# GROUNDWATER QUALITY MONITORING PLAN

# **EDWARDS AQUIFER AUTHORITY**

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#### Acronyms

# ACRONYMS AND ABBREVIATIONS

ASTM bgs COC DQO EAA e-line GW MSL NAWQA psi QA QC SOP	American Society of Testing and Materials below ground surface Chain of Custody data quality objective Edwards Aquifer Authority electronic water level measurement device groundwater mean sea level National Water Quality Assessment pounds per square inch quality assurance quality control standard operating procedure
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TWDB	Texas Water Development Board
USGS	United States Geological Survey
VOA VOC	Volatile Organic Analysis Volatile Organic Compound

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# **SECTION 1**

#### **PURPOSE AND OBJECTIVES**

#### 1.1 PURPOSE AND OBJECTIVES OF THE PLAN

Water quality data provide the primary indicator of the state of water quality in the Edwards Aquifer, and are a key component in assessing its general condition. Water quality samples also provide the primary source of data for understanding and monitoring contaminant loading and migration in the Aquifer. This plan includes sections on data quality objectives (DQOs), sampling programs, analytical methods, field procedures, activities of other agencies, and guidelines for annual plan review.

The purpose of this plan is to provide a guidance document that ensures useful, consistent and defensible water quality data are produced by implementing appropriate procedures and methods when collecting and analyzing water quality samples. Water quality samples are currently collected under five sampling programs at the Edwards Aquifer Authority (the Authority). Data quality requirements vary by program and are discussed in Sections 2 and 3. The water quality sampling programs currently undertaken by the Authority are:

- Routine Water Quality Sampling
- Event Sampling
- Surface Water Sampling
- Spring Sampling
- Confirmation Sampling

The purpose of this plan can be achieved by implementation of the objectives listed below and discussed in detail herein. Each staff member charged with the responsibility of collecting water quality samples should be familiar with this plan, and the objectives and procedures outlined in it. The objectives of this plan are:

- Obtain quality data that are defensible for their intended purpose.
- Analyze field samples in an appropriate and consistent manner such that the results are accurate, and repeatable.
- Collect samples for laboratory analysis in an appropriate and consistent manner that will ensure accurate and reliable analytical results with a minimal amount of anomalous data.
- Select sample sites and time periods that will provide representative water quality data, for a range of aquifer conditions.
- Review and revise the plan on an annual basis as needed.

#### SECTION 2

#### DATA QUALITY OBJECTIVES, DATA LEVELS AND SAMPLE TYPES

The US Environmental Protection Agency (US EPA) has developed criteria for data quality objectives utilizing a seven-step process that optimizes sample collection and analysis based on data uses, fiscal budget, sample quantity and other parameters (US EPA 2000). Other organizations have also developed program documents that utilize DQOs as a tool for developing sampling programs. Data quality objectives herein are designated by classifying data at Levels I – III, where each data level is specific to the requirements of the sampling program. As the data level increases, so does the amount of associated quality assurance/quality control (QA/QC), cost, and level of effort required to obtain the final result.

Level I data are data derived from samples collected and analyzed in the field. These data are quick and inexpensive to obtain. Typically no elaborate QA/QC procedures, such as duplicate and matrix samples are taken in association with Level I data. In addition, the analytical methods associated with these data do not require a rigorous procedure for completion, such as a standard reference method would require. However, Level I data are very valuable especially when properly performed and available for a significant period of record at one sample location. These data provide an indicator tool, or screening tool, that may be used to detect emerging changes in water quality.

Level II data are derived from samples collected in the field and analyzed in the laboratory by standard analytical method. The primary difference between Level II and Level III data are the QA/QC samples. Level II data do not have QA/QC samples associated with the parent sample, trip blanks for VOC analysis being the single exception. Since a full suite of QA/QC samples are not associated with Level II, the cost per sample point is less than Level III data. Most routine water quality samples will fall under this data category.

Level III data are at the other end of the spectrum from Level I. Samples taken for Level III data must be collected with exacting procedures and applicable QA/QC samples must be collected and analyzed in association with the parent sample. Full field documentation is a requisite also. All Level III data are analyzed using standard reference methods under laboratory conditions.

#### 2.1 DATA QUALITY OBJECTIVES

Data quality objectives are defined by the United States Environmental Protection Agency (US EPA) through a seven-step process. The process is iterative, and may be modified by the planning team to incorporate changes as required. The seven steps are outlined below.

State the Problem

Define the problem, identify the planning team, examine the budget, and schedule.

**Identify the Decision** 

State the decision, identify study questions, define alternative actions.

Identify the Inputs to the Decision

Identify information needed for the decision, such as information sources, basis for action level, sampling and analyses methods.

**Define the Boundaries of the Study** Specify sample characteristics, define spatial/temporal limits, units of decision making.

Develop a Decision Rule Define statistical parameter (mean, median); specify action level, develop logic for action.

Specify Tolerable Limits on Decision Errors Set acceptable limits for decision errors relative to consequences (health effects, costs).

Optimize the Design for Obtaining Data Select resource-effective sampling and analysis plan that meets the performance criteria.

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

Therefore, for the purposes of this plan, DQOs are met by assigning a level of precision and procedural techniques that are appropriate for the sample type, and monitoring program. While it is the purpose of this plan for all data produced to be defensible, this does not mean that all data must be analyzed by reference methods in the analytical laboratory utilizing a full suite of QA/QC samples. The majority of water quality samples are intended only as a check on the general condition of the aquifer. Very few of

the samples are used as a tool for assessing risk to public health, or the effectiveness of a remedial action.

Therefore, DQOs for analytical data discussed in this plan are designed to provide data of adequate quality, and quantity, to reflect the sample type, and program type applicable to the data. With the exception of confirmation sampling, the objective of water quality samples are to provide information concerning the absence or presence of compounds that do not occur in the environment naturally, or to measure the variations in concentration or quantity of compounds that do occur naturally. These results are compared to historical data (in most cases) for the sample point. In the case of confirmation sampling, the objective is to ascertain with 95% confidence that a suspect compound is present, and to measure the quantity of that compound if present.

## 2.2 DATA QUALITY LEVELS

The objectives for data quality vary by sample and program type. In order to obtain data in a cost-effective manner, the data are assigned Levels I – III in this plan. Each level represents an acceptable DQO, its associated level of QA/QC, and relative cost to the programs. Data levels, and their respective definitions and QA/QC requirements are summarized in the Table 2-1. Level I data are collected under all sampling programs, while Level III data are normally only collected under the confirmation sampling program.

Data Level		Comments
Level I	Samples analyzed in the field, using field analytical techniques, such as Hach kits, dissolved oxygen (DO) meters, pH meters, or other equipment. Standard parameters are DO, pH, Temperature, Turbidity, Conductivity, and Alkalinity. Or, samples analyzed using a method with less precision inherent in the analysis such that the analytical precision has a relatively high error tolerance for quantification (such as bacteriological counts).	Rigorous QA/QC sampling is not associated with this data level, and these analyses are normally performed in the least controlled environment (analyzed in the field).
Level II	Samples analyzed in the laboratory, but not associated with a full suite of QA/QC samples, analyses may be by a standard reference method (SW-846) or other recognized analytical method. VOC trip blanks may be collected in association with these samples.	Most routine water quality samples are collected as Level II data samples. In addition, spill sampling may frequently fall under this DQO.

Table	2-1,	Analytical	Data	Levels
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Table 2-1, Analytical Data Levels (continued)			
Level III	Samples analyzed in the laboratory by a standard analytical reference method (such as SW-846 Methods), with a full suite of QA/QC samples associated such as trip blanks, equipment blanks, ambient blanks, field duplicates, and MS/MSDs. Also, full field notebook documentation is a requisite for this level of analysis (see Section 5.3).	Confirmation samples will most often fall into this category. This is due to the likelihood that confirmation sampling will be used to assess the degree of accuracy and precision of a predecessor sample.	

# **2.3 SAMPLE TYPES**

Many sample parameters are frequently referred to in this plan as a group. Specifically, QA/QC parameters, field parameters, and general water quality parameters each represent a sample group that may be analyzed for more than one parameter. Each sample type (QA/QC, field parameters, and general water quality parameters) is defined in this section. Other sample parameters utilized and discussed in this plan are method specific and do not require a separate discussion.

# 2.3.1 Quality Control and Quality Assurance Samples

In order to adhere to the data quality process, additional samples for QA/QC must be taken and analyzed to achieve Level III data, and some Level II data. The various types of QA/QC samples applicable to this plan are outlined in the following paragraphs.

# 2.3.2 Matrix Spike and Matrix Spike Duplicate

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

The MS/MSD is spiked and analyzed, if the spiked analytes are recovered within a method specific percentage, then matrix effects are deemed minimal, and no matrix data flag is attached to the results. However, if the spike recovery does not fall within the designated percentage, then analytical results will be flagged with an M-flag, indicating a matrix effect is present. The sample name for MS/MSDs is identical to the parent

sample, with the MS/MSD attached as a modifier at the end of the sample name. The MS/MSD should also be noted on the chain of custody.

# 2.3.3 Ambient Blanks

Ambient blanks are taken to assess the possibility of site specific atmospheric contamination of VOC samples. Ambient blanks are only taken when an area is suspect of having detectable quantities of atmospheric VOCs present (for example if VOC samples are being collected in the vicinity of a fueling operation). Ambient blanks are prepared by pouring ASTM II, reagent grade water directly into a 40 milliliter (ml), volatile organic analyses (VOA), container at the sample site, during collection activities. The VOA is allowed to remain open and exposed to the atmosphere for the duration of the sample collection process. The water is treated and analyzed as a sample from this point forward, with the designation AB on the chain of custody (COC). Ambient blanks are only applicable to Level III, VOC samples.

# 2.3.4 Equipment Blanks

Equipment blanks consist of ASTM II, reagent grade water poured over/through any sampling equipment used for collection of definitive samples. Most sample collection equipment is disposable, however, in some cases, an equipment blank may be required. Equipment blanks are used to assess the effectiveness of decontamination procedures, (for new materials provided to the Authority or from Authority decontamination processes) and are designated as EB on the COC. The frequency of collection of equipment blanks will depend upon the sampling routine, and sampling equipment in use. In most cases however, they will be collected only on a limited basis for Level III data.

# 2.3.5 Trip Blanks

Trip blanks are applicable only to VOC samples. They are prepared and supplied by the analytical laboratory. Trip blanks are to be shipped from the laboratory, and maintained with the VOC samples collected in the field. The purpose of trip blanks is to assess any potential contamination that may be introduced during the shipping and sample handling process. Trip blanks are designated on the COC using the letters TB. Trip blanks are not to be opened in the field. Trip blanks are applicable to Level II and III, VOC samples only.

# 2.3.6 Duplicate or Replicate Samples

Duplicate and replicate samples are intended to assess the precision or repeatability of the analytical process. Typically, one in ten samples should have a duplicate sample collected. However, for the purposes of this plan, duplicates are applicable only to Level III data. The collection frequency of 1 duplicate per 10 samples is generally acceptable.

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Note however, that if a confirmation sampling event involves only 3 wells, then the duplicate (as well as other) QA/QC samples are still required. Stated another way, duplicates comprise 10% of the sample set such that a sample population of 10 would contain 1 duplicate. However a sample population of 11 would contain 2 duplicates. The calculated number of duplicates is always rounded to the next whole number.

A duplicate sample is a second sample collected at the same location as the parent, either simultaneously, or immediately following collection of the first sample (AFCEE 2001). Both samples are collected, stored, and transported in identical fashion. A replicate sample, sometimes called a split sample is defined as a single sample divided into two samples (AFCEE 2001). As with a duplicate, collection, storage, and transport of the resulting samples must be identical. Duplicate and replicate samples each have unique identifiers (see Section 4.4).

## 2.3.7 Field Parameters

The term "field parameters" are frequently used to describe the sample set taken, and analyzed in the field by the sampling team. Field parameters are analyzed using Hach kts, DO meters, pH meters, or other equipment in the Authority's inventory, and are common to all sampling programs. Some of the parameters listed are also analyzed in the laboratory as Type II data. Field parameters are all of Type I data and consist of the following specific parameters:

Field Parameters Analyses List

- DO
- pH
- Temperature
- Turbidity
- Conductivity
- Alkalinity
- Bacteriological

# 2.3.8 General Water Quality Parameters

General water quality parameters are frequently used to describe a basic sample set common to all sampling programs discussed herein. These parameters provide basic information about water quality at each sample site, and are analyzed as Type II data, in the laboratory. Their usefulness becomes more important when the data set is available for a significant period of record in order to establish water quality trends at sample points. Some of the parameters are duplicated in the field parameter list. However, this provides a check on the field parameter data quality, as well as a measure of potential sample quality changes that occur between collection time and laboratory analyses. General water quality parameters are: General Water Quality Analyses List

- Alkalinity
- Bicarbonate
- Carbonate
- Calcium
- Magnesium
- Sodium
- Potassium
- Chloride
- Sulfate
- Fluoride
- Silica
- Strontium
- Nitrate
- pH
- Total Dissolved Solids
- Total Suspended Solids

## **SECTION 3**

#### SAMPLING PROGRAMS AND OBJECTIVES

Water quality samples are collected under one of the five Authority programs previously listed in Section 1, and discussed in detail in this section. The routine water quality and event based sampling programs are further subdivided in this Section. Routine water quality samples vary dependent upon land use surrounding the sample point. This is due to differences in potential contaminants associated with variations in land use. For example, pesticide and herbicide residuals are more likely in an agricultural setting than in association with an urban hydrocarbon storage facility. As such, this program maintains slightly different analytical parameters for urban and agricultural areas. However, parameters for any site may vary dependant upon site history, or other site specific information. The event based program is aimed at two types of events: 1) continuous monitoring for effects of storm water, and 2) monitoring for contaminants associated with a hazardous material release.

The remaining programs, (spring sampling, surface water sampling, and confirmation sampling) are also discussed in detail in this section. Water quality sample locations for calendar year 2002 are shown in Appendix A.

#### 3.1 ROUTINE WATER QUALITY SAMPLING PROGRAM

The Routine Water Quality Sampling Program is the basic sampling program used by the Authority to assess water quality in the Edwards Aquifer. Sampling routines and parameters for this program are based on two broad land use categories, urban and agricultural. Sample parameters are designed to assess contaminants that may be present as a result of land use category. This program is also used as a tool to monitor trends in basic water quality, within the aquifer. During the year 2001, a total of 76 wells across the region were sampled under this program.

In the next revision of this document, a list of water quality index wells will be identified. These water quality index wells shall be selected based on criteria that will be established prior to the next revision. The intent being that these wells will provide reference data points that will assist in assessing Edwards Aquifer water quality trends. Additional samples will be collected from wells throughout the region under the Routine Water Quality Sampling Program, however, these wells may be selected randomly in order to ascertain potential problem areas in the aquifer.

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# 3.1.1 Routine Water Quality Sampling for Urban Wells

Urban wells, in this application are wells (domestic, public water supply, or irrigation), that are located in an area with a primarily urban land use. As such, sampling parameters are designed to detect the presence of compounds that might be expected to occur more frequently in an urban setting. It is worth noting however, the parameters listed below may be changed if conditions warrant, as analyzed on a site conditional basis. Standard analyses performed under this program are listed below.

- Field Parameters (Level I)
- General Water Quality Parameters (Level II)
- Selected Metals (Level II)
- Semi-volatile Organic Compounds (SVOC) (Selected Locations\*) (Level II)
- Volatile Organic Compounds (VOC) (Selected Locations\*) (Level II)
- Bacteriological (Fecal Strep and Fecal Coliform) (Level II)

\* Indicates that all wells sampled under this program are not analyzed for these parameters

# 3.1.2 Routine Water Quality Sampling for Agricultural Wells

Agricultural wells in this application, are wells (domestic, public water supply, or irrigation), that are located in an area with a primarily agricultural land use. As such, sampling parameters are designed to detect the presence of compounds that might be expected to occur more frequently in an agricultural setting. It is worth noting however, the parameters listed below may be changed if conditions warrant, as evaluated on a site conditional basis. Standard analyses performed under this program are listed below.

- Field Parameters (Level I)
- General Water Quality Parameters (Level II)
- Selected Metals (Level II)
- Herbicides (Level II)
- Pesticides (Level II)
- Bacteriological (Fecal Strep., and Fecal Coliform) (Level II)

# 3.2 EVENT BASED SAMPLING PROGRAM

There are two categories of event based sampling, the first category, continuous monitoring, is aimed at monitoring the effects of stormwater runoff into the aquifer. The second category, hazardous materials releases, is designed to assess the impact of spills, or other unauthorized releases of contaminants into the aquifer.

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# **3.2.1 Continuous Monitoring**

Continuous monitoring for changes in conductivity related to recharge is performed to assess aquifer characteristics as part of the optimization technical studies program. To date, the program has been implemented by using a downhole probe (In-Situ®, MP Troll) capable of recording changes in potentiometric pressure (converted into water level) and conductivity on a near continuous basis. As this program is developed, sample parameters may be added, based on established changes in conductivity in response to groundwater flux.

# 3.2.2 Groundwater Sampling in Response to Hazardous Material Releases

Groundwater quality sampling in response to a release of hazardous materials is extremely important in understanding pollutant loading in the aquifer. Another aspect of this sampling program involves detection of contaminants to prevent accidental ingestion of pollutants by the general population via public or private water supply wells. This type of monitoring also provides additional input to other regulatory agencies in charge of determining clean-up criteria for spills.

Knowing the exact number and location of release events in advance is an impossible task. However, spill probabilities typically increase in population and industrial centers, and along the length of major transportation routes. In addition, some historical spills are worthy of periodic sampling to monitor the status of any associated groundwater plumes.

The procedure to be followed in performing spill sampling will be based on directives from the Aquifer Science Program Manager (PM). The PM will meet with the Chief Technical Officer (CTO), and senior aquifer science staff, to assess the situation and develop directives for staff to implement sampling activities. The directives will designate sample locations, and outline analytical parameters specific to the substance spilled or otherwise released into the aquifer. Typically, spill sampling will be performed as Level II sampling for the laboratory analyses, however, in some cases Level III data may be required.

# 3.3 SPRING SAMPLING

Groundwater discharging at five spring sites is sampled three-times annually by the Authority. San Antonio Springs, San Pedro Springs, Comal Springs (spring orifices One and Seven), Hueco Springs (spring orifices A and B), and San Marcos Springs (spring orifices Deep and Aquarena Hotel) are the spring sample locations. This provides a total of eight sample points at five spring sites. Analytical parameters and data quality levels are listed below for spring sampling.

• Field Parameters (Level I)

- General Water Quality Parameters (Level II)
- Selected Metals (Level II)
- Semi-volatile Organic Compounds (SVOC) (Selected Locations) (Level II)
- Volatile Organic Compounds (VOC) (Selected Locations) (Level II)
- Bacteriological (Fecal Strep and Fecal Coliform) (Level II)
- Chlorinated Herbicides (Level II)
- Organophosphorous Compounds (Level II)
- Polychlorinated Biphenyl (PCB) (Level II)
- Organochlorine Pesticides (Level II)
- Nitrate / Nitrite (Level II)
- Total Phosphorous (Level II)

# 3.4 SURFACE WATER SAMPLING

Surface water samples are collected quarterly from eight sites within the Authority's jurisdictional area. The eight sites are the Nueces River at Laguna, Dry Frio River at Reagan Wells, Sabinal River at Sabinal, Seco Creek at Miller Ranch, Frio River at Concan, Hondo Creek at Tarpley, Medina River at Bandera, and the Blanco River at Wimberley. Most of the surface water sample data are collected upstream of the recharge zone, and are generally used to assess the quality of surface waters that may subsequently be introduced as recharge into the aquifer. Surface water samples are analyzed for the following parameters at the indicated levels of data quality.

- Field Parameters (Level I)
- General Water Quality Parameters (Level II)
- Selected Metals plus Silver (Level II)
- Bacteriological (Fecal Strep and Fecal Coliform) (Level II)
- Chlorinated Herbicides (Level II)
- Organophosphorous Compounds (Level II)
- Polychlorinated Biphenyl (PCB) (Level II)
- Organochlorine Pesticides (Level II)
- Nitrate / Nitrite (Level II)
- Total Phosphorous (Level II)
- Biochemical Oxygen Demand (Level II)

# 3.5 CONFIRMATION SAMPLING

At times, sample results may appear erroneous, or questionable, or may be contested by an outside party. These or other conditions may result in a need to re-sample a location. This type of sampling is generally referred to as confirmation sampling. For example, if

a well shows the presence of benzene, but has never tested positive for it in the past, it may require confirmation sampling.

However prior to conducting a confirmation sampling event, the possibility of a false positive result should be assessed. This can be done by review of field notes, and analytical laboratory QA/QC for the sample group in question. This is not always conclusive, and a confirmation sample is sometimes the only alternative. The need to collect confirmation samples does not occur frequently, but should be taken into account for scheduling and budgeting purposes each year. Confirmation samples will be generally performed as Level III samples. Prior to collection of any confirmation samples, approval of the Aquifer Science PM is required.

## **SECTION 4**

#### ANALYTICAL METHODS AND CUSTODY PROCEDURES

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

#### 4.1 ANALYTICAL METHODS

A variety of analytical methods are used in the various water quality sampling programs. Table 4-1 lists standard analytical reference methods applicable to the programs, while Table 4-2 summarized other methods utilized.

Analysis	Method
Volatile Organic Compounds (VOCs)	SW-8260b
Semivolatile Organic Compounds (SVOC)	SW-8270c
Chlorinated Herbicides	SW-8151
Organophosphorus Compounds	SW-8141
Non-volatile Compounds by HPLC	SW-8321
Organochlorine Pesticides	SW-8081
Polychlorinated Biphenyls (PCBs)	SW-8082
Polynuclear Aromatic Hydrocarbons (PAH)	SW-8310
Determination of Triazine Pesticides	EPA-619
Organonitrogen Pesticides in Industrial / Municipal Wastewater	EPA-633
Oryzalin in Industrial / Municipal Wastewater	EPA-638
Total Petroleum Hydrocarbons (TPH)	TX-1005
Metals (except mercury)	SW-6010b
Mercury	SW-7470A
Cyanide	SW-9010B

#### **Table 4-1, Analytical Reference Methods**

Analysis	Method	]
Alkalinity	EPA-310.1	
Common Anions	SW-9056	
Sulfate (SO <sub>4</sub> )	EPA 300.0	
pH	SW-9040B	
Total Dissolved Solids (TDS)	EPA 160.1	
Total Suspended Solids (TSS)	EPA 160.2	
Ortho-Phosphate	EPA 365.3	
Nitrate / Nitrite (both as N)	EPA 353.2	K
Ammonia (as N)	EPA 350.3	
Kjeldahl (as N)	EPA 351.3	
Total Organic Carbon (TOC)	EPA 415.1 or	
-	SW-9060	
Biological Oxygen Demand (BOD)	EPA 405.1	5 /A 600 878
Sulfide	EPA 376.2	( ° °°0 %/2
Bacteriological	=	K
Fecal Strep.	SM 9230.C	LAB Chance
Fecal Coliform	SM 9222.D	to SM 92

# Table 4-1, Analytical Reference Methods (Continued)

# 4.2 DATA FLAGGING CONVENTIONS

The analytical data must be qualified by the analytical laboratory. This is accomplished in a summary fashion by the addition of data flags to the data result. Table 4-3 provides a summary of the data flagging convention used in this plan (modified from AFCEE, 2001).

# Table 4-2 Data Flags

Flag	Description
J	The analyte was positively identified, the quantitation is an estimation.
U	The analyte was analyzed for, but not detected. The associated numerical value is at or below the method detection limit (MDL).
F	The analyte was positively identified but the associated numerical value is below the reporting limit (RL).
R	The data are rejected due to deficiencies in the ability to analyze the sample and meet QC criteria.
В	The analyte was found in an associated blank, as well as in the sample.
М	A matrix effect was present.
S	To be applied to all Level I field analyses
Т	Tentatively identified compound (using GC/MS)
	No flag indicates the analyte was detected at the reported concentration.

# 4.3 SAMPLE CONTAINERS AND HOLD TIMES

Samples sent to the analytical laboratory must be properly containerized, preserved, and analyzed within specified hold times for the method in order for the data to be of defensible quality. In addition to a general requirement for samples to be chilled to 4° C,  $\pm$  2°, some analytical methods require the sample to be maintained at specific pH values. As such, Table 4-3 lists acceptable container types, preservatives, and hold times for common analytical methods. The table is modified from AFCEE, 2001.

	Analytical			Minimum Sample Volume or	Maximum Holding
Name	Methods	Container*	Preservation <sup>b,e</sup>	Weight	Time
Alkalinity	E310.1	P, G	4°C	50 mL	14 days
Common anions	SW9056	P, G	None required	50 mL	28 days for Br', F', Cl', and SO <sub>4</sub> <sup>-2</sup> ; 48 hours for NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> and PO <sub>4</sub> <sup>-3</sup>
Cyanide, total and amenable to chlorination	SW9010A SW9012	P, G, T	4°C; NaOH to pH > 12, 0.6 g ascorbic acid	500 mL or 4 ounces	14 days (water and soil)
Total Dissolved Solids (TDS)	E160.1	P, G	4°C	100 mL	7 days
Total Suspended Solids (TDS)	E160.2	P, G	4°C	100 mL	7 days
Hydrogen ion (pH) (W, S)	SW9040/ SW9045	P, G	None required	N/A	Analyze immediately
Nitrogen, nitrate+nitrite	E353.1	P, G	$4^{\circ}$ C, H <sub>2</sub> SO <sub>4</sub> to pH < 2	500 mL	28 days
Conductance	SW9050	P, G	None required	N/A	Analyze immediately
Temperature	E170.1	P, G	None required	N/A	Analyze immediately
Dissolved oxygen	E360.1	G	None required	500 mL	Analyze immediately
Turbidity	E180.1	P, G	4°C	N/A	48 hours
Settleable Solids	E160.5	P,G	None required	N/A	Analyze immediately
Total organic carbon	SW9060	P, G, T	4°C, HCl or H <sub>2</sub> SO <sub>4</sub> to pH < 2	500 mL or 4 ounces	28 days (water and soil)
Chromium (VI)	SW7196A	P, G, T	4°C	500 mL or 8 ounces	24 hours (water and soil) <sup>d</sup>
Mercury	SW7470 SW7471	P, G, T	HNO <sub>3</sub> to pH < 2, 4°C	500 mL or 8 ounces	28 days (water and soil)
Metals (except chromium (VI) and mercury)	SW6010A SW6020 and SW-846 AA methods	P, G, T	HNO3 to pH < 2, 4°C	500 mL or 8 ounces	180 days (water and soil)

Table 4-3, Sample Containers	, Preservatives,	and Hold Times
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a. Polyethylene (P); glass (G); brass sleeves in the sample barrel, sometimes called California brass (T).

b. No pH adjustment for soil.

c. Preservation with 0.008 percent  $Na_2S_2O_3$  is only required when residual chlorine is present.

d. The maximum recommended holding time for completion of extraction into water is 48 hours. The extract shall be analyzed within 24 hours of completion of extraction

Table 4-3, Sample Containers, Preservatives	s, and Hold Times (Continued)
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Name	Analytical Methods	Container*	Preservation <sup>be</sup>	Minimum Sample Volume or Weight	Maximum Holding Time
Total petroleum hydrocarbons (TPH)-C <sub>6</sub> - C <sub>35</sub>	TX 1005	G, Teflon®- lined septum, T	4°C, HCl to pH < 2	3 x 40 mL or	14 days (water); to extraction, and 14 days after extraction
Volatile aromatics	SW8020A	G, Teflon®- lined septum, T	4°C, HCl to pH < 2, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	2 x 40 mL or 4 ounces	14 days (water and soil); 7 days if unpreserved by acid
Halogenated volatiles	SW8021A	G, Teflon®- lined septum, T	4°C, HCl to pH < 2, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	2 x 40 mL or 4 ounces	14 days (water and soil); 7 days if unpreserved by acid
Nitrosamines	SW8070	G, Teflon®- lined cap, T	4°C	1 liter or 8 ounces	7 days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Chlorinated herbicides	SW8150B SW8151	G, Teflon®- lined cap, T	4°C, pH 5–9	1 liter or 8 ounces	7 days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)

a. Polyethylene (P); glass (G); brass sleeves in the sample barrel, sometimes called California brass (T).

b. No pH adjustment for soil.

c. Preservation with 0.008 percent  $Na_2S_2O_3$  is only required when residual chlorine is present.

Name	Analytical Methods	Container <sup>2</sup>	Preservation <sup>be</sup>	Minimum Sample Volume or Weight	Maximum Holding Time
Organochlorine pesticides and polychlorinated biphenyls (PCBs)	SW8080A, SW8081,	G, Teflon®- lined cap, T	4°C, pH 5–9	1 liter or 8 ounces	7 days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Organophosphorus pesticides/ compounds	SW8140 SW8141A	G, Teflon®- lined cap, T	4°C, pH 5–9	1 liter or 8 ounces	7 days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Semivolatile organics	SW8270B	G, Teflon®- lined cap, T	4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1 liter or 8 ounces	7 days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)
Volatile organics	SW8240B, SW8010B, SW8260A	G, Teflon®- lined septum, T	$4^{\circ}$ C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (HCl to pH < 2 for volatile aromatics by SW8240 and SW8260) <sup>6</sup>	2 x 40 mL or 4 ounces	14 days (water and soil); 7 days if unpreserved by acid
Polynuclear aromatic hydrocarbons (PAHs)	SW8310	G, Teflon®- lined cap, T	4°C, store in dark, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1 liter or 8 ounces	7 days until extraction and 40 days after extraction (water); 14 days until extraction and 40 days after extraction (soil)

a. Polyethylene (P); glass (G); brass sleeves in the sample barrel, sometimes called California brass (T).

b. No pH adjustment for soil.

c. Preservation with 0.008 percent  $Na_2S_2O_3$  is only required when residual chlorine is present.

Name	Analytical Methods	Container <sup>*</sup>	Preservation	Minimum Sample Volume or Weight	Máximum Holding Time
Dioxins and furans	SW8280 SW8290	G, Teflon®- lined cap, T	4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1 liter or 8 ounces	30 days until extraction and 45 days after extraction (water and soil)
Ethylene dibromide (EDB)	SW8011	G, Teflon®- lined cap, T	4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	2 x 40 mL	28 days (water)
Explosive residues	SW8330	P, G, T	Cool, 4°C	1 liter or 8 ounces	7 days to extraction (water); 14 days to extraction (soil); analyze-within 40 days after extraction
Sulfide	EPA 376.2	P, G	4°C, ZnAc/NaOH	250 ml	7 days
Kjeldahl Nitrogen (TKN)	EPA 351.3	P, G	4°C, H <sub>2</sub> SO <sub>4</sub>	500 ml	28 days
Ortho-Phosphate	EPA 365.3	P, G	4°C	250 ml	48 hours
Ammonia	EPA 350.3/350.2	P, G	4°C, H <sub>2</sub> SO <sub>4</sub>	500 ml	28 days
Biochemical Oxygen Demand (BOD)	EPA 405.1	P, G .	4°C	1 liter	48 hours

Table 4-3, Sample	Containers.	Preservatives.	and Hold Ti	imes (Continued)
Table 4-3, Dumple	Concarnerby	I I COCL THEIT CO	HEG HIVIG I	

a. Polyethylene (P); glass (G); brass sleeves in the sample barrel, sometimes called California brass (T).

b. No pH adjustment for soil.

c. Preservation with 0.008 percent  $Na_2S_2O_3$  is only required when residual chlorine is present.

# 4.4 SAMPLE IDENTIFICATION AND CUSTODY

Each sample must have a unique identifier in order to differentiate it from other samples. In addition, proper custody and custody documentation are absolutely critical to providing data that are defensible.

# 4.4.1 Sample Identification

The primary method for sample identification will be to use the State Well Registration Number for wells (and springs as applicable), or the USGS station number for surface water samples. For example:

• The unique identifier, for use on the chain of custody for Comal Springs, Orifice 1 is:

Comal # 1, DX 68-23-301

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• The unique identifier, for use on the chain of custody for the Nueces River at Laguna is:

Nueces 8190000

For QA/QC samples, a modifier is added to the sample name to indicate the QA/QC type for example, Comal #1, if an MS/MSD sample were collected, a separate set of samples named Comal #1, DX 68-23-301 MS/MSD would be collected. The appropriate modifier for each QA/QC sample is listed in Table 4-3.

Sample Type	Modifier
Matrix Spike / Matrix Spike Duplicate	MS/MSD*
Ambient Blank	AB#
Equipment Blank	EB#
Trip Blank	TB#
Duplicate	FD*
Replicate	FR*

\* - Requires a sample, with same sample name as parent + modifier at end

# - Numerical suffix to be attached and referenced in field notebook, suffix starts at 1 at the beginning of each calendar year.

In some cases no well number, or other recognized registration number will exist for the sample point. In this case, full documentation for the sample location and time, as well as sample parameters must be recorded in the field notebook for future reference. In cases such as this the sample will be named for the property owner (if available). For example:

• The unique identifier for a sample taken from the Smith residence at 123 Main Street, a private well with no well registation number would be:

# Smith Well, 123 Main Street

If no owner name is available, then the sample point should be named for the street address, or nearest intersection, for example: 7237 Bitters Rd., or Bitters & 281 No 1. Again, proper documentation to include collection location, sample name, sample parameters, date, and time are extremely important and should be recorded in the field log for cross reference to the COC.

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# 4.4.2 Sample Custody

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

Furthermore, the laboratory COC form is to be filled out completely by the sample custodian in the field. The form must contain all required information for proper sample identification. In addition, samples must remain in control of the sample custodian. Once collected, samples must be under the supervision of the sample custodian, or secured in a manner that no reasonable chance of unauthorized access to the samples exists. Furthermore, if samples are shipped by a common courier (i.e., Federal Express), then the sample custodian must note on the COC when the samples were released to the courier, and why. The analytical laboratory will sign the COC upon receipt. A breach of sample custody can invalidate the defensibility of the sample set.

# 4.4 DATA VALIDATION

Analytical data requires review in order to be validated prior to publication. The amount of review (or level of review) is a function of the data type. Authority Level I data results are reviewed in the field, by the analyst. One of the best ways for the field analyst to assess the acceptability of field data and subsequently validate it, is to compare the results to historical data. This comparison combined with proper equipment calibration, maintenance, and analytical technique will provide an adequate validation process for Level I data. In the event that the analyst finds a discrepancy in the field data, a second analyses for the parameter in question may be performed, or the data may be flagged (per Table 4-3).

Authority Level II data shall receive a 100% analyst review at the analytical laboratory, prior to posting analytical results. A subsequent analytical laboratory review, by the QA/QC section is required prior to the analytical laboratory's certification of the results. A subsequent 10% review by EAA staff of the analytical data is required upon receipt of the final analytical report. The analytical report shall contain the equivalent of a US EPA Level III data package, which provides the numerical analytical results for the field data, as well as the laboratory QA/QC samples (i.e. LCS, Method blanks, etc.). No Raw Data is included in the analytical report.

Authority Level III data shall receive the standard analytical laboratory review (by analyst and QA/QC section) prior to posting of results. In addition, the analytical data report shall provide copies of all "raw data" including calibration curves, run logs, and

bench sheets. This data report is equivalent to and EPA "level IV" data package. Upon receipt by the Authority, the data shall be subject to a 10% review as a check on the data quality.

Level II and III data are to have data flags assigned by the analytical laboratory. The 10% review performed by Authority staff shall assess the accuracy of the data flags as part of the review process.

# SECTION 5

# FIELD PROCEDURES

Significant factors in any successful sample collection effort are the procedures, and documentation that occur in the field. Field procedures to include sample equipment decontamination, sample collection procedures for well, spring and surface water samples, potential sources of contamination, and proper use of field notebooks, is included in this section.

#### 5.1 EQUIPMENT DECONTAMINATION

In order to obtain samples that are reliable and defensible all (non-disposable) sample collection equipment must be decontaminated prior to use. When possible, sample collection from a wellhead valve directly to a sample container is best. When this is not possible (no valve, or spring / surface water sample) disposable equipment is preferable.

If neither option above is plausible, then non-disposable sample collection devices must be used. Sampling equipment that is exposed directly to sample media (pumps, tubing, reusable bailers or other devices) shall be washed in a non-phosphate, laboratory grade detergent such as Alconox®, followed by a double rinse in potable water. A final rinse of deionized or distilled water shall be applied after completion of the initial decontamination process.

Equipment that will not be used immediately must be kept clean by wrapping in aluminum foil, or placed inside clean plastic bags. This will prevent recontamination of the equipment prior to use.

#### 5.2 SOURCES OF SAMPLE CONTAMINATION

Samples can very easily become contaminated during the sample collection process. It is the responsibility of the sampler to prevent this from occurring. A multitude of potential cross contamination sources is present in the field environment. Since many of the analytical methods used are able to quantify various analytes in parts per billion, even minute sources can potentially contaminate a sample. For example Table 5-1 below summarizes some of the potential sources that can cause a false positive reading in a sample. These should be considered when collecting samples in the field. Also note that water has a strong affinity for several types of contaminants. Use of good judgement is another aspect of collecting defensible data. Take steps to avoid cross contamination of samples, if the sampler suspects the possibility of cross contamination, it should be noted in the field log for the sample set in question.

Source	Possible Contaminant
Fuels – generators, or work vehicles	BTEX / TPH / VOC / SVOC
Exhaust Fumes – generators, vehicles, heavy traffic	BTEX / TPH / VOC / SVOC
Oil/Grease residue on tools, gloves, etc.	TPH / SVOC
Таре	VOC
Insect Spray	VOC / SVOC / Pesticides
Insect Repellent	SVOC / VOC / Pest.
Sunscreen	VOC/SVOC
Soil / Debris	Bacteriological / Metals / SVOCs

# Table 5-1, Potential Sources of Cross Contamination

# 5.3 FIELD NOTEBOOKS

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

# 5.4 SAMPLE COLLECTION

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

# 5.4.1 Well Samples

Each well must be gauged, and sounded (if possible). Note the general condition of the well in the field notebook. After gauging the water level, calculate the purge volume for the well by the following equation.

 $V = H \times F$ ,

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

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

# Table 5-2, Well Casing Volume in Gallons per Foot

The relationship:

 $F = \pi (D/2)^2 \times 7.48 \text{ gallons/ft}^3$ 

can be used to calculate pipe volumes not listed in the table. Note that D = pipe diameter in feet.

A minimum of three well volumes shall be purged from all wells prior to sampling. Wells that go dry prior to this volume shall be purged to dryness (except for drinking water supply or irrigation wells). During purging, water shall be monitored for temperature, pH, DO, conductivity and turbidity. Stabilization of the parameters listed below in conjunction with three purge volumes will indicate the well is ready to sample.

Stabilization is defined as: Temperature fluctuations limited to  $\pm 1^{\circ}$  C, pH  $\pm 0.1$  unit, conductivity  $\pm 5\%$ , turbidity  $\pm 10$  NTU. Should these parameters not stabilize, a maximum of 6 well volumes shall be purged prior to sample collection. Once the well has stabilized, or the maximum purge volume is reached, and the well has recovered to at least 80% of its initial level, it is ready to sample.

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# 5.4.2 Spring Samples

Samples of spring water should be as representative of the spring/orifice as possible and not be "contaminated" with surrounding surface waters. When necessary, use a peristaltic pump to collect the spring water sample by placing the intake portion of the tube in the spring orifice. This allows for filling of sample jars without overflowing them, and losing any preservatives in the bottle. In addition, it will reduce the amount of "surface" water collected with the spring sample. This technique is not feasible for all spring sites, but should be utilized as appropriate. When sampling from a spring site and not utilizing a pump, consider collecting samples in a clean container (such as a 1000 milliliter amber glass container or similar) and using this container to transfer water in to subsequent containers. This will prevent the loss of any preservatives that may be in individual containers. However, the action should be performed with as little agitation to the sample as possible to preserve potential VOCs in the parent sample.

Current information and observations concerning springflow at the time of sample collection should be entered in the field notebook. For example, approximate flow volume, does this represent an extreme volume (high or low), observed water quality (clear, cloudy, or murky), and other observations deemed appropriate by the sampler.

## 5.4.3 Surface Water Samples

Surface water samples should be collected without disturbing the sediment if possible. The presence of sediment in the sample may bias the results. Samples should be collected from the flowing portions of the stream, on the upstream side of the sample collector. Samples should not be collected from stagnant areas. Samples should also be taken from approximately the same location each time. Sample jars should be filled by collecting the water sample in a clean jar, and pouring the sample into the final jar. However, use caution to prevent overfilling the jars and diluting any preservatives that may be in the container.

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

# 5.4.4 Sediment Samples

Although sediment sampling is not one of the regular sampling programs currently pursued by the Authority the possibility exists that staff may be required to collect samples of this type on occasion. As such, a brief discussion of this type of sample is included herein. Sediment samples may be collected from below the water line, or from a dry stream bed, or other situation where sediments may collect. The collection technique will depend upon the conditions. For example, a push tube for collection of sediments below the water surface is needed. However, if sediments are being collected

from a dry area, then they may be collected using a trowel, hand auger, or push tube of some type. As with all soil related samples, VOC samples must be collected in a manner that will minimize the loss of in-situ volatiles. As such, sediment samples for VOC analyses shall not be composited or homogenized in the field. Samples for VOC analyses are to be collected first.

The field notebook should note details related to the sediment samples, for example, was the sediment dry or below water, how was it collected, was it discolored or other details as deemed appropriate by the sampler.

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# SECTION 6

## PROCEDURES FOLLOWED BY OTHER AGENCIES

Similar sampling programs are conducted by the US Geological Survey (USGS), the Texas Water Development Board (TWDB), San Antonio Water System (SAWS), and Texas Commission on Environmental Quality (TCEQ). However, the purpose and objectives of the other agencies programs varies from that of the Authority's program for water quality monitoring as discussed below.

#### 6.1 US GEOLOGICAL SURVEY

The USGS has been gathering water quality data for a number of years. One of their primary water quality programs is the NAWQA program. The NAWQA program is designed to assess surface and groundwater across the nation.

The NAWQA program was implemented by the USGS in 1991, in order to assess groundwater and surface water quality in approximately 50 basins nationwide (<u>http://water.usgs.gov/nawqa/about.html</u>). The NAWQA program is founded on the premise of providing answers to three questions:

- 1) What is the condition of our nations streams and groundwater?
- 2) How are these conditions changing over time?
- 3) How do natural features and human activities affect these conditions?

Several NAWQA wells are located within the jurisdictional area of the Authority. Many of them are sampled by the Authority as part of the routine water quality program.

#### 6.2 TEXAS WATER DEVELOPMENT BOARD

TWDB collects water quality and quantity data from surface water and groundwater locations to facilitate the planning, development, conservation and protection of water resources.

The TWDB groundwater database contains information for more than 123,500 sites around Texas. This database includes water wells, springs, oil/gas tests, water levels and water quality. This data goes back to 1965. Around 7,100 water wells are classified as current observation wells with as least one annual measurement.

The TWDB also collects surface water quality data. Currently 77 reservoirs across the state are monitored for the water quantity they hold.

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#### 6.3 SAN ANTONIO WATER SYSTEM

As a supplier of water to the public, San Antonio Water System (SAWS) is under State mandate to provide water quality sampling under the public water supply (PWS) rules. The PWS water quality samples include analyses for the following general constituents:

- Organic
- Inorganic
- Synthetic organic Contaminants
- VOC's
- Radiological Contaminants
- Microbial bacteriological

The monitoring frequency is determined by the population size, and whether the source of the water is surface or groundwater, if the groundwater is under the influence of surface water and if they have had any violations or are under enforcement.

Additional nuances apply if the PWS is a "community water system," a "non-transient non community water system," or a "transient non-community water system,". The public water supply rules can be viewed in detail in Title 30 of the Texas Administrative Code, Chapter 290.

#### 6.4 THE TEXAS COMMISSION ON ENVIRONMENTAL QUALITY

The Texas Commission on Environmental Quality (TCEQ) is the state lead agency for water resources. They administer both state and federal mandated programs, which require conducting various water protection programs, contamination prevention and remediation if contamination exist. Also they have responsibilities to conduct education, permitting and enforcement activities.

The TCEQ is designated as the lead agency for the Texas Groundwater Protection Committee (TGPC) as created by the 71<sup>st</sup> Texas Legislature in 1989. The TGPC was intended to optimize water quality protection by improving coordination among the participating state agencies.

#### **SECTION 7**

#### ANNUAL REVIEW

#### 7.1 ANNUAL REVIEW OF GROUNDWATER QUALITY PLAN

In accordance with the guidance set forth under Section 3.1.2 of the 2002-2006 Edwards Aquifer Authority Strategic Plan, data collection efforts described in this plan will be reviewed by May 31, each year. The review will be directed at ensuring that all data collection efforts herein are necessary, properly performed, and properly staffed. Furthermore, the review will ascertain if the methodologies in use are still appropriate for their intended purpose. The review process will include the wells, springs, and streams sampled, as well as the methods used to collect and analyze those samples.

Results of the annual review, and resulting recommendations will be summarized in a letter report to the Aquifer Science PM each year after the annual review process. The Aquifer Science PM must approve modifications to the Groundwater Quality Monitoring Plan prior to implementation.

In addition to review of this plan, senior staff members shall develop a field sampling plan (FSP) annually. The FSP shall accommodate updates made to this plan, as well as provide direction for sample sites, analytical methods, and procedures. The number and type of samples shall be outlined in the FSP for all known sample sites. In addition frequency for collection of samples shall be summarized in the FSP.

Section 8

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#### **SECTION 8**

#### REFERENCES

AFCEE, (2001), Air Force Center for Environmental Excellence, Quality Assurance Project Plan, Ver. 3.1, Brooks AFB, TX

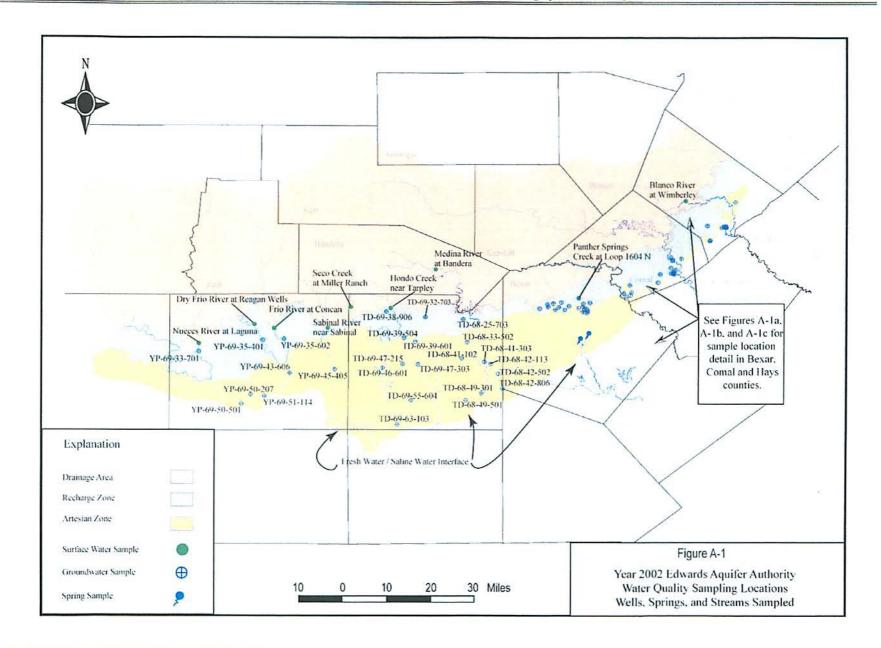
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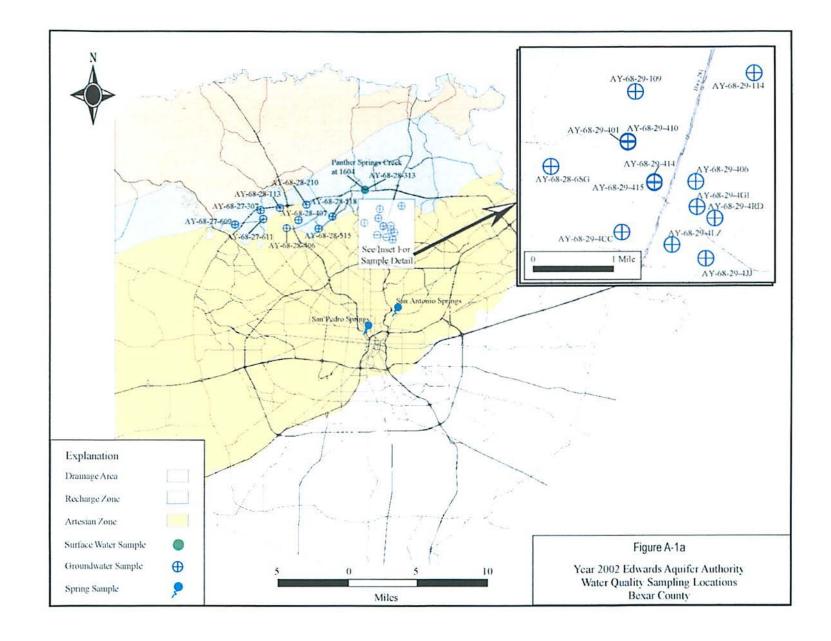
US EPA, (2000), EPA QA/G-4, Guidance for the Data Quality Objectives Process

### **APPENDIX A – Water Quality Sample Locations (Year 2002)**

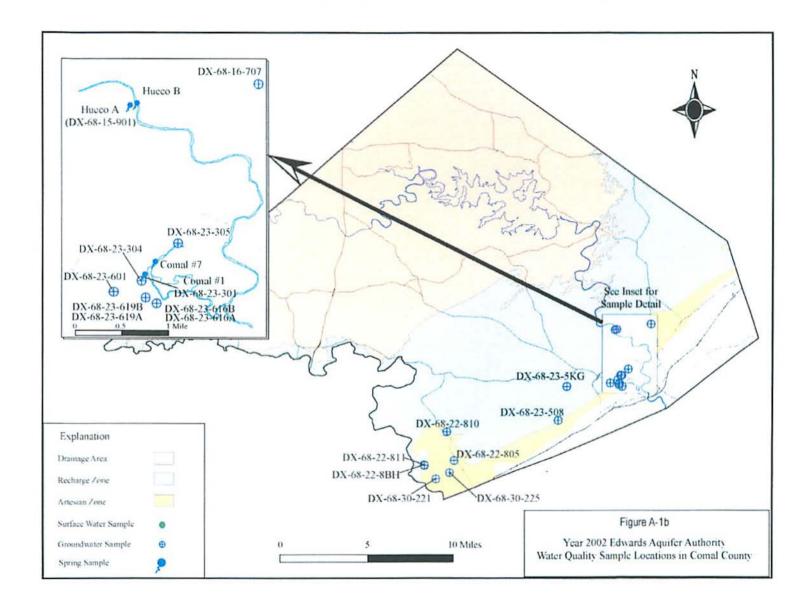
Groundwater Quality Monitoring Plan Edwards Aquifer Authority



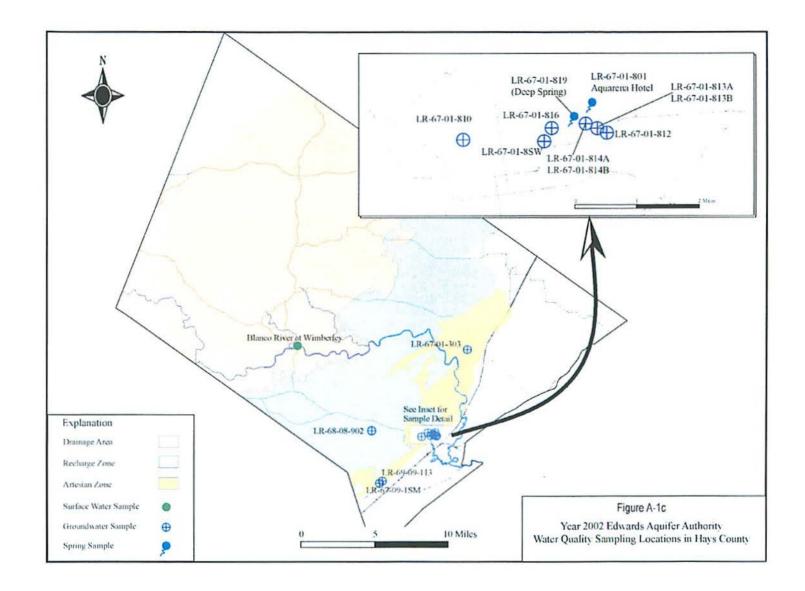
Groundwater Quality Monitoring Plan Edwards Aquifer Authority



Groundwater Quality Monitoring Plan Edwards Aquifer Authority



Groundwater Quality Monitoring Plan Edwards Aquifer Authority



### **APPENDIX B - Glossary of Terms**

Ambient Blank A sample known not to contain target analytes, which is used to assess airborne contaminants at the site. The ambient blank is opened at the site and exposed to site (ambient) conditions and subsequently treated as an environmental sample thereafter. AB samples are applicable to VOC analysis only.

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- Equipment Blank A 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 analyzed for parameters of concern (to match the sampling routine applicable to the site).
- Field Duplicate A second sample collected simultaneously from the same source as the parent sample, but it is submitted and analyzed as a separate sample. Generally this sample should be identified such that the laboratory is not aware that is a field duplicate.
- Field Replicate Sometimes referred to as a split sample, a replicate is defined as a single sample divided into two (or more) samples.
- Matrix Spike The matrix spike is a sample used to determine the effect of the matrix on a method's recovery efficiency. A known amount of the target analyte is added to a specified amount of matrix sample for which an independent estimate of the target analyte concentration is available. Duplicate samples must be available as well (matrix spike duplicate or MSD).
- MDL The MDL or method detection limit is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero as determined from analysis of a sample containing the analyte in a given matrix.
- PQL The PQL or practical quantitation limit is the smallest concentration of the analyte that can be reported with a specific degree of confidence.

RL	The RL or reporting limit is the smallest concentration of an analyte that is reported by the laboratory to a customer. The RL is never less than the PQL, and is generally twice the MDL.
Trip Blank	The trip blank or TB is a sample known to be free of contamination (for target analytes) that is prepared in the laboratory, and treated as an environmental sample after receipt by the sampler. TB samples are applicable to VOC analysis only.

## **APPENDIX C - Field Equipment Calibration**

All equipment maintenance and calibration must be documented in the laboratory notebook, or in the field notebook. This documentation is an important part of assuring that data collection, and results are "defensible".

#### pH Meter Calibration

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

#### Manual Calibration (with two reference solutions)

- 1. Attach or verify the pH indicating electrode and the automatic temperature compensator (ATC) are on the display unit.
- 2. Remove the rubber filling solution plug (if so equipped) to allow equilibration of the internal solution to the ambient air. Allow approximately five minutes for the equilibration process, and replace the plug.
- 3. Turn on the unit and select the calibration mode.
- 4. Rinse both electrodes with de-ionized water and dry (carefully) any excess water.
- 5. Rinse the pH electrode with the first pH buffer (reference) solution. After rinsing, emerse the electrode in a container of the first reference solution, stir to remove bubbles on the electrode.
- 6. Allow the display to read "ready" and begin flashing. If the pH reading is within manufactures specifications (see equipment manual), press "yes". If not, press "no" and repeat the procedure. The first standard will subsequently be locked into the units memory.
- 7. To calibrate the meter to the second pH reference solution, repeat steps 4, 5, and 6 with the second solution.

8. Remove and rinse probes with de-ionized water and begin sample analysis or the meter may be turned off and it will keep calibration as long as the power source remains intact.

#### Electrode Care and Maintenance for pH Meters

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

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

#### **Conductivity Probes**

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Orion Conductivity/Temperature Meters, Models 122, 126, 128, and 1230 Conductance refers to the ability of a substance to carry and electrical current. These probes are used to define the physical parameters of conductivity. Conductivity is the algebraic reciprocal of electrical resistance and is expressed in the SI unit of microSeimens per centimeter. Specific conductance is the electrical conductance measured across a one-centimeter cube of liquid (sample) between opposing faces of two platinum electrodes at 25 °C. Conductivity is the same parameter measured at ambient temperature that has not been temperature-compensated to 25 °C.

#### Calibration

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

#### **Calibration Steps**

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

#### Maintenance

- 1 The meter electrode must be clean in order to obtain accurate readings. Laboratory grade soap may be used to clean dirt, and oil deposits from the meter. For mineral deposits, a 1M HCl solution may be used to in 10 parts de-ionized water, and 10 parts isopropyl alcohol as a soaking agent for their removal.
- 2 The conductivity probe may be stored dry. After each use however, the probe should be rinsed in de-ionized water and blotted dry.
- 3 The unit will indicate a low battery by flashing "LOBAT" in the upper left-hand corner of the LCD display. The 9-volt disposable battery should be changed out with the unit OFF, to prevent damage.

#### **HACH Digital Titrator**

Titrations are performed using the HACH digital titrator. This instrument provides very accurate and precise results when properly operated.

#### Operation

1. Select a sample volume and titration cartridge corresponding to the expected sample concentration.

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

#### Calculations

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

#### Maintenance

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

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

#### Alkalinity Determination using the HACH Digital Titrator

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

#### Procedure

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

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

Collect a second alkalinity sample every 10-samples as a field duplicate, and analyze as outlined above. The field duplicate percent difference should not exceed + or -5%. Where %D is defined as:

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

In addition, a monthly reference sample is to be run and recorded in the laboratory notebook. The reference sample is prepared by dispensing 25-ml de-ionized water into a beaker.

- 1. Take an alkalinity measurement of the DI water, this will act as the blank.
- Using the alkalinity standard solution ampule add 0.5 ml of standard to 50 ml of DI water, mix well and pour 25 ml into a beaker. This will produce a standard with an alkalinity of 250 mg/l (+ or 5%).
- 3. Measure the alkalinity of the standard to verify. Record the results in the laboratory notebook.

#### YSI Dissolved Oxygen Meter

The YSI 57 Dissolved Oxygen (DO) Meter is used to determine DO concentrations and temperature values for field and laboratory samples of surface and groundwater. Measurements of DO are very important to the water quality assessment process. However, DO measurements are easily skewed by improper measurement techniques. As such, the information below should be read and understood by all individuals charged with operation of the DO meter.

#### Calibration

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Prior to starting the calibration process, the meter must be prepared for use. Place the meter in its intended operating position and proceed as follows:

- 1. Disconnect the probe cable from the meter body, be careful not to stress the threads or cable in the process.
- 2. With the meter set to OFF, adjust the needle to Zero with the screw on the front of the display panel.
- 3. Switch to RED LINE and adjust the RED LINE knob until the needle aligns with the red line at the 31 °C position.
- 4. Switch to ZERO and adjust the needle to the zero mark.

5. Reattach the probe to the PROBE connection and begin calibration steps.

#### Air Calibration

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- 1. Pull off the storage lid covering the membrane and insure the sponge in the bottom of the container is moist. Place the probe back into the storage lid, slightly ajar. This allows for a water saturated atmosphere for the calibration of the meter. Wait 10 minutes for temperature stabilization.
- 2. Switch the function knob to TEMP, read and record. Consult Table I (Solubility of Oxygen in Fresh Water) for the calibration value.
- 3. Determine the altitude or atmospheric correction factor from Table II (Altitude Correction Factors) and multiply the calibration value from Table I by the correction factor.
- 4. Switch to the appropriate mg/l range with the salinity set to zero and by using the CALIBRATE knob adjust the meter until the needle reads at the correct calibration value. Wait a couple of minutes to verify the calibration stability, readjust if necessary.

### **Operation and Use**

- 1. Dissolved oxygen measurements are read when the function indicator switch is directed toward the calibration knob. The range of DO values used will depend on the application.
- 2. Temperature will be read when the function indicator switch is directed to the TEMP. knob.
- 3. Note that the oxygen in the test solution is consumed during the test. The user must keep the probe or sample solution moving at all times to prevent false low readings due to local reductions in dissolved oxygen.
- 4. Membrane life will depend on use. When installed properly and stored in humid atmospheres the probe membrane will have the best longevity. The average interval between membrane change is two to four weeks, however, realize that usage is sporadic for this instrument. For example, the instrument may not be used for one or two weeks, and subsequently may be used 8 to 10 hours a day for several days. Therefore, breaks in sampling should be utilized as maintenance periods, and the membrane should be changed at these times.
- 5. The user should also be aware that there are environments that will deteriorate the probes ability to produce accurate readings in addition to those environments that will

give false readings independent of the mechanics of the probe. If erratic readings occur, check the membrane, anode and cathode, and replace if needed.

6. Always store the probe in the plastic bottle provided with a damp cloth or sponge in the bottom. This provides a humid atmosphere and prevents the membrane from drying out.

#### Maintenance

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#### Battery Replacement

The YSI 57 requires two "C" size batteries, which are located inside the case on the meter end. These should be replaced when the RED LINE knob prohibits correct calibration steps.

#### Membrane Renewal

Membrane replacement will be dictated by the frequency of use. However, if the membrane becomes fouled or damaged, or the electrolyte evaporates due to an old or improperly fitted membrane (producing air bubbles under the membrane) then, immediate replacement should be performed.

To change the membrane follow the steps below:

- 1. Make sure fresh electrolyte solution is available or dissolve the KCl crystals in the maintenance kit with de-ionized water. Fill the provided bottle to the top and shake until all the crystals are dissolved.
- 2. Unscrew the sensor guard from the probe and remove the black O-ring from the probe body. The old membrane will slide off with the removal of the O-ring.
- 3. Replenish the filling solution in the probe and prepare for the installation of a new membrane by creating a meniscus on the top of the probe, (covering the gold cathode).
- 4. Secure a single membrane between the probe body and your thumb, be sure the meniscus is still over the top of the probe. With a continuous motion, stretch the membrane up, over and down the other side of the probe. This will form the membrane to the contour of the probe. Secure the membrane with you forefinger, freeing a hand for the O-ring addition.
- 5. Roll the O-ring over the end of the probe, being careful not to touch the membrane surface. If wrinkles should appear in the membrane an attempt should be made to

pull them out by tugging on the edges of the membrane beyond the O-ring. If wrinkle persist remove the membrane and begin again.

6. Remove the excess membrane with scissors or a sharp knife and reinstall the sensor guard. Be sure to submerge the probe in de-ionized water prior to its introduction to samples for analysis.

#### **Probe Cleaning**

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The gold cathode on the head of the probe should always be bright and free of tarnish. During normal use the cathode will become tarnished with silver which can only be removed with the YSI 5680 probe reconditioning kit. In this kit, abrasive paper and a sanding tool are provided with filling solution as a lubricant to remove the silver tarnish from the cathode.

The silver anode may also become contaminated over time, which will interfere with calibration efforts. If this should occur soak the probe in a 3% ammonia solution overnight and ten replace the filling solution and membrane.

Should any further issues with the equipment be encountered, contact YSI at 800-765-9974.

#### **Quality Check**

The Winkler titration will provide verification of successful calibration and insure the DO meter is operating correctly. Each time the membrane is changed and/or after an extended period of storage the Winkler titration must be performed. Accuracy will be assessed for the "true" Winkler result against the analytical DO meter result. The accuracy will be calculated as the percent difference (%D), which is defined as:

 $[(X1 - X2) / X1] \times 100 = \%D$ 

Ideally, the %D shall not exceed 3% for the two measurements. The Winkler titration and subsequent %D calculations will be performed twice (using a different sample each time) to assess the precision of the process. Upon completion of this process, the results shall be recorded in the laboratory notebook.

The Winkler titration shall be performed as follows with the HACH reagent kit:

- 1. Collect a water sample in a clean 60 ml glass BOD bottle with a ground glass stopper.
  - Allow the water to gently overflow the bottle and make sure no air bubbles are

present on the walls of the bottle, or suspended in the water column. Keep 200 ml of this same water (in a separate sealed container) for the DO meter analyses.

- 2. Introduce the contents of DO reagent 1 powder pillow, followed by the contents of DO reagent 2 pillow into the 60 ml BOD bottle.
- 3. Insert the stopper, making sure no air is trapped in the bottle. Invert the bottle several times to mix the two reagents.
- 4. A flocculate precipitate will form and will gradually result in an orange-brown layer on the bottom of the bottle. Allow 10 minutes for this to occur and then re-invert the bottle several times to remix the contents. The flocculate will again settle (allow 10 minutes for this process).
- 5. Remove the stopper and introduce the contents of Dissolved Oxygen Reagent 3 to the bottle and replace the stopper without trapping any air in the bottle. Invert the bottle several times until the reagent has completely dissolved.
- 6. Uncap and pipette 20 ml of the solution into a titration flask and perform a hand held titration with the HACH digital titrator and a 0.2000 N cartridge of sodium thiosulfate. The titration endpoint will be the change of solution color from yellow to clear.
- 7. The number of digits o the titrator at the endpoint will be multiplied by 0.1 to determine the actual concentration of DO in mg/l.
- 8. Measure the original sample with the DO meter and calculate the %D.

#### **Bacteriological Analysis**

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The Authority commonly performs Level I analyses for fecal streptococcus (FS) and fecal coliform (FC) as part of its water quality assessment programs. The following is a discussion of bacteriological sample analyses and preparation. While FS and FC are not pathogenic bacteria, they are commonly used as indicator bacteria to assess the likelihood for the presence of pathogens in water.

Standard analysis for FC and FS is completed by means of membrane filter procedures on agar specific to each type of bacteria. The coliform organisms are defined as those that will produce various shades of blue colonies on m-FC medium at 44.5° C  $\pm$  2° C within 24 hours of incubation exposure. The streptococcus organisms are defined as those which produce dark red to pink colonies of KF streptococcus medium at 35° C  $\pm$  0.5° C within 48 hours of incubation exposure. The Authority does not have certification as a

microbiology laboratory according to the US EPA 1978 Interim guidance. However, the quality assurance steps and techniques described herein will provide for reliable bacteria counts for use as Level I data.

### **Equipment Preparation**

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FC and FS are destroyed by the presence of residual chlorine. Therefore, in cases where chlorine may be present in a sample, it must be removed completely in order to make an accurate determination of bacterial colonies. As such, all glassware and sampling equipment must be pre-treated with a sodium thiosulfate solution to eliminate residual chlorine before sterilization. Approximately 1.0 ml of a 10% stock sodium thiosulfate solution (100 g sodium thiosulfate in 1 liter of de-ionized water) added to 1 liter sample bottles before sterilization will produce a 100 mg/L concentration in the sample and will neutralize approximately 15 mg/L of residual chlorine. In addition, all glassware and sampling devices used should be sterilized prior to use, or purchased pre-cleaned (sterile).

#### Preparation of Media

Bacteria media for the incubation of fecal coliform and fecal streptococcus are prepared in the laboratory prior to field sampling. Each type of media has particular attributes and users are advised to closely follow the specifications for production, use, and holding times specific to each media.

#### Ingredients for Fecal Coliform Media (m-FC agar)

m-FC Agar ---- 10.4 g Rosolic Acid --- 0.2 g 0.2N Sodium Hydroxide Solution - 20 ml Distilled Water - 200 ml

#### Preparation for m-FC agar

The ingredients listed above are sufficient to make 30 agar plates with an 1/8-inch base in 47 mm Petri dishes.

1. Combine Rosolic Acid and 0.2 N Sodium Hydroxide (in quantities listed above), in a "sealed" sterile bottle. Shake the combined contents vigorously until all the crystals have dissolved. Set aside for use later.

- 2. Place the m-FC Agar into a (sterile) 250 ml beaker and add the 200 ml of distilled water while stirring. Continue stirring until all limps are broken down and there is no agar adhering to the sides of the beaker.
- 3. Slowly heat the m-FC Agar solution to 90 °C with the laboratory hot plate. Monitor the temperature with a mercury thermometer and stir continuously to prevent scorching.
- 4. When the mixture reaches 90 °C, add 2 ml of the Rosolic Acid Solution to the beaker and continue monitoring the temperature.
- 5. As the mixture begins to boil (at 100 °C) remove the beaker from the hot plate and set aside to cool.
- 6. When the beaker is cool enough to touch with the bare hand, pour the medium into the 47 mm Petri dishes to a depth of 1/8 inch. Allow to cool for 5 minutes and replace the lids.
- 7. The m-FC Agar plates are ready to use when the medium has completely hardened. If they are not used immediately they may be stored in darkness at 4 °C for a maximum of three days. To prevent dehydration and contamination of the agar during storage, the prepared plates may be sealed in sterile plastic bags.

#### Ingredients for Fecal Streptococcus Media (KF Streptococcus agar)

KF Streptococcus Agar ---- 15.28 g Triphenyltetazolium Chloride TTC 1% Solution (Sterile) -- 2 ml Distilled Water - 200 ml

#### Preparation for KF Streptococcus agar

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The ingredients listed above are sufficient to make 30 agar plates with an 1/8-inch base in 47 mm Petri dishes.

- 1. Place the KF Streptococcus agar into a 250 ml beaker and add the 200 ml of water while stirring. Continue stirring until all the lumps are broken down and no agar is adhering to the sides or bottom of the beaker.
- 2. Slowly heat the KF Streptococcus agar mixture with the laboratory hot plate. Monitor the temperature with a mercury thermometer and stir continuously to prevent scorching.
- 3. At the boiling point (100 °C) allow the mixture to simmer at this temperature for 5 minutes. Remove the beaker from the heat and allow to cool to approximately 55 °C.

- 4. At this temperature add 2 ml of sterile TTC solution and mix well.
- 5. When the beaker is cool enough to touch with the bare hand, pour the medium into the 47 mm Petri dishes to a depth of 1/8-inch. Allow to cool for 5 minutes and replace the lids.
- 6. The KF Streptococcus agar plates are ready to use when the media has completely hardened. If not used immediately, store in darkness at 4 °C for a maximum of two weeks. To prevent dehydration and contamination of the agar during storage, the plates may be sealed in sterile plastic bags.

#### Sample Dilution for High Bacteria Counts

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Sample dilution and rinsing of filters and funnels during the filtration process is completed with sterile buffered solution. Laboratory stock solutions and the preparation of buffer water are outlined below. These solutions are sterile and should be stored at 4 °C with an estimated storage life of three months. Indication of the loss of sterility will be reflected in formation of a flocculate or cloudiness in the solutions. If this occurs the solutions are to be discarded and replaced with new solutions.

#### **Stock Phosphate Buffer Solution Preparation**

- 1. Dissolve 34.0 grams of potassium dihydrogen phosphate in 500 ml of deionized water.
- 2. Adjust the pH to 7.2 with 1N sodium hydroxide and dilute to one liter with deionized water.
- 3. Autoclave in a glass bottle for 30 minutes at a pressure of 17 19 psi.
- 4. Refrigerate after opening.

#### **Preparation of Sterile Buffered Water**

- 1. Add 1.2 ml of the stock phosphate buffer solution to one liter of deionized water containing 1 gram of Difco peptone in a glass container.
- 2. Autoclave in a glass bottle for 30 minutes at a pressure of 17 to 19 psi.
- 3. Refrigerate after opening and observe expiration dates.

#### Membrane Filtration Analytical Procedure

Bacterial sample preparation is achieved using the Millipore Microfil System. This system allows for quick processing of samples with minimum risk of contamination due to sampling error.

The steps required to process samples are:

- 1. Flame the surface of the microfil support for 3 to 5 seconds with a propane flame. Make sure the entire surface has been exposed to the heat.
- 2. With flamed forceps, set the appropriate membrane filter (0.7 micrometer pore size for FC, and 0.45 micrometer pore size for FS) on the center of the stainless steel support.
- 3. Attach a Microfil funnel to the manifold support by grasping the funnel from the middle and carefully lowering it onto the support. Note: Do not touch the inside of the funnel and be careful not to bend the flexible seal area. The funnel is then snapped into position by pressing downward on the top rim until a click is heard.
- 4. Attach the vacuum syringe to the manifold vacuum line and issue the sample to the Microfil funnel.
- 5. The vacuum syringe will draw in the filtered sample solution as the plunger is pulled outward. When the capacity of the syringe has been reached move the plunger inward to eject the waste sample from the tip of the syringe. Repeat this action until all of the sample has been passed through the membrane.
- 6. A membrane and funnel rinse with sterile buffer water may be initiated at this point if the sample feels there is a possibility that residual sample may be remaining on the funnel walls.
- 7. Close the vacuum valve and remove the Microfil funnel.
- 8. Vacuum venting and membrane lifting is achieved in the same step by depressing the lever positioned on the manifold support. Remove the membrane with flamed forceps.
- 9. The membrane is hen transferred to a solid medium Petri dish. Use a rolling motion as the membrane is laid onto the media to prevent air bubbles from being trapped under the membrane. Transfer the Petri dish to an incubator with the membrane side down.

### **Counting and Calculation of Bacterial Colonies**

The objective in preparing sample plates is to achieve filtrate volumes that will provide colony counts in an ideal range for enumeration. The volume of sample to be filtered must be such that after incubation one or more of the plates will have a count of 20 to 60 FC colonies, or 20 to 100 FS colonies.

Fecal coliform colonies are defined as those that produce various shades of blue colonies on M-FC media within 24 hours of incubation. Those colonies, which are gray to cream color, are not to be included in total numbers.

Fecal Streptococcus colonies are those defined as producing dark red to pink colonies on the KF streptococcus media within 48 hours of incubation. Enumeration may be aided with the use of magnification.

Within the range of any given set of filtrate volumes there are several possible end results from the incubation period. It could be possible that only one of the filtrate volumes is within the ideal range or possibly more than one would be suitable. Filtration volumes may produce far too many colonies to count or I contrast produce too few. Due to this the analyst must make observations on the most accurate form of enumeration and choose the appropriate calculation of colony density.

When dealing with colony counts within the ideal range use the following formula to calculate bacteria colonies per 100 ml of sample:

Bacteria colonies/100ml = (Bacteria colonies counted X 100) / (vol. of sample filtered)

Note: If dilutions were made from the original sample before filtration, the volume of filtered sample in the above equation must be the volume of actual sample used in the dilution

Should two or more filtrate volumes produce colony counts within the ideal range both should be used in the formation of a weighted average, calculated below:

Bacteria colonies/100ml = (Sum of Bacteria colonies counted X 100) / (Sum of samples filtered)

Note: Do not calculate the colonies /100 ml for each filter and then average them, a weighted average is required to maintain accuracy.

If the dilution series does not result in any plates being within the required range, the plate closest to the required range should be counted and reported as bacteria colonies/100ml followed by the statement Estimation based on non-ideal colony count.

#### Method Quality Assurance Checks (QA/QC)

Quality assurance procedures for the bacteriological studies will be implemented during each sample set, outlined in the section below.

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- 1. For each range of given filtrate volumes the sampler must start the set with a blank, by filtering 50 ml of buffered water through a membrane and setting this membrane up for incubation. This will announce possible contamination from storage and travel between sites.
- 2. At the end of a filtrate sample set another blank will be run by filtering 100 ml of buffered water through a new membrane and setting this up for incubation. This will indicate if the sterilization process continues to be adequate between samples.
- 3. In addition to the blanks one Petri dish will be incubated with a membrane soaked in sterile water during the incubation period for true samples. This will be an indicator for any cross contamination during the incubation process.

## **APPENDIX D - Field Forms**

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### er Authority Water Quality Field Data Sheet Surface Water

Site Int	formation		Alkalin	ity:				
Station Name:			·	mL of Sample	n pH	mL of Acid	Total Al	k.
Location:			Rep.1					7
Owner/Contact:			Rep.2			†	<del> </del>	1
Address:	·		1	Fie	Id Rea	1	I	J
A001635.						ungs		
<u></u>			<u>Time S</u>	ampled:	· ·		<u> </u>	
County:		<u></u>	<u>pH:</u>					
Point of Collection:			Tempe	rature:				
Date:	Time:	•	Conduc	tivity:				
Ambient Temp.	Collector(s):		Dissolv	ed Oxyg	ien:			
Weather:			Turbidit	v:		. —		
Instrument C	alibration				ncremer	nt Metho	bc	
Conductivity Meter #			Transect	-				
Standard	Meter	Reading						
500			Number		S:			
			Flow/App					
1000			Bacteri	<u>a:</u>	<u> </u>			
10000			Set up Co	onditions	(circle all t	that apply	)	
pH Meter #			Field Vehicl	ð	Open Field		Hotel	Lab
Standard	Meter	Reading	Coliform, fe	cal, Membri	ane Filter m	-FC agar at	44.5 C	•
Buffer 4.0			mL of Sample	Blank	3	10	30	100
Buffer 7.0			# Colonies	<u></u>				
Buffer 10.0			Boostod				ldeal	non ideal
			Reported			•		
DO Meter #	Condition		Streptococc					
Sampling	Condition	15	mL of Semple	Blank	1	5	25	100
Gage Readings	Time	Level	# Colonies	_				
Before Sampling		·	Reported	<u>#: /1</u>	100mL		ideal	non ideal
After Sampling	· ·							
Hydrologic Event		c Condition		• •	circle all th			
Storm		ie. Low	Std. Chem	VOC's	Herb/Pest	800	TOC	TSS
Drought		ling	Other:				•	
Spill		e, High	Data Base	e Entry:		Commen	IS:	
Regulated Flow		sing						
Routine Sample	Stable	Normal						

### Edwards Aquifer Authority Water Quality Field Data Sheet Groundwater

Well In	formation	Alkalin	ity:				
Owner/Contact:			mL of Sample	pH	mL of Acid	Total All	۲.
Well ID #:		Rep.1					
County:		Rep.2					1
Address:			Fie	ld Rea	adings		┛
	<u></u>				T		
Well Name / #:		Started Put	nping:		Time Sam	pled:	
Point of Collection:		Time	Тетр	Cond.	рН	DO	_
Well Use:							
Date:	Time:	_					
Flow Rate: gpm	Collector(s):						
Water Level:	Well Depth:						
Casing Dia.:	3 x well volume=						]
Instrument Ca	alibration						
		Turbidity:			<u> </u>		-
Conductivity Meter # Standard	Meter Reading	Bacteri					-
500					the stars h	<u> </u>	
1000		Set up Co Field Vehid		Open Field		) Hotel	Lab
10000		┥└───					
<u></u>		Coliform, fe	cal, Membra Blank	ane Filter m 3	1-FC agar at	44.5 C	100
pH Meter #	Meter Reading	# Colonies					
Standard	Meter Kedung	~					
Buffer 4.0		Reported	<u>#: /1</u>	100mL	-	ideal	non ideal
Buffer 7.0		Streptococc			T	T	1
Buffer 10.0		mL of Sample	Blank	1	5	25	100
Notes:		# Colorsies			<u> </u>		
		Reported	#: /1	100mL	-	ideal	non ideal
		Type of A	nalysis: (	circle all t	hat apply)	· · · · ·	
		Std. Chem	VOC's	Herb/Pest	Minora	Nutrients	
	·	Other:			······		
Latitude	Longitude	Data Bas	e Entry:		Commer	nts:	

	2002FY	TWDB Water	Quality Fie	Id Data	<u>Sheet</u>			
State Well Number:		Name:				Sampl	e ID Number:	
- County:	· · · ·	Address:					Date:	
- County Code:	·····	-					Sampler(s):	
Aquifer Code:		- Phone Number:						
Aquifer Id:		Attention:		•			Calibration Ve	erification Readings
		Well Name or #:					pН	7.00
	CIRCLE EACH SA	MPLE FRACTION COLLEC	TED:					4 or 10
. 1	2	3			5		SLP ≖	
500ml (filtered)	500ml (filtered)	250ml (filtered)				•	Conductivity	500
Anions / Total Alk.	Cations	Nitrate						1000
ice	Nitric (HNO3)	Ice + H2SO4		•				2000
	Proper preservation re	quires adding enough of the con	rect acid to each sample fract	ion to bring the pH i	below 2.0 .			5000
Time In:	·	Time Out:						
						Field Al	kalinity Titratio	
V. L. depth from LSD (ft.):		- VV.L. remark:	<b></b>	_ <sup>M.P. ≠</sup> -			_Start pH	
				-		<u> </u>	_mL Sample Si	
Pumping Since:		_ Sampling Point:				}	_	I for Phenol ( > 8.3)
								<u>i for Total (8.3 - 4.5)</u>
			S.P.S. readings					cid added x 20 = Alkalinky
							noi Alkaliniky (\$2244);	
Power:	•	- Longitude:		_		To	tel Albellally (39086);	mg/L
· Samole Time·		Filter pressure:	hand pump / line				literns Below Celculat	ad Later From Results:
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•							1	(as CaCO3):
							1	Balanced:
Vater Quality Stabilizat	tion Parameters T	able (at least 3 rea	adings at five minute inte	vals)	Notes:			
Time:					_			
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Celsius Temp. (00010)					_	•	•	······································
Conductivity (µS/cm):					—	Data Entered (	By Sampler Into Datebase	yes / no



### **Edwards Aquifer Authority**

### Chain of Custody Record

1615 N. St. Mary's San Antonio, TX 78215 Phone: (210) 222-2204/ 1(800) 292-1047 Fax: (210) 222-9869

Project Numbe	r:	Project	Name:				Project Location:	
Sample ID Number	Date/Time	Grab	Comp.	Sample Container (Size/Material)	Preservative	Sample Matrix	Analysis/Method Requested	Laboratory Remarks
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	(signature)	•			Time:	(algnature)	)	Time:
	Relinquished	by:(print)			Date:	Receive	ed By:(print)	Date:
	(signature)		_		Time:	(signature)	)	Time:
Remarks/Prec	autions on sam	pling pro	cedures	or chemical analysi	s:		Anaytical Results Sent To:	
							Edwards Aquifer Authority Attn: 1615 N. St. Mary's	
							San Antonio, TX 78215 (210) 222-2204	

TRENT	STL Corpus Christi 1733 N. Padre Island D	rivo												Ν	<b>o.</b> 00523	0
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1-800-880-4616

435 Isom Road, Suite 228

(210) 340-0343

## **APPENDIX E – US EPA Drinking Water Standards**

United States Environmental Protection Agency

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Office of Water (4606)

# SEPA National Primary Drinking Water Standards

Contaminant	MCLG <sup>1</sup> (mg/L) <sup>2</sup>	Common sources of contaminant in drinking water		
MICROORGANISMS				
Cryptosporidium	as of 01/01/02: zero	as of 01/01/02: TT <sup>3</sup>	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and fecal animal waste
Giardia lamblia	zero	TT	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste
Heterotrophic plate count (HPC)	n/a	ΤT	HPC has no health effects; it is an analytic method used to measure the variety of bacteria that are common in water. The lower the concentration of bacteria in drinking water, the better maintained the water system is.	HPC measures a range of bacteria that are naturally present in the environment
Legionella	zero	TT'	Legionnaire's Disease, a type of pneumonia	Found naturally in water; multiplies in heating systems
Total Coliforms (including fecal coliform and <i>E. colf</i> )	zero	5.0%*	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present <sup>3</sup>	Total coliforms are naturally present in the environment; fecal coliforms and <i>E. colt</i> come from human and animal fecal waste.
Turbidity	n/a	Soil runoff		
Viruses (enteric)	zero	ΤΤ <sup>3</sup>	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste
DISINFECTANTS AND DISINF	FECTION BYPRO	DUCTS		
Bromate	as of 01/01/02: zero	as of 01/01/02: 0.010	Increased risk of cancer	Byproduct of drinking water disinfection
Chloramines (as Cl <sub>2</sub> )	as of 01/01/02: MRDLG=41	as of 01/01/02: MRDL=4.01	Eye/nose irritation; stomach discomfort, anemia	Water additive used to control microbes
Chlorine (as Cl <sub>2</sub> )	as of 01/01/02: MRDLG=41	as of 01/01/02: MRDL=4.0 <sup>1</sup>	Eye/nose irritation; stomach discomfort	Water additive used to control microbes
Chlorine dioxide (as ClO <sub>2</sub> )	as of 01/01/02: MRDLG=0.81	as of 01/01/02: MRDL=0.8 <sup>1</sup>	Anemia; infants & young children: nervous system effects	Water additive used to control microbes
Chlorite	as of 01/01/02: 0.8	as of 01/01/02: 1.0	Anemia; infants & young children: nervous system effects	Byproduct of drinking water disinfection
Haloacetic acids (HAA5)	as of 01/01/02: n/a <sup>6</sup>	as of 01/01/02: 0.060	Increased risk of cancer	Byproduct of drinking water disinfection
Total Trihalomethanes (TTHMs)	none <sup>7</sup> as of 01/01/02: n/a <sup>4</sup>	0.10 as of 01/01/02: 0.080	Liver, kidney or central nervous system problems; increased risk of cancer	Byproduct of drinking water disinfection
INORGANIC CHEMICALS				
Antimony	0.006	0.006	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder
Arsenic	none'	0.05	Skin damage; circulatory system problems; increased risk of cancer	Erosion of natural deposits; runoff from orchards; runoff from glass and electronics production wastes
Asbestos fibers >10 micrometers)	7 million fibers per Liter (MFL)	7 MFL	Increased risk of developing benign intestinal polyps	Decay of asbestos cement in water mains; erosion of natural deposits
Barium 2 2 Increase in blood pressure				Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits

Contaminant	MCLG <sup>1</sup> (mg/L) <sup>2</sup>	MCL or TT <sup>1</sup> (mg/Ĺ) <sup>2</sup>	Potential health effects from exposure above the MCL	Common sources of contaminant in drinking water
Beryllium	0.004	0.004	Intestinal lesions	Discharge from metal refineries and coal-burning factories; discharge from electrical, aerospace, and defense industries
Cadmium	0.005	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Chromium (total)	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Copper	1.3	TT <sup>e</sup> : Action Level= 1.3	Short term exposure: Gastrointestinal distress Long term exposure: Liver or kidney damage People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	Corrosion of household plumbing systems; crosion of natural deposits
Cyanide (as free cyanide)	0.2	0.2	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories
Fluoride	4.0	4.0	Bone disease (pain and tenderness of the bones); Children may get mottled teeth	Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories
Lead	zero	TT <sup>4</sup> ; Action Level= 0.015	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; crosion of natural deposits
Mercury (inorganic)	0.002	0.002	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Nitrate (measured as Nitrogen)	10	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits
Nitrite (measured as Nitrogen)	1	1	Infants below the age of six months who drink water containing nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits
Scienium	0.05	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleurn refineries; erosion of natural deposits; discharge from mines
Thallium	0.0005	0.002	Hair loss; changes in blood; kidney, intestine, or liver problems	Leaching from oro-processing sites; discharge from electronics, glass, and drug factories
ORGANIC CHEMICALS				
Acrylamide	2010	TT'	Nervous system or blood problems; increased risk of cancer	Added to water during sewage/wastewater treatment
Alachlor	zero	0.002	Eye, liver, kidney or spleen problems; anemia; increased risk of cancer	Runoff from herbicide used on row crops
Atrazine	0.003	0.003	Cardiovascular system or reproductive problems	Runoff from herbicide used on row crops
Benzene	zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills
Benzo(a)pyrene (PAHs)	2210	0.0002	Reproductive difficulties; increased risk of cancer	Leaching from linings of water storage tanks and distribution lines
Carbofuran	0.04	0.04 1	Problems with blood, nervous system, or reproductive system	Leaching of soil fumigant used on rice and alfalfa
Carbon tetrachloride	22270	0.005	Liver problems; increased risk of cancer	Discharge from chemical plants and other industrial activities
Chlordane	ZETO	171207 1	Liver or nervous system problems; increased risk of cancer	Residue of banned termiticide
Chlorobenzene	0.1	0.1	Liver or kidney problems	Discharge from chemical and agricultural chemical factories
,4-D	0.07	0.07	Kidney, liver, or adrenal gland problems	Runoff from herbicide used on row crops
Dalapon	0.2	0.2	Minor kidney changes	Runoff from herbicide used on rights of way
,2-Dibromo-3- hioropropane (DBCP)	zero		Reproductive difficulties; increased risk of cancer	Runoff/leaching from soil furnigant used on soybeans, cotton, pincapples, and orchards
Dichlorobenzene	0.6	0.6	Liver, kidney, or circulatory system problems	Discharge from industrial chemical factories

Conteminent	MCLG <sup>1</sup> (ing/L) <sup>1</sup>	MCL or TT <sup>1</sup> (mg/L) <sup>2</sup>	Potentiel health effocts from apposure above the MCL	· · · Common sources of contaminant in drinking water
p-Dichlorobenzene	0.075	0.075	Anemia; liver, kidney or spleen damage; changes in blood	Discharge from industrial chemical factories
1,2-Dichloroethane	zero	0.005	Increased risk of cancer	Discharge from industrial chemical factories
1,1-Dichloroethylene	0.007	0.007	Liver problems	Discharge from industrial chemical factories
cis-1,2-Dichloroethylene	0.07	0.07	Liver problems	Discharge from industrial chemical factories
trans-1,2- Dichloroethylene	0.1	0.1	Liver problems	Discharge from industrial chemical factories
Dichloromethane	zero	0.005	Liver problems; increased risk of cancer	Discharge from drug and chemical factories
1,2-Dichloropropane	zero	0.005	Increased risk of cancer	Discharge from industrial chemical factories
Di(2-ethylhexyl) adipate	0.4	0.4	General toxic effects or reproductive difficulties	Discharge from chemical factories
Di(2-ethylbexyl) phthalate	ZETO	0.006	Reproductive difficulties; liver problems; increased risk of cancer	Discharge from rubber and chemical factories
Dinoseb	0.007	0.007	Reproductive difficulties	Runoff from herbicide used on soybeans and vegetables
Dioxin (2,3,7,8-TCDD)	2010	0.00000003	Reproductive difficulties; increased risk of cancer	Emissions from waste incineration and other combustion; discharge from chemical factories
Diquat	0.02	0.02	Cataracts	Runoff from herbicide use
Endothall	0.1	0.1	Stomach and intestinal problems	Runoff from herbicide use
Endrin	0.002	0.002	Liver problems	Residue of banned insecticide
Epichlorohydrin	2010	TT'	Increased cancer risk, and over a long period of time, stomach problems	Discharge from industrial chemical factories; an impurity of some water treatment chemicals
Ethylbenzene	0.7	0.7	Liver or kidneys problems	Discharge from petroleum refineries
Ethylene dibromide	2010	0.00005	Problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer	Discharge from petroleum refineries
Glyphosate	0.7	0.7	Kidney problems; reproductive difficulties	Runoff from herbicide use
Heptachlor	zero	0.0004	Liver damage; increased risk of cancer	Residue of banned termiticide
Heptachlor epoxide	zero	0.0002	Liver damage; increased risk of cancer	Breakdown of heptachlor
Hexachiorobenzene	ZETO	0.001	Liver or kidney problems; reproductive difficulties; increased risk of cancer	Discharge from metal refineries and agricultural chemical factories
Hezachlorocyclopentadiene	0.05	0.05	Kidney or stomach problems	Discharge from chemical factories
Lindane	0.0002	0.0002	Liver or kidney problems	Runoff/leaching from insecticide used on cattle, lumber, gardens
Methoxychlor	0.04	0.04	Reproductive difficulties	Runoff/leaching from insecticide used on fruits, vegetables, alfalfa, livestock
Oxamyi (Vydaie)	0.2	0.2	Slight nervous system effects	Runoff/leaching from insecticide used on apples, potatoes, and tomatoes
Polychlorinated biphenyls (PCBs)	zero	0.0005	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer	Runoff from landfills; discharge of waste chemicals
Pentachlorophenol	2010	0.001	Liver or kidney problems; increased cancer risk	Discharge from wood preserving factories
Picloram	0.5	0.5	Liver problems	Herbicide runoff
Simazine	0.004	0.004	Problems with blood	Herbicide runoff
Styrene	0.1	0.1	Liver, kidney, or circulatory system problems	Discharge from rubber and plastic factories; leaching from landfills
Tetrachloroethylene	zero	0.005	Liver problems; increased risk of cancer	Discharge from factories and dry cleaners
Toluene	1	1	Nervous system, kidney, or liver problems	Discharge from petroleum factories
Toxsphene	zero	0.00.5		Runoff/leaching from insecticide used on cotton and cattle
2,4,5-TP (Silvex)	0.05	0.05	Liver problems	Residue of banned herbicide
1,2,4-Trichlorobenzene	0.07	0.07	Changes in adrenal glands	Discharge from textile finishing factories
1,1,1-Trichloroethane	0.20	0.2	Liver, nervous system, or circulatory problems	Discharge from metal degreasing sites and other factories
1.1.2-Trichloroethane	0.003	0.005	Liver, kidney, or immune system problems	Discharge from industrial chemical factories

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