

**SAMPLING PLAN FOR DETERMINING GEOCHEMICAL
FATE AND TRANSPORT MECHANISMS
AFFECTING ARSENIC CONCENTRATIONS
IN GROUNDWATER
VICINITY OF KOPPERS AND MURPHREE WELLFIELD**

**Prepared for Gainesville Regional Utilities
By Jones Edmunds & Associates, Inc.**

April 2004

1.0 INTRODUCTION

This work plan describes activities that are planned for the purposes of confirming the arsenic concentrations detected in Gainesville Regional Utilities groundwater monitoring wells MWTP-MW-1 and MWTP-MW-2 and determining whether the arsenic is of manmade or natural origin. In addition, the results of this work can be used to gain an understanding of arsenic concentrations in the Floridan Aquifer in the vicinity of the Murphree Wellfield, Alachua County, Florida.

1.1 BACKGROUND

The Gainesville Regional Utilities operates the Murphree Wellfield and the Murphree Water Treatment Plant in order to supply water to residents of the City of Gainesville and adjacent communities. Wells at the Murphree Wellfield extract water from the Floridan aquifer. The Cabot/Koppers Superfund Site is located approximately 2-miles southeast of the Murphree Wellfield and is within the capture zone of the wellfield.

Site-related contaminants have been detected in groundwater in the Surficial Aquifer, Intermediate (Hawthorn) Aquifer, and the Floridan aquifer beneath the Koppers Industries facility. GRU installed two monitor wells into the Floridan aquifer at locations downgradient of the Koppers facility. Those two wells were free of detectable organic contamination; however, arsenic was detected at concentrations above what is generally considered natural background concentrations in the Floridan aquifer and above the soon to be enforced 10 ug/L MCL.

1.2 OBJECTIVES

GRU wants to confirm the concentrations of arsenic detected and determine if the arsenic in groundwater monitoring wells MWTP-MW-1 and MWTP-MW-2 is of natural or man-made origin. In addition, GRU wants to increase the level of information on arsenic in the Floridan Aquifer in Alachua County specifically near the Murphree Water Treatment Plant. GRU has asked Jones Edmunds & Associates, Inc. (Jones Edmunds) to collect groundwater samples from the two GRU monitoring wells near the Superfund site, ten wells associated with GRU's regional groundwater monitoring network, and from six wells within the Koppers facility to compare selected geochemical parameters and to evaluate the source and fate of the arsenic in the local Floridan aquifer. Well locations are presented in the figure included in Appendix A. A limited number of accessible wells monitored by State and local agencies will be sampled if wells suitably constructed and maintained are identified.

2.0 SAMPLING AND ANALYTICAL METHODOLOGIES

The location of the wells to be sampled, sample collection/preservation/shipping methods, and analytical methods are described below:

2.1 SAMPLE LOCATIONS

Jones Edmunds reviewed data presented in the Addendum Hawthorn Group Field Investigation Report (TRC, August 20003) and the Data Report November Sampling Event Investigation of the Hawthorn Group Formation (TRC, January 2004) to identify potential wells from which to collect samples within the Surficial, Intermediate, and Floridan Aquifers at the Koppers facility. Jones Edmunds solicited input from Beazer (via TRC) regarding sample locations at Koppers and discussed other potential sample locations with the Alachua County Environmental Protection Department.

The following wells are tentatively identified as sample locations:

Table 1 Sample Locations		
Well ID	Owner	Aquifer Monitored
MWTP-MW-1	GRU	Floridan
MWTP-MW-2	GRU	Floridan
F2	GRU	Floridan
F3-F	GRU	Floridan
F4	GRU	Floridan
4-H-3	GRU	Hawthorn
FDOT-H132	GRU	Hawthorn
FDOT-FL32	GRU	Floridan
FDOT-H128	GRU	Hawthorn
FDOT-FL28	GRU	Floridan
M-9BR	Beazer	Surficial
M-23BR	Beazer	Surficial
HG-4D	Beazer	Hawthorn
HG-5D	Beazer	Hawthorn
FW-3	Beazer	Floridan
FW-5	Beazer	Floridan
TBD*		Floridan
TBD*		Floridan
TBD*		Floridan
TBD*		Floridan
TBD*		Floridan
TBD*		Floridan

* Dependent on identifying suitable wells.

The wells selected at the Koppers facility were chosen in order that data will be generated from the Surficial and Intermediate Aquifers as well as the Floridan aquifer. Wells were selected to provide a range of arsenic concentrations and to concentrate on the downgradient portion of the Koppers facility.

A limited number of wells monitored by the FDEP and other local agencies will be identified, evaluated and sampled with input from the ACEPD. At this time, it is not known whether any wells monitored by FDEP or other local agencies are suitable for monitoring due to uncertainty regarding well construction information and accessibility issues.

2.2 GROUNDWATER SAMPLING METHODOLOGY

Groundwater samples will be collected from the GRU monitor wells and from other wells outside Koppers property by Jones Edmunds' Field Services group. Wells MWTP-MW-1 and MWTP-MW-2 will be extensively purged with the intent of eliminating potential influences of water that may have been introduced during drilling (due to lost circulation in the limestone). The goal is to purge approximately 200 gallons of water from each well; however, the total volume purged may be modified based on the rate at which the wells produce water. Samples will be collected at the beginning, mid, and end point of purging and analyzed for total arsenic to evaluate the potential impact of lost circulation during drilling and well installation. The wells will then be allowed to stand idle for approximately three days after which a final groundwater sample will be collected for analyses indicated in Table 2. The final set of samples collected from wells MWTP-MW-1 and MWTP-MW-2 and from all other GRU monitor wells will be collected using low-flow SOPs mandated by the Florida Department of Environmental Protection (DEP-SOP -001/01). All sample containers should be filled completely leaving no headspace. Field filtered samples will be collected for determination of arsenic species, oxygen and hydrogen isotopes, hydrogeochemistry (Code-6 and Code-6B), and for field-determination of alkalinity, sulfate, and sulfide. Unfiltered samples will be collected for determination of VOCs, semivolatiles, and total organic carbon. Both filtered and unfiltered samples will be collected for determination of total arsenic concentration.

Where required, alkalinity, sulfate, and sulfide concentrations will be determined in the field using Hach kits supplied by Jones Edmunds.

Sampling of wells at the Koppers facility will be coordinated with Beazer's April 2004 sampling effort. GRU anticipates that Beazer's sampling crew will purge wells located at the Koppers facility and that Jones Edmunds samplers will collect those sample fractions required by GRU. Jones Edmunds staff will be responsible for providing sample kits and preservatives and for delivering samples to GRU's designated laboratory for analysis. GRU understands that wells at the Koppers facility will be sampled using procedures that are compliant with EPA and FDEP low-flow sampling SOPs. Well purge and sampling data, including purging criteria (temperature, conductance, pH, turbidity) will be recorded on appropriate forms. All samples will be maintained under chain of custody during sample collection and shipment.

Table 2 Sample Matrix													
Well ID	Owner	As Total **	As Species @	O ² /H ² Isotopes @	TOC	Code 6 @	Code 6B @	Alkalinity @	Sulfate/Sulfide @	pH, Temp, ORP, Conductivity	VOCs	SVOCs	
MWTP-MW-1	GRU	x	x	x	x	x	x	x	x	x	x	x	
MWTP-MW-2	GRU	x	x	x	x	x	x	x	x	x	x	x	
F2	GRU	x	x		x	x	x	x	x	x	x	x	
F3-F	GRU	x	x		x	x	x	x	x	x	x	x	
F4	GRU	x	x		x	x	x	x	x	x	x	x	
4-H-3	GRU	x	x		x	x	x	x	x	x	x	x	
FDOT-H132	GRU	x	x		x	x	x	x	x	x	x	x	
FDOT-FL32	GRU	x	x		x	x	x	x	x	x	x	x	
FDOT-H128	GRU	x	x		x	x	x	x	x	x	x	x	
FDOT-FL28	GRU	x	x		x	x	x	x	x	x	x	x	
M-9BR	Beazer	x	x	x	x	x	x	x	x	x			
M-23BR	Beazer	x	x	x	x	x	x	x	x	x			
HG-4D	Beazer	x	x	x	x	x	x	x	x	x			
HG-5D	Beazer	x	x	x	x	x	x	x	x	x			
FW-3	Beazer	x	x	x	x	x	x	x	x	x			
FW-5	Beazer	x	x	x	x	x	x	x	x	x			
TBD*		x	x	x	x	x	x			x			
TBD*		x	x	x	x	x	x			x			
TBD*		x	x	x	x	x	x			x			
TBD*		x	x	x	x	x	x			x			
TBD*		x	x	x	x	x	x			x			
TBD*		x	x	x	x	x	x			x			

* Private wells monitored by FDEP or local agencies if suitable wells are identified and access is granted.

** Filtered and unfiltered fractions required

@ Filtered fraction only

The method used to collect samples from those wells monitored by the FDEP and local agencies will depend on the construction and plumbing, including the presence/absence of a pump in the well. Samples may be collected from a tap/sampling port if an operating pump is in the well. Environmental sampling pumps may be used to recover the sample if a pump is not present in the well.

Where required, filtration of groundwater samples will be conducted in the field using a new 0.45 micron in-line filter at each well. The use of a 0.45 micron filter is intended to eliminate most colloids from the sample.

2.3 SAMPLE ANALYSES

Table 2 identifies the parameters to be analyzed for each well. Table 3 identifies for each parameter the analytical method, laboratory conducting the analysis, and the rationale for conducting the analysis.

Table 3 Analytical Requirements			
Parameter	Analytical Method	Laboratory	Rationale
As species (As^3 , As^5) @	Atomic Fluorescence Spectrometry	Pichler	Fate and Transport
As total **	Atomic Fluorescence Spectrometry	Pichler	Compliance / Fate and Transport
oxygen and hydrogen isotopes (filtered) @	Isotope Ratio Mass Spectrometry (IRMS)	Pichler	Source of Water
VOCs	SW846-8260	Enco	Groundwater Quality
Semivolatile Organics	SW846-8270	Enco	Groundwater Quality
oxidation/reduction potential	field	sample crew	Fate and Transport
total organic carbon	EPA 415.1	Enco	Fate and Transport
Hydrogeochemistry parameters (Code 6) @	ICP/MS	Activation Labs	Fate and Transport
Hydrogeochemistry parameters (Code 6B) @	Ion Chromatography	Activation Labs	Fate and Transport
pH , temp., conductivity	field	sample crew	
alkalinity @	field	sample crew	
sulfate/sulfide @	field (Hach kit)	sample crew	Fate and Transport

@ Filtered fraction only

** Filtered and Unfiltered fractions are required. Samples will be filtered in the field using a new 0.45 micron filter at each well.

Total arsenic analysis and arsenic speciation will be conducted by Dr. Thomas Pichler (University of South Florida Department of Geology, Center for Water and Environmental Analysis). Total arsenic concentration will be determined by converting soluble arsenic into arsine gas via hydride generation. The arsine gas will then be analyzed using atomic fluorescence spectrometry (arsine gas will be excited by a hydrogen flame and resulting fluorescence will be measured). Arsenic speciation will also be performed by Dr. Pichler. The arsenic species arsenite (AsIII), DMA, MMA and arsenate (AsV) will be separated using high pressure liquid chromatographic columns. The resulting aliquots containing separate arsenic species will then be

analyzed using the technique described for total arsenic. All nonstandard analyses conducted at the University of South Florida Center for Water and Environmental Analysis (Center) will be in accordance with the Center's formal quality control program (so the accuracy of the testing is guaranteed). The Center operates in strict compliance with all requirements mandated by the EPA Office of Water as stipulated by the Environmental Monitoring Methods Council. This includes formats, conventions, regulation of methods, standards, reagents, sample collection, preservation, storage, quality control, calibration, standardization, procedure, data analysis, calculations, and method performance. All standards are purchased from reputable sources and are diluted with de-ionized type I reagent grade 18MW -cm resistance water or better. An independently certified standard (QCS, ERA or SPEX) is inserted after every twenty samples to ensure ongoing running accuracy. The calibration curve is verified on each working run and after every twenty samples. Spikes are also inserted every twenty runs with 10% of the working stock and 90% of sample. Recovery for all controls (both independent and in house) must fall within + or - 10% of expected result.

Activation Laboratories, located in Ontario, Canada, will conduct analysis of certain hydrogeochemical parameters. The lab will conduct analysis of metals by ICP/MS. This analysis is identified by the lab as "Code 6". Fluoride, chloride, bromide, nitrite, nitrate, phosphate, and sulfate will be determined by Activation Labs using ion chromatography (Code 6B).

Oxygen and hydrogen isotopes will be determined by Dr. John Humphrey, Colorado School of Mines using isotope ratio mass spectrometry (IRMS). The oxygen and hydrogen isotope data will be collected to investigate whether the water in wells MWTP-MW-1 and MWTP-MW-2 is different from the water below the Koppers plant.

Sulfate and sulfide will be measured in the field by the sampling crew using Hach kits provided by Jones Edmunds. Field determination of sulfate and sulfide is required because of geochemical changes that will invariably occur between the time the sample is collected and the time it is analyzed in the laboratory.

All other parameters are typically determined in the field by the sampling crew during well purging.

2.4 SAMPLE CONTAINER, VOLUME, AND PRESERVATION

Requirements for sample containers, sample volume, sample preservation and shipment of samples to laboratories are presented in Table 4 below.

Field filtered samples only will be collected for determination of arsenic species, oxygen and hydrogen isotopes, hydrogeochemistry (Code-6 and Code-6B), and for field-determination of alkalinity, sulfate, and sulfide. Unfiltered samples will be collected for determination of VOCs, semivolatiles, and total organic carbon. Both filtered and unfiltered samples will be collected for determination of total arsenic concentration.

What is this program

really?
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Table 4 Requirements for Sample Containers, Volume, and Preservation

Parameter	Sample Container/Volume	Sample Preservation	Laboratory
As species (As^3 , As^5) @	125 ml plastic	HCl (1%); 4° C	Pichler
As total **	125 ml plastic	HCl (1%); 4° C	Pichler
oxygen and hydrogen isotopes @	125 ml plastic	4° C	Pichler
oxidation/reduction potential	<i>field</i>	4° C	<i>field</i>
VOCs	SW846-8260	HCl, 4° C	Enco
Semivolatile Organics	SW846-8270	4° C	Enco
total organic carbon	40 ml Amber vial	H_3PO_4 ; 4° C	Enco
Hydrogeochemistry parameters (Code 6) @	100 ml plastic	Nitric Acid; 4° C	Activation Labs
Hydrogeochemistry parameters (Code 6B) @	100 ml plastic	4° C (No Acid)	Activation Labs
pH , temp., conductivity	<i>field</i>	none	<i>field</i>
alkalinity @	<i>field</i>	none	<i>field</i>
sulfate/sulfide @	<i>field</i>	none	<i>field</i>

@ Filtered fraction only

** Filtered and Unfiltered fractions are required.

field This parameter will be determined in the field.

All samples will be chilled to 4° C immediately upon collection and addition of preservatives (if required). Helpful hints for sample preservation are presented in Appendix B. Samples will be shipped such that sufficient time is allowed for meeting all extraction and analytical holding times. The sampling crew will contact the appropriate laboratory to confirm the shipping schedule before sending the samples. Addresses for laboratories are presented in Appendix C.

3.0 DATA EVALUATION AND REPORTING

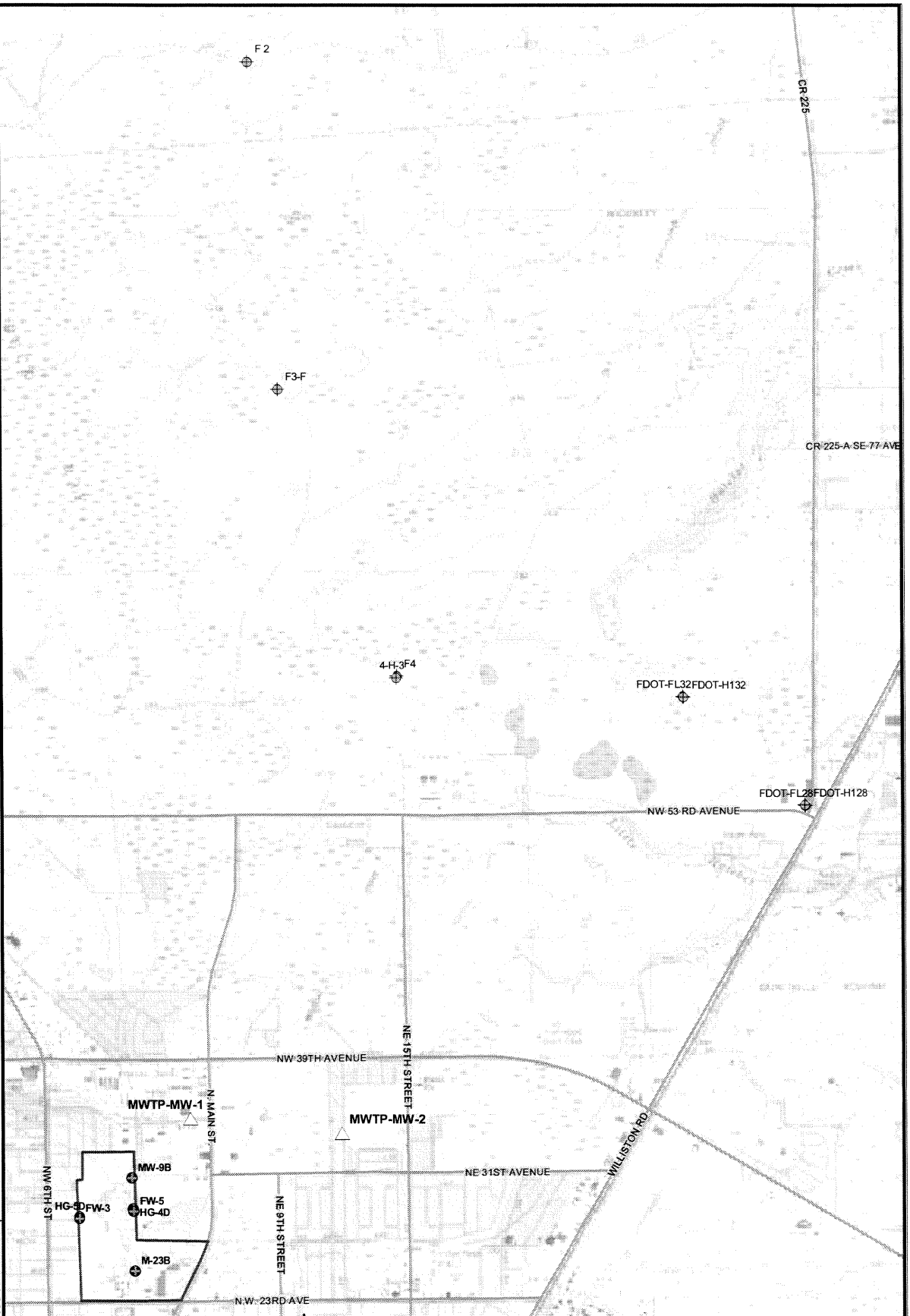
Analytical data will be evaluated and reported to GRU with an emphasis on determining if the arsenic detected in groundwater monitoring wells MWTP-MW-1 and MWTP-MW-2 is of natural or man-made origin. In addition, GRU wants to increase the level of information on arsenic in the Floridan Aquifer in Alachua County specifically near the Murphree Water Treatment Plant. An attempt will be made to determine whether the arsenic detected in wells at and downgradient of the Koppers facility is anthropogenic or natural in origin. All preliminary data for wells sampled on the Superfund site will be reported to Beazer at the same time that the data is reported to GRU.

The report will include a summary of the analytical data and results of the evaluation, field sampling forms, and final analytical reports issued by the laboratories. The report will be submitted to Beazer and other local agencies upon completion by Jones Edmunds and review by GRU. The final report is anticipated to be completed by June 30, 2004.

Appendix A

Map of Sample Locations

07125018 AprilProposedGroundWaterSample.mxd CMM 4/02/04



*Jones
Edmunds &
Associates, Inc.* **JEA**
CONSULTING ENGINEERS AND SCIENTISTS

Proposed April 2004
Groundwater Sample Locations

0 1,000 2,000
Feet



Appendix B

Sample Preservation Helpful Hints

- Nitric and hydrochloric acid should be added to the sample container after the container is partially filled with formation water. Add 1% acid by volume.
- When filling the bottle, it should be rinsed with the sample water at least three times (if sufficient sample is available) before retaining the sample. It should then be acidified. We want to minimize handling of samples after collection; therefore, testing the pH of the sample using pH paper is discouraged.
- Do not freeze water as it will cause precipitation of some elements.
- Samples should be shipped to the lab as soon as possible for analysis. Stability tests indicate most samples are stable for at least 30 days (Code-6 ICP/MS).
- Samples for ion chromatography should not be preserved at all.

(Modified from Activation Labs Helpful Hints)

Appendix C

Laboratory Addresses

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