



EDWARDS AQUIFER  
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# Universal Passive Samplers and the Aliasing Problem in Groundwater Sampling

# UNIVERSAL PASSIVE SAMPLERS AND THE ALIASING PROBLEM IN GROUNDWATER SAMPLING

## Abstract

The Edwards Aquifer Authority (EAA) evaluated the role of passive sampling devices for improving the collection of representative samples for its water quality monitoring program. The purpose of this study was to investigate the use of universal passive samplers to overcome aliasing which reflects the inability of grab samples to capture a complete record of groundwater contaminant concentrations. Monitoring well (AY-68-29-418, Rio Seco) was sampled with universal passive samplers with exposure times of one hour, 48 hours, and ten days. Grab samples were collected after each exposure period. Tetrachloroethene (PCE) was detected in all of the universal passive samples; total petroleum hydrocarbon (TPH) was detected in 80% of the samples; benzene, toluene, ethylbenzene, and xylenes (BTEX) was detected in 33% of the samples; toluene was detected in 26% of the samples; chloroform was detected in 20% of the samples; and benzene was detected in 7% of the samples. Only PCE was detected in the grab samples. These findings indicated that universal passive samplers can detect contaminants at lower concentrations than grab samples, and the PCE concentrations were directly proportional to exposure time rather than the maximum concentration in the groundwater. Consequently, universal passive samplers only partially overcome aliasing by indicating the presence or absence of contaminants in groundwater.

## 1. Introduction

The EAA and its predecessor agency, the Edwards Underground Water District (EUWD), in cooperation with the United States Geological Survey (USGS) and the Texas Water Development Board (TWDB), have maintained a water quality sampling program since 1968. Analyses of these data have been used by the EAA to assess aquifer water quality. This annual sampling program involved the analyses of a broad spectrum of parameters in wells, springs, and streams across the region. Generally, the sampling program consisted of a minimum of 76 wells, eight streams, and major springs across the region at frequencies ranging from annually to monthly. This study involved well AY

68 29 418, that has been historically sampled by EAA. The San Antonio Segment of the Balcones Fault Zone Edwards Aquifer in south central Texas is one of the largest and most important karst aquifer systems in the United States. The aquifer occupies an area approximately 180 miles long and five to forty miles wide and is the primary water source for most of this area including the City of San Antonio. In addition, the Edwards Aquifer is the principal source of water for agriculture and industry in the region and provides springflow required for endangered species habitat, as well as recreational purposes and downstream uses in the Nueces, Medina, Guadalupe, and San Marcos River basins.

The Edwards Aquifer is contained within the Cretaceous age Edwards Group limestone (Edwards Limestone) and associated units. It is generally capped by the Del Rio Clay and overlays the Glen Rose Formation (upper unit of the Trinity Aquifer). As a karst aquifer, it is characterized by the presence of sinkholes, sinking streams, caves, large springs, and a well-integrated subsurface drainage system. It is one of the most productive groundwater systems in the United States, characterized by extremely high capacity water wells and high spring discharges.

### 1.1. Purpose and scope

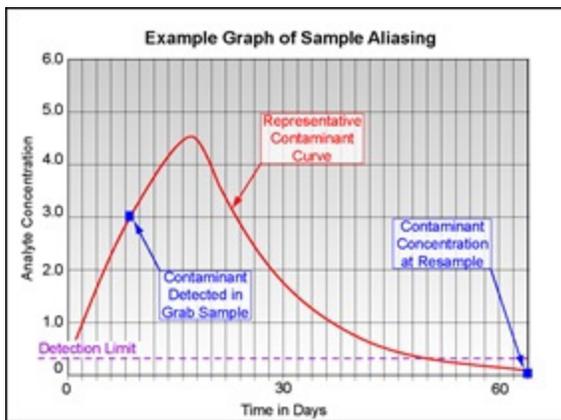
The EAA evaluated the role of passive sampling devices for improving the collection of representative samples for its water quality monitoring program. Historically, EAA's water quality sampling consisted of the collection of "grab" samples from wells, streams, or springs in compliance with the requirements of EAA's Groundwater Quality Monitoring Plan (2013, unpublished). However, due to the karstic nature of the Edwards Aquifer, groundwater composition changes rapidly during rainfall events, and grab samples may not be representative, because they provide only an instantaneous snapshot of water quality at the sample point. Consequently, groundwater analyses that contain detectable anthropogenic compounds often are not repeatable when sampled weeks or months later. Incomplete data due to insufficient sampling frequency is referred to as "aliasing". In contrast, universal passive samplers

involve diffusion and adsorption onto adsorbent material during an extended exposure period that can be utilized for volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and a limited number of pesticide compounds. Universal passive samplers may help to improve the representativeness of groundwater samples by its relatively longer exposure period in groundwater compared to grab samples.

The purpose of this study was to investigate the use of universal passive samplers as a way to overcome aliasing in groundwater sampling. The study consisted of deploying universal passive samplers in a well over a 12-day period and comparing the analyses with grab samples.

## 1.2 Aliasing

Most grab samples collected by the EAA are considered to be discrete samples collected at a certain time and may miss the peak and recession of pollutant concentrations. Historical sampling results indicate contaminant concentrations in the aquifer to be very transient in general. In some cases, it appears that groundwater flow in the aquifer behaves much like



surface water in that velocities are very high. As a result, contaminants travel very quickly through the system, and grab samples may miss the maximum contaminant concentrations. Moreover, grab samples may not detect pollutants at trace levels. Figure 1 discusses aliasing in groundwater.

Figure 1. Aliasing in groundwater.

Besides universal passive samplers, two other solutions to capture pollutants are to increase the sampling frequency or to install automatic samplers. Both

solutions are time consuming and highly costly. Many analytical parameters require preservatives or other sample collection requirements such as refrigeration and/or no head space in the container. These requirements greatly complicate or invalidate some sample analytical parameters collected utilizing auto samplers.

Universal passive samplers are ideal to monitor water quality since these samplers can be deployed for longer periods of time, collect a history of pollutants, and are relatively cheaper than increasing the sampling frequency or installing automatic samplers. Utilization of passive samplers may help to improve the understanding of contaminant flux in the system and improve representativeness of the water quality monitoring program. An objective of this study is to ascertain if universal passive samplers may detect the maximum concentration of contaminants and to improve the understanding of contaminant flux.

## 2. Previous Research

### 2.1. Environmental Technology Verification Report – Groundwater Sampling Technologies

To date, there is limited research on utilizing passive samplers in groundwater monitoring programs. The United States Environmental Protection Agency (EPA) investigated the universal passive sampler in groundwater monitoring wells in 2000 (EPA, 2000). The scope of EPA's study was to determine the accuracy and precision of universal passive samplers in five shallow wells for an exposure time of 48 hours. The water depth for these wells ranged from two feet to ten feet, and each well had a history of containing VOC-contaminated groundwater. These conditions are ideal for universal passive samplers since they are designed to provide adsorption for VOCs and SVOCs at the same time while minimizing the loss of gasses.

The results from the EPA (2000) study indicated that universal passive samplers could detect lower concentration levels of contaminants in groundwater than grab samples and established a direct correlation between universal passive samplers and grab samples.

EPA (2000) determined that universal passive samplers were adequate to study changes in groundwater quality and could illustrate contaminant changes in areas of interest.

## 2.2. Passive Sampling Study

The EAA investigated to evaluate the role of passive sampling devices for improving the collection of representative samples for its water quality monitoring program. (EAA, in preparation, 2016). The scope of the EAA's study was to examine the efficacy of passive sample collection techniques other than the historical purge and sample method. Passive samples may be collected without purging, because groundwater diffuses across a membrane or sorbs onto applicable media. Three devices were utilized for this study; the Polyethylene Diffusion Bag Sampler (RPPS) and the Rigid Porous Polyethylene (RPB) sampler that collect samples by diffusion across a membrane, and the universal passive sampler that works by diffusion and sorption to media. The universal passive sampler was selected over the RPPS and PRB since deployment and retrieval was simple, reduces field labor and costs, was more sensitive than grab samples, and can detect a wide range of VOCs and SVOCs.

The EAA selected 21 monitoring wells to sample with universal passive samplers, either once or multiple times, and a subset of seven wells systematically sampled with universal passive samplers. The study included four wells in Bexar County, one well in Hays County, one well in Medina County, and one well in Uvalde County. All of these wells are within the recharge zone of the Edwards Aquifer except for the well in Medina County, which is in the artesian zone.

Amplified Geochemical Imaging, LLC, (AGI) manufactures and analyzes the universal passive sampler using proprietary techniques. AGI recommends that the universal passive samplers be deployed for no more than 14 days. The EAA varied the exposure time for the universal passive samplers from one hour to approximately 83 days to determine the maximum deployment duration and whether they are a solution to aliasing.

The results from EAA (2015) showed that universal passive samplers as they were used in the study were

most effective as indicators of the presence or absence of organic compounds, which is a partial solution to aliasing. In addition, they were able to detect lower concentration levels of contaminants in groundwater compared to grab samples. Therefore, universal passive samplers could be deployed for long period of time and would record all of the organic compounds that occurred at the monitoring site.

## 3. Methods

### 3.1. Sample Location

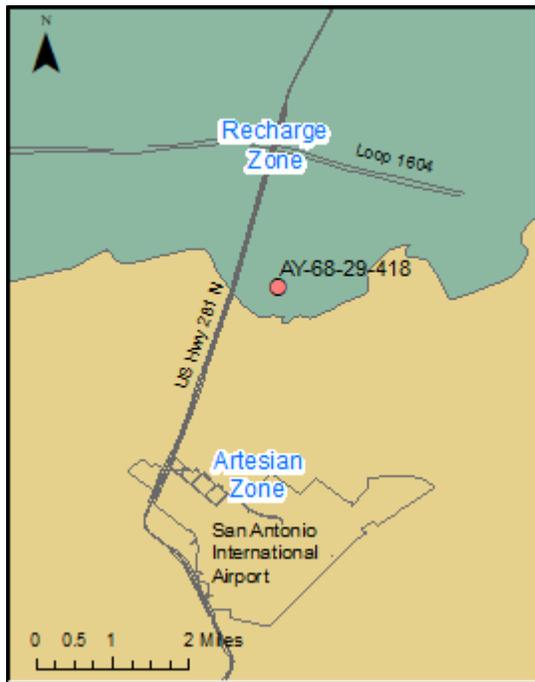
Throughout this 12-day study, one monitoring well (AY-68-29-418, Rio Seco) was sampled with universal passive samplers and grab samples because historical water quality results from January 2008 through March 2015 indicated the presence of chloroform and tetrachloroethene (PCE). Chloroform was detected in 44% of the grab samples with a concentration range of 0.511 micrograms per Liter ( $\mu\text{g/L}$ ) to 0.202  $\mu\text{g/L}$ . PCE was detected in 92% of the grab samples with a concentration range of 0.593  $\mu\text{g/L}$  to 4.96  $\mu\text{g/L}$ . The source of PCE contamination is unknown, although it may be associated with a former dry cleaning facility at Waterford Square at 4202 Thousand Oaks, which is in TCEQ's Dry Cleaner Remediation Program. This well is located within the Recharge Zone of the Edwards Aquifer, surrounded by urban development in Bexar County, as shown in Figure 2. Well depth for AY-68-29-418 is 181 feet below ground level, and the water level was 156 feet below ground level.

Figure 2. AY-68-29-418 (Rio Seco), San Antonio, Texas.

### 3.2. Sampling Frequency

AY-68-29-418 (Rio Seco) was sampled over 12 days with universal passive samplers and grab samples. Grab samples were obtained by using a bailer that was attached to a stainless steel cable and secured within AY-68-29-418. Stagnant water from AY-68-29-418 was not purged because the EAA wanted samples of the water within the well column using both techniques. Universal passive samplers and water quality grab samples were sampled for one hour, every 48 hours, and ten days. Sample parameter selection for this

study was generally based on collecting parameters that would be detectable by the universal passive samplers and grab samples. Sample frequency was selected to detect temporal changes in water quality at a single sample point.



### 3.3. One Hour Deployment

One universal passive sampler was deployed for an hour by zip tying it on top of a bailer deployed at a depth of 176 feet below ground level. Once retrieved, the universal passive sampler was inserted back into its designated vial, and a grab sample was obtained by pouring the water from the bailer into three volatile organic analysis (VOA) bottles. After sampling, the sample tube from the bailer was inserted into a clean Ziploc bag and stored with the box that contained the universal passive samplers. This passive sampling and water quality sampling cycle occurred once at the beginning of this study.

### 3.4. 48 Hour Deployment

Two universal passive samplers were deployed for 48 hours. One sampler was labeled AY-68-29-418 (48 hour), and the other sampler was a field duplicate labeled AY-68-29-418 FD (48 hour). These universal passive samplers and grab samples were sampled identically to the one-hour deployment cycle. This passive sampling and grab sampling cycle occurred six times in 12 days.

### 3.5. Ten Day Deployment

Two universal passive samplers were deployed for 10 days. One sampler was labeled AY-68-29-418 (10 day) and the other sampler was a field duplicate labeled AY-68-29-418 FD (10 day). These two universal passive samplers and grab sample were sampled identically to the one-hour deployment cycle. This passive sampling and water quality sampling cycle occurred once at the end of this study.

### 3.6. Grab Samples

Grab samples were obtained by utilizing a bailer that was deployed and retrieved at the same time as the universal passive samplers. No stagnant water was purged because the EAA wanted to sample the same water quality conditions as the universal passive samplers. The VOC sample was collected by inserting the sample tube into the bailer and allowing the sample water to fill three VOA vials. Each VOA vial was completely filled so that the water formed a convex meniscus to prevent air space in the vial. All VOA vials were turned over and tapped to check for bubbles in the VOA vial, which indicated trapped air. If bubbles were observed, the VOA vial was discarded and another sample collected.

### 3.7. Quality Assurance

Grab samples and universal passive samplers were collected in accordance with the criteria set forth in the EAA's Groundwater Quality Monitoring Plan. Quality assurance samples consisted of trip blanks and field duplicates. The purpose of trip blanks was to assess any potential contamination that may be introduced during storing, sample handling, and shipping of universal passive sampler samples. EAA field staff designated at least one universal passive sampler as the trip blank with every universal passive samplers shipment. All trip blanks remained sealed while in EAA's possession and were maintained with the other universal passive sampler samples. Throughout this study, the EAA dedicated two sealed universal passive samplers for trip blanks, and they did not contain any contaminants.

### 3.8. Quality Control

The purpose of field duplicates was to assess sampling and laboratory analysis precision. Field duplicates were deployed and retrieved at the same time as the parent universal passive samplers. A total of seven field duplicates were utilized throughout this study. The relative percent difference (RPD) range for tetrachloroethene (PCE) was 0% to 14 %, which is satisfactory of this study.

## 4. Results and Discussion

### 4.1 Contaminants Detected in Universal Passive Samplers

AGI detected some contaminants at low levels in the AY-68-29-418 universal passive samplers. In these results, PCE was detected in all of the samples and was the most frequent contaminant found. Total petroleum hydrocarbons (TPHs) was detected in 80% of the samples, benzene, toluene, ethylbenzene, and xylenes (BTEX) was detected in 33% of the samples, toluene was detected in 26% of the samples, chloroform was detected in 20% of the samples, and benzene was detected in 7% of the samples. None of these detections were at a concentration in excess of the applicable regulatory standards for drinking water. Table 1 lists the contaminants detected and range of mass found in AY-68-29-418.

Benzene, BTEX, chloroform, toluene, and TPH were detected by the universal passive samplers but not by grab samples. The universal passive samplers detected these contaminants because they were more sensitive and had a lower detection limit than grab samples. PCE concentrations in grab samples are shown in Figure 3. Table 2 lists the contaminants detected in AY-68-29-418. (Continued on next page)

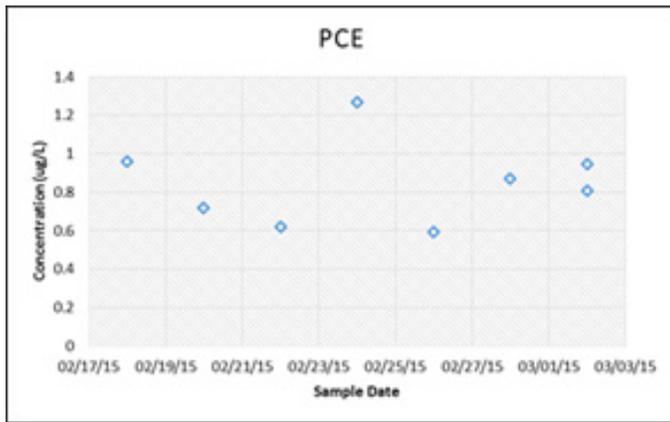


Table 1. Contaminants Detected by AGI and Range of Concentrations in AY-68-29-418.

Chemical Name	Detection Frequency	Percentage of Detections (percent)	Range of Concentrations (µg)
PCE	15	100	<0.02 – 2.26
TPH	12	80	<0.50 – 3.36
BTEX	5	33	<0.02 – 0.08
Toluene	4	26	<0.02 – 0.08
Chloroform	3	20	<0.02 – 0.05
Benzene	1	7	<0.02 – 0.02

Figure 3. Groundwater concentration data from grab sampling.

Table 2. Contaminants Detected in AY-68-29-418 (Rio Seco)

Sample Date	Sample Name and Exposure Duration	Chemical Name	AGI Concentration (µg)	Laboratory Results (µg/L)	Exposure Time for Universal Passive Sampler (in days)
02/18/15	AY-68-29-418 (1 hour)	PCE	0.03	0.958 J	0.040
02/18/15	AY-68-29-418 (1 hour)	TPH	1.06	NA	0.040
02/20/15	AY-68-29-418 (48 hour)	PCE	0.37	0.718 J	1.9
02/20/15	AY-68-29-418 (48 hour)	TPH	0.65	NA	1.9
02/20/15	AY-68-29-418 FD (48 hour)	PCE	0.28	<0.189	1.8
02/22/15	AY-68-29-418 FD (48 hour)	BTEX	0.02	<0.330	1.9
02/22/15	AY-68-29-418 FD (48 hour)	PCE	0.33	<0.189	1.9
02/22/15	AY-68-29-418 FD (48 hour)	Toluene	0.02	NA	1.9
02/22/15	AY-68-29-418 FD (48 hour)	TPH	0.83	NA	1.9
02/22/15	AY-68-29-418 (48 hour)	PCE	0.33	0.618 J	1.9
02/24/15	AY-68-29-418 (48 hour)	PCE	0.46	<0.189	1.9
02/24/15	AY-68-29-418 (48 hour)	TPH	0.66	NA	1.9
02/24/15	AY-68-29-418 FD (48 hour)	PCE	0.48	1.27	1.8
02/24/15	AY-68-29-418 FD (48 hour)	TPH	0.69	NA	1.8
02/26/15	AY-68-29-418 (48 hour)	BTEX	0.06	<0.330	1.9
02/26/15	AY-68-29-418 (48 hour)	PCE	0.38	0.593 J	1.9
02/26/15	AY-68-29-418 (48 hour)	Toluene	0.06	<0.300	1.9
02/26/15	AY-68-29-418 (48 hour)	TPH	1.85	NA	1.9
02/26/15	AY-68-29-418 FD (48 hour)	PCE	0.30	NA	1.8
02/26/15	AY-68-29-418 FD (48 hour)	TPH	0.82	NA	1.8
02/28/15	AY-68-29-418 (48 hour)	Benzene	0.02	<0.330	1.9
02/28/15	AY-68-29-418 (48 hour)	BTEX	0.05	<0.330	1.9
02/28/15	AY-68-29-418 (48 hour)	Chloroform	0.05	NA	1.9
02/28/15	AY-68-29-418 (48 hour)	PCE	0.57	0.870 J	1.9
02/28/15	AY-68-29-418 (48 hour)	Toluene	0.03	<0.300	1.9
02/28/15	AY-68-29-418 (48 hour)	TPH	0.88	NA	1.9
02/28/15	AY-68-29-418 FD (48 hour)	PCE	0.53	NA	1.8
02/28/15	AY-68-29-418 FD (48 hour)	TPH	0.77	NA	1.8
03/02/15	AY-68-29-418 FD (10 day)	PCE	2.26	NA	10.0
03/02/15	AY-68-29-418 FD (10 day)	TPH	0.05	NA	10.0
03/02/15	AY-68-29-418 FD (10 day)	Chloroform	0.04	NA	10.0
03/02/15	AY-68-29-418 (10 day)	Chloroform	0.03	NA	10.0
03/02/15	AY-68-29-418 (10 day)	PCE	2.05	0.807 J	10.0
03/02/15	AY-68-29-418 (10 day)	TPH	0.53	NA	10.0
03/02/15	AY-68-29-418 (48 hour)	PCE	0.39	0.946 J	2.0
03/02/15	AY-68-29-418 FD (48 hour)	BTEX	0.08	<0.330	2.0
03/02/15	AY-68-29-418 FD (48 hour)	PCE	0.39	NA	2.0
03/02/15	AY-68-29-418 FD (48 hour)	Toluene	0.08	NA	2.0
03/02/15	AY-68-29-418 FD (48 hour)	TPH	3.36	NA	2.0

Note: The “J” flags indicate that the result is less than the reporting limit but greater than or equal to the method detection limit, and the concentration is an approximate value. NA means not analyzed.

Figure 4 illustrates data reported from universal passive samplers in units of mass over exposure time in days detected in AY-68-29-418 for chloroform. The data shows no correlation between concentration and exposure time.

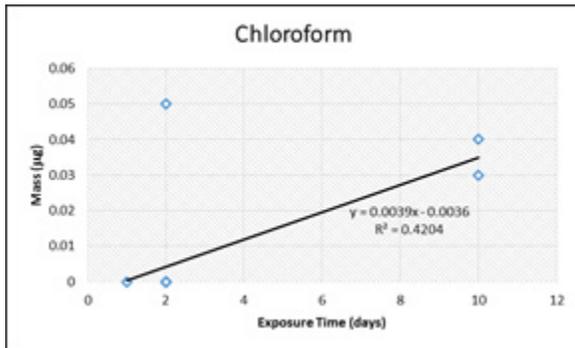


Figure 4. Universal passive sampler data in units of mass over exposure time in days.

Figure 5 illustrates data reported from universal passive samplers in units of mass over exposure time in days detected in AY-68-29-418 for PCE. The data shows there is a correlation between mass and exposure time.

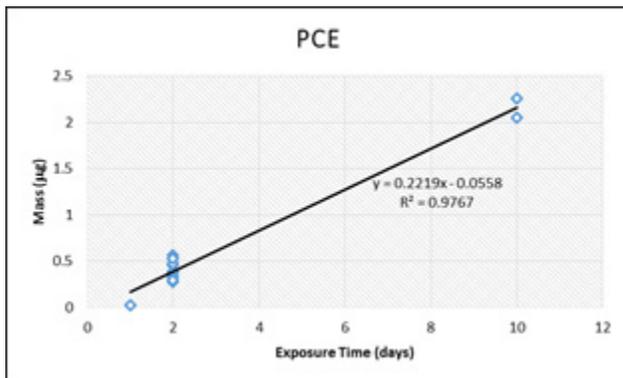


Figure 5. Universal passive sampler data in units of mass over exposure time in days.

Figure 6 illustrates the data reported from the universal passive sampler in units of mass over the grab sample in concentrations for PCE in AY-68-29-418. The data shows there is no correlation between universal passive samplers and grab samples because mass was approximately 0.5 µg in all but two samples while concentrations fluctuated between 0.593 µg/L to 1.27 µg/L.

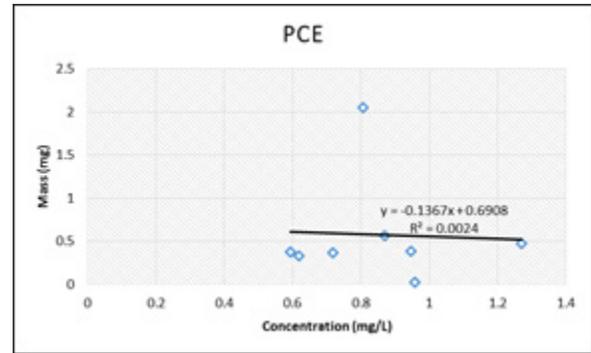


Figure 6. No correlation between universal passive samplers and water quality grab samples for PCE.

Results indicated universal passive samplers had a lower detection limit than grab samples. However, universal passive samplers responded to exposure time and not maximum contaminant. Therefore, universal passive samplers could not be used to calculate maximum concentrations that occurred during the exposure period. Nonetheless, universal passive samplers effectively recorded whether a contaminant was present or absent in groundwater.

## 5. Conclusions

AY-68-29-418 (Rio Seco) was selected for this study because it is within the Recharge Zone of the Edwards Aquifer surrounded by urban development, and water samples contain consistent PCE concentrations. AY-68-29-418 was sampled eight times to determine the correlation between PCE concentrations from universal passive samplers and water quality grab samples. EAA field staff exchanged the universal passive samplers every 48 hours, one universal passive sampler for one-hour exposure time, and two universal passive samplers for ten days exposure time. During each retrieval of universal passive samplers, EAA field staff also obtained a grab sample.

PCE was detected in all universal passive samples and was the most frequent contaminant found in AY-68-29-418. PCE, benzene, BTEX, chloroform, toluene,

and TPH were detected by the universal passive samplers but not detected by the grab samples. The universal passive samplers can detect contaminants at concentrations that are below the detection limit for water quality grab samples. PCE was the only contaminant that established a strong correlation between mass and exposure time.

These findings as well as other studies indicated that universal passive samplers were able to detect low level contaminants that most water quality grab samples would not be able to detect. Universal passive samplers partially overcame aliasing by indicating whether a contaminant was present or absent in groundwater during the exposure period. However, mass adsorbed

by universal passive samplers did not directly correlate with concentration data for the contaminants. This data corroborated the EPA (2000) finding by showing there was a correlation between mass and exposure time for PCE.

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