Edwards Aquifer Habitat Conservation Plan Expanded Water Quality Monitoring Draft Report

May 2021

EXECUTIVE SUMMARY

The Edwards Aquifer Habitat Conservation Plan (EAHCP 2016) Expanded Water Quality Monitoring 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 *Report of the 2016 Expanded Water Quality Monitoring Program Work Group and Report of the 2016 Biological Monitoring Program Work Group and Report of the 2016 Biological Monitoring Program Work Group (EAHCP 2016).* In years 2013 through 2016, the program included surface water (base flow) sampling, sediment sampling, real-time instrument (RTI) water quality monitoring, and stormwater sampling. Passive diffusion sampling was not conducted in 2013 but has been conducted in subsequent years. 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 Springs and San Marcos Springs. Spring flow rates remained above minimum flow rates of 30 cubic feet per second (cfs) at Comal Springs and above 50 cfs at San Marcos Springs from 2013 to 2016; therefore, the groundwater sampling element was not conducted.

In 2016, the EAHCP Program Manager assembled an Expanded Water Quality Monitoring Program Work Group (Work Group) composed of representatives from throughout the Edwards Aquifer Region. The charge of the Work Group was to carry out a holistic review of the existing program and to evaluate possible changes based on the recommendations of the National Academy of Sciences (NAS), the NAS Work Group, the input of the Science Committee, the permittees, and subject matter experts. The Work Group prepared a final report that included the following changes to the program:

- Removing surface water (base flow) monitoring
- Reducing sediment monitoring to once every other year, to be conducted in even years
- Adding one real-time monitoring station per spring system
- Reducing stormwater monitoring to one sampling event per year, with sampling for Integrated Pest Management Plan chemicals plus atrazine in odd years, and the full suite of chemicals in even years
- Continuing passive diffusion sampler (PDS) sampling but adding a pharmaceutical and personal care product (PPCP) membrane to the farthest downstream PDS site in each system
- Removing groundwater monitoring
- Adding biotic tissue (e.g., fish tissue) sampling in odd-numbered years

The Edwards Aquifer Authority contracted with SWCA Environmental Consultants (SWCA) to execute the expanded sampling program through 2014 - 2020, with the exception of RTI water quality monitoring and biotic tissue sampling.

The Comal Springs complex has five sample locations, 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. The San Marcos Springs complex has seven sample locations, beginning at Sink Creek upstream of the headwaters of Spring Lake on the north end of the system and ending downstream of Capes Dam on the south end of the system.

SWCA collected sediment samples in June 2020 from both the Comal Springs and San Marcos Springs systems. No analytes exceeded the probable effect concentration (PEC) to benthic organism values for volatile organic compounds (VOCs), pesticides, herbicides, polychlorinated biphenyls (PCBs), or metals. Three sediment samples from the Comal Springs complex had concentrations of five semi-volatile organic compound (SVOC) constituents above the PEC values. Two sediment samples from the Comal Springs complex had concentrations PEC value. Four SVOC analytes were detected in three samples that exceeded PEC values. Two SVOC analytes were detected in two samples that exceeded PEC values. SWCA conducted one stormwater event in 2020 at the Comal Springs complex on May 16, 2020. SWCA collected samples at five locations: HCS210, HCS240, HCS250, HCS260, and HCS270. SWCA also completed a stormwater sampling event at the San Marcos Springs complex on October 29, 2020. The laboratory results from the San Marcos sampling event are pending.

In the Comal Springs complex, no stormwater sample analyte concentrations exceeded the Texas Commission on Environmental Quality (TCEQ) surface water standards for contact recreation and ecological health for VOCs, pesticides, herbicides, or PCBs (2020). Pentachlorophenol was detected in two samples at concentrations above the TCEQ Acute Surface Water Benchmark (SWB) and the Chronic SWB for aquatic life. Pentachlorophenol also exceeded the TCEQ (2006) Contact Recreation Water Protective Concentrations above the TCEQ Chronic SWB for aquatic life. Lead concentrations exceeded Chronic SWB for aquatic life in one sample. Zinc concentrations exceeded the Acute SWB for aquatic life in one sample. Metals are naturally occurring in soil, sediment, groundwater, and surface water. The water samples for metals analyses were filtered to reduce the potential for sediment impacting the laboratory results; however, the turbidity of the stormwater samples may have contributed to the concentrations of metals detected.

PDSs were deployed in each spring complex for 2-week periods, six times every other month during the year. Polar organic chemical integrative samplers, which are PDSs used for PPCP testing, were deployed at the most downstream sample sites (HCS460 and HSM470) in each spring complex for 1-month periods, six times during the year. PDS samples commonly detected one analyte, tetrachloroethene, in various locations throughout the Comal Springs and San Marcos Springs complexes. Total petroleum hydrocarbon was detected in one sample in the Comal Springs complex and in one sample in the San Marcos Springs complex. Chloroform was detected in August in one Comal Springs complex sample location. The concentrations of these analytes and other less-frequently detected analytes do not exceed the TCEQ surface water standards for contact recreation and ecological health.

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1.0 INTRODUCTION

The Edwards Aquifer Authority (EAA) and its predecessor agency, the Edwards Underground Water District, in cooperation with the U.S. Geological Survey (USGS) and the Texas Water Development Board have maintained a water quality sampling program since 1968. The EAA has used the analyses of these data to assess aquifer water quality. This sampling program has involved the analyses of a broad spectrum of parameters in wells, springs, and streams across the region. The EAA's existing sampling program was expanded with the adoption of the Edwards Aquifer Habitat Conservation Plan (EAHCP 2016) to include collecting additional samples and sample types in the immediate vicinity of Comal Springs and San Marcos Springs. The expanded water quality sampling program was developed in accordance with the directives of the EAHCP (2016) 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 *Report of the 2016 Expanded Water Quality Monitoring Program Work Group and Report of the 2016 Expanded Water Quality Monitoring Program Work Group and Report of the 2016 Biological Monitoring Program Work Group (EAHCP 2016), which herein is referred to as the Work Group Report and is included in Appendix A of this report.*

In years 2013 through 2016, the program included surface water (base flow) sampling, sediment sampling, real-time instrument (RTI) water quality monitoring, and stormwater sampling. Passive diffusion sampling was not conducted in 2013 but has been conducted in subsequent years. 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 Springs and San Marcos Springs. Spring flow rates remained above minimum flow rates of 30 cubic feet per second (cfs) at Comal Springs and above 50 cfs at San Marcos Springs from 2013 to 2016; therefore, the groundwater sampling element was not conducted.

In 2016, the EAHCP Program Manager assembled an Expanded Water Quality Monitoring Program Work Group (Work Group) composed of representatives from throughout the Edwards Aquifer Region. The charge of the Work Group was to carry out a holistic review of the existing program and to evaluate possible changes based on the recommendations of the National Academy of Sciences (NAS), the NAS Work Group, the input of the Science Committee, the permittees, and subject matter experts. The Work Group prepared a final report that included the following changes to the program:

- Removing surface water (base flow) monitoring
- Reducing sediment monitoring to once every other year, to be conducted in even years
- Adding one real-time monitoring station per spring system
- Reducing stormwater monitoring to one sampling event per year, with sampling for Integrated Pest Management Plan chemicals plus atrazine in odd years, and the full suite of chemicals in even years
- Continuing passive diffusion sampler (PDS) sampling but adding a pharmaceutical and personal care product (PPCP) membrane to the farthest downstream PDS site in each system
- Removing groundwater monitoring
- Adding biotic tissue (e.g., fish tissue) sampling in odd-numbered years

The EAA contracted with SWCA Environmental Consultants (SWCA) to execute the expanded sampling program through 2014- 2020, with the exception of RTI water quality monitoring and biotic tissue sampling.

Prior to the implementation of the EAHCP (2016), 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 new parameters. This report presents the stormwater, sediment, passive diffusion sampling, and polar organic chemical integrative sampler (POCIS) data collected by SWCA in 2020. This data set represents the seventh year of the program. Table 1 summarizes the analytical parameters by sample type.

For 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 and stormwater sample locations for Comal Springs and San Marcos Springs is shown in Figures 1 and 2.

Analytical Parameter	Stormwater Samples	Sediment Samples	PDS [†]	POCIS [‡]
Volatile Organic Compounds (VOCs)	Yes	Yes	Yes	No
Semi-volatile Organic Compounds (SVOCs)	Yes	Yes	Yes	No
Organochlorine Pesticides	Yes	Yes	Yes	No
Polychlorinated Biphenyls (PCBs)	Yes	Yes	No	No
Organophosphorus Pesticides	Yes	Yes	No	No
Herbicides	Yes	Yes	No	No
Pharmaceuticals and Personal Care Products	No	No	No	Yes
Metals (Al, Sb, As, Ba, Be, Cd, Cr [total], Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Tl, and Zn)	Yes	Yes	No	No
General water quality parameters (GWQP), total alkalinity (as CaCO3), bicarbonate alkalinity (as CaCO3), carbonate alkalinity (as CaCO3); Cl, Br, NO3, SO4, Fl, pH, total dissolved solids (TDS), total suspended solids (TSS), Ca, Mg, Na, K, Si, Sr, CO3,	Yes	No TDS or TSS	No	No
Phosphorus (total)	Yes	Yes	No	No
Total Organic Carbon (TOC),	Yes	Yes	No	No
Dissolved Organic Carbon (DOC)	Yes	No	No	No
Total Kjeldahl Nitrogen (TKN)	Yes	No	No	No
Bacteria (<i>E. coli</i>)	Yes	No	No	No
Field Parameters (dissolved oxygen [DO], pH, Conductivity, Turbidity, Temperature)	Yes	No	No	No
Caffeine	Yes	No	No	Yes

Table 1. Listing of Analytical Parameters by Sample Type

[†] Passive diffusion samplers (PDSs) samples are analyzed for a modified set of VOCs, SVOCs, and organochlorine pesticides.

* Polar organic chemical integrative samplers (POCIS) samples are analyzed for pharmaceuticals and personal care products.

Figure 1. EAHCP Expanded Water Quality Monitoring Program, Comal Springs and River







1.1 <u>Sediment Samples</u>

Collection of sediment samples within each spring complex was included in the program to help ascertain potential effects on listed species via direct or indirect exposure to sediments. Specifically, five sediment samples were collected from the Comal Springs area and seven locations were sampled within the San Marcos area. In the first two years of the program, sediment samples were collected from the sediment surface to approximately 18 inches below the surface. The EAHCP (2016) Work Plan (Appendix A) reduced the sampling depth to 3 inches below the surface beginning in 2015. Samples were analyzed for the parameters listed in Table 1.

SWCA collected sediment samples as close to each associated surface water sample location as possible. However, for some 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 B 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). Analytical results with a concentration below the TEC are predicted to be nontoxic (on sediment-dwelling organisms), whereas 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 nontoxic. Additional guidelines for chemicals of concern that were not included in MacDonald et al. (2000) were taken from *Conducting Ecological Risk Assessments at Remediation Sites in Texas* (Texas Commission on Environmental Quality [TCEQ] 2014a) and *Guidance for Assessing and Reporting Surface Water Quality in Texas* (TCEQ 2012). Although 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 interests.

1.2 <u>Stormwater Samples</u>

SWCA collected stormwater samples at five Comal Springs locations. As of the date of this report, laboratory analyses are pending from samples collected on October 28, 2020, at seven San Marcos Springs locations. The EAA adopted stormwater sample collection 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. SWCA collected stormwater samples in association with various surface water inputs along each spring complex within the study area. Appendices B and C of this report present the details of each stormwater sample location and any deviations from the EAHCP (2016) Work Plan (Appendix A). Stormwater samples were analyzed for the same parameters as surface water (base flow) samples, as outlined in Table 1.

SWCA collected stormwater samples at three points across the storm hydrograph for the Comal Springs and San Marcos Springs complex. 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 data from the RTIs was available on 15-minute intervals and provided more timely information. Automated sample collection equipment was not utilized for stormwater sample collection due to sample volume, preservation, and analysis limitations. Therefore, sampling was conducted manually. The Comal Springs and San Marcos Springs complexes were each sampled once for stormwater events during calendar year 2020, in accordance with the EAHCP (2016) Work Plan (Appendix A).

Standards for surface water quality vary depending on type of use. For this report, stormwater results are compared with TCEQ (2006) Contact Recreation Water Protective Concentration Levels (PCLs) and with TCEQ (2018a) SWBs for freshwater organisms. The SWBs were developed for acute and chronic exposures. 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.

1.3 <u>Surface Water Passive Diffusion Samples</u>

SWCA deployed Amplified Geochemical Imaging (AGI) PDSs in both spring complexes to measure trace organic constituents. Samplers consisted 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 allowed 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.

SWCA deployed PDSs to each of the 12 sample sites for 2-week periods in February, April, June, August, October, and December 2020. Sample points coincided with surface water collection points, unless prevented by field conditions, and any deviations are discussed in Appendix B.

For this report, PDS results are compared with TCEQ (2006) Contact Recreation Water PCLs and with TCEQ (2018a) SWBs for freshwater organisms. The SWBs were developed for acute and chronic exposures.

1.4 <u>Polar Organic Chemical Integrative Samples</u>

SWCA deployed Environmental Sampling Technologies (EST) POCISs at HCS460 and HSM470 to evaluate PPCP constituents. POCISs are composed of two sheets of microporous (0.1-micrometer [µm] pore size) polyethersulfone membranes encasing a solid phase sorbent (Oasis Hydrophilic-Lipophilic Balance [HLB]), which retains sampled chemicals. The Oasis HLB is a universal solid-phase extraction sorbent widely used for sampling a large range of hydrophilic to lipophilic organic chemicals from water. The high water solubility of polar organic chemicals makes their extraction and detection difficult using standard sampling and analytical techniques. POCISs provide reproducible methods for the concentration of polar organic chemicals in the parts-per-trillion to parts-per-quadrillion range. The POCIS enables estimation of the aqueous exposure of aquatic organism to dissolved polar organic chemicals and permits determination of their time-weighted average concentration in water over extended periods.

SWCA installed three POCISs inside stainless-steel carriers at each sample location. The POCISs were prepared and provided by EST. Following collection, SWCA returned the POCIS samplers to EST for elution. EST then shipped the eluted samples to Weck Laboratories, Inc., for PPCP analyses.

Due to human tampering of deployment devices, SWCA began using two colanders in 2019 to serve as an encasement to hold the POCIS sampler. The colander encasement was locked onto the cable that stretches across the Comal River above the tube chute at sample location HCS460. In the San Marcos Springs complex, the colander encasement was locked onto the PDS deployment device for the first three sample events of 2020. In August 2020, SWCA began attaching the colander encasement onto a cable connected to the bridge foundation at sample location HSM470. SWCA deployed POCISs at HCS460 and HSM470 for 30-day periods in February, April, June, August, October, and December 2020.

2.0 LOGISTICS

A significant number of resources are required to accommodate the needs of the EAHCP's expanded water quality monitoring program. These resources, including sampling equipment, safety gear, trained staff, and sampling schedules, are all key components to the program. Additionally, the program requires developing sampling strategies and planning each sampling event to ensure that resources are used efficiently, and that collection is completed within the scheduled timeframe. The strategies must account for the unpredictable nature of storm events. Below is a short synopsis of events and tasks undertaken to conduct the EAHCP (2016) sampling program.

2.1 <u>Sample Location Detail</u>

Details of individual sample locations for Comal Springs and San Marcos Springs areas are provided in Appendix C.

2.2 <u>Sediment Sampling Program</u>

SWCA acquired sediment sampling equipment in 2014 and purchased an additional core sampler extension handle in 2016 to accommodate sampling at site HCS330, because the water depth was greater than in previous years. In May 2020, SWCA staff acquired sample containers from the contract laboratory for the June 2020 sampling event.

2.3 <u>Stormwater Sampling Program</u>

Prior to each sampling event, SWCA acquired laboratory sample kits and prepared them for use in the field. All other sampling and safety supplies were kept stocked and ready for mobilization in the event a storm occurred. SWCA monitored weather forecasts on a regular basis to determine if teams would be mobilized for a potential sampling event. Prior to mobilization, many logistical concerns had to be addressed, including but not limited to personnel availability, safety, staging area reservation, vehicle availability, sonde rental, and laboratory notifications.

2.4 <u>Surface Water Passive Sampling Program</u>

SWCA acquired PDS from the contract laboratory approximately 2 weeks prior to each sampling event. SWCA constructed sample deployment devices in 2014 and constructed additional deployment devices in 2016, 2017, and 2018 to replace devices lost or damaged in the field. Prior to each deployment, SWCA decontaminated the devices and placed them inside clean plastic bags.

2.5 Polar Organic Chemical Integrated Sampling Program

SWCA acquired POCIS from the contract laboratory approximately 1 week prior to each sampling event. SWCA constructed sample deployment devices in January 2017 and constructed additional deployment devices in 2018 to replace devices lost or damaged in the field. In 2018, the deployment device at location HCS460 was tampered with in February and June; SWCA began using two stainless-steel colanders to serve as an encasement to hold the POCIS. The colander encasement was locked onto a chain with buoys that spans the Comal River above the tube chute. In the San Marcos Springs complex, the colander encasement was locked onto the PDS deployment device for the first three sample events. In August 2020, SWCA began locking the colander encasement onto the bridge foundation located at HSM470. Prior to each deployment, SWCA decontaminated the devices and placed them inside new plastic bags. Colander encasements were used at sample location HCS460 and HSM470 during the 2019 and 2020 sampling program.

3.0 SAMPLE COLLECTION METHODOLOGY

3.1 <u>Sediment Sampling Program</u>

SWCA collected sediment samples once in 2020 from the first 3 inches of sediment below the streambed surface at each of the 12 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 B. Sediment sample collection methods were consistent with the guidelines established in the EAA Groundwater Quality Monitoring Plan (Appendix D). SWCA collected the samples using stainless-steel hand trowels. The trowels were inserted into the sediment 3 inches, and the sample was scooped into sample containers provided by the contract laboratory. SWCA collected two 8-ounce, four 4-ounce and one 2-ounce jars for volatile organic compound (VOC) analysis at each location. Samples were composed of sediment collected at three locations at each sample point, which was combined and homogenized at the contract laboratory prior to analysis.

In compliance with the EAA Groundwater Quality Monitoring Plan (Appendix D) and consistent with the EAA practices of 2013, SWCA collected two field duplicates and one equipment blank. One field duplicate sample is required for each spring complex. SWCA collected the field duplicates at the same locations as two of the field samples, using the same methods as the field samples. One equipment blank was prepared in the laboratory of SWCA's San Antonio office. SWCA collected one equipment blank by pouring ASTM Type II Reagent Grade water over a decontaminated trowel into sample collection containers. The samples were 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 blanks were not analyzed for the following analytes: field parameters, turbidity, field alkalinity, or 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 was maintained at all times. Representative photographs of field activities are included in Appendix E.

3.2 <u>Stormwater Sampling Program</u>

Stormwater samples are designated by the EAHCP (2016) Work Plan (Appendix A) for collection once annually from each spring complex. SWCA collected stormwater samples when rainfall amounts were adequate to initiate at least a 5% rise at the respective USGS gauging locations for each spring complex. SWCA collected samples across the storm-affected stream hydrograph at the rise, peak, and recession limb of the associated stream hydrograph. As with the other sample types, SWCA sampled five locations at Comal Springs. Laboratory analysis of samples from one event at the San Marcos Springs, which included seven sample locations, is pending as of the date of this report. 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. Stream hydrograph data is only updated hourly on the USGS website. The RTI data is updated every 15 minutes, which provides greater resolution regarding the effect of the storm event on the streams and facilitates quicker sampling response times. A graph showing water quality parameters during the Comal Springs storm event is included in Appendix F.

Field parameters were collected first by inserting the sonde probe as close to the sample location as possible. SWCA used only new, disposable equipment for stormwater sampling events.

Stormwater sampling efforts conformed to the protocols outlined in the EAA Groundwater Quality Monitoring Plan (Appendix D) for sample collection, handling, and decontamination. Filtration for methods 6010B (metals), 6020 (metals), dissolved organic carbon, 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. SWCA immediately placed all samples into coolers with ice, which were picked up later by 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.

In compliance with the EAA Groundwater Quality Monitoring Plan (Appendix D), SWCA collected two field duplicates for the Comal Springs complex and three field duplicates for the San Marcos Springs complex. SWCA sampled field duplicates after collection of the parent samples and in the same manner as the field samples. No equipment blanks were collected for stormwater samples because all equipment used was new and disposable.

Analyses for field alkalinity were performed at the field staging area or at SWCA's San Antonio office. 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. Descriptions of conditions specific to each stormwater sampling event are described in Appendix F.

3.3 <u>Surface Water Passive Diffusion Samplers</u>

SWCA deployed the PDS at each of the 12 sample locations during the months of February, April, June, August, October, and December 2020. In general, PDS locations corresponded to surface water sampling points unless prevented by field conditions. Lost PDSs, human tampering, and any variations in deployment locations are discussed in Appendix B.

SWCA staff constructed deployment devices at SWCA's San Antonio office in June 2014. The deployment devices consisted of 2-inch-thick, 18-inch-diameter concrete disks, with a stainless-steel cup set approximately 1 inch deep in the center of each disk. SWCA staff formed handles 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 wet concrete to dedicate each device to a sample location. The concrete was allowed to cure, and each device was decontaminated in accordance with the EAA Groundwater Quality Monitoring Plan guidelines (Appendix D) and placed in a clean plastic bag prior to the first deployment. The same decontamination procedures were followed for subsequent sampling events. SWCA constructed additional deployment devices in 2016, 2017, and 2018 to replace devices lost or damaged in the field. A deployment device is pictured in Figure 3.





Upon arrival at the sample location, the PDS was removed from a dedicated vial and affixed inside of a second stainless-steel 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, staff simply removed the devices from the water and cut the cable ties. Staff then immediately placed the PDS back in the dedicated vial and noted the retrieval date and time. Deployment devices were secured at SWCA offices when PDSs were not deployed.

SWCA collected field duplicates as directed by the EAA Groundwater Quality Monitoring Plan (Appendix D). To collect field duplicates, a second PDS was installed inside selected deployment devices.

Field PDSs were always accompanied by trip blank samplers to monitor for VOC contamination. Deployment devices were dedicated to each sample location to avoid cross contamination and were decontaminated in accordance with the EAA Groundwater Quality Monitoring Plan guidelines (Appendix D) prior to each use. Representative photographs of field activities are included in Appendix E.

3.4 <u>Polar Organic Chemical Integrative Samplers</u>

SWCA deployed the POCIS at HCS460 and HSM470 during the months of February, April, June, August, October, and December 2020. Lost POCISs, human tampering, and any variations in deployment locations are discussed in Appendix B.

SWCA staff constructed deployment devices at SWCA's San Antonio office in 2017 and 2018. The deployment devices consisted of 2-inch-thick, 18-inch-diameter concrete disks, with a stainless-steel basket set approximately 1 inch deep in the center of the disk. SWCA staff formed handles 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 in accordance with the EAA Groundwater Quality Monitoring Plan guidelines (Appendix D) and placed in a clean plastic bag prior to the first deployment. The same decontamination procedures were followed for subsequent sampling events. SWCA constructed additional deployment devices in 2018 to replace devices lost or damaged in the field. In February 2018, the deployment device at HCS460 could not be found possibly due to human tampering. In August 2018, SWCA began using two stainless-steel colanders secured with padlocks to serve as an encasement to hold the POCIS membrane. The colander encasement was locked onto the cable above the tube chute at location HCS460. In the San Marcos Springs complex, the colander encasement was locked onto the PDS deployment device. In August 2020, SWCA began locking the colander encasement onto the concrete bridge foundation located at the HSM470 sampling location.

EST shipped the POCISs to SWCA in two sealed metal containers. Each container held three POCISs already mounted onto a carrier and sealed over argon gas. Upon arrival at each sample location, SWCA staff removed the POCIS carrier from the metal container and then inserted the carrier into a stainless-steel cylindrical basket set in the concrete deployment device. Staff then inverted a second stainless-steel basket and placed it on top of the first basket, thereby enclosing the POCIS inside the two baskets. The two baskets were secured to one another with plastic cable ties and stainless-steel wire. SWCA staff then gently lowered the device into the water. Installation date and time and POCIS identification numbers were noted in the field notebook and on the metal shipping container. To retrieve the POCISs, staff simply removed the devices from the water, cut the cable ties, and removed the stainless-steel wire. Staff then immediately placed the POCIS back in the dedicated metal shipping container and noted the retrieval date and time. Deployment devices were secured at SWCA offices when POCISs were not deployed. Representative photographs of field activities are included in Appendix E.

4.0 SAMPLE RESULTS

The following sections discuss the results from the sampling efforts related to the EAHCP (2016) sampling program. 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 sediment samples, stormwater samples, PDS, and POCIS. Laboratory reports and field parameters are provided in Appendix G of this report. SWCA staff reviewed and validated the laboratory data; the results are presented in Appendix H of

this report. Each sample location (latitude/longitude), name, and other location information are summarized in Appendix I of this report.

4.1 <u>Comal Springs Sample Results</u>

SWCA collected sediment samples at the Comal Springs complex in July 2020. Sediment laboratory results were compared with the standards developed by MacDonald et al. (2000) and TCEQ (2012, 2014a). These standards are based on the probability of a detected compound having a toxic effect on sediment-dwelling organisms, referred to as the TEC and PEC. Detections below the TEC are not considered to be toxic, whereas detections above the PEC are considered to be toxic to sediment-dwelling organisms. Detections above the TEC but less than the PEC are considered equally likely to be toxic or nontoxic. No PECs were exceeded in samples collected from the Comal Springs complex.

Stormwater events were sampled at the Comal Springs complex in May 2020. No TCEQ (2018a) SWBs for aquatic life were exceeded for VOCs, pesticides, herbicides, or polychlorinated biphenyls (PCBs). Two samples, HCS260 Lead and HCS270 Lead, exceeded the Acute SWB and the Chronic SWB for freshwater organisms for pentachlorophenol. One sample, HCS270 Lead, exceeded the PCL for pentachlorophenol. Seven samples, HCS210 Lead 1, HCS210 Lead 2, HCS210 Lead 3, HCS210 Peak, HCS210 Trail, FDHCS260 Trail, and HCS270 Trail, exceeded the Chronic SWB for freshwater organisms for aluminum. One sample, HCS210 Lead 2, exceeded the Chronic SWB for freshwater organisms for lead. The field duplicate, FDHCS260 Trail, exceeded the Acute SWB for freshwater organisms for lead. The field duplicate,

PDS sampling events were conducted at the Comal Springs complex in February, April, June, August, October, and December 2020. As of the date of this report, December PDS results are pending. Generally speaking, various VOCs and total petroleum hydrocarbons (TPH) were detected at various sample locations, but only tetrachloroethene was consistently detected. No TCEQ (2018a) SWBs for aquatic life or TCEQ (2006) Contact Recreation Water PCLs were exceeded.

POCIS sampling events were conducted at the Comal Springs and San Marcos Springs complexes in February, April, June, August, October, and December 2020. Of the 43 PPCP constituents analyzed,20 were detected in the Comal Springs complex and 19 analytes were detected in the San Marcos Springs complex. However, some of the analytes detected were also detected in the extraction blanks analyzed.

4.1.1 Comal Springs Sediment Sampling

4.1.1.1 Sediment – Volatile Organic Compounds

Three VOC compounds were detected in sediment samples collected at HCS310, HCS340, HCS360, and at four sample locations in the Comal Springs complex in 2020. Acetone was detected at three sample locations. 2-Butanone was detected at three sample locations. 4-Isopropyltoluene was detected at sample location HCS360. All the detections were "J" flagged, indicating that the detected concentrations were less than the laboratory reporting limit but greater than the method detection limit. There are no TEC or PEC values established for these compounds. The detections are summarized in Table 2.

Table 2. Sediment Samples - Volatile Organic Compound Detections - Comal Springs Complex

	Date	Acetone	2-Butanone (MEK)	4-lsopropyltoluene
Location	Collected	(µg/kg)	(µg/kg)	(µg/kg)
HCS310	7/06/2020	48.4 J	10.4 J	ND
HCS320	7/06/2020	11.8 J	ND	ND
HCS340	7/06/2020	45.5 J	7.55 J	ND
HCS360	7/06/2020	98.7 J	19.1 J	1.18 J
FDHCS360	7/06/2020	74.1 J	15.6 J	ND
TEC		NE	NE	NE
PEC		NE	NE	NE

µg/kg – Micrograms per kilogram

J – Detected concentration less than the laboratory reporting limit but greater than the detection limit.

- NE Not established
- ND Not detected
- PEC Probable effect concentration

TEC – Threshold effect concentration

4.1.1.2 Sediment – Semi-volatile Organic Compounds (SVOC)

Fourteen semi-volatile organic compound (SVOC) compounds were detected in the sediment samples collected in the Comal Springs complex in 2020. Many of these detections were "J" flagged.¹ None of the SVOC compounds were detected above PEC values.

The SVOC detections are summarized in Table 3. Polycyclic aromatic hydrocarbon (PAH) compounds exceeding the TEC are shown graphically in Figures 4–9. Total PAH detections are shown in Figure 9, where the total PAH concentrations (sum of all detected concentrations for each sample point) are compared with the TEC and PEC values for total PAH concentration established by MacDonald et al. (2000). Sample HCS360 exceeded the TEC for total PAH concentrations.

Two non-PAH compounds, bis(2-ethylhexyl)phthalate and 3&4-methylphenol were detected in the sediment samples collected in the Comal Springs complex in 2020. The compound bis(2-ethylhexyl)phthalate was detected in HCS310, HCS320, HCS340, HCS360 and FDHCS360. The compound 3&4-methylphenol was detected in one sediment sample location, HCS320. There are no TEC or PEC values established for these two non-PAH compounds. The detections are summarized in Table 3.

¹ Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

Table 3. Sediment Samples – Semi-volatile Organic Compound Detections – Comal Springs Complex

Polycyclic Aromatic Hydrocarbon (PAH) Compounds												Non-PAH Compounds				
Location	Date Collected	a) Benzo[a]anthracene (^{gg}	a) Benzo[b]fluoranthene (a)	ସ ଅଧି ଅଧି ଅଧି	a) Benzo[g,h,i]perylene (g	a) Benzo[a]pyrene	ସ୍ଥ ଜ୍ଞି ଅଧ୍ୟ Butyl Benzyl Phthalate	(mg/kg)	ଅ ଅ ଅଧି	(mg/kg	ଅ ଅ (ga (ga (ga (ga (ga (ga)) (ga)	(mg/kg)	euayy A (mg/kg)	(mg/kg)	ଇ ଅନ୍ଥ ଅନ୍ଥ	a) 84 Methylphenol 6
HCS310	7/06/2020	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.870 J B	ND
HCS320	7/06/2020	0.0487 J	0.0918 J	0.0321 J	0.0376 J	0.0792 J	ND	0.0710 J	0.0433 J	0.102 J	0.0666 J	0.0416 J	0.089 J	0.703	0.0952 J B	0.105 J
HCS330	7/06/2020	ND	0.0574 J	0.0212 J	ND	0.0541 J	ND	0.0405 J	ND	0.0604 J	0.0521 J	ND	0.0510 J	0.337	ND	ND
HCS340	7/06/2020	0.0377 J	0.0706 J	0.0303 J	0.0257 J	0.0657 J	0.0503 J	0.0498 J	ND	0.0662 J	0.0602 J	ND	0.0607 J	0.457	0.726 B	ND
HCS360	7/06/2020	0.129 J F2 F1	0.302 J F2 F1	0.116 J F2 F1	0.156 J F2 F1	0.227 J F2 F1	ND	0.210 J F2 F1	0.116 J F2 F1	0.298 J F2 F1	0.214 J F2 F1	0.0708 J F1 F2	0.255 J F1	2.089	0.276 J B F2 F1	ND
FDHCS360	7/06/2020	0.0904 J	0.223 J	0.0858 J	0.0913 J	0.150 J	ND	0.146 J	0.0588 J	0.199 J	0.118 J	0.0433 J	0.175 J	1.37	0.158 J B	ND
TEC		0.108	NE	NE	NE	0.150	NE	0.166	0.033	0.423	NE	0.204	0.195	1.61	NE	NE
PEC		1.05	NE	NE	NE	1.45	NE	1.29	NE	2.23	NE	1.170	1.520	22.8	NE	NE

J – Detection is greater than the method detection limit, but less than the reporting limit

B – Compound was found in the blank and sample

F1 – Matrix spike/matrix spike duplicate (MS/MSD) recovery exceeds control limits

F2 – MS/MSD relative percent difference exceeds control limits

mg/kg – Milligrams per kilogram

ND – Not detected

NE – Not established

PEC – Probable effect concentration

TEC – Threshold effect concentration





Figure 5. Comal Springs Benzo(a)pyrene Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values



Figure 6. Comal Springs Chrysene Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values



Figure 7. Comal Springs Dibenz(a,h)anthracene Detections Compared to Threshold Effect Concentration (TEC) Value



Figure 8. Comal Springs Pyrene Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values



Figure 9. Comal Springs Total PAH Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values



4.1.1.3 Sediment – Pesticides

Sediment samples were analyzed for both organochlorine and organophosphorus pesticides. No pesticides were detected in any of the sediment samples collected in the Comal Springs complex.

4.1.1.4 Sediment – Herbicides

Sediments were analyzed for herbicide compounds to further assess sediment quality at the Comal Springs complex. One herbicide compound was detected in one sediment sample collected from the Comal Springs complex. 2, 4-D was detected at a concentration of $6.06 \,\mu$ g/kg at HCS320. There are no TEC or PEC values established for this compound.

4.1.1.5 Sediment – Polychlorinated Biphenyls (PCBs)

Sediments were analyzed for PCB compounds to further assess sediment quality at the Comal Springs complex. One PCB compound was detected in one sediment sample collected from the Comal Springs complex; Arcelor 1260 was detected at a concentration of 0.0503 mg/kg at HCS340. The detection was "J" flagged.² There are no TEC or PEC values established for this compound.

4.1.1.6 Sediment – Metals

Many metals are naturally occurring within soil, rock, and sediment. Several metals were detected in sediment samples from the Comal Springs complex, generally at low concentrations. Metals detected above the method detection limit and subsequently evaluated in this report for potential toxic effects using the TEC or PEC standards are as follows: arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc.

Other metals detected that do not have a TEC or PEC value available were compared with TCEQ Texasspecific soil background concentrations (TSBC) for soil (TCEQ 2018b). These metals are aluminum, antimony, barium, beryllium, calcium, iron, magnesium, manganese, potassium, sodium, silicon, strontium, and thallium. Two metals, aluminum and strontium, exceeded the TSBC. One metal compound, lead, in one sediment sample collected from the Comal Springs complex, at a concentration of 53.0 mg/kg, exceeded the TEC and TSBC values. None of the metals detected exceeded PEC values.

Metal detections are listed in Table 4.

² Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

Table 4. Sediment Samples – Metal Detections – Comal Springs Complex

Location	Date Collected	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	C Calcium (mg/kg)	(mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	ung/kg)	pea aJ (mg/kg)	(mg/kg)	(mg/kg)	Zunoza Wercunz (mg/kg)	Nickel (mg/kg)	(mg/kg)	maintension (mg/kg)	uojijis (mg/kg)	(mg/kg)	۳ Thailliu (mg/kg)	uin (mg/kg)
HCS310	7/06/2020	2,140	ND	1.88 J	15.7	ND	299,000	0.390 J	4.26 J	3.03 J	3,020	6.11	1,810	81.5	0.0200 J	3.34 J	447 J	ND	1,610	183	ND	21.4 J
HCS320	7/06/2020	1,170	ND	2.21 J	12.4	0.162 J	146,000	0.271 J	3.93 J	4.96 J	2,560	2.74 J	1,160	38.5	ND	2.64 J	249 J	124 J	1,160	110	ND	12.2 J
HCS330	7/06/2020	6,340	ND	4.03 J	28.6	0.557 J	62,400	0.445 J	10.1	5.60 J	6,440	5.58	2,130	83.8	ND	8.03 J	1,080	ND	989	103	ND	20.7
HCS340	7/06/2020	3,220	ND	2.72 J	24.9	ND	120,000	0.383 J	6.17 J	6.06 J	3,100	53.0	1,610	65.1	0.0598 J	4.79 J	626 J	ND	1,690	131	ND	18.4
HCS360	7/06/2020	5,110	ND	2.20 J	35.2	0.234 J	118,000	0.412 J	8.40	6.38 J	4,420	10.1	1,830	74.3	0.0219 J	5.34 J	857	135 J	1,470	164	ND	27.6
FDHCS360	7/06/2020	4,890	ND	2.56 J	33.5	0.293 J	128,000	0.425 J	9.03	6.49 J	4,250	14.2	1,850	78.7	0.0328 J	5.59 J	794	117 J	1,910	155	ND	27.0
TEC		NE	NE	9.79	NE	NE	NE	0.99	43.4	31.6	NE	35.8	NE	NE	0.18	22.7	NE	NE	NE	NE	NE	121
PEC		NE	NE	33	NE	NE	NE	4.98	111	149	NE	128	NE	NE	1.06	48.6	NE	NE	NE	NE	NE	459
TSBC		30,000	1	5.9	300	1.5	NE	NE	NE	15	15,000	15	NE	300	0.04	10	NE	NE	NE	100	NE	30

B – Compound was found in the laboratory blank and sample

J – Detection is greater than the method detection limit, but less than the reporting limit

mg/kg – Milligrams per kilogram

ND – Not detected

NE – Not established

PEC – Probable effect concentration

TEC – Threshold effect concentration

TSBC – Texas-specific background concentration

4.1.2 Comal Springs Stormwater Sampling

Stormwater samples were collected during one storm event at the Comal Springs complex. SWCA sampled the event according to the guidelines in the EAHCP (2016) Work Plan (Appendix A). The event occurred on May 16, 2020. Total rainfall for the May 2020 event was approximately 1.0 to 1.5 inches (National Oceanic and Atmospheric Administration 2020). Streamflow measurements from the USGS gauge increased from approximately 265 cfs to a peak of 280 cfs (USGS 2020). That is an increase of 5.7%, which qualifies the rain event for sampling. Rain fell in the area in the early morning of Saturday, May 16, 2020. The first lead samples were collected beginning at approximately 03:30. The peak samples were collected around 06:00. The trail samples were collected as the river recovered around 09:00, as a second large wave of thunderstorms approached.

E coli samples were placed on ice and transported to San Antonio Testing Laboratory on Saturday, May 16, 2020. Due to the timing of the storm event on a Saturday and Eurofins' working hours, it was not possible to deliver samples the same day of collection. Therefore, samples were brought back to the SWCA San Antonio office and were packaged for transport the next business day, Monday, May 18, 2020. The samples were successfully picked up by Eurofins personnel and delivered to their laboratory located in Corpus Christi, Texas, on Monday, May 18, 2020.

4.1.2.1 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 (MPN) 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 Texas Administrative Code 307.7). The geometric mean for stormwater samples collected from the Comal Springs complex during May 2020 was approximately 1,874 MPN/100 mL. Bacteria counts ranged from 183 MPN/100 mL to >2,419 MPN/100 mL, with all samples exceeding the individual sample limit. Individual detections are listed in Table 5 and shown in relation to stream discharge and specific conductivity in Figure 10. Due to the timing of storm events and laboratory working hours, it was not possible to deliver all samples to the laboratory within the sample holding time of 8 hours (see discussion in Appendix B). All sample results were included in the range and geometric mean calculations.

Table 5. Stormwater Samples – Bacteria Counts – Comal Springs C	omplex
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Location	Date	Count (MPN/100 mL)
HCS210 Lead 1	5/16/2020	183
HCS210 Lead 2	5/16/2020	1,730
HCS210 Lead 3	5/16/2020	>2,419
HCS210 Peak	5/16/2020	>2,419
HCS210 Trail	5/16/2020	1,730
HCS240 Lead	5/16/2020	>2,419
HCS240 Peak	5/16/2020	2,420
HCS240 Trail	5/16/2020	727
FDHCS240 Trail	5/16/2020	727
HCS250 Lead	5/16/2020	>2,419

Location	Date	Count (MPN/100 mL)
HCS250 Peak	5/16/2020	2,420
HCS250 Trail	5/16/2020	Not Collected
HCS260 Lead 1	5/16/2020	2,420
HCS260 Lead 2	5/16/2020	1,730
HCS260 Lead 3	5/16/2020	1,550
HCS260 Peak	5/16/2020	>2,419
HCS260 Trail	5/16/2020	1,550
FDHCS260 Trail	5/16/2020	1,410
HCS270 Lead	5/16/2020	>2,419
HCS270 Peak	5/16/2020	1,550
HCS270 Trail	5/16/2020	>2,419
MSHCS270 Trail	5/16/2020	1,730
MSDHCS270 Trail	5/16/2020	2,420

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





4.1.2.2 Stormwater – Volatile Organic Compounds

There were two VOC detections in stormwater samples during the May 2020 storm event. Acetone was detected at a concentration of 9.75 μ g/L in HCS270 Lead and 5.95 μ g/L in HCS210 Lead 3. Naphthalene was detected at a concentration of 0.320 μ g/L in HCS210 Lead 1. Detections are listed in Table 6. None of the detected concentrations exceeded the TCEQ (2018a) SWBs for aquatic life or the TCEQ (2006) Contact Recreation Water PCLs.

		Acetone	Naphthalene
Location	Date	(µg/L)	(ug/L)
HCS210 Lead 1	5/15/2020	ND	0.320 J
HCS210 Lead 3	5/16/2020	5.94 J	ND
HCS270 Lead	5/15/2020	9.75 J	ND
TCEQ Acute SWB for Aquatic Life	e [†]	607,400	148
TCEQ Chronic SWB for Aquatic L	ife [†]	101,200	250
Contact Recreation Water PCL [‡]		780,000	2,550

 Table 6. Stormwater Samples – Volatile Organic Compound Detections – Comal Springs Complex

J - Detection is greater than the method detection limit, but less than the reporting limit

μg/L – Micrograms per liter

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

[‡] Contact Recreation Water PCL Table (TCEQ 2006)

4.1.2.3 Stormwater – Semi-volatile Organic Compounds

Generally, SVOCs were analyzed because their detection can indicate the presence of chemicals originating from anthropogenic sources and, therefore, can be used to evaluate potential impacts on water quality. Two SVOCs, bis(2-ethylhexyl) phthalate (DEHP) and pentachlorophenol, were detected in two samples from the May 2020 stormwater sampling event. All the detections were "J" flagged.³ The bis(2-ethylhexyl) phthalate detection in HCS260 Trail did not exceed the TCEQ (2018a) SWBs for aquatic life. The pentachlorophenol detection of 13.2 μ g/L in HCS270 Lead exceeded the TCEQ (2018a) acute and chronic SWBs for aquatic life and the TCEQ (2006) Contact Recreation Water PCL. The pentachlorophenol concentration of 13.2 μ g/L was detected by SVOC analysis (U.S. Environmental Protection Agency [EPA] Method 8270C). Pentachlorophenol was also detected in sample HCS270 Lead at a concentration of 0.0745 μ g/L by herbicide analysis (EPA Method 8151A), which does not exceed either the TCEQ (2018a) SWBs for aquatic life or the TCEQ (2006) Contact Recreation Water PCL. SVOC detections are listed in Table 7.

³ Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

Table 7. Stormwater Samples – Semi-volatile Organic Compound Detections – Comal Springs Complex

		Bis(2-Ethylhexyl)Phthalate (DEHP)	Pentachlorophenol		
Location	Date	(μg/L)	(µg/L)		
HCS270 Lead	5/16/2020	ND	13.2 J*		
HCS270 Peak	5/16/2020	ND	0.03636 J		
HCS260 Trail	5/16/2020	8.15 J	ND		
TCEQ Acute SWB for Aquat	ic Life [†]	60	3.19		
TCEQ Chronic SWB for Aqu	atic Life [†]	20	2.45		
Contact Recreation Water	PCL [‡]	NE	9.92		

J – Detection is greater than the method detection limit, but less than the reporting limit

 μ g/L – Micrograms per liter

NE – Not established

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

[‡] Contact Recreation Water PCL Table (TCEQ 2006)

* The pentachlorophenol concentration of 13.2 J µg/L was detected by SVOC analysis (EPA Method 8270C). Pentachlorophenol was also detected in sample HCS270 Lead at a concentration of 0.0745 J µg/L by herbicide analysis (EPA Method 8151A).

4.1.2.4 Stormwater – Herbicides and Pesticides

Three herbicides were detected in stormwater samples from the Comal Springs complex in 2020. The herbicide compounds, 2,4-D, 2,4,5-T, and pentachlorophenol, were detected during the storm event in the Comal Springs complex sampled during the May 2020 event. The compound 2,4-D was detected in HCS270 Lead, HCS260 Peak, HCS270 Peak, HCS240 Trail, and HCS260 Trail. The compound pentachlorophenol was detected in HCS270 Lead and HCS270 Peak, and compound 2,4,5-T was detected in HCS260 Trail. The 2,4-D and 2,4,5-T detections in HCS260 Trail were not "J" flagged; however, all other detections were "J" flagged.⁴ None of the detections approach the TCEQ (2006) Contact Recreation Water PCL of 3,920 mg/L for 2,4-D. No SWBs for aquatic life have been established for 2,4, 5-T.

Herbicide detections are summarized in Table 8.

⁴ Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

		2,4-D	2,4,5-T	Pentachlorophenol			
Location	Date	(µg/L)	(µg/L)	(μg/L)			
HCS270 Lead	5/16/2020	0.0266 J	ND	0.0745 J*			
HCS260 Peak	5/16/2020	0.139 J	ND	ND			
HCS270 Peak	5/16/2020	0.184 J	ND	0.0363 J			
HCS240 Trail	5/16/2020	0.0238 J	ND	ND			
HCS260 Trail	5/16/2020	1.82	1.82 0.0286 N				
TCEQ Acute SWB for Aqu	atic Life †	510	NE	3.19			
TCEQ Chronic SWB for Ac	luatic Life [†]	85	NE	2.45			
Contact Recreation Wate	r PCL [‡]	3,920	14,000	9.92			

Table 8. Stormwater Samples – Herbicide Detections – Comal Springs Complex

J - Detection is greater than the method detection limit, but less than the reporting limit

µg/L –Micrograms per liter

NE – Not established

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

^{*} Contact Recreation Water PCL Table (TCEQ 2006)

* The pentachlorophenol concentration of 0.0745 J μg/L was detected by herbicide analysis (EPA Method 8151A). Pentachlorophenol was also detected in sample HCS270 Lead at a concentration of 13.2 J μg/L by SVOC analysis (EPA Method 8270C).

4.1.2.5 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 PCB compounds during the May 2020 sampling event.

4.1.2.6 Stormwater – Metals

Stormwater samples were analyzed for metals in accordance with the EAHCP (2016) Work Plan (Appendix A). Several positive metal detections were noted in the sample set. Eight samples, HCS210 Lead 1, HCS210 Lead 2, HCS210 Lead 3, HCS210 Peak, HCS210 Trail, HCS260 Trail, FDHCS260 Trail, and HCS270 Trail, exceeded the Chronic SWB for aquatic life for aluminum. HCS210 Lead 2 slightly exceeded the Chronic Surface Benchmark for aquatic life for lead. None of the detected metal concentrations exceeded the TCEQ (2006) Contact Recreation Water PCLs. Metal results are presented in Table 9.

Table 9. Stormwater Samples – Metals – Comal Springs Complex

Location	Date Collected	(mg/L)	Arsenic (mg/T)	Barin (mg/L)	Calcium (mg/L)	Chromium Chromium (mg/L)	ba da O O (mg/L)	Б <u>л</u> (mg/L)	Lead (mg/T)	(mg/L)	(mg/r)	Mercury (mg/L)	(T/ ⁸ m)	Emipos (mg/L)	uojiicon (mg/L)	Strontium (m8/T)	uz iz (mg/L)	(mg/L)
HCS210 Lead 1	5/15/2020	0.210	ND	0.0217	0.0285 B	ND	ND	0.218 J	ND	0.0143 J	4.84	ND	1.90	3.60	1.73	0.185	0.00557 J	0.00355 J
HCS210 Lead 2	5/16/2020	0.804	0.0011 J	0.0268	0.0372 B	0.00162 J	0.00259 J	0.753	0.00174 J	0.0295 J	5.23	ND	2.10	3.78	2.87	0.203	0.0132 J	0.00521
HCS210 Lead 3	5/16/2020	0.117	ND	0.0252	0.0321 B	ND	ND	0.107 J	ND	0.0167 J	6.50	ND	1.93	475	1.83	0.248	0.00919 J	0.00357 J
HCS210 Peak	5/16/2020	0.310	ND	0.0221	0.0281 B	ND	ND	0.288	ND	0.0166 J	4.63	ND	2.05	3.27	2.14	0.177	0.00823 J	0.00382 J
HCS210 Trail	5/16/2020	0.170	ND	0.0265	0.0352 B	ND	ND	0.159 J	ND	ND	6.80	ND	2.15	4.73	2.11	0.272	0.00595 J	0.00352 J
HCS240 Lead	5/16/2020	ND	ND	0.0485	0.0725 B	ND	ND	ND	ND	ND	14.2	ND	2.15	978	4.88	0.569	ND	0.00302 J
HCS240 Peak	5/16/2020	ND	ND	0.523	0.0768B	ND	ND	ND	ND	ND	15.2	0.000164 J	1.79	11.1	5.07	0.609	ND	0.00281 J
HCS240 Trail	5/16/2020	ND	ND	0.0528	0.0795 B	ND	ND	ND	ND	ND	16.1	ND	1.46	11.2	5.15	0.638	ND	0.00271 J
FDHCS240 Trail	5/16/2020	ND	ND	0.0553	0.0820 B	ND	ND	ND	ND	ND	16.5	ND	1.56	11.2	5.16	0.657	ND	0.00280 J
HCS250 Lead	5/16/2020	0.0586 J	ND	0.0385	0.0586 B	ND	ND	0.101 J	ND	ND	11.3	ND	1.49	7.74	3.83	0.450	0.00739 J	0.00257 J
HCS250 Peak	5/16/2020	ND	ND	0.0473	0.0712 B	ND	ND	ND	ND	ND	14.1	ND	1.78	9.82	4.74	0.565	ND	0.00274 J
HCS250 Trail	5/16/2020	ND	ND	0.0523	0.0786 B	ND	ND	ND	ND	ND	15.8	ND	1.68	11.1	5.22	0.634	ND	0.00265 J
HCS260 Lead 1	5/16/2020	0.0600 J	ND	0.0431	0.0671 B	ND	ND	ND	ND	ND	13.2	ND	1.79	9.28	4.26	0.520	ND	0.00250 J
HCS260 Lead 2	5/16/2020	ND	ND	0.0442	0.0661 B	ND	ND	ND	ND	ND	12.8	ND	1.68	9.26	4.12	0.511	0.00513 J	0.00270 J
HCS260 Lead 3	5/16/2020	0.0604 J	ND	0.0417	0.0591 B	ND	ND	ND	ND	0.0135 J	11.3	ND	1.75	8.51	3.74	0.449	0.00520 J	0.00291 J
HCS260 Peak	5/16/2020	0.0607 J	ND	0.0399	0.0557 B	ND	ND	ND	ND	ND	10.2	0.000175 J	2.10	8.12	3.56	0.409	0.00371 J	0.00334 J
HCS260 Trail	5/16/2020	0.0968 J	0.00125 J	0.0558	0.0738 B	ND	ND	ND	ND	0.0219 J	12.8	ND	2.9	16.8	5.10	0.563	ND	0.00406 J
FDHCS260 Trail	5/16/2020	0.378	0.00154 J	0.0572	0.0707 B	0.00269 J	ND	0.392	ND	0.0309 J	12.3	ND	3.14	17.3	5.52	0.542	0.0708	0.00446 J
HCS270 Lead	5/16/2020	ND	ND	0.0444	0.0685 B	ND	ND	ND	ND	ND	13.3	ND	1.68	9.50	4.31	0.534	ND	0.00265 J
HCS270 Peak	5/16/2020	ND	ND	0.0262	0.0375 B	ND	ND	ND	ND	0.132	6.71	ND	2.26	6.12	2.47	0.270	0.00526 J	0.00204 J
HCS270 Trail	5/16/2020	0.542	0.00139 J	0.0495	0.0680 B	0.00140 J	ND	0.484	ND	0.0190 J	11.6	ND	2.72	11.6	5.27	0.486	0.00540 J	0.00509
TCEQ Acute SWB fo	or Aquatic Life [†]	0.99	0.34	123	NE	0.32	0.00739	NE	0.03014	2.37	NE	0.0024	NE	NE	NE	14.53	0.0651	0.015
TCEQ Chronic SWB	for Aquatic Life [†]	0.087	0.15	20.5	NE	0.042	0.00524	1.00	0.00170	1.310	NE	0.0013	NE	NE	NE	10.7	0.0657	NE
Contact Recreation	Water PCL [‡]	403	0.0285	64.9	NE	126	33.1	NE	NE	40.9	NE	0.0973	NE	NE	NE	338	201	108

J – Detection is greater than the method detection limit, but less than the reporting limit

mg/L – Milligrams per liter

NE – Not established

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

⁺ Contact Recreation Water PCL Table (TCEQ 2006)

4.1.2.7 Stormwater – Nitrates

Stormwater samples were analyzed for nitrate-nitrite as nitrogen, in accordance with the EAHCP (2016) Work Plan (Appendix A). All nitrate results were below the TCEQ (2018a) SWBs for aquatic life and the TCEQ (2006) Contact Recreation Water PCLs. During the May 2020 event, the range of nitrate results was 0.408 mg/L to 1.76 mg/L, with an average of 1.18 mg/L. The samples were not analyzed within the EPA Method holding time, because the samples were collected on Saturday and could not be delivered to the laboratory until Monday. Nitrate results are summarized in Table 10.

I	1 4	J		
Location	Date	Concentration (mg/L)		
HCS210 Lead 1	5/16/2020	0.423 J H H3		
HCS210 Lead 2	5/16/2020	0.433 J H H3		
HCS210 Lead 3	5/16/2020	0.423 J H H3		
HCS210 Peak	5/16/2020	0.412 J H H3		
HCS210 Trail	5/16/2020	0.408 J H		
HCS240 Lead	5/16/2020	1.74 H H3		
HCS240 Peak	5/16/2020	1.72 H H3		
HCS240 Trail	5/16/2020	1.76 H H3		
FDHCS240 Trail	5/16/2020	1.75 H H3		
HCS250 Lead	5/16/2020	1.19 H H3		
HCS250 Peak	5/16/2020	1.52 H H3		
HCS250 Trail	5/16/2020	1.66 H H3		
HCS260 Lead 1	5/15/2020	1.44 H		
HCS260 Lead 2	5/16/2020	1.45 H H3		
HCS260 Lead 3	5/16/2020	1.31 H H3		
HCS260 Peak	5/16/2020	1.11 H H3		
HCS260 Trail	5/16/2020	1.36 H H3		
FDHCS260 Trail	5/16/2020	1.35 H H3		
HCS270 Lead	5/16/2020	1.08 H H3		
HCS270 Peak	5/16/2020	0.862 H H3		
HCS270 Trail	5/16/2020	1.38 H H3		
TCEQ Acute SWB for Aquatic Life [†]		1,320		
TCEQ Chronic SWB for Aquatic Life	550			
Contact Recreation Water PCL [‡]		13		

Table	10	Stormwater	Sample	s _ Nitrate	Detections _	Comal	Snrings	Comn	lev
I able	10.	Stormwater	Sample	s – Iviti ate	Detections -	Comai	springs	Comp	юл

J - Detection is greater than the method detection limit, but less than the reporting limit

H – Sample was prepped or analyzed beyond the specified holding time

H3 – Sample was received and analyzed past holding time

mg/L – Milligrams per liter

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

[‡] Contact Recreation Water PCL Table (TCEQ 2006)

4.1.2.8 Stormwater – Caffeine

Stormwater was analyzed for caffeine, which can indicate an anthropogenic source. Caffeine may enter surface water from leaking sewer or septic systems, or it may be present in the aquifer from similar sources
in the recharge zone (EPA 2012). Potential ecological effects are currently unknown but could include reduced reproductive success of aquatic organisms (EPA 2012). Caffeine detections in stormwater samples from Comal Springs in May 2020 ranged from 14 ng/L to 110 ng/L. There is no regulatory standard or expected value for comparison. These results are shown in Table 11.

	Date	Caffeine			
Location	Collected	(ng/L)			
HCS210 Lead 1	5/16/2020	93			
HCS210 Lead 2	5/16/2020	78			
HCS210 Lead 3	5/16/2020	94			
HCS210 Peak	5/16/2020	44			
HCS210 Trail	5/16/2020	49			
HCS240 Lead	5/16/2020	37			
HCS250 Lead	5/16/2020	52			
HCS250 Peak	5/16/2020	22			
HCS250 Trail	5/16/2020	14			
HCS260 Lead 1	5/16/2020	47			
HCS260 Lead 2	5/16/2020	60			
HCS260 Lead 3	5/16/2020	74			
HCS260 Peak	5/16/2020	110			
HCS260 Trail	5/16/2020	48			
FDHCS260 Trail	5/16/2020	31			
HCS270 Lead	5/16/2020	88			
HCS270 Peak	5/16/2020	83			
HCS270 Trail	5/16/2020	39			

Table 11. Stormwater Samples – Caffeine Detections – Comal Springs Complex

ng/L – Nanograms per liter

4.1.3 Comal Springs Surface Water Passive Sampling

PDSs were installed in the Comal Springs complex in February, April, June, August, October, and December 2020. Any changes to deployment locations or non-recovered samplers are discussed in Appendix B.

Rain events did occur during some PDS deployment periods during 2020. Figures 11–16 show specific conductivity and discharge for each PDS deployment period.

No suitable set of regulatory standards exists for comparison with the PDS results; rather, the data are a qualitative tool for evaluating the presence of trace concentrations of organic compounds. PDSs were analyzed for a suite of SVOCs, VOCs, and organochlorine pesticides. Few compounds were detected, the most notable are relatively consistent detections of tetrachloroethene. Positive detections are shown in Table 12. None of the detected concentrations exceeded the TCEQ (2018a) SWBs for aquatic life or the TCEQ (2006) Contact Recreation Water PCLs.

The specific conductivity values for Figures 11–16 values were obtained from the New Channel RTI station (Contrail 2020).

Figure 11. Passive Diffusion Sampling – February 2020 Stream Discharge and Specific Conductivity – Comal Springs Complex



Figure 12. Passive Diffusion Sampling – April 2020 Stream Discharge and Specific Conductivity – Comal Springs Complex



Figure 13. Passive Diffusion Sampling – June 2020 Stream Discharge and Specific Conductivity – Comal Springs Complex



Figure 14. Passive Diffusion Sampling – August 2020 Stream Discharge and Specific Conductivity – Comal Springs Complex



Figure 15. Passive Diffusion Sampling – October 2020 Stream Discharge and Specific Conductivity – Comal Springs Complex



Figure 16. Passive Diffusion Sampling – December 2020 Stream Discharge and Specific Conductivity – Comal Springs Complex



 Table 12. Passive Diffusion Sampling –Volatile and Semi-volatile Organic Compound Detections –

 Comal Springs Complex

Location	Month 2020	Chloroform (hã/r)	여 A Tetrachloroethene (기	표 (µg/L)	Huorene Huorene
	February	ND	0.013	ND	ND
	April	ND	0.018	ND	ND
1105440	June	ND	0.020	ND	ND
HC5410	August	0.013	0.015	0.074	ND
	October	0.033	0.012	ND	ND
	December	ND	0.011	ND	ND
	February	ND	0.057	ND	ND
	April	ND	0.076	ND	ND
HCC420	June	ND	0.053	ND	ND
ПС3420	August	ND	0.038	ND	ND
	October	ND	0.064	ND	ND
	December	ND	0.060	ND	ND
	February	ND	0.080	ND	ND
	April	ND	0.108	ND	ND
	June	ND	0.071	ND	ND
103430	August	ND	0.057	ND	ND
	October	ND	0.077	ND	ND
	December	ND	0.072	ND	ND
	February	ND	0.056	ND	ND
	April	ND	0.070	ND	ND
	June	ND	0.032	ND	ND
1103440	August	ND	0.040	ND	ND
	October	ND	0.060	ND	ND
	December	ND	0.062	ND	ND
	February	ND	0.059	ND	ND
	April	ND	0.064	ND	ND
	June	ND	0.045	ND	ND
	August	ND	0.035	ND	ND
	October	ND	0.053	ND	ND
	December	ND	0.064	ND	0.105

Location	Month 2020	(1/¤π)	知 知 て、 T イ	Η Ε (μg/L)	ene Fluorene (µg/L)
	February	ND	0.039	ND	ND
	April	ND	0.042	ND	ND
1105460	June	ND	0.036	ND	ND
HC3460	August	ND	0.026	ND	ND
	October	ND	0.034	ND	ND
	December	ND	0.037	ND	ND
TCEQ Acute SWB for Aquatic L	.ife [†]	5,370	3,840	NE	64
TCEQ Chronic SWBfor Aquatic	Life [†]	1,790	1,280	NE	11
Contact Recreation Water PCL	*	2,350	148	28,100*	2,110

 μ g/L – Micrograms per liter

NE – Not established

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

TPH – Total petroleum hydrocarbons

* Value for C>16-21 Aromatics presented for TPH

[†] Aquatic Life SWBTable (TCEQ 2018a)

⁺ Contact Recreation Water PCL Table (TCEQ 2006)

4.1.4 Comal Springs Polar Organic Chemical Integrative Sampling

POCISs were installed at the farthest downstream sample location, HCS460, in the Comal Springs complex in February, April, June, August, October, and December 2020.

Rain events did occur during all POCIS deployment periods during 2020. Figures 17–22 show conductivity and discharge for each POCIS deployment period.

No suitable regulatory standards are available to compare to POCIS results; however, the data can be used as a qualitative tool to evaluate the presence of trace concentrations of PPCP constituents. Of the 43 PPCP constituents analyzed, 20 were detected in the Comal Springs complex. Positive detections are shown in Table 13.

The specific conductivity values for Figures 17–22 were obtained from the New Channel RTI station (Contrail 2020).



Figure 17. Polar Organic Chemical Integrative Sampling (POCIS) – February 2020 Stream Discharge and Conductivity – Comal Springs Complex









Figure 20. Polar Organic Chemical Integrative Sampling (POCIS) – August 2020 Stream Discharge and Conductivity – Comal Springs Complex





Figure 21. Polar Organic Chemical Integrative Sampling (POCIS) – October 2020 Stream Discharge and Conductivity – Comal Springs Complex

Figure 22. Polar Organic Chemical Integrative Sampling (POCIS) – December 2020 Stream Discharge and Conductivity – Comal Springs Complex



Table 13. Polar Organic Chemical Integrative Sampling – Pharmaceutical and Personal Care Products – Comal Springs Complex

Location	Month 2020	(J ⁸ Bisphenol A	(ng/L)	(ng/L)	ubuprofen (ug/L)	Naproxen	(ng/L)	(ug/L)	u ^{la}) Ciprofloxacin	Lu u (ng/L)	u) (T) (T)) (ng/L)	(ngesterone	(ug/r) Quinoline) Sucralose	(J ^r Sulfamethoxazole	(ng/L)	u) Acetaminophen	G H J J L J L J	d d Ung/L)	Ad DOL (ng/L)
	February	ND	ND	2,100	ND	4,200	33,000	6,500	6,300	33,000	21,000	13,000	ND	66,000	ND	ND	33,000	820,00 0	4,000	100,000	3,200
	April	3,100	ND	1,600	ND	ND	ND	5,000	ND	35,000	17,000	14,000	ND	110,000	ND	ND	38,000	ND	5,000	170,000	12,000
HCS460	June	5,700	ND	1,100	5,800	6,700	ND	13,000	ND	210,000	39,000	42,000	ND	36,000	13,000	ND	12,000	ND	10,000	270,000	15,000
	August	8,300	ND	2,400	3,600	2,200	ND	13,000	ND	130,000	58,000	18,000	3,300	ND	25,000	1,100	21,000	ND	3,200	86,000	6,300
	October	ND	8,200	ND	ND	ND	ND	4,500	ND	47,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	51,000	ND
	December	ND	11,000	ND	ND	ND	8,700	ND	ND	25,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	February	ND	ND	ND	ND	ND	ND	2,400	ND	21,000	11,000	5,500	ND	11,000	ND	ND	19,000	ND	3,200	69,000	1,200
	April	ND	ND	ND	ND	ND	20,000	2,500	ND	18,000	10,000	4,100	ND	3,000	ND	ND	ND	ND	2,800	54,000	1,400
Extraction	June	ND	ND	ND	ND	ND	ND	3,100	ND	35,000	33,000	1,200	ND	8,800	ND	ND	16,000	ND	6,000	110,000	2,600
Blank	August	ND	ND	ND	ND	ND	ND	3,800	ND	43,000	72,000	5,400	ND	ND	ND	ND	12,000	ND	3,400	66,000	ND
	October	ND	ND	ND	ND	ND	ND	ND	ND	20,000	ND	ND	ND	ND	ND	ND	ND	ND	63,000	ND	ND
-	December	ND	ND	ND	ND	ND	ND	ND	ND	14,000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

DEET – N,N-Diethyl-meta-toluamide

HHCB – 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta--2-benzopyran

TCEP – Tris(2-carboxyethyl)phosphine

TCPP - Tris (chloropropyl)phosphate

TDCPP – Tris(1,3-dichloroisopropyl)phosphate

ng/L – Nanograms per Liter

ND – Not detected

4.2 San Marcos Springs Sample Results

Sediments at the San Marcos Springs complex were sampled in July 2020. Sediment results were compared with the standards developed by MacDonald et al. (2000). These standards are based on the probability of a detected compound having a toxic effect on sediment-dwelling organisms, referred to as the TEC and PEC. Detections below the TEC are not considered to be toxic, whereas 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 nontoxic. Two analytes were detected at concentrations exceeding TEC values. Six analytes were detected at concentrations exceeding PEC values.

A stormwater event was sampled on October 28, 2020. No TCEQ (2018a) SWBs for aquatic life or PCLs were exceeded for VOCs, SVOCs, pesticides, herbicides, or polychlorinated biphenyls (PCBs). One sample, HSM250 Peak exceeded the Chronic SWB for freshwater organisms for lead.

PDS sampling events were conducted at the San Marcos Springs complex in February, April, June, August, and October 2020. Generally speaking, various VOCs and TPH were detected at various sample locations, but only tetrachloroethene was relatively consistently detected. No TCEQ (2018a) SWBs for aquatic life or TCEQ (2006) Contact Recreation Water PCLs were exceeded.

POCIS sampling events were conducted at the San Marcos Springs complex in conjunction with the PDS sampling events at the downstream location HSM470. Of the 43 PPCP constituents analyzed, 19 were detected in the San Marcos Springs complex. However, some of the analytes detected were also detected in extraction blank samples.

4.2.1 San Marcos Springs Sediment Sampling

4.2.1.1 Sediment – Volatile Organic Compounds

VOCs were detected in sediment samples collected at three of the seven sample sites in the San Marcos Springs complex in 2020. Many of these detections were "J" flagged.⁵ None of the detected compounds have established TECs or PECs. The detections are summarized in Table 14.

⁵ Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

	Date	Acetone	Benzene	2-Butanone (MEK)	1,2 Dichloroethane	m-xylene & p-xylene	Toluene	4-Isopropyltoluene	1,2,4-Trimethylbenzene	Xylene, Total
Location	Collected	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)
HSM310	7/8/2020	42.4 J	ND	7.56 J	ND	ND	ND	ND	ND	ND
HSM320	7/8/2020	60.5 J	ND	12.6	7.71	1.17 J	1.47 J	1.98 J	0.612 J	1.57 J
HSM330	7/8/2020	ND	ND	ND	2.76 J	ND	ND	ND	ND	ND
HSM340	7/8/2020	25.7 J	ND	4.84 J	1.62 J	ND	ND	ND	ND	ND
FDHSM340	7/8/2020	22.6 J	ND	3.85 J	ND	ND	ND	ND	ND	ND
HSM350	7/8/2020	34.2 J	1.13 J	6.59 J	0.776 J	ND	ND	1.98 J	0.612 J	ND
HSM360	7/8/2020	ND	0.862 J	ND	5.10 J	ND	ND	ND	ND	ND
HSM370	7/8/2020	29.6 J	ND	6.74 J	ND	ND	ND	ND	0.545 J	ND
TEC		NE	NE	NE	NE	NE	NE	NE	NE	NE
PEC		367.990	45.010	154.260	28.690	2.080 [†]	17.290	5.980	4.580	12.010

Table 14. Sediment Samples – Volatile Organic Compound Detections – San Marcos Springs Complex

J – Detection is greater than the method detection limit, but less than the reporting limit

µg/kg – Micrograms per kilogram

ND – Not detected

NE – Not established

PEC – Probable effect concentration

TEC – Threshold effect concentration

 † Value for m-xylene is presented. No PEC for p-xylene has been established.

4.2.1.2 Sediment – Semi-volatile Organic Compounds

Several SVOC compounds were detected in the sediment samples collected in the San Marcos Springs complex in 2020. Many of these detections were "J" flagged.⁶ The SVOC detections are summarized in Table 15. The discussion of SVOC detections presented below is divided between non-PAH and PAH compounds.

Non-Polycyclic Aromatic Hydrocarbon (PAH) Detections

Three non-PAH SVOC compounds were detected in 2020 sediment samples from the San Marco Springs complex, Bis(2-ethylhexyl)phthalate (DEHP), di-n-butyl phthalate, and 3&4-methylphenol. No TECs or PECs have been established for the three non-PAH SVOC compounds detected.

Based on analysis of 2013 sediment sample laboratory data, the EAA concluded that three detected compounds may have been laboratory artifacts. The compounds were DEHP, di-n-octyl phthalate, and di-n-butyl phthalate. The EAA (2013) noted in the 2013 *EAHCP 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) in 2014, leading SWCA to conclude that it is possible DEHP is present within the sediment and not just a laboratory artifact. DEHP was detected again in three samples in 2015, HSM330, HSM340, and HSM350. In 2016, DEHP was detected in all San Marcos sediment samples except HSM310, with concentrations ranging from 0.0671 mg/kg to 0.668 mg/kg. All detections in 2016 were less than the laboratory reporting limit but were greater than the method detection limits. In the 2018 sampling event, DEHP, di-n-butyl phthalate, and di-n-octyl phthalate were not detected within the sediment samples. In the 2020 sampling event, DEHP was detected in all the sediment samples but was "B" flagged, indicating the compound was found in the laboratory blank sample. Di-n-butyl phthalate was only detected in sediment sample HSM360.

Polycyclic Aromatic Hydrocarbon (PAH) Detections

Sixteen PAH SVOC compounds were detected in 2020 sediment samples from the San Marcos Springs complex. PAH compounds exceeding the TEC or PEC are shown graphically in Figures 23–33. Total PAH detections are shown in Figure 33, where the total PAH concentrations (sum of all detected concentrations for each sample point) are compared with the TEC and PEC values for total PAH concentration established by MacDonald et al. (2000). Sample locations HSM320 and HSM340 exceed the TEC and PEC for total PAH concentrations. Sample locations HSM330, FDHSM340, and HSM350 exceeded only the TEC for total PAH concentrations.

⁶ Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

Table 15. Sediment Samples – Semi-volatile Organic Compounds – San Marcos Springs Complex

	Polycyclic Aromatic Hydrocarbon (PAH) Compounds									Non-PAH Compounds											
Location	Date Collected	(mg/kg)	(mg/kg) (g	(mg/kg)) Benzo(a)anthracene (g	g Benzo(b)fluoranthene (a	(mg/g benzo(k)fluoranthene	(Benzo(g,h,i)perylene	(mg/kg	Chrysene (mg/kg)) B B Dibenz(a,h)anthracene	(mg/kg)	fuorene (mg/kg)	ш ^{gd} /rdeno(1,2,3-cd)ругеne ^{gg}	(^{dwg} /kg)	(mg/kg)	enene (mg/kg)	(mg/kg)	ଇ ଜ୍ଜୁ ଅs(2-ethylhexyl)phthalate	(mg/kg (g	(mg/kg
HSM310	7/8/2020	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.141 J F1	ND	ND	ND	0.141	0.298 J B F1	ND	ND
HSM320	7/8/2020	ND	0.178 J	0.609 J	5.310	9.70	3.29	4.03	6.42	6.56	ND	10.9	0.169 J	3.96	ND	3.75	8.37	63.25	0.304 J B	ND	1.36 J
HSM330	7/8/2020	ND	ND	ND	0.632 J	1.38 J	0.436 J	0.430 J	0.917 J	0.932 J	ND	1.39 J	ND	0.523 J	ND	0.498 J	1.11 J	8.25	0.293 J B	ND	ND
HSM340	7/8/2020	0.208 J	ND	0.462 J	3.47 J	5.94	2.05 J	1.92 J	4.45	4.30	ND	8.03	ND	2.26 J	ND	3.16 J	6.99	43.24	1.02 J B	ND	ND
FDHSM340	7/8/2020	ND	ND	ND	1.04 J	2.04 J	0.692 J	0.649	1.48 J	1.59 J	ND	2.72	ND	0.807 J	ND	1.43 J	2.69	15.14	0.757 J B	ND	ND
HSM350	7/8/2020	ND	ND	ND	0.290 J	0.476 J	0.200	0.145 J	0.354 J	0.420 J	0.118 J	0.752 J	ND	0.201 J	0.0574 J	0.270 J	ND	3.28	0.289 J B	ND	ND
HSM360	7/8/2020	ND	ND	ND	ND	ND	ND	ND	0.0495 J	ND	ND	ND	ND	0.0696 J	ND	ND	ND	0.2661	0.161 J B	0.147 J	ND
HSM370	7/8/2020	ND	ND	ND	0.0925 J	0.223 J	ND	0.0482 J	0.153 J	0.0972 J	ND	0.121 J	ND	0.115 J	ND	ND	0.118 J	0.968	0.176 J B	ND	0.107 J
TEC		NE	NE	0.0572	0.108	NE	NE	NE	0.150	0.166	0.033	0.423	0.0774	NE	0.176	0.204	0.195	1.610	NE	NE	NE
PEC		0.089	0.130	0.845	1.050	NE	NE	NE	1.450	1.290	0.140	2.230	0.536	NE	0.561	1.170	1.520	22.800	NE	0.043	NE

J – Detection is greater than the method detection limit, but less than the reporting limit

B – Compound was found in blank and sample

F1 – Matrix spike/matrix spike duplicate (MS/MSD) recovery exceeds control limits

mg/kg – Milligrams per kilogram

ND – Not detected

NE – Not established

PEC – Probable effect concentration

TEC – Threshold effect concentration





Figure 24. San Marcos Springs Sediment Benzo(a)Pyrene Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values







Figure 26. San Marcos Springs Sediment Fluoranthene Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values







Figure 28. San Marcos Springs Sediment Phenanthrene Detections Compared to Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) Values







Figure 30. San Marcos Springs Sediment Acenaphthene Detections Compared Probable Effect Concentration (PEC) Values















4.2.1.3 Sediment – Pesticides

Sediment samples were analyzed for both organochlorine and organophosphorus pesticides. No pesticides were detected in the sediment samples from the seven sample locations in the San Marcos complex.

4.2.1.4 Sediment – Herbicides

Sediments were analyzed for herbicide compounds to further assess sediment quality at the San Marcos Springs complex. One herbicide, mecoprop, was detected in HSM330 with a concentration of 272 μ g/kg. The result was "J" flagged.⁷ There are no TEC or PEC values established for this compound.

4.2.1.5 Sediment – Polychlorinated Biphenyls (PCBs)

Sediments were analyzed for PCB compounds to further assess sediment quality at the San Marcos Springs complex. One PCB, Aroclor 1260, was detected in HSM350 with a concentration of 0.0284 mg/kg. The result was "J" flagged.⁷ There are no TEC or PEC values established for this compound.

4.2.1.6 Sediment – Metals

Many metals are naturally occurring within soil, rock, and sediment. 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

⁷ Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

effects using the TEC and PEC standards are as follows: arsenic, cadmium, chromium, copper, lead, manganese, mercury, nickel, and zinc.

Other metals detected that do not have a TEC or PEC value are: aluminum, antimony, barium, beryllium, iron, and selenium, which were compared with TSBC (TCEQ 2018b). Several samples exceeded one or more of these limits in 2020. Arsenic detection in HSM320 exceeded the TSBC. Antimony detection in HSM330 and HSM340 exceeded the TSBC. Lead detections exceeded the TSBC in samples HSM320, HSM330, HSM340, and HSM360. Lead detections exceeded the TEC value in HSM330 and HSM340. The manganese detection exceeded the TSBC at HSM350. The zinc concentration exceeded the TSBC in samples HSM310 and HSM320.

Selenium detections exceeded the TSBC in samples HSM310, HSM320, HSM330, and HSM340. Sediment studies of selenium concentrations have shown that levels below 4 mg/kg are not likely to bioaccumulate in the food chain or have adverse impacts on the reproduction of fish or aquatic birds (Lemly 1995; Moore et al. 1990; Van Derveer and Canton 1996). Selenium detections did not exceed 4 mg/kg in 2020 San Marcos sediment samples.

Metal detections are listed in Table 16. Metals with detections above an established TEC, TSBC, or PEC value for arsenic, antimony, lead, manganese, mercury, selenium, strontium, and zinc are displayed graphically in Figures 34–41, respectively.

	Date	Aluminum	Antimony	Arsenic	Barium	Beryllium	Calcium	Cadmium	Chromium	Copper		(cut)	Manganese	Magnesium	Mercury	Nickel	Potassium	Selenium	Silicon	Sodium	Strontium	(allium	Zinc
Location		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
HSM310	//8/2020	6,260	ND	4.80 J	44.2	0.678J	84,400	0.896 J	17.9	12.6	9,170	13.4	146	2,300	0.0843 J	12.0	1/00	3.24	2,910	111 J	160	ND	37.9
HSM320	7/8/2020	2,680	ND	6.78	39.7	0.393 J	58,500	0.265 J	4.34	8.05	6,990	15.1	131	1,320	0.0207 J	2.75	1270	0.439 J	646	64.0 J	80.6	ND	45.3
HSM330	7/8/2020	953	1.30 J	4.46	18.4	0.173 J	214,000	0.382 J	24.4	4.33	5,410	66.5	194	6,110	0.0216 J	5.90	287	1.19	794	82.9 J	98.4	0.122 J	25.2
HSM340	7/8/2020	2,080	1.55 J	2.50	26.6	0.254 J	316,000	0.323 J	6.76	23.7	3,310	38.8	87.1	2,460	ND	4.66	791	1.31	1,410	43.3 J	81.8	ND	24.9
FDHSM340	7/8/2020	1,950	ND	1.49 J	18.6	0.158 J	244,000	0.179 J	3.82	5.60	2,050	13.0	77.8	1,330	0.0465 J	3.13	507	ND	827	80.7 J	126	ND	21.1
HSM350	7/8/2020	2,120	ND	4.35 J	23.8	0.273 J	129,000	0.581 J	6.76	4.61 J	5,250	11.1	323	1,660	ND	5.73 J	397 J	ND	1,190	210 J	169	ND	21.9
HSM360	7/8/2020	1,650	ND	2.30 J	18.1	ND	156,000	0.394 J	5.18 J	2.26 J	3,210	16.3	178	1,420	0.0138 J	2.50 J	320 J	ND	728	127 J	137	ND	12.0 J
HSM370	7/8/2020	2,930	ND	3.68 J	47.2	0.271 J	211,000	0.539 J	7.26	7.50 J	5,970	11.3	212	1,500	ND	6.67 J	398 J	ND	1,210	658 J	347	ND	26.7
TEC		NE	NE	9.79	NE	NE	NE	0.99	43.4	31.6	NE	35.8	460	NE	0.18	22.7	NE	NE	NE	NE	NE	NE	121
PEC		NE	25	33	NE	NE	NE	4.98	111	149	40,000	128	1,100	NE	1.06	48.6	NE	NE	NE	NE	NE	NE	459
TSBC		30,000	1	5.9	300	1.5	NE	NE	NE	15	15,000	15	300	NE	0.04	10	NE	0.3	NE	NE	100	NE	30

Table 16. Sediment Samples – Metal Detections – San Marcos Springs Complex

J – Detection is greater than the method detection limit, but less than the reporting limit

mg/kg – Milligrams per kilogram

NE – Not established

ND – Not detected above laboratory minimum detection limit

PEC – Probable effect concentration

TEC – Threshold effect concentration

TSBC – Texas-specific background concentration

Figure 34. San Marcos Springs Sediment Arsenic Detections Compared to Texas-specific Background Concentration (TSBC), Threshold Effect Concentration (TEC), and Probable Effect Concentration (PEC) Values



Figure 35. San Marcos Springs Sediment Antimony Detections Compared to Texas-specific Background Concentration (TSBC)



Figure 36. San Marcos Springs Sediment Lead Detections Compared to Texas-specific Background Concentration (TSBC), Threshold Effect Concentration (TEC), and Probable Effect Concentration (PEC) Values



Figure 37. San Marcos Springs Sediment Manganese Detections Compared to Texasspecific Background Concentration (TSBC), and Threshold Effect Concentration (TEC), and Probable Effect Concentration (PEC) Values



Figure 38. San Marcos Springs Sediment Mercury Detections Compared to Texas-specific Background Concentrations (TSBC), Threshold Effect Concentration (TEC), and Probable Effect Concentration (PEC) Values



Figure 39. San Marcos Springs Sediment Selenium Detections Compared to Texas-specific Background Concentration (TSBC)







Figure 41. San Marcos Springs Sediment Zinc Detections Compared to Texas-specific Background Concentration (TSBC), Threshold Effect Concentration (TEC), and Probable Effect Concentration (PEC) Values



4.2.2 San Marcos Springs Stormwater Sampling

Stormwater samples were collected during one storm event at the San Marcos Springs complex. SWCA sampled the event according to the guidelines in the EAHCP (2016) Work Plan (Appendix A). The event occurred on October 28, 2020. Total rainfall for the October 2020 event was approximately 0.1 to 0.5 inches (National Oceanic and Atmospheric Administration 2020). Streamflow measurements from the USGS gauge increased from approximately 164 cfs to a peak of 179 cfs (USGS 2020). SWCA consulted with Chad Furl, PhD. with the EAA, who indicated SWCA should go ahead and sample the event at the San Marcos Spring Complex. Very light rain began falling around midnight, 00:00, on October 28, 2020. The rainfall intensified slightly while SWCA staff watched precipitation collect in puddles and then begin to coalesce into small rivulets that made their way toward storm drain inlets. The first lead samples were collected at 01:40. Steady rain fell throughout collection of the lead and peak samples, and SWCA staff observed runoff flowing into the San Marcos River at the area of each of the sample locations during the storm event. The peak samples were collected around 03:00. The first trail samples were collected approximately 0.1 to 0.5 inch of rain fell in the northern San Marcos area, based on NOAA data, as presented in the figure below.

E coli samples were placed on ice and transported to San Antonio Testing Laboratory on Wednesday October 28, 2020. Samples were brought to the SWCA San Antonio office and were packaged for transport on the afternoon of Wednesday October 28, 2020. The samples were successfully picked up by Eurofins personnel and delivered to their laboratory located in Corpus Christi, Texas, on Wednesday, October 28, 2020.

4.2.2.1 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 (MPN) 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 Texas Administrative Code 307.7). The geometric mean for stormwater samples collected from the San Marcos Springs complex during October 2020 was approximately 590 MPN/100 mL. Bacteria counts ranged from34 MPN/100 mL to 17,300 MPN/100 mL, with all samples exceeding the individual sample limit. Individual detections are listed in Table 17 and shown in relation to stream discharge and specific conductivity in Figure 42. Due to the timing of storm events and laboratory working hours, it was not possible to deliver all samples to the laboratory within the sample holding time of 8 hours (see discussion in Appendix B). All sample results were included in the range and geometric mean calculations.

Complex	Table 17. Stormwater Samples – Bacteria Counts – San Marcos Spi	rings
	Complex	

Location	Date	Count (MPN/100 mL)
HSM210 Lead 1	10/28/2020	109
HSM210 Lead 2	10/28/2020	34
HSM210 Peak	10/28/2020	75
HSM210 Trail	10/28/2020	134
HSM230 Lead 1	10/28/2020	959
HSM230 Lead 2	10/28/2020	15,500

Location	Date	Count (MPN/100 mL)
HSM230 Peak	10/28/2020	17,300
HSM230 Trail	10/28/2020	11,200
FDHSM230 Trail	10/28/2020	8,160
HSM231 Lead 1	10/28/2020	17,300
HSM231 Peak	10/28/2020	529
HSM231 Trail	10/28/2020	512
MSHSM231 Trail	10/28/2020	345
MSD HSM231 Trail	10/28/2020	282
HSM240 Lead	10/28/2020	119
HSM240 Peak	10/28/2020	2,760
HSM240 Trail	10/28/2020	689
FDHSM240 Trail	10/28/2020	537
HSM250 Lead	10/28/2020	175
HSM250 Peak	10/28/2020	620
HSM250 Trail	10/28/2020	272
MDHSM250 Trail	10/28/2020	262
HSM260 Lead	10/28/2020	75
HSM260 Peak	10/28/2020	259
HSM260 Trail	10/28/2020	776
FDHSM260 Trail	10/28/2020	631
HSM270 Lead	10/28/2020	256
HSM270 Peak	10/28/2020	594
HSM270 Trail	10/28/2020	410

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





4.2.2.2 Stormwater – Volatile Organic Compounds

There were five VOC detections in stormwater samples during the October 2020 storm event. Acetone was detected at a concentration of 8.75 μ g/L in HSM231 Lead. There four VOC detections in HSM230 Lead 2, Ethylbenzene at was detected at 0.308 μ g/L, Total Xylene at 1.90 μ g/L, o-xylene at 0.487 μ g/L, and m,p-xylenes at 1.41 μ g/L. Detections are listed in Table 18. None of the detected concentrations exceeded the TCEQ (2018a) SWBs for aquatic life or the TCEQ (2006) Contact Recreation Water PCLs.

1 8 1						
		Acetone	Ethylbenzene	Xylenes, Total	o-xylene	m -xylene & p- xylene
Location	Date	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
HSM231 Lead	10/28/2020	8.75 J	ND	ND	ND	ND
HSM230 Lead 2	10/28/2020	ND	0.308 J	1.90 J	0.487 J	1.41 J
TCEQ Acute SWB for Aquatic	Life [†]	607,400	NE	4,020	NE	NE
TCEQ Chronic SWB for Aquat	ic Life [†]	101,200	NE	1,340	NE	NE
	+					

Table 18. Stormwater Samples – Volatile Organic Compound Detections –
San Marcos Springs Complex

J - Detection is greater than the method detection limit, but less than the reporting limit

µg/L – Micrograms per liter

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

4.2.2.3 Stormwater – Semi-volatile Organic Compounds

Generally, SVOCs were analyzed because their detection can indicate the presence of chemicals originating from anthropogenic sources and, therefore, can be used to evaluate potential impacts on water quality. None of the stormwater samples from the San Marcos Springs complex indicated positive detections of SVOC compounds during the October 2020 sampling event.

4.2.2.4 Stormwater – Herbicides and Pesticides

Two herbicides were detected in stormwater samples from the San Marcos Springs complex in 2020. The herbicide compounds, 2,4-D and 2,4,5-T were detected during the storm event in the San Marcos Springs complex sampled during the October 2020 event. The compound 2,4-D was detected in HSM270 Peak. The compound 2,4,5-T was detected in HSM230 Lead 2 and HSM230 Trail. The 2,4,5-T detections in HSM230 Trail was not "J" flagged; however, all other detections were "J" flagged.⁸ None of the detections approach

⁸ Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

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the TCEQ (2006) Contact Recreation Water PCL of 3,920 mg/L for 2,4-D and 14,000 mg/L for 2,4,5-T. No SWBs for aquatic life have been established for 2,4, 5-T.

There was one pesticide detection in stormwater samples during the October 2020 storm event. Alpha-BHC was detected at a concentration of 0.00357 μ g/L in HSM240 Trail, 0.00328 μ g/L in HSM260 Lead, 0.00747 μ g/L in HSM260 Peak, and 0.00399 μ g/L in HSM260 Trail.

Herbicide detections are summarized in Table 19.

Table 19. Stormwater Samples – Herbicide and Pesticide Detections – San
Marcos Springs Complex

		2,4-D	2,4,5-T	Alpha-BHC
Location	Date	(µg/L)	(µg/L)	(μg/L)
HSM230 Lead 2	10/28/2020	ND	0.0663 J p	ND
HSM 230 Trail	10/28/2020	ND	0.148 p	ND
HSM240 Trail	10/28/2020	ND	ND	0.00357
HSM260 Lead	10/28/2020	ND	ND	0.00328
HSM260 Peak	10/28/2020	ND	ND	0.00747
HSM260 Trail	10/28/2020	ND	ND	0.00399
HSM270 Peak	10/28/2020	0.0238 J p*	ND	ND
TCEQ Acute SWB for Aquation	c Life [†]	510	NE	447
TCEQ Chronic SWB for Aqua	85	NE	74	
Contact Recreation Water P	3,920	14,000	0.42	

J - Detection is greater than the method detection limit, but less than the reporting limit

µg/L –Micrograms per liter

NE – Not established

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

⁺ Contact Recreation Water PCL Table (TCEQ 2006)

* The pentachlorophenol concentration of 0.0745 J μ g/L was detected by herbicide analysis (EPA Method 8151A). Pentachlorophenol was also detected in sample HCS270 Lead at a concentration of 13.2 J μ g/L by SVOC analysis (EPA Method 8270C).

4.2.2.5 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 San Marcos Springs complex indicated positive detections of PCB compounds during the October 2020 sampling event.

4.2.2.6 Stormwater – Metals

Stormwater samples were analyzed for metals in accordance with the EAHCP (2016) Work Plan (Appendix A). Several positive metal detections were noted in the sample set. None of the detected metal

concentrations exceeded the Acute SWB, Chronic SWB, and TCEQ (2006) Contact Recreation Water PCLs. Metal results are presented in Table 20.

Table 20. Stormwater Samples – Metals – San Marcos Springs Complex

	Date	Aluminum	Antimony	Barium	Calcium	Chromium	Copper	Iron	Lead	Manganese	Magnesium	Potassium	Sodium	Silicon	Strontium	Thallium	Zinc	Vanadium
Location	Collected	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
HSM210 Lead 1	10/28/2020	ND	ND	0.0355	84.4	ND	ND	ND	ND	0.0202 J	20.0	1.75	13.60	4.91	0.675	0.00129 J	0.00628 J	0.00192J
HSM210 Lead 2	10/28/2020	ND	ND	0.0303	85.9	ND	ND	ND	ND	ND	19.7	1.96	15.2	4.91	0.708	ND	0.00357 J	0.00151 J
HSM210 Peak	10/28/2020	ND	ND	0.0312	83.7	ND	ND	ND	ND	ND	19.7	1.79	13.7	4.83	0.675	ND	ND	0.00183 J
HSM 210 Trail	10/28/2020	ND	ND	0.0322	81.5	ND	ND	ND	ND	ND	19.5	1.75	13.5	4.80	0664	ND	ND	0.00184 J
HSM230 Lead	10/28/2020	0.116	ND	0.0417	96.3	ND	ND	ND	ND	ND	16.9	1.75	13.1	5.51	0.537	0.00076 J	0.00509 J	0.00243
HSM230 Lead 2	10/28/2020	0.0844 J	ND	0.00121	029.0	ND	0.00272 J	ND	ND	ND	3.74	5.38	5.59	1.50	0.110	ND	0.0134 J	0.0015J
HSM230 Peak	10/28/2020	ND	0.00188 J	0.0217	46.6	ND	0.00419 J	ND	ND	ND	7.29	4.38	6.92	2.56	0.224	ND	0.0211 J	0.00261 J
HSM230 Trail	10/28/2020	ND	ND	0.0281	64.2	ND	0.00251 J	ND	ND	ND	10.9	3.25	9.69	3.68	0.347	ND	0.0123 J	0.00243 J
FDHSM230 Trail	10/28/2020	ND	ND	0.0295	62.0	ND	ND	ND	ND	ND	10.5	3.30	9.31	3.57	0.331	ND	0.00744 J	0.00217 J
HSM231 Lead	10/28/2020	ND	ND	0.037	81.1	ND	0.00373 J B	ND	ND	ND	14.8	1.49	10.5	4.62	0.463	ND	0.0107 J	0.00221 J
HSM231 Peak	10/28/2020	ND	ND	0.0396	90.9	ND	ND	ND	ND	ND	17.5	1.36	10.7	5.24	0.516	ND	0.0052 J	0.0024 J
HSM 231 Trail	10/28/2020	ND	ND	0.0367	90.8	ND	ND	ND	ND	ND	17.4	1.38	10.6	5.26	0.512	0.00476	0.0045 J	0.00225 J
HSM 240 Lead	10/28/2020	ND	ND	0.0412	90.6	ND	ND	ND	ND	ND	17.5	1.41	11.4	5.28	0.527	0.00162	ND	ND
HSM240 Peak	10/28/2020	ND	ND	0.0364	86.0	ND	ND	ND	ND	ND	16.4	1.62	10.9	4.97	0.501	0.000918 J	ND	0.0015 J
HSM240 Trail	10/28/2020	ND	ND	0.0392	89.9	0.00306 J	ND	ND	ND	ND	17.1	1.55	11.7	5.21	0.526	ND	ND	ND
FDHSM240 Trail	10/28/2020	ND	ND	0.0388	87.6	ND	ND	ND	ND	ND	16.9	1.46	11.6	5.20	0.512	ND	ND	ND
HSM250 Lead	10/28/2020	ND	ND	0.0405	90.1	ND	ND	ND	ND	ND	17.2	1.42	11.5	5.30	0.520	0.00102 J	ND	0.00155 J
HSM250 Peak	10/28/2020	ND	ND	0.0367	87.6	ND	ND	ND	0.00942	ND	ND	1.39	10.9	5.15	0.507	ND	ND	ND
HSM250 Trail	10/28/2020	ND	ND	0.038	91.0	ND	ND	ND	ND	ND	17.5	1.48	11.2	5.29	0.527	ND	0.00498 J	0.00158 J
HSM260 Lead	10/28/2020	ND	ND	0.0397	91.6	ND	ND	ND	ND	ND	17.4	1.42	11.7	5.37	0.533	ND	ND	ND
HSM260 Peak	10/28/2020	ND	ND	0.0397	90.4	ND	ND	ND	ND	ND	17.4	1.47	11.3	5.37	0.522	ND	ND	ND
HSM260 Trail	10/28/2020	ND	ND	0.042	90.9	ND	ND	ND	ND	ND	17.3	1.49	11.8	5.24	0.518	0.00105 J	ND	0.0015
FDHSM260 Trail	10/28/2020	ND	ND	0.0384	90.7	ND	ND	ND	ND	ND	17.2	1.46	11.7	5.19	0.512	ND	ND	ND
HSM270 Lead	10/28/2020	ND	ND	0.0397	91.0	ND	ND	ND	ND	ND	17.5	1.43	11.4	5.66	0.528	ND	ND	0.00153 J
HSM270 Peak	10/28/2020	ND	ND	0.0389	90.2	ND	ND	0.484	ND	ND	17.3	1.43	11.1	5.23	0.527	0.00129 J	ND	ND
HSM270 Trail	10/28/2020	ND	ND	0.0412	89.0	ND	ND	ND	ND	ND	ND	1.45	11.7	5.28	0.521	ND	ND	ND
TCEQ Acute SWB fo	or Aquatic Life [†]	0.99	NE	123	NE	0.32	0.00739	NE	0.03014	2.37	NE	NE	NE	NE	14.53	NE	0.0651	0.015
TCEQ Chronic SW Life [†]	B for Aquatic	0.087	NE	20.5	NE	0.042	0.00524	1.00	0.00170	1.310	NE	NE	NE	NE	10.7	NE	0.0657	NE

	Date	Aluminum	Antimony	Barium	Calcium	Chromium	Copper	Iron	Lead	Manganese	Magnesium	Potassium	Sodium	Silicon	Strontium	Thallium	Zinc	Vanadium
Location	Collected	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Contact Recreatio	n Water PCL [‡]	403	0.199	64.9	NE	126	33.1	NE	NE	40.9	NE	NE	NE	NE	338	0.0661	201	108

J – Detection is greater than the method detection limit, but less than the reporting limit

mg/L – Milligrams per liter

NE – Not established

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

[‡] Contact Recreation Water PCL Table (TCEQ 2006)

4.2.2.7 Stormwater – Nitrates

Stormwater samples were analyzed for nitrate-nitrite as nitrogen, in accordance with the EAHCP (2016) Work Plan (Appendix A). All nitrate results were below the TCEQ (2018a) SWBs for aquatic life and the TCEQ (2006)528 mg/L to 1.69 mg/L, with an average of 1.18 mg/L. Four samples, HSM231 Lead 1, HSM230 Lead 2, HSM250 Lead, and HSM260 Peak were not analyzed within the EPA Method holding time. Nitrate results are summarized in Table 21.

A		
Location	Date	Concentration (mg/L)
HSM210 Lead 1	10/28/2020	0.530
HSM210 Lead 2	10/28/2020	0.528
HSM210 Peak	10/28/2020	0.552
HSM210 Trail	10/28/2020	0.530
HSM230 Lead 1	10/28/2020	1.69
HSM230 Lead 2	10/28/2020	0.784 H
HSM230 Peak	10/28/2020	1.02
HSM230 Trail	10/28/2020	1.29
FDHSM230 Trail	10/28/2020	1.25
HSM231 Lead	10/28/2020	1.34 H
HSM231 Peak	10/28/2020	1.27
HSM231 Trail	10/28/2020	1.29
HSM240 Lead	10/28/2020	1.29
HSM240 Peak	10/28/2020	1.23
HSM240 Trail	10/28/2020	1.28
FDHSM240 Trail	10/28/2020	1.27
HSM250 Lead	10/28/2020	1.30 H
HSM250 Peak	10/28/2020	1.28
HSM250 Trail	10/28/2020	1.27 F1
HSM260 Lead	10/28/2020	1.28
HSM260 Peak	10/28/2020	1.27 H
FDHSM260 Trail	10/28/2020	1.28
HSM270 Lead	10/28/2020	1.28
HSM270 Peak	10/28/2020	1.28
HSM270 Trail	10/28/2020	1.27
TCEQ Acute SWB for Aquatic Life [†]	1,320	
TCEQ Chronic SWB for Aquatic Life	550	
Contact Recreation Water PCL [‡]	13	

Table 21. Stormwater Samples – Nitrate Detections –San Marcos Springs
Complex

J – Detection is greater than the method detection limit, but less than the reporting limit

H – Sample was prepped or analyzed beyond the specified holding time

mg/L – Milligrams per liter

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

[†] Aquatic Life SWB Table (TCEQ 2018a)

⁺ Contact Recreation Water PCL Table (TCEQ 2006)

4.2.2.8 Stormwater – Caffeine

Stormwater was analyzed for caffeine, which can indicate an anthropogenic source. Caffeine may enter surface water from leaking sewer or septic systems, or it may be present in the aquifer from similar sources in the recharge zone (EPA 2012). Potential ecological effects are currently unknown but could include reduced reproductive success of aquatic organisms (EPA 2012). Caffeine detections in stormwater samples from San Marcos Springs in October 2020 ranged from 12 ng/L to 1,000 ng/L. There is no regulatory standard or expected value for comparison. These results are shown in Table 22.

	Date	Caffeine
Location	Collected	(ng/L)
HSM210 Lead 1	10/28/2020	29
HSM210 Lead 2	10/28/2020	62
HSM210 Peak	10/28/2020	12
HSM210 Trail	10/28/2020	ND
HSM230 Lead 2	10/28/2020	1,500
HSM230 Peak	10/28/2020	1,000
HSM230 Trail	10/28/2020	670
FDHSM230 Trail	10/28/2020	720
HSM231 Peak	10/28/2020	29
HSM231 Trail	10/28/2020	19
HSM240 Peak	10/28/2020	110
HSM240 Trail	10/28/2020	38
FDHSM240 Trail	10/28/2020	32
HSM250 Peak	10/28/2020	22
HSM250 Trail	10/28/2020	13
HSM260 Peak	10/28/2020	12
HSM260 Trail	10/28/2020	20
FDHSM260 Trail	10/28/2020	19
HSM270 Trail	10/28/2020	17

 Table 22. Stormwater Samples – Caffeine Detections – San Marcos Springs

 Complex

ng/L – Nanograms per liter

4.2.3 San Marcos Springs Surface Water Passive Sampling

PDSs were installed in the San Marcos Springs complex in February, April, June, August, October, and December 2020. A sampler was lost due to vandalism or was carried downstream in August 2020. Any changes to deployment locations or unrecovered samplers are discussed in Appendix B.

Rain events occurred during all PDS deployment periods during 2020. Figures 43–48show conductivity and stream discharge rates for each PDS deployment period. The specific conductivity values presented in Figures 43–48 were obtained from the Rio Vista RTI station (Contrail 2020).

PDSs were analyzed for a suite of SVOCs, VOCs, and organochlorine pesticides. Tetrachloroethene was detected in every sample analyzed, except for samples from the most upstream location, HSM410. TPH
was detected in several samples; however, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, undecane, oxylenes, and m-, p-xylenes had few incidents of detection. None of the detected concentrations exceeded the TCEQ (2018a) SWBs for aquatic life or the TCEQ (2006) Contact Recreation Water PCLs. The TCEQ comparison standards and positive detections are presented in Table 17.





Figure 44. Passive Diffusion Sampling – April 2020 Stream Discharge and Specific Conductivity – San Marcos Springs Complex



Figure 45. Passive Diffusion Sampling – June 2020 Stream Discharge and Specific Conductivity – San Marcos Springs Complex



Figure 46. Passive Diffusion Sampling – August 2020 Stream Discharge and Specific Conductivity – San Marcos Springs Complex



Figure 47. Passive Diffusion Sampling – October 2020 Stream Discharge and Specific Conductivity – San Marcos Springs Complex







Table 23. Passive Diffusion Sampling – Volatile and Semi-volatile Organic Compound Detections – San Marcos Springs Complex

Location	Month 2020	(ug/L)	(1) m,p,xylene	도 고 고	anon Toluene (ng/L)	E (ug/L)
	February	ND	ND	ND	ND	ND
	April	ND	ND	ND	ND	0.159
	June	ND	ND	ND	ND	ND
HSM410	August	0.013	ND	ND	ND	0.058
	October	ND	ND	ND	ND	ND
	December	ND	ND	ND	ND	0.059
	February	ND	ND	0.045	ND	ND
	April	ND	ND	0.042	ND	ND
1101420	June	ND	ND	0.040	ND	ND
HSM420	August	ND	0.020	0.026	0.022	ND
	October	ND	ND	0.034	ND	ND
	December	ND	ND	0.028	ND	ND
FDHSM420	June	ND	ND	0.044	ND	ND
	February	ND	ND	0.076	ND	ND
	April	ND	ND	NA	ND	NA
	June	ND	ND	0.102	ND	ND
ПЗIVI430	August	ND	ND	0.077	ND	ND
	October	ND	ND	0.082	ND	ND
	December	ND	ND	0.078	ND	ND
	February	ND	ND	0.016	ND	ND
	April	ND	ND	0.041	ND	ND
	June	ND	ND	NA	ND	NA
113101440	August	ND	ND	0.020	ND	ND
	October	ND	ND	0.025	ND	ND
	December	ND	ND	0.023	ND	ND
	February	ND	ND	0.013	ND	ND
	April	ND	ND	0.016	ND	ND
HSM450	June	ND	ND	NA	ND	NA
13141-30	August	ND	ND	0.010	ND	ND
	October	ND	ND	0.014	ND	ND
	December	ND	ND	0.019	ND	ND

Location	Month 2020	(handorm) (1/ ⁸⁴⁾	(ha, μ, xylene	始 石 (ア	an Toluene (μg/L)	표 (μg/L)
FDHSM450	February	ND	ND	0.013	ND	ND
	April	ND	ND	0.017	ND	ND
	June	ND	ND	NA	ND	NA
	August	ND	ND	0.010	ND	ND
	October	ND	ND	0.016	ND	ND
	December	ND	ND	0.017	ND	ND
	February	ND	0.006	0.025	ND	0.052
HSM460	April	ND	ND	0.023	ND	ND
	June	ND	ND	0.018	ND	ND
	August	ND	ND	NA	ND	NA
	October	ND	ND	0.018	ND	ND
	December	ND	ND	0.021	ND	ND
	February	ND	ND	0.009	ND	ND
	April	ND	ND	NA	ND	NA
	June	ND	ND	0.014	ND	ND
H3IVI470	August	ND	ND	0.014	ND	ND
	October	ND	ND	ND	ND	ND
	December	ND	ND	0.013	ND	ND
TCEQ Acute SWB for Aquatic Life [†]		5,370	32*	3,840	10,210	NE
TCEQ Chronic SWB for Aquatic Life [†]		1,790	1.8*	1,280	3,400	NE
Contact Recreat	ion Water PCL [‡]	2,350	2,080*	148	16,500	28,100**

 μ g/L – Micrograms per liter

NA – Not analyzed

NE – Not established

PCL – Protective concentration level

TCEQ – Texas Commission on Environmental Quality

TPH – Total petroleum hydrocarbons

* Value for m-xylene is presented.

** Value for C>16-21 Aromatics presented for TPH

[†] Aquatic Life SWB Table (TCEQ 2018a)

⁺ Contact Recreation Water PCL Table (TCEQ 2006)

4.2.4 San Marcos Springs Polar Organic Chemical Integrative Sampling

POCIS were installed in the San Marcos Springs system at the farthest downstream sampling location, HSM470, in February, April, June, August, October, and December 2020. Any changes to deployment locations or unrecovered samplers are discussed in Appendix B.

Rain events occurred during all POCIS deployment periods during 2020. Figures 48-53 show conductivity and discharge for each POCIS deployment period. The specific conductivity for Figures 48-53 were obtained from the Rio Vista RTI (Contrail 2020).

No suitable regulatory standards are available to compare to POCIS results; however, the data can be used as a qualitative tool to evaluate the presence of PPCP constituents. Of the 43 PPCP constituents analyzed, 19 were detected in the San Marcos Springs complex. Positive detections are shown in Table 18.









Figure 51. Polar Organic Chemical Integrative Sampling (POCIS) – June 2020 Stream Discharge and Conductivity – San Marcos Springs Complex



Figure 52. Polar Organic Chemical Integrative Sampling (POCIS) – August 2020 Stream Discharge and Conductivity – San Marcos Springs Complex











Location	Month 2020	lo tri (ng/L)	eurone Estrone (ng/L)	(JV Progesterone	ug/L) Bisphenol A	ubrofen (ug/L)	(ug/r)	Naproxen (Jaguana)	Triclosan (ng/L)	Caffeine Ulagene	u) Ciprofloxacin	(ug\r)	표 여 (ng/L)	u) (T/ Galaxolide (HHCB)	u) Oxybenzone	(ug/L) Quinoline	Sucralose	습 IJ (ng/L)	d T (ng/L)	e D L (ng/L)
	February	ND	1,200	ND	ND	1,400	ND	13,000	34,000	11,000	11,000	ND	32,000	20,000	11,000	95,000	5,600	3,700	110,000	3,600
	April	ND	2,300	2,100	9,000	ND	ND	ND	36,000	6,800	ND	ND	44,000	27,000	13,000	54,000	7,200	5,900	190,000	14,000
	June	ND	1,400	ND	5,800	ND	12,000	11,000	16,000	28,000	ND	2,000	300,000	72,000	22,000	71,000	31,000	14,000	370,000	14,000
113101470	August	ND	2,300	ND	6,400	5,000	ND	3,000	22,000	30,000	ND	ND	170,000	46,000	17,000	9,100	28,000	2,300	94,000	9,600
	October	11,000	ND	ND	ND	ND	ND	ND	ND	10,000	ND	ND	160,000	ND	ND	ND	ND	ND	ND	ND
	December	6,600	ND	ND	ND	ND	ND	ND	15,000	ND	ND	ND	13,000	ND	ND	ND	ND	ND	ND	ND
	February	ND	ND	ND	ND	ND	ND	ND	19,000	2,400	ND	ND	21,000	11,000	5,500	11,000	ND	3,200	69,000	1,200
	April	ND	ND	ND	ND	ND	ND	ND	20,000	2,500	ND	ND	18,000	10,000	4,100	3,000	ND	2,800	54,000	1,400
Extraction Blank	June	ND	ND	ND	ND	ND	ND	ND	160,000	3,100	ND	ND	35,000	33,000	1,200	8,800	ND	6,000	110,000	2,600
	August	ND	ND	ND	ND	ND	ND	ND	12,000	3,800	ND	ND	43,000	72,000	5,400	ND	ND	3,400	66,000	ND
	October	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20,000	ND	ND	ND	ND	63,000	ND	ND
	December	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	14,000	ND	ND	ND	ND	ND	ND	ND

Table 24. Polar Organic Chemical Integrative Sampling – Pharmaceutical and Personal Care Products – San Marcos Springs Complex

DEET – N,N-Diethyl-meta-toluamide

HHCB – 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta--2-benzopyran

TCEP – Tris(2-carboxyethyl)phosphine

TCPP – Tris(2-chloroethyl) phosphate

TDCPP – Tris(1,3)-dichloroisopropyl)phosphate

ND – Not detected

ng/L – Nanograms per liter

5.0 SUMMARY OF RESULTS

In 2020, SWCA staff collected sediment, stormwater, passive diffusion samples, and POCIS samples from Comal Springs and San Marcos Springs complexes. The sampling events met the requirements of the EAHCP (2016) and provided background data for these two systems. The limited number of detections above comparative standards is indicative of generally high water quality. Specific compounds detected above a TCEQ (2018a) SWB for aquatic life or TCEQ (2006) Contact Recreation Water PCL (for water) or PEC (for sediment) are listed in Table 19.

Sample Location	Sample Type	Date	Analyte	Concentration	PCL or PEC	
HCS270 Lead	Stormwater	5/16/2020	Pentachlorophenol	13.2 μg/L	3.19 μg/L	SWB Acute
HCS270 Lead	Stormwater	5/16/2020	Pentachlorophenol	13.2 μg/L	2.45 μg/L	SWB Chronic
HCS210 Lead 1	Stormwater	5/16/2020	Aluminum	0.210 mg/L	0.087 mg/L	SWB Chronic
HCS210 Lead 2	Stormwater	5/16/2020	Aluminum	0.804 mg/L	0.087 mg/L	SWB Chronic
HCS210 Lead 2	Stormwater	5/16/2020	Aluminum	0.117 mg/L	0.087 mg/L	SWB Chronic
HCS210 Peak	Stormwater	5/16/2020	Aluminum	0.310 mg/L	0.087 mg/L	SWB Chronic
HCS210 Trail	Stormwater	5/16/2020	Aluminum	0.170 mg/L	0.087 mg/L	SWB Chronic
HCS260 Trail	Stormwater	5/16/2020	Aluminum	0.0968 mg/L	0.087 mg/L	SWB Chronic
FDHCS260 Trail	Stormwater	5/16/2020	Aluminum	0.378 mg/L	0.087 mg/L	SWB Chronic
HCS210 Lead 1	Stormwater	5/16/2020	Lead	0.00174 mg/L	0.00170 mg/L	SWB Chronic
HSM250 Peak	Stormwater	10/28/2020	Lead	0.00942 mg/L	0.00170 mg/L	SWB Chronic

 Table 25. Compounds Detected above Protective Concentration Levels or Probable Effect

 Concentrations

Sample Location	Sample Type	Date	Analyte	Concentration	PCL or PEC	
HSM320	Sediment	7/8/2020	Benzo(a)anthracene	5.310 mg/kg	1.05 mg/kg	PEC
HSM340	Sediment	7/8/2020	Benzo(a)anthracene	3.47 mg/kg	1.05 mg/kg	PEC
HSM320	Sediment	7/8/2020	Benzo(a)pyrene	6.42 mg/kg	1.45 mg/kg	PEC
HSM340	Sediment	7/8/2020	Benzo(a)pyrene	4.45 mg/kg	1.45 mg/kg	PEC
FDHSM340	Sediment	7/8/2020	Benzo(a)pyrene	1.48 mg.kg	1.45 mg/kg	PEC
HSM320	Sediment	7/8/2020	Chrysene	6.56 mg/kg	1.29 mg/kg	PEC
HSM340	Sediment	7/8/2020	Chrysene	4.30 mg/kg	1.29 mg/kg	PEC
FDHSM340	Sediment	7/8/2020	Chrysene	1.59 mg/kg	1.29 mg/kg	PEC
HSM320	Sediment	7/8/2020	Fluoranthene	10.9 mg/kg	2.23 mg/kg	PEC
HSM340	Sediment	7/8/2020	Fluoranthene	8.03 mg/kg	2.23 mg/kg	PEC
FDHSM340	Sediment	7/8/2020	Fluoranthene	2.72 mg/kg	2.23 mg/kg	PEC
HSM320	Sediment	7/8/2020	Phenanthrene	3.75 mg/kg	1.17 mg/kg	PEC
HSM340	Sediment	7/8/2020	Phenanthrene	3.16 mg/kg	1.17 mg/kg	PEC
FDHSM340	Sediment	7/8/2020	Phenanthrene	1.43 mg/kg	1.17 mg/kg	PEC
HSM320	Sediment	7/8/2020	Pyrene	8.37 mg/kg	1.52 mg/kg	PEC
HSM340	Sediment	7/8/2020	Pyrene	6.99 mg/kg	1.52 mg/kg	PEC
FDHSM340	Sediment	7/8/2020	Pyrene	2.69 mg/kg	1.52 mg/kg	PEC
HSM320	Sediment	7/8/2020	Total PAH	63.25 mg/kg	22.8 mg/kg	PEC
HSM340	Sediment	7/8/2020	Total PAH	43.24 mg/kg	22.8 mg/kg	PEC

PAH – Polycyclic aromatic hydrocarbon

PCL – Protective concentration levels

PEC – Probable effect concentrations

SWB Acute – Acute SWB for aquatic life

SWB Chronic – Chronic SWB for aquatic life

Metals in Stormwater

In stormwater samples, no analytes exceeded the TCEQ (2018a) surface water standards for contact recreation and ecological health for VOCs, pesticides, herbicides, or PCBs. In 2020, pentachlorophenol was detected in one sample at a concentration above the TCEQ acute and chronic ecological health freshwater

benchmarks. Aluminum was detected in seven samples at concentrations above the TCEQ chronic ecological health freshwater benchmark. A lead concentration exceeded the chronic ecological health benchmark in one sample. Metals are naturally occurring in soil, sediment, groundwater, and surface water. The water samples for metals analyses were filtered to reduce the potential for sediment impacting the laboratory results; however, the turbidity of the stormwater samples may have contributed to the concentrations of metals detected.

Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment

PAHs are a group of SVOCs common in urban runoff (Mahler et al. 2005) that can have adverse effects on aquatic life, including plants, invertebrates, and fish. The effects of exposure vary but can include organ damage, reproductive harm, or immune system weakening (Mahler et al. 2005). Coal-tar parking lot sealants have been identified as a significant source of PAHs in urban waterways and were banned from use in areas surrounding the recharge zone of the Edwards Aquifer within Comal and Hays Counties by the EAA in 2012. In each sample year thus far, levels of total PAH in sediment samples have exceeded TECs and PECs at location HSM320 in the San Marcos Springs complex.

Bis(2-Ethylhexyl)Phthalate (DEHP) in Sediment

In 2013, DEHP was detected in the majority of sediment samples from the Comal Springs and San Marcos Springs complexes. However, DEHP results were noted in the laboratory blank samples for October 2013 surface water (base flow) sampling event and were considered likely post collection contaminants or false positive detections. In general, DEHP is quite problematic, in that it is common in plastics and other materials. Therefore, the EAA considered DEHP as a likely laboratory or sampling equipment artifact. DEHP was not detected in water quality samples from either spring complex in 2014 or 2015. In 2016, DEHP was detected in multiple surface water (base flow) and stormwater samples collected from both spring complexes. However, DEHP detections were "J" flagged.⁹ In 2018, DEHP was detected in three stormwater samples in the San Marcos Springs complex and three stormwater samples in the Comal Springs complex. None of the detected concentrations exceeded TCEQ (2018a) SWBs for aquatic life or TCEQ (2006) Contact Recreation Water PCLs. DEHP was not detected in any sediment samples from either the Comal Springs or San Marcos Springs complexes in 2018. In 2020, DEHP was detected in all but one of the sediment samples; however, all of the concentrations were "J" flagged.⁸ Also in 2020, DEHP was detected in the laboratory's method blank sample, indicating it was a laboratory contaminant.

Lead in Sediment

Lead has been detected at concentrations of 56.0 mg/kg, 235 mg/kg, 63.5 mg/kg, and 260 mg/kg in years 2013, 2014, 2015, and 2016, respectively, at sample location HSM340. In 2018, the TEC and PEC for lead were 35.8 and 128 mg/kg, respectively. In 2018, lead exceeded the TEC at HSM360. Although the detection level of 127 kg/mg did not exceed the PEC at HSM360, the detection was relatively close to the PEC level of 128 mg/kg. In 2020, lead was detected at a concentration of 53.0 mg/kg at HCS340, which exceeded the TEC value. Additionally, lead was detected at concentrations of 66.5 mg/kg at HSM330 and 38.5 mg/kg at HSM340, which both exceeded the TEC. Lead concentrations detected in sediment in 2020 did not exceeded the PEC.

⁹ Detections that are "J" flagged had concentrations that were greater than the method detection limit, but less than the laboratory reporting limit.

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Tetrachloroethene Detected in Passive Samplers

PDS testing conducted in both spring complexes detected tetrachloroethene in the majority of samples analyzed in 2020. TPH was detected in February in HSM460 and in August in HCS410. Chloroform was detected in August in HCS410. None of the detected concentrations exceeded TCEQ (2018a) SWBs for aquatic life or TCEQ (2006) Contact Recreation Water PCLs.

PPCP Detections in Passive Samplers

POCIS testing was conducted five times during 2020 at HCS460 and HSM470. Of the 43 PPCP constituents analyzed, 20 were detected in the Comal Springs complex and 19 were detected in the San Marcos Springs complex. No suitable regulatory standards are available to compare to POCIS results; however, the data can be used as a qualitative tool to evaluate the presence of trace concentrations of PPCP constituents.

An overview of the scope of work for 2020 is shown in Table 20.

Sample Type	Frequency					
Sediment	Sample biennially in even years					
Stormwater	 One sampling event was conducted in each spring complex Full suite of analyses conducted, as in previous even years Two samples were added to the rising limb of the hydrograph for a total of five samples at two locations in each spring complex, when possible 					
Passive Diffusion Samplers	 Sampling conducted every other month Included pharmaceutical and personal care product membrane only at the bottom of the channel in both systems 					

Table 26. Overview of the Scope of Work for 2020

6.0 DATA QUALITY OBJECTIVES

SWCA evaluated each sampling event to determine whether procedures should be modified to improve data collection to ensure data quality objectives are met. Appendix B discusses problems encountered, deviations to the Work Plan, and resolutions to these circumstances. The only ongoing challenge recognized is the inability to consistently deliver *E. coli* samples to a laboratory within hold times during stormwater sampling events. This inability is inherent to stormwater sampling events due to the occurrence of storms during nonworking hours. SWCA uses additional SWCA office staff or an extra member of the sampling team to deliver samples to the laboratory as early as possible to minimize hold-time exceedances.

Given the procedures implemented to correct or improve data collection methods and the relatively low significance of the deviations, the circumstances described in Appendix B do not compromise the integrity of the study or this report.

7.0 **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).
AGI	Amplified Geochemical Imaging
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.
В	Compound was found in the blank and sample
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.
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.
cfs	cubic feet per second
Channel	A long, narrow excavation or surface feature that conveys surface water and is open to the air.
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.
DEHP	bis(2-ethylhexyl) phthalate
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.
Drainage	The collection, conveyance, containment, and/or discharge of surface and stormwater runoff.
EAA	Edwards Aquifer Authority
ЕАНСР	Edwards Aquifer Habitat Conservation Plan
EST	Environmental Sampling Technology
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.
GC-MS	gas chromatography coupled with a mass spectrometry detector
Groundwater	Water found beneath Earth's surface that fills pores between materials, such as sand, soil, or gravel.
GWQP	General Water Quality Parameters
Habitat	The specific area of environment in which a particular type of plant or animal lives and grows.
НСР	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.
HLP	Hydrophilic-Lipophilic Balance
J	Detection is greater than the method detection limit, but less than the reporting limit

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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.					
mg/kg	Milligrams per kilogram					
MPN	Abbreviation for most probable number. An analytical method used to detect the presence of coliforms in a water sample and estimate their numbers.					
NAS	National Academy of Sciences					
РАН	Polycyclic aromatic hydrocarbon					
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.					
PDS	Passive diffusive sampling					
PEC	Probable effect concentration					
Peak	Maximum instantaneous flow at a specific location resulting from a given storm condition.					
рН	A measure of the alkalinity or acidity of a substance. Also defined as the negative logarithm of the hydrogen ion concentration $(-\log 10[H^+])$ 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.					
POCIS	Polar organic chemical integrative sampler					
РРСР	Pharmaceutical and personal care product					
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.					

Recession	End of runoff event, which is defined as the point in time when the recession limb of the hydrograph is $< 2\%$ of the peak or is within 10% of the pre-storm base flow, whichever is greater.
Representative	Said of samples collected that are similar to those of groundwater in its in situ condition.
RTI	Real time instrument
Runoff	Precipitation, snowmelt, 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.
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	Water that forms and remains above ground, such as lakes, ponds, rivers, streams, bays, and oceans.
SWB	Surface Water Benchmark
SWCA	SWCA Environmental Consultants
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.
TCEQ	Texas Commission on Environmental Quality
TEC	Threshold effect concentration
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.
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 particulates are not transferred from the sample by the lab analyst and are not part of the TOC measurement.

- TPH Total petroleum hydrocarbons
- TSBC Texas-specific Background Concentrations as established by the Texas Commission on Environmental Quality.
- 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 blankSample 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 Unites States Geological Services. USGS is a federal research organization that provides impartial information on health of ecosystems and environment, natural hazards that may threaten us, natural resources, impacts of climate and land use change, and core science systems which provide timely, relevant, and useable information.

μm Micrometer

- 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, 1,2dichloroethane, and carbon tetrachloride.
- Work Group Expanded Water Quality Monitoring Program Work Group

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