Quality Assurance Program Plan

For Activities of the
Agricultural Chemicals & Groundwater
Protection Program

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Project Management

This Quality Assurance Project Plan (QAPP) outlines all of the necessary information pertaining to the monitoring of Colorado groundwater for the presence of agricultural chemicals, which is the responsibility of the Agricultural Chemicals and Groundwater Protection Program (ACGP) as established under C.R.S. 25-8-205.5(1). Activities mentioned by this QAPP are grouped into Data Generation and Acquisition, Data Validation and Evaluation, and Reporting. All aspects of how the program decides on sample site selection, sampling frequency, which compounds to monitor for, monitoring well installation specifications, and program standard operating procedures are covered in Data Generation and Acquisition. How data quality is controlled and the program's process for data review and statistical analysis are covered in Data Validation and Evaluation. And finally Reporting includes the normal methods of how the data is reported to cooperating owners, the program's advisory committee, and to the general public through the creation of monitoring reviews and factsheets.

Organization of the Program

The ACGP is a collaboration of three separate entities. The Colorado Department of Agriculture (CDA) is the lead entity and is responsible for the conductance of all groundwater monitoring activities in Colorado. The Colorado Department of Public Health & Environment has an employee that serves as a liaison between the ACGP and the Water Quality Control Commission. Furthermore this position serves as an unbiased reviewer and interpreter of measurements and data collected by the program and provides technical assistance with regard to hydrogeology and geochemistry of the various compounds measured by the program. Lastly, Colorado State University Extension (CSUE) works to evaluate data collected by the program and use it to formulate remedies to discovered groundwater contamination in the form of best management practices, which are communicated to various land user types to encourage voluntary implementation. Additionally, CSUE provides public education in the classroom and to the general public about ways to improve management of fertility, pests, irrigation, and crop selection in order to minimize future contamination of groundwater with agrichemicals.

The ACGP also has its own laboratory which is part of the Biochemistry Laboratory in the Inspection & Consumer Services Division of CDA. The chemists working in this laboratory serve the program to conduct the majority of the measurements desired for an adequate investigation of groundwater quality samples. Occasionally, the program will utilize outside laboratories to obtain results for procedures its own lab is not capable of doing, but the vast majority of work is accomplished in house.

Problem Definition/Background

Alluvial groundwater in some parts of Colorado has been found to be contaminated with nitrate at levels that exceed water quality standards set by the Colorado Water Quality Control Commission. The program was created to consistently monitor and report on such contamination in the initially discovered areas but also to spread the investigation to all groundwater in Colorado that has an intrinsic vulnerability to agrichemical contamination and is relied upon by various users, which include: domestic, municipal, industrial/commercial, and agriculture. The goal of the program in conducting this monitoring is to provide useful information that helps to protect human, animal and environmental health.

Proper sampling network development is essential for accurately depicting both current contamination and spacial-temporal contamination trends. Data collected from these efforts provide private well owners with information they can utilize to ensure a safe drinking water supply. Furthermore, agriculture users of groundwater can benefit from knowing what types of agrichemicals are being discovered in groundwater and can improve their management approaches to help prevent further contamination. Monitoring information is also useful to general public and research efforts of other entities such as the U.S. Geological Survey (USGS), U.S. EPA Region 8, Colorado municipalities, local stakeholders, universities and private consultants.

Data Generation & Acquisition

This section provides details about how the program uses various tools to determine sampling location and frequency, what compounds to screen for in samples, and references the standard operating procedures used for field and laboratory work. The information discussed in this section was developed to create a standardized and uniform theory behind how the program operates with respect to collecting essential data through time and space. The Standard Operating Procedures (SOPs) used by field personnel to collect samples are mentioned in this section but the details can be found in the program's stand-alone manual, *Field Standard Operating Procedures for Activities of the Agricultural Chemicals & Groundwater Protection Program* (Mauch and Ross, 2014). Details on the laboratory's standard operating procedures can be found in the document *Analytical Work Plan for Activities of the Agricultural Chemicals & Groundwater Protection* Program (Wegner, 2013). Furthermore, detailed procedures for creating vulnerability maps and drilling and installing groundwater quality monitoring/observation holes is best described in stand-alone manuals either created by program personnel or a third party.

Sampling Network Design Process

The program determines how to distribute sampling locations within a particular aquifer or watershed through the use of several tools. Each investigation should be to determine the intrinsic vulnerability of an area with respect to agrichemical contamination. Several data variables are utilized in the creation of a vulnerability map that is useful in prioritizing sample distribution in order to cover the most vulnerable areas. Once this map is created other information needs to be compiled to assist in determining the number of samples to take in a particular area and the frequency at which to sample them. Part of this information comes from conducting pesticide use surveys. Data collected from these surveys provides insight to the intensity of pesticide use and the types of pesticides being used in different parts of Colorado. Similarly, fertilizer sales and or usage records can provide insight to the intensity of nitrogen fertilizer use within an area. This information combined with historical measurements of groundwater quality (if available), vulnerability maps, and aquifer usage details gives the information necessary for creating a long-term sampling plan. If part of the desired focus, results from BMP implementation within the study area can be incorporated into the long-term monitoring plan as well. The long-term sampling plan is intended to create a strategically designed, uniform frequency of sampling for various networks which assists in analysis of long-term trends in water quality data. Furthermore it serves as guidance for the program to ensure that sampling efforts are being prioritized to locations determined to be at highest risk for new or continued groundwater contamination with agrichemicals.

Vulnerability Assessment – SIMPLE

A detailed procedure on how this assessment is conducted and the resulting outputs obtained through it is explained in depth in Relative Sensitivity of Colorado Groundwater to Pesticide Impact (Hall, 1998). In general this assessment takes into account several key criteria that can serve as indicators to land areas and aquifers that are prone to contribute to or be impacted by agrichemical contamination. Some of the used parameters include soil characteristics such as surface texture, hydrologic group, % organic matter, and depth to a restrictive layer. The depth to groundwater is very important as it relates to how much soil and geologic material a contaminant must travel through before it reaches groundwater and impacts quality. The presence of irrigated agriculture is also included in conducting a vulnerability assessment primarily because the presence of such a land use provides a source of agrichemicals that may not normally be seen in natural areas. Furthermore, the additional infiltration of water due to irrigation practices usually exceeds the mean annual precipitation for areas monitored by the program and this additional flux can result in accelerated leaching of residual agrichemicals. This vulnerability assessment can be conducted for a regional area, a watershed, or statewide. The main restriction on which scale can be used is the study area requirements and the working scale of the input data. The final vulnerability assessment is quintessential to determining which areas of either the state, or the watershed in question, are in need of water quality testing.

Agrichemical Use Surveys

It is very beneficial to the program's purpose if reliable information is available on what types and quantities of agrichemicals are being used throughout Colorado. Such information can be leveraged into creating a strong long-term monitoring plan that takes aim at monitoring vulnerable groundwater in areas where agrichemical intensity is greatest. Given the limited personnel resources of the program, it is important that efforts are efficiently aligned with the program's purpose.

The program has attempted to conduct two pesticide use surveys – the first in 1997, and the second over a two year period from 2007-2008. The problem with both surveys is that the response rates were insufficient for providing adequate representation of pesticide use. While the first survey (a mailed hardcopy survey) garnered greater than a 30% response rate the second survey (an internet-based electronic survey) only mustered about 10%. It is believed that both surveys failed to obtain a large response rate primarily because of the lack of incentives to encourage the polled pesticide applicators to respond. The program will have to brainstorm ways to encourage those in the target population to take the survey because the information provided to the program is important.

For the purposes of determining the long-term sampling plan and strategy, the program can estimate needed values by utilizing sales records and survey results from the USDA's National Agricultural Statistics Service which are usually conducted on an annual basis. One issue with having to rely on NASS survey data is that very few of the questions are aimed at deciphering how much or what types of agrichemicals are used. For the most part the only question answered is whether or not a farm operation uses agrichemicals, and such information is not incredibly helpful to the program's planning efforts. There should be an attempt to acquire this information at least once every decade which is roughly the same desired frequency of updating the program's long term monitoring strategy and plan.

Best Management Practice Surveys

These surveys are conducted nearly exclusively by the program's personnel working at Colorado State University Extension. These surveys are aimed at getting details on what types of best management practices (BMPs) are being implemented on various farming operations, for what reasons, and at what cost. For the cost questions it is desired to understand what the trend is on whether a producer may sacrifice their input costs or net income to accommodate BMPs the may help reduce agrichemical contamination. Such BMPs are typically aimed at fertility, pest, and water management along with crop type rotations which aid in breaking up pest populations.

Knowing where specific BMPs are being implemented versus where they may not be assists the program two-fold. First, such information is useful in interpreting the groundwater quality results obtained under the current monitoring strategy and plan; and second, it helps the program adjust its future sampling strategy to attempt to study the specific impacts that some BMPs are having on improving or preventing groundwater contamination with agrichemicals. CSU Extension has conducted three surveys in attempt to obtain this useful information. The most recent was conducted in 2011 (Bauder et al., 2013) and obtained a usable response rate of 37%. This survey was the first conducted since 2002 but normally such surveys are conducted more often than once per decade. Results from these reports are used by the program along with information obtained from agrichemical use surveys to update the long term monitoring strategy and plan.

Long-term Monitoring Strategy and Plan

The program has decided that conducting a review of all monitoring data, along with any new information on land use change, BMP and agrichemical use information from available from surveys, and more up to date knowledge on the hydrogeology of various areas, and new water uses and demands, is essential for keeping the program on target with its monitoring objectives. The long-term monitoring strategy and plan is updated every ten years. The exact

details of how the plan is developed can be discovered in the current long-term plan titled *Long-Term Groundwater Monitoring Strategy and Plan*(Naugle et al., 2007) which can be found on the program's publications webpage. The development of all future long-term plans should follow the basic methodology used in this report and therefore it serves as essential guidance for accomplishing this component of the QAPP.

Pesticide Properties Database

The program is responsible for determining which agrichemical compounds should be screened for in the groundwater samples it collects. For the most part all samples collected undergo analysis for the complete list of nutrient and pesticide compounds. The main limitations to which nutrients are monitored is budget and laboratory instrumentation. The program will at a minimum monitor for nitrate and phosphate which are the two nutrients of main interest to the program. Which pesticide compounds are being used in Colorado may vary over time so it is important to evaluate how necessary it is to be screening for particular pesticide compounds. The program's approach towards this end has been to create a pesticide properties database that houses all known information on pesticide active ingredients. Of course the list of pesticide active ingredients is quite extensive so multiple criteria are evaluated to create a final priority list.

The first criteria is whether or not a pesticide has been detected in Colorado's groundwater through the program's monitoring efforts or by monitoring efforts of other groups, such as USGS. Generally compounds discovered at any point in time will likely remain indefinitely on the priority list unless future conditions warrant its removal. The second criteria used, is whether or not a pesticide product, registered for use here in Colorado, has a Groundwater Advisory on its label. Such advisories are usually only present when the product contains a pesticide active ingredient that has a propensity for leaching into groundwater. However the labeling process used by U.S. EPA does not always identify these compounds and therefore it is necessary to use other criteria such as the Groundwater Ubiquity Score (GUS) which is a calculation based on a compound's solubility, half-life, and octanol-water coefficient (Kow). Pesticide compounds with scores less than 2.0 are believed to have low to no propensity to leach under normal conditions. A score greater than 2.75 is believed to have a greater likelihood of leaching under normal conditions. These scores can be used as a supplement to a Groundwater Advisory label or in conjunction with. An additional criteria is whether or not there is a U.S. EPA drinking water standard for the pesticide compound. There are very few pesticide compounds that have been thoroughly evaluated to the extent that it is known whether or not they need a standard. While the program focuses primarily on maximum

contaminant level (MCL) standards, lifetime health advisory levels are also of interest when it comes to determining the need to include a particular pesticide compound in the screening list.

The more of the above criteria a pesticide compound meets, then the more important it is for the program to be monitoring for it. Currently the program has about 100 compounds on its priority list and the Biochemistry Lab currently screens for about 95 of those compounds. The program plans to keep the pesticide properties database up to date with new compounds over a ten year period and then use the priority ranking to adjust the screening list as necessary. This will coincide with an update to the long-term monitoring strategy and plan.

Monitoring Well Installation

The program's focus is mainly on monitoring the uppermost portion of alluvial or coarse grained, unconfined aquifers. In most cases this is where contamination migrating through the soil and the unsaturated vadose zone will first impact the saturated zone of the aquifer. This, therefore, provides an early detection mechanism for aquifer contamination. Since the majority of domestic and irrigation wells are drilled deeper into an alluvial aquifer to ensure a strong yield and production longevity, monitoring wells designed to sample the top of the aquifer should provide adequate warning in the event a contaminant of concern is discovered. A drawback to installing monitoring wells near the unsaturated-saturated boundary of an alluvial aquifer in Colorado is the potential for static water levels to drop below the screened interval. This is not controllable, but can be accounted for with proper placement of the well. Furthermore, the program strives to install monitoring wells for the purpose of conducting 20-30 years of monitoring or longer which makes it critical that they are properly installed, developed, and maintained according to industry standards. The program adheres to the guidance provided in chapters 2 thru 12 of the Practical Handbook for Environmental Site Characterization and Ground-Water Monitoring (Nielsen, 2006).

Chapter 2 (pp. 35-197) provides information on the value of conducting an environmental site characterization of the area to be monitored prior to implementing a monitoring program. This process ensures that the area is well understood; and by establishing data quality objectives for each area, the program will be efficient in its placement of monitoring wells. Furthermore, conducting site characterization can involve collecting baseline sample data for an area if such data is not available. Doing this provides guidance for deploying monitoring wells in areas that have a likelihood of depicting the nature and extent of agrichemical contamination. The program accomplishes this partly through vulnerability assessments and development of a long-term monitoring strategy and plan. Obviously for new areas with no availability of historical data, the program will rely more on the contents of this chapter to help develop an effective, and study focused monitoring network.

There is also valuable instruction and guidance provided in Chapter 5 (pp. 297-343) pertaining to selecting the appropriate drilling methods, collecting soil samples during borehole drilling, logging of boreholes, and advice on how to develop focused and detailed drilling contracts. Information collected using these methods is essential for fulfilling the requirements of Water Well Construction Rules (2 CCR 402-2) with regard to filing necessary forms and documentation about the well during the permitting process. The program's usual course of action regarding the permitting process for a new monitoring well is explained in more detail in Appendix I, Monitoring Well Installation Procedures, of its comprehensive publication titled *Agricultural Chemicals & Groundwater Protection in Colorado* (CWI Special Report No. 23, 2012) The Division of Water Resources in the Department of Natural Resources has a document titled *Guide to Colorado Well Permits, Water Rights, and Water Administration* (State of Colorado, 2012) that provides essential information for this process.

In Nielsen, 2006, Chapter 6 (pp. 345-472) discusses in-depth the use of direct-push technologies that may be appropriate for certain areas of Colorado. Since the program's monitoring responsibility and focus is primarily on groundwater, Chapters 8 – 12 (pp. 517-882) provide all necessary guidance for properly installing and developing a monitoring well to meet the study-specific data quality objectives. ASTM Standard D5092 and ASTM Standard D5521 are documents referenced in Nielsen (2006) that provide additional insight.

Field Standard Operating Procedures

The program strives to obtain scientifically defensible results in samples fully representative of the groundwater aquifer being studied. The most important factors that help assure this is to develop standardized methods for all field work and laboratory work. For more detailed descriptions of the procedures that are currently implemented by the program, the *Field Standard Operating Procedures* are available within the Program Guidance Documents portion of the programs Publications webpage at www.colorado.gov/ag/gw.

In general the program follows industry standards for collection of groundwater samples to be analyzed for inorganic and/or organic compounds. The routine inorganic compounds studied by the program include fluoride, sulfate, dissolved orthophosphate, nitrite, nitrate, bromide, and chloride. Occasionally the program may send a sample to a third-party laboratory to be analyzed for other inorganic constituents like dissolved or total metals. The program's main interest with regard to organic compounds is pesticide compounds. Currently there are nearly 100 pesticide compounds screened for in most of the groundwater samples collected. These include parent and breakdown compounds of herbicides, fungicides, and insecticides. The detection limits tend to be less than one part-per-billion but some compounds are screened for at levels 10- to 100-fold lower. While the program is responsible as a whole for deciding which

compounds are desired to be screened for in Colorado, laboratory personnel are responsible for developing the correct methodology for conducting the analysis. Once these methods are developed in the lab, any information pertaining to the requirements for sample filtration and preservation are conveyed to field personnel and are included in the field SOPs.

The specific methodology that is used for each sample site depends on the type of groundwater well that is being sampled (domestic, irrigation, monitoring, municipal, etc.) and how deep the pump inlet would have to be set at if one is being used. Field personnel should strive to utilize the same sampling methodology for each and every sampling event once the methodology is proven effective. Where this QAPP is essential for field operations is in the guidance of several key elements that are normally part of every sampling event regardless of the SOP. These include: documentation requirements with regard to SOP forms and Chain-of-Custody forms; quality control sample requirements; work area safety and security; sampling specifics (identification, collection, preservation, and transport/shipping); and inventory/maintenance of sampling equipment.

Documentation Requirements

It is important to complete the SOP forms as thoroughly as possible for each sampling event. The information on these forms, when thoroughly populated, provides details critical to the interpretation of laboratory results. A black or blue ink pen should be used to record information. Care should be taken to ensure that the appropriate site name is recorded on the forms being used during the sampling event. In general the program uses ASTM Standard D6089 (ASTM, 2004n) as a guide for determining what information should be collected during a groundwater sampling event. Additional information used by the program can be found in Chapter 15 (pp. 959-1112) of Practical Handbook for Environmental Site Characterization and Ground-water Monitoring (Nielsen, 2006).

Field personnel need to work within the Chain-of-Custody (COC) requirements of laboratory to which samples will be delivered. Most samples will be delivered to CDA's Biochemistry Lab and must therefore be accompanied by their specific form which can be found in the lab's analytical work plan. The sample IDs on the COC must match the sample IDs on bottle labels as well as the time/date the sample was collected. ASTM Standard D4840 also provides insight towards ensuring thorough and accurate use of sample COCs. Another document that must be cross-referenced to the field forms is the calibration record detail for the multi-parameter and dissolved oxygen instruments if they are being used for purging during a sampling event. The most recent calibration data and time on the form SED-1 must match what is in the calibration record book.

Instrument Calibration

The calibration procedures for the multi-parameter instrumentation being used by the program may vary over time due to changes in equipment. Therefore the procedure to be followed as part of this QAPP is based on manufacturer recommendations which should be compiled into the Calibration Procedure & Log which can be found on the program's webpage under Publications → Program Guidance Documents. All field personnel should become familiar with the most recent version of this document.

Instrumentation should be calibrated as necessary to ensure that the values recorded during a sampling event are accurate. At a minimum, calibration of instruments to be used for sampling of a specific sampling network should occur before the first well and then once per week until the entire network is sampled. In addition to full calibration, field personnel will check instrument calibration with YSI's Confidence Solution before every sampling event that the instrument will be used on. The dissolved oxygen calibration will require comparison to true percentage of saturated dissolved oxygen. This can be obtained by dividing the barometric reading at the site by 760 (mm Hg at sea level) and multiplying by 100 for a percentage. If the calibrated % saturation is within 1% of this value then the sensor is adequately calibrated.

Field personnel should record calibration standard lot numbers and expiration dates. This is to ensure that expired standards are not being used for calibration. Furthermore, electrical conductivity standards should not be used beyond one week of being opened regardless of how far out the expiration date may be. Calibration standards for pH are more stable and can be used until extinguished or until their expiration date. The ORP calibration standard is sensitive and care should be taken to keep it away from ultraviolet light and temperatures above 25˚C for prolonged times.

Temperature is a quintessential variable for calibrating instruments. Therefore it is important that the thermistor on the instrument is checked for accuracy at the beginning of every field season and as necessary during the field season. Furthermore, since parameter calibration is sensitive to temperature, it is recommended that instrument calibration is conducted first thing in the morning or in a temperature-controlled environment.

The date and time of the most recent calibration is to be recorded on Form SEF-1 as outlined in the Field SOP Manual for any sampling event that is utilizing the instrument(s) for data collection.

Quality Control Sample Requirements

The program follows the suggested guidance found in Chapter 15 of Nielsen (2006). Specifically, the suggestions on purging to stabilization of indicator parameters, low-flow sampling

techniques, and protocols for collecting field QC samples. Currently the program does not do trip blanks as part of its normal sampling regime unless they are required as part of a collaborative effort with a separate entity (i.e. Dept. of Public Health & Environment needing VOC samples collected which requires a trip blank QC sample). Likewise the program does not normally collect Field Spike Samples as part of QC requirements. The regular QC samples collected by the program include equipment blanks, blind duplicate samples, and duplicate samples. Equipment blanks are a two sample set which includes one sample that is of the source water supply and another that is of the source water after it has been cycled through the decontaminated equipment setup. It is important that source water is passed through all parts of the equipment setup that is relevant to the collection of the groundwater sample.

Work Area Safety & Security

Field personnel need to ensure that access to and around a well to be sampled is safe. It is important to cut back weeds prior to backing a field truck up to the well for multiple reasons which include eliminating trip hazards, preventing contamination of samples during collection due to dust or pollen being at or above the work surface, and prevention of sparking a fire due to excessive vegetation being in contact with the truck. Another safety concern is mostly related to lifting hazards as some of the equipment used for a sampling event can be upwards of 50 lbs and must be moved into and out of the field truck. It is important to use proper lifting techniques to avoid injury.

If a sampling event is taking place within or beside a normal vehicle or bicycle traffic lane, then it is required that field personnel emplace cones and signs to provide warning to passersby of the work taking place. Additionally, in areas when vehicles are a safety hazard it is mandatory that an ANSI Class 2 high visibility vest is being worn by all field personnel for the duration of the sampling event.

During borehole drilling and monitoring well installation activities, program personnel are to follow the requirements of the contracted well drilling company while working on site. However, at a minimum, program personnel are required to wear a hardhat, eye protection, full-length pants, and work boots (preferably steel- or composite-toed) when it is expected that any work will be conducted within a working circumference of the drilling point that is no less than the working height of the rig mast.

It is important to note any well security issues like a broken lock, missing cap, or foreign debris so such information is available during interpretation of laboratory results. If any parts are missing or damaged it is important to get the well repaired as soon as possible. In the event a

sampling site is in an area requiring gate access it is the responsibility of the field personnel to ensure that the landowner's property is secured upon conclusion of sampling activities.

Sampling Specifics

Well Purging

Wells being sampled by program personnel must be adequately purged as appropriate for the well type being sampled and the methodology being used. On average the typical length of purge time for any well that has a normal yield is 15-20 minutes. For most wells the purging time should be a function of purging parameter stabilization. ASTM Standard D6452 provides suggestions on the purging methods for wells used for groundwater quality investigations. This information in addition to that provided in ASTM Standard D6771 (low-flow purging and sampling for wells and devices used for groundwater quality investigations) supports the basic premise behind the program's purging protocols seen in the field SOPs which is to purge until selected parameters (pH, EC, D.O., and ORP) have met their respective stabilization criteria. ASTM Standard D6771 was withdrawn in 2011 per regulations governing ASTM technical committees because the standard was not updated by the end of its eighth year. For this matter the program also follows guidance provided by Puls and Barcelona (1996) in *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*.

In the program's SOP GPP-3, it is noted that purging time length for irrigation and domestic wells can be limited to how long the well owner desires for the well to be ran if it is not already running upon arrival. Even in these circumstances it is important to purge the well for as long as possible prior to collecting a sample. When applicable, it is important to select a pump for purging and sampling a monitoring well that does not affect water chemistry or the constituents being measured in the field or at the lab. ASTM Standard D6634 discusses selection of purging and sampling devices in order to prevent alteration of sample representativeness or constituent concentrations.

Sample Labeling

It is required that all sample bottles are labeled (preferably with waterproof labels) to indicate site ID, date, time, personnel, and analysis needed. Whatever information that is written on the sample label must be replicated onto the Chain-of-Custody form and the SOP Forms verbatim. Additional information about whether the particular sample was filtered or pretreated in any way should also be documented as necessary on the COC and SOP Forms. If the sample ID is different than the site ID then the SOP field forms must accurately cross-reference the two IDs.

Sample Filtration

Generally all samples collected by the program must be filtered in the field to at least 0.7 micron with an appropriate filter media that does not interfere with the analytes being measured. The most common filtration media used by the program should be borosilicate micro-fiber glass without binder. In the event disposable filters are used it is important to ensure the filter media does not conflict with measured analytes. Some analyte procedures may require the sample to be filtered to as low as 0.2

micron and this should be conducted in stepwise fashion to prevent premature clogging of the filter. If any of the samples to be collected are for dissolved metals it is imperative that the filter housing is not constructed of stainless steel or any other material that may bias sample quality.

Sample Collection Order

The collection order of samples has normally been from most sensitive to least sensitive with regard to sensitivity of compounds to changes in temperature, pressure, and subsequently water chemistry. This is of concern in the event that a grab sample is collected and split up between the various sample bottles (i.e. a surface water grab sample, or a bailer groundwater sample). Since this program predominantly uses a consistent pumping rate to purge and sample monitoring wells it is not imperative that any particular sample order is followed. It is more important that all samples are collected in a fashion that minimizes the chances of cross-contamination or biasing of the aquifer formation water quality. For example, if a particular sample bottle has a pretreatment chemical that the laboratory had added to it, it is important the bottle is not pre-rinsed or overfilled. If no pretreatment chemical is being used, then all sample bottles must be pre-rinsed one time prior to collection of the sample as outlined in the Field SOP Manual. Another point to consider when determining the sample fill order is whether or not the analyte may become impacted by being left out in hot and high sunlight conditions. If there is concern about this then such samples should be collected last to minimize the amount of time filled bottles may be sitting in such conditions.

Sample Preservation and Storage

Currently none of the samples collected for inorganic anion or pesticide analysis at CDA's laboratory require chemical pretreatment. In the event field personnel are collecting samples for collaborative purposes, then the collaborating lab needs to supply the bottles and pretreatment/preservation chemicals along with instructions on their specific requirements. In nearly all cases, it is required that samples are promptly stored in a wet ice cooler or an electric refrigerator/freezer at a temperature of 4˚C. Samples should not be frozen for transport from the field to the laboratory so use of dry ice is not recommended. The maximum temperature that any samples should be stored at for an extended period of time is 10˚C. Samples collected for some analyses, like Boron, do not require preservation, but even these samples should not be stored in excessive heat or direct sunlight for extended periods of time.

Sample Transport and Shipping

The program primarily has the same field personnel collecting and delivering samples to the lab. In these instances the main precaution is to ensure that samples are protected from breakage during transport. Samples transported in a wet ice cooler or an electric refrigerator/freezer should be placed in a cardboard separator or wrapped in bubble wrap, whichever is most appropriate for the conditions. In the event a wet ice cooler is used necessary measures should be taken by field personnel to ensure that sample labels remain adhered to the sample bottle and that the information written on them does not rub off or become unreadable.

When it is necessary to ship samples, it is important that they are properly preserved in ice to maintain their necessary temperature. This includes the use dry ice if samples must be shipped frozen. Furthermore each shipping box of samples must be accompanied by the COC that is populated with the corresponding sample labels. If shipping more than one box of samples it is important to include a sheet that documents the total number of samples and boxes in the shipment. A copy of this should be placed in each box along with that box's specific COC. ASTM Standard D6911 deals with more specific requirements and regulations governing the shipment of environmental samples for laboratory analysis.

Inventory/Maintenance of Sampling Equipment

All equipment used by the program for the purpose of collecting, storing, and transporting/shipping samples to a laboratory need to be tracked and maintained according to manufacturer suggestions (where appropriate). A list of current equipment and its status (active, inactive, in need of repair) needs to be maintained by field personnel. Additionally, since equipment may be stored in multiple locations it is important to document where each piece of equipment is located.

Most of the equipment used for pumping groundwater (pump, tubing, generator, air compressor) are used on a frequent basis and should be monitored throughout the field season for maintenance needs. The Teflon bladder in a pneumatic bladder pumps may collapse over time and result in a decreased fill volume which lessens the maximum pumping rate. It is essential that field personnel monitor its condition so as to prevent excessive pressures from being used which can alter water chemistry. All sample tubing used by the program for down-hole applications is Teflon-lined polyethylene tubing. This tubing is fairly durable and can withstand the repeated decontamination procedures that are necessary, but it should be monitored for kinks or damage.

Since most of the program's monitoring wells that utilize portable pumps for sampling do not have excessive sediment, the water is usually not abrasive. However, over time the stainless steel check balls in the pneumatic bladder pump may become etched and will not properly seat and seal. This can decrease pumping efficiency and may result in excessive pressures being used which can affect water chemistry. Furthermore, excessive sediment may begin to clog the intake screen.

The inverter generator that is used by the program is gas-powered and therefore must be maintained similar to any small engine. The oil must be changed every 300 hours of operation per manufacturer suggestions and the air filter must be kept clean of excessive dust in order to ensure optimal operation. The inverter generator powers an electric oil-less air compressor. Even though the program does not analyze samples for hydrocarbons, it is the program's prerogative to use an oil-less compressor to minimize any effects such compounds may have on pesticide measurements. It is imperative that the air tanks on the air compressor are drained at the end of every work day in order to prevent air from cooling overnight and creating condensate which may lead to internal rusting and weakening of the tank's integrity. Abuse of this type over time may result in an explosion. The air compressor's air intake has a filter that should be checked occasionally to ensure it is not clogged.

A peristaltic pump is used fairly regularly by the program because many monitoring wells have their screened intake in groundwater that is less than 25 ft below ground surface which is approximately the maximum vacuum lift obtainable by a peristaltic pump for the altitudes of most of the program's study areas in Colorado. Aside from the sampling shallow wells the peristaltic pump is used as part of the decontamination procedure for the pneumatic bladder pump scheme as part of GPP SOP 2 in the field SOP manual. The pump cartridge utilizes thick-walled silicone tubing and this tubing must rebound after being squeezed in order for a suction to be created. Over time this tubing can be worn out because of the way it is constantly squeezed and stretched in the cartridge. It is important to monitor the condition of the tubing to ensure that the loss of pumping efficiency is not requiring the pump to be operated at excessive speeds which can impart additional, unwanted negative pressure on the sample water.

The electric refrigerator/freezer that is used for sample storage and transport needs to be maintenance according to manufacturer suggestions and should be monitored for efficiency during use throughout the field season. Similarly, the multi-parameter and optical dissolved oxygen instruments require constant calibration monitoring throughout the field season and these calibration records should be recorded in a calibration record book. It is important to keep these instruments from being in direct sunlight or extreme heat for prolonged periods of time as such conditions could affect the calibration or damage the instrument.

Data Validation and Evaluation

In order for the program to ensure that data being used in study area evaluation and statistical interpretation are accurate, it is important that all data collected is done within the constraints of this QAPP, the Calibration Procedure & Log, the field SOPs, and the analytical work plan being used by the laboratory. This requires quality assurance in field procedures and lab procedures and validation and review of methods.

Quality Assurance and Control

As described earlier in Field Standard Operating Procedures, the program utilizes equipment blanks, duplicate blanks, and blind duplicate blanks to ensure sampling procedures in the field are accurate and precise. Aside from QC sample collection it is critical that instruments are properly calibrated as outlined in the Calibration Procedure & Log, that storage coolers are maintaining the appropriate temperatures, and that field forms are thoroughly and accurately completed.

Data Review

All data received from the laboratory is reviewed to ensure its suitability for including in long-term trends for networks. Part of this process involves the program's groundwater monitoring specialist screening the laboratory results to check for any reporting errors and to determine the accuracy of QC samples submitted to the laboratory. If any errors are discovered in the lab's reports it is important that they are resolved promptly so a rerun of a sample can occur in a timely fashion.

The program also utilizes its liaison with the Colorado Department of Public Health & Environment (CDPHE) to review the laboratory data. Any samples containing constituents that exceed a water quality standard as defined by Regulations No. 41 and No. 42 of the Colorado Water Quality Control Commission will be dealt with under the authority of CDPHE. If a sample has a water quality standard exceedance, it is the liaison's responsibility to notify the Commissioner of Agriculture at CDA. Furthermore, if a particular action (such as an unpermitted discharge) is suspected to be associated with the impacted groundwater quality, the liaison is responsible under CDPHE's authority to investigate the mater further. Due to the time sensitive nature of environmental contamination, it is important that the laboratory, field personnel, and the CDPHE liaison work together quickly in evaluating preliminary and final data from the laboratory in order to ensure necessary actions are taken to protect human, animal, and/or environmental health.

Statistical Techniques

The vast majority of data collected by the program's efforts consists of environmental data that is usually not normally distributed. Therefore, it is important to not utilize techniques that require a normal distribution unless the data have been properly transformed. The program will primarily utilize non-parametric/non-normal statistical techniques for conducting statistical evaluation of data.

The book Statistics for Censored Environmental Data Using Minitab and R (Helsel, 2012) provides guidance to the program with respect to utilizing the currently recognized and appropriate statistical techniques. Of particular importance is how censored data – reported values that are non-detects – are accommodated in the dataset. The program will not use data biasing techniques such as data substitution (substituting ½ the detection limit for a non-detect) nor should data be deleted from the dataset without ample evidence that it should be. Outliers should be included in statistical techniques testing for differences in median between years or in testing for long-term trends unless there is strong reason to drop them from the analysis (i.e. result is due to verified point source contamination).

Reporting

All data collected by the program is done for the purpose of protecting human, animal, and environmental health from degradation of groundwater quality due to agrichemical contamination. Part of responsibility of the program is to report the data to the various stakeholders which include cooperating land- or well-owners, the program's advisory committee, the Commissioner of Agriculture, and the general public. It is important that in any form of reporting that program personnel adequately ensure that water well owner anonymity is maintained.

Owner Results

The program's monitoring efforts operate mostly on private lands, primarily under the cooperation of the land- and/or well-owner. Unless required by law (especially when working with municipalities) there are no contracts signed between the program and a cooperating owner. It is the program's objective to provide owners with a copy of all monitoring results from testing that occurs on their land, either by use of their domestic or irrigation well or by use of a monitoring well. This is done to both show appreciation for their cooperation and to provide them with information on the water quality of groundwater they may or may not be using for domestic, stock, or lawn/crop irrigation.

It is important that program personnel creating these reports ensure that the data being reported to a particular owner is accurate and highlights any items of concern. Primarily these items will be water quality constituents that are exceeding an established water quality standard (Colorado Water Quality Commission Regulations No. 41 and 42). It is also essential that the report is in a lay-person readable format and that the necessary program personnel contacts are provided if the owner has questions. Either a mailed report with results, or notification on how the owner can access their data on the program's online database, should be provided to the owner no later than March in the year following the year of sampling.

Advisory Committee

The program has a panel of 13 people from a variety of stakeholder interests that meet, on average, once per year to discuss program matters and review results from recent groundwater monitoring activities. Program personnel must compile the results from the prior year's sampling events into a summary that compares the data to historic measurements or discoveries made in the sampled networks. Any areas of the state which are of concern with regard to persistent agrichemical contamination should be disclosed and open for discussion on actions or directions the program should take.

Standard Exceedance

It is the program's responsibility to bring to the attention of the liaison with CDPHE, any occurrence of a water sample that is found to exceed an established water quality standard. While this means that any agrichemical exceeding a standard should be reported, nitrate-nitrogen contamination over the U.S. EPA

Drinking Water Standard of 10.0 ppm is commonplace in some locales in Colorado, and the urgency of notifying the liaison is not as critical. However, there has been very limited occurrence of pesticide compounds exceeding a standard partly because there are not many pesticide compounds screened for by the program that have an established standard, but mostly because concentrations tend to be very small (< 1.0 parts-per-billion) in comparison to nitrate-nitrogen. Therefore when a discovery is made of a pesticide concentration exceeding an established standard it is imperative that the program's liaison is notified as soon as possible to determine the next steps. It is then the liaison's responsibility to notify the Commissioner of Agriculture about the exceedance and make recommendations on what actions to take, if necessary.

It is important to assure that all field and laboratory quality assurance and data integrity has been verified prior to reporting to the liaison, and subsequently the Commissioner of Agriculture, that a pesticide has been detected over an established standard. It is important to minimize the potential of taking action and wasting resources on a false positive.

Reviews and Factsheets

On an annual basis the program should create a summary review discussing the monitoring activities that occurred in the prior year. This should be made available to the public before the start of the next year's monitoring season. The review should discuss the following details:

- The network areas sampled and the dates of sampling
- The general statistics of water quality constituents screened for by the lab
- Any notable discoveries such as standard exceedances or noticeable data trends
- Any regulatory action being taken due to a result
- The sampling plans for the upcoming sample year
- Any plans for other program work in the upcoming year that relates to sampling network maintenance, design, or expansion

From time to the time the program should compile results from a network, or multiple networks, into a factsheet that discusses major discoveries over the various sampling events, data trends, and any correlation of data results to auxiliary data like climate, land use change, BMP implementation, or other variable. Attempt should be made in these factsheets to provide statistical evidence of how the data is behaving or how it is being affected by other auxiliary data. It is important for the program's field personnel to collaborate with other program colleagues at CSU Extension and CDPHE in order to conduct an adequate investigation into the data. These factsheets should be created on a frequency that allows enough data to be collected in order to allow the best chance to draw definitive conclusions for the study area(s) being discussed within it. The program's monitoring schedule as depicted in its Long-Term Monitoring Strategy and Plan provides guidance on how often a network factsheet should be revised or created.

The program currently has a comprehensive publication that documents all work that has been conducted by all facets of the Agricultural Chemicals & Groundwater Protection Program. This includes information on program oversight and regulation; groundwater monitoring; and education and training. This document should be revised at a frequency that is found reasonable given the progress and/or advances of the program in these different areas.

If monitoring activities result in a discovery that is of concern or could result in significant impact to human, animal, or environmental health, then it may be necessary to create a factsheet that discusses this discovery and its potential impacts. Such a factsheet should be created as soon as the program's liaison with CDPHE's Water Quality Control Division and the Commissioner of Agriculture qualify the need for one.

Online Database

All data collected by the program is organized into an online database that is available to the public. It is the program's desire to make this database easy to use for the general public. It must provide opportunities for a user to query the data, view the data, and download the data. The database should also interface with a map viewing tool that allows a user to see the approximate area that a sample or sampling network is pertaining to. It is important that the program ensure steps are taken to maintain well- and land-owner anonymity. For the water quality data this requires that any identifying fields are not provided to the general public and for the geospatial location of sampling sites on the map viewer this requires that location offsets are sufficient enough to preserve its ambiguity.

The database should be updated during the program's offseason which is the period of time in between sampling years. Before any data is uploaded to the database it should have undergone Data Validation and Evaluation and before the new data is available to the public, the query and mapping functionality of the database should verify the accuracy of the reporting and the preservation of owner anonymity.

The Online Database can be accessed at www.erams.com/co_groundwater.

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Revisions

All revisions made to any portion of this document after its inception, should be listed in a format similar to the one shown below in the box.

Revision: Adjust decontamination protocol
Date of Revision: January 08, 2007
Revision made by: Karl Mauch
Position Title: Groundwater Monitoring Specialist
Description of Revision:

- Updated the header and footer as necessary
- Included final peer reviewed SOPs for field tasks

Revision: Initial documentation and development of Quality Assurance Program Plan

Date of Revision: February 2014

Revision made by: Andrew Ross & Karl Mauch

Position Title: CDPHE & CDA

Description of Revision(s):

- Created the initial format and content of this manual

Revision:

Date of Revision:

Revision made by:

Position Title:

Description of Revision: