Characterization of Natural and Anthropogenic Sources of Arsenic in Groundwater in the Tampa Bay Region of Florida

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Executive Summary

A number of authors have indicated that land use, lithology, and water levels can all affect arsenic concentrations in groundwater (Price and Pichler, 2006; Arthur et al., 2008; Kjoller et al., 2004; Hering and Stumm, 1990; Miller et al., 1933; Garbarino et al., 2003; Berg et al., 2008; and Harvey et al., 2006). In addition, the Florida Department of Environmental Protection (the Department), the Florida Department of Health (DOH), and the Southwest Florida Water Management District (SWFWMD) have each noted in their monitoring activities, that total arsenic concentrations in some of their sampled wells occasionally exceed the maximum contaminant level (MCL) of 10.0 µg/L.

For these reasons, the Department's Florida Geological Survey (FGS), Ground Water Protection (GWP) Section, and Watershed Monitoring Section (WMS) initiated a series of studies with SWFWMD and DOH to better understand the geological processes that may affect arsenic concentrations in groundwater. This report represents one of those studies.

This study used factorial design experiments to evaluate the relationships between land use, lithology, and seasonal changes in groundwater levels, and how they affect total arsenic concentrations. Due to a relative abundance of existing groundwater data from the Tampa Bay area, and relatively high concentrations of arsenic in many of the groundwater samples, the study focused on this area. For the experiments, 48 wells were selected based on aerial distribution within the study area and on the aquifer system they tapped. Wells were sampled in 2009 during both the dry and wet seasons.

Land use coverages as defined by the Florida Department of Transportation (DOT) (2009) were used to evaluate the generalized land use surrounding each well. In addition, micro land use (localized land use) data were obtained at the well head by WMS project samplers. Land use and micro land use were then used to classify each well as having either: (1) minimal or (2) high potential for arsenic contamination. Of the wells selected, 12 tapped the surficial aquifer system (SAS), 6 tapped the intermediate aquifer system (IAS), and 30 were completed into the Floridan aquifer system (FAS). The predominant lithology of the SAS is silica sands, whereas the IAS and the FAS are composed primarily of carbonate rocks. Most of the selected wells (30) are part of the Department's Status Monitoring Network, a network that randomly selects wells in order to monitor ambient, statewide groundwater resources. The remaining 18 wells were selected from a list of DOH wells that had previously been sampled for arsenic.

The DOH wells were originally sampled in the 1990s and 2000s because DOH suspected the wells may have had concentrations of arsenic above the MCL. The wells were "targeted".

The first factorial design experiment revealed that, at the scale of the investigation, land use contributed significantly to arsenic concentrations, while lithology and seasonal water level changes did not make significant contributions. Because DOH wells might have biased the results of the first experiment, a second factorial design experiment, excluding the DOH wells, was conducted. It was believed that if arsenic data from the DOH wells did not have an adverse impact on the initial evaluation, the results of the second experiment would be very similar to the first. However, if the wells did skew the first experiment, then the second would shed valuable information on the relationships among the three factors.

The second experiment revealed that even without the DOH wells, land use was the most significant factor affecting arsenic concentrations in groundwater. Again, lithology and water levels were not significant factors. However, lithology was found to interact with land use. In the future, environmental management practices designed to mitigate arsenic in groundwater will not only need to consider sources of arsenic from land use, but will also need to consider the complex relationships between the sources of arsenic due to land use and those due to lithology.

Background

Lazareva (2004) and Price and Pichler (2006) noted that arsenic and other trace metals can occur naturally in the matrix of Florida's aquifers. Other authors noted that trace metals interact with recharged water during aquifer storage and recovery activities (Arthur et al., 2001; Arthur et al., 2005; and Arthur et al., 2008). The interactions resulted in undesirable trace metals such as arsenic being released from the aquifer matrix material into the recovered water. The release can cause concentrations to exceed the state or federal MCL for arsenic. Groundwater levels can affect the pH and redox potential which, in turn, can affect trace metal concentrations such as arsenic (Kjoller et al., 2004; Hering and Stumm, 1990). Land use activities are also known to affect arsenic concentrations in groundwater. For example, between 1910 and 1961, Florida cattle were routinely dipped in arsenic solutions to control tick infestation (Todd et al., 2004). Arsenic has been used as a control of insects in citrus production (Miller et al., 1933). Arsenic has also been added to chicken feed to control parasites and enhance weight gain (Garbarino et al., 2003). These examples all represent sources of arsenic contamination in

groundwater, and furthermore, the Department, DOH, and SWFWMD have often measured arsenic concentrations above the current MCL in monitoring and private supply wells.

For these reasons, the Department's FGS, GWP, and WMS, in cooperation with SWFWMD and DOH, initiated several investigations to evaluate and characterize the natural and anthropogenic sources of arsenic (and other trace metals) in groundwater. This study is one of them.

By considering the variables: (1) land use, (2) aquifer matrix material (lithology), and (3) seasonal changes in groundwater levels as factors that have the potential to affect arsenic concentrations (the response to the factors), it was believed that factorial design experiments could shed some light upon the relationships among the three factors. The major questions are:

> Does land use significantly affect arsenic concentrations in groundwater?
> Does aquifer lithology significantly affect arsenic concentrations in groundwater?
> Do seasonal water level changes significantly affect arsenic concentrations in groundwater?
> Do the above factors significantly interact with each other to adversely affect arsenic concentrations?

If interactions proved to be significant, then it might be necessary to account for the interactions so that the Department and other entities can develop appropriate strategies to mitigate high arsenic concentrations in groundwater. Because the cooperating agencies had a relative abundance of groundwater data in the Tampa Bay area, and because arsenic concentration often exceeded the MCL, it was decided to conduct the study primarily in Hernando, Pasco, Pinellas, and Hillsborough Counties, as well as portions of Citrus, Sumter, Lake, Polk, Hardee, and Manatee Counties (Figure 1). Additional information depicted in Figure 1 will be discussed later.

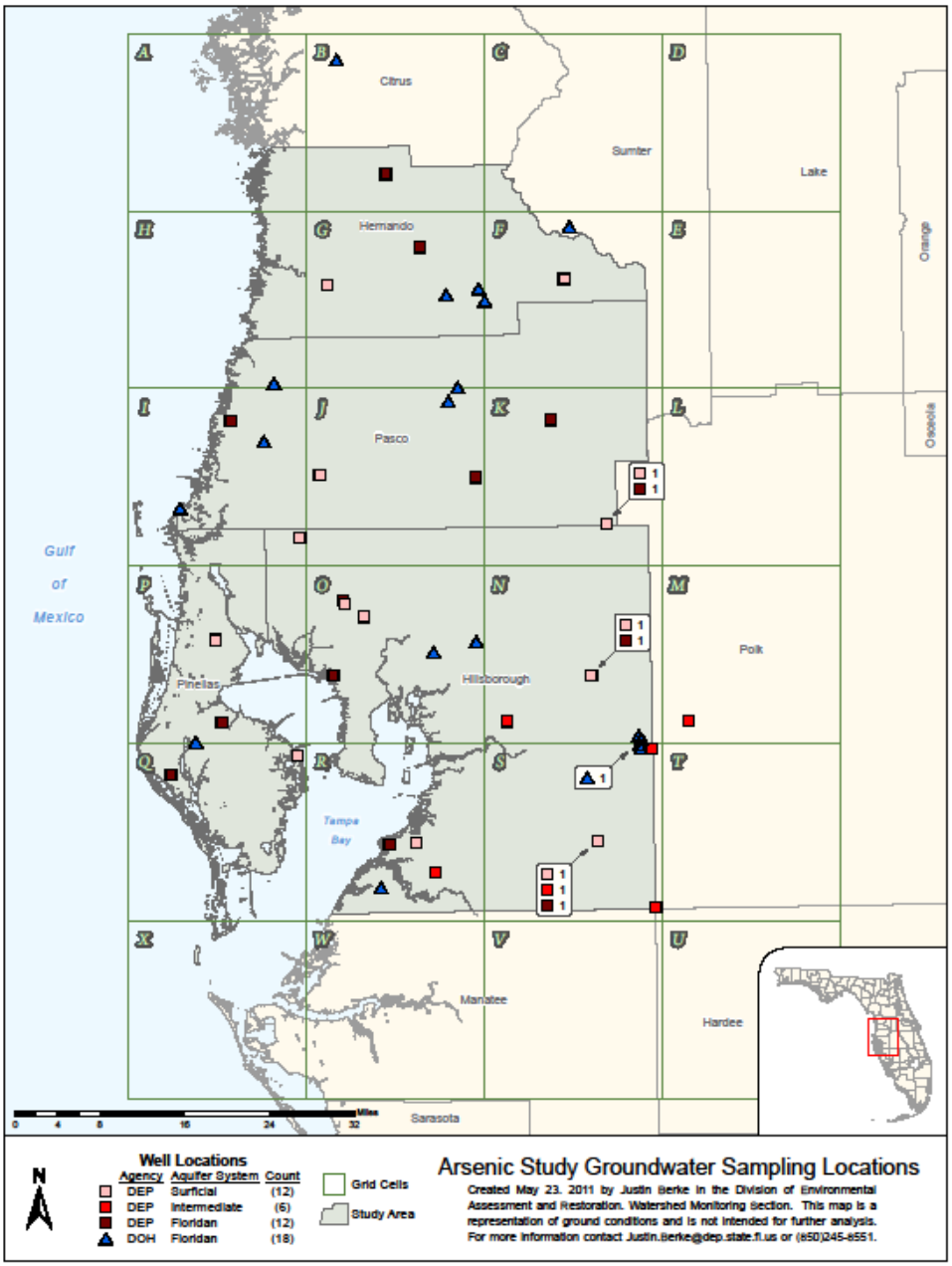

Figure 1. Arsenic Study Area

Factorial Design Experiments

Montgomery (1976) indicated that a factorial design experiment (FDE) consists of two or more factors, each with discrete possible values or levels. A full factorial design allows the investigator to study the effects of each factor on the response, as well as the effects of the interactions among factors.

The simplest factorial experiments are designed so that each factor has only two levels. If, for example, there are two factors without replicates, then there are four treatment combinations in total. The design is

referred to as a "2^2" factorial design. The main statistical tool used to analyze factorial designs is the analysis of variance (ANOVA) procedure (Montgomery, 1976). If levels are designed to be at fixed, known levels, then the models are called fixed-effects models. However, when the treatment levels are not fixed, which is often the case in field studies, the designs are referred to as the random-effects models. The models used in this study are random-effects models.

The effect of a factor is defined as the change in the response produced by a change in the level of the factor. This is frequently called a main effect because it refers to the primary factors of interest. For this study, the response is the concentration of arsenic in micrograms per liter (µg/L) to different levels of the three factors (lithology, groundwater levels, and land use). As an example, the main effect of the lithology factor could be thought of as the difference between the average response at the first level of lithology (silica sands) and the average response at the second level (carbonate rock) within the study area. That is, increasing Factor A from level 1 (silica) to level 2 (carbonate) causes an average response increase in the concentration of arsenic by "x" amount. Refer to Table 1 below. Let Factor A be lithology, level 1 be silica, and level 2 be carbonate. Let Factor B represent land use. For our demonstration, let level 1 land use represent a minimal potential source of arsenic, while level 2 represents a high potential source of arsenic. The values in the table refer to hypothetical measured responses in arsenic concentrations.

Table 1. Hypothetical Relationship between Main Effects of Factor A and Factor B

		Land Use (Factor B)	
		Level 1 (Low)	Level 2 (High)
Lithology (Factor A)	Level 1 (Silica)	0.20	0.30
	Level 2 (Carbonate)	0.40	0.52

Again, the main effect of Factor A can be thought of as the difference between the average response at the first level of A and the average response at the second level. In our example, it is

$$A = (0.40 + 0.52)/2 – (0.20 + 0.30)/2 = 0.21 \text{ µg/L of arsenic.}$$

Similarly, the main effect of Factor B (land use) is:

$$B = (0.30 + 0.52)/2 – (0.20 + 0.40)/2 = 0.11 \text{ µg/L of arsenic.}$$

Triola (1998) indicated that there is an interaction between two factors if the effect of one of the factors changes for different levels of the other factor. When an interaction effect is present, the impact of one factor depends on the level of the other factor. In our example, the signs of the effects of both A and B are the same (positive).

Suppose that we discovered a different set of responses, as shown in Table 2.

Table 2. Hypothetical Relationship of Factors A and B, Displaying Interactions

		Land Use (Factor B)	
		Level 1 (Low)	Level 2 (High)
Lithology (Factor A)	Level 1 (Silica)	0.20	0.40
	Level 2 (Carbonate)	0.50	0.12

At the first level of Factor B, the A effect is

A = 0.50 - 0.20 = 0.30 µg/L of arsenic.

At the second level of Factor B, the A effect is

A = 0.12 - 0.40 = -0.28 µg/L of arsenic.

Since the effect of A depends on the level chosen for B, there is an interaction between A and B. Note in our example that the sign of the effect of the first level is positive, while the sign of the effect of the second level is negative. In this situation, the opposite sign indicates that there is an interaction between A and B. Although the opposite sign is a definite indicator of interaction, an interaction can also exist even if the signs are the same. A complete FDE analysis is needed in order to make the determination. Again, if the impact of one factor depends on the level of the other factor, then an interaction exists.

Montgomery (1976) stated that an analyst can evaluate one factor at a time. If no interactions are present, evaluating the factors in this manner will suffice. However, if interactions are present, then determining which single factor has the most influence on the response can be misleading. For example, the interaction between factors may produce a greater effect than either factor on its own; thus, a full factorial design is the method employed in this study.

Assumptions of ANOVA

The first assumption is that each case (in our situation, a water sample) is independent of the others. This can be due to temporal or spatial separation. Dai (2009) indicated that if groundwater samples are collected no more frequently than once per three months, then time dependence is generally a minor issue. However, the vertical and lateral proximity of well samples could potentially affect the outcomes of statistical analysis. One might conclude that a factor significantly affects the response when in reality there is no effect. The second assumption is that the data are normally distributed. For this study, if normality proved to be a problem, then the data were transformed to a normal distribution. The third assumption is that the variances of the groups of data are statistically equal. Tabachnik and Fidell (2001) stated that ANOVA tests work well as long as the variance of one group is no more than ten times greater than the group with the smallest variance.

Experiment Setup

For the experiments the factors were: (1) land use, (2) lithology of the aquifer system matrix material, and (3) seasonal water levels. Regarding land use, a modification of the DOT (2009) land use classification was used. The classifications were broken down into a group of land uses categorized as having a minimal potential to contaminate groundwater with arsenic, and a group having the maximum potential for contamination. The groupings, developed by the author, will be discussed shortly.

Three aquifer systems exist within the study area: the SAS, the IAS and the FAS (Southeastern Geological Society, 1986). Within the study area, the SAS is predominantly made up of silica sands, along with clay material. The IAS is made up of sands, clays, dolostones and limestones, while the FAS consists mostly of dolostones and limestones (Yobbi, 2000). Based on lithologic and trace metal inspection of cores from the Tampa Bay area, Adel Dabous (Personal Communications, FGS, 2010) indicated that arsenic concentrations were generally lowest in sediments making up the SAS, whereas the concentrations are often twice as high within the sediments of the IAS and FAS. For this reason, the experiment was designed to compare arsenic concentrations in the predominantly silica sands of the SAS to the predominantly carbonate sediments of the IAS and FAS. Based on historical rainfall data (Southeast Regional Climate Center, 2010) it was determined that the dry season is March – May, while the wet season is July – September.

Forty-eight wells were sampled for arsenic during both the dry and wet seasons. Data from these wells regarding location, aquifer system tapped, land use, water levels, and arsenic concentrations are found in

Appendix A. Thirty of the wells are part of the Department's Status Monitoring Network (Florida Department of Environmental Protection, 2009). Many of those wells are maintained by SWFWMD. Based on well construction data, 12 of the wells tap the SAS, 6 tap the IAS, and 12 tap the FAS. The remaining 18 wells were selected from a list of wells sampled previously by DOH. As noted, DOH sampled these wells because they were suspected of having high concentrations of arsenic. The author attempted to obtain a "balanced" set of DOH wells for this study. He did this by selecting 9 DOH wells that, from previous sampling events, had arsenic concentrations greater than the MCL (10 µg/L), and 9 that were at or near the laboratory detection level. Construction data were not available for the DOH wells; however, the GWP Section discovered that most private wells in the area tap the FAS. In addition, GWP Section staff found data on existing wells in the study area, and estimated that the 18 selected wells tapped the FAS. The location of the wells, the aquifer system tapped, and monitoring agency are depicted in Figure 1. The grid cells in the figure simply represent arbitrary subdivisions. The goal was to obtain, if possible, groundwater data from each grid cell in order to have evenly spaced data across the study area.

For a variety of reasons, data were not available for one of the wells and the dry season datum was not available for a second well. Thus, arsenic data were available for 47 wells. In addition to arsenic the samples were analyzed for field analytes, major ions, and numerous trace metals. Those data were used in associated studies. For this particular study, arsenic was the only laboratory analyte of concern. Plumbing issues prevented access of water level indicator devices in many of the wells. However, water levels were obtained from 23 wells during the wet and the dry season. The purpose was to evaluate water level changes between the wet and the dry seasons.

Sampling and Lab Analysis

Groundwater samples were collected using WMS protocols (Florida Department of Environmental Protection, 2009). Samples were shipped to a commercial laboratory (Activation Laboratories Ltd.) using approved protocols (Florida Department of Environmental Protection, 2009). The laboratory was certified (#E87979) by DOH complying with Florida Administrative Code 64E-1 regarding the chemical analysis of metals for environmental samples. The arsenic analytical method was ICP-MS 200.8 (total arsenic). Specific details regarding field sampling and analytical protocols are found in Appendix B.

During laboratory analyses, reported concentrations of total arsenic below their method detection limit (MDL) varied. For statistical analyses, if an arsenic sample concentration was below the MDL, the reported MDL was used.

Land Use Classifications

During each sampling event of this study, field crews obtained micro land use (MLU) data. MLU is the predominant land use within 300 feet of the well head. There are five MLU categories: (1) Low Impact, (2) Urban/Suburban, (3) Mining, (4) Intensive Agriculture, and (5) Industrial (Florida Department of Environmental Protection, 2009). In addition, a variety of land use maps were available (1974, 1995, 2003, and 2006). These maps represent predominant land use polygons. They represent a coarser scale than MLU.

Prior to selecting the land use map to be used in this study, the author assigned a land use category to each well based on the various maps (one for each land use map year). In the opinion of the author, the 2006 data (jointly developed in 2010 by SWFWMD and the Department) tended to correlate best with the samplers' in-the-field MLU data. For this reason, the author selected the 2006 data set for use in the factorial design experiments.

Using 2006 land use data, Level II or III land use codes (DOT, 2009) were assigned to each well site. The author then classified the land use at each well into one of two broad, major land use categories based on the author's perception of the site's vulnerability to groundwater contamination. The major categories were based on: (a) the samplers' MLU data and (b) 2006 land use.

The two land use categories are: (a) minimal impact potential, labeled -1 (Table 3, first column), and (b) high impact potential, labeled 1 (Table 3, second column). In order for a well site to be labeled -1 in the FDE, it had to be classified as "minimal" in the 2006 land use and as MLU category 1 or 2 (Low Impact or Urban/Suburban). The 2006 land use code, the MLU code, and the land use code adopted for FDE experiments (LUCode) are in Appendix A.

Table 3. Land Use Classifications Used for Study

Minimal Impact Potential (Level -1 for FDE)	**High Impact Potential (Level 1 for FDE)**
Institutional (170)*	Cropland and Pastureland (210 - 260)
Recreational (180)	Commercial (140)
Rangeland (300) Swamp (600)	Extraction (160)
a. Residential Low or Medium (110-129) plus b. Low Impact or Urban/Suburban MLU	a. Residential Low or Medium (110 – 129) plus b. Mining, Industry or Intensive Agriculture MLU
Forest, Hardwood (400 - 450)	Residential High (130-139)
	Industrial (150), Utilities (800)
	Nurseries, Tree Crops (220 - 224)
	Open Land (190)

*Numbers in parentheses represent DOT (2009) land use codes.

Initial Factorial Design Experiment

Figure 2 depicts the conceptual diagram of the initial, three factor, two level (3^2) FDE design. The factors were: (A) land use – minimal impact potential (code = -1) and high impact potential (code 1), (B) lithology – predominant sands of the SAS (code = -1) and predominant carbonates of a combination of the IAS and FAS (code = 1), and (C) seasonal changes in groundwater levels – wet season (code = -1) and dry season (code = 1).

The Minitab statistical software package (Minitab, version 15.1.1.0 [2007]) was used for all statistical tests. For each test, the level of significance (α) was pre-set at 0.05. Thus, for any statistical test, if the resulting probability value (p-val) was ≤ 0.05, then the corresponding null hypothesis was rejected.

To test for normality, the Ryan-Joiner (RJ) test (Minitab, 1996) was used. For the test, the null hypothesis (H_0) was that the data were normally distributed, while the alternate hypothesis (H_A) was that the data were not. The test revealed that the arsenic concentrations did not have a normal distribution (p-val < 0.01). The data were then transformed into a normal distribution. This was accomplished by

substituting the corresponding n-score (NSc) (Minitab, 1996) for each arsenic datum. The resulting p-val (> 0.10) of the RJ test indicated that the NSc data had a normal distribution.

For an FDE, an equal number of replicate samples at each combination level is desirable. Thus, for the "3^2" design used in this experiment, it would have been ideal to collect an equal number of replicates for each of the eight combination levels (see Table 4, row 2). Funds were not available for the drilling of new wells, so only existing wells were used. Consequently, some of the eight combinations had many samples, while others only had a few.

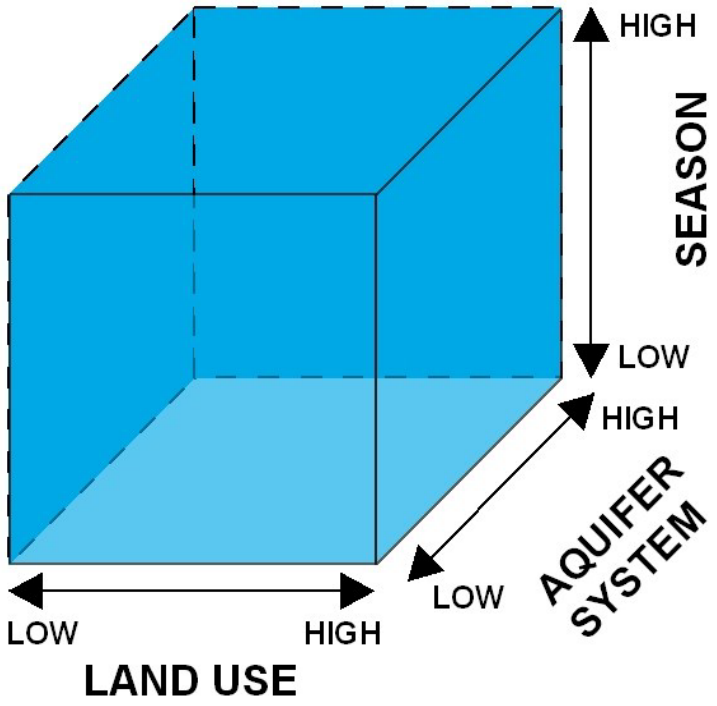

Figure 2. Three-Dimensional Concept of Factorial Design Experiment. The low and high levels of each factor represent expected response concentrations of arsenic.

Table 4 displays the data used for the initial factorial design experiment (IFDE). The second row in the table lists the eight combination levels. Beginning with the fourth row, the table displays both the arsenic concentrations and the corresponding NSc values. Four of the combination levels (-1-1-1, -1-11, 1-1-1, and 1-11) had six NSc values. The six values were replicates and they were each used in the IFDE analysis. The remaining four combinations (-11-1, -111, 11-1, and 111) had more than six values, so Minitab's random number generator was used to select six values from the available replicates. The

randomly selected replicates are indicated in Table 4 as bold, highlighted cells. For the IFDE, each of the eight combination levels ended up with six replicates.

Table 4. Initial Factor Design Experiment Factors and Combinations

Note: "As" is the arsenic concentration (in µg/L); "NSc" is the transformed arsenic concentration.

Factor Combinations: Land Use (-1 or 1), Aquifer (Lithology) (-1 or 1), and Water Level (-1 or 1)															
-1 -1 -1		**-1 -1 1**		**-1 1 -1**		**-1 1 1**		**1 -1 -1**		**1 -1 1**		**1 1 -1**		**1 1 1**	
As	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**
0.30	-0.67	0.30	-0.67	0.30	-0.67	0.30	-0.67	0.30	-0.67	7.20	1.05	0.44	**0.08**	0.62	**0.20**
0.21	-1.76	0.36	-0.11	0.30	**-0.67**	0.30	-0.67	0.30	-0.67	0.35	-0.13	0.30	**-0.67**	0.42	0.00
0.30	-0.67	0.30	-0.67	0.30	-0.67	0.30	**-0.67**	0.30	-0.67	0.30	-0.67	2.15	0.60	2.29	**0.63**
0.62	0.20	0.30	-0.67	1.48	0.44	0.39	**-0.07**	5.22	0.96	4.83	0.88	10.94	1.55	11.90	**1.39**
0.24	-1.65	0.30	-0.67	1.10	**0.39**	1.00	**0.29**	0.50	0.11	0.33	-0.16	0.27	0.7	2.13	0.56
0.53	0.16	0.42	0.00	0.30	-0.67	0.30	-0.67	0.39	-0.67	1.66	0.47	3.01	0.73	0.43	**0.05**
				0.30	**-0.67**	0.30	-0.67					2.74	2.11	0.30	-0.67
				3.13	0.80	2.73	**0.70**					2.61	**2.15**	1.17	0.42
				0.30	**-0.67**	0.30	-0.67					0.30	-0.67	0.30	-0.67
				1.00	0.29	1.09	0.36					4.44	0.67	4.91	0.92
				0.11	**-1.91**	0.30	-0.67					2.02	**1.91**	74.80	2.47
				5.48	1.01	7.29	1.10					0.51	**0.13**	0.30	**-0.67**
				2.03	0.55	1.94	0.50					0.30	-0.67	0.42	0.00
				0.30	-0.67	0.30	-0.67					1.13	**1.23**	8.36	**1.15**
				0.30	-0.67	0.30	-0.67								
				10.20	1.23	11.90	1.33								
				1.02	0.33	0.76	0.24								
				16.80	1.65	12.80	**1.47**								
				17.60	1.76	0.30	-0.67								
				0.29	-1.47	0.30	**-0.67**								
				0.30	**-0.67**										

The factorial design experiments actually had several null hypotheses (H_0). They were:

H_0: The effect of land use was insignificant.

H_0: The effect of lithology was insignificant.

H_0: The effect of water level was insignificant.

H_0: The interaction between land use and lithology was insignificant.

H_0: The interaction between land use and water level was insignificant.

H_0: The interaction between lithology and water level was insignificant.

H_0: The interactions between land use, lithology and water level were insignificant.

The alternate hypothesis (H_A) in each situation was that the null hypothesis was false.

Results

Tables 5a and 5b display the results of the IFDE experiment. Table 5a indicates that land use (Factor A) was significant (p-val = 0.024). In addition, the ANOVA Table 5b indicates that the overall effects of two-way and three-way interactions were not significant. Thus, according to the IFDE, land use was the only significant factor that affects arsenic concentrations in groundwater.

Table 5a. Factorial Fit: NSc versus Factors A (land use), B (lithology), and C (seasonal groundwater level) for Initial Factor Experiment

Note: X*Y indicates the interaction between Factor X and Factor Y. For a discussion of Factorial Designs and terms, refer to Minitab (1996).

Term	Effect	*Coef	**SE Coef	***T	P-val
Constant		-0.1635	0.1122	-1.46	0.153
A	0.5281	0.2640	0.1122	2.35	**0.024**
B	0.3500	0.1750	0.1122	1.56	0.127
C	0.3081	0.1541	0.1122	1.37	0.177
A*B	0.0153	0.0076	0.1122	0.07	0.946
A*C	-0.2625	-0.1313	0.1122	-1.17	0.249
B*C	-0.1497	-0.0748	0.1122	-0.67	0.509
A*B*C	-0.4517	-0.2258	0.1122	-2.01	0.051

* Coef – the mathematical effect of factors (and combination of factors)

** SE Coef – The standard error of the factors

*** T – The corresponding T-statistic

Table 5b. Analysis of Variance for Arsenic Nscor (coded units) for Initial Factor Experiment

For a discussion of Factorial Designs and terms, refer to Minitab (1996).

Source	*DF	**Seq SS	***Adj SS	****Adj MS	*****F	P-val
Main Effects	3	5.957	5.957	1.9855	3.29	**0.030**
2-Way Interactions	3	1.099	1.099	0.3662	0.61	0.615
3-Way Interactions	1	2.448	2.448	2.4479	4.05	0.051
Residual Error	40	24.176	24.176	0.6044		
Pure Error	40	24.176	24.176	0.6044		
Total	47	33.679				

* DF – Degrees of freedom

** Seq SS – Sequential sum of squares

*** Adj SS – Adjusted sum of squares

**** Adj MS – Adjusted mean square error

*****F – The corresponding F-Statistic

Second Factorial Design Experiment

Earlier, it was mentioned that 18 selected wells had been sampled by DOH because they were located in or near areas known to be contaminated with arsenic. They were “targeted” wells. The author believed that arsenic concentrations from the DOH wells might have biased the results of the IFDE experiment. For this reason, a second factorial design experiment (SFDE) was conducted without the DOH wells. Table 6 displays combination levels and data used in the SFDE. The author believed that if the wells did not bias the experiment, the results of the SFDE would be very similar to the IFDE. On the other hand, if the wells did have an undue impact, the SFDE would shed additional light on the relationships among the three factors.

For the SFDE, because DOH well data were eliminated, NSc data were re-computed. Each of the first six combination levels had 6 samples (replicates). Each sample was used. However, the last two combination levels (11-1, and 111) had 11 samples. In order to have an equal number of replicates for each combination, the Minitab random number generator was used to select 6 replicates from the last two combination levels. These are indicated in bold, highlighted font in Table 6.

Table 6. Second Factor Design Experiment Factors and Combinations

Note: "As" is the arsenic concentration (in µg/L); "Nsc" is the transformed arsenic concentration.

Combination Levels - Land Use(-1 or 1), Aquifer (Lithology) (-1 or 1) , and Water level (-1 or 1)															
-1 -1 -1		**-1 -1 1**		**-1 1 -1**		**-1 1 1**		**1 -1 -1**		**1 -1 1**		**1 1 -1**		**1 1 1**	
As	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**	**As**	**NSc**
0.30	-0.49	0.30	-0.49	0.30	-0.49	0.30	-0.49	0.30	-0.49	7.20	1.30	0.44	0.37	0.62	0.59
0.21	-1.69	0.36	0.15	0.30	-0.49	0.30	-0.49	0.30	-0.49	0.35	0.30	-0.30	-0.49	0.42	0.29
0.30	-0.49	0.30	-0.49	0.30	-0.49	0.30	-0.49	0.07	-2.30	0.30	-0.49	2.15	0.84	2.29	0.91
0.62	0.59	0.30	-0.49	0.11	-1.91	0.30	-0.49	5.22	1.21	4.83	1.12	12.90	**1.91**	12.00	**1.69**
0.24	-1.54	0.30	-0.49	0.29	-1.31	0.30	-0.49	0.50	0.42	0.33	0.06	2.76	1.04	2.13	**0.78**
0.53	0.52	0.42	0.28	0.30	-0.49	0.30	-0.49	0.39	0.19	1.66	0.73	26.00	**3.00**	0.30	**-0.49**
												2.61	**0.97**	1.17	**0.67**
												0.30	**-0.49**	0.30	-0.49
												0.51	0.46	0.30	**-0.49**
												0.25	**-1.41**	0.42	**0.28**
												10.20	**1.54**	8.36	1.41

Results

Tables 7a and 7b display the results and illustrate that, by excluding the DOH wells, land use (Factor A) was highly significant (p-val = 0.000). It also indicates that a significant interaction between land use and lithology (Factor B) did exist (p-val = 0.037). Of note, the ANOVA Table 7b indicated that the overall effects of two-way and three-way interactions were not significant.

Evaluation of Land Use Effects

Based on the results of the two FDEs, a comparison of arsenic concentrations by land use was in order. For this evaluation, the 18 DOH wells were excluded. Table 8 shows the arsenic values and descriptive statistics within each of the two land use levels. The concentrations represent the mean concentration of arsenic at each site (average of the wet and dry seasons). The two land use categories are minimal impact potential and high impact potential. The terms Q1, Q2, and Q3 represent the 25^{th}, 50^{th} (median), and 75^{th} percentiles.

Because the data were not normally distributed, a two-sided Mann-Whitney (MW) test (Conover, 1999) was used to compare the median arsenic concentration values of the two land uses, where H_0 was that the medians were equal and H_A was that the medians were not. The MW test revealed that the concentrations were significantly different between the two land use categories (p-val = 0.001).

Table 7a. Factorial Fit: Nscor versus Factors A(land use), B (lithology), and C(seasonal groundwater level) for Second Factor Experiment

Note: X*Y indicates the interaction between Factor X and Factor Y.

Term	Effect	Coef	SE Coef	T	(P-val)
Constant		-0.0318	0.1161	-0.27	0.786
A	1.0016	0.5008	0.1161	4.31	**0.000**
B	0.2094	0.1047	0.1161	0.90	0.373
C	0.2008	0.1004	0.1161	0.86	0.392
A*B	0.5008	0.2504	0.1161	2.16	**0.037**
A*C	-0.1159	-0.0579	0.1161	-0.50	0.621
B*C	-0.2878	-0.1439	0.1161	-1.24	0.222
A*B*C	-0.3426	-0.1713	0.1161	-1.48	0.148

Table 7b. Analysis of Variance for Arsenic Nscor (coded units) for Second Factor Experiment

Source	DF	Seq SS	Adj SS	Adj MS	F	P-val
Main Effects	3	13.0486	13.0486	4.3495	6.72	**0.001**
2-Way Interactions	3	4.1646	4.1646	1.3882	2.15	0.110
3-Way Interactions	1	1.4083	1.4083	1.4083	2.18	0.148
Residual Error	40	25.8858	25.8858	0.6471		
Pure Error	40	25.8858	25.8858	0.6471		
Total	47	44.5073				

Table 8. Descriptive Statistics on Arsenic Concentrations (in µg/L) versus Land Use Category

	N	Mean	St.Dev	Min	Q1	Q2	Q3	Max
Minimal (-1)	12	0.32	0.08	0.21	0.29	0.30	0.30	0.48
High (1)	17	3.18	4.31	0.19	0.35	1.02	4.39	13.15

Evaluation of Lithology

Table 9 shows the descriptive statistics on arsenic values within each of the two lithology levels. Again, the concentrations represent the average value of the wet and dry seasons. For this analysis, DOH wells were included. Recall that the two lithology levels were: (a) SAS (predominantly silica sands, assigned level -1) and (b) a combination of the IAS and FAS (predominantly carbonate rock; level 1).

Table 9. Descriptive Statistics on Arsenic Concentrations (in µg/L) versus Major Aquifer System Category

	N	Mean	St.Dev	Min	Q1	Q2	Q3	Max
SAS (-1)	12	1.08	1.58	0.30	0.30	0.37	0.89	5.03
IAS/FAS (1)	*35	4.55	8.90	0.30	0.30	0.94	4.68	47.50

*One FAS well was not sampled.

Since the data were not normally distributed, a two-sided MW test was used to compare the median arsenic concentration values. The H_0 was that the medians were equal and H_A was that the medians were not. The resulting p-val (0.257) indicated that the concentrations were not significantly different. Earlier it was mentioned that lithologies were separated based on: (a) silica sands and (b) carbonate rocks. Table 10 displays the descriptive statistics, based on the specific aquifer system tapped by each well.

To determine if there were differences in the median arsenic concentrations among the three aquifer systems, a two-sided Kruskal-Wallis (KW) test (Conover, 1999) was used. The H_0 was that the medians were equal and H_A was that the median value in at least one category was not equal to the other two. The resulting p-val (0.516) indicated that the concentrations in the three aquifer systems were not significantly different.

Table 10. Descriptive Statistics on Arsenic Concentrations (in µg/L) versus Specific Aquifer System

	N	Mean	St.Dev	Min	Q1	Q2	Q3	Max
SAS (-1)	12	1.08	1.58	0.30	0.30	0.37	0.89	5.03
IAS (1)	6	3.01	4.73	0.30	0.30	1.29	4.95	12.45
FAS (1)	29*	4.87	9.57	0.30	0.30	0.94	5.53	47.50

*One FAS well was not sampled.

Evaluation of Groundwater Levels

Even though the FDEs showed no significant relationship between seasonal water level changes and arsenic concentrations, a comparison of water levels in the wet and dry seasons was still of interest. Water levels were not obtainable in all sampled wells. However, water levels were obtained both in the wet and the dry seasons in 23 of the wells. The analyte measured was depth to water (DtoW) (from the

measuring point). Thus, during the dry season, DtoW was expected to be greater than during the dry season. Descriptive statistics for the two seasons are found in Table 11 below.

Table 11. Descriptive Statistics on Depth to Water (DtoW, in feet) for the Wet and Dry Seasons

	N	Mean	St.Dev	Min	Q1	Q2	Q3	Max
Wet Season	23	21.73	26.41	2.81	6.10	9.50	35.85	107.95
Dry Season	23	25.75	29.94	3.65	7.50	11.61	37.56	109.95
Difference	23	- 4.03	7.00	-31.07	- 4.30	-2.00	-0.40	0.71

The mean difference in DtoW between the wet and dry seasons (wet minus dry) was - 4.03 feet, while the median change was - 2.00 feet. To determine if the difference was due to a minority of the wells having a large change or due to a more uniform change across the study area, a one-sample sign test (Conover, 1999) was used. Conover stated that the sign test is useful in testing whether the difference between (X, Y) pairs of data tends to be positive, negative, or simply no significant difference. The wet season values for DtoW were subtracted from the dry season for the 23 wells. The signs (plus or minus) were recorded. If there was no change, data were not counted. The H_0 was that the median of all of the difference signs was equal to zero (the median = 0.00), while H_A was that the median did not equal zero. If the median equaled zero, then water levels in approximately half of the wells should have increased and the other half should have decreased. For the study area, 21 of the 23 wells had a greater DtoW value during the dry season. The sign test resulted in a p-val equal to 0.001.

The RJ test indicated (p-val <0.01) that water levels were not distributed normally. Thus, a MW test was used to compare the median groundwater levels between the two seasons. Using the same H_0 and H_A as the other MW tests, the resulting p-val was 0.482. The magnitude of water level change was statistically insignificant. Even though the water levels were lower in the dry season from an aerial perspective, the magnitude of the change was insignificant.

Figure 3 displays the average change per grid cell during the study. The number in the center of each cell is an absolute value (positive sign) and represents the mean change for all wells in the corresponding cell. Of note is that the magnitude of change per cell tends to increase inland.

Seasons

Table 12 describes the distribution of arsenic concentrations during the wet and dry seasons. DOH wells were included. Note that the mean was greater during the dry season, while the median (Q2) was greater during the wet season.

Table 12. Descriptive Statistics on Arsenic Concentrations (in µg/L) for the Wet and Dry Seasons.

	N	Mean	St.Dev	Min	Q1	Q2	Q3	Max
Wet Season	47	3.57	5.99	0.30	0.30	0.50	3.01	26.00
Dry Season	46	3.66	11.24	0.30	0.30	0.41	2.17	74.80

Since arsenic concentrations were not normally distributed, a MW test was used to determine if there was a significant difference in concentrations between the wet and dry seasons. Using the two-sided MW test, plus the corresponding null and alternate hypotheses, there was not a significant difference in arsenic concentrations during the wet and the dry seasons (p-val = 0.767). Finally, a sign test was used to determine if the differences in arsenic concentrations during the two seasons were uniformly distributed over the study area. The test indicated that by subtracting the dry season concentrations from the wet season, 18 wells showed increases, 17 showed decreases, while 11 showed no difference. The corresponding p-val was 1.000. Thus, there was no aerial difference in arsenic concentrations in the wet versus dry seasons.

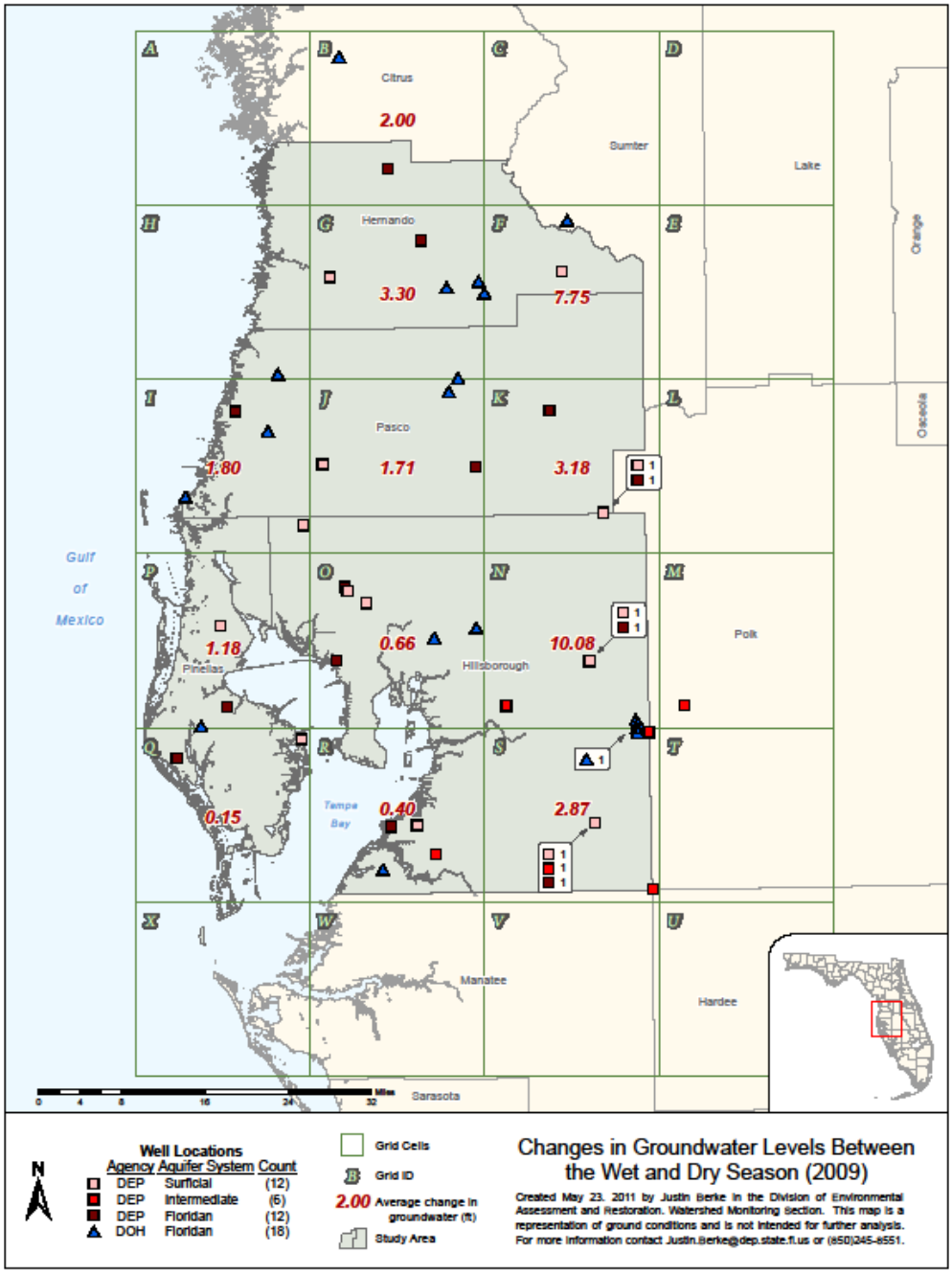

Figure 3. Magnitudes of Changes in Groundwater Levels between the Wet and Dry Seasons (2009)

The value in the center of each cell represents the mean change in groundwater level in absolute values for all wells located in the cell, independent of aquifer system tapped.

Discussion

Previous investigations cited in the "Background" section of this report indicated that land use, lithology, and changing groundwater levels are all significant factors in the concentration of arsenic in groundwater. This investigation found that only land use was significant. None of the earlier studies evaluated the effects of land use, lithology, and water level changes simultaneously. The FDEs of this study did so and also allowed for evaluation of the interactions of the three factors.

Previous studies in Bangladesh and in Vietnam demonstrated that groundwater levels can affect the geochemical processes near water wells and thus influence arsenic concentrations. Harvey et al. (2006) indicated that changing groundwater levels due to extensive irrigation practices in Bangladesh have altered geochemical and biogeochemical processes. These processes release arsenic from sediments into groundwater. Likewise, Berg et al. (2008) discovered that elevated levels of arsenic in groundwater near Hanoi, Vietnam were caused by reductive geochemical conditions. The latter authors mentioned that excessive groundwater extraction contributed to the reductive conditions. When those conditions exist, arsenic-rich sediments and aquifer matrix material release arsenic into solution. In both investigations, the changing water levels were man-induced and of longer duration than naturally occurring seasons. This suggests that relative to the Bangladesh and Vietnam studies, seasonal groundwater level fluctuations observed in the FDE study are simply not long enough in duration to observe significant changes in arsenic concentrations due to geochemical modifications. This interpretation is supported by an investigation of shallow groundwater in northern Argentina (Claesson and Fagerberg, 2003). The authors determined arsenic concentrations in groundwater during a wet and a dry season in 2002. As with the current study, Claesson and Fagerberg did not find a significant difference between the two seasons. However, not only did they analyze for total arsenic, they also determined arsenic(III) ($H_2AsO_3^-$ and H_3AsO_3) concentrations for each sample and then calculated the ratio of arsenic(III) to total arsenic. They noticed that the ratio was lower during the dry season for each well sampled. Claesson and Fagerberg speculated that the decrease in the ratio was due to oxidation of arsenic(III) and was probably a consequence of a decrease in redox potential. If their speculation is correct, then given sufficient time, the changes in redox potential and probable changes in arsenic concentrations in groundwater would be expected.

In Florida, arsenic-laden chemicals have been applied to land surfaces (e.g. Miller et al., 1933; Todd et al., 2004). These chemicals represent sources that are known to have directly found their way into groundwater. In addition, arsenic-bearing sediments underlie the study area (Lazareva, 2004). For these

reasons, both land use and lithology represent potential sources of arsenic in groundwater. However, this study found that land use was, by far, the most important contributor. It also found that the interaction between lithology and land use also contributed significantly. With this in mind, several questions still need to be addressed. Which land use activities contribute the most to elevated concentrations of arsenic in groundwater? Do land use activities cause the release of naturally occurring arsenic from the underlying rock material into the aquifer? If one considers groundwater extraction to be a land use activity, then Harvey et al. (2006) and Berg et al. (2008) have already addressed this issue. The answer is yes. However, other related questions remain unanswered. If applied at land surface, and if it finds its way to groundwater, how does chemical "X" affect geochemical and/or hydrogeochemical processes that influence the mobility of arsenic from the sediments and the aquifer matrix material? What are the long-term consequences? Since land use is a much greater contributor to elevated arsenic concentrations than lithology, is there a threshold value that could be established that segregates the two sources? For example, if the arsenic concentration from a well is above this theoretical threshold, with what "Y" percent of confidence (preferably a high value), can an investigator state that the predominant cause for the elevated arsenic is derived from anthropogenic (land use) activities? This study was not designed to address these types of questions. However, they represent issues that need further research.

The behavior of arsenic in groundwater is a complex issue. Environmental management practices, designed to effectively mitigate arsenic in groundwater, not only need to consider sources of arsenic from land use, but also need to consider the complex geochemical processes that mobilize arsenic from lithologic sources.

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Appendix A. Well Data

*LU Code represents code used in Factorial Design Experiments.

Latitude	Longitude	Station Name	2006 Land Use Class	MLU	LU Code*	Aquifer System
28 10 24.751 N	82 07 20.151 W	CF Ind CPI 27S	Extractive	Industrial	1	S
28 30 36.774 N	82 10 54.753 W	ROMP 99x-SHA	Residen L Den	Urban/Suburban	-1	S
27 57 59.986 N	82 08 53.262 W	ROMP DV-2 Surf	Utilities	Urban/Suburban	1	S
27 58 00.075 N	82 08 53.155 W	ROMP DV-2 Floridan	Utilities	Urban/Suburban	1	F
28 01 19.323 N	82 43 44.322 W	ROMP TR 14-3 Surf	Recreational	Urban/Suburban	-1	S
27 44 27.182 N	82 08 32.992 W	ROMP 48 WT MONIT	Crop/Pasture	Low Impact	1	S
27 44 27.121 N	82 08 33.238 W	ROMP 48 FLORIDAN	Crop/Pasture	Low Impact	1	F
27 44 27.144 N	82 08 33.212 W	ROMP 48 HAWTH	Crop/Pasture	Low Impact	1	I
28 03 06.049 N	82 29 54.451 W	CARROLLWOOD ELM Sf	Institutional	Urban/Suburban	-1	S
27 52 47.014 N	82 04 21.276 W	290265201	Residen L Den	Urban/Suburban	-1	F
27 54 09.157 N	81 59 58.265 W	KAISER PROCESS	Industrial	Industrial	1	I
27 38 52.351 N	82 03 14.772 W	ROMP 40 HAWTHORN	Shrub/Brush	Low Impact	-1	I
27 51 47.919 N	82 36 12.013 W	FL0000132_MWA-146	Utilities	Industrial	1	S
27 50 17.345 N	82 47 59.477 W	275017082475201	Residen M Den	Urban/Suburban	-1	F
27 51 57.762 N	82 03 22.883 W	W E BUGG-HRS	Residen L Den	Intense Ag	1	I
28 12 10.741 N	82 46 53.640 W	510012701	Residen M Den	Urban/Suburban	-1	F
27 52 58.211 N	82 45 38.315 W	520015601	Industrial	Industrial	1	F
28 09 40.964 N	82 35 46.707 W	CMP KEYSTN WRAP 30-S	Residen M Den	Low Impact	-1	S
28 00 56.197 N	82 19 31.603 W	290186501	Residen L Den	Urban/Suburban	-1	F

28 04 11.194 N	82 31 40.004 W	FL00368820_MWB-01	Utilities	Industrial	1	S
27 54 32.125 N	82 43 13.308 W	ROMP TR 13-2X SUW	Industrial	Urban/Suburban	1	F
27 58 19.132 N	82 32 50.127 W	ROMP TR 12-1Dp (New)	Open Land	Urban/Suburban	1	F
27 44 27.619 N	82 25 21.888 W	ROMP TR 9-3	Crop/Pasture	Urban/Suburban	1	S
27 40 49.142 N	82 28 37.781 W	290164501	Residen M Den	Urban/Suburban	-1	F
27 44 22.482 N	82 27 50.041 W	ROMP TR 9-1	Recreational	Urban/Suburban	-1	F
27 53 01.735 N	82 04 34.549 W	290241401	Hard/Conif Mix	Low Impact	-1	F
27 42 02.018 N	82 23 35.084 W	C.J VONSEE-HRS	Residen L Den	Urban/Suburban	1	I
27 51 59.821 N	82 04 25.103 W	290241701	Residen L Den	Urban/Suburban	-1	F
27 52 20.028 N	82 04 30.932 W	290255701	Residen L Den	Urban/Suburban	-1	F
28 19 03.083 N	82 12 19.442 W	281904082122401	Residen M Den	Urban/Suburban	-1	F
28 21 49.991 N	82 20 56.839 W	510014701	Residen L Den	Urban/Suburban	-1	F
28 20 41.861 N	82 21 49.436 W	510032201	Crop/Pasture	Urban/Suburban	1	F
28 00 07.911 N	82 23 30.727 W	290084101	Industrial	Industrial	1	F
28 34 54.765 N	82 10 20.203 W	600004301	Residen L Den	Urban/Suburban	-1	F
28 48 50.569 N	82 31 51.352 W	90005501	Residen L Den	Urban/Suburban	-1	F
28 29 54.146 N	82 18 52.142 W	270058801	Hard/Conif Mix	Low Impact	-1	F
28 17 35.215 N	82 39 02.133 W	510012301	Residen M Den	Low Impact	-1	F
28 22 21.442 N	82 38 01.772 W	510016301	Residen L Den	Urban/Suburban	-1	F
28 28 54.530 N	82 18 18.846 W	2700052801	Residen L Den	Urban/Suburban	-1	F
28 29 25.895 N	82 21 54.420 W	270043101	Hard/Conif Mix	Low Impact	-1	F
28 39 25.127 N	82 27 23.424 W	ROMP 107	Crop/Pasture	Low Impact	-1	F
28 30 24.204 N	82 32 59.441 W	SPR HL BELL TOW SH	Residen M Den	Urban/Suburban	-1	S

28 33 22.289 N	82 24 15.633 W	ROMP B105 SH FL	Industrial	Urban/Suburban	1	F
28 14 45.559 N	82 33 52.861 W	E. STARKEY CD 3AE	Cypress	Urban/Suburban	-1	S
27 54 21.467 N	82 16 48.038 W	275349082164701	Nurs/Vineyard	Intense Ag	1	I
28 14 25.160 N	82 19 25.330 W	ROMP 85 AVON PARK	Residen M Den	Urban/Suburban	-1	F
28 19 17.082 N	82 42 06.670 W	ROMP TR 17-1 DEEP	Open Land	Urban/Suburban	1	F
28 04 29.258 N	82 31 53.691 W	W.VILLIAGE Dr. FL	Residen M Den	Urban/Suburban	-1	F

Appendix A. (Continued) Well Data

Note: DEP is the Florida Department of Environmental Protection; LSE is Land Surface Elevation; MSL is Mean Sea Level; Avg is Average.

Station Name	**Aquifer Category**	**Cell**	**Agency**	**LSE (MSL)**	**Well Depth ft**	**As (Dry) µg/L**	**As (Wet) µg/L**	**As (Avg) µg/L**	**DtoW (Wet) ft**	**DtoW (Dry) ft**
CF Ind CPI 27S	-1	K	DEP	90	10	7.20	0.30	3.75	6.10	7.50
ROMP 99x-SHA	-1	F	DEP	75	61	0.30	0.30	0.3	39.65	46.8
ROMP DV-2 Surf	-1	N	DEP	100	35	0.35	0.30	0.33	3.65	6.10
ROMP DV-2 Floridan	1	N	DEP	100	130	0.62	0.44	0.53	38.30	56.00
ROMP TR 14-3 Surf	-1	P	DEP	95.23	30	0.36	0.30	0.33	6.90	8.15
ROMP 48 WT MONIT	-1	F	DEP	101	14	0.30	0.070	0.30	9.50	11.52
ROMP 48 FLORIDAN	1	F	DEP	101.04	541	0.42	0.30	0.36	61.80	92.87
ROMP 48 HAWTH	1	F	DEP	101	61	2.29	2.15	2.22	12.90	17.68
CARROLLWOOD ELM SF	-1	0	DEP	46.1	17	0.30	0.30	0.30	9.00	11.61
290265201	1	0	DOH			0.30	0.30	0.30		
KAISER PROCESS	1	M	DEP	120	175	12.00	12.90	12.45		

ROMP 40 HAWTHORN	1	S	DEP	137.94	180	0.30	0.30	0.3	15.20	16.82
FL0000132_MWA-146	-1	Q	DEP		8	4.83	5.22	5.03	3.50	3.65
275017082475201	1	Q	DEP		187	0.30	0.30	0.30		
W E BUGG-HRS	1	S	DEP	108	300	2.13	2.76	2.45		
510012701	1	I	DOH			0.39	1.48	0.94		
520015601	1	P	DOH			0.43	3.01	1.72		
CMP KEYSTN WRAP 30-S	-1	I	DEP	45	27	0.30	0.62	0.46	10.80	15.10
290186501	1	O	DOH		150	1.00	1.10	1.05		
FL00368820_MWB-01	-1	O	DEP	47.3	18	0.33	0.50	0.42	7.75	7.77
ROMP TR 13-2X SUW	1	P	DEP	17.49	279	0.30	26.00	13.2	14.6	15.7
ROMP TR 12-1Dp (New)	1	O	DEP	7	132	1.17	2.61	1.89	4.90	4.61
ROMP TR 9-3	-1	R	DEP	6.57	25	1.66	0.39	1.03	5.60	6.00
290164501	1	R	DOH			0.30	0.30	0.30		
ROMP TR 9-1	1	R	DEP	3.86	288	0.30	0.30	0.30		
290241401	1	N	DOH			2.73	3.13	2.93		
C.J VONSEE-HRS	1	R	DEP	42	200	0.30	0.30	0.30		
290241701	1	S	DOH			0.30	0.30	0.30		
290255701	1	S	DOH			1.09	1.00	1.05		
281904082122401	1	K	DEP		115	0.30	0.11	0.30		
510014701	1	J	DOH			7.29	5.48	6.39		
510032201	1	J	DOH			4.91	4.44	4.68		
290084101	1	O	DOH			74.8	20.2	47.50		
600004301	1	F	DOH			1.94	2.03	1.99		

90005501	1	B	DOH			0.30	0.30	0.30		
270058801	1	G	DOH			0.30	0.30	0.30		
510012301	1	I	DOH			11.9	10.20	11.05		
510016301	1	H	DOH			0.76	1.02	0.89		
2700052801	1	F	DOH			12.8	16.80	14.80		
270043101	1	G	DOH				17.60	17.60		
ROMP 107	1	B	DEP	116.03	240	0.30	0.30	0.30	107.95	109.95
SPR HL BELL TOW SH	-1	G	DEP	37	35	0.30	0.30	0.30	16.45	19.95
ROMP B105 SH FL	1	G	DEP	102	95	0.30	0.51	0.41	69.70	72.80
E. STARKEY CD 3AE	-1	S	DEP	45.9	20	0.42	0.53	0.48	2.81	7.77
275349082164701	1	N	DEP		240	0.42	0.30	0.36		
ROMP 85 AVON PARK	1	J	DEP	107.94	505	0.30	0.30	0.30	35.85	37.56
ROMP TR 17-1 DEEP	1	F	DEP	10.91	139	8.36	10.20	9.28	8.20	7.49
W.VILLIAGE Dr. FL	1	O	DEP	42.85	52	0.32			8.60	8.90

Appendix B. Sampling and Analytical Protocols

Background

Each water sample will be analyzed for major cations (Ca, Mg, Na, K), major anions (Cl, SO4, PO4, NO2, NO3, Br, F) plus TDS, Alkalinity, Temp., pH, DO, Sp. Cond.) and trace metals (50 metals - research grade). All samples will be delivered to Activation Labs near Ontario, Canada. FGS, the Groundwater section, and SWFWMD are funding all equipment, supplies, shipping, and sample analysis for the study. WMS is contributing sampling organization and coordination, preparation, orientation, site reconnaissance, Quality Assurance and Quality Control (QA/QC), and sampling for the study.

Field Procedures

Introduction

Navigate to the designated lat/long, and record its coordinates in the Trimble GeoXT data logger. Field measurements (pH, DO, specific conductance, temperature, etc.) will be measured. **Collect the field measurements prior to collecting arsenic samples**. If a representative arsenic sample cannot be accessed at the lat/long provided, (due to lack of permission, inactive well, etc.), contact the Project Manager or the Watershed Monitoring Section Quality Assurance Officer (QAO) for guidance.

Field Sheets and Custody Sheets

All information is documented on the “Arsenic Groundwater Study” field sheet. All sections must be completed with nothing left blank; indicate “NA” or draw a line through any section that is not applicable.

All samples need to be documented on the “Arsenic Groundwater Study” custody sheet as a single entry for each site. Place a station label in the appropriate space, enter the final (primary) field measurement information (pH, DO, etc.) after reaching stability, record the collection date and time for the cations and anions, and note the matrix as “water”. Complete the preservation section of the custody sheet by confirming that the water samples were properly acidified (as applicable) and placed on ice. The sample collection time entered on the custody sheet (and on the sample container) must match the “Time Sampling Begins” recorded on the front of the field sheet.

If a QA/QC blank is collected, it must be recorded on the custody sheet as a separate entry from the collected water samples. Place a label in the appropriate space, enter “NA” or place a dash for the field measurement information (pH, DO, etc.), record the collection date and time, and note the matrix as

"water". Complete the preservation section of the custody sheet by confirming that the QA/QC sample was properly acidified and placed on ice. See QA/QC section below for more information.

Label Sample Containers

Two water sample containers are included in each kit; both are 125 mL Nalgene bottles. Place a station identification bar code label vertically on each of the two sample bottles. For both bottles, use a permanent marker to write the sampler name, date and time (24 hour format) on the container.

The QA/QC blank kit is comprised of one 125 mL Nalgene sample container per 20 sample sites; all containers should be labeled with a station identification label ("QA/QC Blank"), along with the sample collection date and time. Therefore, a total of three blanks/48 sites will be collected.

Replacing a pH probe with a pH/ORP probe

After replacing the pH probe with a pH/ORP probe, press the menu key on the datalogger. This will add the ORP probe to the drop-down menu screen; otherwise, it might not show up on this menu. After you select ORP, press <enter>.

"Calibration:"

Successful "calibration" of the ORP probe depends on successfully calibrating the accompanying pH sensor first, as well as observing the ambient temperature during the second part of the process.

1. Conduct a 3-point calibration for pH using pH 7, 4, and 10 reference standards, in that order.
2. Rinse the probe with deionized (DI) water.
3. Next, go outside to continue the ORP calibration because:

    Zobell's Solution is TOXIC (Potassium ferrocyanide & Potassium ferricyanide)

    Wear protective eyewear, gloves, and a mask. Don't inhale!

    The process should take place in a shaded area to preclude the probe and Zobell's solution heating up.

4**.** Read and note the outside temperature on the datalogger.
5. Rinse the probe with enough Zobell's solution to cover the probe, and discard the solution into a special waste container just for Zobell's solution.
6. Fill with enough Zobell's to cover the pH/ORP probe head when the sonde is probe down (very important!).

7. Screw cap onto probe cover, invert the sonde so that probe is down, and select ORP on the datalogger screen.

8. Immediately prior to ORP calibration, record the ORP value in Run mode. This serves as the CCV. Continue on to calibration.

9. The datalogger screen will provide a space to enter the correct mV value. To find this value, match the ambient temperature with the correct mV value on the accompanying table[1] (see example below). Do not interpolate; use the value closest to the ambient temperature.

Temp	Ag/AgCl
in ^{o}C	in mV
20	237.5

10. Wait until mV value stabilizes within +- 10 mV, although it may actually stabilize within +- 50mV, and still be considered OK to use.

11. Record the temperature and the mV reading on the calibration sheet. If there are problems with stabilizing the mV reading, please note that also.

12. After calibration, put the ORP probe into "Run" mode for the ICV. Discard the used Zobell's solution into the Zobell's waste container.

14. Calibrate once per week, and run the CCV right before the calibration. Essentially, this is a balancing act between assuring accuracy and the potential of degrading the Zobell's solution when opened. That is, conducting frequent calibration of the probes will, by its nature, result in the degradation of the Zobell's solution when opened.

15. If the ORP probe values appear to "drift" over a period of time, "calibrate" the probe in use and the backup probe; compare their values to determine whether it is the probe or the Zobell's solution that needs to be replaced.

16. If possible, take a backup sonde that includes an ORP probe into the field. The ORP probe should be "calibrated" on this backup also.

Storage of Zobell's Solution

Because Zobell's solution is highly reactive with light, temperature fluctuations, and air, it is best kept in small quantities in lightproof containers within a temperature-controlled environment. It should be capped apped immediately after each usage, and stored right away. According to knowledgeable

sources, it should not be carried into the field, due to its toxicity and the potential of accelerated degradation.

As with standards, buffers, and acids, the lot number of the Zobell's solution and the date it is opened should be documented in the Standards & Buffers Log. The date of first use should also be written on the bottle with a waterproof Sharpie.

Field Measurements

1. Navigate to the site's designated lat/long, and/or street address. Use all known information about the well to ensure that it's the correct well. If there are any doubts concerning the well's identity, contact the Project Manager to discuss options. If the well is clearly the selected one, but is inoperative or destroyed, select an alternate well from the selection sheet provided by R. Copeland.
2. Record the lat/long coordinates in the Trimble GeoXT data logger.
3. Purge the well as described in Section 4, Ground Water Sampling Protocols, January 2009 WMS Sampling Manual.
4. During the purging and stabilization process, pay close attention to the dissolved oxygen measurements as these will often predict the range of values provided by ORP field measurements. For example, if the percent saturation of D.O. is high (around 20%), the ORP mV value is likely to be positive rather than negative. A low percent saturation D.O. should result in a negative mV reading. The ORP measurement may take 15-30 minutes to stabilize. If the percent saturation D.O. value and the ORP mV value are contradictory, it may mean that the ORP or the DO probe(s) is (are) "drifting", at which point the backup sonde(s) should be used.
5. The Standard Operating Procedures (SOPs) for Purging Completion (pgs. 25-26) of Section 4, WMS Sampling Manual, should be followed.

Collection of Lab Analytes

1. Prior to collecting the samples, use a Sharpie to write the sampler's name, date, and time (24 hour format) on both bottles.
2. Once the well measurements have stabilized, fill the 125 mL bottle labeled CATION & Metals sample. Preserve with nitric acid, test with a narrow-range pH strip to ensure it's properly acidified, and put on ice.
3. Attach the barrel filter and flush with 250 mL of sample water. Completely fill the 125 mL bottle labeled ANION and Alkalinity sample so that there is no headspace. Preserve only with ice.

Field Cleaning

Clean pumps and equipment between each well, either in the field or at the office, and document in the Equipment Cleaning Log Book (January 2009 Sampling Manual, pg. 118).

1. Protect equipment - use ground cover if in field.
2. Fill dedicated container with sudsy water, and pump 3 volumes through tubing.
3. Clean with soapy water and brush, and use sudsy water to clean outside.
4. Pump tap water, then DI water through tubing.
5. Omit isopropanol and acid rinse.
6. Protect clean pump.

FLUWID Tags

If the well does not have a FLUWID (Florida Unique Well Identification) tag, please put three tags of the same number in conspicuous places on the well, and record the FLUWID number. Do not attach FLUWID tags if the well already has one or several. Instead, record the number of the original.

QA/QC Blanks

During the project, a total of six QA/QC blanks will be collected for the arsenic samples, three for each set of 48 sites, e.g. during each season.

Field Reference Samples (FRSs)

During the project, a total of ten FRSs will be collected for the arsenic samples, five for each set of 48 sites, e.g. during each season.

Shipping and Handling

Pack the samples following the procedures outlined in the Status and Temporal Variability Monitoring Networks Sampling Manual in the custody and shipment section, making sure to include the white copy of the custody sheet and the letter to Activation Labs. The outside pocket on the cooler should contain the Federal Express Inc. (FedEx) international waybill and three copies (one signed original) of a completed FedEx customs document. The coolers should be delivered to Activation Labs in Ancaster, Ontario, Canada. The analytical holding times for the samples permit the opportunity to collect samples throughout the week and ship all coolers at one time at the beginning of the next week. All samples must be kept at <=6 deg. C; add ice as necessary until shipping. After the shipment is sent, the samplers FAX a copy of the custody sheet and the letter to the analytical laboratory via the FGS.

Laboratory Procedures

Hydrogeochemistry cation analyses (from Activation Laboratories Ltd.)

Samples must be acidified prior to analysis. Water samples are analyzed by Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS. A blank and two water standards are run at the beginning and end of each group of 32 samples. A reagent blank is run at the beginning of the group and every tenth sample is run in duplicate. If instrument suppression occurs, sample(s) affected are re-run at appropriate dilutions until response is normal. Dilution factors will increase by the same factor that samples were diluted. For analysis of marine waters or brines, detection limits will be correspondingly elevated depending on the dilution necessary to run the water samples. Sample introduction, ionization, detection and data output are controlled by the system computer. Values which exceed the upper limits should be analyzed by Code 6 inductively coupled plasma - optical emission spectrometer (ICP/OES).

The ICP technique relies on placing the sample material into solution using specific partial leaches, single acids, mixed acids or fusion techniques using fluxes. The sample solution is then introduced into a radio frequency excited plasma (~8000°K). Atoms within the samples are excited to the point that they emit wavelength-specific photons or light which is characteristic of a particular element. The number of photons produced is directly related to the concentration of that element in the sample.

Ion Chromatography

Un-acidified water samples are analyzed using the DIONEX DX-120 Ion Chromatography System to determine and quantify a group of seven anions. This analysis is applicable to concentrations less than 75 mg/L for Cl, NO_2 and NO_3; less than 50 mg/L for F; less than 125 mg/L for PO_4; less than 250 mg/L for Br and less than 375 mg/L for SO_4. Samples exceeding this range (with high total dissolved solids) must be diluted to avoid over-saturation. Measurement uncertainty is evaluated and controlled by an appropriate quality assurance program, including the use of regular laboratory duplicates of samples and verification of the precision/calibration of the instrument through regular runs of various primary dilution standard solutions.