardous waste clean-up sites, which often represent a threat to public health and the environment. However, sampling programs at the EAA differ in that most samples taken are “clean” and are not used to assess the success of a clean-up action.

Therefore, for the purposes of this plan, DQOs are met by assigning a level of precision and procedural techniques and parameter suites that are appropriate for the sample type and monitoring program. Whereas it is the purpose of this plan for all data produced to be representative and fully defensible, all data do not necessarily need to be analyzed by reference methods in the analytical laboratory utilizing a full suite of QA/QC samples. Most water quality samples collected are intended for monitoring the general status of water quality within the Edwards Aquifer, with one potential exception. In some cases, contingency sampling may be used to assess the impact of an event (i.e., a spill) to the Edwards Aquifer that has the potential for public health implications.

Therefore, DQOs developed for this document are designed to provide data of quality and quantity adequate to reflect the needs of the sample program under which a particular sample is collected. Most analytical data collected are designed to assess

- The presence or absence of anthropogenic compounds in the sample.
- Changes to chemical quality of the sample point when compared with prior data,
- Development of data adequate to establish a record of water quality such that future changes to water quality can be measured,
- Measurement of changes to water quality against changes in hydrologic conditions, and
- In the case of confirmation samples, assessment with a high degree of confidence the presence or absence of a compound of interest.

SECTION 3

SAMPLING PROGRAMS AND OBJECTIVES

Water quality samples are collected under one of the EAA sample programs described in detail in this section. Sample parameters vary with the sample program. For a better understanding of the sampling programs and sample distribution, typical water quality sample locations, see Appendix A, which is a listing of sample type and program. EAHCP sample locations are also provided.

3.1 SAMPLE TYPES AND SAMPLE PROGRAMS

Sample type is simply defined by source and media. The EAA collects samples from wells, springs, surface water, and, at times, groundwater in caves. Samples of soil or sediment may also be collected under some circumstances. As such, sample types are:

- Wells (applies to groundwater samples and includes water collected in caves),
- Springs,
- Surface water,
- Soil or sediment, and
- Stormwater.

Sample programs exist for each sample type, driving the DQO process for a given sample. Each sample program has a defined sample frequency and analytical parameter list. However, the analytical parameter list is always subject to future revision to accommodate changing circumstances. Table 3-1 summarizes current sample types and individual sample programs conducted by the EAA.

Table 3-1. Sample Types and Sample Programs

Sample Type	Sample Program	Sample Frequency	Analytical Parameters
Wells	Passive	Quarterly	FP, GWQP, VOC, TPH, TOC, PAH, metals, bacteria
	NAWQA	Annually	FP, GWQP, VOC, 8081B, 8141A, 8151A, 8082A, TOC, PAH, metals, bacteria
	Routine	Annually	FP, GWQP, VOC, 8081B, 8141A, 8151A, TOC, PAH, metals, bacteria
	TWDB	Annually	FP, GWQP, VOC, 8081B, 8141A, 8151A, TOC, PAH, metals, bacteria
	PPCP	Annual	FP, PPCP (limited to nine wells annually)
	Contingency	As needed	Defined by contingency event
	Confirmation	As needed	Defined by detection needing confirmation
	QA/QC	Per QA needs	Defined by QA program
	EAHCP	Water level dependant	FP, GWQP, TOC, TDS
Springs	Primary	Quarterly (noncritical period) Monthly (critical period)	FP, GWQP, SVOC, VOC, 8081B, 8141A, 8151A, 8082A, TOC, metals, total phosphorous, bacteria, orthophosphate as P
	Secondary	Annually	FP, GWQP, SVOC, VOC, 8081B, 8141A, 8151A, 8082A, TOC, metals, total phosphorous, bacteria
	PPCP	Annually	FP, PPCP (limited to six spring samples annually)
	Contingency	As needed	Defined by contingency event
	Confirmation	As needed	Defined by detection needing confirmation
	QA/QC	Per QA needs	Defined by QA program
Surface water	Primary	Twice annually	FP, GWQP, 8081B, 8141A, 8151A, 8082A, TOC, PAH, metals, total phosphorous, bacteria
	Secondary	Annual	FP, GWQP, 8081B, 8141A, 8151A, 8082A, TOC, PAH, metals, total phosphorous, bacteria
	EAHCP	Twice annually	FP, GWQP, VOC, SVOC, 8081B, 8141A, 8151A, 8082A, TOC, metals, total phosphorous, bacteria, TKN, DOC
	PPCP	Annually	FP, PPCP (limited to two surface water samples annually)
	Contingency	As needed	Defined by contingency event
	Confirmation	As needed	Defined by detection requiring confirmation
	QA/QC	Per QA needs	Defined by QA program
Soil/sediment	EAHCP	Annually	FP, GWQP, VOC, SVOC, 8081B, 8141A, 8151A, 8082A, TOC, metals, total phosphorous
	Contingency	As needed	Defined by contingency event
	Confirmation	As needed	Defined by detection requiring confirmation
	QA/QC	Per QA needs	Defined by QA program
Stormwater	EAHCP	Twice annually	FP, GWQP, VOC, SVOC, 8081B, 8141A, 8151A, 8082A, TOC, metals, total phosphorous, bacteria, TKN
	Confirmation	As needed	Defined by detection requiring confirmation
	QA/QC	Per QA needs	Defined by QA program

FP=field parameter, GWQP=general water quality parameters, SVOC=semivolatile organic compound, VOC=volatile organic compound, TOC=total organic carbon, TKN=total kjeldahl nitrogen, PPCP=personal care and pharmaceutical products., PAH=polynuclear aromatic hydrocarbons, TPH=total petroleum hydrocarbons, DOC=dissolved organic compounds

3.2 SAMPLE PROGRAM DETAIL

The sample types and programs summarized in Table 3-1 comprise the various analytical samples collected and analyzed by the EAA. Specific details of each program are provided in this section.

Sample Programs for Well Sample Types

1. Passive Sampling Program

The passive sampling program is a program to provide continuous monitoring of particular wells (referred to as sentinel wells) through the use of a passive sampling device. The device currently used is the Amplified Geochemical Imaging (AGI), LLC passive diffuse sample module (aka, Gore Module). This device utilizes a sorbent material encased in GoreTex® fabric that is capable of detecting certain analytes for volatile and semivolatile compounds, as well as petroleum hydrocarbon compounds. The Gore Modules are hung at specific intervals continuously in a sentinel well and replaced each month. The module is then shipped to AGI, LLC. for analysis (which is included as part of the module cost). Currently six wells designated as sentinel wells are located in Medina, Bexar, and Hays counties. These wells are sampled via grab sample quarterly. Sample parameter selection for this sample type is generally based on collecting parameters that are also detectable by the Gore Module, plus some additional parameters of value to an understanding of long-term trends in water quality. Sample frequency is also selected to detect temporal changes in water quality at a single sample point.

2. National Water Quality Assessment (NAWQA) Program

The NAWQA wells are a series of thirty wells installed by the USGS for long-term assessment of water quality on a regional and national scale. Ten of these wells (all in the recharge zone of Bexar County) are sampled annually. The sample parameter list is selected on the basis of the NAWQA program and is used to contribute data to that study, as well as to build a historical record of water quality for the EAA data set. Ten out of 30 NAWQA wells are sampled annually, and every well must be sampled within a three-year period.

3. Routine Water Quality Monitoring

Routine water quality samples are collected from a variety of well types (monitoring, domestic, agricultural, industrial, and municipal) to provide a data set for water quality regionwide for different well types. Sample parameters are broad in spectrum and designed to detect the most common anthropogenic compounds, as well as to document changes in concentrations of common cations and anions. These wells are generally sampled annually or less frequently.

4. Texas Water Development Board (TWDB)

Twenty TWDB samples are collected at designated wells using a split-sample technique, such that a sample set is sent to the TWDB contract laboratory (at no cost to the EAA). The remaining sample is sent to the EAA contract laboratory and analyzed for some of the same (TWDB) parameters, as well as additional parameters. This sample type provides a cost-effective tool for evaluation and comparison of analytical results for certain parameters (metals and anions). These wells (or springs, in some cases) are sampled annually under this program for a wide variety of parameters and are also used to assess the health of the system and to establish potential changes or trends in quality.

5. Pharmaceuticals and Personal Care Products (PPCPs)

These parameters detect various compounds found in common personal care products, as well as medications and household items. The primary value in this sample group is the conclusiveness of the data. Because the detection limits are low and the percentage of detections (at low concentrations) to date is high, this sample program appears to provide the most conclusive evidence of anthropogenic impacts on the Edwards Aquifer. The current sample budget allows for nine wells, six springs, and two surface waters to be sampled annually for these parameters. The same locations are sampled each year (with some exceptions) to provide a temporal record of water quality changes associated with the compounds. This program is being evaluated for an increase in sample frequency at some locations.

6. Contingency Samples

Contingency samples are collected only on an as-needed basis to assess potential contamination events related to spills or similar contingencies that have a high potential for affecting water quality in the Edwards Aquifer. Sample parameters and sample frequency are determined on the basis of type of spill (or other contingency), as well as the size of the event. Sample parameters and frequency are decided on by management. EAA staff members are subsequently directed to an appropriate course of action on the basis of assessment of the event by management.

7. Confirmation Samples

Confirmation samples are samples collected in response to an unexpected detection at a site where additional confirmation is needed in order to assess the probability that detection is not a sampling artifact or otherwise false detection. Confirmation detections are method and analyte specific and are taken at the direction of management.

8. QA/QC Samples

QA/QC samples are discussed in detail in Section 3.3.

9. EAHCP Drought Contingency-Sampling of transect wells and Springs

Well samples collected for the EAHCP are collected only when certain springflow criteria are met—specifically, low-flow situations at Comal and San Marcos springs. For Comal Springs, when flows fall below 30 cubic feet per second (cfs), weekly monitoring at three wells is to be conducted for DO, conductivity, pH, and temperature. The next trigger at Comal Springs is 20 cfs, and weekly monitoring is conducted using the same parameters plus nutrients, TDS, and TOC. For San Marcos Springs, the first trigger is 50 cfs, and the second trigger is 30 cfs.

Sample Programs for Spring Sample Types**1. Primary Springs**

Primary springs are Comal, Hueco, and San Marcos. They are sampled monthly during critical periods (critical period = a ten-day average when water levels at Bexar, County, index well J-17 of below 660 feet msl, and/or a ten-day average springflow rate at either Comal or San Marcos springs is less than 225 cfs for Comal Springs and less than 96 cfs for San Marcos Springs). During noncritical periods, sampling is generally conducted quarterly. Sample parameters are extensive because the springs represent a composite sample of aquifer water and are directly associated with habitat for threatened and endangered species.

2. Secondary Springs

Secondary springs generally produce a smaller volume of springflow and may or may not be located within the San Antonio Segment of the Edwards Aquifer. These springs are Las Moras (Fort Clark Springs), San Pedro, San Antonio, Government Canyon, and other springs that may be designated for infrequent sampling. Las Moras is generally sampled annually, whereas the others are sampled quarterly or annually if flowing. Sample parameters are the same as those for the primary springs, except that sample frequency differs between primary and secondary.

3. Pharmaceuticals and Personal Care Products (PPCPs)

These parameters detect various compounds found in common personal care products, as well as medications and household items. The primary value in this sample group is the conclusiveness of the data. Because the detection limits are low and the percent of detections (at low concentrations) to date are high, this sample program appears to provide the most conclusive evidence of anthropogenic impacts on the aquifer. The current sample budget allows for nine wells, six springs, and two surface waters to be sampled annually for these parameters. The same locations are sampled each year (with some exceptions)

to provide a temporal record of water quality changes associated with the compounds. This program is being evaluated for an increase in sample frequency at some locations.

4. Contingency Samples

Contingency samples are collected only on an as-needed basis to assess potential contamination events related to spills or similar contingencies that have a high potential for affecting water quality in the Edwards Aquifer. Sample parameters and sample frequency are determined on the basis of type of spill (or other contingency), as well as the size of the event. Sample parameters and frequency are decided on by management. EAA staff members are subsequently directed to an appropriate course of action on the basis of assessment of the event by management.

5. Confirmation Samples

Confirmation samples are samples collected in response to an unexpected detection at a site where additional confirmation is needed in order to assess the probability that detection is not a sampling artifact or otherwise false detection. Confirmation detections are method and analyte specific and are taken at the direction of management.

6. QA/QC Samples

QA/QC samples are discussed in detail in Section 3.3.

7. Drought Contingency-Sampling of transect wells and Springs

Sample Programs for Surface Water Sample Types

1. Primary Surface Water

Primary surface waters are collected twice annually from eight locations: Nueces River at Laguna, Dry Frio River at Reagan Wells, Frio River at Concan, Sabinal River near Sabinal, Seco Creek at Miller Ranch, Hondo Creek near Tarpley, Medina River at Bandera, and Blanco River at Wimberley. These sample locations have a significant historical sample record and provide information regarding the quality of waters that effectively provide recharge to the Edwards Aquifer. Sample parameter lists are fairly significant, but do not generally include VOCs because of the low probability of detection of these compounds in a surface water environment.

2. Secondary Surface Water

Secondary surface water sites may have varying locations and are generally sampled only annually. They are generally sites of interest because of their ability to provide recharge to the aquifer, or they may be indicators of water

quality from springs issuing forth from the Trinity Aquifer. Sample parameter lists are fairly significant but do not generally include VOCs because of the low probability of detection of these compounds in a surface water environment.

3. EAHCP Surface Water Samples

EAHCP surface water samples are collected at Comal and San Marcos springs; Comal Springs has five sample locations, whereas San Marcos has seven sample locations, which are situated upstream and downstream of the spring orifice locations. Parameters provide a broad spectrum of analyses so that water quality might be better understood in detail at these locations. The parameters list will also be used to study trends in water quality at these locations over time. Sample frequency is twice annually.

4. Pharmaceuticals and Personal Care Products (PPCPs)

These parameters detect various compounds found in common personal care products, as well as medications and household items. The primary value in this sample group is the conclusiveness of the data. Because the detection limits are low and the percent of detections (at low concentrations) to date high, this sample program appears to provide the most conclusive evidence of anthropogenic impacts on the aquifer. The current sampling budget allows for nine wells, six springs, and two surface waters to be sampled annually for these parameters. The same locations are sampled each year (with some exceptions) to provide a temporal record of water quality changes associated with the compounds. This program is being evaluated for an increase in sample frequency at some locations.

5. Contingency Samples

Contingency samples are collected only on an as-needed basis to assess potential contamination events related to spills or similar contingencies that have a high potential for affecting water quality in the Edwards Aquifer. Sample parameters and sample frequency are determined on the basis of type of spill (or other contingency), as well as the size of the event. Sample parameters and frequency are decided on by management. EAA staff members are subsequently directed to an appropriate course of action on the basis of assessment of the event by management.

6. Confirmation Samples

Confirmation samples are samples collected in response to an unexpected detection at a site where additional confirmation is needed in order to assess the probability that detection is not a sampling artifact or otherwise false detection. Confirmation detections are method and analyte specific and are taken at the direction of management.

7. QA/QC Samples

QA/QC samples are discussed in detail in Section 3.3.

Sample Programs for Sediment Sample Types**1. EAHCP Sediment Samples**

EAHCP sediment samples will be collected for a broad spectrum of parameters to establish a base-line data set for sediments in and around Comal and San Marcos springs. These sample data are important to an understanding of potential issues with disturbing sediments in these areas.

2. Contingency Samples

Contingency samples are collected only on an as-needed basis to assess potential contamination events related to spills or similar contingencies that have a high potential for affecting water quality in the Edwards Aquifer. Sample parameters and sample frequency are determined on the basis of type of spill (or other contingency), as well as the size of the event. Sample parameters and frequency are decided on by management. EAA staff members are subsequently directed to an appropriate course of action on the basis of assessment of the event by management.

3. Confirmation Samples

Confirmation samples are samples collected in response to an unexpected detection at a site where additional confirmation is needed in order to assess the probability that detection is not a sampling artifact or otherwise false detection. Confirmation detections are method and analyte specific and are taken at the direction of management.

4. QA/QC Samples

QA/QC samples are discussed in detail in Section 3.3

Sample Programs for Stormwater Sample Types**1. EAHCP Stormwater Samples**

EAHCP stormwater samples are collected twice annually for a broad spectrum of parameters to establish a base-line data set for stormwater quality in and around Comal and San Marcos springs. Stormwater samples are collected across the hydrograph at three points (rising, peak, and recession) to ascertain changes in water quality associated with storm flow.

2. Confirmation Samples

Confirmation samples are samples collected in response to an unexpected detection at a site where additional confirmation is needed in order to assess the probability that detection is not a sampling artifact or otherwise false detection. Confirmation detections are method and analyte specific and are taken at the direction of management.

3. QA/QC Samples

QA/QC samples are discussed in detail in Section 3.3

3.3 QUALITY CONTROL AND QUALITY ASSURANCE SAMPLES (QA/QC)

So that the data quality process is adhered to, additional samples for QA/QC must be taken and analyzed on occasion so that the quality of the sample collection and analysis process might be assessed. The various types of QA/QC samples applicable to this plan are outlined in the following paragraphs. Approximately ten percent of all samples will be QA/QC samples.

3.3.1 Matrix Spike and Matrix Spike Duplicate

Matrix spike and matrix spike duplicate samples (MS/MSD) are used to assess the effects of the sample matrix on the analytical process. The MS/MSD is a split (or replicate) of a parent sample collected in the field concurrently during the normal sample-collection process. Ideally, one MS/MSD is collected for each media type (soil, water, sludge, etc.) every 20 samples for each analysis being performed. For most sampling, no media changes will be encountered; i.e., most samples will be water. However, should the samples vary significantly in turbidity, collection of a specific MS/MSD for a sample with elevated turbidity may be advisable.

The MS/MSD is spiked and analyzed, and if the spiked analytes are recovered within a method-specific percentage, then matrix effects will be deemed minimal and no matrix data flag will be attached to the results. However, if spike recovery does not fall within the designated percentage, then analytical results will be flagged with an M-flag, indicating that a matrix effect is present. The sample name for MS/MSDs is identical to that of the parent sample, with the MS/MSD attached as a modifier at the end of the sample name. The MS/MSD will also be noted on the chain of custody (COC).

3.3.2 Ambient Blanks

Ambient blanks are taken to assess the possibility of site-specific atmospheric contamination of VOC samples. Ambient blanks are taken only when an area is suspected of having detectable quantities of atmospheric VOCs present (e.g., if VOC samples are being collected near a fueling operation). Ambient blanks are prepared by pouring ASTM

II, reagent-grade water directly into a 40-milliliter (mL), VOA container at the sample site during collection. The VOA is allowed to remain open and exposed to the atmosphere for the duration of the sample-collection process. The water is treated and analyzed as a sample from this point forward, with the designation *AB* on the COC. Ambient blanks are applicable to VOC samples.

3.3.3 Equipment Blanks

Equipment blanks consist of ASTM II, reagent-grade water poured over/through any sampling equipment used for collection of definitive samples. Most sample-collection equipment is disposable; however, in some cases, an equipment blank may be required. Equipment blanks are used to assess the effectiveness of decontamination procedures (for new materials provided to the EAA or from EAA decontamination processes) and are designated as *EB* on the COC. The frequency of collection of equipment blanks will depend on the sampling routine and sampling equipment in use.

3.3.4 Trip Blanks

Trip blanks are applicable only to VOC samples and are prepared and supplied by the contracted analytical laboratory. Trip blanks are to be shipped from the laboratory and maintained along with the VOC samples collected in the field. The purpose of trip blanks is to assess any potential contamination that may be introduced during shipping and sample handling. Trip blanks are designated on the COC as *TB*. Trip blanks are not to be opened in the field.

3.3.5 Duplicate or Replicate Samples

Duplicate and replicate samples are intended to assess the precision or repeatability of the analytical process. Typically one in ten samples should have a duplicate sample collected. The collection frequency of one duplicate per ten samples is generally acceptable. Note, however, that if a confirmation sampling event involves only three wells, then the duplicate (as well as other) QA/QC samples are still required. In other words, duplicates compose 10% of the sample set such that a sample population of ten would contain one duplicate. However, a sample population of 11 would contain two duplicates. The calculated number of duplicates is always rounded to the next whole number. Duplicates will generally be collected only at the 10% level for EAHCP analysis. For other programs, duplicate analysis is covered generally by the application of a TWDB sample set. Exceptions may apply and will be designated by management.

A duplicate sample is a second sample collected at the same location as that of the parent, either simultaneously or immediately following collection of the first sample (AFCEE, 2001). Both samples are collected, stored, and transported identically. A replicate sample, sometimes called a *split sample* is defined as a single sample divided into two samples (AFCEE, 2001). As with a duplicate, collection, storage, and transport of the resulting

samples must be identical. Duplicate and replicate samples each have unique identifiers (see Section 4).

3.3.6 Spike Samples

Spike samples are used as part of EAA's quality control on the contracted laboratory. EAA sampling staff members collect and subsequently spike twelve liters of water at one of the major springs, the spike containing a known percentage of a substance (contaminant). The spiked sample is then submitted to the contracted laboratory for analysis. If the contracted laboratory reports the findings within the specified amount, then EAA has confidence in their data. However, if the contracted laboratory is unable to detect or report the spikes, then EAA will pursue corrective action with the help of laboratory personnel to resolve the discrepancy. The corrective-action process will be initiated by the Hydrogeology Supervisor.

3.3.7 Recording QA/QC Samples in Analytical Workbook

Samples collected for QA/QC or spiked samples are to be recorded in chronological order in the laboratory notebook. The laboratory notebook is to be kept in the EAA Camden Building in the water quality area with the calibration notebook.

SECTION 4**ANALYTICAL METHODS, SAMPLE IDENTIFICATION, AND CUSTODY PROCEDURES**

This section will discuss analytical methods applicable to the EAA sampling program, as well as provide a summary of analytical hold times, acceptable sample containers, and preservation techniques. In addition, a discussion of proper identification and sample custody procedures is provided herein.

4.1 ANALYTICAL METHODS

A variety of analytical methods are used in the various water quality and sediment sampling programs. Table 4-1 lists standard analytical reference methods that have possible application to the various programs. Recall, too, that Table 3-1 provides a current listing of analytical methods/parameters for each sample type and program.

Table 4-1. Analytical Reference Methods

Analysis	Method
VOC	SW-8260b
SVOC	SW-8270c
Chlorinated herbicides	SW-8151a
Organophosphorus compounds	SW-8141a
Nonvolatile compounds by HPLC	SW-8321
Organochlorine pesticides	SW-8081b
Polychlorinated biphenyls (PCBs)	SW-8082a
PAH	SW-8310
Determination of triazine pesticides	EPA-619
Organonitrogen pesticides in industrial/municipal wastewater	EPA-633
Oryzalin in industrial/municipal wastewater	EPA-638
TPH	TX-1005
Metals (except mercury)	SW-6010b or SW-6020
Mercury	SW-7470A
Cyanide	SW-9010B

Table 4-1. Analytical Reference Methods (continued)

Analysis	Method
Alkalinity	EPA-310.1
Common anions	SW-9056
Sulfate (SO ₄)	EPA 300.0
pH	SW-9040B
Total dissolved solids (TDS)	EPA 160.1
Total suspended solids (TSS)	EPA 160.2
Ortho-phosphate	EPA 365.3
Nitrate/nitrite (both as N)	EPA 353.2
Ammonia (as N)	EPA 350.3
Kjeldahl (as N)	EPA 351.3
Total organic carbon (TOC)	EPA 415.1 or SW-9060
Sulfide	EPA 376.2
Dissolved organic compound	SM 5310C- 2000
E-coli most probable number (MPN)	SM9223B-2004
Dissolved orthophosphate lab	EPA 365.3- 1978
Ammonia as N-nondistilled	SMA4500 NH3D-1997
Bromide	EPA 300.0- 1993
Chloride	EPA 300.0- 1993
Nitrate as N	EPA 300.0- 1993
Total phosphorous	EPA 365.3- 1978
Enterococci	ENTEROLERT
Eshcerichia coli-colilert	SM 9223B 20Ed
Total coliform_colilert	SM 9223B 20Ed
TWDB anions	EPA 300.1
TWDB cations	EPA 200
TWDB nitrate	EPA 353.2
Anti-bacterial agents	1694
Pharmaceuticals	1694
Steroids/hormones	1698

SIM analysis	MS-SIM-GX/MS
Nonylphenols	WS-MS-0010
General water quality parameters (GWQP), general chemistry—(alkalinity, bicarbonate, carbonate, Ca, Mg, Na, K, Cl, SO ₄ , F, Si, Sr, bromide, nitrate as N, pH, TDS, and TSS)	Methods listed in table

4.2 DATA-FLAGGING CONVENTIONS

Analytical data must be qualified by the EAA-contracted analytical laboratory, which is done summarily by the addition of data flags to the data result. Table 4-2 provides a summary of the data-flagging convention used in this plan (modified from AFCEE, 2001).

Table 4-2. Data Flags

Flag	Description
J	Analyte positively identified. Quantitation is an estimation because the associated numerical value is below the reporting limit (RL).
U or ND	Analyte analyzed for, but not detected. Associated numerical value at or below method detection limit (MDL).
R	Data rejected because of deficiencies in ability to analyze sample and meet QC criteria.
B	Analyte found in associated blank, as well as in sample.
M	Matrix effect present.
T	Tentatively identified compound (using GC/MS).
No flag	Analyte detected at reported concentration.

4.3 SAMPLE CONTAINERS AND HOLD TIMES

Samples sent to the analytical laboratory must be properly containerized, preserved, and analyzed within specified hold times for the method for the data to be of defensible quality. In addition to the requirement for samples to be chilled to 4°C, ±2°, some analytical methods require the sample to be maintained at specific pH values. As such, Table 4-3 lists acceptable container types, preservatives, and hold times for common analytical methods. The table includes all scheduled analyses for the various sampling programs. In the event an analysis is required that is not included in the table, Aquifer Science Team members listed herein (hydrogeology supervisor or hydrologic data coordinator) will communicate with the EAA contracted laboratory regarding appropriate containers, preservatives, and hold times for the methods in question.

Table 4-3. Sample Containers, Preservatives, and Hold Times

Analyte or Method ¹	Container	Preservation	Minimum Sample Volume	Holding Times
Volatile organic compounds (SW8260B)	G, Teflon®-lined septum, T	4°C, HCl to pH <two	3× 40 mL with no head space or (1) 250 mL amber bottle with no head space	14 days (water and soil); seven days if unpreserved by acid
Semivolatile organic compounds (SW8270C)	G, Teflon®-lined cap, T	4°C	1L or 8 ounces/soil	Seven days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Chlorinated herbicides (SW8151a)	G, Teflon®-lined cap, T	4°C	1L or 8 ounces/soil	Seven days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Organophosphorus compounds (SW8141A)	G, Teflon®-lined cap, T	4°C	1L or 8 ounces/soil	Seven days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Organochlorine pesticides (SW8081)	G, Teflon®-lined cap, T	4°C	1L or 8 ounces/soil	Seven days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Polychlorinated biphenyls (SW8082)	G, Teflon®-lined cap, T	4°C	1L or 8 ounces/soil	Seven days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)

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Analyte or Method ¹	Container	Preservation	Minimum Sample Volume	Holding Times
Polynuclear aromatic hydrocarbons (SW8310)	G, Teflon®-lined cap, T	4°C	1L or 8 ounces/soil	Seven days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Total petroleum hydrocarbons (TX1005)	G, Teflon®-lined septum, T	4°C, HCl to pH <2	3× 40 mL with no head space or (1) 250 mL amber bottle with no head space	14 days (water); to extraction, and 14 days after extraction
General water quality parameters (alkalinity, bicarbonate, carbonate, Ca, Mg, Na, K, Cl, SO ₄ , F, Si, Sr, bromide, nitrate (as N), pH, TDS, and TSS)	P, G	4°C	250 mL	28 days
Cyanide	P, B	4°C; NaOH to pH >12	500 mL or four ounces /soil	14 days (water and soil)
Ortho-phosphate (as P)	P, G	4°C	50 mL	48 days
Nitrate (as N) and nitrite (as N)	P, G	4°C	250 mL	48 days
Ammonia (as N)	P, G	4°C	250 mL	28 days
Kjeldahl (as N)	P, G	4°C	250 mL	28 days
Total organic carbon	P, G	4°C, H ₂ SO ₄ to pH <2	250 mL	28 days
Dissolved organic carbon	P, G	4°C, H ₂ SO ₄	400 mL	28 days
Phosphorus	P, G	4°C, H ₂ SO ₄	500 mL	28 days
Alkalinity E310.1	P, G	4°C	50 mL	14 days
Common anions SW9056	P, G	None required	50 mL	28 days for Br ⁻ , F ⁻ , Cl ⁻ , and SO ₄ ²⁻ ; 48 hours for NO ₃ ⁻ , NO ₂ ⁻ , and PO ₄ ³⁻
Cyanide, total and amenable to chlorination SW9010A SW9012	P, G, T	4°C; NaOH to pH >12, 0.6 g ascorbic acid	500 mL or four ounces /soil	14 days (water and soil)
Total dissolved solids (TDS) E160.1	P, G	4°C	100 mL	Seven days
Total suspended solids (TSS) E160.2	P, G	4°C	100 mL	Seven days
Biological oxygen demand (BOD), five-day	P, G	4°C	1L	48 hours
Sulfide	P, G	4°C	1L	Seven days

Section 4

Analyte or Method ¹	Container	Preservation	Minimum Sample Volume	Holding Times
Total inorganic carbon	P, G	4°C	250 mL	28 days
Escherichia coli-colilert	P, G, WP	4°C, dark, sodium thiosulfate, one-inch headspace	100–250 mL	Six + two h (this holding time represents six field hours and two lab hours)
Enterococci	P, G, WP	4°C, dark, sodium thiosulfate, one-inch headspace	100–250 mL	Six + two h (this holding time represents six field hours and two lab hours)
Total coliform-colilert	P, G, WP	4°C, dark, sodium thiosulfate, one-inch headspace	100–250 mL	Six + two h (this holding time represents six field hours and two lab hours)
TWDB anions	P, G	4°C, filtered on site	500 mL	28 days
TWDB cations	P, G	4°C, HNO ₃ , filtered on site	250 mL	28 days
TWDB nitrate	P, G	4°C, H ₂ SO ₄ , filtered on site	500 mL	28 days
1694 Pharmaceuticals (LCMS/MS) Acetaminophen Caffeine Carbamazepine Cotinine DEET Diltiazem Fluoxetine Gemfibrozil Ibuprofen Lincomycin Naproxen Sulfamethoxazole Trimethoprim Tylosin Iopromide	G, Teflon®-lined cap, T	4°C	1L or 8 ounces/soil	Seven days (unpreserved), 14 (days preserved)
1694 Antibacterial (LCMS/MS) Triclobarban Triclosan	G, Teflon®-lined cap, T	4°C	1L or 8 ounces/soil	Seven days (unpreserved), 14 (days preserved)

Section 4

Analyte or Method ¹	Container	Preservation	Minimum Sample Volume	Holding Times
1698 Steroids/hormones (LCMS/MS) 17a-Estradiol 17a-Ethynyl estradiol 17b-Estradiol Equilenin Estriol Estrone Progesterone Testosterone	G, Teflon®-lined cap, T	4°C, H ₂ SO ₄	1L or 8 ounces/soil	Seven days (unpreserved), 14 (days preserved)
Nonylphenols/ethoxylates/bisphenol-A (GCMS) Bisphenol-A Nonylphenol diethoxylate (tech.) Nonylphenol monoethoxylate (tech.) p-Nonyphenol (tech.) p-tert-octylphenol para-n-nonylphenol	G, Teflon®-lined cap, T	4°C, H ₂ SO ₄	1L or 8 ounces/soil	Seven days (unpreserved), 14 (days preserved)
Selected metals—6020 (Al, Sb, As, Ba, Be, Cd, Cr (total), Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Tl, and Zn)	P, G, T	HNO ₃ to pH <2, 4°C	500 mL or 8 ounces/soil	180 days (water and soil)
Hg—Cold vapor 7470.7471	P, G	HNO ₃ to pH <2, 4°C	250 mL	28 days (14 days if in plastic bottle)
Selected metals—(ICP unless otherwise noted) 6020/7470/7471 (Al, Sb-ICP-MS or GFAA, As, Ba, Be, Cd, Cr (total), Cu, Fe, Pb, Mn, Hg-ICP-MS or CVAA, Ni, Se-ICP-MS or GFAA, Ag, Tl-ICP-MS or GFAA, and Zn)	P, G, T	HNO ₃ to pH <2, 4°C	500 mL or 8 ounces/soil	180 days (water and soil)
Hg- ICP-MS or CVAA 7470/7471	P, G	HNO ₃ to pH <2, 4°C	250 mL	28 days (14 days if in plastic bottle)

- Polyethylene (P); glass (G); brass sleeves in sample barrel, sometimes called California brass (T).
- No pH adjustment for soil.
- Preservation with 0.008 percent Na₂S₂O₃ only required when residual chlorine present.

4.4 SAMPLE IDENTIFICATION

Each sample must have a unique identifier so that it can be differentiated from other samples. In addition, sample names must meet the required criteria for entry into the data base and subsequent electronic storage and retrieval of the data. Therefore, sample names must conform to the guidelines herein.

4.4.1 Sample Identification, for Non-EAHCP Samples

The primary method for non-EAHCP sample identification will be to use the state well registration number for wells (and springs as applicable) or the site name for surface water samples. When no well number is available for a spring, then an abbreviation for the spring name and orifice will be used. For example,

- The unique identifier, for use on the COC for Comal Springs, Orifice 1 is DX 68-23-301,
- The unique identifier for use on the COC for Comal Springs Orifice 3 (no state well number) is CS3,
- The unique identifier for use on the COC for the Nueces River at Laguna is Nueces@Laguna, and
- For wells that are sampled in more than one location within the borehole, the interval number is attached to the well name. For example, well LR-67-09-101 is regularly sampled at two intervals, so the COC name is LR-67-09-101-1 (interval 1 or upper interval) and LR-67-09-101-4 (interval 4, or the deepest interval).

Note that to the extent possible, custody forms and sample-container labels will be preprinted by the laboratory.

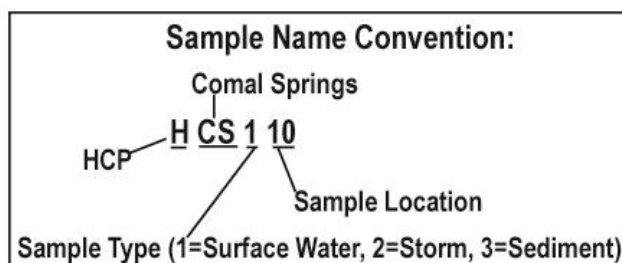
In some cases no well number or other recognized registration number will exist for the sample point. Then documentation for the sample location will require location (latitude/longitude and address if available) and name of well owner. Photographic documentation is also required. The subsequent sample name will be a *pseudo* state well number derived from the well location and owner name. For example,

The unique identifier for a sample taken from the Mary Smith residence in San Antonio, a private well with no state well registration number and located in Bexar County (abbreviation AY) at state well grid location 68-23-8, would be AY-68-23-8MS.

When wells of this type are sampled, proper documentation to include collection location, sample name, sample parameters, date, and time is extremely important and will be recorded in the field log for cross reference to the COC.

4.4.2 Sample Identification, for EAHCP Samples

For samples collected under the EAHCP, sample names are designed to provide additional data regarding sample type. Specifically the sample name will indicate the sample as an EAHCP-related sample, the spring group (Comal or San Marcos), sample type (surface water, stormwater, or sediment), and sample location. In the example below, the sample name refers to an EAHCP sample at Comal Springs, collected for surface water, at location 10. Sample locations are noted on the sample-collection maps for the EAHCP (included in Appendix A with calendar year 2013 non-EAHCP sample locations).



4.4.3 Sample Identification, QA/QC

For QA/QC samples, a modifier is added to the sample name to indicate the QA/QC type, for example, DX-68-23-301 (Comal Spring 1). If an MS/MSD sample were collected, a separate set of samples named DX-68-23-301MS/MSD would be collected. The appropriate modifier for each QA/QC sample is listed in Table 4-4.

Table 4-4. QA/QC Sample Nomenclature

Sample Type	Modifier
Matrix spike/matrix spike duplicate	MS/MSD*
Ambient blank	AB [#]
Equipment blank	EB [#]
Trip blank	TB [#]
Duplicate	FD*
Replicate	FR*

* Requires sample, with same sample name as parent + modifier at end.

[#] Numerical suffix to be attached and referenced in laboratory notebook; suffix starts at 1 at beginning of each calendar year. Details for location, etc. included in field notebook documentation.

4.5 SAMPLE CUSTODY

All samples shipped to the analytical laboratory must have proper custody documentation. One person on each sampling team is to have primary responsibility for sample custody (generally the lead sampler). This person will be designated as the *sample custodian* for sample collection. A person has custody of a sample group if samples are (1) in his/her possession, (2) in his/her view after being in his/her possession, (3) placed in a secure area by the sample custodian.

Furthermore, the laboratory COC form is to be filled out completely by the sample custodian in the field. The form must contain all required information for proper sample identification (if not preprinted) and must contain appropriate signatures. In addition, samples must remain in control of the sample custodian. Once collected, samples must be under the supervision of the sample custodian or secured in a manner such that no reasonable chance of unauthorized access to the samples exists. Furthermore, samples shipped by a common courier (i.e., Federal Express), require that the sample custodian note on the COC when the samples were released to the courier and why. The contracted analytical laboratory will sign the COC upon receipt. A breach of sample custody can invalidate the defensibility of the sample set.

4.6 DATA VALIDATION

Analytical data require review in order to be validated prior to publication. The amount of review (or level of review) is a function of the sample type. Field-collected data results are reviewed in the field by the analyst. One of the best ways for the field analyst to assess the acceptability of field data and subsequently validate them is to compare the results with historical data. This comparison, combined with proper equipment calibration, maintenance, and analytical technique, will provide an adequate validation process for field-parameter data. In the event that the analyst finds a discrepancy in the field data, a second analysis for the parameter in question should be performed. If the analyst feels that the data may be inaccurate because of issues with the field analysis, this fact is to be noted on the sample field sheet.

Contract analytical-laboratory data will receive a 100% analyst review at the analytical laboratory prior to posting of analytical results. A subsequent analytical laboratory review by the QA/QC section is required prior to the analytical laboratory's certification of the results. A subsequent 10% review by EAA staff of the analytical data is required upon receipt of the final analytical report. The analytical report will contain numerical analytical results for the laboratory QA/QC samples (i.e., LCS, method blanks, etc.). These laboratory analytical data are to have data flags assigned by the analytical laboratory.

SECTION 5

FIELD PROCEDURES AND SAMPLE COLLECTION

Possibly the most significant part of any successful sample collection is the field procedures and documentation that occur in the field. Field procedures to include sample equipment decontamination; sample-collection procedures for well, spring, surface water, and sediment samples; a listing of potential sources of contamination; and the proper use of field notebooks are included in this section.

5.1 RESPONSIBILITIES

The CTO and hydrogeology supervisor for the data-collection program will ensure that the samples obtained represent the environment being investigated. The hydrologic data coordinator will ensure that all field crews are provided with the necessary information, equipment, and supplies to successfully schedule and complete sampling. The hydrologic data coordinator will also be the primary point of contact between the contract analytical laboratory project manager and the EAA sampling team(s). The hydrologic data coordinator will report sampling deviations to the CTO and hydrogeology supervisor. Sample-collection staff (generally, environmental science technicians) are responsible for being familiar with the instructions provided in this SOP and for collection of samples in accordance with this SOP. For most sample-collection events, a sample team of two people will be utilized. Teams will have a lead sampler (according to experience level) who is directly responsible for adherence to directives of the SOP.

5.2 EQUIPMENT DECONTAMINATION

In order to obtain samples that are reliable and defensible, all (nondisposable) sample-collection equipment must be decontaminated prior to use. When possible, sample collection from a wellhead valve directly to a sample container is best. When this kind of collection is not possible, disposable equipment is preferable.

If neither option is plausible, then nondisposable sample-collection devices (constructed of Teflon® when possible) must be used. Sampling equipment that is exposed directly to sample media (pumps, peristaltic or submersible pump tubing, reusable bailers, or other devices) will be washed in a nonphosphate, laboratory-grade detergent such as Alconox®, followed by a double rinse in potable water. A final rinse of deionized or distilled water will be applied after completion of the initial decontamination process.

Equipment that will not be used immediately must be kept clean by wrapping in aluminum foil or placed inside clean plastic bags. Such storage will prevent

contamination of the equipment prior to use. See Appendix G for additional detail regarding equipment-decontamination procedures.

5.3 SOURCES OF SAMPLE CONTAMINATION

Samples can easily become contaminated during the sample-collection process. It is the responsibility of the sampler to prevent contamination from occurring. A multitude of potential cross-contamination sources are present in the field environment. Because many of the analytical methods used can quantify various analytes in parts per billion or less, even minute sources can potentially contaminate a sample. For example, Table 5-1 summarizes some of the potential sources that can cause a false-positive reading in a sample. These should be considered when samples are collected in the field. Also note that water has a strong affinity for many anthropogenic compounds. Use of good judgment is another aspect of collecting defensible data. Steps should be taken to avoid cross-contamination of samples. If the sampler suspects the possibility of cross-contamination, he/she should note it in the field log for the sample set in question, or the site should be sampled again if necessary.

Table 5-1. Potential Sources of Cross-Contamination

Source	Possible Contaminant
Fuels—generators, work vehicles	BTEX/TPH/VOC/SVOC
Exhaust fumes—generators, vehicles, heavy roadway traffic, overhead air traffic	BTEX/TPH/VOC/SVOC
Oil/grease residue on tools, gloves, etc.	TPH/SVOC
Tape	VOC
Insect spray	VOC/SVOC/pesticides
Insect repellent	SVOC/VOC/pesticides
Sunscreen	VOC/SVOC/PPCP
Soil/debris	Bacteriological/metals/SVOCs
Foods/drinks/medications and other personal care products such as soap, makeup, deodorant, etcetera.	PPCPs

5.4 FIELD NOTEBOOKS

The field notebook is a legal document and should be treated as such. All pertinent site information should be in the notebook, including site name, weather information, site conditions, well condition (if applicable), equipment problems, sample-collection notes such as approximate sample times, and any other information that may be deemed valuable. The names of individuals on the sample team, as well as visitors to the site, should also be recorded in the notebook. All information recorded in the field notebook should follow the format described herein. No blank spaces are to be left on pages. All blank areas should be marked through with a single line and initialed by the author. The top of each page should have the date and sample site. The base of each page should contain the initials of the author. Mistakes are to be crossed out with a single line and initialed. Field notebooks are to be recorded in black ink only.

5.5 SAMPLE COLLECTION

Field personnel must wear clean (disposable) nitrile gloves during the sample-collection process. Generally samples for field water quality parameters are to be collected first, followed by VOC, SVOC, and metals samples. Any required information is to be recorded in the field notebook before, during, and after sampling.

5.5.1 Well Samples

Each well must be gauged and sounded (if possible). The general condition of the well will be noted in the field notebook. After the water level is gauged, the purge volume for the well will be calculated by the following equation,

$$V = H \times F,$$

where V is one well volume, H is the difference between depth of the well and depth to water in feet (i.e., length of water column in well), and F is the number of gallons per foot of water for the well size (Table 5-2).

Table 5-2. Well-Casing Volume in Gallons per Foot

Casing Diameter (in inches)	F (gallons per foot of water in well)
2	0.16
4	0.65
6	1.47
8	2.6
10	4.1
12	5.9
16	10.4

The relationship $F = \pi (D/2)^2 \times 7.48$ gallons/ft³ can be used to calculate pipe volumes not listed in the table. Note that D = pipe diameter in feet and F = volume per foot.

A well may be sampled upon achieving *one* of the following: a minimum of three well volumes are purged from the well or field-parameter readings are stabilized for a minimum of three parameter measurements. Wells that go dry prior to purging the three well volumes, or the field-parameter readings have not stabilized, shall be purged to dryness (except for drinking-water supply or irrigation wells). During purging, water will be monitored for the following field parameters: *temperature, pH, DO, conductivity, and turbidity*.

Stabilization is defined as

- Temperature fluctuations limited to $\pm 1^\circ \text{C}$,
- pH fluctuations ± 0.1 unit,
- DO fluctuations ± 0.3 milligrams per liter (mg/L),
- Conductivity fluctuations $\pm 5\%$, and
- Turbidity ± 10 NTU.

In the event that these parameters do not stabilize (after purging of three well volumes), a maximum of six well volumes will be purged prior to sample collection (if the field parameters stabilize at any point, the well is considered ready to sample, and purging may cease). Once the well has stabilized or the maximum purge volume is reached, and the well has recovered to at least 80% of its initial level, it is ready to sample.

5.5.2 Spring Samples

Springwater samples should be as representative of the actual water issuing forth from the spring as possible and not be “contaminated” by surrounding surface waters. As such, various sample-collection techniques may be necessary. For spring orifices located below surface water, samplers should use a peristaltic pump to collect the springwater sample by placing the intake part of the pump tubing in the spring orifice. This placement allows for filling of sample bottles without introducing surface waters or overflowing the bottles and losing any preservatives inside. This technique is not feasible or necessary for all spring sites but should be utilized as appropriate. When a spring that can be sampled without a pump is being sampled, then a typical grab sample may be collected. In some cases (high flow volume) it may be necessary to collect samples in a clean bottle (such as a clean 1,000-mL amber glass bottle, clean Teflon beaker, or something similar) and the container used to transfer water into subsequent containers. Doing so will prevent the loss of any preservatives that may be in sample bottles. However, the action should be performed with as little agitation to the sample as possible to preserve potential VOCs in the parent sample.

Note: If preservatives in the sample container are diluted or lost because of the collection technique, a new bottle should be used. If a new bottle is unavailable, the lack of preservatives must be communicated to the laboratory to ensure that the sample remains valid by being analyzed within the appropriate hold time.

Current information and observations concerning springflow at the time of sample collection should be entered in the field notebook. For example, approximate springflow volume (can be listed as low, medium, high) is the flow representative of an extreme volume (high or low); observed water quality should be noted (clear, cloudy, or murky), along with other observations deemed appropriate by the lead sampler.

5.5.3 Surface Water Samples

Surface water samples should be collected without disturbing the sediment, if at all possible. The presence of sediment in the sample may bias the results. Samples should be collected from the flowing parts of the stream on the upstream side of the sample collector. Samples are not to be collected from stagnant areas, and they should also be taken from approximately the same location for each sample event. Sample bottles should be filled by collecting the water sample in a clean bottle or by using a peristaltic pump and transferred into the final sample bottle. Caution should be used to prevent overfilling of the sample bottle and diluting any preservatives that may be in the bottle.

Note: If preservatives in the sample container are diluted or lost because of the collection technique, a new bottle should be used. If a new bottle is unavailable, the lack of preservatives must be communicated to the laboratory to ensure that the sample remains valid by being analyzed within the appropriate hold time.

Information regarding the sample point in the stream, streamflow, and water conditions, as well as other information deemed appropriate by the sampler, should be entered into the field notebook at the time of sample collection.

5.5.4 Sediment Samples

Sediment samples are scheduled for collection by the EAHCP sampling program. Furthermore, the possibility exists that EAA staff may be required to collect samples of this type on occasion for other programs. As such, a brief discussion of this type of sample is included herein. Sediment samples may be collected from below the water line, from a dry stream bed, or from any other source in which sediments or soils may collect. The collection technique will depend on conditions. For example, a push tube for collection of sediments below the water surface is generally needed. However, if sediments are being collected from a dry area, then they may be collected using a trowel, hand auger, or push tube of some type. As with all sediment/soil-related samples, VOC samples must be collected in a manner that will minimize the loss of in situ volatiles. As

such, sediment samples for VOC analysis will not be composited or homogenized in the field. Samples for VOC analysis are to be collected first.

In the event that the discreet-interval sediment sampler is used for collection of sediments, the procedure for device operation is as follows:

1. Insert the lower-half of the lead internal rod using a $\frac{3}{8}$ -inch coupler (first stage) into the internal drive tip. Pull down on the brass ring, push the grooved end of the lead internal rod into the recess, and gently release the brass ring.
2. Insert the internal drive tip and lead internal-rod assembly into the external drive tip.
3. Connect the upper lead internal rod using the $\frac{3}{8}$ -inch coupler (second stage) to the lower lead internal rod (first stage).
4. Insert a four-ft liner, with the hole in the liner oriented to the top, into the sample tube (the sample tube has a two-inch outside diameter and consists of two parts, a double female lead section and a male \times female extension). If the EAA staff chooses to use a two-ft liner instead of a four-ft liner, the process is the same, except that the male \times female upper extension is not used.
5. Insert a plastic core catcher (white) in the bottom of the sample tube, with the dome pointing toward the top.
6. Insert the internal drive tip/external drive tip assembly into the sampler tube.
7. Insert the metal core catcher into the top of the main sampler tube, with the dome pointing upward.
8. Install the internal tip chamber to the top of the main sampler tube.
9. Install the top drive head adapter to the top of the internal tip chamber.
10. Install the thread protector cap or internal rod with external drive extensions (if using $1\frac{1}{8} \times 3$ ft external extensions with $\frac{3}{8}$ -inch internal rods, place a $\frac{3}{8}$ -inch coupler on the top of the internal rods prior to installing the top drive head adapter). Install the thread protector cap at the top of the internal rod prior to connecting the vented drive head (install the correct number of internal/external extensions necessary to lower the sampler to the surface and arrive at the desired sampling point).
11. Install the vented hammer adapter, already attached to the slide hammer.

The field notebook will note details related to the sediment samples; for example, was the sediment dry or below water, how was it collected, was it discolored, at what depth (from the surface) was the sample collected? If sediments are field screened with a photoionization detector (PID), readings from the various intervals will be recorded. Other details will be recorded as deemed appropriate by the sampler.

Also, if a hand trowel is used, it must be constructed of stainless steel, and it must be decontaminated prior to each use. For sites at which multiple samples will be collected, multiple hand trowels may be used, or a single trowel may be used if it is decontaminated in the field (Alconox wash, double rinse in potable water, followed by a DI water rinse).

5.5.5 Stormwater Samples

Stormwater samples are scheduled for collection under the EAHCP program at each spring group, twice annually. Stormwater sample collection offers additional challenges and safety issues, as compared with that of other samples collected under EAA programs. This section provides a general summary of stormwater sampling, additional detail regarding this sample type being provided in Appendix F.

Stormwater samples are scheduled for collection across three points on the storm hydrograph. One sample collected from the initial rise on the hydrograph, a second sample from the peak area of the hydrograph, and a final sample along the recession limb of the graph. In addition, water quality parameters obtained from EAA-installed real-time water quality monitors, flow data from the U.S.G.S. springs gauges, and local weather radar maps will be used to define the behavior of the systems and help guide sample-collection timing. The real-time monitors collect data at 15-minute intervals for conductivity, DO, pH, temperature, and turbidity.

A stormwater event will be dictated by a rainfall event sufficient to cause a significant rise in springflow at either Comal or San Marcos springs. The significant rise in springflow is to be further defined in conjunction with real-time data systems. See Appendix F for details on stormwater sampling procedures.

SECTION 6

ANNUAL REVIEW OF PLAN

6.1 ANNUAL REVIEW OF GROUNDWATER QUALITY PLAN

Data collection described in this plan will be reviewed by May 31 each year. The review will be directed at ensuring that all data collection herein is necessary, properly performed, and properly staffed. Furthermore, the review will ascertain whether the methodologies in use remain appropriate for their intended purpose. The review process will include all sample types and programs, as well as methods used to collect and analyze these samples.

Postreview, modifications will be made, if needed, to accommodate changes to EAA sampling. Changes will be initiated by the management and staff of the EAA Aquifer Science Team.

SECTION 7

CONTINUING EDUCATION CREDITS FOR SAMPLE-COLLECTION PERSONNEL

7.1 CONTINUING EDUCATION

Staff members assigned to sample-collection teams must attain a minimum of 12 hours of continuing education each year. Opportunities for continuing education will be provided either in-house by the EAA, or, in some cases, staff may be sent to an offsite facility to attend a class. One hour of credit is considered to be one classroom or contact hour. Staff may also carry credits over into the following year if more than 12 hours of credit are obtained in a calendar year. It is the responsibility of each staff member to document his/her credit hours annually and submit them to the hydrogeology supervisor by December 1 of each year.

SECTION 8

REFERENCES CITED

- AFCEE, 2001, Quality Assurance Project Plan, Version 3.1: Air Force Center for Environmental Excellence, Brooks AFB, Texas.
- EAA, 2012, Water Quality Monitoring Program Strategy for Comal Springs and San Marcos Springs in Support of the Edwards Aquifer Habitat Conservation Plan.
- SARA, 2013, Watershed Monitoring, San Antonio River Authority.
- U.S. EPA, 2000, EPA QA/G-4, Guidance for the Data Quality Objectives Process.

SECTION 9

REFERENCES NOT CITED

- Driscoll, F.G., 1995, Groundwater and Wells: St. Paul, Johnson Screens, 1089 p.
- Nielsen, D.M., 2006, Environmental Site Characterization and Ground-Water Monitoring: New York, Taylor and Francis, 1318 p.

APPENDIX A—Sample Locations (2013)







APPENDIX B—Glossary of Terms

Ambient blank	Sample known not to contain target analytes, which are used to assess airborne contaminants at the site. The ambient blank [AB] is
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	opened at the site and exposed to site (ambient) conditions and subsequently treated as an environmental sample thereafter. AB samples are applicable to VOC analysis only.
Anion	Negatively charged ion.
Aquifer	Underground geological formation or group of formations containing water; source of groundwater for wells and springs.
Cation	Positively charged ion.
DOC	Abbreviation for dissolved organic carbon, a broad classification of organic molecules of varied origin and composition within aquatic systems. Organic carbon compounds are a result of decomposition processes from dead organic matter, such as plants.
DQO	Abbreviation for data quality objectives, a process used to develop performance and acceptance criteria or data quality objectives that clarify study objectives, define the appropriate type of data, and specify tolerable levels of data needed to support decisions.
Equipment blank	Sample used to assess the effectiveness of the decontamination process on sampling equipment. The equipment blank is prepared by pouring reagent-grade water over/through sampling equipment and analyzing for parameters of concern (to match the sampling routine applicable to the site).
Field duplicate	Second sample collected simultaneously from the same source as the parent sample, but which is submitted and analyzed as a separate sample. This sample should generally be identified such that the laboratory is unaware that it is a field duplicate.
Field replicate	Sometimes referred to as a <i>split sample</i> , a single sample divided into two (or more) samples.
Groundwater	Water found beneath Earth's surface that fills pores between materials, such as sand, soil, or gravel.
Initial rise	Initial surface runoff of a rainstorm. During this phase, water pollution entering storm drains in areas with high proportions of impervious surfaces is typically more concentrated during first flush than it is during the remainder of the storm.

Matrix spike	Sample used to determine the effect of the matrix on a method's recovery efficiency. A known amount of the target analyte is added to a specified amount of matrix sample for which an independent estimate of the target analyte concentration is available. Duplicate samples must be available as well (matrix spike duplicate, or MSD).
MDL	Abbreviation for method detection limit, minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, as determined from analysis of a sample containing the analyte in a given matrix.
Peak	Maximum instantaneous flow at a specific location resulting from a given storm condition.
PQL	Abbreviation for practical quantitation limit, which is the smallest concentration of the analyte that can be reported with a specific degree of confidence.
Precision	State or quality of being precise; exactness. The ability of a measurement to be consistently reproduced.
Purge	To remove standing water in a well.
Recession	End of runoff event, which is defined as the point in time when the recession limb of the hydrograph is <two% of the peak or is within ten % of the prestorm base flow, whichever is greater.
Recharge zone	Where an aquifer is replenished with water by the downward percolation of precipitation through soil and rock.
Representative	Said of samples collected that are similar to those of groundwater in its in situ condition.
RL	Abbreviation for reporting limit [RL], the smallest concentration of an analyte reported by the laboratory to a customer. The RL is never less than the PQL and is generally twice the MDL.
Spike sample	One of any known concentrations of specific analytes that have been added to minimize change in the matrix of the original

sample. Every spike sample analyzed should have an associated reference to the spike solution and the volume added.

Spring	Water coming naturally out of the ground.
Surface water	That which forms and remains above ground, such as lakes, ponds, rivers, streams, bays, and oceans.
SVOC	Abbreviation for semivolatile organic compounds, which is a group of chemicals composed primarily of carbon and hydrogen that have a tendency to evaporate (volatilize) into the air from water or soil. Some of the compounds that make up asphalt are examples of SVOCs.
TDS	Abbreviation for total dissolved solids, or the total amount of all inorganic and organic substances, including minerals, salts, metal, cations, or anions that are dispersed within a volume of water.
Temporal	Over a period of time.
TKN	Abbreviation for total kjeldahl nitrogen, which is the total concentration of organic and ammonia nitrogen in wastewater.
TOC	Abbreviation for total organic carbon, which is the gross amount of organic matter found in natural water. Suspended-particulate, colloidal, and dissolved organic matter are part of the TOC measurement. Settable solids consisting of inorganic sediments and some organic particulate are not transferred from the sample by the lab analyst and are not part of the TOC measurement.
Trip blank	Sample known to be free of contamination (for target analytes) that is prepared in the laboratory and treated as an environmental sample after receipt by the sampler. Trip blank [TB] samples are applicable to VOC analysis only.
TSS	Abbreviation for total suspended solids, which are the nonfilterable residue retained on a glass-fiber disk filter mesh measuring 1.2 micrometers after filtration of a sample of water or wastewater.
VOC	Abbreviation for volatile organic compounds, which are often used as solvents in industrial processes and are either known or suspected carcinogens or mutagens. The five most toxic are vinyl

chloride, tetrachloroethylene, trichloroethylene, 1,2-dichloroethane, and carbon tetrachloride.

Well Bored, drilled, or driven shaft whose purpose is to reach underground water supplies.

APPENDIX C—Equipment Use and Calibration

DOCUMENTATION PROCEDURES

All equipment maintenance and calibration must be documented in the laboratory notebook kept at the EAA Camden Building. This documentation is an important part of ensuring that data-collection results are “defensible.” Calibration details, equipment type, date, calibration statement, and sampler’s signature must appear in the book for each day that the equipment is used.

EAA currently uses the YSI 556 MPS field instrument to collect pH, DO, conductivity, and temperature at each sample point. Calibration procedures for this instrument are detailed next.

CALIBRATION PROCEDURES

Calibration Procedures for YSI 556 MPS

Accessing the Calibrate Screen

1. Press the **On/Off** key to display the run screen.
2. Press the **Escape** key to display the main menu screen.
3. Use the arrow keys to highlight the **Calibrate** selection

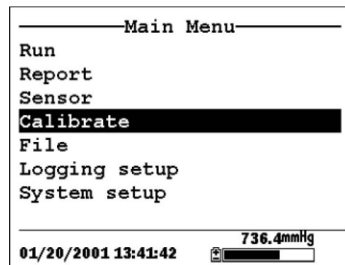


Figure 6.1 Main Menu

4. Press the **Enter** key. The Calibrate screen will be displayed.

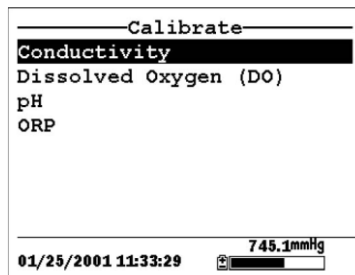


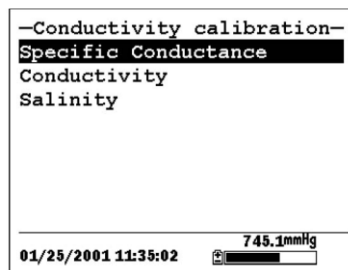
Figure 6.2 Calibrate Screen

Conductivity Calibration

This procedure calibrates specific conductance (recommended), conductivity, and salinity.

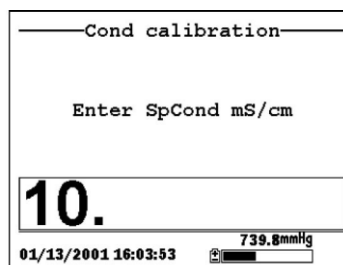
Calibrating any one option automatically calibrates the other two.

1. Go to the Calibrate screen
2. Use the arrow keys to highlight the **Conductivity** selection.
3. Press **Enter**. The Conductivity Calibration Screen is displayed.



Conductivity Calibration Selection Screen

4. Use the arrow keys to highlight the Specific Conductance selection.
5. Press **Enter**. The Conductivity Calibration Entry Screen is displayed.



Conductivity Calibration Selection Screen

6. Place the correct amount of conductivity standard into a clean, dry or pre-rinsed transport/calibration cup.

WARNING: Calibration reagents may be hazardous to health. See information on label.

NOTE: For maximum accuracy, the conductivity standard you choose should be within the same conductivity range as the samples you are preparing to measure. However, we do not recommend using standards less than one mS/cm. For example:

- For freshwater use a one-mS/cm conductivity standard.
- For brackish water use a ten-mS/cm conductivity standard.
- For seawater use a 50-mS/cm conductivity standard.

NOTE: Before proceeding, ensure that the sensor is as dry as possible. Ideally, rinse the conductivity sensor with a small amount of standard that can be discarded. Be certain that cross-contamination of solutions be avoided. Make certain that no salt deposits are around the oxygen or pH/ORP sensors, particularly if standards of low conductivity are being employed.

7. Carefully immerse the sensor end of the probe module into the solution.
8. Gently rotate and/or move the probe module up and down to remove any bubbles from the conductivity cell.

NOTE: The sensor must be completely immersed past its vent hole. Using the recommended volumes and ensure that the vent hole is covered.

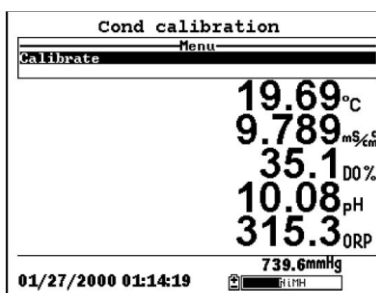
9. Screw the transport/calibration cup onto the threaded end of the probe module and securely tighten.

NOTE: Do not over tighten because doing so could damage the threaded parts.

10. Use the keypad to enter the calibration value of the standard being used.

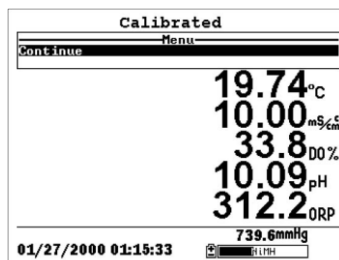
NOTE: Be sure to enter the value in **mS/cm at 25°C**.

11. Press **Enter**. The Conductivity Calibration Screen is displayed.



Conductivity Calibration Screen

12. Allow at least one minute for temperature equilibration before proceeding. The current values of all enabled sensors will appear on the screen and will change with time as they stabilize.
13. Observe the reading under Specific Conductance. When the reading shows no significant change for approximately 30 seconds, press **Enter**. The screen will indicate that the calibration has been accepted and prompt pressing of **Enter** again to Continue.



Calibrated

14. Press **Enter** to return to the Conductivity Calibrate Selection Screen
15. Press **Escape** to return to the Calibrate menu. See Figure 6.2 Calibrate Screen.
16. Rinse the probe module and sensors in tap or purified water and dry.

Dissolved Oxygen Calibration

This procedure calibrates dissolved oxygen. Calibrating any one option (% or mg/L) automatically calibrates the other.

1. Go to the calibrate screen as described in Section 6.2.1 *Accessing the Calibrate Screen*.

NOTE: The instrument must be on for at least 10 to 15 minutes to polarize the DO sensor before calibrating.

2. Use the arrow keys to highlight the **Dissolved Oxygen** selection. See Figure 6.2 Calibrate Screen.
3. Press **Enter**. The Dissolved Oxygen Calibration Screen is displayed.

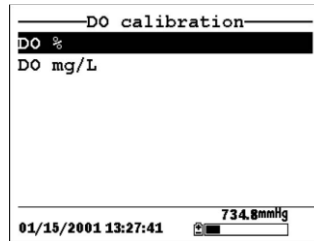


Figure 6.7 DO Calibration Screen

DO Calibration in Percent Saturation

1. Use the arrow keys to highlight the DO% selection.
2. Press **Enter**. The DO Barometric Pressure Entry Screen is displayed.

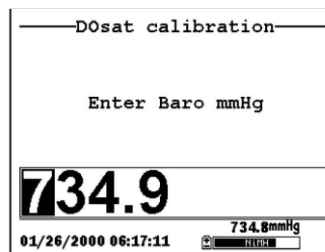


Figure 6.8 DO Barometric Pressure Entry Screen

3. Place approximately 3 mm ($\frac{1}{8}$ inch) of water in the bottom of the transport/calibration cup.
4. Place the probe module into the transport/calibration cup.
NOTE: Ensure that the DO and temperature sensors are **not** immersed in the water.
5. Engage only one or two threads of the transport/calibration cup to ensure that the DO sensor is vented to the atmosphere.
6. Use the keypad to enter the current local barometric pressure.

NOTE: If the unit has the optional barometer, no entry is required.

NOTE: Barometer readings that appear in meteorological reports are generally corrected to sea level and must be uncorrected before use

7. Press **Enter**. The DO% Saturation Calibration screen is displayed.

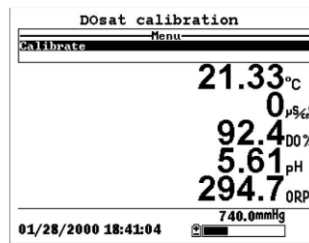


Figure 6.9 DO Sat Calibration Screen

8. Allow approximately ten minutes for the air in the transport/calibration cup to become water saturated and for the temperature to equilibrate before proceeding.
9. Observe the reading under DO %. When the reading shows no significant change for approximately 30 seconds, press **Enter**. The screen will indicate that the calibration has been accepted and prompt pressing of **Enter** again to Continue. See Figure 6.6 Calibrated.
10. Press **Enter** to return to the DO Calibration Screen, See Figure 6.7 DO Calibration Screen.
11. Press **Escape** to return to the calibrate menu. See Figure 6.2 Calibrate Screen.
12. Rinse the probe module and sensors in tap or purified water and dry.

pH Calibration

1. Go to the Calibrate Screen as described in *Section 6.2.1 Accessing the Calibrate Screen*.
2. Use the arrow keys to highlight the **pH** selection. See Figure 6.2 Calibrate Screen.
3. Press **Enter**. The pH Calibration screen is displayed.

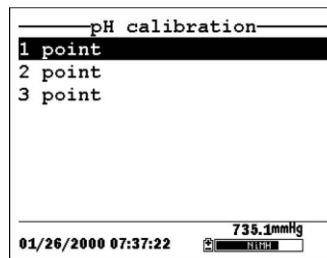


Figure 6.12 pH Calibration Screen

4. Select the **one-point** option only if adjusting a previous calibration. If a two-point or three-point calibration has been performed previously, the calibration can be adjusted by carrying out a one-point calibration. The procedure for this calibration is the same as for a two-point calibration, but the software will prompt a selection of only one pH buffer.
5. Select the **two-point** option to calibrate the pH sensor using only two calibration standards. Use this option if the media being monitored is known to be either basic or acidic. For example, if the pH of a pond is known to vary between 5.5 and seven, a two-point calibration with pH seven and pH four buffers is sufficient. A three-point calibration with an additional pH ten buffer will not increase the accuracy of this measurement because the pH is not within this higher range.
6. Select the **three-point** option to calibrate the pH sensor using three calibration solutions. In this procedure, the pH sensor is calibrated with a pH seven buffer and two additional buffers. The three-point calibration method assures maximum accuracy when the pH of the media to be monitored cannot be anticipated. The procedure for this calibration is the same as for a two-point calibration, but the software will prompt a selection of a third pH buffer.
7. Use the arrow keys to highlight the **two-point** selection.
8. Press **Enter**. The pH Entry Screen is displayed.

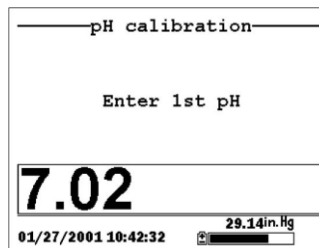


Figure 6.13 pH Entry Screen

9. Place the correct amount (see Table 6.1 Calibration Volumes) of pH buffer into a clean, dry, or prerinsed transport/calibration cup.

NOTE: Always calibrate with buffer seven first, regardless of whether performing a one-, two-, or three-point calibration.

WARNING: Calibration reagents may be hazardous to health. See reagent label for more information.

NOTE: For maximum accuracy, the pH buffers chosen should be within the same pH range as the water being prepared for sampling.

NOTE: Before proceeding, ensure that the sensor is as dry as possible. Ideally, rinse the pH sensor with a small amount of buffer that can be discarded. Be certain to avoid cross-contamination of buffers with other solutions.

10. Carefully immerse the sensor end of the probe module into the solution.
11. Gently rotate and/or move the probe module up and down to remove any bubbles from the pH sensor.

NOTE: The sensor must be completely immersed. Using the recommended volumes from Table 6.1 Calibration Volumes should ensure that the sensor is covered.
12. Screw the transport/calibration cup onto the threaded end of the probe module and securely tighten.

NOTE: Do not overtighten because doing so could damage the threaded parts.

13. Use the keypad to enter the calibration value of the buffer being used **at the current temperature**.

NOTE: pH vs. temperature values are printed on the labels of all YSI pH buffers.

14. Press **Enter**. The pH Calibration Screen is displayed.

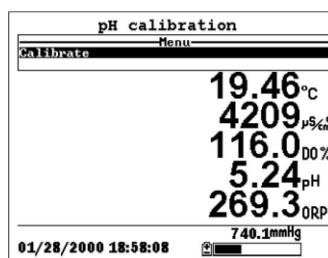


Figure 6.14 pH Calibration Screen

15. Allow at least one minute for temperature equilibration before proceeding. The current values of all enabled sensors will appear on the screen and will change with time as they stabilize.

16. Observe the reading under pH. When the reading shows no significant change for approximately 30 seconds, press **Enter**. The screen will indicate that the calibration has been accepted and prompt **Enter** to be pressed again to continue.
17. Press **Enter** to return to the specified pH Calibration Screen, See Figure 6.13 pH Entry Screen.
18. Rinse the probe module, transport/calibration cup, and sensors in tap or purified water and dry.
19. Repeat steps 6 through 13 using a second pH buffer.
20. Press **Enter** to return to the pH Calibration Screen. See Figure 6.12 pH Calibration Screen.
21. Press **Escape** to return to the Calibrate menu. See Figure 6.2 Calibrate Screen.
22. Rinse the probe module and sensors in tap or purified water and dry.

Return to Factory Settings.

1. Go to the Calibrate screen as described in Section 6.2.1 *Accessing the Calibrate Screen*.
2. Use the arrow keys to highlight the **Conductivity** selection. See Figure 6.2 Calibrate Screen.

NOTE: We will use the Conductivity sensor as an example; however, this process will work for any sensor.

3. Press **Enter**. The Conductivity Calibration Selection Screen is displayed. See Figure 6.3 Conductivity Calibration Selection Screen.
4. Use the arrow keys to highlight the **Specific Conductance** selection.
5. Press **Enter**. The Conductivity Calibration Entry Screen is displayed. See Figure 6.4 Conductivity Calibration Entry Screen.
6. Press and hold the **Enter** key down, and press the **Escape** key.

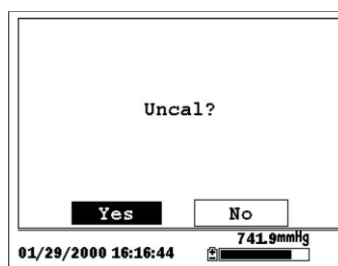


Figure 6.17 ORP Calibration Screen

7. Use the arrow keys to highlight the **YES** selection.

CAUTION: Pressing **YES** returns a sensor to the factory settings. For example, in the selection to return specific conductance to the factory setting, salinity and conductivity will automatically return to their factory settings.

8. Press **Enter** to return you to the Conductivity Calibrate Selection Screen. See Figure 6.3 Conductivity Calibration Selection Screen. .
9. Press **Escape** to return to the Calibrate menu. See Figure 6.2 Calibrate Screen.

HACH Digital Titrator (for Alkalinity) Primary Method

Titration are performed using the HACH digital titrator. This instrument provides precise results when properly operated.

Basic Operation

1. Select a sample volume and titration cartridge corresponding to the expected sample concentration.
2. Insert the cartridge into the titrator slide and lock it into place with the plunger. Remove the polyethylene cap from the cartridge and insert a clean delivery tube into the end of the cartridge. (Note: use a straight tube with a hook on the end for hand-held titrations and a 90° tube with a hook at the end for stationary setups.)
3. To start the titrant flow, hold the tip of the cartridge upward while turning the delivery knob until the air is expelled and several drops of solution flow from the tip of the delivery tube.
4. Use the counter reset knob (the smaller of the two knobs) to set the digital counter back to zero, then blot any titrant from the delivery tube.
5. Proceed with titration by submerging the tip of the delivery tube into the sample and turning the delivery knob to dispense the titrant. (Note: during the titration process, samples must be continuously stirred either manually or with the magnetic stirrer)

Calculations

HACH titration cartridge solutions are designed to give those numbers used in the titrations (reading from the digital meter) to be actual sample concentration in mg/L, or they are marked with conversion factors. If in the process of sample preparation, the amount of SAMPLE becomes less than 100 mL, the titration number must be multiplied by the divisional factor. For example, if the intended 100-mL sample is reduced to 25 mL ($\frac{1}{4}$ of 100 mL) during the sample-preparation process, then the final result must be multiplied by 4 ($25 \text{ mL} \times 4 = 100 \text{ mL}$) to obtain the result.

General Maintenance

1. For long-term storage the delivery tube should be removed, the polyethylene cap reattached, and the cartridge removed from the titrator body. DO NOT attempt to remove the cartridge from the titrator without recapping.
2. After use and removal from the cartridges, rinse the delivery tubes with deionized water to prevent clogging.

The titration process should be checked monthly by titration of a standard solution and recorded in the laboratory notebook. Acceptable results are obtained if the titration is within $\pm 3\%$ of the standard solution.

Alkalinity Determination Using the HACH Digital Titrator

Alkalinity of water is defined by its acid-neutralizing capacity. Once a sample has been collected, geochemical changes can alter the sample's alkalinity. Therefore, alkalinity samples are to be analyzed in the field or immediately upon returning to the EAA laboratory.

Procedure

Sample alkalinity is determined by titration with sulfuric acid to a pH of 4.5 and includes all carbonate, bicarbonate, and hydroxide present within the sample. Values are recorded as mg/L calcium carbonate.

1. Follow the steps outlined in HACH digital titrator usage, with the sulfuric acid cartridge as the active titrant and the 90° delivery tube as a stationary setup.
2. Set up the HACH titrator unit and attach the digital titrator to the rotational holder and clamp securely.
3. The pH and temperature probes should also be connected to the titrastir at the end of the rotational holder. For best results, attempt to have the ends of the delivery tube, pH probe, and temperature probe at the same level.
4. Rinse a 25-mL pipette three times with deionized water and then three times with the sample water to be tested. Pipette 25 mL of this sample into a clean 50-mL beaker. Record this amount on the corresponding field sheet.
5. Place the beaker on the stir plate, put a stir bar in the beaker, and turn on the stirring function.
6. Rotate the titrastir arm toward the sample beaker, submerging the probes and delivery tube. Note: ensure that the titrator counter is reset to zero and the outside of the delivery tube is free of sulfuric acid before submerging.
7. Turn on the pH meter and record the stabilized pH reading of the sample. Record this value on the corresponding field data sheet.
8. Titrate by turning the delivery knob until the pH is reduced to 4.5, which is the endpoint, and the amount of titrant used should be recorded.
9. Calculate the alkalinity by multiplying the amount of titrant used by the dilution factor, and record on the appropriate field data sheet.

Collect a second alkalinity sample every ten samples as a field duplicate, and analyze as outlined above. The field duplicate percent difference should not exceed $\pm 5\%$, where %D is defined as

$$[(X1 - X2) / X1] \times 100 = \%D \text{ (X1 = original sample, X2 = duplicate sample)}$$

(see next page for additional alkalinity procedures)

Additional Procedures for Alkalinity Analyses, University of Minnesota Methodology (to be incorporated into the EAA methodology)

Good Titration Practices

Aliquot Measurement

- ◆ Sample aliquots should be measured with the most accurate method available.
- ◆ Rinse the volumetric flask with sample water.
- ◆ Never rinse the titration flask with sample water.
- ◆ Rinse the titration flask with De-Ionized water between samples and air dry (glass) or shake dry (PMP plastic).
- ◆ An electronic balance is preferred over a volumetric flask is preferred over a graduated cylinder.
- ◆ A 0.1g scale is comparable to a volumetric flask.
- ◆ An electronic balance allows the size of sample aliquots to be varied.
- ◆ An electronic balance allows aliquot size to be reduced in high alkalinity samples which reduces titration time.

Titration Equipment

- ◆ Digital titrator should be periodically lubricated.
- ◆ Titrant cartridges must be kept tightly capped to prevent evaporation.
- ◆ Old, partially used titrant cartridges should be replaced.
- ◆ Don't try to use every drop of acid in the titrant cartridge - when it gets low start a new cartridge.
- ◆ Delivery tubes should be flushed with fresh titrant before use and rinsed after use.
- ◆ A magnetic stirrer (battery powered for field use) helps ensure thorough mixing.

Titration Procedures

- ◆ All chemical analyses should be replicated.
- ◆ Titrations are done in triplicate to allow comparison of results ensuring that reproducible results are obtained.
- ◆ Replicates that vary by more than two percent indicate interference or analytic error.
- ◆ Real time analysis of the results allows additional titrations and/or a change in procedure to identify the sources of the interference or error.
- ◆ Work consistently and quickly to limit degassing and precipitation in your sample bottle.
- ◆ Add acid uniformly to each aliquot as if performing the first titration.

Colorimetric

- ◆ Bromocresol Green / Methyl Red indicator dyes.
- ◆ pH 4.8 to 4.5 buffer solutions.
- ◆ Adding acid too quickly and incomplete equilibration will produce irregular results.
- ◆ Use buffered indicator solutions to define endpoint.
- ◆ Relies on human color interpretation.

Potentiometric

pH Endpoint

- ◆ Meter calibration is critical.
- ◆ Adding acid too quickly and incomplete equilibration will produce irregular results.
- ◆ Must allow for solution equilibration and meter stabilization.
- ◆ Uses one data point to determine endpoint.

Δ pH/ Δ v acid

- ◆ Must be done in uniform steps through the endpoint.
- ◆ Adding acid too quickly and incomplete equilibration will produce irregular results.
- ◆ Organics may shift endpoint.
- ◆ Uses two data points to determine endpoint.

Figure 1 shows a typical “S” shaped titration curve. The inflection point represents the true alkalinity of the sample and may not occur at exactly pH 4.5.

Gran Titration

- ◆ Uses many data points.
- ◆ Must be carried well past the endpoint.
- ◆ Requires graphical interpretation or linear regression.
- ◆ Adding acid too quickly and incomplete equilibration will produce non-linear trend.
- ◆ Presence of organics will produce non-linear trends.
- ◆ Least susceptible to operator error or chemical interference but should still be backed up by replicate measurements - replicate may be by colorimetric or potentiometric methods.

To calculate the alkalinity, use the formula $(V_{\text{aliquot}} + V_{\text{titrant}}) \times 10^{(4.65-\text{pH})}$ to plot an ascending line after the endpoint with apparent alkalinity on the x-axis; V_{aliquot} in ml, $V_{\text{titrant}} = \text{titrator digits}/800$ and 4.65 is the assumed endpoint. A linear regression can then be used to calculate an x-intercept. Use only the points well after the endpoint to get the best regression as shown in Figure 2.

Common Interferences

◆ **Highly colored waters**

Organic-rich waters with humic and fulvic acids.
Often have low pH and correspondingly low alkalinity.

Solutions

Perform Gran Titration - by extrapolating from points below pH 4.5 a fairly precise determination of alkalinity can be made.

Add a second packet of indicator dye to intensify green and red colors.

◆ **Chlorinated waters**

Color change at endpoint goes from green to yellow.

Solution: Add 5 drops and 2N Sodium Thiosulfate to scavenge any free chlorine before titrating.

◆ **Clay-rich waters**

Colors of indicators are "off" often tending towards an orange endpoint.
Commonly associated with poorly developed monitoring wells.

Solution: Filter the sample before titrating.

◆ **Muddy waters**

Suspended sediment may contain carbonates or clays that could react with the acid titrant.
Thick sediment may mask the color changes.

Solution: Filter the sample, preferably after allowing sediment to settle.

References

Determination of the Equivalent Point in Potentiometric Titrations, 1950, Gunnar Gran, Acta Chemica Scandinavica, pp 559-577.

Determination of the Equivalence Point in Potentionmetric Titrations - Part II, 1952, Gunnar Gran, The Analyst, International Congress on Analytical Chemistry, V. 77, pp 661-671.

Field Guide for Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program, Larry R. Shelton, 1994, U.S. Geological Survey Open-File Report 94-455, 42 pp.

Field and Laboratory Methods, 1998, Scott C. Alexander and E.C. Alexander Jr., Hydrogeochemistry Lab, Dept. of Geology & Geophysics, Univ. of Minnesota, 21 pp.

EPA Method 310.1: Alkalinity determination to a colorimetric end-point.

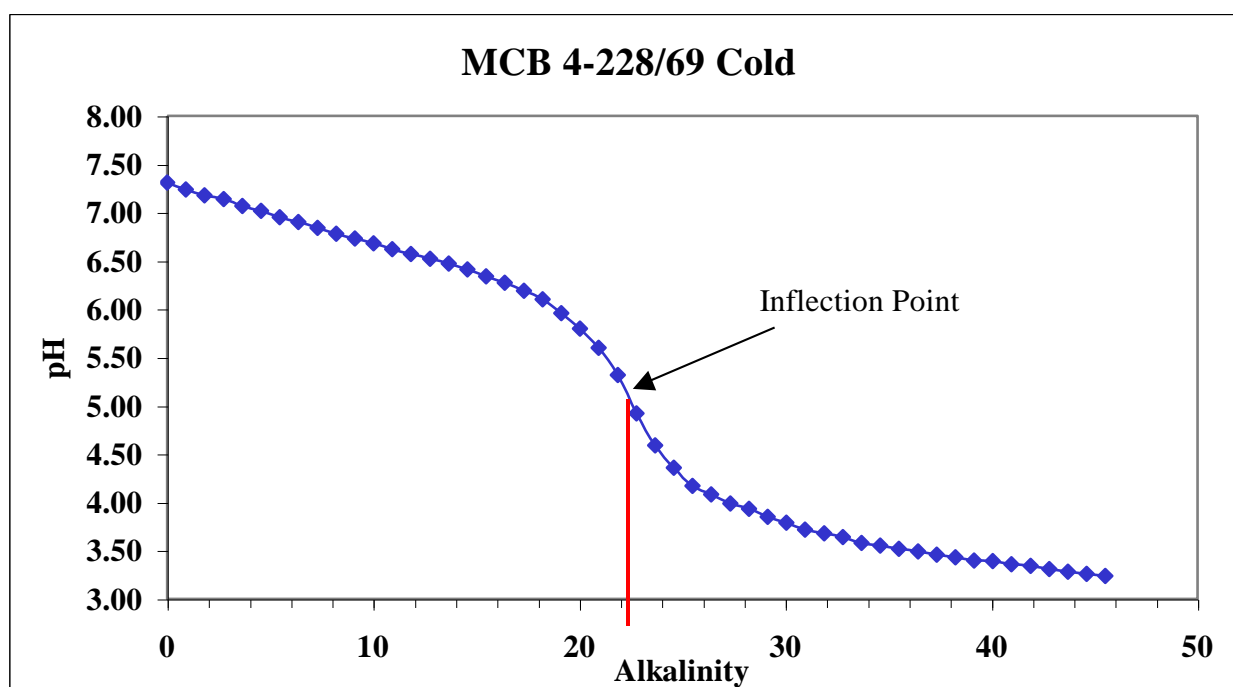


Figure 1. Example of pH titration

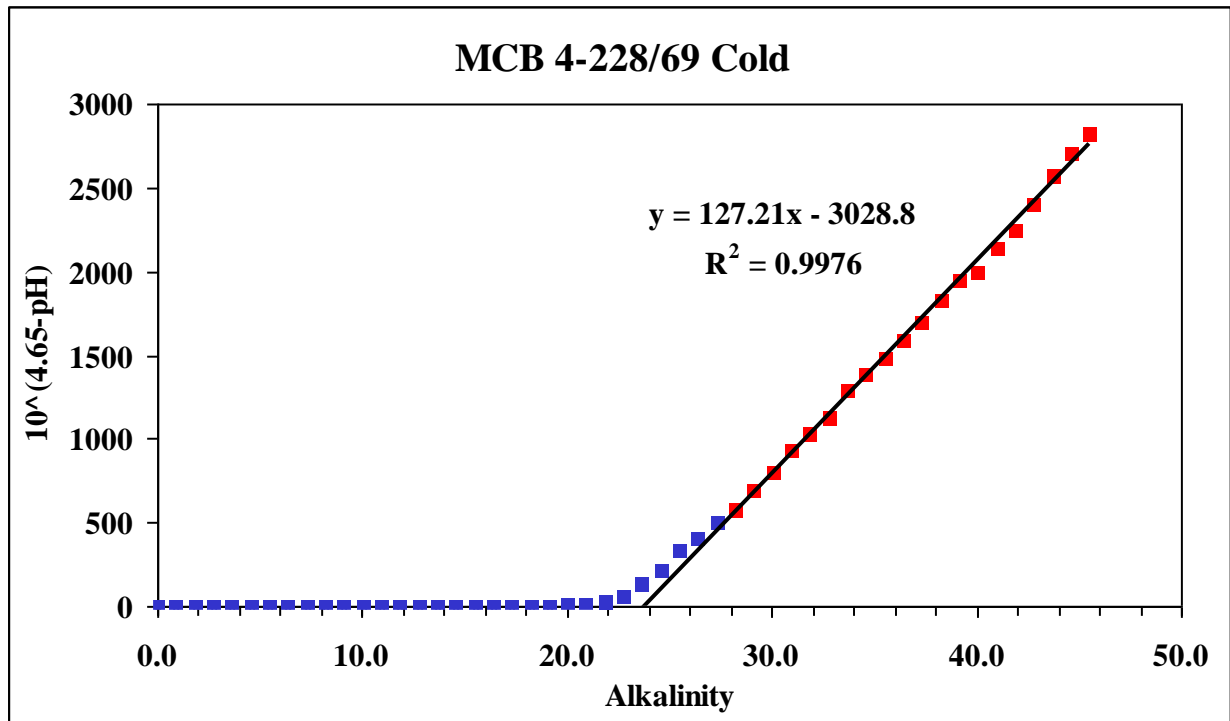


Figure 2. Example of Gran Titration

Use of the DR2800 Portable Spectrophotometer for Alkalinity Measurements (Secondary Method for Alkalinity Determination)

EAA currently uses the DR2800 Portable Spectrophotometer for measuring alkalinity values of samples in the event the Hach Digital Titrator is not available. Measurements are made at the EAA Camden building following the field sample-collection event. All measurements are to be recorded in the alkalinity notebook and on the field sheet. Operation procedures for this instrument are detailed next.

Alkalinity, Total

DOC316.53.01257

Colorimetric Method

Method 10239

25 to 400 mg/L CaCO₃

TNTplus™ 870

Scope and Application: For drinking water, wastewater and boiler water.

Test preparation

Before the test:

DR 2800 only: Install the light shield in Cell Compartment #2 before performing this test.

Read the safety advice and expiration date on the package.

The recommended sample and reagent temperature is 15–25 °C (59–77 °F).

The recommended reagent storage temperature is 15–25 °C (59–77 °F).

TNTplus™ methods are activated from the Main Menu when the sample vial is inserted into the sample cell holder.

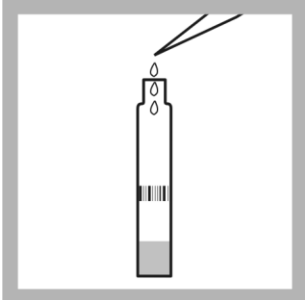
Collect the following items:

Description	Quantity
Total alkalinity TNT870 vials	variable
Light shield (DR 2800 only)	1
Pipette for 2.0-mL sample	1
Pipette for 0.5-mL sample	1
Pipette tips	variable

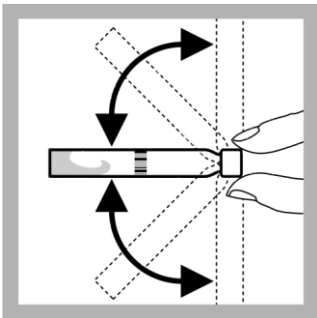
TNTplus™ method



1. Pipette 2.0 mL of **Solution A** into test vial.



2. Pipette 0.5 mL of sample into vial.



3. Cap and invert vial until contents are well mixed.



4. Wait 5 minutes.



5. After timer expires, wipe vial and insert it into cell holder. Instrument reads barcode, selects method, and make measurement. No instrument zero required. Results are in mg/L CaCO_3 .

Interferences

If samples contain particles, remove the particles by filtration through a 0.45- μm filter.

Sample collection, preservation, and storage

- Collect samples in clean plastic or glass bottles. Fill completely and cap tightly.
- Prevent excessive agitation or prolonged exposure to air. Complete the test procedure as soon as possible after collection for best accuracy.
- The sample can be stored for 24 h if cooled to 4 °C (39 °F) or below. Warm to room temperature before the test begins.

Accuracy check

Standard solution method required for accuracy check:

- Alkalinity Voluette® Ampule Standard Solution, 25,000 mg/L CaCO_3 (0.500 N)
- Ampule breaker
- Variable-volume pipette
- Pipette tips
- 100-mL volumetric flask, Class A
- Deionized water

1. Prepare a 250-mg/L CaCO_3 standard solution as follows:

- a.** Pipette 1.0 mL of alkalinity standard solution, 25,000 mg/L as CaCO_3 , into a clean 1.0-mL volumetric flask.
 - b.** Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
- 2.** Use this solution in place of the sample. Follow the TNTplus™ method test procedure. The result should be within 10% of the expected value.

Summary of method

Carbonates and other buffers react with the reagent in the vial to change the pH. The pH affects the color of the indicator, which is measured photometrically at 615 nm.

Calibration Procedures for Backup Instruments

The following pages contain a discussion of proper use of “backup” instrumentation owned by the EAA, but not in regular use. These instruments may be utilized during a contingency sampling event, or in the case where newer instrumentation is not available due to damage or other issues.

Calibration Procedures for Luminescent Dissolved Oxygen Probe Model LDO10101 with HQ30d Meter

Before calibration:

The probe must have the correct service-life time stamp. Set the date and time in the meter before the probe is attached.

It is not necessary to recalibrate when moving a calibrated probe from one HQd meter to another if the additional meter is configured for the same calibration options.

To view the current calibration, push Select View Probe Data, then select View Current Calibration.

If any two probes are connected, push the **UP** or **DOWN** arrow to change to the single display mode in order to show the Calibrate option.

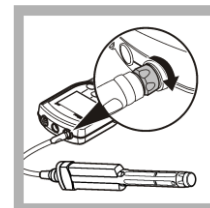
Calibration notes:

- % saturation or mg/L calibration methods are available in the Modify Current Settings menu.
- Slope value is the comparison between the latest calibration and the factory calibration shown as a percentage.
- Calibration is recorded in the probe and the data log. Calibration is also sent to a PC, printer, or flash memory stick if connected.

- Air bubbles under the sensor tip when submerged can cause slow response or error in measurement. If bubbles are present, gently shake the probe until bubbles are removed.

Water-saturated air (100%) calibration procedure:

1. Connect the probe to the meter. Ensure that the cable locking nut is securely connected to the meter. Turn on the meter.



2. Push **Calibrate**.



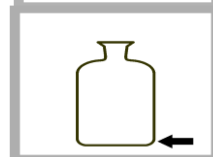
3. Push **Methods**. Select User Cal-100%. Push **OK**.



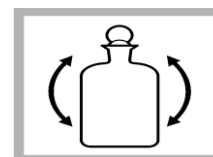
4. Rinse the probe cap with deionized water. Blot dry with a lint-free cloth.



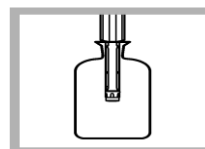
5. Add approximately ¼ inch (6.4 mm) of reagent water to a narrow-neck bottle, such as a BOD bottle.



6. Put a stopper in the bottle and shake the bottle vigorously for approximately 30 seconds to saturate the entrapped air with water. Allow up to 30 minutes for contents to equilibrate to room temperature.



7. Remove the stopper. Carefully dry the probe cap using a nonabrasive cloth. Put the probe in the bottle.



8. Push **Read**. The display shows “Stabilizing” as the probe stabilizes. The display shows the standard value when the reading is stable.

9. Push **Done** to view the calibration summary.

10. Push **Store** to accept the calibration and return the measurement mode. If a rugged probe, install the shroud on the probe.



Calibration Procedures for Conductivity Model 5197500 or 5197503 with sensION™ 5 (Backup Instrumentation)

Before the test:

Collect samples in clean plastic or glass bottles.

Analyze samples as soon as possible after collection. However, samples may be stored at least 24 h by cooling to 4 °C (39 °F) or below (all storage temperatures have changed to 0 to 6 °C as per the EPA MUR, March 2007). When solutions are measured that are not at reference temperature, the meter automatically adjusts the conductivity value to reference temperature from 20 or 25 °C.

Water samples containing oils, grease, or fats will coat the electrode and affect the accuracy of the readings. If this coating occurs, clean the probe with a strong detergent solution, then thoroughly rinse with deionized water.

Mineral buildup on the probe can be removed with a diluted 1:1 hydrochloric acid solution. Refer to the meter user's manual.

Calibration instructions are given in the operation section of the meter manual. For most accurate results, calibrate before use or check the accuracy of the meter using a known conductivity standard.

Calibrating with a Known Standard

1. Place the probe in a conductivity standard that is in the expected range of the samples. On the meter, choose one of four ranges that corresponds to the sample range. Agitate the probe to dislodge bubbles in the cell. Avoid resting the probe on the bottom or sides of the container.
2. Press **CAL**. Functional keys will appear in the lower-left part of the display. **CAL?** and **1.000 1/cm** will appear in the upper display. If the meter has been calibrated, the last calibration value will appear. The numeric keypad will become active.
3. Press the arrow keys to scroll to the factory-calibration options (1000 µS/cm or 18 mS/cm). To calibrate using one of

these standards, press **ENTER**.

4. If using a standard with a different value, use the number keys to enter the standard conductivity at 25 °C, then press **ENTER**. The meter will automatically correct the calibration measurement to 25 °C using the NaCl-based, non-linear temperature coefficient.

If the standard has a value of 25 °C in the $\mu\text{S}/\text{cm}$ range, enter the value when 1000 $\mu\text{S}/\text{cm}$ is displayed. If the standard has a value of 25 °C in the mS/cm range, enter the value when 18 mS/cm is displayed. All four places have a number entered in them. If a number entry error occurs, start over by pressing **SETUP/CE**.

5. When the reading is stable, the calibration is automatically stored, and the instrument returns to reading mode.

Calibration Procedures for Turbidimeter

Note: *for best accuracy, use the same sample cell of four matched sample cells for all measurements during calibration. Always insert the cell so that the orientation mark placed on the cell during the matching procedure is correctly aligned.*

Calibration

1. Rinse a clean sample cell with dilution water several times. Then fill the cell to the line (~15 mL) with dilution water or use StablCal <0.1 NTU standard. *Note: the same dilution water used for preparing the standards must be used in this step.*
2. Insert the sample cell in the cell compartment by aligning the orientation mark on the cell with the mark on the front of the cell compartment. Close the lid, and press **I/O**. *Note: choose signal average mode option (on or off) before pressing CAL—the SIGNAL AVERAGE key in calibration mode.*
3. Press **CAL**. The CAL and S0 icons will be displayed and will flash. The four-digit display will show the value of the S0 standard for the previous calibration. If the blank value were forced to 0.0, the display would be blank (as shown.) Press **→** for a numerical display.

Hach Company recommends the use of StableCal® Stabilized Formazin or formazin standards only for the calibration of Hach turbidimeters. Hach Company cannot guarantee the performance of the turbidimeter if calibrated with co-polymer styrene divinylbenzene beads of other suspension. DO NOT calibrate with Gelex® Secondary Standards.

4. Press **READ**. The instrument will count from 60 to 0 (67 to 0 if signal average is on), read the blank, and use it to calculate a correction factor for the 20 NTU standard measurement. If the dilution water is less than or equal to 0.5 NTU, E 1 will appear when the calibration is calculated. The display will automatically increment to the next standard. Remove the sample cell from the cell compartment. *Note: turbidity of the dilution water can be “forced” to zero by pressing → rather than reading the dilution water. The display will show S0 NTU, and the up arrow key must be pressed to continue with the next standard.*
5. The display will show the S1 (with the 1 flashing) and 20 NTU, or the value of the S1 standard for the previous calibration. If the value is incorrect, edit the value by pressing the → key until the number that needs editing flashes. Use the up arrow key to scroll to the correct number. After editing, fill a clean sample cell to the line with well-mixed 20 NTU StablCal Standard of 20 NTU formazin standard. Insert the sample cell compartment by aligning the orientation mark on the cell with the mark on the front of the cell compartment. Close the lid.
6. Press **READ**. The instrument will count from 60 to 0 (67 to 0 if signal average is on), measure the turbidity, and store the value. The display will automatically increment to the next standard. Remove the sample cell from the cell compartment. *Note: for potable water applications with low turbidity values, instrument calibration may be stopped after the 20 NTU StablCal Standard has been read. Press CAL after reading the 20-NTU standard. Instrument calibration is now complete for the range of 0–20 NTU only. The instrument will continue to read turbidity values above 20 NTU. These values were not updated during the 0–20 NTU calibration.*
7. The display will show the S2 (with the 2 flashing) and 100 NTU of the value of the S2 standard for the previous calibration. If the value is incorrect, edit the value by pressing the → key until the number that needs editing flashes. Use the up arrow key to scroll to the correct number. After

editing, fill a clean sample cell to the line with well-mixed 100 NTU StableCal Standard or 100 NTU formazin standard. Insert the sample cell into the cell compartment by aligning the orientation mark on the cell with the mark on the front of the cell compartment. Close the lid.

8. Press **READ**. The instrument will count from 60 to 0 (67 to 0 if signal average is on), measure the turbidity and store the value. Then the display will automatically increment to the next standard. Remove the sample cell from the cell compartment.
9. The display will show the S3 (with 3 flashing) and 800 NTU, or the value of the S3 standard for the previous calibration. If the value is incorrect, edit the value by pressing the → key until the number that needs editing flashes. Use the up arrow key to scroll to the correct number. After editing, fill a clean sample cell to the line with well-mixed 800 NTU formazin standard. Insert the sample cell into the cell compartment by aligning the orientation mark on the cell with the mark on the front of the cell compartment. Close the lid.
10. Press **READ**. The instrument will count from 60 to 0 (67 to 0 if signal average is on), measure the turbidity, and store the value. Then the display will increment back to the S0 display. Remove the sample cell from the cell compartment.
11. Press **CAL** to accept the calibration. The instrument will return to measurement mode automatically. *Note: pressing CAL completes the calculation of the calibration coefficients. If calibration errors occurred during calibration, error messages will appear after CAL is pressed. If E1 or E2 appear, check the standard preparation and review the calibration; repeat the calibration if necessary. If CAL? appears, an error may have occurred during calibration. If CAL? is flashing, the instrument is using the default calibration.*

Notes

- If the **I/O** key is pressed during calibration, the new calibration data are lost, and the old calibration will be used for measurements. Once in calibration mode, only the **READ**, **I/O**, ↑, and → keys function. Signal averaging and range mode must be selected before the

calibration mode can be entered.

- If **E 1** or **E 2** is displayed, an error occurred during calibration. Check the standard preparation and review the calibration; repeat the calibration if necessary. Press **DIAG** to cancel the error message (**E 1** or **E 2**). To continue without repeating the calibration, press **I/O** twice to restore the previous calibration. If **CAL?** is displayed, an error may have occurred during calibration. The previous calibration may not be restored. Either recalibrate or use the calibration as is.
- To review a calibration, press **CAL** and then \uparrow to view the calibration standard values. As long as **READ** is never pressed and **CAL** is not flashing, the calibration will not be updated. Press **CAL** again to return to the measurement mode.

pH Meter Calibration

The pH meter must be calibrated before daily use. The calibration may be accomplished in the laboratory or in the field. In addition to a “preuse” calibration, it is strongly recommended that the meter be checked with a standard buffer solution at least once during the day in order to observe any instrument drift that may have occurred.

Manual Calibration (with two reference solutions)

1. Attach or verify that the pH-indicating electrode and the automatic temperature compensator (ATC) are on the display unit.
2. Remove the rubber filling solution plug (if so equipped) to allow equilibration of the internal solution to the ambient air. Allow approximately five minutes for the equilibration process, and replace the plug.
3. Turn on the unit and select the calibration mode.
4. Rinse both electrodes with deionized water and dry (carefully) any excess water.
5. Rinse the pH electrode in the first pH buffer (reference) solution. After rinsing, immerse the electrode in a container of the first reference solution, and stir to remove bubbles on the electrode.
6. Allow the display to read **READY** and begin flashing. If the pH reading is within the manufacturer’s specifications (see equipment manual), press **YES**. If not, press **NO** and repeat the procedure. The first standard will subsequently be locked into the unit’s memory.
7. To calibrate the meter to the second pH reference solution, repeat steps 4, 5, and 6 USING the second solution.
8. Remove and rinse probes IN deionized water, and begin sample analysis. Otherwise the meter may be turned off; it will keep calibrating as long as the power source remains intact.

Electrode Care and Maintenance for pH Meters

The pH electrodes discussed above are of the temperature-compensating triode design. These probes are delicate and require careful handling. The probes should not be allowed to freeze and **MUST** be stored in a vial of the storage solution.

1. Inspect the probe for damage before each use. Verify that probes contain the appropriate levels of filling solution.
2. If filling-solution levels are low, more solution should be added. Use the Hach solution for Hach probes and the Orion solution for Orion probes.
3. If the probe appears sluggish when readings are taken, the filling solution should be drained and refilled with fresh solution.
4. During normal operations, the probe will become fouled with scale deposits and oils. Clean with laboratory-grade soap by soaking the probe in the soap solution and rinsing in deionized water. If fouling is not removed by this procedure, then a 0.1-N solution of HCL or HNO₃ can be used as a soaking media.
5. Probes must be stored in the electrode storage solution or in a 4.0-pH buffer solution. If probes are allowed to dry out, irreversible damage to the probe may occur.

Conductivity Probes

Orion Conductivity/Temperature Meters, Models 122, 126, 128, and 1230

Conductance, refers to the ability of a substance to carry an electrical current. These probes are used to define the physical parameters of conductivity. Conductivity is the algebraic reciprocal of electrical resistance and is expressed in SI units of microSeimens per centimeter. Specific conductance is electrical conductance measured across a one-cm cube of liquid (sample) between opposing faces of two platinum electrodes at 25°C. Conductivity is the same parameter measured at ambient temperature that has not been temperature compensated to 25°C.

Calibration

The conductivity meter must be calibrated in the laboratory or in the field daily. Conductance standards should be chosen to closely reflect the values expected in the sample groups. For example, if historical conductivity values for an area to be sampled range below 1000 µS/cm, the 500-µS/cm solution should be chosen. The meters are designed to provide a nonlinear-function temperature coefficient to correct calculations; however, best results may be obtained when samples are 25°C.

Calibration Steps

- 1 Select conductivity measurement by turning the meter's conductivity/temperature selector knob from **OFF** to **CONDUCTIVITY** (labeled Δ).
- 2 Submerge the probe into THE selected conductivity standard (past the open area within the probe), and stir briefly to eliminate any air bubbles.
- 3 Maintain the probe in solution, wait for the reading to stabilize, and record the final value.
- 4 No manual adjustment for the meter exists; therefore, the process described herein provides a reference check. If the conductivity reading obtained from steps 1 through 3 is within $\pm 3\%$ of the given standard value, the meter is deemed to be within tolerance limits. If repeated attempts fail to obtain readings within the acceptable range, the meter will require factory service.

Maintenance

- 1 The meter electrode must be clean for readings to be accurate. Laboratory-grade soap may be used to clean dirt and oil deposits from the meter. For mineral deposits, a 1-M-HCl solution may be used in ten parts deionized water, and ten parts isopropyl alcohol as a soaking agent for their removal.
- 2 The conductivity probe may be stored dry. After each use, however, the probe should be rinsed in deionized water and blotted dry.
- 3 The unit will indicate a low battery by flashing **LOBAT** in the upper-left-hand corner of the LCD display. The nine-volt disposable battery should be changed out with the unit **OFF**, to prevent damage.

APPENDIX D—Forms



**EDWARDS AQUIFER
AUTHORITY**

Water Quality Field Data Sheet

HCP SEDIMENT

Site Information

Station Name:	
Location:	
Owner/Contact: Edwards Aquifer Authority	
Address: 900 East Quincy	
County:	
Point of Collection:	
Date: / / 201	Time:
Ambient Temp.	Collector(s):
Weather:	

Equal-Width-Increment Method

Transect Width:
Number of Verticals:
Flow/Appearance:

Type of Analysis: (circle all that apply)					
GWQP	Select. Met.	8081	8082	8141	8151
T.					
TOC	Phosphorous	SVOCs	TB	DOC	VOC

Notes

Latitude:	Longitude:
Datum: _____	

updated 06/06/13



**EDWARDS AQUIFER
AUTHORITY**

Water Quality Field Data Sheet

HCP STORM WATER

Site Information

Station Name:	
Location:	
Owner/Contact: Edwards Aquifer Authority	
Address: 900 East Quincy	
County:	
Point of Collection:	
Date: / / 201	Time:
Ambient Temp.	Collector(s):
Weather:	

Field Readings

Time Sampled:
pH:
Temperature:
Conductivity:
Dissolved Oxygen:
Turbidity:

Equal-Width-Increment Method

Transect Width:
Flow/Appearance:

Instrument Calibration

Conductivity Meter #	
Standard	Meter Reading
500	
1000	
10000	

pH Meter #	
Standard	Meter Reading
Buffer 4.0	
Buffer 7.0	
Buffer 10.0	

pH Meter #	
Standard	Meter Reading
DI water in bottle	

Alkalinity

Alkalinity Meter:	DR 2800 TNT870
Total Alkalinity	

Type of Analysis: (circle all that apply)					
GWQP	Selet. Met.	8081	8082	8141	8151
TOC	T. Phosphorous	TKN	E-Coli MPN	DOC	VOC
TB	SVOCs				

Latitude:	Longitude:
-----------	------------

Datum: _____

Sampling Conditions

Gage Readings	Time	Level
Before Sampling		
After Sampling		
Hydrologic Event	Hydrologic Condition	
Storm	Stable, Low	
Drought	Falling	
Spill	Stable, High	
Regulated Flow	Rising	
Routine Sample	Stable, Normal	

updated 12/21/12



**EDWARDS AQUIFER
AUTHORITY**

Water Quality Field Data Sheet

HCP SURFACE WATER

Site Information

Station Name:
Location:
Owner/Contact: Edwards Aquifer Authority
Address: 900 East Quincy
County:
Point of Collection:
Date: / / 201 Time:
Ambient Temp. Collector(s):
Weather:

Field Readings

Time Sampled:
pH:
Temperature:
Conductivity:
Dissolved Oxygen:
Turbidity:

Equal-Width-Increment Method

Transect Width:
Flow/Appearance:

Instrument Calibration

Conductivity Meter #	
Standard	Meter Reading
500	
1000	
10000	
pH Meter #	
Standard	Meter Reading
Buffer 4.0	
Buffer 7.0	
Buffer 10.0	
pH Meter #	
Standard	Meter Reading
DI water in bottle	

Alkalinity

	mL of Sample	mL of Acid	Total Alk	
Rep.1				Ave. Total Alk. <div></div>
Rep. 2				
Rep3.				

Type of Analysis: (circle all that apply)

GWQP	Selct. Met.	8081	8082	8141	8151
TOC	T. Phosphorous	TKN	E-Coli MPN	DOC	VOC
TB	SVOCs				

Latitude:	Longitude:
-----------	------------

Datum: _____

Sampling Conditions

Gage Readings	Time	Level
Before Sampling		
After Sampling		
Hydrologic Event	Hydrologic Condition	
Storm	Stable, Low	
Drought	Falling	
Spill	Stable, High	
Regulated Flow	Rising	
Routine Sample	Stable, Normal	

updated 12/21/12



Water Quality Field Data Sheet

SPRINGS

Spring Information

State well ID #: NA	
Owner/Contact: New Braunfels Parks & Rec.	
Address:	
Phone Number:	
County: Comal	
Spring Name / #: Comal Springs 7	
Point of Collection: Springs Oriface	
Spring Use: Springs	
Date:	Time:
Weather:	Collector(s):

Field Readings

Time Sampled:				
Turbidity:				
Time	Temp	Cond.	pH	DO

Alkalinity

	mL of Sample	mL of Acid	Total Alk	
Rep. 1				Ave. Total Alk. <div style="border: 1px solid black; width: 50px; height: 20px; margin: 0 auto;"></div>
Rep. 2				
Rep. 3				

Instrument Calibration

Conductivity Meter	
Standard	Meter Reading
500	
1000	
pH Meter	
Standard	Meter Reading
Buffer 4.0	
Buffer 7.0	
Buffer 10.0	
DO Meter	
Standard	Meter Reading
DI water in bottle	

Type of Analysis: (circle all that apply)

GWQP	Select. Met.	8081	8082	8141	8151
8260	Trip Blank	SVOC'S	TOC	T. Phosphorous	Ortho-phosphate as P
E-Coli MPN	TPH	PAH	PPCP		

Latitude:	Longitude:
-----------	------------

Datum: _____

Sampling Conditions

Spring Flow	Low	Medium	High
Flow Appearance	Clear	Cloudy	Murky

updated 12/21/12



**EDWARDS AQUIFER
AUTHORITY**

Water Quality Field Data Sheet

SURFACE WATER

Site Information

Station Name:
Location:
Owner/Contact:
Address:
County:
Point of Collection:
Date: Time:
Ambient Temp. Collector(s):
Weather:

Field Readings

Time Sampled:
pH:
Temperature:
Conductivity:
Dissolved Oxygen:
Turbidity:

Equal-Width-Increment Method

Transect Width:
Number of Verticals:
Flow/Appearance:

Instrument Calibration

Conductivity Meter #	
Standard	Meter Reading
500	
1000	
10000	
pH Meter #	
Standard	Meter Reading
Buffer 4.0	
Buffer 7.0	
Buffer 10.0	
pH Meter #	
Standard	Meter Reading
DI water in bottle	

Alkalinity

	mL of Sample	mL of Acid	Total Alk	
Rep.1				Ave. Total Alk.
Rep. 2				
Rep3.				

Type of Analysis: (circle all that apply)

GWQP	Select. Met.	8081	8082	8141	8151
TOC	T. Phosphorous	Ortho-phosphate as P	E-Coli MPN	TPH	PAH
PPCP					

Latitude:	Longitude:
-----------	------------

Datum: _____

Sampling Conditions

Gage Readings	Time	Level
Before Sampling		
After Sampling		
Hydrologic Event	Hydrologic Condition	
Storm	Stable, Low	
Drought	Falling	
Spill	Stable, High	
Regulated Flow	Rising	
Routine Sample	Stable, Normal	

updated 12/21/12



Water Quality Field Data Sheet
GROUNDWATER

Well Information

Field Readings

State well ID #:	Started Pumping:
Owner/Contact:	Time Sampled:
Address:	Turbidity:
Phone Number:	Time Temp Cond. pH Do
County:	
Well Name / #:	
Point of Collection:	
Well Use:	
Weather:	
Date: Time:	
Flow Rate: gpm Collector(s):	
Water Level: Well Depth:	
Casing Dia.: 3 x well volume=	

Alkalinity

	mL of Sample	mL of Acid	Total Alk	
Rep.1				Ave. Total Alk. <div></div>
Rep. 2				
Rep3.				

Instrument Calibration

Conductivity Meter #	
Standard	Meter Reading
500	
1000	
10000	
pH Meter #	
Standard	Meter Reading
Buffer 4.0	
Buffer 7.0	
Buffer 10.0	
DO Meter	
Standard	Meter Reading
DI water in bottle	

Latitude:	Longitude:
------------------	-------------------

Datum:

Type of Analysis: (circle all that apply)					
GWQP	Selct. Met.	8081	8082	8141	8151
8260	Trip Blank	SVOC'S	TOC	T. Phosphorous	Ortho-phosphate as P
E-Coli MPN	TPH	PAH	PPCP		

Updated on 12/21/12

Page 1 of 1

**APPENDIX E—Drinking-Water Standards and Chemical Health Effects,
from 30 TAC 290, RG-346, and U.S. EPA, July 2002**

(Note, regulatory limits change frequently for certain compounds, the data herein are for general comparisons. The reader should utilized the most recent data available online from TCEQ and EPA if sample results exceed regulatory limits)

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water^	Sources of Contaminant in Drinking Water^
Temperature (°C) EPA 170.1	NE	NA	NA
pH measured at 25°C EPA 150.1	>7.0*	NA	NA
Turbidity (NTU)	NE	NA	NA
Dissolved oxygen (DO) (mg/L)	NE	NA	NA
Alkalinity total as CaCO ₃ SM 2320 B (mg/L)	NE	NA	NA
Specific conductance µS/cm	NE	NA	NA
Laboratory		NA	NA
Alkalinity total as CaCO ₃ SM 2320 B	NE	NA	NA
Bicarbonate (HCO ₃) SM 2320 B	NE	NA	NA
Fecal coliform (CFU/100 mL)	0 MCLG ¹	NA	NA
Fecal strep (CFU/100 mL)	0 MCLG ¹	NA	NA
E. coli (CFU/100 mL)	0 MCLG ¹	NA	NA
pH measured at 25°C EPA 150.1	>7.0*	NA	NA
Specific conductance µS/cm	NE	NA	NA
Nutrients (mg/L)			
Nitrate-nitrite as N EPA354.1/300.0	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water^	Sources of Contaminant in Drinking Water^
Nitrate as N E300	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits
Orthophosphate EPA 365.3	NE	NA	NA
Ammonia as N SM 4500	NE	NA	NA
Phosphorus	NE	NA	NA
Major Ions (mg/L)		NA	NA
Sulfate (SO ₄) EPA 300.0	300*	NA	NA
Solids total dissolved (TDS) EPA 160.1	1,000*	NA	NA
Solids total suspended (TSS) EPA 160.2	NE	NA	NA
Bromide (Br) EPA 300.0	NE	NA	NA
Chloride (Cl) EPA 300.0	300*	NA	NA
Fluoride (F) EPA 340.2	2.0*	Bone disease (pain and tenderness of the bones); children may get mottled teeth	Water additive that promotes strong teeth, erosion of natural deposits, discharge from fertilizer and aluminum factories
Metals by EPA 200.7 and 200.8 (µg/L)		NA	NA
Aluminum	24,000**	NA	NA
		NA	NA
Antimony	6	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries, fire retardants, ceramics, electronics, solder
Arsenic	5	Skin damage or problems with circulatory systems and increased risk of cancer	Erosion of natural deposits; runoff from orchards and glass and electronics production wastes

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
Barium	2,000	Increase in blood pressure	Discharge of drilling wastes, discharge from metal refineries, erosion of natural deposits
Beryllium	4	Intestinal lesions	Discharge from metal refineries and coal-burning factories. erosion of natural deposits
Boron	4,900**		
Cadmium	5	Kidney damage	Corrosion of galvanized pipe, erosion of natural deposits, discharge from metal refineries, runoff from waste batteries and paints
Chromium	100	Allergic dermatitis	Discharge from steel and pulp mills, erosion of natural deposits
Cobalt	1,500**	NA	NA
Copper	1,300*	Short-term exposure, gastrointestinal distress; long-term exposure, liver or kidney damage. People with Wilson's disease should consult their personal doctor if the amount of copper in their water exceeds the action level.	Corrosion of household plumbing systems, erosion of natural deposits
Iron	300*	NA	NA
Lead	15	Infants and children: delays in physical or mental development; children could show slight deficits in attention span and learning abilities. Adults: Kidney problems, high blood pressure	Corrosion of household plumbing systems, erosion of natural deposits
Lithium	490**	NA	NA
Manganese	1,100*	NA	NA
Molybdenum	120**	NA	NA
Nickel	490**	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water^	Sources of Contaminant in Drinking Water^
Selenium	50	Hair or fingernail loss, numbness in fingers or toes, circulatory problems	Discharge from petroleum refineries, erosion of natural deposits, discharge from mines
Silver	120*	NA	NA
Strontium	15,000**	NA	NA
Thallium	2	Hair loss; changes in blood; kidney, intestine, or liver problems	Leaching from ore processing sites; discharge from electronics, glass, and drug factories
Uranium	30	NA	NA
Vanadium	1.7**	NA	NA
Zinc	7,300*	NA	NA
		NA	NA
Metals by E200.8 (mg/L)			
Calcium	NE	NA	NA
Magnesium	NE	NA	NA
Potassium	NE	NA	NA
Sodium	NE	NA	NA
Metals by SW-7470A (mg/L)			
Mercury	0.002	Kidney damage	Erosion of natural deposits, discharge from refineries and factories, runoff from landfills and croplands
Total Organic Carbon by E415.1 (mg/L)			
TOC	NE	NA	NA
Herbicides by SW-8141 (µg/L)			
Azinphosmethyl	37**	NA	NA
Bolstar (Sulprofos)	73**	NA	NA
Chlorpyrifos	73**	NA	NA
Coumaphos	170**	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
Demeton-O	1.0**	NA	NA
Demeton-S	0.98**	NA	NA
Diazinon	22**	NA	NA
Dichlorvos	3.1**	NA	NA
Dimethoate	4.9**	NA	NA
Disulfoton	0.98**	NA	NA
EPN	0.24**	NA	NA
Ethoprop	2.4**	NA	NA
Famphur	0.73**	NA	NA
Fensulfothion	24**	NA	NA
Fenthion	1.7**	NA	NA
Malathion	490**	NA	NA
Merphos	7.3**	NA	NA
Methyl parathion	6.1**	NA	NA
Mevinphos (Phosdrin)	0.61**	NA	NA
Mononcrotophos	15**	NA	NA
Naled	49**	NA	NA
Parathion	150**	NA	NA
Phorate	4.9**	NA	NA
Ronnel	1,200**	NA	NA
Stirophos (Tetrachlorvinphos)	1,000**	NA	NA
Sulfotepp (Tetraethyl dithiopyrophosphate)	12**	NA	NA
Tokuthion (Prothiofos)	2.4**	NA	NA
Trichloronate	73**	NA	NA
Thionazin	1.7**	NA	NA
Herbicides by SW-8151 (µg/L)			
2,4,5-T	240	NA	NA
2,4,5-TP (Silvex)	50	Liver problems	Residue of banned herbicide

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water^	Sources of Contaminant in Drinking Water^
2,4- D	70	Kidney, liver, or adrenal gland problems	Runoff from herbicide used on row crops
2,4-DB	200	NA	NA
Dalapon	200	Minor kidney changes	Runoff from herbicide used on rights of way
Dicamba	730	NA	NA
Dichoroprop	240	NA	NA
Dinoseb	7	Reproductive difficulties	Runoff from herbicide used on soybeans and vegetables
MCPA	12	NA	NA
MCP (mecoprop)	24	NA	NA
Pentachlorophenol	1	Liver or kidney problems, increased cancer risk	Discharge from wood-preserving factories
Pesticides by SW-8081 (µg/L)			
4, 4'-DDD	3.8**	NA	NA
4, 4'-DDE	2.7**	NA	NA
4, 4'-DDT	2.7**	NA	NA
Aldrin	0.05**	NA	NA
Alpha-bhc (Alpha-hexachlorocyclohexane)	0.1**	NA	NA
Alpha-chlordane	2.6**	NA	NA
Beta-bhc (Beta-hexachlorocyclohexane)	0.5**	NA	NA
Chlordane	2.0**	Liver or nervous system problems, increased risk of cancer	Residue of banned termiticide
Delta-bhc (Delta-hexachlorocyclohexane)	0.5**	NA	NA
Dieldrin	0.57**	NA	NA
Endosulfan I	49**	NA	NA
Endosulfan II	150**	NA	NA
Endosulfan sulfate	150**	NA	NA
Endrin	2.0**	Liver problems	Residue of banned insecticide

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
Endrin aldehyde	7.3**	NA	NA
Endrin ketone	==		
Gamma-bhc (Lindane)	7.3**	NA	NA
Gamma-chlordane	0.2	Liver or kidney problems	Runoff/leaching from insecticide used on cattle, lumber, gardens
	2.6**	NA	NA
Heptachlor epoxide	0.4	Liver damage, increased risk of cancer	Residue of banned termiticide
Methoxychlor	0.2	Liver damage, increased risk of cancer	Breakdown of heptachlor
Toxaphene	40	Reproductive difficulties	Runoff/leaching from insecticide used on fruits, vegetables, alfalfa, livestock
PCBs by SW-8082 (µg/L)	3	Kidney, liver, or thyroid problems; increased risk of cancer	Runoff/leaching from insecticide used on cotton and cattle
Aroclor 1016			
Aroclor 1221	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals
Aroclor 1232	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals
Aroclor 1242	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals
Aroclor 1248	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water^	Sources of Contaminant in Drinking Water^
Aroclor 1254	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals
Aroclor 1260	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals
Aroclor 1262	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals
Aroclor 1268	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals
	0.5	Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer	Runoff from landfills, discharge of waste chemicals
SVOCs by SW-8270C (µg/L)			
1,2- dichlorobenzene	600**	NA	NA
1,2,4- trichlorobenzene			
2, 4, 5-trichlorophenol	70**	Changes in adrenal glands	Discharge from textile finishing factories
2, 4, 6-trichlorophenol	2,400**	NA	NA
2, 4-dichlorophenol	24**	NA	NA
2, 4-dimethylphenol	73**	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
2, 4-dinitrophenol	490**	NA	NA
2-chlorophenol	49**	NA	NA
2-methylnaphthalene	120**	NA	NA
2-methylphenol (o-cresol)	98**	NA	NA
2-nitroaniline	1,200**	NA	NA
2-nitrophenol	7.3**	NA	NA
3 & 4 methylphenol (m&p cresol)	49**	NA	NA
3-nitroaniline	1,200**	NA	NA
4, 6-dinitro-2-methylphenol	7.3**	NA	NA
4-chloro-3-methylphenol	2.4**	NA	NA
4- chloroaniline	120**	NA	NA
4-nitroaniline	4.6**	NA	NA
4-nitrophenol	46**	NA	NA
Naphthalene	49**	NA	NA
Nitrobenzene	490**	NA	NA
Pentachlorophenol	49**	NA	NA
Phenanthrene	1	NA	NA
Phenol	730**	NA	NA
Pyrene	7,300**	NA	NA
N-nitrosodi-n-propylamine	730**	NA	NA
N-nitrosodiphenylamine	0.13**	NA	NA
Acenaphthene	190**	NA	NA
Acenaphthylene	1,500**	NA	NA
Anthracene	1,500**	NA	NA
Benzo(a)anthracene (1 2-benzanthracene)	7,300**	NA	NA
Benzo(b)fluoranthene	1.3**	NA	NA
Benzo(k)fluoranthene	1.3**	NA	NA
Benzo(ghi)perylene	13**	NA	NA
Benzo(a)pyrene	730**	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water^	Sources of Contaminant in Drinking Water^
Benzyl Alcohol	0.2	Reproductive difficulties, increased risk of cancer	Leaching from linings of water storage tanks and distribution lines
Butyl benzyl phthalate	2,400**	NA	NA
Bis(2-chloroethoxy)methane	480**	NA	NA
Bis(2-chloroethyl)ether	0.83**	NA	NA
Bis(2-ethylhexyl)phthalate	0.83**	NA	NA
4-bromophenyl phenyl ether	6	NA	NA
4-chloroaniline	0.061**	NA	NA
2-chloronaphthalene	4.6**	NA	NA
4-chlorophenyl phenyl ether	2,000**	NA	NA
Chrysene	0.061**	NA	NA
Dibenz(a,h)anthracene	130**	NA	NA
Dibenzofuran	0.2**	NA	NA
3 3-dichlorobenzidine	98**	NA	NA
Diethyl phthalate	2**	NA	NA
Dimethyl phthalate	20,000**	NA	NA
Di-n-butyl phthalate	20,000**	NA	NA
Di-n-octyl phthalate	2,400**	NA	NA
2 4-dinitrotoluene	980**	NA	NA
2 6-dinitrotoluene	1.3**	NA	NA
Fluoranthene	1.3**	NA	NA
Fluorene	980**	NA	NA
Hexachlorobenzene	980**	NA	NA
Hexachlorobutadiene	1**	Liver or kidney problems, reproductive difficulties, increased risk of cancer	Discharge from metal refineries and agricultural chemical factories
Hexachlorocyclopentadiene	12**	NA	NA
Hexachloroethane	50	Kidney or stomach problems	Discharge from chemical factories
Indeno(1,2,3-cd)pyrene	24**	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
Isophorone	1.3**	NA	NA
VOCs SW-8260b (µg/L)	960**	NA	NA
1, 1, 1, 2-tetrachloroethane			
1, 1, 1-trichloroethane	35.0**	NA	NA
1, 1, 2, 2-tetrachloroethane	200	Liver, nervous system, or circulatory problems	Discharge from metal degreasing sites and other factories
1, 1, 2-trichloroethane	4.6**		
1, 1-dichloroethane	5	Liver, kidney, or immune system problems	Discharge from industrial chemical factories
1, 1-dichloropropene	4,900**	NA	NA
1, 1-dichloroethene (Vinylidene chloride)	9.1**	NA	NA
1- chlorohexane	7	NA	NA
1-octene	980**	NA	NA
1, 2, 3-trichlorobenzene	NE	NA	NA
1, 2, 3-trichloropropane	73**	NA	NA
1, 2, 4-trichlorobenzene	0.03**	NA	NA
1, 2, 4-trimethylbenzene	72**	NA	NA
1, 2-dibromo-3-chloropropane	1,200**	NA	NA
1, 2-dibromoethane (EDB)	0.2	Reproductive difficulties, increased risk of cancer	Runoff/leaching from soil fumigant used on soybeans, cotton, pineapples, and orchards
1, 2-dichlorobenzene	NE	NA	NA
1, 2-dichloroethane (EDC)	600**	NA	NA
1, 2-dichloropropane	5	Increased risk of cancer	Discharge from industrial chemical factories
1, 3, 5-trimethylbenzene	5	Increased risk of cancer	Discharge from industrial chemical factories
1,3- butadiene	1,200**	NA	NA
1, 3-dichlorobenzene	NE	NA	NA
1, 3-dichloropropane	730**	NA	NA
1, 4-dichlorobenzene	9.1**	NA	NA
1, 4-dioxane	75**	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
2, 2-dichloropropane	9.1**	NA	NA
2- chloro-1,3- butadiene	13	NA	NA
2-chlorotoluene	NE	NA	NA
2-hexanone	490**	NA	NA
2-nitropropane	120**	NA	NA
1,3,5- trichlorobenzene	3.4**	NA	NA
3- chloro-1- propene	73**	NA	NA
4-chlorotoluene	NE	NA	NA
4-isopropyltoluene	490**	NA	NA
4-methyl-2-pentanone (MIBK)	2,400**	NA	NA
Acetone	1,950**	NA	NA
Acetonitrile	22,000**	NA	NA
Benzene	780**	NA	NA
Benzyl chloride	5	Anemia, decrease in blood platelets, increased risk of cancer	Discharge from factories, leaching from gas storage tanks and landfills
Bromobenzene	5.4**	NA	NA
Bromochloromethane (chlorobromomethane)	200**	NA	NA
Bromodichloromethane	980**	NA	NA
Bromoform (Tribromomethane)	15**	NA	NA
Bromomethane (methyl bromide)	120**	NA	NA
Carbon disulfide	34**	NA	NA
Carbon tetrachloride	2,400**	NA	NA
Chlorobenzene	5	Liver problems, increased risk of cancer	Discharge from chemical plants and other industrial activities
Chloroethane (ethyl chloride)	100	Liver or kidney problems	Discharge from chemical and agricultural chemical factories
Chloroform	9,800**	NA	NA
Chloromethane (methyl chloride)	240**	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
Cis-1, 2-dichloroethene	70**	NA	NA
Cis-1, 3-dichloropropene	70	NA	NA
Cis-1,4- dichloro-2- butene	2.0**	NA	NA
Cyclohexane	NE	NA	NA
Cyclohexanone	120,000**	NA	NA
Dibromochloromethane	120,000**	NA	NA
Dibromomethane	11**	NA	NA
Dichlorodifluoromethane	NE	NA	NA
Ethylbenzene	4,900**	NA	NA
Ethyl acetate	700**	Liver or kidney problems	Discharge from petroleum refineries
Ethyl ether	22,000**	NA	NA
Ethylene oxide	4900**	NA	NA
Ethyl methacrylate	0.89**	NA	NA
Hexane	2,200**	NA	NA
Hexachlorobutadiene	1,500**	NA	NA
Iodomethane	12**	NA	NA
Isobutyl alcohol	34**	NA	NA
Isooctane	7,300**	NA	NA
Isopropylbenzene (cumene)	NE	NA	NA
Methacrylonitrile	700 / 2,400**	NA	NA
Methyl ethyl ketone (2-butanone)	2.4**	NA	NA
Methyl methacrylate	15,000**	NA	NA
Methylene chloride (dichloromethane)	34,000**	NA	NA
Naphthalene	5**	NA	NA
n-Butylbenzene	490**	NA	NA
n-Heptane	1,200**	NA	NA
n-Propylbenzene	1,500**	NA	NA
Pentachloroethane	980**	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
Propionitrile	10**	NA	NA
sec-Butylbenzene	9.8**	NA	NA
Styrene	980**	NA	NA
tert-Butylbenzene	100	NA	NA
Tert-butyl methyl ether (mtbe)	980**	NA	NA
Tetrachloroethene	240**	NA	NA
Toluene	5	NA	NA
Trans-1, 2-dichloroethene	1,000	Nervous system, kidney, or liver problems	Discharge from petroleum factories
Trans-1, 3-dichloropropene	100	NA	NA
Trans-1,4- dicloro-2-butene	9.1**	NA	NA
Trichloroethene	NE	NA	NA
Trichlorofluoromethane	5	NA	NA
Vinyl Acetate	7,300**	NA	NA
Vinyl chloride (chloroethene)	24,000**	NA	NA
m-p-xylene	2	Increased risk of cancer	Leaching from PVC pipes, discharge from plastic factories
o-xylene	10,000**	NA	NA
Xylenes, Total	10,000**	NA	NA
	10,000**	Nervous system damage	Discharge from petroleum factories, discharge from chemical factories
Total coliforms (including E. Coli MPN)			
1694 Pharmaceuticals (LCMS/MS)	0	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present.	Coli forms are naturally present in the environment, as well as feces; fecal coli forms and E. coli only come from human and animal fecal waste.
1694 Pharmaceuticals (LCMS/MS)	NA	NA	NA
1694 Pharmaceuticals (LCMS/MS)	NA	NA	NA
1694 Pharmaceuticals (LCMS/MS)	NA	NA	NA

Parameter, Method, and Units	Maximum Contaminant Levels or Secondary Standards	Potential Health Effects from Ingestion of Water[^]	Sources of Contaminant in Drinking Water[^]
Turbidity	NA	NA	NA
	NA	Turbidity is a measure of the cloudiness of water. It is used to indicate water quality and filtration effectiveness (e.g., whether disease-causing organisms are present). Higher turbidity levels are often associated with higher levels of disease-causing microorganisms such as viruses, parasites, and some bacteria. These organisms can cause symptoms such as nausea, cramps, diarrhea, and associated headaches.	Soil runoff

Maximum contaminant level and secondary standards from 30 TAC 290 Subchapter F.

** Numerical value for risk reduction not an MCL, but provides a measure of desirable concentrations, from RG-346 (www.sos.state.tx.us).

[^]From EPA 816-F-02-013 July 2002.

APPENDIX F—Stormwater-Sampling Detail

Stormwater-Sampling Program for Comal and San Marcos Springs in Support of the Edwards Aquifer Habitat Conservation Plan

PURPOSE

The purpose of this technical procedure is to describe the methodology for collecting grab samples from stormwater runoff in surface waters at Comal and San Marcos springs. Sample frequency is twice annually, with samples collected across three points on the hydrograph. The EAA samples storm waters at Comal Springs at the following five locations (see Appendix A for map):

1. Upper Springs (near Blieders Creek),
2. New Channel—(below confluence with Dry Comal Creek),
3. Upper Old Channel—(at Elizabeth Street),
4. Lower Old Channel—(above Hinman Island), and
5. Comal River—(above confluence with Guadalupe River).

The EAA samples stormwaters at San Marcos Springs at the following seven locations (see Appendix A for map):

1. Sink Creek, upstream of Spring Lake,
2. Sessoms Creek,
3. Dog Beach Outflow,
4. Hopkins Street Outflow,
5. Purgatory Creek (above San Marcos River),
6. I-35 Reach, and
7. Willow Creek (above San Marcos River).

SCOPE

This procedure applies to all EAA personnel and subcontractors who sample storm water.

DEFINITIONS

1. Stormwater runoff as stated by the US EPA, “is generated when precipitation from rain and snowmelt events flows over land or impervious surfaces and does not percolate into the ground” (US EPA Stormwater Program, epa.gov).
2. Rivers are sources of water that flow on top of the ground in volume.
3. Sample intervals (for the EAHCP stormwater sampling program) are defined as:
 - a. Initial rise, or rising limb of the hydrograph;
 - b. Peak area of hydrograph; and
 - c. Recession limb of the hydrograph.

GENERAL

Weather permitting, EAA will sample two stormwater events per year to evaluate stormwater quality from urban landscapes that discharge to Comal and San Marcos springs.

STORM-EVENT SELECTION CRITERIA

According to the *Water Quality Monitoring Program Strategy for Comal Springs and San Marcos Springs in Support of the Edwards Aquifer Habitat Conservation Plan*, (EAHCP Workplan “a storm water sampling event will be triggered when a local rainfall event causes a significant increase in spring flow at the historic Comal Springs gauging station and the San Marcos Springs gauging station.” Furthermore, data collected from real-time instrumentation for surface water quality will be used to further refine the type of stormwater event(s) to be sampled. Real-time data are collected for the following parameters at 15-minute intervals from the stations shown on Comal and San Marcos springs EAHCP maps (Appendix A):

- Conductivity,
- DO,
- pH,
- Temperature, and
- Turbidity.

EAA field staff will monitor incoming storms by radar to determine whether the storm will produce one-half inch or more of localized precipitation and determine whether the storm is safe for stormwater sampling. Because of the nature of storms, stormwater sampling may be canceled as a result of false starts, safety issues, or if a new storm interrupts the stormwater sampling. Aquifer Science Management will make the final determination regarding go/no go for stormwater sampling.

Minimum Antecedent Dry Period Requirements

The following is a guideline to determine whether watersheds have returned to “normal” flow conditions. Each watershed will be evaluated separately because one watershed may return to “normal” flow conditions faster and technically be ready for another stormwater sampling event before another watershed, as noted below:

- One day wait if the previous rain event was limited to light rain/drizzle, producing only a surface wetting and no runoff
- Three days wait if the previous rain event did not produce enough rainfall to result in a measurable increase in discharge at the sample location(s)

- Minimum of five days wait if preceded by a rainfall of at least one-half inch at a sample location. The antecedent dry period may be longer if the sample location(s) are still being impacted by runoff from a previous rain event (SARA, 2013).

Canceling a Stormwater-Sampling Event

- A stormwater-sampling event may be canceled because of excessive lightning, hail, high winds, or flooding. If a storm does become severe during a stormwater-sampling event, the event will be postponed, cancelled, or suspended under some circumstances.
- A stormwater sampling event may be suspended because of a new rain event. For example, if samples are collected during the 10% of baseline flow conditions and another storm event interrupts this sampling event, then sampling will be suspended. The second storm will represent a new stormwater event.

RESPONSIBILITIES

CTO and Hydrogeologist Supervisor—Aquifer Science

The CTO and hydrogeologist supervisor—aquifer science will determine which parameters need to be sampled and will ensure that the samples obtained represent the environment being investigated. Sampling parameters are listed in the EAHCP workplan.

Hydrologic Data Coordinator

The hydrologic data coordinator will schedule sampling events and ensure that all field crews are provided with the information and equipment necessary to successfully complete scheduled sampling (i.e., location ID and selected analyses). Furthermore, the coordinator will organize and interface with local entities as needed to ensure that all notifications are in place for each river/spring complex as needed.

Environmental Science Technicians

Environmental science technicians will generally be responsible for collection of samples. Other individuals may also be asked to participate in sample-collection activities. However, each sample team of two people will have a lead sampler who reports back to the hydrogeologist supervisor—aquifer science. Reports will include

problems and issues in the field, inability to sample because of unforeseen or changing circumstances, and any deviations from the sample-collection plan and protocols.

PROCEDURE

Supplies and Equipment

Major Equipment Items

- Sample dipper
- Peristaltic pump with inert sample tubing
- 500- or 1,000-mL Teflon™ beakers affixed to telescoping rods
- Two gallon buckets for field-parameter readings

Equipment Support Items

- Trash bags
- Gloves (nitrile)
- Kim wipes/towels
- Rope
- Garden wagon

Sampling Supplies

- Sample bottles
- COC forms
- Sample labels
- Bailer (for filtration)
- 0.45-micron filter
- Ice chest
- Ice for sample preservation
- Ziplock bags
- Field sheet
- Pen and waterproof permanent marker

Monitoring Equipment

- pH and temperature meter
- Specific conductance meter
- Dissolved-oxygen meter
- Turbidity meter

Health and Safety Items

- First-aid kit and emergency eye-wash kit
- Fire extinguisher
- Mobile phone
- Helmet with head lamp
- Hand sanitizer
- Mud boots
- Raincoat
- Life vests with reflective markings
- Throw rope
- Computer access to real-time flow, water quality, and weather data

Field Equipment Decontamination

Proper decontamination between sites is essential to the avoidance of introducing contaminants from the sampling equipment. Before sampling, all hoses, buckets, water quality probes, and other sampling equipment should be decontaminated at EAA before fieldwork. Procedures specified in the EAA's *Field Sampling Plan* should be followed for decontamination of field equipment.

Instrument Usage and Measurement of Water Quality Parameters

Before going into the field, the environmental science technician should verify that all field instruments are operating properly. Calibration will be done on pH, specific conductivity, dissolved oxygen, and turbidity meters, and calibration information should be recorded in the calibration log book.

Purging

No purging is required for stormwater runoff to be sampled in the Comal and San Marcos rivers.

Sample Collection

According to the EAHCP work plan, “three water quality samples will be collected from each surface water sampling location during the sampling event. Sample times will be spaced to reflect changes in the stream hydrograph.” The first sample will be during the initial rise in the hydrograph. The second sample will be collected near the peak of flow. The final sample will be collected along the recession limb of the storm hydrograph. In some circumstances, additional samples may be collected during the storm event such

that sample groups may be subsequently compared to hydrograph data and the most representative samples groups sent for analyses. Following is the sampling procedure:

At EAA Offices

- EAA field staff will monitor local weather forecasts and Doppler radars to determine whether an incoming storm meets the criteria for a stormwater sampling event.
- If the incoming storm DOES NOT meet the criteria, no action will be taken.
- If the incoming storm DOES meet the criteria, EAA field staff will monitor weather conditions, estimate a time of arrival of the incoming storm, and determine whether weather conditions are safe for stormwater sampling (CTO or hydrogeologist supervisor will make the final go/no go decision).
- EAA field staff will notify the contracted laboratories for the possibility of samples.
- Labels for the sample bottles will be filled out.
- Aquifer Science CTO or Hydrogeologist supervisor will make the final determination regarding go/no-go with regard to the storm event.

In the Field

- Field personnel must wear clean (disposable) nitrile gloves during the sample-collection process.
- Sample water will be collected in a two-gallon bucket for parameter readings, and sample water will be collected in a 500- or 1000-mL Teflon™ beaker attached to telescoping rods, or, if needed, a peristaltic pump with inert tubing will be used.
- Meter(s) will be inserted into a two-gallon bucket and measurements recorded on a field sheet, or, if a peristaltic pump is being used, a flow chamber will be used.
- Samples will be collected using beakers or a peristaltic pump.
 - Herbicides and pesticides
 - General water quality parameters
 - Selected metals
 - Turbidity
 - Bacteria (E-coli most probable number)
 - Total phosphorous
 - Total organic carbon
 - Dissolved organic carbon
 - Total kjeldahl nitrogen
 - All containers will be filled almost full, except for alkalinity and VOCs
 - Alkalinity

- A bailer attached with a filter will be used or a filter will be attached onto tubing from the peristaltic pump
 - Alkalinity must have no head space.
- Selected metals
 - A bailer attached with a filter will be used or a filter will be attached onto tubing from the peristaltic pump
- VOC
 - The VOC sample vial will be completely filled so that the water forms a convex meniscus at the top and then capped so that no air space exists in the vial. The vial must be turned over and tapped to check for bubbles in the vial, which indicate trapped air. If bubbles are observed, the vial should be discarded and another sample collected.
- Any required information will be recorded on the field sheet before, during, and after sampling. Parameter readings will be measured in a two-gallon bucket and recorded on field sheets.
- Preservatives (if any) will be placed in the bottles by EAA-contracted laboratories.
- After the samples have been collected, they will be immediately placed in an ice-filled cooler.
- Prior to departure from the field, field documentation, including the COC form, will be completed, and all EAA field employees will clean their hands with hand sanitizer.
- Field notebooks will be used to record basic information for each event, such as magnitude of storm, issues related to sample collection, weather conditions, time of day samples were collected, and other information deemed pertinent by the lead sampler and/or coordinator.

The second sample will be collected near the peak of flow and will follow the same procedure as that of the initial rise on the hydrograph sample. The third sample will be collected along the recession limb of the hydrograph and will follow the same procedure as that of the other two sampling events. Again, the possibility exists that additional sample may be collected during the event with the most representative three sample groups being submitted for analyses (based on comparison with the appropriate stream hydrograph).

Contracted Laboratories

EAA field staff will drop off samples at EAA-contracted laboratories or have samples picked up at the EAA offices. Samples will be analyzed within proper holding times.

Equipment Blanks

Equipment blanks consist of ASTM II, reagent-grade water poured over/through any sampling equipment used for collection of definitive samples. Most sample-collection equipment is disposable; however, in some cases, an equipment blank may be required. Equipment blanks are used to assess the effectiveness of decontamination procedures (for new materials provided to the EAA or from EAA's decontamination processes) and are designated as *EB* on the COC. The frequency of collection of equipment blanks will depend on the sampling routine and sampling equipment in use. Collection of equipment blanks will be designated prior to sample-collection events.

Trip Blanks

Trip blanks are used to assess potential volatile organic contamination during sample custody in the field and shipment to the receiving laboratory. Trip blanks are submitted with characteristic samples to the laboratory to verify that volatile organic contamination has not occurred from outside influences during sample handling to transport (such as absorption through the septa.)

Trip blanks consist of two 40-mL vials filled with ASTM Type II reagent-grade water prepared by the contracted laboratory. Trip blanks will remain unopened until they are received at the contracted laboratory.

Sample Identification, Handling, and Documentation

Samples will be identified, handled, and recorded as described in the preceding sections of this document.

Records

Field sheets and COCs will be kept in a bound field log book. The following will be recorded using waterproof ink on these sheets and in the field notebook:

- Names of sampling personnel
- Weather conditions
- Project name
- Date and time of sampling
- Analyses to be performed by EAA-contracted laboratory
- Equipment-calibration information
- Field-parameter measurements
- Irregularities, problems, or delays

APPENDIX G—Equipment-Decontamination Procedures

Decontamination

Proper decontamination of all equipment used in the sample-collection process is essential to obtaining quality, representative samples. Improperly decontaminated equipment is capable of causing cross-contamination between sample sites, resulting in samples that are not representative of in situ site conditions. The objective of this appendix is to provide a set of decontamination procedures applicable to various EAA equipment and sampling programs.

Whereas many different protocols exist for decontamination, ASTM Standard D 5088 is perhaps the most commonly referenced protocol. The methods outlined here are tailored to EAA sampling environments and programs.

Basic Decontamination Procedure—Groundwater, Surface Water, and Spring Sampling Equipment

When possible, equipment that comes into contact with sample media will be single-use (disposable) equipment or dedicated equipment. Having such equipment helps reduce the possibility of cross-contamination of samples. However, for many sample types, such dedicated equipment may not be possible. As such, a listing of equipment that may be used to collect a water sample (groundwater, surface water, or spring) would include

- Grundfos submersible pump and associated pump tubing
- Peristaltic pump tubing
- Sample dippers
- Surface water churn

Other equipment that *may* come into direct contact with sample media of concern includes

- Water level measurement devices (steel tape and e-lines)
- Field-parameter probes
- Downhole geophysical equipment

Equipment that will have direct contact with any sample media will be decontaminated prior to use for sample collection or prior to introduction into the well, surface water site, or spring vent, as applicable.

Grundfos Submersible Pumps

Decontamination will be accomplished as follows for submersible well pumps. Sampler will wear new, disposable, nitrile (or equivalent) gloves to perform the decontamination.

Materials needed:

- Submersible pump, pump controller, and pump tubing
- 33-gallon trashcan (dedicated for decon use only)
- Alconox® or laboratory-grade soap
- DI water
- Large plastic bags or foil
- Plastic sheeting
- Clean scrub brush(es)

The designated trashcan will be rinsed with fresh, potable water and subsequently filled with potable water and laboratory-grade soap (per soap label directions).

When the container is approximately 80% full, the pump will be lowered, with heat shield attached, into the trashcan. The pump should be suspended at least six inches off the bottom of the trashcan. The pump will then be activated and allowed to discharge outside of the trashcan for at least 30 seconds. After the initial discharge, pump tubing will be directed into the trashcan such that the decontamination mixture is recirculated through the pump and tubing. The pump should run/recirculate a minimum of ten pump-tubing volumes (about 40 gallons) through the system. This process should take about 15 to 20 minutes.

Note: in the event that the pump or tubing has sediment or other foreign matter on it, a step will be added. A clean scrub brush will be used to remove any sediment or other foreign matter from the equipment manually prior to the circulation process.

Next, the decontamination mixture will be allowed to pump out of the trashcan into the sink (the pump should not be allowed to run dry or cavitate). The pump and tubing will be placed on a clean surface (plastic sheet) and the trashcan rinsed in clean water. The pump will be rinsed and placed back into the trashcan. The pump is to be allowed to discharge outside of the trashcan until the soapy water is evacuated from the tubing. The discharge tubing will then be placed back into the trashcan and more clean water added if needed. The freshwater will be recirculated through the pump and into the trashcan for a minimum of ten volumes (about 40 gallons). Once circulation is complete, the pump will be allowed to discharge outside the trashcan until nearly empty (again, the pump should not be allowed to run dry or cavitate). Next, a final rinse of DI water will be provided on the pump and tubing, an adequate volume being used to ensure that the pump and tubing are well rinsed.

Upon completion of the decontamination procedure, the pump will be sealed in a clean plastic bag, and the end of the pump tubing will be sealed in its own clean plastic bag. A

rubber band can be used to affix the bags around the apparatus. Pump and hose assembly are to be stored indoors when not in use, away from any sources of cross-contamination.

Tubing Decontamination for Peristaltic Pumps:

Decontamination should be accomplished as follows for peristaltic pump tubing. Sampler will wear new, disposable, nitrile (or equivalent) gloves to perform the decontamination.

Materials needed:

- Four five- or seven-gallon plastic buckets (for decon use only)
- Alconox® or laboratory-grade soap
- DI water
- Large plastic bags that can be sealed (large zip-top bags)
- Plastic sheeting
- Clean scrub brush(s)

The designated buckets will be rinsed in fresh, potable water. The first bucket will be subsequently filled with potable water and laboratory-grade soap (per soap label directions). The next two buckets will be filled with clean tap water. All three decontamination buckets are to be placed on top of a clean sheet of plastic sufficiently long to provide a clean surface on which all decontamination can take place. Decon buckets are to be placed in order on the sheet, with the soap bucket first, followed by the two rinse buckets. Decontamination should proceed such that each step is always followed in order from most contaminated to least contaminated (i.e., from prewash if needed, to soap–water mixture, to first rinse bucket, to second rinse bucket, to final DI water rinse).

Any excess foreign material will be removed from the tubing, first by wiping or scrubbing with soap and water mixture (if needed). The suction side of the tubing will be lowered into the soap–water bucket. The pump will be activated and allowed to discharge outside of the bucket until the soap–water mixture has initially purged the tubing. After the initial discharge, the pump tubing will be directed into the bucket such that the decontamination mixture is recirculated through the tubing. The pump will be allowed to run a minimum of ten pump-tubing volumes through the system (or about eight to ten gallons).

Next, the suction end of the tubing will be placed into the first rinse bucket and the pump allowed to discharge into the soap bucket until the soapy water is evacuated from the tubing. The discharge side of the tubing will then be placed back into the first rinse bucket. The freshwater will be allowed to recirculate through the pump and into the first rinse bucket for a minimum of ten volumes (or about eight to ten gallons). Once circulation is complete, the process will be repeated using the second rinse bucket. Final rinse is to be accomplished by pumping/recirculating DI water through the tubing for a minimum of ten volumes, using the third rinse bucket filled with DI water. Next, a final

rinse of DI water will be provided on the outside of the tubing using an adequate volume to ensure that the tubing is well rinsed. This final rinse will complete the decontamination process.

Upon completion of the decontamination procedure, the tubing will be allowed to dry and the tubing seal placed in a plastic bag to prevent exposure to cross-contamination. Bagged tubing is to be stored indoors when not in use away from any sources of cross-contamination.

Note: peristaltic tubing for EAHCP samples is dedicated tubing and is to be stored in *labeled* bags. The bag label will have the name of the sample point written on the outside of it. EAHCP-related tubing is not to be used for any other applications.

Decontamination of Other Equipment Used in Collection of Water or Soil Samples

Decontamination will be accomplished as follows for other equipment that will come into direct contact with sample media (dippers, churns, sample probes—if placed into sample media, water level measurement devices, soil sampling devices, or trowels). Sampler will wear new, disposable, nitrile (or equivalent) gloves to perform the decontamination.

Materials needed:

- Sample-collection device (dipper, churn, etc.) or field meter (applies only to that part of the probe exposed to sample media) or water level measurement device
- Three five- or seven-gallon plastic buckets (for decon use only)
- Alconox® or laboratory-grade soap
- DI water
- Large plastic bags or foil
- Plastic sheeting
- Clean scrub brush

Designated buckets will be rinsed in fresh, potable water. The first bucket will be subsequently filled with potable water and laboratory-grade soap (per soap label directions). The remaining two buckets will be filled with clean tap water. All three decontamination buckets are to be placed on top of a clean sheet of plastic sufficiently long to provide a clean surface on which all decontamination will take place. Decon buckets are to be placed in order on the sheet, with the soap bucket first, followed by the two rinse buckets. Decontamination will proceed such that each step is always followed in order from most contaminated to least contaminated (i.e., from prewash if needed, to soap–water mixture, to first rinse bucket, to second rinse bucket, to final DI water rinse).

Any excess sediment or foreign matter will be removed from the device by gentle scrubbing and rinsing with water prior to placement into the soap–water mixture. The

sampling device will be placed into the soap–water mixture and gently scrubbed (all surfaces that will come into contact with sample media must be cleaned).

Note: the surface water churn may not fit in the bucket(s), as such the churn may be cleaned in the 33-gallon trashcan, or it may be cleaned by some of the soap–water mixture being poured into the churn. The churn will be cleaned with the soap–water mixture; double rinsed in clean, potable water; and provided a final rinse in DI water.

Upon completion of the soap–water wash, each device being decontaminated must be double rinsed (i.e., buckets two and three) in clean, potable water, followed by a final rinse in DI water. Upon completion of decontamination, equipment will be allowed to dry and stored such that it is not exposed to potential contaminants. Equipment should be stored in plastic bags or wrapped in foil to further insulate it from potential contamination.

Note: decontamination buckets are to be monitored when used for multiple items to ensure that the soap–water mixture does not become spent or ineffective. They are to be replaced as needed. Also, rinse water should be replaced regularly when it appears to have a significant accumulation of soap.

Special Decontamination Procedures

Downhole or soil-sampling equipment may be decontaminated generally by one of the applicable processes outlined above. However, in rare cases, a tool or device that is not disposable may be exposed to hydrocarbon residue or, in rarer cases, high concentrations of heavy metals may occur. In such a scenario, the tool may (at the discretion of management) require a more elaborate decontamination procedure.

Exposure to Hydrocarbons

In the event that a tool is exposed to free-product hydrocarbons, an additional step in the decontamination process may be required that will involve spraying the tool with pesticide-grade methanol or hexane prior to the final DI water rinse. Use of solvents in this case serves to remove any hydrocarbon residual from the tool.

Exposure to Heavy Metals

In the event that a tool or device is exposed to heavy metals, and the sample media are being analyzed for these same metals, another step in the decontamination process may be required. In this case, the tool may require a spray rinse with dilute (10%) hydrochloric or nitric acid prior to DI water rinse. Use of acid in this situation will act to remove residual metals from the tool.

Note: use of solvents or acids is only to be pursued if directed by management. Use of these products can be hazardous and can also present issues regarding disposal of the waste products themselves. Use of the products may also damage sampling equipment in

some cases. In the vast majority of cases, the standard washing and rinsing procedures described herein are adequate for proper decontamination of sampling equipment. Analysis of equipment blanks will be pursued when needed so that the decontamination process might be assessed. It is the responsibility of the sampler to notify management if a tool is suspected of any unusual exposure

APPENDIX E

PHOTOGRAPHIC LOG

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 1.

Reconnaissance site visit with SWCA Environmental Consultants (SWCA) and Edwards Aquifer Authority (EAA) staff, January 22, 2014; sample location HSM110.



PHOTOGRAPH 2.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HSM120.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 3.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HSM130.



PHOTOGRAPH 4.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HSM231.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 5.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HSM150.



PHOTOGRAPH 6.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HSM160.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 7.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HSM170.



PHOTOGRAPH 8.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HCS110.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 9.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HCS140.



PHOTOGRAPH 10.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HCS130.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 11.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HCS250.



PHOTOGRAPH 12.

Reconnaissance site visit with SWCA and EAA staff, January 22, 2014; sample location HCS160.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 13.
Reconnaissance site visit with SWCA and EAA staff, January 22,
2014; sample location HCS270.



PHOTOGRAPH 14.
Construction of PDS deployment devices.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 15.
Construction of PDS deployment devices.



PHOTOGRAPH 16.
Construction of PDS deployment devices.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 17.
PDS prior to deployment.



PHOTOGRAPH 18.
PDS after deployment on June 23, 2014; sample location.

PHOTOGRAPHIC LOG

Comal and San Marcos springs, Texas



PHOTOGRAPH 19.

Discovery of PDS deployment device that had been opened by a vandal. The PDS was still present. The device was secured with an additional cable-tie and left in-place; sample location HSM470.



PHOTOGRAPH 20.

Storage of storm water sample kits and supplies within SWCA San Antonio office.

APPENDIX F

RECORD OF STORMWATER SAMPLING

COMAL SPRINGS COMPLEX

January through March 2014 - Necessary supplies and equipment were acquired and assembled. Site visits were made and plans were developed.

March 2014 (and prior to each subsequent event) - Sample kits, labels and Chain-of-Custody (COC) forms were received from the contract laboratory and sampling containers, and coolers were labeled by SWCA staff. Staff went on standby for sampling events.

June 9, 2014 - Staff mobilized to the New Braunfels area in response to forecasts and significant rainfall indicated by weather radar. The precipitation changed course, and New Braunfels did not receive sufficient rainfall for sampling.

June 25, 2014 - An SWCA sediment sampling team had planned to operate in the Comal Springs system but rain was indicated in the forecast that morning. The sediment team mobilized with stormwater kits, and additional staff were put on call. The rainfall did not occur. Stormwater sampling was cancelled, and sediment sampling was carried out.

August 8, 2014 - Replacement sample kits, labels and COC forms were received from the contract laboratory, and sampling containers and coolers were labeled by SWCA staff.

September 12, 2014 - Staff mobilized to New Braunfels in anticipation of a stormwater event. Staff monitored the EnviroNet water quality parameters but the amount of precipitation was not enough to trigger an event.

September 17, 2014 - Weather reports indicated a significant chance of rain in New Braunfels. Staff mobilized but upon arrival, radar was clear, and the forecast showed diminished chances. The sampling effort was called off.

September 25, 2014 - Weather forecasts predicted a slight chance of rain overnight with increased chances the following evening. While collecting surface water samples in Comal Springs, SWCA staff noticed the chances of precipitation increasing, and the predictive radar showing high probability of rain. After completing surface water collection efforts for the day, two staff members mobilized to New Braunfels for the night to monitor conditions. Weather dissipated, and surface water collection continued on Friday, September 26, 2014.

September 26, 2014 - After completing surface water sample collections in both Comal and San Marcos springs, SWCA staff mobilized to New Braunfels in response to promising forecasts and radar. The storm event began at approximately 19:00, and trail samples were collected at approximately 07:00 Saturday, September 27, 2014. The storm produced approximately 0.75 to 1.0 inches of rain (NOAA, 2014) and caused an increase in streamflow from approximately 84 cfs to 101 cfs at USGS Gauge 08169000 (USGS, 2014). Streamflow and water quality parameter data from RTIs used to determine timing of stormwater sample collection can be found in Appendix A. Heidelberg Lodges, adjacent to sampling site

HCS210, was used as a home base for staging, sample filtration, alkalinity and packaging for shipment. As the storm occurred on a weekend, all samples were taken to the SWCA San Antonio office and housed on ice until they could be shipped to the laboratory on Monday morning. E. coli samples were submitted Saturday at approximately noon at the San Antonio River Authority (SARA).

October 2, 2014 - Forecasted precipitation chances reached 100% for the overnight hours Thursday evening. Staff mobilized to New Braunfels at approximately 19:00. Precipitation chances began to diminish at approximately 22:00. The storm cell anticipated to develop over New Braunfels developed just south of the springs complex. An insignificant amount of rain fell for a short time but it was insufficient for sampling. At approximately midnight all but two sampling team members returned home, and the remaining team continued monitoring the radar in case another cell developed overnight. No additional rain fell, and the sampling effort was officially called off the morning of October 3, 2014.

October 10-11, 2014 - High chances of precipitation were forecasted overnight Friday night. Stormwater crews monitored the radar and forecast from home overnight and mobilized to New Braunfels at approximately 06:00 when precipitation chances peaked. Light rain fell from approximately 08:00 to 11:00 but only caused a 5% change in water quality parameters. The sampling event was called off at noon when no further rain was on the radar or forecast.

November 4-5, 2014 – SWCA staff went on call when a large storm was forecast for the area. The stormwater team mobilized to New Braunfels at approximately 5pm. Precipitation began to fall at approximately 8pm. The lead sample collection was initiated at approximately 8:30pm. Rain fell consistently throughout the night. Water quality parameters peaked and began to rise at approximately 12:45 am on November 5, 2014. Peak sample collection was initiated at this time. Rain continued to fall into the early morning but water quality parameters continued to recover to baseline levels. Trail sample collection was initiated at approximately 7:00 am. The storm produced approximately 2 to 3 inches of rain (NOAA, 2014) and caused an increase in streamflow from approximately 91 cfs to 151 cfs at USGS Gauge 08169000 (USGS, 2014). Streamflow and water quality parameter data from RTIs used to determine timing of stormwater sample collection can be found in Appendix A. Alkalinity analysis occurred at the Heidelberg Lodge used as a home base by SWCA staff during the event. E. coli samples were delivered to the San Antonio River Authority lab upon its opening on the morning of November 5, 2014. The remaining samples were packaged and shipped to the CalScience lab also on the morning of November 5, 2014.

SAN MARCOS SPRINGS COMPLEX

May 8, 2014 - Local weather forecasts indicated a high chance of rain in the San Marcos area. SWCA staff mobilized to the San Marcos Nature Center at 04:00 to attempt to sample the San Marcos Springs Complex. At approximately 17:00, the effort was cancelled due to insufficient rainfall.

May 9, 2014 - Staff mobilized to the San Marcos Nature Center to sample in San Marcos Springs. The effort was again called off when the storm dissipated without sufficient rainfall to sample.

May 12, 2014 - Two sampling teams mobilized to the San Marcos Nature Center in advance of substantial predicted rainfall. The sampling event began at approximately 22:45 and continued until approximately 11:00 on May 13, 2014. The storm produced approximately 3 to 4 inches of rain (NOAA, 2014) and caused an increase in streamflow from approximately 107 cfs to 286 cfs at USGS Gauge 08170500 (USGS, 2014). Streamflow and water quality parameter data from RTIs used to determine timing of stormwater sample collection can be found in Appendix A. The staff utilized the San Marcos Nature Center as a home base staging area and a location to conduct sample processing which included filtering and alkalinity titrations.

July 15, 2014 - Two sampling teams mobilized to San Marcos in response to high chances of precipitation. A sampling event began at approximately 21:15. Additional staff members arrived at approximately 22:30 to assist with sample collection and processing. The staff again utilized the San Marcos Nature Center for staging and sample processing. The last sample was collected at approximately 05:00 on July 16, 2014. The storm produced approximately 0.5 to 1.0 inches of rain (NOAA, 2014) and caused an increase in streamflow from approximately 138 cfs to 361 cfs at USGS Gauge 08170500 (USGS, 2014). Streamflow and water quality parameter data from RTIs used to determine timing of stormwater sample collection can be found in Appendix A. Following the final sample collection, SWCA staff took the remaining samples for processing back to the SWCA San Antonio office as the San Marcos Nature Center had programs beginning early that morning. All samples remained on ice and in secure custody during this transition.

APPENDIX G

ANALYTICAL RESULTS

Laboratory reports have been provided to the
Edwards Aquifer Authority in a digital format.

APPENDIX H

ANALYTICAL DATA VALIDATION DISCUSSION

Introduction

This appendix provides an overview of the SWCA's post analyses review of the eurofins/Calscience (Calscience), San Antonio River Authority (SARA), Aqua-Tech Laboratories, Inc. (ATI), and Amplified Geochemical Imaging, LLC (AGI) analytical data set. In general, the data are considered valid for the intended purpose of assessing the baseline of sediment quality, stormwater runoff quality, surface water (under base flow conditions) and passive diffusion samplers (PDS) at a screening level for Comal and San Marcos Springs. Analyses with any associated laboratory issues are listed herein.

Worth note in this assessment are the detection of plasticizer compounds such as bis(2-ethylhexyl) phthalate (DEHP) and other phthalate compounds. While it is possible these compounds were introduced post-sample collection from either sampling equipment, or laboratory equipment, they should not be completely dismissed. The 2013 Edwards Aquifer Habitat Conservation Plan Expanded Water Quality Report concluded further assessment of the presence or absence of these compounds may be warranted in the future. Multiple phthalate compounds were detected in the all five Comal Springs sediment samples and the field duplicate. Six of seven field sediment samples from San Marcos Springs in 2013 detected phthalate compounds including DEHP.

Based on analysis of 2013 laboratory data, the EAA concluded that three compounds detected in sediment samples may have been laboratory artifacts. The compounds were DEHP, di-n-octyl phthalate, and di-n-butyl phthalate. The EAA noted in the 2013 Edwards Aquifer Habitat Conservation Plan Expanded Water Quality Report that as the data set grows, additional conclusions could be drawn. The 2014 laboratory analyses of sediment samples did not detect di-n-octyl phthalate or di-n-butyl phthalate. However, DEHP was detected in three of the sediment samples (HSM320, HSM330, and HSM350).

DEHP was not detected in the laboratory method blank or trip blank, and a different laboratory and sampling equipment was used by SWCA in 2014. Therefore, it appears DEHP may be present within sediment samples. Future analyses may help better understand the possible presence of DEHP within sediments in both Comal and San Marcos Spring complexes. The concentrations of DEHP ranged from 2.1 mg/kg to 9.2 mg/kg.

Analytical results are discussed by analytical laboratory sample data group number, and by sample event type and date. Each event (surface water/base flow, stormwater, PDS, or sediment) is discussed by sample data group with sample names and date outlined for each event in the beginning of the discussion.

A key to sample names is provided below:

Key to Sample Names

H CS 1 10

H=HCP

CS=Comal Springs (**SM**=San Marcos Springs)

1=Sample Type (1=Surface Water, 2=Storm, 3=Sediment, 4=PDS)

10=Sample Location

Field Duplicates are identified with the prefix FD followed by the sample identification described above. Trip Blank samples are denoted with the prefix “TB” followed by a sequential number.

Corrective Action Comments

TPH was consistently detected in PDS Trip Blanks from AGI. AGI had provided an annual supply of PDS. SWCA will return unused PDS and request a new batch of PDS for the December 2014 and all 2015 sampling events. SWCA will request PDS for each sample event be sent separately.

Calscience packaged three VOA vials within a tight zip-lock bag within a bubble wrap pouch. Frequently, some of the VOA vials broke during return shipping. During the last two sampling events, SWCA individually wrapped the VOA vials as opposed to having the three vials packaged together.

Field duplicates were not collected, trip blanks were not shipped, and decontamination procedures were not properly followed for two sample locations during the first stormwater sampling event in May 2014 at San Marcos Springs. These actions were corrected in subsequent stormwater sampling events.

Analytical Data Review Summary for HCP samples collected in 2014.

Data Group Numbers (HCP surface water/base flow samples collected March 25, 2014, and April 29, 2014, Comal and San Marcos springs):

<i>114-03-2143-1</i> (HCS 110)	<i>14-03-2143-8</i> (HSM 110)
<i>14-03-2143-2</i> (HCS 120)	<i>14-03-2143-9</i> (HSM 120)
<i>14-03-2143-4</i> (HCS 130)	<i>14-03-2143-10</i> (HSM 130)
<i>14-03-2143-3</i> (HCS 140)	<i>14-03-2143-11</i> (HSM 140)
<i>14-03-2143-7</i> (HCS 160)	<i>14-03-2143-12</i> (HSM 150)
<i>14-03-2143-5</i> (Trip Blank)	<i>14-03-2143-13</i> (HSM 160)
<i>14-03-2143-6</i> (HCS 130 FD)	<i>14-03-2143-13</i> (HSM 170)

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. pH values are collected in the field at the time of sample collection and are listed in the field parameters for each sample event. As such, the laboratory pH values which are flagged for hold time exceedances are not used for sample assessment purposes.

Trip Blank (Comal – March 25, 2014)

There were no detections in the trip blank associated with this sample set.

QA/QC Discussion – Comal and San Marcos Springs Surface/Base Flow Samples (Sampled March 25, 2014)

Issues associated with all surface samples

Beta-BHC was detected at a concentration of 0.048 ug/L within the Method Blank, but was not detected in any of the subject samples.

Samples collected on March 25, 2014, were placed on ice prior to overnight delivery; however, at the time the samples were checked into the laboratory the temperatures measured of blank samples exceeded criteria.

Nitrate sample hold times were exceeded for the samples collected on March 25, 2014; however, resampling occurred for nitrates on April 29, 2014. Therefore the March 25, 2014, results were not used.

Metals samples were preserved with nitric acid, but had not been filtered. Therefore, resampling for metals occurred on April 29, 2014, and the March 25, 2014, results were not used.

Method SW8260B - The Matrix Spike (MS) or Matrix Spike Duplicate (MSD) for batch 140401S007 was below control limits for chlorobenzene. Recovery of the MS or MSD

compound was out of control due to suspected matrix interference. This analyte was not detected in the associated samples. The associated Laboratory Control Sample (LCS) recovery was in control; therefore, the results are accepted.

Method 8270C SVOCs – The LCS Recovery Percentage is within Marginal Exceedance (ME) Control Limit range (+/- 4 SD from the mean) for 4-nitrophenol. The results are accepted.

Issues specific to individual samples

HCS 110 – For analytes calcium, magnesium and silicon, spike recovery and Relative Percent Difference (RPD) control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

The *E. coli* analysis was conducted out of Hold Time by less than one hour.

Data Group Numbers (HCP surface water/base flow samples collected September 25-26, 2014, Comal and San Marcos springs):

<i>14-09-2120-1</i> (HCS 110)	<i>14-09-2402-4</i> (HSM 130)
<i>14-09-2120-2</i> (HCS 120)	<i>14-09-2402-5</i> (HSM 140)
<i>14-09-2120-3</i> (HCS 140)	<i>14-09-2402-6</i> (HSM 150)
<i>14-09-2120-4</i> (FDHCS 140)	<i>14-03-2402-7</i> (HSM 160)
<i>14-09-2402-1</i> (HCS 130)	<i>14-03-2402-8</i> (HSM 170)
<i>14-09-2402-2</i> (HSM 110)	<i>14-09-2402-9</i> (HCS 160)
<i>14-09-2402-3</i> (HSM 120)	<i>14-09-2402-10</i> (FDHSM 160)
	<i>14-09-2402-11</i> (Trip Blank 6)

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. pH values are collected in the field at the time of sample collection and are listed in the field parameters for each sample event. As such, the laboratory pH values which are flagged for hold time exceedances are not used for sample assessment purposes.

Trip Blank (Comal and San Marcos)

Trip Blank (TB-6) associated with this sample set had a detection of 0.65 ug/L for 1,2-dichloroethane and 1.6 ug/L for toluene. Neither of these constituents was detected in the subject samples.

**QA/QC Discussion – Comal and San Marcos Springs Surface/Base Flow Samples
(Sampled September 25-26, 2014)**

Issues associated with all surface samples

Magnesium was detected at a concentration of 0.00809 mg/L in batch 141001L5FF within the Method Blank, which is below the Reporting Limit, but above the Method Detection Limit. It was therefore “J” flagged. Due to the low concentration and lack of issues with magnesium concentrations in the subject samples, the results are accepted.

The laboratory hold time was exceeded for some of the samples for nitrate because samples were collected on Friday afternoon, September 26, 2014, at the same time a storm was approaching. SWCA staff mobilized to collect stormwater samples and were unable to package the surface water grab samples for overnight delivery until the following Monday morning, September 29, 2014, when the courier service was able to deliver samples overnight.

Method EPA 365.1 - The MS and/or the MSD for batches 140929S01A were above control limits for phosphorous, total. Recovery of the MS or MSD compound was out of control due to suspected matrix interference. The results were biased high and the associated LCS recovery was in control; therefore, the results are accepted.

Method SM 5310 B - The MSD for batch E0926DOCS1 was below control limits for Carbon, Dissolved Organic. Recovery of the MSD was out of control due to suspected matrix interference. The associated LCS recovery was in control; therefore, the results are accepted.

For analytes calcium, magnesium, sodium, strontium, and silicon, spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

Method EPA 6020 - Recovery of the MSD compound was out of control due to suspected matrix interference. The associated LCS recovery was in control. The MS/MSD RPD was out of control due to suspected matrix interference. The result was biased high and the results are accepted.

Method EPA7470A - The MS/MSD RPD was out of control due to suspected matrix interference.

Issues specific to individual samples

HCS 120 – For analytes calcium, magnesium, and silicon spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

Recovery of the MS and MSD compound was out of control for potassium, sodium, and aluminum due to suspected matrix interference. The associated LCS recovery was in control. Results are accepted.

The MS/MSD RPD was out of control for cadmium and aluminum due to suspected matrix interference.

LCS Recovery Percentage is within Marginal Exceedance (ME) Control Limit range (+/- 4 SD from the mean) for selenium.

FDHSM160 - Recovery of the MS compound was out of control for phosphorous, total due to suspected matrix interference. The associated LCS recovery was in control and results were biased high. Results are accepted.

Data Group Numbers (HCP stormwater samples collected May 23-13, 2014, at San Marcos springs):

Test Blank-Beta *14-05-1026-1*
Test Blank-Pole *14-05-1026-2*
HSM 210-lead *14-05-1026-3*
HSM 210-trail *14-05-1026-4*
HSM 210-peak *14-05-1026-5*
HSM 230-lead *14-05-1026-6*
HSM 230-trail *14-05-1026-7*
HSM 230-peak *14-05-1026-8*
HSM 231-lead *14-05-1026-9*
HSM 231-trail *14-05-1026-10*
HSM 231-peak *14-05-1026-11*
HSM 240-lead *14-05-1026-12*
HSM 240-trail *14-05-1026-13*
HSM 240-peak *14-05-1026-14*
HSM 250-lead *14-05-1026-15*
HSM 250-trail *14-05-1026-16*
HSM 250-peak *14-05-1026-17*
HSM 260-lead *14-05-1026-18*
HSM 260-trail *14-05-1026-19*
HSM 260-peak *14-05-1026-20*
HSM 270-lead *14-05-1026-21*
HSM 270-trail *14-05-1026-22*
HSM 270-peak *14-05-1026-23*

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. pH values are collected in the field at the time of sample collection and are listed in the field parameters for each sample event. As such, the laboratory pH values which are flagged for hold time exceedances are not used for sample assessment purposes.

Trip Blank

No Trip Blank sample was analyzed, but was corrected in following sampling events.

Equipment Blanks

Equipment Blanks were collected after triple rinsing the Beta Sampler and Sampling Pole with store-bought distilled water. The water used for the equipment blanks was also store-bought distilled water as opposed to ASTM Type II Reagent Grade water. A sample of the distilled water was analyzed separately for comparison. Standard minerals were detected in both the Equipment Blanks and the distilled water in similar concentrations. The Beta Sampler and Sampling Pole were only used at two sample locations for a collection of four total samples out of the 21 samples collected. Therefore, the validity of the sample set is not considered to be compromised.

QA/QC Discussion – San Marcos Springs Stormwater Samples (Sampled May 12-13, 2014)

Issues associated with all stormwater samples

Magnesium was detected at a concentration of 0.00809 mg/L in batch 141001L5FF within the Method Blank, which is below the Reporting Limit, but above the Method Detection Limit. It was therefore “J” flagged. Due to the low concentration and lack of issues with magnesium concentrations in the subject samples, the results are accepted.

Method EPA6010B - Recovery of the MS or MSD compound was out of control due to suspected matrix interference for sodium. The results were biased high and associated LCS recovery was in control. The MS/MSD RPD was out of control due to suspected matrix interference. Results are accepted.

Method EPA 6010B - For analytes calcium, magnesium, potassium, sodium, strontium, and silicon, spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

Method EPA 6020 – For selenium, the Pulse Digestion Spike/Pulse Digestion Spike Duplicate associated with this batch of samples was out of control due to suspected matrix interference. For zinc, spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

Method 8270C – For 2,4-dinitrotoluene, LCS Recovery Percentage is within Marginal Exceedance (ME) Control Limit range (+/- 4 SD from the mean) in batches 140516L06 and 140516L07. Results are accepted.

Issues specific to individual samples

HSM 260-trail – For caffeine, sample was extracted past end of recommended maximum holding time. Caffeine concentrations are within the expected range, and the results appear acceptable even with the hold time violation.

Data Group Numbers (HCP stormwater samples collected July 15-16, 2014, at San Marcos springs):

HSM 210 lead *14-07-1141-1*
HSM 210 peak *14-07-1141-2*
HSM 210 trail *14-07-1141-3*
FDHSM 210 trail *14-07-1141-4*
HSM 230 lead *14-07-1141-5*
HSM 230 peak *14-07-1141-6*
HSM 230 trail *14-07-1141-7*
FDHSM 230 trail *14-07-1141-8*
HSM 231 lead *14-07-1141-9*
HSM 231 peak *14-07-1141-10*
HSM 231 trail *14-07-1141-11*
FDHSM 231 trail *14-07-1141-12*
HSM 240 lead *14-07-1141-13*
HSM 240 peak *14-07-1141-14*
HSM 240 trail *14-07-1141-15*
HSM 250 lead *14-07-1141-16*
HSM 250 peak *14-07-1141-17*
HSM 250 trail *14-07-1141-18*
HSM 260 lead *14-07-1141-19*
HSM 260 peak *14-07-1141-20*
HSM 260 trail *14-07-1141-21*
HSM 270 lead *14-07-1141-22*
HSM 270 peak *14-07-1141-23*
HSM 270 trail *14-07-1141-24*
VOC Blank *14-07-1141-25*
TB#3 *14-07-1141-26*

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. pH values are collected in the field at the time of sample collection and are listed in the field parameters for each sample event. As such, the laboratory pH values which are flagged for hold time exceedances are not used for sample assessment purposes.

Trip Blanks

Two Trip Blanks sample were analyzed for VOCs. No VOCs were detected in either sample.

Equipment Blanks

No equipment blanks were collected because samples were either collected directly in the sample bottles or were collected with new, disposable, single-use bailers with new rope.

QA/QC Discussion – San Marcos Springs Stormwater Samples (Sampled July 15-16, 2014)

Issues associated with all surface samples

Magnesium was detected at a concentration of 0.0172 mg/L in batch 140718LA3F and 0.0172 mg/L in batch 140718LA4F within the Method Blanks. The detected concentrations are below the Reporting Limit, but above the Method Detection Limit. It was therefore “J” flagged. Due to the low concentration and lack of concerns with magnesium concentrations in the subject samples, the results are accepted.

Method EPA6010B (Batch No. 140718SA3) - Recovery of the MSD compound was out of control due to suspected matrix interference for potassium and sodium. The results were biased high and associated LCS recovery was in control. For potassium, the MS/MSD RPD was out of control due to suspected matrix interference. The results may be biased high; the results are accepted.

Method EPA 6010B (Batch No. 140718SA3) - For analytes calcium, magnesium, and silicon, spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

Method EPA 6010B (Batch No. 140718SA4) - Spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

Method 6020 (Batch No. 140718S05) – For chromium and selenium, recovery of the MSD compound was out of control due to suspected matrix interference. The associated LCS recovery was in control; therefore the results are accepted.

Method 7470A (Batch 140722S07) – For mercury, recovery of the MSD compound was out of control due to suspected matrix interference. The associated LCS recovery was in control; therefore the results are accepted.

Method EPA1694 (M) Caffeine (Batch 140722L15) – For caffeine, the RPD between the LCS Percent Recovery and LCS Duplicate (LCSD) Percent Recovery was out-of-range. The result was biased high. Therefore, the results are accepted.

Method EPA 8082 – For Aroclor-1260, the LCS Percent Recovery was out-of-range. The result was biased high. Therefore, the results are accepted.

Method 8270C – For 4-nitrophenol and pentachlorophenol, the RPD was out-of-range. The LCS %Rec. and LCSD %Rec. were both in range. Results are accepted.

Issues specific to individual samples

HSM 210 peak – For cadmium, recovery of the MSD compound was out of control due to suspected matrix interference. The associated LCS recovery was in control; therefore the results are accepted.

HSM 240 trail – For caffeine, recovery of the MSD compound was out of control due to suspected matrix interference. The associated LCS recovery was in control; therefore the results are accepted.

HSM 260 trail – For caffeine, recovery of the MSD compound was out of control due to suspected matrix interference. The associated LCS recovery was in control; therefore the results are accepted.

Data Group Numbers (HCP stormwater samples collected September 26-27, 2014, at Comal springs):

HCS 210 Lead *14-09-2403-1*
HCS 240 Lead *14-09-2403-2*
HCS 250 Lead *14-09-2403-3*
HCS 260 Lead *14-09-2403-4*
HCS 270 Lead *14-09-2403-5*
HCS 240 Peak *14-09-2403-7*
HCS 250 Peak *14-09-2403-8*
HCS 260 Peak *14-09-2403-9*
HCS 270 Peak *14-09-2403-10*
HCS 210 Trail *14-09-2403-11*
HCS 240 Trail *14-09-2403-12*
HCS 250 Trail *14-09-2403-13*
HCS 260 Trail *14-09-2403-14*
HCS 270 Trail *14-09-2403-15*
FDHCS 260 Trail *14-09-2403-16*
FDHCS 270 Trail *14-09-2403-17*
TB-5 *14-09-2403-18*

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. pH values are collected in the field at the time of sample collection and are listed in the field parameters for each sample event. As such, the laboratory pH values which are flagged for hold time exceedances are not used for sample assessment purposes.

The hold times for all field samples were exceeded for nitrates analyses. This is due to the fact that samples were collected during a storm event that occurred on a Friday evening, September 26, 2014 and early Saturday morning, September 27, 2014. Samples were shipped on Monday September 29, 2014 for overnight delivery. The recommended holding time for nitrates analysis is 48 hours. The results obtained appear consistent with other results obtained from other stormwater events and base flow conditions.

Trip Blanks

Trip Blank, TB-5, sample was analyzed for VOCs. 1,2-dichloroethane was detected as a concentration of 0.34 ug/L, which is above the minimum detection limit, but below the reporting limit. It was therefore “J” flagged. 1,2-dichloroethane was not detected in any of the field samples or the method blank.

Equipment Blanks

No equipment blanks were collected because samples were either collected directly in the sample bottles or were collected with new, disposable, single-use bailers with new rope.

QA/QC Discussion – Comal Springs Stormwater Sampled (Sampled September 26-27, 2014)

Issues associated with all surface samples

Aluminum was detected at a concentration of 0.00890 mg/L in batch 141001L09F within the Method Blank. The detected concentration is below the Reporting Limit, but above the Method Detection Limit. It was therefore “J” flagged. Due to the low concentration and lack of concerns with aluminum concentrations in the subject samples, the results are accepted.

Method EPA 6010B (Batch No. 141001SA3) - For analytes calcium, magnesium, and silicon, spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

Method EPA 6020 (Batch No. 141001L09F) – For selenium, LCS Recovery Percentage is within Marginal Exceedance Control Limit range (+/- 4 SD from the mean). The acceptable number of Marginal Exceedance compounds for 16 LCS compounds is one. Only one Marginal Exceedance compound was present. Therefore the LCS Marginal Exceedance validation passed. The results are accepted.

Issues specific to individual samples

HCS 210 Lead – For aluminum, the Pulse Digestion Spike %Rec. associated with this batch of samples was out of control due to suspected matrix interference. The result was biased high. The results are accepted.

Data Group Numbers (HCP stormwater samples collected November 4-5, 2014, at Comal springs):

HCS 210 Lead *14-11-0442-1*
HCS 240 Lead *14-11-0442-2*
HCS 250 Lead *14-11-0442-3*
HCS 260 Lead *14-11-0442-4*
HCS 270 Lead *14-11-0442-5*
HCS 210 Peak *14-11-0442-6*
HCS 240 Peak *14-11-0442-7*
HCS 250 Peak *14-11-0442-8*
HCS 260 Peak *14-11-0442-9*
HCS 270 Peak *14-11-0442-10*
HCS 210 Trail *14-11-0442-11*
HCS 240 Trail *14-11-0442-12*
HCS 250 Trail *14-11-0442-13*
HCS 260 Trail *14-11-0442-14*
HCS 270 Trail *14-11-0442-15*
FDHCS 260 Trail *14-11-0442-16*
FDHCS 270 Trail *14-11-0442-17*
TB-8 *14-11-0442-18*

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. pH values are collected in the field at the time of sample collection and are listed in the field parameters for each sample event. As such, the laboratory pH values which are flagged for hold time exceedances are not used for sample assessment purposes.

At the stormwater base camp when alkalinity analysis were being conducted by SWCA staff a very low pH value of 2.32 was discovered in the water within a cubitainer for sample FDHCS 270 Trail. The pH measured in the stream at the time of sample collection was 7.22. The cubitainer was used to collect and filter water for metals and field alkalinity analyses. The cubitainer and bottle for metals analyses were shipped with the rest of the sample bottles to Calscience for analyses. Measurement of alkalinity was not possible because of the low pH value.

The cubitainer pH value measured by SWCA was 2.32. Calscience measured a pH value of 2.4 in the cubitainer. The pH measured with a sonde in the stream at the time of sample collection was 7.22. It appears acid was somehow introduced into the cubitainer prior to or during filling of the cubitainer. The source of acid is unknown. The cubitainer has a volume of approximately 2.5 gallons. Therefore preservative acid from one of the 1-liter bottles does not seem sufficient to have lowered the pH in the larger cubitainer to as low as 2.32 or 2.4, but it is the most likely source of acid that could have been emptied into the cubitainer during sample collection. A bottle filled with preservative acid could have mistakenly been used to fill the cubitainer. Because the sample was a field duplicate, the parent sample was not affected, and those results are still valid. In addition, water for VOC, SVOC, pesticide, herbicide, and PCB analyses was not taken from

the cubitainer; and therefore, would not be affected. The only analyses potentially affected by acid within the cubitainer would be pH, metals, alkalinity, and other general water quality parameters. While the TDS and sulfates appear elevated in the field duplicate above the parent sample, the water quality parameters appear relatively consistent with the parent sample. The parent sample is valid and all results from the field duplicate appear valid with the exception of pH, alkalinity, TDS, and sulfates.

Trip Blanks

No analytes were detected in the trip blank sample TB-8.

Equipment Blanks

No equipment blanks were collected because samples were either collected directly in the sample bottles or were collected with new, disposable, single-use bailers with new rope.

QA/QC Discussion – Comal Springs Stormwater Sampled (Sampled July 15-16, 2014)

Issues associated with all stormwater samples

Magnesium was detected at a concentration of 0.00853 mg/L in batch 141107L5FF within the Method Blank. The detected concentration is below the Reporting Limit, but above the Method Detection Limit. It was therefore “J” flagged. Due to the low concentration and lack of concerns with magnesium concentrations in the subject samples, the results are accepted.

Method 365.1 (Batch No. 141110S01) – For phosphorous, total, the recovery of the MS and MSD was out of control due to suspected matrix interference. The associated LCS recovery was in control. The result was biased high. The results are accepted.

Method EPA 6010B (Batch No. 141001SA3) - For analytes calcium, magnesium, and silicon, spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. Results are accepted.

Method EPA 6020 (Batch No. 141107S03) – For zinc and aluminum, the Pulse Digestion Spike associated with this batch of samples was out of control due to suspected matrix interference. The concentration was biased high. The results are accepted.

Method EPA 8141A (Batch No. 141108L03) – For phorate, the LCS % Recovery is out-of-range. However, the LCS Recovery Percentage is within Marginal Exceedance (ME) Control Limit range (+/- 4 SD from the mean).

Issues specific to individual samples

There were no issues specific to individual samples.

Data Group Numbers (HCP sediment samples collected June 25, 26, and 26-27, 2014, at Comal springs):

HCS360 *14-06-2074-1*
HCS330 *14-06-2074-2*
HCS340 *14-06-2074-3*
FDHCS360 *14-06-2074-4*
HCS310 *14-06-2078-1*
HCS320 *14-06-2078-2*
HSM370 *14-06-2078-3*
HSM340 *14-06-2078-4*
HSM310 *14-07-0162-1*
HSM350 *14-07-0162-2*
FDHSM350 *14-07-0162-3*
HSM360 *14-07-0162-4*
HSM320 *14-07-0162-5*
HSM330 *14-07-0162-6*
EB1 *14-07-0163-1*

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. Samples were collected in plastic sleeves within the core barrel. The ends of the plastic sleeves were capped with Parafilm and plastic caps. The laboratory extracted a portion of the sample for VOC analysis, then homogenized the remainder of the sample for other analyses.

Trip Blanks

No trip blank was submitted for analysis. No VOCs were detected in any of the sediment samples.

Equipment Blanks

One equipment blank was collected by pouring ASTM Type II Reagent Grade water through a sample tube and into sample containers. A total organic carbon concentration of 0.67 mg/L and a chloroform concentration of 3.5 ug/L. Neither of these detected concentrations is anticipated to have significantly impacted the results of the sediment analyses.

QA/QC Discussion – Comal and San Marcos Springs Sediment Samples

(Sampled June 25, 26, and 30, 2014)

Issues associated with all sediment samples

Method 6010B (MS/MSD Batch 140701S02) – For barium, zinc, aluminum, iron, and manganese, spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. For Antimony, recovery of the MS and MSD compound was out of control due to suspected matrix interference. The MS/MSD RPD was out of control due to suspected matrix interference. The associated LCS recovery was in control. Results are accepted.

Method 6010B (MS/MSD Batch No. 140707S02) – For aluminum, iron, and manganese, spike recovery and RPD control limits do not apply—resulting from the parameter concentration in the sample exceeding the spike concentration by a factor of four or greater. For thallium, recovery of the MSD compound was out of control due to suspected matrix interference. The associated LCS recovery was in control. Results are accepted.

Method EPA 8270C (MS/MSD Batch No. 140705S05) – For pentachlorophenol, the MS/MSD RPD was out of control due to suspected matrix interference. The MS %Rec. and MSD %Rec. were both within Control Limits. The results are accepted.

Method EPA 8260B (MS/MSD Batch No. 140709S005) – For p/m-xylene, recovery of the MSD compound was out of control due to suspected matrix interference. The associated LCS recovery was in control. Results are accepted.

Issues specific to individual samples

There were not issues specific to individual samples.

Data Group Numbers (HCP PDS deployed March 24 – April 29, 2014, at Comal and San Marcos springs):

HSM 120 **00732920**
HSM 110 **00732926**
HCS 130 **00732938**
HSM 160 **00732945**
HSM 150 **00733520**
HCS 110 **00733525**
Trip Blank **00733528**

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. PDS were deployed from March 24, 2014, through April 29, 2014.

Trip Blanks

Toluene was detected at a concentration of 0.03 ug/L. Toluene was detected in sample HSM 110 at a concentration of 0.05 ug/L, and 0.04 ug/L in sample HSM 150, which are both similar to the Trip Blank concentrations. Therefore, concentrations detected in field samplers may be the result of impacts other than those detected in the PDS environment when deployed.

TPH was detected at a concentration of 0.89 ug/L in the Trip Blank. The concentrations of TPH detected in the field PDS ranged from 0.03 ug/L to 0.07 ug/L. Therefore, concentrations detected in field samplers may be the result of impacts other than those detected in the PDS environment when deployed.

Equipment Blanks

No equipment blanks were not practicable due to sampler type.

QA/QC Discussion – Comal and San Marcos Springs PDS

(Deployed March 24-April 29, 2014)

Issues associated with all PDS

No analytes were detected in the Method Blank.

Issues specific to individual samples

There were not issues specific to individual samples.

Data Group Numbers (HCP PDS deployed June 23, 2014, through July 7, 2014, at Comal and San Marcos springs):

HSM420 00733579
HSM460 00733580
HSM440 00733581
HSM450 00733582
HSM410 00733585
TB2 00733587
HSM470 00733588
HCS460 00733591
HCS430 00733597
HCS440 00733603
HCS440 00733603D
HCS420 00733609
HSM430 00733615
HSM430 00733615D
HCS410 00733621

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. PDS were deployed from June 23, 2014, through July 7, 2014.

Trip Blanks

TPH was detected at a concentration of 0.83 ug/L in the Trip Blank. The concentrations of TPH detected in the field PDS were all higher than the Trip Blank concentration (1.49, 1.34, 1.81, 1.17, 2.56, 2.14, 3.09, 1.00, 1.81, 1.62, 1.03, 2.57, 2.02, and 2.64 ug/L). Although TPH was detected in the Trip Blank sampler, it appears it may also have been detected in the river environments.

Equipment Blanks

No equipment blanks were not practicable due to sampler type.

QA/QC Discussion – Comal and San Marcos Springs PDS

(Deployed June 23, 2014, through July 7, 2014)

Issues associated with all PDS

No analytes were detected in the Method Blank.

Issues specific to individual samples

There were not issues specific to individual samples.

Data Group Numbers (HCP PDS deployed August 12 – August 26, 2014, at Comal and San Marcos springs):

TB4 00733531
HCS410 00733583
HCS420 00733584
HCS440 00733586
HCS460 00733590
HSM410 00733592
HSM420 00733593
HSM430 00733594
HSM440 00733595
HSM450 00733596
HSM460 00733598
HSM470 00733599
FDHSM430 00733600
FDHCS440 00733601

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. PDS were deployed from August 12, 2014, through August 26, 2014.

Trip Blanks

TPH was detected at a concentration of 1.50 ug/L in the Trip Blank. The concentrations of TPH detected in the field PDS ranged from 0.07 ug/L to 0.12 ug/L. Therefore, concentrations detected in field samplers may be the result of impacts other than those detected in the sampler environment when deployed.

Equipment Blanks

No equipment blanks were not practicable due to sampler type.

QA/QC Discussion – Comal and San Marcos Springs PDS

(Deployed August 12-August 26, 2014)

Issues associated with all PDS

No analytes were detected in the Method Blank.

Issues specific to individual samples

There were not issues specific to individual samples.

Data Group Numbers (HCP PDS deployed October 2 – October 16, 2014, at Comal and San Marcos springs):

TB4 **00733619**
HCS410 **00733604**
HCS420 **00733605**
HCS430 **00733606**
HCS440 **00733607**
HCS460 **00733608**
HSM410 **00733602**
HSM420 **00733610**
HSM430 **00733611**
HSM440 **00733612**
HSM450 **00733613**
HSM460 **00733614**
HSM470 **00733616**
FDHSM430 **00733618**
FDHCS440 **00733617**

General Comments

Although some analytical issues are noted for the data group, unless otherwise noted in the detailed discussion, the data are considered valid for the purposes of the investigation. PDS were deployed from October 2, 2014, through October 16, 2014.

Trip Blanks

TPH was detected at a concentration of 1.14 ug/L in the Trip Blank. The concentrations of TPH detected in the field PDS ranged from 1.13 ug/L to 2.19 ug/L. Therefore, concentrations detected in field samplers may be the result of impacts other than those detected in the sampler environment when deployed.

Equipment Blanks

No equipment blanks were not practicable due to sampler type.

QA/QC Discussion – Comal and San Marcos Springs PDS

(Deployed October 2-October 16, 2014)

Issues associated with all PDS

No analytes were detected in the Method Blank.

Issues specific to individual samples

There were no issues specific to individual samples.

Data Group Numbers (HCP PDS deployed December 1 – December 15, 2014, at Comal and San Marcos springs):

HCS410 00753365
HCS420 00753366
HCS440 00753367
FDCS440 00753368
HCS430 00753369
HCS460 00753370
HSM410 00753371
HSM420 00753372
HSM430 00753373
HSM450 00753374
HSM440 00753375
HSM460 00753376
HSM470 00753377
FDHSM430 00753378
TB9 00753379

General Comments

No analytical issues are noted for this data group, and the data are considered valid for the purposes of the investigation. PDS were deployed from December 1, 2014, through December 15, 2014.

Trip Blanks

No analytes were detected in the Trip Blank (TB9).

Equipment Blanks

No equipment blanks were not practicable due to sampler type.

QA/QC Discussion – Comal and San Marcos Springs PDS

(Deployed December 1-December 15, 2014)

Issues associated with all PDS

No analytes were detected in the Method Blank.

Issues specific to individual samples

There were no issues specific to individual samples.

Relative Percent Differences (RPD) values for parent samples and associated duplicate samples are provided in the table below. In general, the RPD are low indicating parent and duplicate sample constituent concentrations are close to the same. Some differences observed in water samples may be the result of concentrations that vary naturally due to stream flow. Because the streams sampled are constantly flowing, constituent concentrations can change, or fluctuate during the time period in which multiple sample bottles, which are all part of the same sample, are filled. Although sediment sample cores were collected in close proximity to one another, soil concentrations may vary spatially, which can cause differences between parent and duplicate sample constituent concentrations.

The differences observed do not show wide variations where a parent sample concentration exceeds a regulatory threshold or comparison value and a duplicate does not, or vice versa.

Efforts to minimize RPDs were implemented during sample collection, but greater measures may be employed such as simultaneous bottle filling, as opposed to sequential bottle filling. It should be noted that the RPDs between parent and duplicate field samples not only show differences between the parent and duplicate samples but also include differences inherent to laboratory procedures when the two separate samples are analyzed. Therefore, the laboratory RPDs contribute to the parent and field duplicate constituent concentration RPDs.

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
Surface Water								
HCS130	3/25/2014	Calcium	(mg/L)	84.0		86.1		2.5%
		Magnesium	(mg/L)	17.6	B 0.00464J	17.6	B 0.00464J	0.0%
		Potassium	(mg/L)	1.43		1.40		-2.1%
		Sodium	(mg/L)	13.8		14.2		2.9%
		Strontium	(mg/L)	0.671		0.687		2.4%
		Silicon	(mg/L)	6.21		6.37		2.6%
		Barium	(mg/L)	0.0569		0.0578		1.6%
		Copper	(mg/L)	0.000351	J	0.000222	J	-36.8%
		Nickel	(mg/L)	0.00173		0.00174		0.6%
		Selenium	(mg/L)	0.000464	J	0.000513	J	10.6%
		Zinc	(mg/L)	0.0109		0.0192		76.1%
		Aluminum	(mg/L)	0.0593		0.00644	J	-89.1%
		Iron	(mg/L)	0.0170	J	0.0180	J	5.9%
		Fluoride	(mg/L)	0.23		0.23		0.0%
		Chloride	(mg/L)	18		18		0.0%
		Bromide	(mg/L)	0.068	J	0.087	J	27.9%
		Nitrate	(mg/L)	1.7	H	1.7	H	0.0%
		Sulfate	(mg/L)	33		33		0.0%
		Total alkalinity	(mg/L)	233		233		0.0%
		Bicarbonate	(mg/L)	233		233		0.0%
HSM170	4/29/2014	Total dissolved solids	(mg/L)	360		357		-0.8%
		Total Kjeldahl Nitrogen	(mg/L)	0.70		0.56		-20.0%
		Nitrate	(mg/L)	1.1		1.1		0.0%
		Calcium	(mg/L)	91.9		96.4		4.9%
		Magnesium	(mg/L)	17.8		18.5		3.9%
		Potassium	(mg/L)	1.39		1.47		5.8%
		Sodium	(mg/L)	11.2		11.8		5.4%
		Strontium	(mg/L)	0.502		0.532		6.0%
		Silicon	(mg/L)	5.82		6.02		3.4%
		Barium	(mg/L)	0.0388		0.0379		-2.3%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
HCS140	9/25/2014	Nickel	(mg/L)	0.00157		0.00142		-9.6%
		Zinc	(mg/L)	0.0376		0.0404		7.4%
		Iron	(mg/L)	0.0504		0.0502		-0.4%
		Calcium	(mg/L)	85.3		86.7		1.6%
		Magnesium	(mg/L)	17.2		17.1		-0.6%
		Potassium	(mg/L)	1.47		1.47		0.0%
		Sodium	(mg/L)	13.0		13.1		0.8%
		Strontium	(mg/L)	0.673		0.687		2.1%
		Silicon	(mg/L)	5.43		5.42		-0.2%
		Barium	(mg/L)	0.0565		0.0562		-0.5%
		Chromium	(mg/L)	0.000474	J	0.000491	J	3.6%
		Copper	(mg/L)	0.000510	J	0.000482	J	-5.5%
		Lead	(mg/L)	<0.0000898		0.000103	J	14.7%
		Nickel	(mg/L)	0.00332		0.00327		-1.5%
		Selenium	(mg/L)	0.000438	J	0.000339	J	-22.6%
		Zinc	(mg/L)	0.0117		0.0124		6.0%
		Aluminum	(mg/L)	0.00601	J	0.00567	J	-5.7%
		Iron	(mg/L)	0.0889		0.0649		-27.0%
		Manganese	(mg/L)	0.00140		0.000975	J	-30.4%
		Fluoride	(mg/L)	0.25		0.23		-8.0%
		Chloride	(mg/L)	17		17		0.0%
		Bromide	(mg/L)	0.071	J	0.080	J	12.7%
		Nitrate	(mg/L)	1.6		1.6		0.0%
		Sulfate	(mg/L)	29		29		0.0%
		Total alkalinity	(mg/L)	244		240		-1.6%
		Bicarbonate	(mg/L)	244		240		-1.6%
		Total dissolved solids	(mg/L)	340		350		2.9%
		Total suspended solids	(mg/L)	1.7		1.1		-35.3%
		pH		7.40	H	7.39	H	-0.1%
		Total organic carbon	(mg/L)	12		10		-16.7%
		Dissolved organic carbon	(mg/L)	8.8		6.9		-21.6%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		<i>E. coli</i>	(MPN/100mL)	260		290		11.5%
		Average Field alkalinity	(mg/L)	205		199		-2.9%
HSM160	9/26/2014	Calcium	(mg/L)	93.0		95.1		2.3%
		Magnesium	(mg/L)	17.8	B 0.00809J	18.2	B 0.00809J	2.2%
		Potassium	(mg/L)	1.39		1.38		-0.7%
		Sodium	(mg/L)	12.7		12.7		0.0%
		Strontium	(mg/L)	0.519		0.530		2.1%
		Silicon	(mg/L)	5.49		5.63		2.6%
		Barium	(mg/L)	0.0380		0.0393		3.4%
		Chromium	(mg/L)	0.000530	J	0.000544	J	2.6%
		Copper	(mg/L)	0.000879	J	0.000444	J	-49.5%
		Nickel	(mg/L)	0.00378		0.00349		-7.7%
		Selenium	(mg/L)	0.000263	J	0.000309	J	17.5%
		Zinc	(mg/L)	0.00418	J	0.00393	J	-6.0%
		Aluminum	(mg/L)	0.00566	J	0.00676	J	19.4%
		Iron	(mg/L)	0.0755		0.0991		31.3%
		Manganese	(mg/L)	0.00215		0.00200		-7.0%
		Caffeine	(ng/L)	19		48		152.6%
		Fluoride	(mg/L)	0.21		0.21		0.0%
		Chloride	(mg/L)	19		19		0.0%
		Bromide	(mg/L)	0.080	J	0.085	J	6.3%
		Nitrate	(mg/L)	1.3	H	1.3	H	0.0%
		Sulfate	(mg/L)	26		26		0.0%
		Total phosphorous	(mg/L)	0.02	J	<0.020		-5.0%
		Total alkalinity	(mg/L)	261		263		0.8%
		Bicarbonate	(mg/L)	261		263		0.8%
		Total dissolved solids	(mg/L)	355		345		-2.8%
		Total suspended solids	(mg/L)	1.4		1.1		-21.4%
		pH		7.44	H	7.49	H	0.7%
		Total Kjeldahl Nitrogen	(mg/L)	0.28	J	<0.28		-0.4%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		Total organic carbon	(mg/L)	6.9		5.8		-15.9%
		Dissolved organic carbon	(mg/L)	10		12		20.0%
		<i>E. coli</i>	(MPN/100mL)	96		72		-25.0%
		Average Field alkalinity	(mg/L)	177		189		6.8%
Stormwater								
HCS260 Trail	9/27/2014	Calcium	(mg/L)	81.8		82.1		0.4%
		Magnesium	(mg/L)	15.7		16.0		1.9%
		Potassium	(mg/L)	1.97		1.90		-3.6%
		Sodium	(mg/L)	13.8		13.5		-2.2%
		Strontium	(mg/L)	0.615		0.615		0.0%
		Silicon	(mg/L)	5.45		5.50		0.9%
		Antimony	(mg/L)	0.000142	J	<0.0000995		-29.9%
		Arsenic	(mg/L)	0.000744	J	0.000443	J	-40.5%
		Barium	(mg/L)	0.0551		0.0538		-2.4%
		Chromium	(mg/L)	0.000680	J	0.000574	J	-15.6%
		Copper	(mg/L)	0.000960	J	0.000817	J	-14.9%
		Lead	(mg/L)	0.000122	J	<0.0000898		-26.4%
		Nickel	(mg/L)	0.00440		0.00427		-3.0%
		Selenium	(mg/L)	0.000503	J	0.000341	J	-32.2%
		Zinc	(mg/L)	0.0256		0.00484	J	-81.1%
		Aluminum	(mg/L)	0.00844	J,B0.00890 J	0.00483	J,B0.00890 J	-42.8%
		Iron	(mg/L)	0.0664		0.0776		16.9%
		Manganese	(mg/L)	0.00522		0.00501		-4.0%
		Caffeine	(ng/L)	120		130		8.3%
		Fluoride	(mg/L)	0.23		0.24		4.3%
		Chloride	(mg/L)	17		17		0.0%
		Bromide	(mg/L)	0.085	J	0.076	J	-10.6%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		Nitrate	(mg/L)	1.4	H	1.4	H	0.0%
		Sulfate	(mg/L)	31		31		0.0%
		Total alkalinity	(mg/L)	212		212		0.0%
		Bicarbonate	(mg/L)	212		212		0.0%
		Total dissolved solids	(mg/L)	355		330		-7.0%
		Total suspended solids	(mg/L)	3.0		4.0		33.3%
		pH		7.71	H	7.71	H	0.0%
		Total Kjeldahl Nitrogen	(mg/L)	0.56		0.49	J	-12.5%
		Total organic carbon	(mg/L)	2.6		3.1		19.2%
		Dissolved organic carbon	(mg/L)	2.6		3.8		46.2%
		<i>E. coli</i>	(MPN/100mL)	3300		3700		12.1%
		Average Field alkalinity	(mg/L)	174		170		-2.3%
HCS270 Trail	9/27/2014	Calcium	(mg/L)	81.1		81.9		1.0%
		Magnesium	(mg/L)	15.7		15.9		1.3%
		Potassium	(mg/L)	2.07		2.08		0.5%
		Sodium	(mg/L)	14.1		13.5		-4.3%
		Strontium	(mg/L)	0.605		0.608		0.5%
		Silicon	(mg/L)	5.34		5.39		0.9%
		Antimony	(mg/L)	0.000417	J	<0.0000995		-76.1%
		Arsenic	(mg/L)	0.000758	J	0.000678	J	-10.6%
		Barium	(mg/L)	0.0545		0.0535		-1.8%
		Chromium	(mg/L)	0.000753	J	0.000647	J	-14.1%
		Copper	(mg/L)	0.000617	J	0.00110		78.3%
		Lead	(mg/L)	0.000296	J	0.0000958	J	-67.6%
		Nickel	(mg/L)	0.00435		0.00448		3.0%
		Selenium	(mg/L)	0.000428	J	0.000337	J	-21.3%
		Zinc	(mg/L)	0.0748		0.00809		-89.2%
		Aluminum	(mg/L)	0.0283	J,B0.00890 J	0.0122	J,B0.00890 J	-56.9%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		Iron	(mg/L)	0.137		0.0827		-39.6%
		Manganese	(mg/L)	0.00439		0.00376		-14.4%
		Caffeine	(ng/L)	120		600		400.0%
		Fluoride	(mg/L)	0.24		0.25		4.2%
		Chloride	(mg/L)	18		18		0.0%
		Bromide	(mg/L)	<0.037		0.079	J	114.1%
		Nitrate	(mg/L)	1.4	H	1.4	H	0.0%
		Sulfate	(mg/L)	32		32		0.0%
		Total alkalinity	(mg/L)	212		210		-0.9%
		Bicarbonate	(mg/L)	212		210		-0.9%
		Total dissolved solids	(mg/L)	335		325		-3.0%
		Total suspended solids	(mg/L)	5.0		5.0		0.0%
		pH		7.76	H	7.74	H	-0.3%
		Total Kjeldahl Nitrogen	(mg/L)	0.42	J	0.70		66.7%
		Total organic carbon	(mg/L)	3.4		3.4		0.0%
		Dissolved organic carbon	(mg/L)	3.2		2.9		-9.4%
		<i>E. coli</i>	(MPN/100mL)	3100		5500		77.4%
		Average Field alkalinity	(mg/L)	174		173		-0.6%
HCS260 Trail	11/5/2014	Calcium	(mg/L)	70.9		76.1		7.3%
		Magnesium	(mg/L)	14.8	B0.00853J	15.6	B0.00853J	5.4%
		Potassium	(mg/L)	1.82		1.81		-0.5%
		Sodium	(mg/L)	12.4		13.3		7.3%
		Strontium	(mg/L)	0.591		0.632		6.9%
		Silicon	(mg/L)	5.08		5.43		6.9%
		Barium	(mg/L)	0.0485		0.0541		11.5%
		Copper	(mg/L)	0.00141	J	0.00180	J	27.7%
		Nickel	(mg/L)	0.00181	J	0.00134	J	-26.0%
		Zinc	(mg/L)	0.0185	J	0.0812		338.9%
		Aluminum	(mg/L)	0.517		0.458	J	-11.4%
		Manganese	(mg/L)	0.00383	J	0.00328	J	-14.4%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		Caffeine	(ng/L)	98		81		-17.3%
		Fluoride	(mg/L)	0.20		0.21		5.0%
		Chloride	(mg/L)	16		16		0.0%
		Bromide	(mg/L)	0.11		0.13		18.2%
		Nitrate	(mg/L)	1.5		1.4		-6.7%
		Sulfate	(mg/L)	28		28		0.0%
		Total alkalinity	(mg/L)	201		200		-0.5%
		Bicarbonate	(mg/L)	201		200		-0.5%
		Total dissolved solids	(mg/L)	330		310		-6.1%
		Total suspended solids	(mg/L)	5.7		5.5		-3.5%
		pH		7.76	H	7.75	H	-0.1%
		Total Kjeldahl Nitrogen	(mg/L)	0.56		0.56		0.0%
		Total organic carbon	(mg/L)	5.6		4.4		-21.4%
		Dissolved organic carbon	(mg/L)	3.2		4.8		50.0%
		<i>E. coli</i>	(MPN/100mL)	510		1100		115.7%
		Average Field alkalinity	(mg/L)	160		165		3.1%
HCS270 Trail	11/5/2014	Calcium	(mg/L)	56.1		57.0		1.6%
		Magnesium	(mg/L)	11.8	B0.00853J	12.0	B0.00853J	1.7%
		Potassium	(mg/L)	3.44		3.64		5.8%
		Sodium	(mg/L)	12.4		13.2		6.5%
		Strontium	(mg/L)	0.449		0.445		-0.9%
		Silicon	(mg/L)	4.48		4.54		1.3%
		Barium	(mg/L)	0.0398		0.0380		-4.5%
		Copper	(mg/L)	0.00204	J	0.00437	J	114.2%
		Nickel	(mg/L)	0.00136	J	0.00132		-2.9%
		Zinc	(mg/L)	0.0363	J	0.0413	J	13.8%
		Aluminum	(mg/L)	0.112	J	1.06		846.4%
		Manganese	(mg/L)	0.00331	J	0.00638	J	92.7%
		Caffeine	(ng/L)	130		95		-26.9%
		Beta-BHC	µg/L	0.10		0.039	J	-61.0%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		1,2-Dichloroethane	µg/L	0.84		<0.24		-71.5%
		Fluoride	(mg/L)	0.18		0.94		422.2%
		Chloride	(mg/L)	13		14		7.7%
		Bromide	(mg/L)	<0.037		0.093		152.0%
		Nitrate	(mg/L)	1.2		1.2		0.0%
		Sulfate	(mg/L)	23		530		2204.3 %
		Total phosphorous	(mg/L)	0.036	J	0.036		0.0%
		Total dissolved solids	(mg/L)	250		740		196.0%
		Total suspended solids	(mg/L)	7.0		3.7		-47.1%
		pH		7.77	H	2.44		-68.6%
		Total Kjeldahl Nitrogen	(mg/L)	0.56		0.56		0.0%
		Total organic carbon	(mg/L)	6.3		5.4		-14.3%
		Dissolved organic carbon	(mg/L)	4.8		2.4		-50.0%
		<i>E. coli</i>	(MPN/100mL)	980		650		-33.7%
HSM210 Trail	7/16/2014	Calcium	(mg/L)	81.9		56.7		-30.8%
		Magnesium	(mg/L)	20.5	B0.0172J	7.80	B0.0172J	-62.0%
		Potassium	(mg/L)	2.46		2.38		-3.3%
		Sodium	(mg/L)	16.1		7.78		-51.7%
		Strontium	(mg/L)	0.679		0.246		-63.8%
		Silicon	(mg/L)	5.30		3.39		-36.0%
		Barium	(mg/L)	0.0332		0.0244		-26.5%
		Copper	(mg/L)	0.00133	J	0.00324	J	143.6%
		Nickel	(mg/L)	0.00303	J	0.00231	J	-23.8%
		Zinc	(mg/L)	0.0382		0.0460		20.4%
		Aluminum	(mg/L)	<0.0165		0.0654	J	296.6%
		Iron	(mg/L)	<0.0463		0.0637	J	37.6%
		Caffeine	(ng/L)	100		660		560.0%
		Fluoride	(mg/L)	0.34		0.30		-11.8%
		Chloride	(mg/L)	24		9.9		-58.8%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		Bromide	(mg/L)	0.12		<0.037		-69.3%
		Nitrate	(mg/L)	0.27		1.3		381.5%
		Sulfate	(mg/L)	32		28		-12.5%
		Total phosphorous	(mg/L)	0.041	J	0.081		97.6%
		Total alkalinity	(mg/L)	228		134		-41.2%
		Bicarbonate	(mg/L)	228		134		-41.2%
		Total dissolved solids	(mg/L)	310		210		-32.3%
		Total Kjeldahl Nitrogen	(mg/L)	0.70		0.84		20.0%
		Total organic carbon	(mg/L)	5.6		22		292.9%
		Dissolved organic carbon	(mg/L)	1.5		4.8		220.0%
		<i>E. coli</i>	(MPN/100mL)	17000	H	10000	H	-41.2%
		Field alkalinity	(mg/L)	228		131		-42.5%
HSM230 Trail	7/16/2014	Calcium	(mg/L)	54.8		78.7		43.6%
		Magnesium	(mg/L)	7.62	B0.0172J	19.7	B0.0172J	158.5%
		Potassium	(mg/L)	2.33		2.30		-1.3%
		Sodium	(mg/L)	7.47		15.6		108.8%
		Strontium	(mg/L)	0.245		0.647		164.1%
		Silicon	(mg/L)	3.31		5.08		53.5%
		Barium	(mg/L)	0.0229		0.0325		41.9%
		Copper	(mg/L)	0.00324	J	0.000922	J	-71.5%
		Nickel	(mg/L)	0.00225	J	0.00225	J	0.0%
		Zinc	(mg/L)	0.0182	J	0.0340		86.8%
		Caffeine	(ng/L)	990		23		-97.7%
		Fluoride	(mg/L)	0.32		0.35		9.4%
		Chloride	(mg/L)	9.8		24		144.9%
		Bromide	(mg/L)	<0.037		0.13		252.3%
		Nitrate	(mg/L)	1.3		0.24		-81.5%
		Sulfate	(mg/L)	27		33		22.2%
		Total phosphorous	(mg/L)	0.088		0.040	J	-54.5%
		Total alkalinity	(mg/L)	111		227		104.5%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		Bicarbonate	(mg/L)	111		227		104.5%
		Total dissolved solids	(mg/L)	205		320		56.1%
		Total Kjeldahl Nitrogen	(mg/L)	1.1		0.84		-23.6%
		Total organic carbon	(mg/L)	26		29		11.5%
		Dissolved organic carbon	(mg/L)	7.3		5.2		-28.8%
		<i>E. coli</i>	(MPN/100mL)	10000	H	9800	H	-2.0%
		Field alkalinity	(mg/L)	131		225		71.8%
HSM231 Trail	7/16/2014	Calcium	(mg/L)	91.3		93.5		2.4%
		Magnesium	(mg/L)	18.3	B0.0172J	18.6	B0.0172J	1.6%
		Potassium	(mg/L)	1.83		1.87		2.2%
		Sodium	(mg/L)	13.0		13.5		3.8%
		Strontium	(mg/L)	0.561		0.581		3.6%
		Silicon	(mg/L)	5.80		5.94		2.4%
		Antimony	(mg/L)	0.000782	J	0.000552	J	-29.4%
		Barium	(mg/L)	0.0398		0.0392		-1.5%
		Copper	(mg/L)	0.00137	J	0.00115	J	-16.1%
		Nickel	(mg/L)	0.00274	J	0.00263	J	-4.0%
		Zinc	(mg/L)	0.0320		0.0117	J	-63.4%
		Aluminum	(mg/L)	0.0220	J	0.0169	J	-23.2%
		Caffeine	(ng/L)	32		21		-34.4%
		Fluoride	(mg/L)	0.32		0.32		0.0%
		Chloride	(mg/L)	19		19		0.0%
		Nitrate	(mg/L)	1.2		1.2		0.0%
		Sulfate	(mg/L)	29		29		0.0%
		Total phosphorous	(mg/L)	0.024	J	0.026	J	8.3%
		Total alkalinity	(mg/L)	250		230		-8.0%
		Bicarbonate	(mg/L)	250		230		-8.0%
		Total dissolved solids	(mg/L)	375		365		-2.7%
		Total Kjeldahl Nitrogen	(mg/L)	0.84		0.70		-16.7%
		Total organic carbon	(mg/L)	22		23		4.5%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		Dissolved organic carbon	(mg/L)	1.5		1.2		-20.0%
		<i>E. coli</i>	(MPN/100mL)	8700	H	10000	H	14.9%
		Field alkalinity	(mg/L)	249		251		0.8%
Sediment								
HCS360	6/25/2014	Total organic carbon	(mg/kg)	37000		37000		0.0%
		Barium	(mg/kg)	54.0		68.2		26.3%
		Beryllium	(mg/kg)	0.570		0.715		25.4%
		Chromium	(mg/kg)	11.7		14.5		23.9%
		Copper	(mg/kg)	14.2		14.8		4.2%
		Lead	(mg/kg)	23.7		38.3		61.6%
		Nickel	(mg/kg)	8.47		10.7		26.3%
		Silver	(mg/kg)	<0.516		0.630		22.1%
		Zinc	(mg/kg)	60.4		7.16		-88.1%
		Aluminum	(mg/kg)	6620		7890		19.2%
		Iron	(mg/kg)	6290		8040		27.8%
		Manganese	(mg/kg)	120		148		23.3%
HSM350	6/30/2014	Total organic carbon	(mg/kg)	66000		33000		-50.0%
		Total phosphorous	(mg/kg)	6.1		<5.0		-19.7%
		Arsenic	(mg/kg)	<1.49		8.47		468.8%
		Barium	(mg/kg)	42.5		55.4		30.4%
		Beryllium	(mg/kg)	0.517		0.814		57.4%
		Chromium	(mg/kg)	14.2		20.1		41.5%
		Copper	(mg/kg)	13.5		21.5		59.3%
		Lead	(mg/kg)	35.6		25.0		-29.8%
		Nickel	(mg/kg)	11.7		16.4		40.2%
		Silver	(mg/kg)	0.758		0.749		-1.2%
		Zinc	(mg/kg)	65.7		43.0		-34.6%
		Aluminum	(mg/kg)	5620		9690		72.4%
		Iron	(mg/kg)	9210		15400		67.2%
		Manganese	(mg/kg)	189		351		85.7%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
		Benzo (a) Anthracene	(mg/kg)	2.0		<2.0		-0.5%
		Benzo (a) Pyrene	(mg/kg)	2.5		<2.0		-20.4%
		Benzo (b) Fluoranthene	(mg/kg)	2.4		<2.0		-17.1%
		Benzo (g,h,i) Perylene	(mg/kg)	1.9		<2.0		4.7%
		Benzo (k) Fluoranthene	(mg/kg)	2.0		<2.0		-0.5%
		Bis(2-Ethylhexyl) Phthalate	(mg/kg)	2.1		2.2		4.8%
		Chrysene	(mg/kg)	2.5		<2.0		-20.4%
		Fluoranthene	(mg/kg)	4.3		<2.0		-53.7%
		Phenanthrene	(mg/kg)	2.1		<2.0		-5.2%
		Pyrene	(mg/kg)	4.8		<2.0		-58.5%
<u>PDS</u>								
HCS440	Jun 2014	Tetrachloroethene	µg	0.45		0.45		0.0%
		1,2,4-Trimethylbenzene	µg	0.03		0.03		0.0%
		TPH	µg	1.81		1.62		-10.5%
		Phenanthrene	µg	1.44		<0.05		-96.6%
HSM430	Jun 2014	Tetrachloroethene	µg	0.47		0.47		0.0%
		TPH	µg	2.57		2.02		-21.4%
		Fluoranthene	µg	4.74		4.21		-11.2%
		Phenanthrene	µg	8.70		7.49		-13.9%
		Pyrene	µg	2.21		1.85		-16.3%
		Undecane	µg	<0.05		0.08		63.3%
HCS440	Aug 2014	Toluene	µg	0.02		0.03		50.0%
		Tetrachloroethene	µg	0.41		0.42		2.4%
		Fluorene	µg	0.06		<0.05		-18.3%
		TPH	µg	1.48		1.50		1.4%
		BTEX	µg	0.02		0.03		50.0%
HSM430	Aug 2014	Tetrachloroethene	µg	0.49		0.44		-10.2%
		TPH	µg	1.06		1.13		6.6%
HCS440	Oct 2014	Tetrachloroethene	µg	0.33		0.30		-9.1%
		TPH	µg	1.13		1.51		33.6%

Sample Location	Date Collected	Analyte	Units	Field Sample	Qualifiers	Duplicate	Qualifiers	RPD
HSM430	Oct 2014	Tetrachloroethene	µg	0.38		0.40		5.3%
		TPH	µg	2.15		1.29		-40.0%
HCS440	Dec 2014	Tetrachloroethene	µg	0.53		0.47		-11.3%
HSM430	Dec 2014	Tetrachloroethene	µg	0.43		0.43		0.0%
		TPH	µg	<0.50		0.52		961.2%
B - Analyte detected in the laboratory method blank at the quantity listed H - Sample exceeded hold time J - Result above the method detection limit but below the reporting limit Method detection limits or reporting limits were used to calculate RPD for results not detected above these limits.								

APPENDIX I

SAMPLE RECORD

COMAL SURFACE WATER

Location / Sample Name	Date Sampled	Time Sampled	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HCS110	3/25/2014	9:33	29.72043	-98.12525	Comal	Upper Springs
HCS120	3/25/2014	10:30	29.718084	-98.131644	Comal	Upper Landa Lake
HCS130	3/25/2014	12:13	29.709566	-98.133749	Comal	Lower Landa Lake
FDHCS130	3/25/2014	12:30	29.709566	-98.133749	Comal	Lower Landa Lake
HCS140	3/25/2014	11:20	29.710221	-98.129534	Comal	Upper Old Channel
HCS160	3/25/2014	13:25	29.707454	-98.122762	Comal	USGS Gauge
Comal TB	3/25/2014	12:15	NA	NA	Comal	VOC Blank
HCS110	4/29/2014	9:45	29.72043	-98.12525	Comal	Upper Springs
HCS120	4/29/2014	11:00	29.718084	-98.131644	Comal	Upper Landa Lake
HCS130	4/29/2014	12:00	29.709566	-98.133749	Comal	Lower Landa Lake
HCS140	4/29/2014	11:40	29.710221	-98.129534	Comal	Upper Old Channel
HCS160	4/29/2014	12:55	29.707454	-98.122762	Comal	USGS Gauge
HCS110	9/25/2014	13:15	29.72043	-98.12525	Comal	Upper Springs
HCS120	9/25/2014	14:19	29.718084	-98.131644	Comal	Upper Landa Lake
HCS130	9/26/2014	8:46	29.709566	-98.133749	Comal	Lower Landa Lake
HCS140	9/25/2014	14:57	29.710221	-98.129534	Comal	Upper Old Channel
FDHCS140	9/25/2014	14:57	29.710221	-98.129534	Comal	Upper Old Channel
HCS160	9/26/2014	15:17	29.707454	-98.122762	Comal	USGS Gauge
TB6	9/26/2014	NA	NA	NA	Comal/Hays	VOC Blank

COMAL STORM WATER

Location / Sample Name	Date Sampled	Time Sampled	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HCS210 Lead	9/26/2014	19:15	29.72043	-98.12525	Comal	Upper Springs
HCS240 Lead	9/26/2014	19:37	29.710221	-98.129534	Comal	Upper Old Channel
HCS250 Lead	9/26/2014	19:20	29.709491	-98.122578	Comal	Lower Old Channel
HCS260 Lead	9/26/2014	19:55	29.708007	-98.127301	Comal	New Channel
HCS270 Lead	9/26/2014	19:40	29.704014	-98.115791	Comal	Comal River above confluence
HCS210 Peak	9/26/2014	22:43	29.72043	-98.12525	Comal	Upper Springs
HCS240 Peak	9/26/2014	23:12	29.710221	-98.129534	Comal	Upper Old Channel
HCS250 Peak	9/26/2014	22:50	29.709491	-98.122578	Comal	Lower Old Channel
HCS260 Peak	9/26/2014	23:31	29.708007	-98.127301	Comal	New Channel
HCS270 Peak	9/26/2014	23:07	29.704014	-98.115791	Comal	Comal River above confluence
HCS210 Trail	9/27/2014	6:22	29.72043	-98.12525	Comal	Upper Springs
HCS240 Trail	9/27/2014	6:47	29.710221	-98.129534	Comal	Upper Old Channel
HCS250 Trail	9/27/2014	6:30	29.709491	-98.122578	Comal	Lower Old Channel
HCS260 Trail	9/27/2014	7:03	29.708007	-98.127301	Comal	New Channel
FDHCS260 Trail	9/27/2014	7:03	29.708007	-98.127301	Comal	New Channel
HCS270 Trail	9/27/2014	7:00	29.704014	-98.115791	Comal	Comal River above confluence
FDHCS270 Trail	9/27/2014	7:00	29.704014	-98.115791	Comal	Comal River above confluence
TB5	9/26/2014	NA	NA	NA	Comal	VOC Blank
HCS210 Lead	11/4/2014	20:41	29.72043	-98.12525	Comal	Upper Springs
HCS240 Lead	11/4/2014	20:58	29.710221	-98.129534	Comal	Upper Old Channel
HCS250 Lead	11/4/2014	21:03	29.709491	-98.122578	Comal	Lower Old Channel
HCS260 Lead	11/4/2014	21:12	29.708007	-98.127301	Comal	New Channel
HCS270 Lead	11/4/2014	21:20	29.704014	-98.115791	Comal	Comal River above confluence
HCS210 Peak	11/5/2014	1:10	29.72043	-98.12525	Comal	Upper Springs
HCS240 Peak	11/5/2014	1:25	29.710221	-98.129534	Comal	Upper Old Channel
HCS250 Peak	11/5/2014	1:29	29.709491	-98.122578	Comal	Lower Old Channel
HCS260 Peak	11/5/2014	1:37	29.708007	-98.127301	Comal	New Channel
HCS270 Peak	11/5/2014	1:51	29.704014	-98.115791	Comal	Comal River above confluence
HCS210 Trail	11/5/2014	6:58	29.72043	-98.12525	Comal	Upper Springs
HCS240 Trail	11/5/2014	7:17	29.710221	-98.129534	Comal	Upper Old Channel
HCS250 Trail	11/5/2014	7:22	29.709491	-98.122578	Comal	Lower Old Channel
HCS260 Trail	11/5/2014	7:31	29.708007	-98.127301	Comal	New Channel
FDHCS260 Trail	11/5/2014	7:31	29.708007	-98.127301	Comal	New Channel
HCS270 Trail	11/5/2014	7:57	29.704014	-98.115791	Comal	Comal River above confluence
FDHCS270 Trail	11/5/2014	7:57	29.704014	-98.115791	Comal	Comal River above confluence
TB8	11/5/2014	NA	NA	NA	Comal	VOC Blank

COMAL SEDIMENT

Location / Sample Name	Date Sampled	Time Sampled	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HCS310	6/26/2014	12:00	29.72043	-98.12525	Comal	Upper Springs
HCS320	6/26/2014	13:00	29.718084	-98.131644	Comal	Upper Landa Lake
HCS330	6/25/2014	14:30	29.709566	-98.133749	Comal	Lower Landa Lake
HCS340	6/25/2014	17:10	29.710221	-98.129534	Comal	Upper Old Channel
HCS360	6/25/2014	14:07	29.707454	-98.122762	Comal	USGS Gauge
FDHCS360	6/25/2014	18:00	29.707454	-98.122762	Comal	USGS Gauge
EB1	7/1/2014	11:40	NA	NA	Comal	Equipment Blank

COMAL PDS

Location / Sample Name	Installed	Retrieved	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HCS410	3/24/2014 9:05	4/29/2014 9:45	29.72043	-98.12525	Comal	Upper Springs
HCS420	3/24/2014 10:30	-	29.718084	-98.131644	Comal	Upper Landa Lake
HCS430	3/24/2014	4/29/2014 12:00	29.709566	-98.133749	Comal	Lower Landa Lake
HCS440	3/24/2014	-	29.710221	-98.129534	Comal	Upper Old Channel
HCS460	3/24/2014	-	29.707454	-98.122762	Comal	USGS Gauge
TB	3/24/2014 9:05	4/29/2014 16:48	NA	NA	Comal/ Hays	Trip Blank
HCS410	4/29/2014	5/12/2014 17:16	29.72043	-98.12525	Comal	Upper Springs
HCS420	4/29/2014	-	29.718084	-98.131644	Comal	Upper Landa Lake
HCS430	4/29/2014	5/12/2014 18:49	29.709566	-98.133749	Comal	Lower Landa Lake
HCS440	4/29/2014	-	29.710221	-98.129534	Comal	Upper Old Channel
HCS460	4/29/2014	-	29.707454	-98.122762	Comal	USGS Gauge
HCS410	6/23/2014 11:30	7/7/2014 10:40	29.72043	-98.12525	Comal	Upper Springs
HCS420	6/23/2014 11:45	7/7/2014 17:40	29.718084	-98.131644	Comal	Upper Landa Lake
HCS430	6/23/2014 12:06	7/7/2014 11:46	29.709566	-98.133749	Comal	Lower Landa Lake
HCS440	6/23/2014 11:55	7/7/2014 11:32	29.710221	-98.129534	Comal	Upper Old Channel
FDHCS440	6/23/2014 11:55	7/7/2014 11:32	29.710221	-98.129534	Comal	Upper Old Channel

Location / Sample Name	Installed	Retrieved	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HCS460	6/23/2014 12:25	7/7/2014 12:05	29.707454	-98.122762	Comal	USGS Gauge
TB2	6/23/2014 11:30	7/7/2014 17:40	NA	NA	Comal/ Hays	Test Blank
HCS410	8/12/2014 8:35	8/26/2014 8:40	29.72043	-98.12525	Comal	Upper Springs
HCS420	8/12/2014 8:52	8/26/2014 8:49	29.718084	-98.131644	Comal	Upper Landa Lake
HCS430	8/12/2014 9:18	-	29.709566	-98.133749	Comal	Lower Landa Lake
HCS440	8/12/2014 9:06	8/26/2014 8:58	29.710221	-98.129534	Comal	Upper Old Channel
FDHCS440	8/12/2014 14:17	8/26/2014 8:58	29.710221	-98.129534	Comal	Upper Old Channel
HCS460	8/12/2014 9:35	8/26/2014 9:26	29.707454	-98.122762	Comal	USGS Gauge
TB4	8/12/2014 8:35	8/26/2014 11:26	NA	NA	Comal/ Hays	Test Blank
HCS410	10/2/2014 9:18	10/16/2014 8:00	29.72043	-98.12525	Comal	Upper Springs
HCS420	10/2/2014 9:35	10/16/2014 8:11	29.718084	-98.131644	Comal	Upper Landa Lake
HCS430	10/2/2014 9:55	10/16/2014 8:34	29.709566	-98.133749	Comal	Lower Landa Lake
HCS440	10/2/2014 9:45	10/16/2014 8:17	29.710221	-98.129534	Comal	Upper Old Channel
FDHCS440	10/2/2014 9:45	10/16/2014 8:17	29.710221	-98.129534	Comal	Upper Old Channel
HCS460	10/2/2014 10:15	10/16/2014 8:45	29.707454	-98.122762	Comal	USGS Gauge
TB7	10/2/2014 9:18	10/16/2014 10:20	NA	NA	Comal/ Hays	Test Blank
HCS410	12/1/2014 10:08	12/15/2014 12:20	29.72043	-98.12525	Comal	Upper Springs
HCS420	12/1/2014 10:19	12/15/2014 12:37	29.718084	-98.131644	Comal	Upper Landa Lake
HCS430	12/1/2014 13:45	12/15/2014 13:45	29.709566	-98.133749	Comal	Lower Landa Lake
HCS440	12/1/2014 10:30	12/15/2014 10:30	29.710221	-98.129534	Comal	Upper Old Channel
FDHCS440	12/1/2014 10:30	12/15/2014 10:30	29.710221	-98.129534	Comal	Upper Old Channel
HCS460	12/1/2014 11:03	12/15/2014 13:14	29.707454	-98.122762	Comal	USGS Gauge
TB9	12/1/2014 10:08	12/15/2014 15:16	NA	NA	Comal/ Hays	Test Blank

SAN MARCOS SURFACE WATER

Location / Sample Name	Date Sampled	Time Sampled	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HSM 110	3/25/2014	15:20	29.893566	-97.927631	Hays	Sink Creek
HSM 120	3/25/2014	16:00	29.890258	-97.934568	Hays	Spring Lake
HSM 130	3/25/2014	16:40	29.889831	-97.935957	Hays	Sessoms Creek
HSM 140	3/25/2014	17:15	29.883955	-97.935295	Hays	City Park
HSM 150	3/25/2014	17:51	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 160	3/25/2014	18:29	29.87469	-97.931603	Hays	1-35 Reach
HSM 170	3/25/2014	19:00	29.868809	-97.930378	Hays	Capes Dam
HSM 110	4/29/2014	13:40	29.893566	-97.927631	Hays	Sink Creek
HSM 120	4/29/2014	14:15	29.890258	-97.934568	Hays	Spring Lake
HSM 130	4/29/2014	15:07	29.889831	-97.935957	Hays	Sessoms Creek
HSM 140	4/29/2014	15:52	29.883955	-97.935295	Hays	City Park
HSM 150	4/29/2014	16:04	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 160	4/29/2014	16:48	29.87469	-97.931603	Hays	1-35 Reach
HSM 170	4/29/2014	17:30	29.868809	-97.930378	Hays	Capes Dam
FDHSM 170	4/29/2014	17:30	29.868809	-97.930378	Hays	Capes Dam
HSM 110	9/26/2014	10:13	29.893566	-97.927631	Hays	Sink Creek
HSM 120	9/26/2014	11:15	29.890258	-97.934568	Hays	Spring Lake
HSM 130	9/26/2014	10:55	29.889831	-97.935957	Hays	Sessoms Creek
HSM 140	9/26/2014	11:57	29.883955	-97.935295	Hays	City Park
HSM 150	9/26/2014	12:25	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 160	9/26/2014	13:22	29.87469	-97.931603	Hays	1-35 Reach
FDHSM 160	9/26/2014	13:22	29.87469	-97.931603	Hays	1-35 Reach
HSM 170	9/26/2014	13:49	29.868809	-97.930378	Hays	Capes Dam

SAN MARCOS STORM WATER

Location / Sample Name	Date Sampled	Time Sampled	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HSM210 Lead	5/12/2014	22:55	29.893566	-97.927631	Hays	Sink Creek
HSM230 Lead	5/12/2014	23:10	29.889831	-97.935957	Hays	Sessoms Creek
HSM231 Lead	5/13/2014	0:15	29.886254	-97.935891	Hays	Dog Beach Outflow
HSM240 Lead	5/13/2014	0:45	29.884145	-97.935554	Hays	City Park
HSM250 Lead	5/12/2014	22:48	29.882213	-97.934867	Hays	Purgatory Creek
HSM260 Lead	5/12/2014	23:11	29.87484	-97.931713	Hays	1-35 Reach
HSM270 Lead	5/12/2014	23:39	29.868809	-97.930378	Hays	Capes Dam
EB Beta	5/13/2014	2:15	NA	NA	Hays	Equipment Blank
EB Pole	5/13/2014	2:15	NA	NA	Hays	Equipment Blank
HSM210 Peak	5/13/2014	2:10	29.893566	-97.927631	Hays	Sink Creek

Location / Sample Name	Date Sampled	Time Sampled	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HSM230 Peak	5/13/2014	2:40	29.889831	-97.935957	Hays	Sessoms Creek
HSM231 Peak	5/13/2014	1:43	29.886254	-97.935891	Hays	Dog Beach Outflow
HSM240 Peak	5/13/2014	2:52	29.884145	-97.935554	Hays	City Park
HSM250 Peak	5/13/2014	2:06	29.882213	-97.934867	Hays	Purgatory Creek
HSM260 Peak	5/13/2014	2:25	29.87484	-97.931713	Hays	1-35 Reach
HSM270 Peak	5/13/2014	2:58	29.868809	-97.930378	Hays	Capes Dam
HSM210 Trail	5/13/2014	8:35	29.893566	-97.927631	Hays	Sink Creek
HSM230 Trail	5/13/2014	9:01	29.889831	-97.935957	Hays	Sessoms Creek
HSM231 Trail	5/13/2014	9:20	29.886254	-97.935891	Hays	Dog Beach Outflow
HSM240 Trail	5/13/2014	9:45	29.884145	-97.935554	Hays	City Park
HSM250 Trail	5/13/2014	10:18	29.882213	-97.934867	Hays	Purgatory Creek
HSM260 Trail	5/13/2014	10:34	29.87484	-97.931713	Hays	1-35 Reach
HSM270 Trail	5/13/2014	10:58	29.868809	-97.930378	Hays	Capes Dam
TB HCP	5/14/2014	16:00	NA	NA	Hays	Equipment Blank
HSM210 Lead	7/15/2014	21:24	29.893566	-97.927631	Hays	Sink Creek
HSM230 Lead	7/15/2014	21:49	29.889831	-97.935957	Hays	Sessoms Creek
HSM231 Lead	7/15/2014	21:05	29.886254	-97.935891	Hays	Dog Beach Outflow
HSM240 Lead	7/15/2014	22:10	29.884145	-97.935554	Hays	City Park
HSM250 Lead	7/15/2014	21:22	29.882213	-97.934867	Hays	Purgatory Creek
HSM260 Lead	7/15/2014	21:40	29.87484	-97.931713	Hays	1-35 Reach
HSM270 Lead	7/15/2014	21:55	29.868809	-97.930378	Hays	Capes Dam
HSM210 Peak	7/15/2014	22:50	29.893566	-97.927631	Hays	Sink Creek
HSM230 Peak	7/15/2014	23:13	29.889831	-97.935957	Hays	Sessoms Creek
HSM231 Peak	7/15/2014	22:50	29.886254	-97.935891	Hays	Dog Beach Outflow
HSM240 Peak	7/15/2014	23:36	29.884145	-97.935554	Hays	City Park
HSM250 Peak	7/15/2014	23:30	29.882213	-97.934867	Hays	Purgatory Creek
HSM260 Peak	7/15/2014	23:35	29.87484	-97.931713	Hays	1-35 Reach
HSM270 Peak	7/15/2014	23:40	29.868809	-97.930378	Hays	Capes Dam
HSM210 Trail	7/16/2014	3:46	29.893566	-97.927631	Hays	Sink Creek
FDHSM210 Trail	7/16/2014	3:46	29.893566	-97.927631	Hays	Sink Creek
HSM230 Trail	7/16/2014	4:15	29.889831	-97.935957	Hays	Sessoms Creek
FDHSM230 Trail	7/16/2014	4:15	29.889831	-97.935957	Hays	Sessoms Creek
HSM231 Trail	7/16/2014	3:45	29.886254	-97.935891	Hays	Dog Beach Outflow
FDHSM231 Trail	7/16/2014	3:45	29.886254	-97.935891	Hays	Dog Beach Outflow
HSM240 Trail	7/16/2014	4:51	29.884145	-97.935554	Hays	City Park
HSM250 Trail	7/16/2014	4:15	29.882213	-97.934867	Hays	Purgatory Creek
HSM260 Trail	7/16/2014	4:40	29.87484	-97.931713	Hays	1-35 Reach
HSM270 Trail	7/16/2014	5:00	29.868809	-97.930378	Hays	Capes Dam
TB3	7/16/2014	5:00	NA	NA	Hays	VOC Blank

SAN MARCOS SEDIMENT

Location / Sample Name	Date Sampled	Time Sampled	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HSM 310	6/30/2014	11:00	29.893566	-97.927631	Hays	Sink Creek
HSM 320	6/30/2014	15:20	29.890258	-97.934568	Hays	Spring Lake
HSM 330	6/30/2014	16:00	29.889831	-97.935957	Hays	Sessoms Creek
HSM 340	6/26/2014	16:30	29.883955	-97.935295	Hays	City Park
HSM 350	6/30/2014	12:00	29.880016	-97.932977	Hays	Rio Vista Dam
FDHSM 350	6/30/2014	12:15	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 360	6/30/2014	14:20	29.87469	-97.931603	Hays	1-35 Reach
HSM 370	6/26/2014	15:15	29.868809	-97.930378	Hays	Capes Dam

SAN MARCOS PDS

Location / Sample Name	Installed	Retrieved	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HSM 410	3/24/2014 13:10	4/29/2014 13:40	29.893566	-97.927631	Hays	Sink Creek
HSM 420	3/24/2014 13:21	4/29/2014 14:15	29.890258	-97.934568	Hays	Spring Lake
HSM 430	3/24/2014	-	29.889831	-97.935957	Hays	Sessoms Creek
HSM 440	3/24/2014	-	29.883955	-97.935295	Hays	City Park
HSM 450	3/24/2014 15:59	4/29/2014 15:59	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 460	3/24/2014 16:08	4/29/2014 16:08	29.87469	-97.931603	Hays	1-35 Reach
HSM 470	3/24/2014	-	29.868809	-97.930378	Hays	Capes Dam
HSM 410	4/29/2014	5/12/2014 18:49	29.893566	-97.927631	Hays	Sink Creek
HSM 420	4/29/2014 14:15	-	29.890258	-97.934568	Hays	Spring Lake
HSM 430	4/29/2014	-	29.889831	-97.935957	Hays	Sessoms Creek
HSM 440	4/29/2014	-	29.883955	-97.935295	Hays	City Park
HSM 450	4/29/2014	-	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 460	4/29/2014	5/12/2014 19:20	29.87469	-97.931603	Hays	1-35 Reach
HSM 470	4/29/2014	-	29.868809	-97.930378	Hays	Capes Dam
HSM 410	6/23/2014 13:55	7/7/2014 14:05	29.893566	-97.927631	Hays	Sink Creek
HSM 420	6/23/2014 14:01	7/7/2014 16:05	29.890258	-97.934568	Hays	Spring Lake
HSM 430	6/23/2014 14:36	7/7/2014 14:23	29.889831	-97.935957	Hays	Sessoms Creek
FDHSM 430	6/23/2014 14:36	7/7/2014 14:23	29.889831	-97.935957	Hays	Sessoms Creek
HSM 440	6/23/2014 15:07	7/7/2014 14:40	29.883955	-97.935295	Hays	City Park
HSM 450	6/23/2014 15:40	7/7/2014 14:51	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 460	6/23/2014 16:00	7/7/2014 15:07	29.87469	-97.931603	Hays	1-35 Reach
HSM 470	6/23/2014 16:15	7/7/2014 13:41	29.868809	-97.930378	Hays	Capes Dam
HSM 410	8/12/2014 10:29	8/26/2014 10:14	29.893566	-97.927631	Hays	Sink Creek
HSM 420	8/12/2014 10:39	8/26/2014 10:23	29.890258	-97.934568	Hays	Spring Lake

Location / Sample Name	Installed	Retrieved	Latitude (dd)	Longitude (dd)	County	Location Generic Name
HSM 430	8/12/2014 10:50	8/26/2014 10:32	29.889831	-97.935957	Hays	Sessoms Creek
FDHSM 430	8/12/2014 13:39	8/26/2014 10:32	29.889831	-97.935957	Hays	Sessoms Creek
HSM 440	8/12/2014 11:05	8/26/2014 10:47	29.883955	-97.935295	Hays	City Park
HSM 450	8/12/2014 11:18	8/26/2014 11:00	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 460	8/12/2014 11:30	8/26/2014 11:09	29.87469	-97.931603	Hays	1-35 Reach
HSM 470	8/12/2014 11:44	8/26/2014 11:26	29.868809	-97.930378	Hays	Capes Dam
HSM 410	10/2/2014 10:58	10/16/2014 9:25	29.893566	-97.927631	Hays	Sink Creek
HSM 420	10/2/2014 11:16	10/16/2014 9:31	29.890258	-97.934568	Hays	Spring Lake
HSM 430	10/2/2014 11:29	10/16/2014 9:35	29.889831	-97.935957	Hays	Sessoms Creek
FDHSM 430	10/2/2014 11:29	10/16/2014 9:35	29.889831	-97.935957	Hays	Sessoms Creek
HSM 440	10/2/2014 11:39	10/16/2014 9:45	29.883955	-97.935295	Hays	City Park
HSM 450	10/2/2014 11:51	10/16/2014 9:59	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 460	10/2/2014 12:05	10/16/2014 10:08	29.87469	-97.931603	Hays	1-35 Reach
HSM 470	10/2/2014 12:13	10/16/2014 10:20	29.868809	-97.930378	Hays	Capes Dam
HSM 410	12/1/2014 11:45	12/15/2014 14:17	29.893566	-97.927631	Hays	Sink Creek
HSM 420	12/1/2014 12:04	12/15/2014 14:30	29.890258	-97.934568	Hays	Spring Lake
HSM 430	12/1/2014 12:11	12/15/2014 14:40	29.889831	-97.935957	Hays	Sessoms Creek
FDHSM 430	12/1/2014 12:11	12/15/2014 14:40	29.889831	-97.935957	Hays	Sessoms Creek
HSM 440	12/1/2014 12:17	12/15/2014 14:48	29.883955	-97.935295	Hays	City Park
HSM 450	12/1/2014 12:27	12/15/2014 15:01	29.880016	-97.932977	Hays	Rio Vista Dam
HSM 460	12/1/2014 12:56	12/15/2014 15:09	29.87469	-97.931603	Hays	1-35 Reach
HSM 470	12/1/2014 13:04	12/15/2014 15:16	29.868809	-97.930378	Hays	Capes Dam