



**RECOMMENDED SAMPLING, ANALYSIS, AND REPORTING  
PROTOCOLS FOR BASELINE GROUNDWATER SAMPLING IN  
ADVANCE OF COALBED GAS DEVELOPMENT IN THE TELKWA  
COAL FIELD, BRITISH COLUMBIA**

**PREPARED FOR THE  
B. C. MINISTRY OF ENERGY, MINES, AND PETROLEUM RESOURCES**

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## **1. INTRODUCTION**

The objective of this report is to recommend standardized baseline groundwater sampling, analysis, and reporting protocols in advance of coalbed gas (CBG) development in the Telkwa coalfield tenure area. As applied here, baseline sampling is intended to provide the foundations for additional groundwater monitoring during future CBG exploration and development activities. Such monitoring will provide a valuable screening tool useful for evaluating whether CBG activities are impacting either groundwater tapped by domestic water wells or water issuing from springs.

The baseline approach proposed here is to sample and test for the most direct, abundant, and obvious signs of contaminants potentially related to CBG development. This will require analyzing and comparing data derived from sampling groundwater sources designated for domestic use, springs, and groundwater in coalbed gas reservoirs. Sample selection criteria will be addressed in a separate document.

Recommendations presented here address the two major environmental concerns related to the potential impact of CGB development on potable groundwater resources. These are: 1. Contamination of aquifers with migrated hydrocarbon gas, and 2. Declining aquifer yield associated with drawdown associated with CBG water production. Consistent baseline sampling and analysis protocols will make it possible to reliably assess potential impacts to the groundwater environment with the highest possible degree of scientific certainty. Although emphasis in this report is placed on sampling cased and completed water wells, similarly rigorous protocols apply to the sampling of open wells, springs, and surface water resources.

Recommendations presented in this report include the following:

- Standard sampling protocols needed to yield consistent analytical results;
- Standard analyses needed to evaluate the origin of natural gas in water resources;
- Standard data maintenance and recording practices and;
- Selected quality assurance and control considerations that allow the information collected to withstand public scrutiny and be scientifically defensible.

Numerous readily available references provide guidelines for surface water and groundwater sampling. To keep this document reasonably brief, established conventional surface water and groundwater sampling protocols will not be repeated.

## **2. FIELD SAMPLING PROTOCOLS**

### **2.1. Conduct and document interviews**

Prior to or upon arrival at a water well site, it is best to speak directly with the water well owner to get information regarding past and current water quality and water yield data. Information collected can be used to supplement or update information that may already be available in a data base. Useful data would include current contact information,



current and historic water usage, the owner's perceptions regarding current and historic water quality and yield, maintenance practices, and the availability of historic documents regarding water well construction and water quality.

## **2.2. Document surroundings**

The surrounding environment near a water sampling site should be documented to help interpret sampling results. This is particularly important for the analyst who is asked to interpret data but who is not present at the time a sample is collected.

### **2.2.1. Inspect the area near a water sample source**

When sampling domestic water wells near homes, it is useful to note or sketch the location of a home, septic tanks, leach field, well head construction, stock pens, storage sheds, or any other features that could impact water quality (Figures 1& 2). Any potential sources of water contamination should also be noted when sampling water resources at any site. For example, surface discharge outfalls, improperly disposed organic or inorganic wastes or containers, spills, abandoned pits, and unlined pits could all be pollutant sources to either surface or groundwater resources. The presence of stressed vegetation may also help identify the presence of contaminants in soil. Observations and sketches made in conjunction with scale-referenced digital photographs are ideal for documenting local conditions.

### **2.2.2. Document mechanical components of a water well**

The type of pump used in a water well can affect water-quality analyses. Suction lift pumps and jet pumps can induce the loss of dissolved atmospheric and hydrocarbon gases and volatile organics due to the drop in pressure caused by a vacuum. Water circulating and mixing with sample water in the venturi of jet pumps can also affect water chemistry. Thus it is helpful to document the type of pump used on a well. Wells with water-lubricated submersible pumps are preferred by the United States Geological Survey (USGS) for their National Water Quality Assessment Program (NAWQA) sampling efforts (Lapham *et al.*, 1995).

Casing materials can affect water quality, particularly if the well is infected with sulfate-reducing, and iron-related bacteria. Stainless steel, carbon steel, and galvanized steel are susceptible to galvanic currents induced by stratified aquifers of differing salinity. Bacterially-mediated chemical reactions, common in most water wells, not only facilitate corrosion but also concentrate mineral constituents in the well bore annulus (Borenstein, 1994). Depending on the type of metal casing used, redox reactions can release iron, manganese, zinc, chromium, cadmium, and other metals into the surrounding aquifer environment. Corroded metal casing can also accommodate aggressive bacterial colonies within a sheath of bacterially-generated mucous (bioslime or biofilm) that is very difficult to eliminate. PVC casing, on the other hand, has a minimal effect on water quality within the aquifer. For these reasons, the casing material in a water well should be noted,





especially when the water column in a well cannot be adequately purged prior to sampling.

The access point for sampling a well must routinely be noted on all data sheets. Water chemistry can change significantly if samples are accessed from a cistern or from the downstream side of a water treatment system, pressure tank, or holding tank. At times, it may be necessary to install a sample valve at or near a well head to obtain a representative aquifer sample. If water treatment systems are present at a sampling site, their function and location should be noted.

### 2.2.3. Document the hydrologic setting

The hydrogeologic setting of every sample site should be considered. For example, if there are bedrock outcrops in the area, a strike and dip measurement could be very useful to predict the likely transport direction of free or dissolved gas in the subsurface. Noting the presence of evaporite minerals at the surface can also help identify an ephemeral spring that may not be flowing during the dry season.



**Figure 1. Example of poorly constructed well, flush to the ground, allowing surface water to enter the casing.**



**Figure 2. Fecal coliform contamination observed in the same well is easily explained.**

When sampling water wells, it is important to document a well's total depth and the depth of screened intervals. A deep water well with a long screened interval may draw water from a number of different water-bearing strata, whereas a shallow well with a short screened interval might only tap a single water-bearing stratum. It is not unusual to observe significant changes in water chemistry within deep wells that are perforated at depth if there are multiple water-bearing zones that infiltrate the well bore through a long gravel pack (Figure 13). Driller's logs will help identify the occurrence of one or more water-bearing horizons. If driller's logs are not on file with an agency, water well owners should be interviewed to determine if they might have access to such information. A geologic map and/or topographic map can at times be used to help establish which aquifers a well taps.



### 2.3. Conduct a hazard assessment

Because sampling environments can be potentially hazardous, reasonable precautions should be taken to ensure a safe working environment. Prior to entering a sampling site, conduct and document a formalized hazard or job safety assessment survey. The survey should identify both potentially hazardous conditions and actions or steps required to mitigate such hazards. If conditions warrant air quality monitoring, appropriate monitors should be available to measure oxygen levels, explosive conditions, and contaminants. Safety contact information should be made available to all field personnel, including emergency phone numbers, and directions to the nearest critical care or health facility.

#### 2.3.1. Observe confined space protocols

Confined or partially confined spaces should not be entered unless field personnel have been adequately trained and certified. There are several types of portable sensors that can be used to determine oxygen levels in confined and semi-confined spaces (McManus, 1999, Chapter 10).

#### 2.3.2. Monitor hydrocarbons in air

When purging a well with water containing dissolved or free hydrocarbons, it is likely that hydrocarbons will accumulate in the immediate environment.

Methane 1% in air –lighter than air @ 15°C
Ethane: 2% in air – heavier than air @ 15°C
Butane: 2% in air – heavier than air @ 15°C

**Table 1. Asphyxiant concentrations of hydrocarbons in air**

If present in sufficiently high concentrations to displace oxygen in air, hydrocarbons will induce symptoms of asphyxia including dizziness, headaches, and impaired judgement (Table 1). At higher concentrations, both the sampling environment and the headspace below the sanitary seal in a well could ultimately become sufficiently saturated with hydrocarbons to reach the lower explosive limit (LEL) by volume in air (Table 2).

**Table 2. Lower explosive limit of hydrocarbons in air**

Methane: 5.3 % of air volume
Ethane: 3.0% of air volume
Propane: 2.1 % of air volume
Butane: 1.6% of air volume
Pentane: 1.5% of air volume

Monitoring ambient air or headspaces at a either a well or sampling bucket with a combustible gas detector will mitigate the above risks. There are numerous brands of portable combustible gas detectors that can be used to monitor methane in air concentrations near a well (Figure 3) and ensure that ambient working conditions at sampling site well are safe.





## 2.4. Decontaminate sampling equipment

Disinfection is important to avoid inoculating water wells with bacteria, and to ensure that any samples collected to detect the presence of bacteria (e.g. BART™ or coliform) have not been contaminated by bacteria from other sites. Decontamination should be performed immediately after sample collection and before sampling equipment is allowed to dry.

Any equipment, buckets, hoses, and probes that may come in contact with well water or surface water sampling apparatus should be cleaned and disinfected. The following process can be modified, depending on the type of sampling conducted in the field.

Step 1. Clean equipment as needed with soft brush using a mild detergent solution (e.g. a dilute solution of Alakanox) and rinse thoroughly (3 times) with distilled water;

Step 2. Clean and rinse equipment with a mixture of 1 part sodium hypochlorite bleach (6.15 % normal household product concentration) to 5 parts distilled water solution for a minimum contact time of two minutes;

Step 3. Soak, rinse, or spray with 70% isopropyl alcohol or methanol solution for a minimum contact time of two (2) minutes;

Step 4. Rinse thoroughly with distilled water for a minimum contact time of two (2) minutes;

Step5. Allow to air dry.



**Figure 3. Field technician using a portable flame ionization detector to monitor well head gas while purging a well.**

## 2.5. Record static water levels

It is desirable but not essential to measure static water levels prior to purging water wells. Static water levels are rarely measured because few want to assume the liability of removing sanitary seals or pump assemblies for the purpose of documenting static water levels. Such measurements can be deferred if there are historic water level document records available. If static water level measurements are required, then any changes made to existing water well component configurations should be conducted under the supervision of a qualified water well professional. At least two measurements should be made within a 30 minute interval using a water level meter. Consecutive measurements should agree with a precision or 5 mm to ensure that a static water

level has been reached in the well. Water usage 24 hours prior to measuring static water should also be documented. Water level measurements in open wells should not pose a problem.



## 2.6. Purge water wells

Most standard water well sampling protocols require purging a minimum of 3 well bore volumes of water prior to collecting water samples. A casing volume to be purged is calculated using well depth, casing diameter, and static water level data. If such data are not available then purging should be based on both documented water usage 24 hours prior to arrival and on field parameter measurements. If it is known that domestic water wells in an area have low yields, then it is prudent to take a conservative approach to purging. Residents should first be questioned about well yield prior to purging and sampling. If yields are very low, then well owners should be encouraged to use their well heavily the day before a sampling team is scheduled to arrive. This will allow a well to recover overnight. If it is not possible to purge 3 casing volumes from a well, then field parameters and/or water levels can be monitored while purging until field parameter values become stable.

Ideally, the U. S. EPA's low flow sampling protocol (Puls and Barcelona, 1995) can be applied to minimize purge volumes. However this requires the use of an adjustable flow rate submersible pump. The pump must be placed adjacent to a well's perforations and the purging flow rate should be low enough so that the static water level does not drop significantly while purging. Stable field parameter data will verify the entry of fresh aquifer water into the well. Most pump assemblies found in the field have fixed pumping rates and it is usually not possible to determine where the pump is set relative to perforations.

## 2.7. Record Field Parameters

Field parameters are important indicators of water well conditions prior to collecting samples. The following field measurements and observations should be documented.

*Static water level:* Initial static water level prior to purging if accessible;

*Purging:* Casing volumes purged, or number of gallons purged;

*From calibrated field sensors:* pH, temperature, specific conductivity (SC), dissolved oxygen (DO), redox potential (Eh), turbidity (NTU's);

*Field test kits:* Dissolved sulfide from HACH tests (mg/L);

*Recording qualitative water quality parameters:* color, clarity, odor, effervescence, sheen, silt, and any sounds coming from a water well;

*Photos:* Should be included to record site conditions and visual water quality at the time sampling commences.

### 2.7.1. Monitor field parameters

Monitoring how field parameters change while purging will provide important clues regarding water sources in the well, oxidation states of well water, and when to collect samples. Field parameters can be measured using individual sensors, or sensors mounted in a flow-through cell. However, if water is effervescent, use of a flow-through cell should be avoided. Small gas bubbles interfere with sensor stability and generate spiked



results because they attach themselves to sensor surfaces thereby impeding their function. In such cases, it is preferable to use individual sensors submersed in a bucket or beaker. Alternatively, a clear plastic flow-through cell can be inverted so that the sensors are pointing upward. Either way, each sensor should be continually observed to mitigate bubble build up. Sensors should not be immersed into a vigorously effervescing water sample until effervescence subsides. Small bubbles attached to sensors can be shaken loose by gently tapping sensors as needed. Field-calibrated sensor parameters should be recorded for every sample collected and sent to laboratories for distribution and inclusion in their final laboratory data report output.

The appropriate time to obtain a water sample is determined when either 3 casing volumes have been purged, or when field parameter measurements become stable, whichever comes first. Field parameters usually stabilize in the following order: pH, temperature (T °C), specific electrical conductance (SC), dissolved oxygen (DO), and turbidity (NTU). According to USGS NAWQA protocols (Holmes *et al.*, 2001, and Koterba *et al.*, 1995), stability is demonstrated when there is no significant change in measured parameters for a duration of 5 consecutive measurements separated by 3-5 minute intervals. A summary of stability criteria required before collecting a water sample is presented in Table 3.

In water wells with yields exceeding 5 gpm, initial purge rates should be slow enough to avoid turbulence that may stir up suspended sediments in the well bore and pump tubing. Laminar flow conditions should be maintained at all times while purging and sampling a well. Wells should be purged slowly at first, while water quality is observed. Flow rates are then gradually increased to a maximum flow rate of 3 to 5 gallons per minute as long as no increase in turbidity is observed. If water well yields are known to be too low to allow field measurement to stabilize without drawing down a well to pump levels, use low flow rates at the outset.

**Table 3. Field parameter stability criteria for collecting water samples.**

<b>FIELD PARAMETER STABILITY CRITERIA (Holmes et al., 2001)</b>		
<b>Measurement</b>	<b>Variability</b>	<b>Recording</b>
<b>pH</b>	<b>+/- 0.1 units</b>	<b>Last measurement at time of sampling</b>
<b>Temperature</b>	<b>+/- 0.2 ° C</b>	<b>Median of last 5 values</b>
<b>SC &lt; 100 uS/cm</b>	<b>+/- 5%</b>	<b>Median of last 5 values</b>
<b>SC &gt; 100 uS/cm</b>	<b>+/- 3%</b>	<b>Median of last 5 values</b>
<b>Redox Potential (Eh)</b>	<b>+/- 5%</b>	
<b>Dissolved Oxygen</b>	<b>+/- 0.3 mg/L</b>	<b>Median of last 5 values</b>
<b>Turbidity</b>	<b>10% of NTU</b>	<b>Median of last 5 values</b>

Using a clean white 5 gallon bucket is the simplest way to measure flow, while allowing the observer to qualitatively monitor water color, odor, and turbidity as a well is purged. After field parameters become stable, the flow rate must be reduced to a rate that is just high enough to prevent the pump from surging. This can usually be attained at flow rates between 0.1 and 1 gallon per minute. Whenever possible, low flow rates should be continued for 15 minutes before the first samples are collected. This allows any free or



dissolved gas to re-equilibrate within the flow system. Collecting samples at low flow rates ensures more representative measurements of dissolved gas and other volatile constituent concentrations. The final sampling data spreadsheet should record the total casing volume purged prior to sampling. If flow rates cannot be controlled, it may be necessary to use a Y fitting with a valve and a secondary line of tubing to fill sample vials and bottles.

If a flow-through cell is used for monitoring water quality field parameters while purging, it should be bypassed for sampling. Most laboratories will provide appropriate sample containers that are prepared in advance of actual sample collection. It is necessary to know which containers contain acids or preservatives so that these additives are not lost or spilled during sampling.

## **2.8. Collect samples**

### **2.8.1. Filter selected water samples**

It is important to decide in advance what types of groundwater samples require filtering and what types of samples do not. In-line filtered water samples should be collected for laboratory analysis of alkalinity, analysis of major cation and anions, dissolved trace metals, and total dissolved solids. Non-filtered samples should be collected for total suspended solids, dissolved hydrocarbon gases, volatile organic compounds (VOCs), and bacterial analyses.

Water wells may contain rich cultures of naturally-occurring bacteria that alter the chemical composition of samples. Filtering helps remove most of these bacteria. Most samples from water wells that are not regularly maintained contain moderate to aggressive colonies of sulfate-reducing bacteria, iron-related bacteria, heterotrophic bacteria, anaerobic bacteria, and slime-producing bacteria. Such bacteria can affect the equilibrium speciation of carbonate species, total organic carbon, and total inorganic carbon concentrations, even when field samples are shipped in coolers and/or stored in refrigerators.

Filtering removes suspended solids that can dissolve in acidic preservatives, and thereby affect the quality of analytical results. Values for pH and conductivity measured in the field are often significantly different than those measured in the laboratory. It is also quite common to observe large differences in charge imbalance (greater than 10%) between the total concentration of cations and anions measured in the laboratory. Such differences are largely due to the dissolution of suspended sediments and minerals because samples collected for cation analysis are shipped and preserved in acid, whereas samples collected for anion analysis are not (Clark, 1994).

If water samples contain very high concentrations of suspended solids, it may not be practical to filter samples in the field. In that case, chain of custody forms should instruct the receiving laboratory to filter samples upon receipt. However, under most sampling conditions, using a 45 micron in-line filter will not severely reduce sampling rates. In-line



filtering also reduces the potential for water samples to react with atmospheric gases. There are many commercially available filters available for groundwater sampling applications (e.g. <http://www.qedenv.com/products/sampling/QuickFilter/QuickFilter.html>).

#### 2.8.1.1. Sampling for alkalinity

Samples acquired for either field or laboratory titration analysis should be filtered. Most regulatory programs recommend using in-line 0.45 µm filters, primarily to remove suspended carbonates that may affect results.

Fill the sample container with filtered water using a low flow rate. Then place the tubing at the end of the filter into the bottom of the sample container and displace 2 sample volumes of water from the bottle. Carefully remove the tubing, and make sure the bottle is sufficiently filled so that it can be capped without a headspace. Cap and seal the bottle. Request a 48 hr. turn around time for alkalinity titration analysis in the chain of custody form.

If in-line filters are not used to collect a sample of water to be titrated, collect a sample in a 5-gallon bucket under a head of water. Pack samples upright in a cooler with at least 1 to 2 times as much ice as the total volume of samples. Samples most likely to deteriorate should be packed closest to ice packs. Glass containers should be separated with plastic containers or ice packs to minimize the potential for breakage during transport. Make arrangements with the laboratory to have the samples filtered upon arrival, and titrated within 48 hours.

### 2.8.2. Sampling for analysis of free and dissolved hydrocarbons

Water samples collected for dissolved methane analysis are normally collected in 40 ml VOA (volatile organic analysis) vials. However, when sampling to analyze for the presence of other dissolved hydrocarbon gas components it is best to use 250 ml sample bottles. A sufficient amount of dissolved gas can be extracted and chromatographically analyzed from larger samples to determine the concentration of all hydrocarbon gas components in the C<sub>1</sub> to C<sub>6</sub> range at part per billion concentrations. Such higher sensitivity provides stakeholders with an effective screening tool for detecting the presence of thermogenic gas and offers early warning of a potentially advancing contaminant plume. Additional chromatographic and stable isotopic analysis would be required if thermogenic gas was detected in a sample, or if measured dissolved methane concentrations exceed 2 mg/L.

#### 2.8.2.1. Sampling for dissolved hydrocarbon gas concentration measurements

Dissolved gas concentrations in well water can vary significantly from year to year as well as from minute to minute. Variability results from changes in static and dynamic water levels relative to pump levels, well bore dilution of aquifer fluids containing dissolved natural gas, mixing between aquifer fluids containing different concentrations of dissolved natural gas from different sources, bacterial hydrocarbon oxidation, and





sampling error (Gorody *et al.*, 2005). For these reasons, it is important to maintain consistent sampling protocols when collecting samples for dissolved hydrocarbon gas analysis. Such consistency is particularly desirable when collecting baseline and subsequent monitoring samples.

Published protocols for collecting water samples for dissolved methane analysis (Kampbell *et al.*, 1990, Kampbell and Vandegrift, 1998, EPA method RSK 175) recommend gradually filling 40 ml VOA vials that contain an acid preservative. This procedure is not recommended here. The disadvantage to collecting samples in this way is that the sample can degas to the air as it is being collected. Acid preservatives which come in contact with water containing high dissolved bicarbonate concentrations will also cause samples to degas CO<sub>2</sub> that can strip out dissolved methane. Accordingly, values reported using the Kampbell sampling method tend to underestimate the amount of dissolved methane in water. Furthermore, if the water sample is effervescent, much of the gas will exsolve, further reducing the amount of dissolved gas it may have contained.

The recommended laboratory holding time for dissolved methane analysis of samples collected without any preservative is 48 hours from the time a sample is collected. In lieu of a preservative, a biocide capsule can be attached to the inside of the septum cap of a 250 ml bottle. This will allow holding times to increase to less than 14 days. Recent unpublished experiments conducted on natural waters collected from the San Juan Basin and the Illinois Basin indicate that natural bacteria begin consuming dissolved hydrocarbons as soon as a sample is collected (Dennis Coleman, IsoTech laboratory, personal communication). Refrigeration only retards hydrocarbon consumption rates.

Samples collected to determine dissolved hydrocarbon gas concentrations should be collected in two 250 ml bottles. Duplicate samples are recommended in the event that one breaks in transit. "Boston round" 250 ml amber glass bottles with a Teflon® silicone septa closures are available from several sources such as from Environmental Sampling Supply, Oakland, CA, Part # 0250-0650-PC. Bottles can be bubble wrapped, placed in a baggie filled with ice, and shipped overnight to the analytical laboratory.



**Figure 4. Collecting a water sample in a 40 ml VOA for dissolved methane analysis. A 250 ml bottle is preferable for dissolved hydrocarbon analysis.**

To collect a sample for dissolved methane from a flowing water well, use an appropriate length of clear ½" polyvinyl tubing to connect to the source tap. An adapter may be required to connect the tap to the clear hose. Such a hose is narrow enough to fit inside either a 40 ml VOA or 250 ml bottle (Figure 4), and visibly ensures that laminar flow through the hose is maintained. Flow rates through the hose should be slow, generally within 0.5 to 1 gpm. Keep the end of the hose submerged in water to minimize the free gas space in the hose. Fill the bottle with





water from the tubing and submerge the bottle into a 5 gallon bucket filled with water. Invert the bottle and insert the tubing to flush the bottle with sufficient water to displace twice its volume. Then slowly remove the nozzle under water, and secure the screw cap under water and as far down towards the bottom of the bucket as possible. In this way, dissolved gas is trapped under the pressure of a head of water and the sample is not easily degassed. After the bottle is capped, take it out of the bucket, turn it upside down and inspect it to ensure that there are no bubbles in the vial. If bubbles are visible, collect another sample. If the water effervesces, then it will be necessary to remove bubbles by briefly tilting the bottle under water. Keep fresh water flowing over the top of the VOA opening when removing excess bubbles under water.

#### 2.8.2.2. Sampling for stable isotopic and chromatographic analysis of free and dissolved gas

Collecting water samples in 1 liter bottles normally provides a sufficient amount of dissolved gas for both chromatographic and stable isotopic analysis of dissolved hydrocarbons. There are 2 types of sample bottles that can be used for this purpose. One liter amber "Boston round" amber glass bottles (made by Qorpak - part # 7724T) with open top, gray septa caps (size 33-430 made by Wheaton - part # 240680) have been traditionally used. However, because they are made of glass, they can break during transit. A second type of 1L stiff plastic bottle (available from U.S. Plastics, part # 66265 32oz Pet® Clear Round Bottle) will not break in transit. However, the sealing caps that come with this bottle (28-400 cap included) must be replaced with a separate cap (U.S. Plastics Part # 66504 28/410 Cap with Liner). A hole is punched into the cap, the liner removed, and a septum is inserted at the analytical laboratory.

Because naturally occurring bacteria in water will consume hydrocarbons even when a sample is refrigerated, adding a biocide to the sample bottle is recommended. The most effective way to add a bactericide is to fill a gelatin capsule (ordered from any drug store) with concentrated benzalkonium chloride (100%). This can be ordered from Alfa Aesar (Stock # 41339). The capsule is then glued to the inside of the septum cap. The gelatin capsule delivers bactericide to water in the bottle as long as the bottle is shipped inverted, so that water is in contact with the capsule. Recent experiments have shown that the component and isotopic composition of hydrocarbons in water samples treated with bactericide will not change over a period of a month. A maximum 14 day holding time is recommended for processing samples. Samples treated with bactericide do not need to be refrigerated during transit and can be more effectively packed to avoid breakage. If no bactericide is added to a collected water sample, call ahead and instruct the analytical laboratory to process the samples and remove dissolved gases from the water matrix within 48 hours of the time the samples are received. It is best to notify the lab on the day of shipment. Such samples must be shipped in ice. Sample preservation and analysis protocols must be decided upon before going out in the field.



#### 2.8.2.2.1. *Sampling non-effervescent water*

Use a clear ½” polyvinyl hose that is small enough to fit inside the neck of the bottle when collecting samples in 1L bottles. This will allow flow to be monitored (see report cover illustration and Figure 5). Make sure that the flow rates through the tubing are low. Remove the cap of the 1L bottle and fill it with water. Once the bottle is filled, immerse it in a 5 gallon bucket full of water, keeping the tubing at the bottom of the bottle. Place the bottle at the bottom of the bucket over a head of water, and keep water flowing at a low rate until another 2 volumes of water have been displaced from the bottle. Then slowly lift the tubing out of the bottle and immediately cap it under water. After the bottle is capped, remove it from the bucket, turn it upside down, and inspect it to ensure that there are no bubbles present. If large bubbles are visible, collect another sample. When finished, tape the cap to the bottle around the neck, pack the bottle upside down in ice, and ship it overnight to the analytical laboratory.



**Figure 5. Filling a 1-L Boston round bottle with water for extraction and analysis of dissolved hydrocarbons.**

Processing a water sample in the laboratory to remove dissolved gas for analysis normally involves the following steps. A volume comprising 5% of the water in a full bottle is first displaced with a helium headspace. The bottle is then agitated mechanically for several hours until the dissolved hydrocarbons elute into the headspace. This method allows the gas to be partitioned between the water and the gas headspace under equilibrium conditions (Henry’s Law). A gas sample is then removed with a syringe and stored in butyl-rubber stopped serum vials that are crimped with an

aluminum cap.

#### 2.8.2.2.2. *Sampling effervescent water*

To collect a headspace gas sample from effervescent water, also use a 1L bottle equipped with a cap. Fill the container with well water using either the tubing or the bucket. Submerge the container in a 5 gallon bucket filled with well water and invert it. Make sure there is no air left in the bottle. Insert the ½ ” polyvinyl tubing into the bottle, increase the flow rate to 2-3 gpm, and allow the bubbling gases to displace water in a headspace until a ⅓ to ½ of the water in the bottle has been displaced. If the bottle opening is too narrow to accommodate the available tubing, a funnel can be used to direct the flow of bubbles into the bottle. Seal the container under water with the septum and screw cap and tighten it securely. Dry the bottle, tape the cap to the bottle, and ship the



container upside down overnight to the sample laboratory. If no bactericide is used, make sure to ship the sample bottle packed in ice.

When sampling gases exsolving in a spring or stream, submerge the 1L bottle and allow water to fill it. Prevent suspended sediment from entering the bottle by allowing water to fill it near the air-water interface. Invert the bottle when filled and place a large funnel into the opening. Allow bubbles to enter the funnel and allow the gases to displace the water in a headspace as described above. Seal the container under water with the septum and screw cap and tighten it securely. Dry the container, tape the cap to the bottle, and ship the container upside down overnight to the sample laboratory. If no bactericide is used, make sure to ship the sample bottle packed in ice.

### 2.8.3. Sampling for volatile organic compounds (VOCs)

Samples collected for VOC analysis are not filtered. Standard 40 mL glass screw-cap VOA vials with Teflon-lined silicone septa and preservatives are routinely used for collecting water samples for volatile analyses. Samples must always be collected in duplicate. Vials should be slowly and completely filled without introducing any air bubbles within the vial. When the septum cap is fitted and sealed, and the vial inverted, no bubbles should be visible. Sample vials must be labeled, inverted, and stored in ice immediately at 4°C.

Water samples containing high dissolved solids concentrations and high alkalinity may effervesce in the presence of an acid preservative. It is therefore important to ensure that no effervescence is observed while filling a VOA vial with an acid preservative. If effervescence is observed, the VOA vial should be thoroughly rinsed with sample water and slowly filled again. The chain of custody should show that the preservative was discarded and should request a 48 hour turn around time for analysis.



**Figure 6. BART sample vials: IRB- red cap; SRB black cap (photo courtesy of Four Corners Geoscience.**

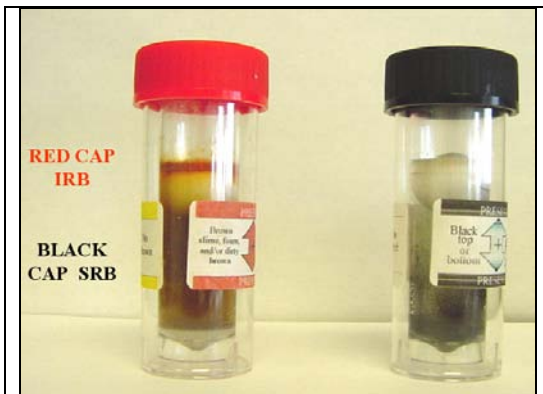
### 2.8.4. Biologic Activity Reaction Test (BART™) Screening

Aside from mechanical failures, the principal cause for complaints of poor water quality and lowered water yields is bacterial fouling of the wellbore environment. Naturally-occurring bacterial consortia systematically remove the available oxygen in water within a series of vertically and laterally stacked biozones. Each biozone

functions to react with specific sources of either dissolved or bound oxygen which is used



to regulate and maintain bacterial respiration and metabolism. If allowed to grow uncontrollably, bacteria will consume all available oxygen in water, generating an anaerobic well bore environment full of unpleasant metabolic byproducts that impact overall water quality. Such stagnant environments are common in water wells. Because similar conditions can arise if natural gas contaminants are present or bubbling through the water column in a well, baseline measurement and monitoring using BART™ tests is useful and therefore recommended (Figures 6&7).



**Figure 7. Colorimetric reactions taking place in BART vials after several days (photo courtesy of COGCC)**

Lateral and vertical gradients of dissolved oxygen concentrations found in stagnant well water are identical in succession to those found in regional aquifer systems from points of recharge to points of discharge (Stumm and Morgan, 1996). The successive loss of oxygen progresses as bacteria first consume dissolved oxygen near the air water interface, and then sequentially consume chemically bound oxygen in nitrates, manganese oxides, iron oxides, sulfate, and dissolved carbon dioxide. Most of these reactions produce carbon dioxide as a byproduct, as well as other byproducts such as manganese and iron sulfide which make water appear gray or black.

Bacterially contaminated wells can be difficult to remediate, particularly if slime-forming bacteria are allowed to generate the biomembranes that protect anaerobic bacteria from



**Figure 8. Clear water with musty odor indicative of Pseudomonas bacteria.**



**Figure 9. Murky water with odor like sewage indicative of enteric bacteria.**



**Figure 10. IRB (Gallionella sp.) and particulate ferric iron account for the orange color and “metallic” odor and taste.**



**Figure 11. Strongly reducing environment with SRB yielding smell of “rotten eggs” and color due to dissolved ferrous iron sulfide.**

oxygen-rich environments. Bacterial colonies and slime can become dense enough to foul perforations, impeding the groundwater flow needed to recharge a well. Bacterial byproducts will not only cause scaling or corrosion but will also generate noxious odors,





and significantly affect water clarity, color, and taste (Figures 8 – 11). Hydrogen sulfide generated by sulfate-reducing bacteria (SRB) is toxic at low concentrations particularly if a resident is exposed over a long time (Chou, 2003).

Biologic activity reaction test (BART™) sampling provides an easy way to determine whether a water well is contaminated with bacteria (Cullimore, 1992). There are different types BART™ sampling containers that are readily available. Each is spiked with different bacterial growth media designed to spur the growth of specific bacterial types. The 9 common BART™ types are the following:

Iron Related Bacteria	IRB-BART™	Red Cap
Sulfate Reducing Bacteria	SRB-BART™	Black Cap
Slime Forming Bacteria	SLYM-BART™	Green Cap
Heterotrophic Aerobic Bacteria	HAB-BART™	Blue Cap
Denitrifying Bacteria	DN-BART™	Grey Cap
Nitrifying Bacteria	N-BART™	White Cap
Fluorescing Pseudomonads	FLOR-BART™	Yellow Cap
Acid Producing Bacteria	APB-BART™	Purple Cap
Biochemical Oxygen Demand	BOD-BART™	Light Blue C

If BART™ vials are not used to collect samples in the field, bulk 1L water samples, filled without a gas headspace can be sent directly to the laboratory performing the analyses. The chain of custody forms should specify that bulk samples be disseminated into the appropriate BART™ containers as soon as they arrive at the laboratory. This will minimize bacterial competition for nutrients in bulk samples that may change the distribution and viability of different bacterial groups.



**Figure 12. HACH™ Test for dissolved sulfide (courtesy of ESN Rocky Mountain).**

### 2.8.5. HACH Tests for dissolved sulfide

The HACH Company provides several field test kits that allow a sampling technician to determine dissolved sulfide concentrations in water colorimetrically (e.g. Hydrogen Sulfide Test Kit, Model HS-C, 0-5 mg/L and Model HS-WR, Color Disc). These tests are useful for confirming the presence of SRB that generate rotten egg smells in water. The procedure is equivalent to USEPA method 376.2 and Standard Method 4500-S2– D used for wastewater.



### 3. ANALYTICAL REQUIREMENTS

The following list of recommended analytes will help identify potential pollutant sources and determine whether dissolved hydrocarbons, if present in a contaminant plume, are increasing or decreasing in concentration over time at a particular location.

#### 3.1. ROUTINE ANALYSES

##### 3.1.1. Dissolved inorganic constituents and physical properties

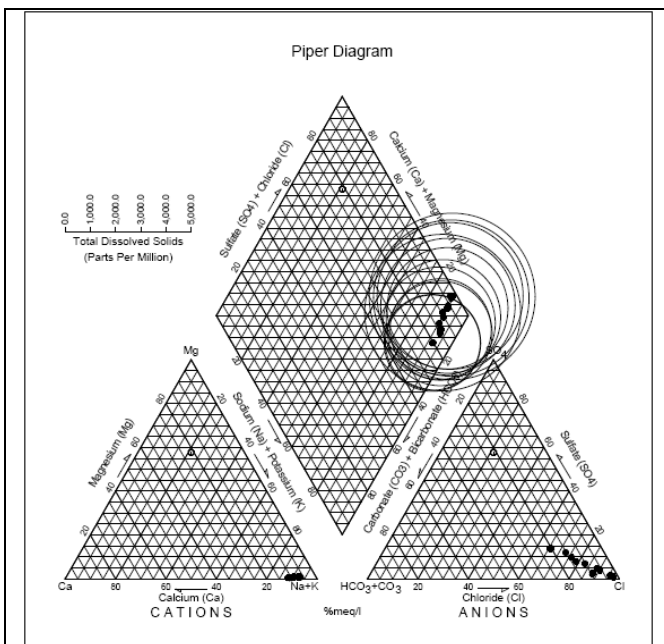
*General water quality parameters;* pH, specific conductance, total dissolved solids (TDS), total suspended solids (TSS);

*Major Ions:* Dissolved (<45  $\mu\text{m}$  filtered): alkalinity, sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl), bicarbonate ( $\text{HCO}_3$ ), carbonate ( $\text{CO}_3$ ), sulfate ( $\text{SO}_4$ );

*Halides:* Fluoride (F), bromide (Br);

*Trace metals:* Dissolved (<45  $\mu\text{m}$  filtered): aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), lithium (Li), iron (Fe), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), silica (Si), silver (Ag), strontium (Sr), thallium (Tl), titanium (Ti), tin (Sn), uranium (U), vanadium (V), and zinc (Zn).

*Nutrients:* Total Nitrogen, nitrate and nitrite ( $\text{NO}_3$  &  $\text{NO}_2$ ), ammonia ( $\text{NH}_3$ ), total organic nitrogen, ortho-phosphate ( $\text{PO}_4$ );



**Figure 13. Monthly data from a single water well in the Piceance basin showing a range in TDS values stretching along a mixing line of differing water composition. There are multiple water sources infiltrating this 200' deep well bore.**

In domestic water wellbore environments, suspended sediment, well bore corrosion, and local bacterial populations and their byproducts dominate the trace element composition of colloids and fine particulates. For this reason we recommend that laboratories only analyze for and report “dissolved” and not “total” values for the listed elemental constituents. Such analyses are more likely to reflect the baseline geochemical environment in the surrounding aquifer and not in the well bore environment.

It should be common practice to analyze the dissolved major ion content of all samples collected. Results are used to monitor the quality of each analysis by





comparing the total concentration of positively charged cations and negatively charged anions using charge balance calculations. Many water wells deeper than 15 meters tap more than one aquifer or water-bearing unit (Figure 13). Repeated sampling and analysis of just the major ions can be used to establish the presence of multiple aquifers, to observe differences in aquifer mixing rates that influence dissolved gas concentrations, to document seasonal changes in precipitation rates, recharge rates, and discharge rates, and to document the influence of irrigation.

Monitoring halides is also very useful in the context of interpreting factors controlling the concentration of dissolved natural gas. The halogens Cl, F, and Br, are relatively conservative, non-reactive constituents in water. When used in conjunction with stable isotopes, halogens are excellent tracers of water sources and mixtures. Fluorine is a common dissolved constituent in alkaline siliciclastic aquifers. Its concentration can vary particularly if it is diluted by cross-flowing fluids originating from shallow aquifers. The Cl/Br ratio is used to identify brines originating from aquifers in communication with connate seawater, evaporites, or a contaminant source. The ratio can also be mapped to identify plumes originating from deep faults, fractures, or point sources.

### 3.1.2. Dissolved atmospheric and hydrocarbon gases

*Fixed Gas Chromatography:* He, H<sub>2</sub>, Ar, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>;

*Hydrocarbon Gas Chromatography:* C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, iC<sub>4</sub>, nC<sub>4</sub>, iC<sub>5</sub>, and nC<sub>5</sub>.

As discussed previously, we recommend using a large volume sample (250 ml) to analyze and quantify the volume of dissolved hydrocarbons in the C<sub>1</sub>-C<sub>4</sub> range. Unless samples are treated with a bactericide, the purge-and-trap extraction of dissolved gas from the water matrix should be completed within 48 hours of sample collection. If thermogenic coalbed gas is detected, or if the methane concentration exceeds 2 mg/L, additional hydrocarbons should be extracted from 1L sample bottles for analysis of stable isotopes. The receiving laboratory can be most easily made aware of such protocols with illustrated decision trees.

Because argon is non-reactive, it is used to normalize the concentration of dissolved gases relative to the concentration of dissolved air. O<sub>2</sub>/Ar, N<sub>2</sub>/Ar, and CO<sub>2</sub>/Ar ratios are used to address the oxidation state of water. C<sub>1</sub>/Ar ratios are positively correlated with measured dissolved methane concentrations. Gas component ratios such as C<sub>1</sub>/C<sub>2</sub>, C<sub>2</sub>/C<sub>3</sub>, iC<sub>4</sub>/C<sub>4</sub>, iC<sub>5</sub>/C<sub>5</sub>, total C<sub>4</sub>/C<sub>5</sub>, gas dryness (C<sub>1</sub>/(Sum C<sub>1</sub>-C<sub>5</sub>)) and gas wetness (C<sub>2</sub>/(Sum C<sub>1</sub>-C<sub>5</sub>)) ratios are all used to characterize free and dissolved hydrocarbon gases collected from water wells. Statistical analysis of these variables will allow investigators to compare results with the composition of a suspected point source of natural gas (Prinzhofer *et al.*, 2000, and Whiticar, 1994 and 1991).

Measuring gas component ratios at either a contaminant or pollutant site can also help establish the role that hydrocarbon-oxidizing bacteria play in altering the original source gas composition. Bacteria preferentially consume chained alkanes over branched alkanes of the same carbon number, and larger carbon number alkanes are consumed



preferentially over smaller carbon number alkanes. Repeated, temporal analysis of dissolved gas composition at a contaminant or pollutant site will reveal the rate at which the source gas is consumed. If the rate at which bacteria consume hydrocarbons is less than the rate at which fresh gas is introduced into the aquifer system, then alkane ratios won't change significantly. Once bacterial consumption rates begin to steadily surpass the rate at which fresh gas is introduced (as when the source gas is shut off), there will be a gradual increase in alkane ratios  $C_2/C_3$ ,  $iC_4/C_4$ ,  $iC_5/C_5$ , and total  $C_4/C_5$ .

### **3.1.3. Volatile Organic Compounds (VOCs) in water**

*Volatile Organic Compounds:* Volatile benzene, toluene, ethylbenzene, and xylene (BTEX) compounds, and MTBE (As listed in EPA methods 8260);  
*Total Extractable Petroleum Hydrocarbons* (TEPH as listed in EPA method 8015);

The principal reason for running both sets of analyses is to help differentiate a natural gas pollutant source from a refined product pollutant source. If BTEX is not detected, then there is no need to run any other analyses. However, if any of the BTEX compounds are detected, then additional sample splits should be tested for MTBE and TEPH. The receiving laboratory must be made aware of such decision trees.

### **3.1.4. BART™**

Routine baseline sampling should test for IRB, SRB, and slime-forming bacteria with IRB-BART™, SRB-BART™, SLYM-BART™ sample vials. These are the most common indicators of potential water well problems related to bacteria. The lag time (in days) or the time to the first visible reaction, is directly related to the number of bacterial colonies present in water. The shorter the lag time, the more colonies have been cultured and the more aggressive the bacteria. BART™ results should be documented in a consistent numeric format such as lag time, or in equivalent numbers that reflect the number of colony-forming units per milliliter of water present. Each BART™ will also generate a visible reaction pattern which have been classified (Cullimore, 1992). The reaction type, designated in a few capital letters, should also be reported in table format.

## **3.2. SPECIAL ADDITIONAL ANALYSIS**

Special analyses should be run if either thermogenic gas components are detected or if dissolved methane concentrations exceed 2mg/L. A water sample with 1 mg/L of dissolved methane will yield enough gas for reliable and reproducible analysis of stable isotopes.

### **3.2.1. Stable isotope analyses**

*Stable Isotopic Analysis of Gas:*  $\delta^{13}C$  of  $C_1$ ,  $\delta D$  of  $C_1$ ,  $\delta^{13}C$  of Dissolved Inorganic Carbon (DIC),  $\delta^{13}C$  of  $C_2$ ,  $C_3$ ,  $iC_4$ , and  $nC_4$  (if in sufficient quantity),

*Stable Isotope Analysis of Water:*  $\delta D$  of well water,  $\delta^{18}O$  of well water (recommended when methane found to occur at concentrations > 2mg/L).



Stable carbon and deuterium isotopes of methane provide an independent means to determine the origin of gases, and are conventionally used to differentiate between biogenic and thermogenic methane sources (James 1993, and Whiticar 1994 and 1999). Biogenic gas sources are derived from bacterially-mediated fermentation and carbon dioxide reduction reactions. Thermogenic sources are generally derived from the progressive burial, heating, and catalytic conversion of sedimentary organic matter to hydrocarbons. Both chromatographic composition and isotope ratios are used to differentiate natural gas sources (Prinzhofer, *et al.*, 2000, Whiticar, 1994). The same analytical methods used to characterize produced natural gas can be applied to characterize free and dissolved natural gases found in groundwater, gas seeps, natural gas encountered in coal seams while drilling, and in bradenhead or surface casing gas.

Hydrocarbon-oxidizing bacteria will predictably alter the isotopic signature of natural gases (Whiticar, 1999). These bacteria consume hydrocarbons, converting them to CO<sub>2</sub>. In doing so, bacteria preferentially consume simple alkanes containing lighter isotopes, leaving the gas pool enriched in heavier isotopes and the CO<sub>2</sub> pool relatively depleted in heavier isotopes. This process is referred to as kinetic fractionation. Accordingly, the effects of in-situ bacterial consumption of such hydrocarbons can be documented by measuring both the stable carbon isotopic ratios of hydrocarbon gases and the corresponding stable carbon isotopic ratios of dissolved inorganic carbon (DIC) in samples. That is why we recommend regularly measuring  $\delta^{13}\text{C}$  of DIC. Routine measurements of  $\delta^{13}\text{C}$  DIC are reliable, and can be readily converted to  $\delta^{13}\text{C}$  values of dissolved CO<sub>2</sub> provided that the ambient temperature of the water sample is accurately recorded in the field (Clark and Fritz, 1997).

Temporal analyses of stable isotopes originating from either contaminant or pollutant natural gas sources in water will provide predictable fractionation trends that help characterize the original, un-oxidized stable isotope composition of source gases. For example, a one part per thousand change in the stable isotopic ratio of carbon in methane will result in an 8.3 per mil change in the stable isotopic ratio of the associated deuterium in methane (Gorody *et al.*, 2005, Coleman *et al.*, 1981 ). Such methane oxidation trends can sometimes also be detected by taking water samples for stable isotopic analysis of dissolved gas before purging and after purging a contaminated or polluted water well.

Initial baseline samples collected should include stable isotopic analyses of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in water if dissolved methane concentrations exceed 2 mg/L. Compared to the major ions and cations normally analyzed for water quality, these stable isotopes are relatively un-reactive. The stable isotopic content of water is routinely used to establish water provenance, mixing between aquifers, and brine contamination from either natural contaminant or pollutant sources. The deuterium data are also used to differentiate the reaction pathways that generate bacterial methane (fermentation vs. CO<sub>2</sub> reduction), and to determine whether bacterial methane is generated in-situ or migrated from another source.



## 4. DATA BASE DESIGN

The previous sections of this report offer recommendations for documenting a large variety of data. A relational data base structure is the most efficient way to keep such data records. A relational database stores related data records within a set of one or more tables. Each table has a unique index or key field, and tables can be linked using common key fields. It is not the intent of this report to specify all the elements of a relational data base structure. Nevertheless this section will illustrate what types of data table structures can be used to store the many field observations, field data, photographs, and lab data previously discussed.

Figure 14 shows an example of six data tables, linked with key index fields, that store different types of information. The tables are named Project, Site, Background, Photo, Sample, Lab, and Contact. Data tables of this type are designed to store data, not to make calculations. Properly designed, such tables can be queried to generate formatted data useful for spreadsheet analysis, plotting data on GIS maps, and any number of different reports. Fields in any given table are shown below in data entry forms.

### 4.1. TABLE STRUCTURES

The example table structures discussed below (Figure 14) are designed to capture a minimum amount of information necessary to document where, when, and what samples are collected during a project, and the observational, field, and analytical results associated with them. The key field links between tables are shown with lines connecting field names. Example data entry forms will be used to show additional fields comprising individual data records within each table. The advantage of using data entry forms is that they can be used as check lists to ensure consistent data collections. Forms also help ensure data integrity among key fields used to link different tables.

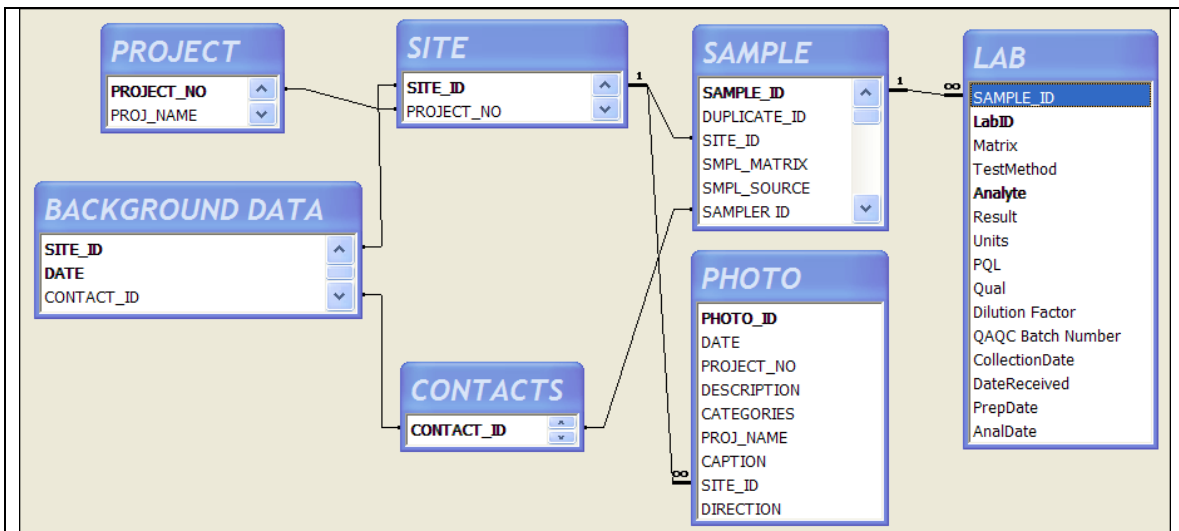


Figure 14. Example of linked relational tables in a Microsoft Access data base.



### 4.1.1. PROJECT Table

A project table is useful for identifying which sites, samples, or other information are linked to a unique zone that can be defined geographically, or on the basis of unique funding sources, or both. Unique geographic zones can be defined on the basis of sedimentary basins, one or more watersheds, or map units. Funding projects, on the other hand, can have unique expenditure numbers such as authorized expenditures (AFE's), purchase orders, or contract numbers. In its simplest form, a single project will define a unique set of sampling locations. This defines a one-to-many relationship where one project can have many different sampling sites or locations.

The screenshot shows a web-based data entry form titled "Project Table". The form is organized into several sections. At the top right, there are two input fields: "Date Started:" and "Date Completed:". Below these, the main form area contains several input fields: "Project Name", "Project ID" (with a placeholder "oNumber"), "Project Type", "Location", "Coalfield", and "Description". To the right of the "Project ID" field is a section titled "Link" in blue, which contains three input fields: "AFE Number:", "Client:", and "Contract #:". The "Description" field has a vertical scroll bar on its right side.

Figure 15. Example Project table data entry form.

### 4.1.2. SITE (Location) Table

A SITE table (Figure 16) documents relevant information regarding a location where special observations have been made and/or where samples have been collected. SITE tables or sheets can be used to designate all sampling sites including surface water locations, water wells, monitor wells, coal exploration wells, gas producing wells, cathodic protection wells, summa canister sites used to monitor air quality, soil probes, etc. Each SITE table must have a unique identifier (SITE\_ID), or key field that will be used to link all related tables. Each key field entry should include a sufficient number of characters to easily differentiate one site from another. When possible, include fields that can be used to link the unique SITE table to a key field in a table from another data base source. For example, a permit number or well tag number identifies a water well in agency records; an API number identifies a producing oil, gas, or coalbed methane well. Some thought should also be given to including site parameters useful for distinguishing different type of sampling sites on a GIS-base map.



SITE_ID: <input type="text"/> PROJECT_NO: <input type="text"/> CATEGORY: <input type="text"/> WWPERMIT#: <input type="text"/> ASSC. WELL#: <input type="text"/> WELL PLATE #: <input type="text"/>	<b>WELL CONSTRUCTION INFORMATION</b> CASGDIAMIN <input type="text"/> UNITS: <input type="text"/> CASG ELEV <input type="text"/> UNITS: <input type="text"/> CASG TYPE <input type="text"/> TOP PERF <input type="text"/> UNITS: <input type="text"/> BTM PERF <input type="text"/> UNITS: <input type="text"/>	<b>SOIL PROBE DATA</b> SOIL PROBE DEPTH: <input type="text"/> UNITS: <input type="text"/>
<b>GEOGRAPHIC DATA</b> WAYPOINT <input type="text"/> ELEVATION <input type="text"/> 0 UNITS: <input type="text"/> LAT <input type="text"/> LONG <input type="text"/> XUTM <input type="text"/> YUTM <input type="text"/> DATUM <input type="text"/> ZONE <input type="text"/> COORDINATE SOURCE: <input type="text"/>	<b>COMMENTS</b> <div style="border: 1px solid black; height: 150px; width: 100%;"></div>	
		<b>OUTCROP INFORMATION</b> DIP ANGLE: <input type="text"/> STRIKE: <input type="text"/> RIGHT HAND RULE

**Figure 16. Example data entry form for a SITE table.**

Fields other than the key field in a SITE sheet should contain variables that are descriptive of the site and not likely to change. In the example form illustrated, there are fields specific to defining the site name with links to other data bases, geographic data, well construction information (water well or monitor well), soil probe information, and outcrop strike and dip information. Strike and dip information should use consistent protocols such as the “right hand rule”. Pull down menus (fields with ▼) use information available from other linked data and lookup tables to avoid data entry errors. Site names in the SITE\_ID should be descriptive and unique.

### 4.1.3. CONTACTS Table

During any environmental sampling program, one comes in contact with many individuals who are in some way involved with a project (contractors, project managers, property owners, realtors, etc.). If a special contact manager program is used to track such information, then the appropriate tables for the project data base should contain a link to the the key fields in the contact data base. Otherwise, a simple CONTACTS table, such as that shown in Figure 17 should suffice. A unique CONTACT\_ID key linking field must be defined. Properly designed, a simple data base will allow linking individuals to sample sites they may own or rent, to related project activities or surveys, or to other tables useful for tracking data reports and their delivery.





## Contact Information

Contact\_ID:  Contact Type:

NameLast:  NameFirst:  NI:

Primary Contact Home Information	Primary Contact Work Information
Home Phone: <input type="text"/> Address: <input type="text"/>	Work Phone: <input type="text"/> Company Address: <input type="text"/>
Mobile Phone: <input type="text"/> City: <input type="text"/>	Company Name: <input type="text"/> Company City: <input type="text"/>
Province: <input type="text"/>	Company Department: <input type="text"/> Company Province: <input type="text"/>
Country: <input type="text"/>	Company Title: <input type="text"/> <b>Company Country:</b> <input type="text"/>
Postal Code: <input type="text"/>	Company Postal Code: <input type="text"/>
Email Address: <input type="text"/>	
Notes: <input style="height: 40px;" type="text"/>	

**Figure 17. Example Contact table.**

### 4.1.4. BACKGROUND DATA Table

## Background Information

Site\_ID:  Date:

Contact ID:  Owner or Occupant:

Participate:  Access to Property:  To Receive Reports:  Permission to Pump/Purge:  Well construction documentation?  Water quality documentation?  Signature:

	Water Quantity
	Pumping Frequency: <input type="text"/> Primary Water Use: <input type="text"/> Number of homes sharing water: <input type="text"/>
	Number of people using the water: <input type="text"/> Average daily acre-feed irrigation: <input type="text"/> Number of stock using water: <input type="text"/>
	Is the water quantity sufficient? <input type="checkbox"/> If no, explain: <input type="text"/>
	Is the water supplemented from another source? <input type="checkbox"/> If yes, explain: <input type="text"/>
	Has there been changes in quantity this past year? <input type="checkbox"/> If yes, explain: <input type="text"/>
	Has there been changes in water uses this past year? <input type="checkbox"/> If yes, explain: <input type="text"/>
	Will there be changes in water use next year? <input type="checkbox"/> If yes, explain: <input type="text"/>
	Are there variations in use? <input type="checkbox"/> If yes, explain: <input type="text"/>
	<b>Maintenance Information</b>
	Was there water quality changes in the past year? <input type="checkbox"/> If yes, explain: <input type="text"/>
	Is there a water treatment system? <input type="checkbox"/> Installation Date: <input type="text"/>
	What are the components? <input type="text"/>
	Has the well been repaired/replaced? <input type="checkbox"/> If yes, explain: <input type="text"/>
	Has the pump been repaired/replaced? <input type="checkbox"/> If yes, explain: <input type="text"/>
	Has the pump been lowered? <input type="checkbox"/> If yes, explain: <input type="text"/>
	Has there been bacteria maintenance this year? <input type="checkbox"/>
	<b>Cap/Cover Status</b>
	Cover Status: <input type="text"/> Cap Status: <input type="text"/>
	Comments: <input style="height: 40px;" type="text"/>

	Water Quality
	Rate water taste: <input type="text"/>
	Rate water odour: <input type="text"/>
	Is there odour from the cold water tap? <input type="checkbox"/>
	Rate water colour: <input type="text"/>
	Rate water clarity: <input type="text"/>
	Rate sediment content: <input type="text"/>
	Rate scaling: <input type="text"/>
	Rate gas content: <input type="text"/>
	Are the fixtures stained? <input type="checkbox"/>
	Are there corroded fixtures/appliances? <input type="checkbox"/>

**Figure 18. Example of a data entry form useful for capturing interview data.**

Previous sections discuss the importance of conducting interviews with water well owners prior to collecting samples. The BACKGROUND DATA table (Figure 18) is



designed to store such information. When sampling water wells in particular, it is helpful to know which individuals (CONTACT\_ID) were contacted and if they gave permission to have sampling crews gain access to their property and water resources. An interview should be conducted each time a given site is accessed. For this reason, there are two concatenated fields needed to define each unique data record: a SITE\_ID and a DATE.

The example form contains 3 main types of information documenting perceptions and observations related to water resource quality, water resource quantity, and well maintenance. Many of the check boxes in the BACKGROUND DATA form allow easy data entry of yes and no answers with options to include explanations of 255 words or less. The “Comments” box is a memo field that will accept information of any length. The form illustrated for the fields in the table can also be printed and used to guide an interview either in the field, or on the phone.

#### 4.1.5. SAMPLE Table

A SAMPLE table is another example of a table with unique records based on concatenated key fields: the SITE\_ID and a SAMPLE\_ID. The SAMPLE\_ID will uniquely identify each sample collected, and is used to relate sample splits sent to each

### Sample Data

<p>SAMPLE_ID: <input type="text"/></p> <p>Site_ID: <input type="text"/></p> <p>ID of Duplicate: <input type="text"/></p> <p>Sample Matrix: <input type="text"/></p> <p>Sample Category: <input type="text"/></p> <p>Sampler_ID: <input type="text"/></p> <p>Sample Date: <input type="text"/></p> <p>Sample Time: <input type="text"/></p>	<p style="text-align: center; color: blue;"><b>Site Preparation</b></p> <p>PriorUsage: <input type="text"/></p> <p>PumpType: <input type="text"/></p> <p>Static Water: <input type="text"/></p> <p># Casing Volumes Purged: <input type="text"/></p> <p># Casing Gallons Purged: <input type="text"/></p>	<p style="text-align: center; color: blue;"><b>Field Parameters</b></p> <p>Was the equipment calibrated? <input checked="" type="checkbox"/></p> <p>Barometric Pressure( mm Hg) <input type="text"/></p> <p>pH <input type="text"/></p> <p>Temperature (C) <input type="text"/></p> <p>Specific Conductivity (uS/Cm) <input type="text"/></p> <p>Dissolved Oxygen (mg/l) <input type="text"/></p> <p>Eh (mv) <input type="text"/></p> <p>Turbidity (NTU) <input type="text"/></p> <p>HACH Test Results <input type="text"/></p>
<p style="text-align: center; color: blue;"><b>Infrared Detection Devices</b></p> <p>IRCO2%: <input type="text"/></p> <p>IRO2%: <input type="text"/></p> <p>IRCH4%LEL: <input type="text"/></p>	<p style="text-align: center; color: red;"><b>Hazard Assessment</b></p> <p>Calibrated Hazard Sensors? <input checked="" type="checkbox"/></p> <p>Initial Headspace FID Reading <input type="text"/></p> <p>Initial Headspace PID Reading <input type="text"/></p> <p>Depth of Soil Gas Probe <input type="text"/></p>	<p style="text-align: center; color: blue;"><b>Observations</b></p> <p>Colour <input type="text"/></p> <p>Clarity <input type="text"/></p> <p>Effervescence <input type="text"/></p> <p>Odour <input type="text"/></p> <p>Sediment <input type="text"/></p> <p>Sound from Well <input type="text"/></p>
<p>COMMENTS <input style="width: 100%;" type="text"/></p>		<p style="text-align: center; color: green;"><b>Production Well Samples</b></p> <p>CASINGPSIG: <input type="text"/></p> <p>CASINGVENTPSIG: <input type="text"/></p>

**Figure 19. Example sample entry form with fields for observations and data.**



analytical laboratory for analysis to the sample number assigned by each laboratory. The SAMPLE\_ID key field should at a minimum contain a sample matrix designation (such as G for gas or W for water) plus a code that contains a date and time stamp for each sample collected. This makes it easy to sort and discriminate between samples taken in one day, at different times, or on different dates. A DUPLICATE\_ID field allows for tracking blind duplicate samples sent to any laboratory. The first sample in a pair is assigned the same SAMPLE ID and DUPLICATE ID values; the second sample in the pair gets a DUPLICATE ID that matches the first sample in the pair, but a different SAMPLE\_ID designation for the chain of custody form. The sample data sheet should

contain columns recording the date the sample was collected, and all the field observations and measurements made when the sample was collected. Comments should also be included at the end of each row. Both SITE\_ID and SAMPLE\_ID designations should be documented on chain of custody forms.

#### 4.1.6. LABORATORY DATA Table

Sample splits are typically sent to different laboratories for analyses. Chain of custody forms will associate sample splits with the laboratory analyses to be conducted. A typical suite of analyses representing a single water well sample may include the following sets of analyses, each potentially completed at a different laboratory:

- Dissolved organic and inorganic constituents,
- Biologic Activity Reaction Tests (BART),
- Dissolved methane concentrations,
- Stable isotopes of water and dissolved inorganic carbon (DIC),
- Chromatographic analysis of free or dissolved hydrocarbon gases,
- Chromatographic analysis of free or dissolved fixed gases,
- Stable isotopic analyses of hydrocarbons gases.

LAB : Table			
	Field Name	Data Type	
	SAMPLE_ID	Text	From Chain of Custody Form
?	LabID	Text	ID assigned by Laboratory
	Matrix	Text	Matrix (G Gas, W Water, N NAPL, S Solid
	TestMethod	Text	e.g. NLAG 110, E310.1, SW8020a, etc.
?	Analyte	Text	
	Result	Number	Measured value
	Units	Text	
	PQL	Number	Practical Quantiation Limit or Reporting Detection Limit
	Qualifier	Text	Analysis qualifier flag if needed, e.g. "J"
	Dilution Factor	Number	
	QAQC Batch Number	Number	Link to Laboratory QAQC
	CollectionDate	Date/Time	From Chain of custody
	DateReceived	Date/Time	
	PrepDate	Date/Time	
	Analysis Date	Date/Time	

Figure 20. Example fields contained in an EDD laboratory report.



Each lab will assign a LABORATORY\_ID or job number to each sample. Each unique laboratory id or job number should be related to a unique SAMPLE\_ID number. At a minimum, a complete sample data record should include a LABORATORY\_ID, a SAMPLE\_ID, associated analytical results, analysis dates, and an associated QC batch number. Proper planning will allow each laboratory to deliver data in any format requested. Advances in modern laboratory information managements systems (LIMS) provide many options for electronic data deliverables (EDD). The list of fields in Figure 20 is a typical example of the number of fields that should be reported, as explained below.

#### 4.1.6.1. Documenting dates

Laboratory data tables should include time stamps for the time a sample was received, the time a sample was prepared for analysis, and the time a sample was analyzed. This helps with QA/QC procedures used to check whether recommended holding times for sample analyses are exceeded. This becomes particularly important for analyses of dissolved hydrocarbons (natural gases and BTEX) and for alkalinity titration which should ideally be performed routinely within 48 hours of the time a sample is collected.

#### 4.1.6.2. Documenting detection limits and qualifier flags

Each laboratory will have different detection limits for each of the various analytes measured. Depending on how the data are treated for statistical analysis, it is necessary to document what those detection limits are. An MDL (method detection limit) is the minimum concentration of a substance that can be measured and reported by an instrument with 99% confidence that the substance is present at a concentration that is greater than zero. The PQL (practical quantitation limit) is the lowest measurable concentration of a substance that can be practically, reliably, and reproducibly quantified using routine laboratory procedures. This is also sometimes referred to as the Reportable Detection Limit (RDL). Most laboratories will assign a qualifier flag, such as a “J” value, to an analytical result if it falls between the MDL and the PQL. This helps a data analyst determine whether an analyte was detected. Different qualifier labels are used to flag other types of conditional data quality constraints. A simple lookup table is used to define each qualifier. All lab qualifier flags should be included in a lab data table field. Analytical results need to document a laboratory’s MDL and/or PQL for all analytes measured.

The best way to avoid mixing alphanumeric and numeric values in data fields is to report results is use blank cells and/or special numbers. Values such as ND (not detected) or NA (not analyzed) cannot be included in numeric data base field. If an analyte is not run, it won’t be reported in a laboratory EDD and will show up as a blank cell in a query. If an analyte is run, but the results fall below detection limits, a numeric entry such as -999.9 can be used. This approach makes it easy to export a spreadsheet file format to a data base file format, and also facilitates data base queries. For example, a query can contain a statement that looks for a -999.9 value. If the statement is true, the query can



then report the detection limit, or a zero, or any value in between for the purposes of statistical analysis.

#### 4.1.6.3. Documenting the analytical method used

Every laboratory runs their analysis using established EPA, ASTM, or other established and qualified analytical methods. The method used must be documented to ensure that analytical results from different laboratories can be compared.


#### 4.1.6.4. Documenting analytical units

There should be a column specifying the concentration units reported for each analyte.

### 4.1.7. PHOTO Table

Photo documentation should be an important part of every baseline study. For example, the environment surrounding a domestic water well may include such features as septic tanks, leach fields, industrial waste containers, buried gasoline tanks, feeding troughs, animal pens, etc. Other water quality features such as effervescence, clarity, and color (Figures 8-11) are all easily documented using digital photography.

Each photo should have its own unique PHOTO\_ID. If the digital image extension is included in the ID (e.g. \*.tif or \*.jpg), the image can be hyperlinked to either a data base or mapping package. Photo documentation should include the xy location at the time a photo was taken as determined using a GPS device. Documentation should also include the compass direction (0° - 359°) that the camera was facing. If the photo is linked to features at a site previously specified for a survey or sampling project, then the related SITE\_ID number should be included. In that case, the SITE\_ID will already be linked to an xy location. Otherwise, each new site should get its own photo SITE\_ID.

	ID	P-060707-003.jpg
	When	06 July 2006
	Where	John Doe Ranch
	Event	John Doe baseline water well sampling
	Description	These are 50 gallon drums that, according to Mr. Doe, were dumped illegally on his ranch. Not sure what the drums actually contain, but they are up-gradient from the water well (to left of photo). Waste oil residue and leaking drums evident in the foreground.
	Caption	50 gallon drums dumped illegally on Mr. Does ranch.
	SITE_ID	60208-F05-OTH
	DIRECTION	160
	Project_No	60208
	<p><b>Figure 22. Example data fields describing the photo on left. The format used is part of photo documentation software (PixFiler™). The information in these fields is exported to Access data base through a comma delimited function.</b></p>	

**Figure 21. Baseline project photo.**

Documentation should also include a photo caption, as well as extended observation notes that may be relevant (Figures 15 and 16).



Formatting photo documentation into a data table format will help link photos to a location on a map. For example, ArcMap™ software allows the user to hyperlink the data table to a directory containing each photo. This lets a user view photo captions on a map, use a mouse to click on a location, and view the photo.

## **5. RECOMMENDED QUALITY ASSURANCE AND CONTROL PRACTICES**

The subject of quality control measures and protocols used for environmental sampling is extensive, and far too large to be covered in great detail here. The reader can refer to various published ISO 9000 standard protocols to get a more comprehensive review of this important topic. However, because data collected to address the origin of gas in water may be subject to rigorous regulatory and scientific review, it is necessary to carefully consider and review sampling and analytical procedures to continually improve good quality control and assurance practices.

Every sampling program should make provisions to document the protocols required for checking data quality. To maximize efficiency and data quality, protocols and procedures should be followed consistently. These should be documented and specified in a sampling and analysis work plan submitted to the client and, if necessary, to the appropriate regulatory agency for approval prior to going into the field.

### ***5.1. CHECK LISTS***

As previously discussed, there are many planning, field collection, and data gathering activities that need to be monitored in the course of field investigation or a baseline measurement and subsequent monitoring program. Field measurement, sampling, and sample handling procedures are most easily controlled by printing formatted daily checklists and data entry forms. Such forms also facilitate training and communication with all contractors and subcontractors. Checklists can include calibration checks, lists of interview questions to ask property owners, lists of field parameters to record, and a list of materials, equipment, and supplies needed for sampling. A printed, empty database entry form can be ideally used as a check list if appropriately designed (Figure 18).

### ***5.2. FIELD CALIBRATION***

Field parameter sensors should be calibrated a minimum of once a day daily using appropriate fresh standards. Some provision should be made on field sheets to document whether or not field instruments were calibrated (Figure 19). Field calibration check lists should be filed with field notes for easy access if necessary.

### ***5.3. BLIND DUPLICATE ANALYSES***

There are several types of errors than can affect the quality of sample data (Morrison, 2002). These can be addressed by maintaining consistent sampling practices, by taking multiple samples at a given site, and by randomly selecting a blind set of duplicate samples for laboratory analysis. Budgetary constraints are likely to practically limit the





number of duplicate samples submitted for analysis. It is generally accepted that 10% of all samples collected should be duplicate samples. At a minimum, however, every baseline measurement and monitoring program should attempt to submit one blind sample duplicate for laboratory analysis for every twenty samples collected (5% of samples). A blind duplicate sample is a second sample set with a SAMPLE\_ID value that is different from the first sample split and not recognizable as such by the receiving laboratory. All duplicate sample results should be reported and routinely monitored to ensure quality control.

A split duplicate sample is normally collected by pooling water into a large container and then distributing samples into smaller sample bottles for duplicate analysis. This allows water to mix, and the resultant error measured can be related to subsequent sample handling and laboratory measurement error. This practice is not recommended because dissolved gases are prone to exsolution and because atmospheric gases can be introduced into solution when water is poured from one source to another. Our experience has shown that it is sufficient to collect paired sample sets into their respective containers as water is delivered at low flow rates directly from the source. Small analytical differences arising from this method provide both a measure of sampling error and laboratory error.

For example, historic data from the San Juan basin collected by regulators, state and federal agencies, and gas production companies show that average maximum dissolved methane concentrations differ from minimum concentrations among sample pairs by a factor of 1.14 (14%) times the minimum concentration + 0.05 mg/L (Gorody *et al.* 2005). Among duplicate sample pairs collected by trained field crews in the Piceance Basin, maximum dissolved methane concentrations differ from minimum concentrations by a factor of 1.08 (8%) times the minimum concentration + 0.02 mg/L. In the Piceance basin, the highest concentration values found among paired samples were either at or slightly below the maximum amount of dissolved methane that water can hold at ground level elevations. Such variance must be documented to determine whether dissolved methane concentrations vary systematically with time and to address whether rates of gas contaminant influx to a water well site are increasing or decreasing.

#### ***5.4. TRIP AND EQUIPMENT BLANKS***

If there is a potential for cross-contamination of samples from hydrocarbon emission sources in the sampling area, then the use of trip and equipment blanks should be anticipated and collected. A trip blank of packaged distilled water will record sources of VOC contamination during round-trip sample transportation as well as laboratory sources of VOC contamination. An equipment blank will determine if field equipment provide sources of VOC contamination and will also record sources of laboratory contamination. Such samples must be collected when analyzing for volatile constituents (e.g. dissolved methane and VOCs). Equipment blank samples should be regularly collected and analyzed after each time that portable water pumping and distribution equipment is used and then cleaned in the field. Trip blank samples should at a minimum be required each time a sample team leaves a laboratory that provides them with sample vials and bottle sets.



### **5.5. PROCESS CHARTS, DECISION TREES**

Maximum cost efficiency and optimum communication between contractors and subcontractors is achieved by using and publishing simple decision trees. Decision trees are easier to understand and manage than procedural manuals. For example, a receiving laboratory must know that if they detect either thermogenic hydrocarbons or more than 2 mg/L of methane in their samples, they must ensure that stable isotopic analyses of natural gases and water are ordered. If thermogenic gas is detected, a laboratory must know to follow up with BTEX analyses. And finally, if BTEX components are detected, a laboratory must know to proceed with gasoline range and MTBE analyses.

### **5.6. LABORATORY RESULTS**

Simple ways to routinely evaluate the quality of laboratory data may include the following:

- Compare measured TDS vs. calculated TDS values (adding the results of all analyses);
- Calculate charge balance using the total charge of dissolved cation concentration and the total dissolved anion concentration;
- Compare field pH and laboratory pH;
- Compare specific conductivity and total dissolved ion charge;
- Compare analytical results of duplicate samples.

Regular review of such results may quickly reveal systematic field or laboratory errors that may arise from poor calibration procedures or substandard sample collection practices. Alternatively, obvious inconsistencies may be due to analytical error introduced in the laboratory. In most cases, comparison of pH and conductivity measured in the field and in the laboratory will show changes in water quality that normally occur in transit.

Analytical laboratories should be asked to include their daily internal quality control measurements used for handling batch samples with every data report. These include measurements made to ensure that their instrumentation is functioning properly, that false positives are not reported, that false negatives are not reported, and that results of duplicate sample analyses are consistent. Ideally, the laboratory quality control data derived from batch samples can be tracked using a separate data table. A LABORATORY\_ID and a DATE can be used as key fields linking the dates that laboratory run their internal dates with the dates that sample analyses are run.

### **5.7. REPORTING**

Field parameter and laboratory results should not be released until all the data for a sample have been received and the data quality has been checked. Nothing defeats the objectives and perceived integrity of independent baseline sampling and analysis projects more than releasing data with errors.



At a minimum each water well owner should receive correspondence within some period of time documenting both field and laboratory results as well as the internal laboratory QA/QC data run for batch samples analyzed on the day the owner's sample was analyzed. Any interpretative report included should at a minimum reflect the adequacy of the water for its proposed use (e.g. drinking water, stock water, or irrigation water) and a list of Canadian drinking water standards.

## 6. CONCLUSIONS

The advent of baseline groundwater sampling, analysis, and monitoring in the oil and gas industry in advance of drilling new wells is a relatively new concept. However, the recommendations in this report have been gradually developed and successfully tested over a period of 15 years. Observing consistent sampling and analysis protocols will minimize natural variability that can sometimes be confused with trends of either decreasing or increasing contaminant concentrations in groundwater. Observing a consistent set of analytical measurements will facilitate the forensic analysis required to reliably determine whether a contaminant plume is increasing or decreasing in intensity with the greatest degree of scientific certainty. Maintaining a relatively consistent and standardized data reporting format will allow all stakeholders to compare results obtained by different service providers and operating companies. This will help make it easy for all stakeholders to reliably evaluate whether groundwater in a producing basin is being adversely impacted as a result of oil and gas operations. And finally, maintaining consistent quality control and assurance practices will ensure that available data are defensible when subjected to public or scientific scrutiny.

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