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RRD-GAS-02

SINKHOLE WATER QUALITY DEPTH PROFILE SAMPLING

RECOMMENDED REQUIREMENTS DOCUMENT

Subject: **Sinkhole Water Quality Depth Profile Sampling**

1.0 Background

The Blue Ribbon Commission (BRC) Gas Group recommends that reducing and maintaining methane gas formation pressures in the Mississippi River Alluvial Aquifer (MRAA) to equal to hydrostatic pressure across the Bayou Corne gas area as one metric necessary in order to lift the mandatory evacuation order. This Recommended Requirements Document (RRD) defines the technical requirements for obtaining sinkhole depth profile water quality data needed to address this overall objective. The intent of this RRD is to provide recommended requirements for use by the appropriate state agencies when directing the development of a comprehensive work plan for addressing the RRD objective.

This RRD for collecting sinkhole water quality depth profile data has been prepared with consideration of the following site conditions and data requirements:

- Since the formation of the sinkhole, natural gas and crude oil have been percolating up from depth and into the sinkhole waters. During periodic sinkhole "burps" where the amount of gas migration to the surface appears to increase, trees and other debris float to the surface for a short period of time, and the amount of crude oil on the surface of the sinkhole also typically increases.
- The available water quality data from the sinkhole illustrate that there is a substantial degradation of water quality from the surface to the 100-foot water depth in the sinkhole with total dissolved solids concentration increasing from approximately 5,000 mg/L at the surface to over 50,000 mg/L at a depth of 100 feet (Hecox and Saxton, 2013).
- Establishing a more complete chemical profile of the sinkhole water quality including dissolved gas concentration will provide a more defined picture of the water column in the sinkhole and will help to determine if the water column contains distinct layers or if there is a chemical gradient throughout the water column.
- The potential exists that reducing conditions in the bottom of the sinkhole are conducive to microbial degradation of sulfate in the presence of methane is producing hydrogen sulfide in the deeper portions of the sinkhole. This sampling will determine if this is occurring and quantify hydrogen sulfide concentrations, if any.
- Data collected from monthly sampling will be used to monitor changes in the sinkhole water quality and how sinkhole events, such as the periodic "burps" or subsidence events, affect the chemical composition of the sinkhole waters.

This RRD has been prepared as part of the overall GAS-04 BRC task. This BRC task addresses the need for chemical constituent concentration data in the sinkhole water for use in quantitative evaluations of gas migration and mitigation. The quantitative evaluation requirements are addressed in other RRDs. This RRD establishes the procedures and equipment required to collect these data.

2.0 Objective and Requirements

The objective of this RRD is to quantify and monitor the inorganic and organic chemical constituents and concentrations in the sinkhole for the entire water column from the water surface to the bottom of the sinkhole. The specific laboratory and testing programs shall be specified in the work plan addressing this RRD.

3.0 Requirements

The requirements of this RRD for sinkhole water quality depth profile data are:

1. Conduct monthly sinkhole depth-profile water and dissolved gas sampling of the water column from the surface to the bottom of the sinkhole. Due to ongoing changes in the sinkhole configuration, the location of the deepest portion may change over time. As such, the location of the deepest portion for a given sampling event will be determined by the results of the most current bottom survey conducted prior to each sampling event.
2. Field water quality parameters shall be measured and include pressure, specific conductance, temperature, pH, dissolved oxygen (DO), turbidity, and oxidation-reduction potential (ORP).
3. Water samples shall be collected at the water surface and at 25-foot depth intervals down to the bottom of the sinkhole.
4. Water and dissolved gas samples should be analyzed for parameters in **Table 1**. As data are obtained, this parameter list can be adjusted. Both total and dissolved (0.45 μ filter) metals shall be analyzed.

Table 1. Sinkhole Water Quality Laboratory Analyte List

Gas Analysis	Trace Metals	Major Ions and General Parameters	Organic Compounds
Argon	Aluminum	Total Alkalinity (as CaCO3)	Total Petroleum Hydrocarbons, GRO
Butane	Antimony	Alkalinity, Bicarbonate (as CaCO3)	Total Petroleum Hydrocarbons, DRO
Carbon Dioxide	Arsenic	Alkalinity, Carbonate (as CaCO3)	Aliphatic C6-C8
del 13C1	Barium	Calcium	Aliphatic >C8-C10
del 13C2	Beryllium	Chloride	Aliphatic >C10-C12
del 13C3	Boron	Magnesium	Aliphatic >C12-C16
del 13IC4	Bromide	Potassium	Aliphatic >C16-C35
del 13NC4	Cadmium	Sodium	Aromatic >C8-C10
del Dc1	Chromium, Total	Sulfate (as SO4)	Aromatic >C10-C12
Ethane	Cobalt	Total Dissolved Solids (Residue, Filterable)	Aromatic >C12-C16
Ethene	Copper	Total Suspended Solids	Aromatic >C16-C21
Helium	Iron	Water Density	Aromatic >C21-C35
Hexanes + heavier	Lead		Benzene
Hydrogen	Lithium		Ethylbenzene
hydrogen Sulfide	Manganese		Toluene
Isobutane	Mercury		Xylene, total
Isopentane	Nickel		
Methane	Selenium		
Nitrogen	Silver		
Oxygen	Strontium		
Pentane	Thallium		
Propane	Vanadium		
Propene	Zinc		
Specific Gravity			

Appendix 1 presents suggested procedures for data collection to meet the above objective and requirements. These procedures can be modified or replaced as appropriate to meet the objectives and requirements.

APPENDIX 1
SUGGESTED PROCEDURES

1.0 Introduction

This appendix is intended for use as a procedural reference for obtaining the data required in the RRD. The procedures in this section have been used by one or more Blue Ribbon Commissioners to obtain or generate the data specified in Section 3.0 of the RRD. In preparing the work plan to address this RRD, other procedures can be used provided the objectives and data requirements in Sections 2 and 3 are met.

2.0 Contract Services

2.1 Isotech Laboratories, Inc.

Water samples submitted for compositional gas analysis and isotopes should be submitted to Isotech Laboratories, Inc. in Champaign, Illinois or an equivalent laboratory specializing in analysis of dissolved gases.

2.2 Louisiana Accredited Analytical Laboratory

With the exception of samples submitted for compositional gas analysis and isotopes, all other samples submitted for laboratory analysis should be analyzed by a laboratory accredited under the Louisiana Department of Environmental Quality's (LDEQ) Louisiana Environmental Laboratory Accreditation Program (LELAP).

3.0 Specialized Field Equipment

3.1 Boat Equipped with a Sample Winch/Depth Meter

The sampling boat shall be equipped with a manual or electric sample winch with the cable marked in feet or an attached depth counter. The winch should have a minimum of 300 feet of cable. A second supply boat is recommended for handling decontamination activities and storage of sample coolers, sample containers, and sampling supplies.

3.2 Tag Line

A tag line, with a minimum of 500 feet of line weighted at the end and marked in feet and tenths of feet or equivalent, should be provided for depth measurements.

3.3 In-Situ Troll® 9500 and Rugged Reader®

The In-Situ Troll® 9500 with cable-coupled RDO dissolved oxygen sensor (http://www.in-situ.com/products/water-quality/troll-9500-sensors/rdo-sensors-for-the-troll-9500) and 9500 magnetic stirrer, is a water quality instrument that can measure up to nine (9) water quality parameters which can be recorded and saved on the Rugged Reader®. At a minimum the following water quality parameters should be measured in the sinkhole: pressure, pH, temperature, conductance, DO, ORP, and turbidity. The Troll is programmed and data recorded with a Rugged Reader or smarTROLL iPhone app.

3.4 Van Dorn Samplers

Van Dorn-style samplers are recommended to collect samples at various depths of the water column to maintain integrity of the dissolved gases in the water sample. The sampler should have a minimum of 4.2 liter capacity although the 6.2 liter sampler may reduce field time if a properly configured winch is used. A vertical Van Dorn sampler is recommended as this allows for easier dissolved gas sample retrieval. Two Van Dorn samplers are recommended to allow for one to be decontaminated while the other one is being used to collect a sample.

3.5 Sample Filtering Equipment

Peristaltic pump and 0.45 micron high-capacity filters and tubing should be provided in sufficient quantity for the number of anticipated samples.

3.6 Sampling Supplies

Appropriate sample containers (sufficient quantity for the number of anticipated samples), coolers, labels, chain-of-custody forms, nitrile or latex gloves, and miscellaneous sampling supplies should be provided.

3.7 Decontamination Supplies

Appropriate tubs, brushes, decon fluids (distilled or deionized water, Alconox soap or equivalent), brushes, paper towels, and foil should be provided. It is recommended that a decon station be set up on a second boat for this sampling.

3.8 GPS Unit

A portable global positioning system (GPS) unit with sub-meter accuracy and real-time tracking capability is recommended.

4.0 Definitions

The following definitions are applicable to this appendix:

- *Van Dorn Sampler*—specialized sampling device capable of collecting dissolved gas and water samples at a specific depth.

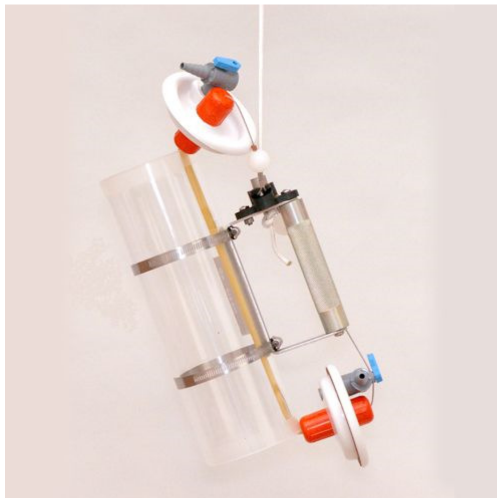


Figure 1. Vertical Van Dorn sampler

- *LELAP*— Louisiana Environmental Laboratory Accreditation Program. Laboratory data generated by commercial environmental laboratories that are not accredited under these regulations will not be accepted by the department in accordance with LAC 33:I.4501.A.2. Whenever samples are subcontracted to another environmental testing laboratory, the original laboratory shall maintain a verifiable copy the results with a chain of custody. The procedure may not be used to circumvent proper accreditation or any state requirements. The original laboratory is responsible for ensuring that the secondary laboratory used is properly accredited for the scope of testing performed in accordance with LAC 33:I.5307.D.

5.0 Procedure

The following procedures are recommended for the collection of depth-profile water quality samples from the sinkhole. These procedures are based on previous experience with sampling surface water and water at depth along the Louisiana Gulf Coast. The sampling should be conducted using a primary sample boat with a second supply boat for handling decontamination, sample coolers, ice, and bottles.

5.1 Sinkhole Access/Seismic Clearance

Before launching the boats, meet with the site seismic monitoring authority to obtain the current Seismic Activity Level Code which will indicate if personnel can enter and perform work on the sinkhole. The depth-profile sampling can only be conducted during periods when the Seismic Activity Level Code is at Level 1/Green. A competent and knowledgeable person should monitor the seismic helicorders when personnel are working on the sinkhole. Cell-phone or OEP radio communications will be used during the sampling.

5.2 Route and Sample Location Tracking

Upon leaving the boat launch, turn on the GPS unit in tracking mode and allow it to record the track of the entire sample event. Place the unit in the location where it has a clear signal from the sky, away from any other electronic or magnetic equipment that could cause interference, but is out of the way for sampling. Turn the unit off only after sampling is complete and the boats are back at the dock.

5.3 Boat Positioning/Sample Location

Position the sampling boat over the deepest depth location in the sinkhole, based on the most recent depth profiles. Since it may not possible to anchor the boats, procedures for maintaining proper location over the deepest part of the sinkhole should be coordinated with the boat operators.

5.4 Depth Gauging

Once the boat has been positioned over the deepest part of the sinkhole, sound the bottom of the sinkhole using the tag line. Record the depth of the sinkhole at this location.

5.5 Water Quality Measurements

With the In-Situ, Inc. Troll® 9500, measure pressure, pH, specific conductance, temperature, DO, turbidity, and ORP at 10-foot depth intervals from the water surface down to just above the bottom of the sinkhole. Attach the tag line to the Troll® sensor for measuring the depth—it is not possible to use pressure to determine depth because of the variable density water in the sinkhole. Use the Troll® logging function (In-Situ, Inc. Rugged Reader® required) to continuously record the data and write down the final values at each 10-foot depth interval on the sample collection log. It may take several minutes for the DO and ORP readings to stabilize at a given depth; the magnetic stirrer facilitates stabilization.

5.6 Surface Water Sample Collection

Using a peristaltic pump and new, clean Teflon tubing, collect water and dissolved gas samples at approximately 1-foot below the water surface. Place the proper aliquots in the labeled sample bottles. Filter the sample that will be submitted for dissolved metals analysis. Use the Isobag and peristaltic pump for collecting the dissolved gas samples.

5.7 Depth Profile Water Sample Collection

Using the Van Dorn sampler (Lane et al., 2003), collect depth profile water samples at depths of 10 feet, 25 feet, 50 feet, and every 25 feet thereafter to the bottom of the sinkhole. The last sample should be approximately 5 feet above the bottom of the sinkhole. As a guide for the final sample, if the bottom of the sinkhole is at 160 feet, it is not necessary to collect a sample at 155 feet and the 150-foot sample will be the bottom sample. If the bottom of the sinkhole is at 165 feet, then the bottom sample will be collected at the 160-foot depth.

It is important that the boat location be maintained close to the deepest portion of the sinkhole during all sampling. It is recommended that the GPS unit be operated in tracking mode to document any changes in boat location during the sampling events.

A water sample at the selected depths should be collected as follows using a Van Dorn sampler which has been properly decontaminated. Any sampling personnel that will come into contact with the sampling device and/or sampling containers shall wear a new, clean pair of nitrile or latex gloves during all sampling activities. The gloves should all be changed in between each sample. Below are the general sampling procedures that are recommended:

1. Confirm that the winch cable is securely attached to the sampling device. Check that the sample valves (located on the sampler end caps) on the Van Dorn sampler are both closed. Set the end cap trigger mechanism as per manufacturer instructions.
2. Using the winch with depth meter on the boat, lower the Van Dorn sampler to the target depth. Make sure that the rope attached to the sampler is free of knots and kinks so that the messenger (weighted cylinder) can reach the sampling device.
3. Upon reaching the desired depth, release the messenger (weighted cylinder) to trigger the closing of the sampler end caps.
4. Retrieve the Van Dorn sampler into the boat using the winch.
5. Hold the sampling device in the vertical position then open the top sample port. **The sampler will be under pressure and so caution must be used when opening the valves.**
6. Open the bottom valve and using the attached sample port and Teflon tubing, fill the dissolved gas Isobag first followed by the VOC vials. As pressure is relieved in the Van Dorn sampler, open the top sample port to allow for water flow out of the bottom port.
7. New Teflon tubing will be used for each new sample depth.
8. After these samples are collected, fill the appropriate bottles including the filtered dissolved metals container. For dissolved metals, it is preferable to connect tubing to the bottom sample port and pump directly from that port, through the filter into the sample bottle.
9. Properly label each sample at the time of collection. At a minimum, the label should contain the following information: Sample I.D., Depth, Date and Time collected, Sampler's name, requested analysis.
10. Except for the Isobags, samples will be placed on ice in coolers immediately following sample collection.
11. The sampler will hold approximately 4 or 6 liters of water. Make repeated trips to the sample depth as necessary to fill all sample bottles.
12. Decontaminate the sampler on the decon boat using the proper materials and procedures. Because there will likely be oil film on the sampler, a mild (phosphate-free) detergent may be necessary for thorough decontamination. Two samplers are recommended so one can be decontaminated while the second on is being used for sampling.

5.8 Sample Handling and Shipment

Upon returning to the dock, pack the samples for shipping to the appropriate laboratory. Add ice if necessary/required. Complete the Chain-of-Custody forms. Transport the samples to the laboratory, laboratory courier, or shipper (i.e. Fed-Ex or UPS).

5.9 Sample Analysis

The water samples from each sample depth will be submitted to the appropriate laboratories, following proper chain-of-custody procedures, for analyses. The following analyses will be requested:

5.9.1 Isotech Laboratories

The Isobags should be submitted to Isotech Laboratories in Champaign, Illinois or equivalent dissolved gas laboratory for analysis of:

- Compositional Gas (see Table 1 for list of components)
- Compound-specific isotope Ratios (see Table 1 for list of isotopes)

5.9.2 LELAP Laboratory

The remaining samples from each depth should be submitted to the selected LELAP laboratory for the following analyses:

- Alkalinity by Method 2320 or equivalent
- Benzene, Toluene, Ethylbenzene, Xylene (BTEX) by U.S. Environmental Protection Agency (EPA) Method 8260 or equivalent
- Chloride by Method SM4500 or Method 9056 or equivalent
- Inorganic Anions by Method 9056 or equivalent
- Metals (dissolved and total) – EPA Method 6010 or equivalent (see Table 1 for metals list)
- Specific Conductance by Method SM2510 or equivalent
- Total Dissolved Solids by Method SM2540 or equivalent
- Total Petroleum Hydrocarbons – Gasoline Range Organics/Diesel Range Organics/Oil Range Organics by EPA Method 8015 or equivalent
- Total Petroleum Hydrocarbon fractions (aliphatics >C6–C35, and aromatics >C8–C35) by Massachusetts TPH Method
- Total suspended solids by Method 160.2 or equivalent
- Water density by hydrometer or equivalent

5.10 Equipment Decontamination

At the conclusion of the sampling event, all sampling equipment should be thoroughly decontaminated and placed in proper storage pending future sampling. All disposable equipment shall be properly disposed.

5.11 Submittal of Data

All field activities should be documented and reported to LDNR in an electronic format and reasonable time frame. Upon receipt, analytical results shall also be submitted to LDNR in PDF and Excel or similar electronic data transfer format.

6.0 Attachments

- ***Attachment 1***—Isobag fill procedures

7.0 Forms

- Daily Field Activity Log
- Chain-of-Custody Document
- Sample Collection Log

8.0 References

Hecox, G. R., and Saxton, D. C., 2013, Bayou Corne Sinkhole Status Report to Blue Ribbon Commission, Baton Rouge, LA, CB&I, 121 plus appendices p.:

Lane, S. L., Flanagan, S., and Wilde, F. D., 2003, Chapter A2, Book 9, Selection of Equipment For Water Sampling, Handbooks for Water-Resources Investigations, National Field Manual for the Collection of Water-Quality Data, Reston, VA, U.S. Geological Survey, v. A2, 123 p.:

ATTACHMENT 1

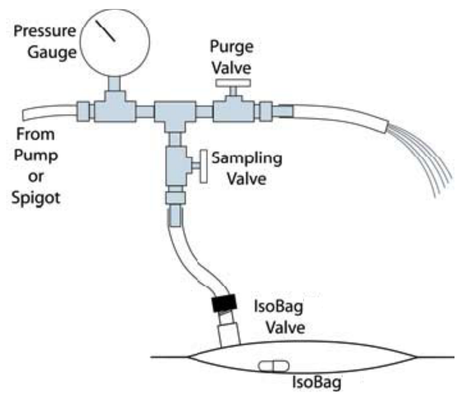
ISOBAG FILL PROCEDURES

ISOTECH
ISOTECH LABORATORIES INC
1308 Parkland Court Champaign, IL 61821 • (877) 362-4190 • www.isotechlabs.com

Collection of Ground Water Samples from Domestic and Municipal Water Wells for Dissolved Gas Analysis

1. **Sampling source:** Water samples should either be collected from a pressurized water system or by using a suitable water pump. When sampling from a pressurized water system, it is recommended to use an outdoor spigot or other source which bypasses any water treatment systems (i.e. water softeners, etc.). When using a pump, it should be capable of maintaining a constant pressure at or above that which exists within the aquifer. This is to ensure that gases dissolved in the water within the aquifer remain dissolved until the water is transferred into an IsoBag®. If using a pulsating pump such as a bladder pump, please contact Isotech for additional recommendations.

2. **Sampling Mechanism:** After purging the well, a mechanism consisting of a pressure gauge in line with two valves should be attached to the spigot or pump output (see figure). The ***purge valve*** (see figure) allows water to be pumped through the system to purge both the well and the tubing. The ***sampling valve*** (which should point downward), provides a point whereby a sample split can be slowly "bled" off from that water which is being continuously purged out of the system via the ***purge valve***. Sampling in this manner allows for collection of a sample over a longer period of time, and as such should provide a sample that is more representative of the water source, in essence creating an "averaging effect" during collection.



3. **IsoBags:** The gas bags provided have been evacuated in advance. A capsule filled with bactericide has also been inserted.

4. **Collection of samples:** Slowly open the ***purge valve*** to purge any gas or air from the tubing. The flow rate should be controlled so as to allow a reasonable flow, while also maintaining a pressure close to the maximum pressure of the water system or pump. When the line has been adequately purged and a steady state situation is achieved, open the sampling valve slightly to purge the air from it. Then, with the water still running at a low rate, connect the fitting to the valve on the IsoBag and proceed to fill the bag (note: the slower the filling rate, the greater the "averaging effect"). The bag should be filled with approximately 500 cc of water (i.e. to a thickness of about 1 inch). When sufficient sample has been collected, close the sampling valve and quickly disconnect the fitting from the IsoBag. The water flow can now be turned off and the hose disconnected. Reattach the cap to the valve of the IsoBag.

5. **Submission of samples.** After recording the sample identification on the attached label, the bag should be placed in its protective box and packed **laying flat**. Complete a Chain-of-Custody/Analysis Request form and include it with the sample(s). **If possible, samples should be shipped the same day collected, via an overnight delivery service. Client MUST inform Isotech of shipment prior to arrival.** Please note Isotech's receiving hours of **Monday thru Friday** 8:00 am to 4:30 p.m.

   Ship samples to:

   Isotech Laboratories, Inc.
   1308 Parkland Court
   Champaign, IL 61821

These instructions have been provided to simplify the collection of samples for dissolved gas analysis. Although we try to foresee and avoid problems in the field, it is never possible to predict every situation. If you encounter any difficulties, or if any additions or changes in these instructions would be beneficial, please let us know.

Isotech Laboratories, Inc. makes no warranty as to the applicability and/or safety of the procedures described herein.