FINAL

FINAL TECHNICAL REPORT

Arsenic Mobilization in Two Suwannee Limestone Aquifer Storage Recovery Systems

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Contents

Appendices

Figures

Tables

Executive Summary

Arsenic mobilization during cycle testing represents a major challenge to aquifer storage recovery (ASR) feasibility, particularly for storage in permeable zones of the Suwannee Limestone. Strategies to minimize arsenic mobility require definition of the major geochemical, microbiological, and hydraulic controls. In this report, we examine two large water-quality datasets obtained during cycle testing at contrasting ASR systems, both of which store water in the Suwannee Limestone. In addition, two complementary investigations also were completed. First, microcosm experiments were performed to simulate native microbiological physiology and community changes in mixed ground water samples. Second, detailed lithological characterization of Suwannee Limestone samples were obtained from the Tampa-Rome Avenue Park (TRAP) ASR system, using scanning electron microscopy and trace element analyses.

The TRAP ASR system dataset consists of water-quality analyses from six cycle tests, conducted between 2002 and 2006. Prior to recharge, water is disinfected using ozone. Oxic water (dissolved oxygen at supersaturation) reacts with pyrite in the Suwannee Limestone during the ASR cycle test, releasing arsenic. A consistent pattern of arsenic concentrations occurs at this ASR system throughout each cycle test, consisting of the following features. During recharge, arsenic is released by pyrite oxidation. However, arsenic is rarely detected at monitor wells located approximately 350 feet (ft) from the ASR well during recharge or storage phases. During recovery, a consistent pattern of arsenic concentration is observed at 5 of 8 ASR wells. Arsenic concentrations increase, reaching an asymptote value after approximately 50 percent recovery (about 80 million gallons [MG] recovered volume). During successive cycles, the asymptote arsenic concentration declines exponentially. This pattern appears consistently at 5 of 8 wells in the TRAP ASR system, during cycles 2 through 6. This reproducible pattern is observed throughout the wellfield, and suggests that arsenic is being removed progressively from the flowpath during successive ASR cycles by extensive pyrite oxidation. A predictive model simulates arsenic concentrations during cycles 7 through 9. In this model, 2 ASR wells show asymptote arsenic concentrations below 10 micrograms per liter (µg/L) during cycle 7. Other ASR wells will show declining arsenic concentrations through cycle 9, but will still remain above the 10-µg/L maxima.

The Peace River Facility ASR system at Wellfield 2 (PRF ASR WF2) dataset consists of water-quality analyses from cycles 2 through 5 conducted between 2003 and 2006. Prior to recharge, water is disinfected using chloramines treatment. Compared to the TRAP ASR system, recharge water is oxic, but generally shows dissolved oxygen concentrations at or near saturation. PRF ASR WF2 recharge water is considered less oxidizing than that at TRAP. A consistent pattern of arsenic concentrations occurs at this ASR system, but the pattern differs from the one at TRAP. During recharge, arsenic is released by pyrite oxidation, and like TRAP, arsenic is only rarely detected at monitor wells approximately 350 ft away from the ASR well. During recovery, arsenic concentration shows a linear relationship with recovered water volume. During successive cycles, the slope of this linear relationship declines. Comparison of data from successive cycles at a common point (at a recovered volume of 50 MG, or at approximately 80 percent recovery cycles 2 through 4). This relationship indicates that arsenic concentration will decline below 10 µg/L between cycles 5 and 7, at 7 of 12 ASR wells.

The geochemical controls on arsenic mobility at both ASR systems undoubtedly relate to redox evolution of the aquifer system throughout an ASR cycle. Unfortunately, water-quality data to quantify aquifer and ground water redox conditions are lacking. Arsenic sequestration during recharge and release during recovery are inferred at both systems using existing water-quality data, geochemical modeling, and interpretations from other ASR systems in south Florida.

Arsenic sorption likely occurs by iron oxyhydroxide or other surface that is stable under oxic conditions during recharge. Arsenic adsorption and complexation by metal oxyhydroxide surfaces is well-known in the geochemical literature. Iron oxyhydroxides are not detected (less than 5 percent by weight) in the Suwannee Limestone, but trace abundance of these surfaces represents a sufficient mass to adsorb low (parts per billion [ppb]) arsenic concentrations along the flowpath between ASR and monitor wells.

Arsenic release occurs when the iron oxyhydroxide surfaces become unstable. Sulfate-reducing conditions that evolve during storage and recovery are proposed as the mechanism for destabilizing the adsorbed arsenic. Reductive dissolution of iron oxyhydroxide surfaces is also known in the geochemical literature, typically at significantly negative Eh values (approximately -250 millivolts). Reductive dissolution leading to arsenic release is the mechanism that explains increasing arsenic concentrations in ASR wells during recovery, without significant detections of arsenic at monitor wells. Data that support this geochemical control on arsenic include: 1) a pulse of iron (up to 200 µg/L) that coincides with increased arsenic during recovery at TRAP and PRF ASR WF2; 2) preliminary geochemical model simulations at the Olga-Lee County ASR system (where the redox couple sulfate/sulfide concentrations were measured); and 3) the presence of hydrogen sulfide in samples obtained early during recovery at TRAP, suggesting that sulfate-reducing conditions prevail during storage and recovery.

The different patterns of arsenic concentrations shown at TRAP and PRF ASR WF2 probably result from the magnitude of oxic conditions during recharge. At TRAP, more extensive oxidation occurs during each cycle due to higher initial dissolved oxygen concentrations. More arsenic is released, sorbed, then ultimately removed from the flowpath during recovery. Our working “scorched earth” hypothesis appears to be fulfilled at TRAP.

Microcosm experiments were conducted at the US Geological Survey to quantify changes in microbial physiology and community that result from mixing between native Floridan Aquifer System (FAS) water and recharge water. Experimental parameters showed consistent changes in the microcosms over a 2-week duration. Specifically, these microcosms showed increased dissolved oxygen consumption rates, changes in bacterial community-level physiological profiles (CLPP) that differed from those of the end-member microcosms, greater bacterial community productivity, and changing bacterial community diversity compared to that in pure end-member microcosms. The overall conclusion from these data is that mixing between recharge and native FAS waters stimulates microbial growth and replication while the redox environment is still largely under oxic conditions.

1.0 Arsenic Concentration Trends in Recovered Water at the Tampa-Rome Avenue Park (TRAP) ASR System

1.1 Introduction

Water-quality data were compiled from cycle tests 2 (2002) through 6 (2006) at the Tampa-Rome Avenue Park (TRAP) ASR (aquifer storage recovery) system. TRAP water-quality datasets consist of field parameters (specific conductance, pH, temperature, and Oxidation-Reduction Potential, [ORP]) and some major constituents (alkalinity, chloride, sulfate, fluoride), trace constituents (iron, manganese), plus species of regulatory concern (arsenic, total trihalomethanes, gross alpha, and radium 226+228). To evaluate water-quality changes as recovery proceeds, concentrations are plotted as a function of total volume recovered (in million gallons [MG]), or percent recovery. Percent recovery is calculated as the volume of water recovered at the sampling event/total volume of water recharged during that cycle, multiplied by 100. At the TRAP ASR system, typical recharge and recovery cycles target approximately 100 percent recovery of the stored water, regardless of water quality since this water is blended with other water prior to distribution and use as a potable water supply. Because arsenic mobilization and transport are of primary interest at this ASR system, arsenic is the only constituent considered in the following discussion. All water-quality data from TRAP appear in an Excel spreadsheet entitled "Tampa_RomeAve_CycleTests_Alldata" (CD).

The TRAP ASR system consists of 8 ASR (recharge/recovery) wells and 10 storage zone monitor wells (Figure 1). Prior to distribution in the ASR system, surface water is treated at the David L. Tippin Water Treatment Facility (DLT WTP) to comply with Federal and State safe drinking water-quality criteria, and is disinfected using ozone. Treated surface water from the facility travels approximately 3 miles to the TRAP ASR system, where it is recharged and stored in permeable zones within the Suwannee Limestone. Recharge water is stored at depths between 300 and 430 ft below land surface (bls) (Figure 2). Recharge water quality is characterized by low concentrations of dissolved constituents (Appendix A), but does show dissolved oxygen concentrations ranging between 10 and 20 milligrams per liter (mg/L) (median value 12.4 mg/L), and therefore is in an oxidant (electron-acceptor) condition.

Six ASR system cycle tests have been completed at the TRAP ASR system between 2002 and 2006 (Figure 3). Cycle 7 recovery began in March 2007 but results were not available at the time this draft report was published. During each cycle, approximately 1 billion gallons of ozone-treated water are recharged seasonally (May to October) in the wellfield, stored for approximately 4 to 6 months, then recovered during the dry season (March-May). Volumes recovered at individual ASR wells typically range between 100 and 150 MG per cycle, with more uniform recovery volumes recorded during each successive cycle. By cycle 6, 123 +/- 4 MG were recovered from each of eight ASR wells. Percent recoveries for ASR wells at TRAP

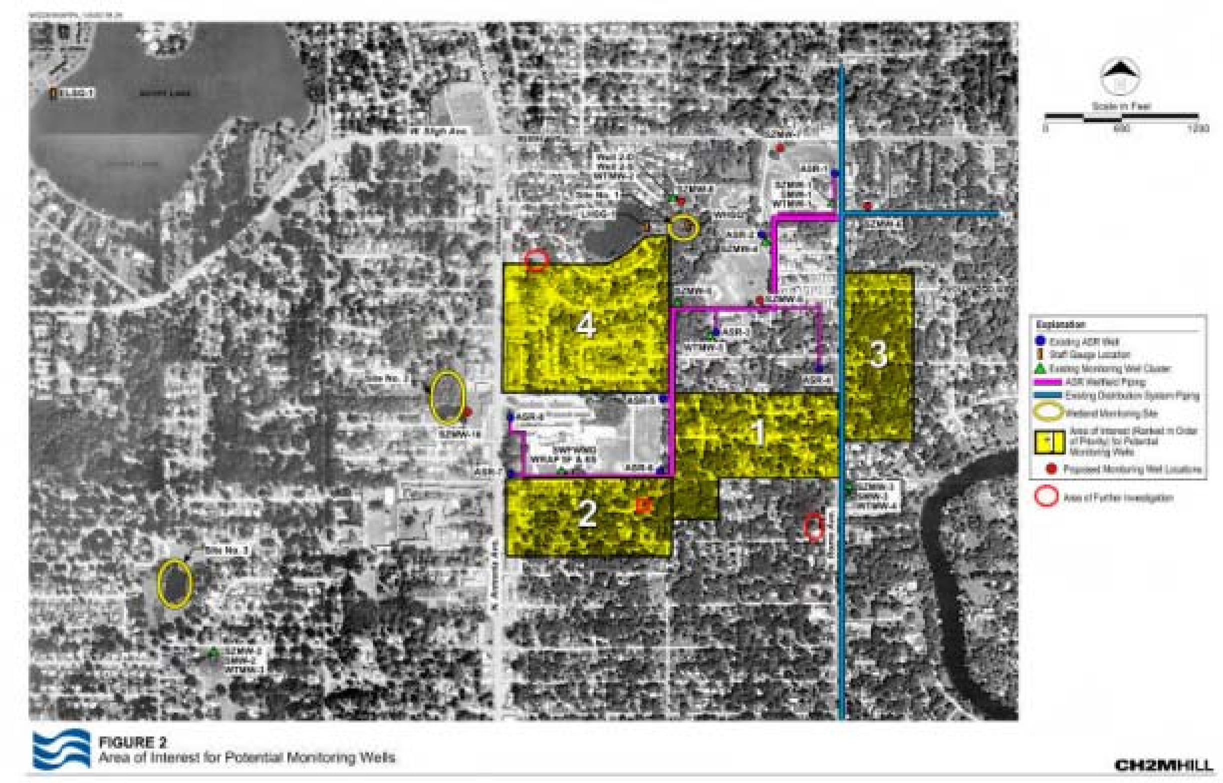

FIGURE 1
Locations of ASR Wells and Existing and Proposed Monitor Wells at the Tampa-Rome Avenue Park ASR System. Figure from CH2M HILL (2006)

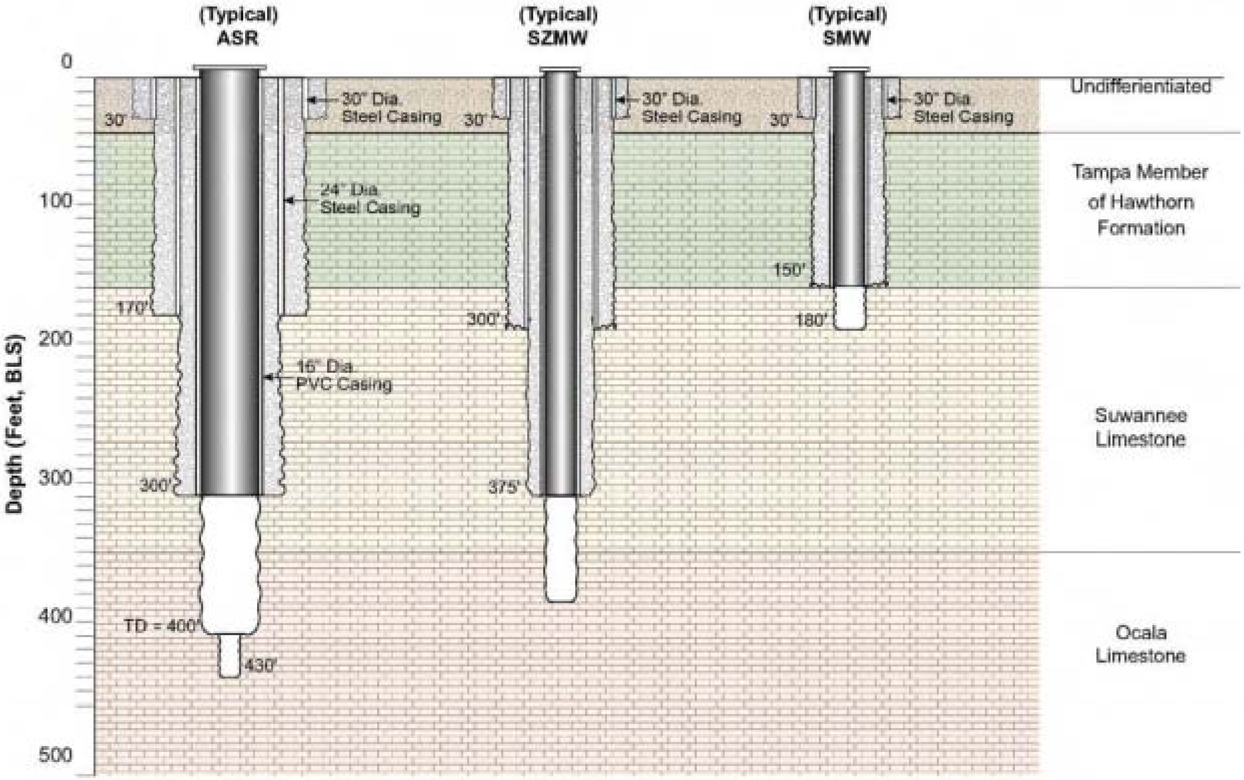

FIGURE 2

Representative Geologic Cross-Section Across Tampa-Rome Avenue Park ASR System

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generally range between 80 and 120 percent. However, during later cycles the ASR system was operated to recover approximately 100 percent at each well, in an attempt to reduce arsenic concentrations in the storage zone prior to beginning the next recharge event. The cumulative pattern of recharge and recovered volumes for the entire TRAP wellfield shows this consistent recharge-recovery pattern (Figure 3; Appendix E).

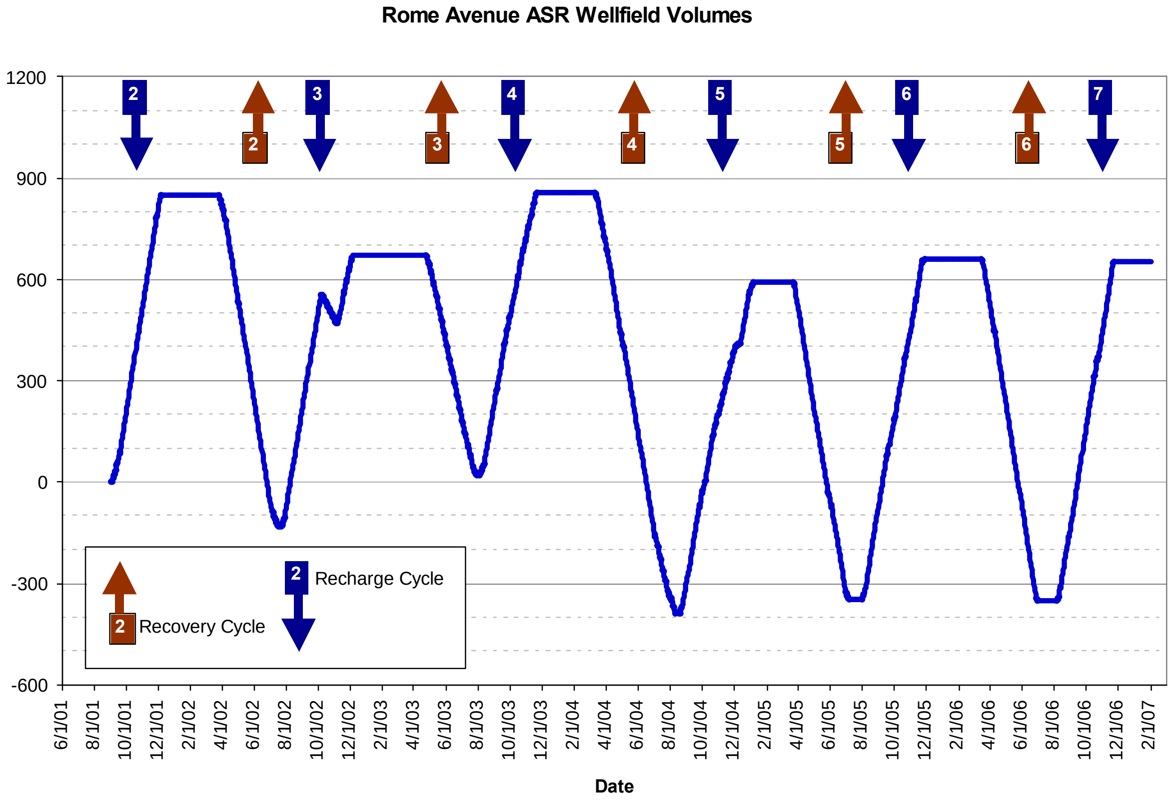

FIGURE 3
Diagram Showing Cumulative Wellfield Recharge and Recovery Volumes through 6 Cycles at the Tampa-Rome Avenue Park ASR System

1.2 Arsenic Trends During Successive TRAP ASR Cycle Tests

Arsenic concentrations were measured regularly throughout each cycle test (1999 to present), in samples from both ASR and monitor wells at TRAP. At ASR wells, arsenic concentrations in recovered water regularly exceeded the Federal and State maximum contaminant level (MCL) (0.010 mg/L). The patterns of measured arsenic concentration during recovery in successive cycles at each ASR well form the basis of a model to simulate and predict arsenic concentrations during later cycles at the TRAP ASR system.

Characteristic patterns of arsenic concentrations are observed as recovery proceeds at each ASR well (Figure 4). However, trends observed during cycle 2 differ from later cycles. Cycle 2 data exhibit a "bell curve" shape in most wells, compared to later curves that show curves that rise to an asymptote. Cycle 2 trends differ from successive cycles primarily because different disinfection methods were used. In 2002, chloramine treatment was used to disinfect water prior to recharge. Recharge water-quality data from 2001 (in Tampa_Rome_Cycle Tests_alldata.xls) suggest less oxidizing conditions, characterized by negative ORP values and dissolved oxygen concentrations less than 7 mg/L. From cycle 3 (2003) to present, ozone treatment was used as the primary disinfectant of recharge water. Recharge water-quality data during ozone treatment show greater dissolved oxygen concentrations and high, positive ORP values (CD and Appendix A). Introduction of a more powerful oxidant into the storage zone affected the redox environment of the aquifer during recharge, and enhanced arsenic mobility. Arsenic released during recharge becomes more mobile during recovery, for reasons that will be discussed in Section 1.4. The result is a reproducible pattern of arsenic concentrations during recovery in cycles 3 through 6. In subsequent discussion and interpretations, the patterns of arsenic concentrations in cycle 2 are considered atypical for the TRAP ASR system, and are not included in the following modeling and analysis.

During recovery in cycles 3 through 6, trends in arsenic concentration more closely resemble an exponential curve that reaches an asymptote. The asymptote occurs generally after 70 percent recovery, and when total volumes recovered exceed 70 MG. This trend appears at all ASR wells except ASR-8, and is observed regardless of the x-axis parameter used (percent recovery or volume recovered). The most important feature of these trends is that the arsenic concentrations at the asymptote of each curve indicate a trend of lower arsenic concentrations in recovered water with each successive cycle. This pattern of declining maximum arsenic concentration is observed in plots of raw data (Figure 4), and is observed at 7 of 8 TRAP ASR wells. Because the pattern is reproduced in most ASR wells in the wellfield, these data and trends form the basis for model development.

A significant observation for the TRAP ASR system is that arsenic remains below the MCL throughout each cycle in all monitor wells except SZMW-1. Water-quality data collected during 6 cycle tests at all 5 storage zone monitor wells (SZMW-1 through 5; Tampa_Rome_Cycle Tests_alldata.xls) provide limited information about the distance that arsenic is transported away from the ASR well during recharge. TRAP monitor well samples generally show arsenic concentrations below the MCL or below detection level (0.003 mg/L) throughout 6 cycle tests. Only at SZMW-1 do maximum arsenic concentrations exceed the MCL, and these generally range between 0.020 and 0.030 mg/L. SZMW-1 is located approximately 190 ft south of ASR-1, and arsenic is transported along a flowpath in this area. In comparison, SZMW-4 is within 150 ft of ASR-2, and yet few samples exceed 0.010 mg/L (14 of 270 samples over 4 years). The few MCL exceedances in SZMW-1 occur during recharge and storage, not during recovery in the well. It is possible that preferential flow paths in fractured Suwannee Limestone exert some control on recharge water, and hence arsenic mobility between ASR-1 and monitor well SZMW-1.

SZMW-5, located approximately 350 feet from ASR-3, showed declining peaks of 0.021 mg/L (2003), 0.012 mg/L (2003), and 0.001 mg/L (2004) before showing a slight increase in 2005 to 0.003 mg/L. In all cases SZMW-5 rose during recharge events and quickly declined once recovery from the ASR wellfield commenced. Arsenic concentrations are below the MCL in all other monitor well samples throughout each cycle.

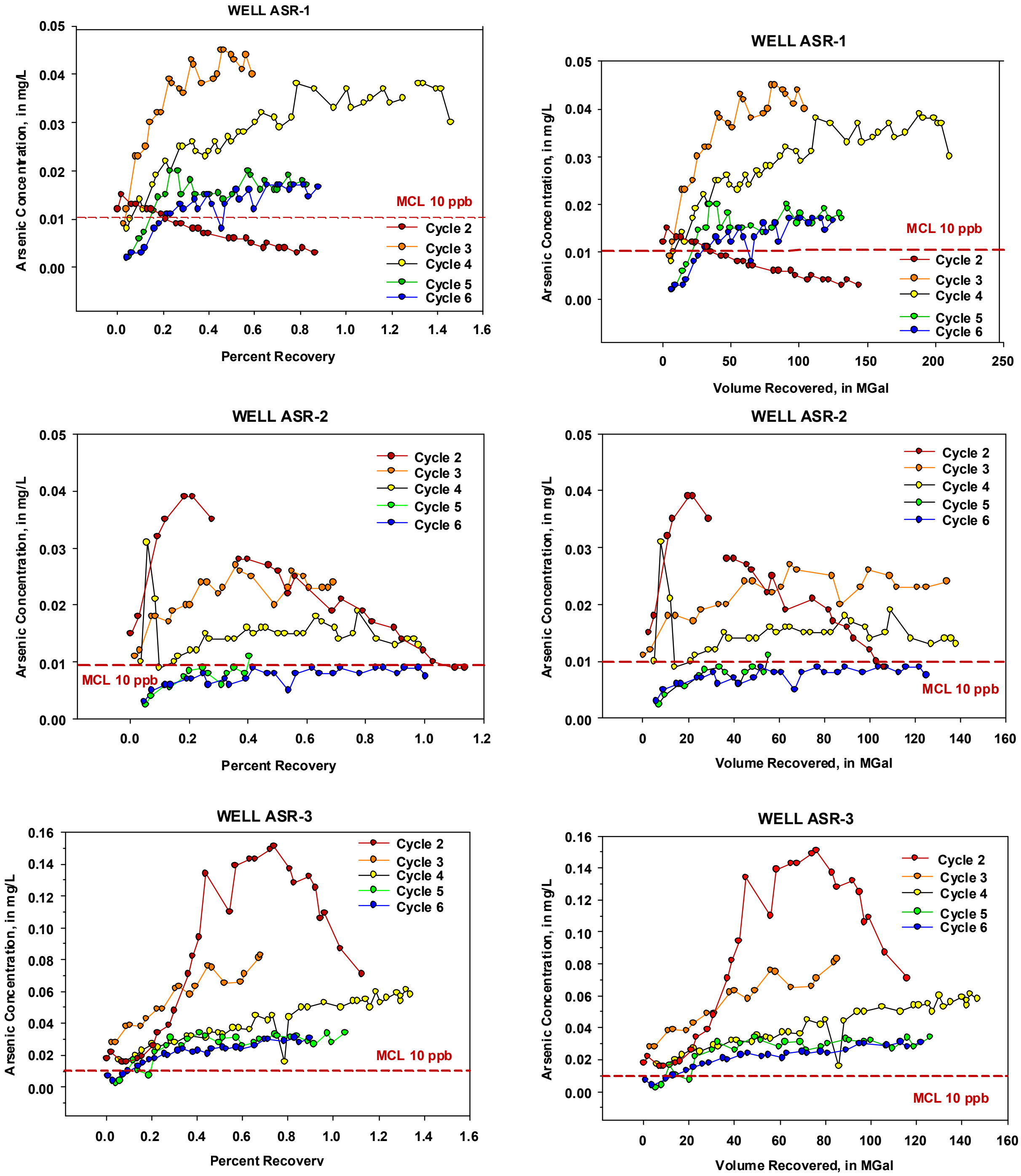

FIGURE 4
Plots Showing Arsenic Concentration Versus Percent Recovery (left) or Volume Recovered (right) During Recovery, as Measured in ASR Well Samples at the Tampa-Rome Avenue ASR System

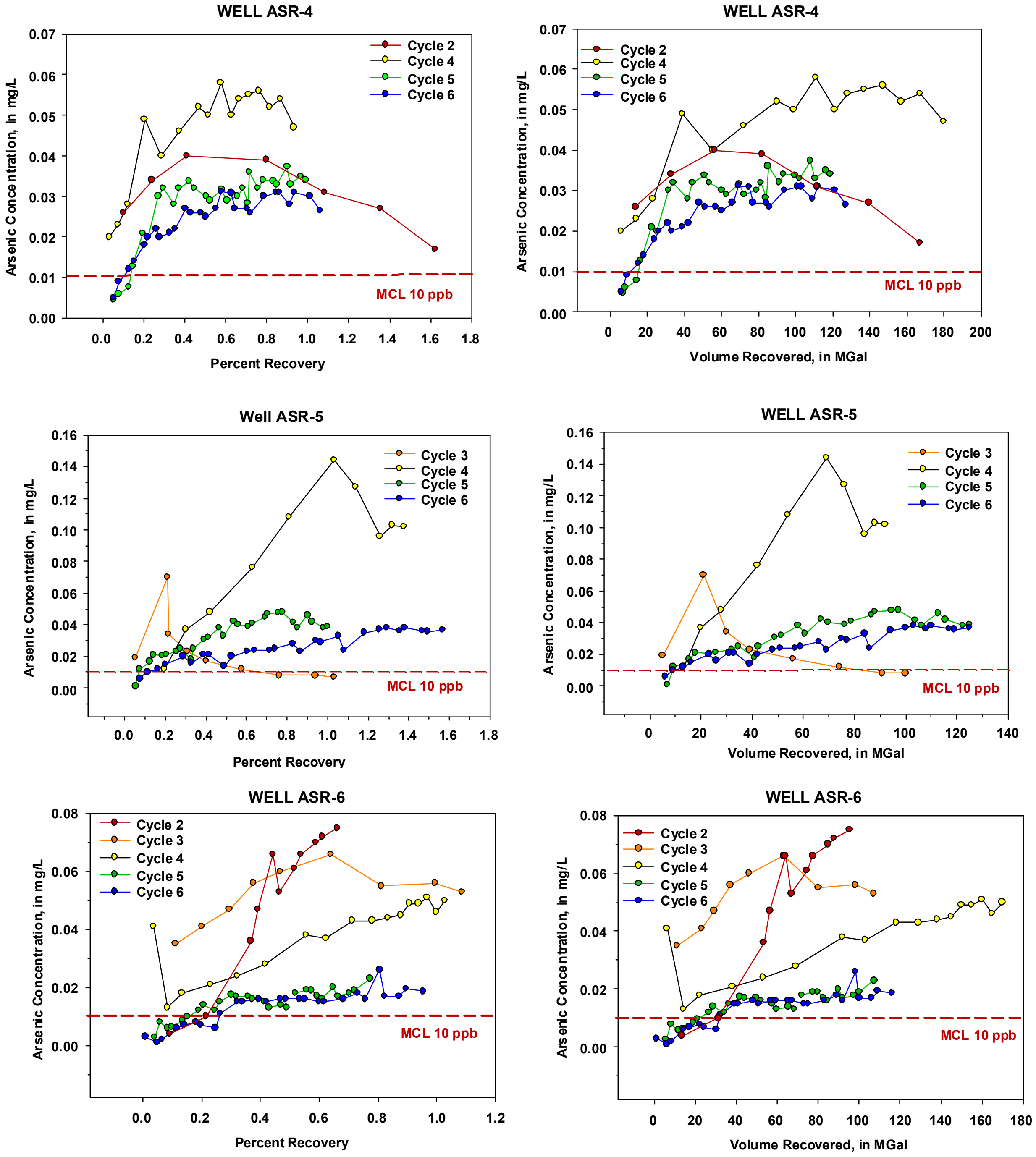

FIGURE 4 (*CONTINUED*)
Plots Showing Arsenic Concentration Versus Percent Recovery (left) or Volume Recovered (right) During Recovery, as Measured in ASR Well Samples at the Tampa-Rome Avenue ASR System

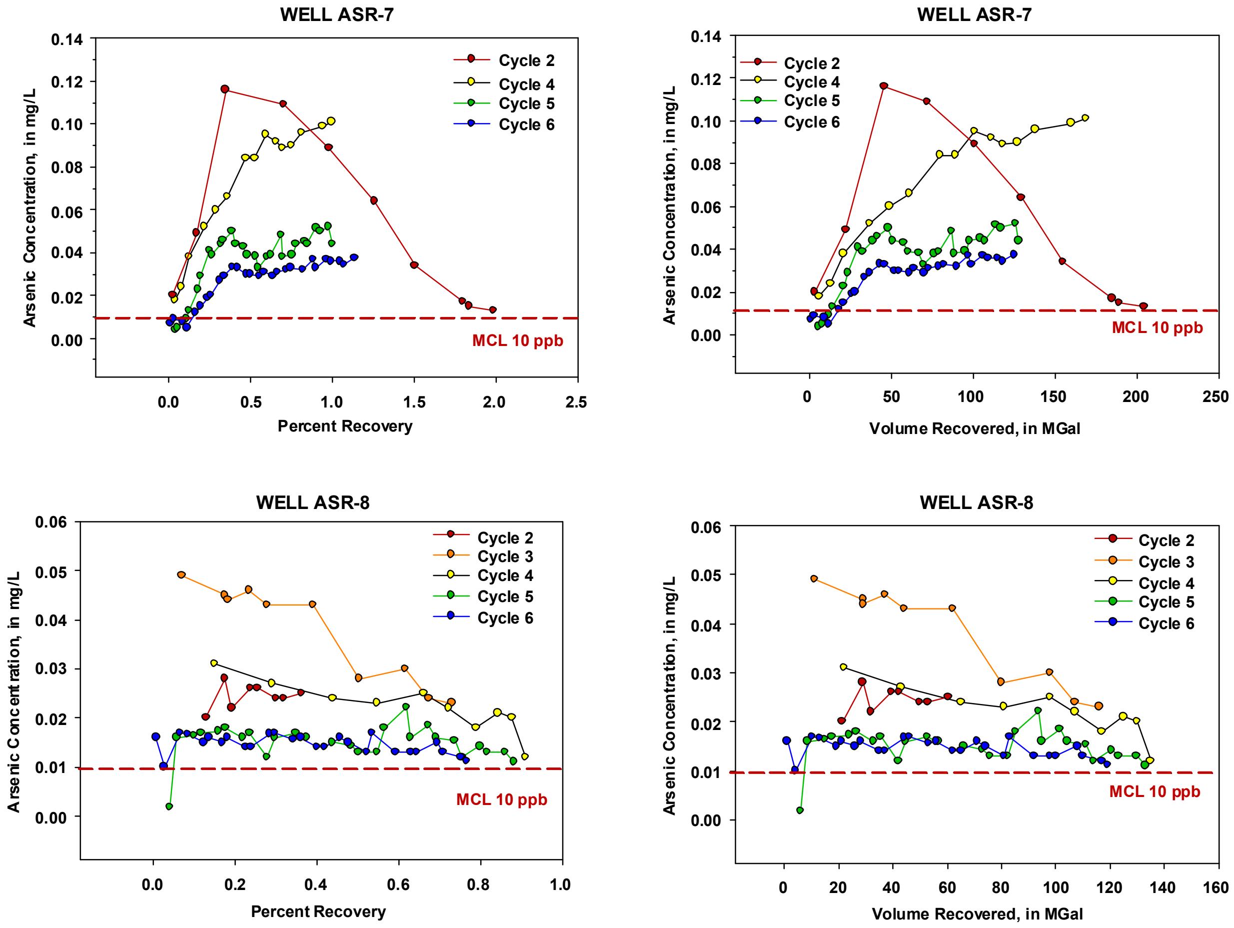

FIGURE 4 (*COMPLETED*)
Plots Showing Arsenic Concentration Versus Percent Recovery (left) or Volume Recovered (right) During Recovery, as Measured in ASR Well Samples at the Tampa-Rome Avenue ASR System

In summary, the following observations characterize arsenic mobility at TRAP:

- Arsenic is released into the aquifer during recharge, but rarely is detected at monitor wells located 50 to 350 ft away from ASR wells;
- Arsenic is detected in ASR wells at concentrations often exceeding the MCL only during recovery;
- Arsenic concentrations increase asymptotically during successive recovery phases at 7 of 8 ASR wells;
- The asymptote or maximum arsenic concentration during recovery can be estimated after approximately 70 MG have been recovered (70 percent recovery);
- The maximum arsenic concentration during recovery declines exponentially during successive cycles at most TRAP ASR wells

These trends can be simulated with a simple analytical model for predicting arsenic concentrations during future recovery cycles.

1.3 Simulating Arsenic Concentration Trends in Recovered Water During Successive ASR Cycle Tests at TRAP

The pattern of arsenic concentration during a single recovery event resembles an exponential curve that reaches an asymptote. Successive cycles show consistently declining asymptotes between cycles 3 or 4 through 6. The mathematical expression to simulate arsenic concentration values at the successively declining asymptotes (cycles) is a 4-parameter exponential curve:

$$[As] = (cS_0 + cS_1 * \exp(-\text{cycle number}/b))*(1-\exp(-3[\text{Volume Recovered}]/a) \qquad (1)$$

where:

[As]	is arsenic concentration at the asymptote, in mg/L,
cS_0	is the minimum [As] at the end of a recovery cycle,
cS_1	is the difference between the maximum and minimum [As],
a	is the recovery volume where [As] equals 95% of the maximum [As] during a cycle,
b	is an arbitrary coefficient that relates magnitude of the asymptote between cycles

cycle number	actual cycle number
volume recovered	recovered water volume, in MG

The TRAP recovered water dataset was estimated consistently with the 4-parameter, cS_0, cS_1, a, and b model. The solved equation generates a curve or series of curves to fit input data (arsenic concentrations and volumes) for cycles 3 through 6. Once the curve fits are established, the family of generated curves (the exponential model) predicts the asymptote [As] for cycles 7 through 9. The model is one of exponential growth to an asymptote, with successive asymptotes declining in a manner similar to exponential decay. This model simulates maximum arsenic concentrations in successive cycles based on reproducible observations in most wells, and predicts maximum arsenic concentrations in future cycles. The model assumes that future operation of the ASR wellfield will be similar to operation between cycles 3 through 6.

In this model, data are weighted such that later cycles have more influence than early cycles. The declining pattern of asymptotes at each well is based primarily on later cycles. This is a conservative approach because the difference between cycles 3 and 4 asymptotes is greater than that of cycles 5 and 6. Consequently, the predicted asymptotes [As] for cycles 7 through 9 tend toward higher concentrations. The goodness-of-fit of model to data from each well is summarized by r^2 and sum-of-squares values. Model input and output for each TRAP ASR well are in Excel spreadsheet format (Tampa_RomeAve_CurveFit_AllWells.xls; CD).

1.4 Exponential Model of Arsenic Mobility During Cycle Testing at the TRAP ASR System: Model Interpretations

A pattern of declining arsenic concentrations during successive recovery phases of cycles 3 through 6 is suggested in the raw cycle test data in 7 of 8 ASR wells at TRAP (Figure 4). The exponential model to quantify this pattern confirms this decline in 5 of 8 ASR wells at TRAP (Figure 5). Declining asymptote arsenic concentration in successive cycles is quantified in all wells except ASR-5, ASR-6, and ASR-8. No significant change in asymptote arsenic concentrations was simulated in ASR-5 and ASR-6. No satisfactory model fit could be obtained using data from ASR-8. A summary of model output and goodness-of-fit is presented in Table 1.

The best model fit for the greatest number of cycles was developed at wells ASR-1, ASR-2, and ASR-3. Asymptote arsenic concentrations decline between 42 and 53 percent from cycles 3 to 6. Excellent model fits were obtained for wells ASR-4 and ASR-5, but are based on fewer cycles (cycles 4 to 6). Asymptote arsenic concentrations decline between 18 and 60 percent from cycles 4 to 6 in these wells. Good model fits were obtained at wells ASR-5 and ASR-6; however, no pattern of declining asymptote arsenic can be discerned because only data from cycles 5 and 6 were used for these simulations. The model is not sensitive enough to define the change in asymptote between cycles 5 and 6 data, although some raw arsenic concentration data suggest minor improvement (Figure 4). Model simulations were not possible using data from well ASR-8.

This model allows prediction of asymptote arsenic concentration in cycles 7 through 9, for 5 of 8 wells at TRAP, and predicted values can be compared to the MCL (Table 1). Predicted asymptote arsenic concentrations will be at or below the MCL during cycle 7 at wells ASR-1 and ASR-2. Although significant declines have occurred in wells ASR-3, ASR-4, and ASR-7, the predicted asymptote arsenic concentration remains in excess of the MCL through cycle 9, ranging between 0.025 and 0.035 mg/L. More data are necessary to simulate the pattern at wells ASR-5 and ASR-6.

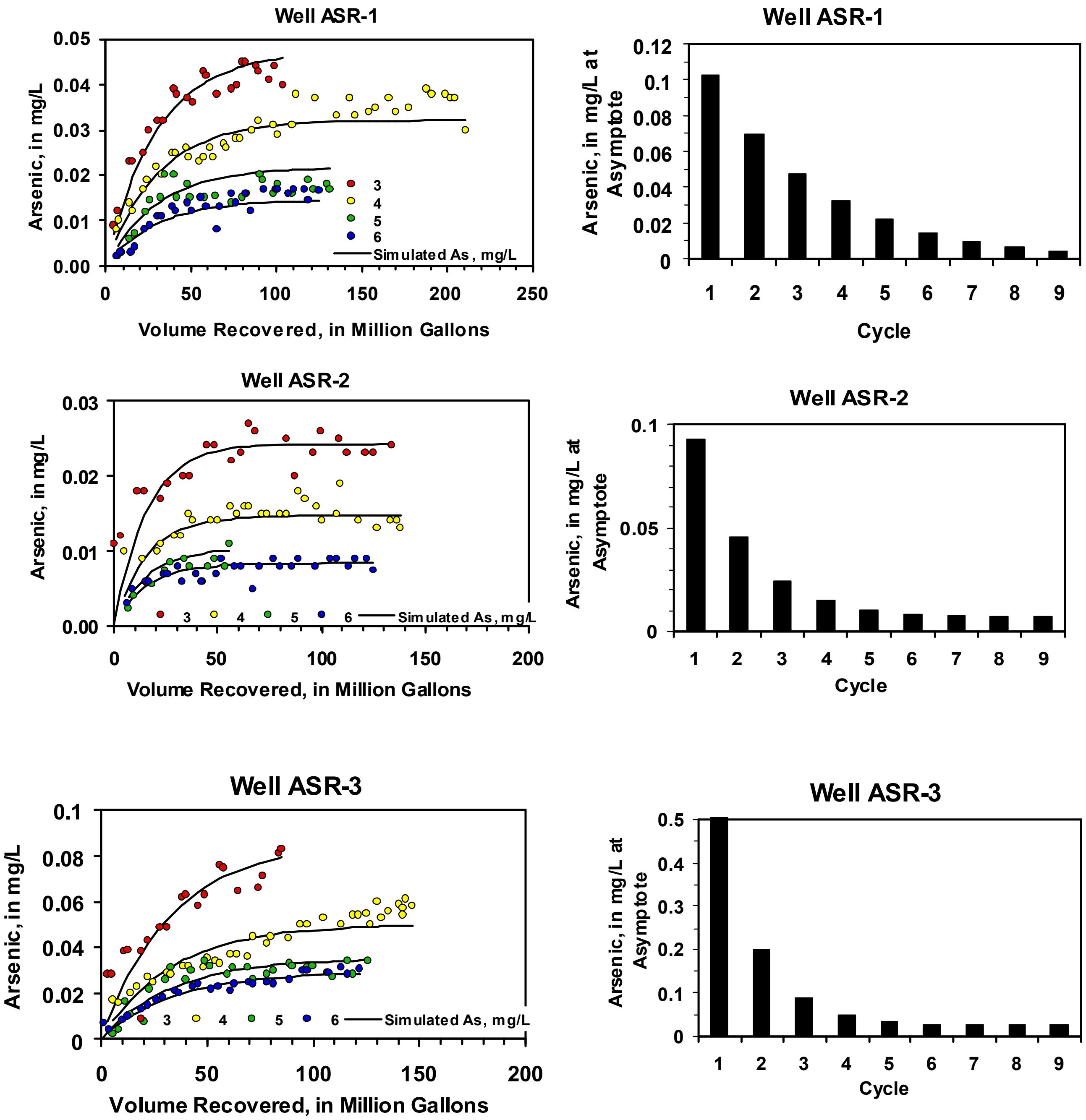

FIGURE 5
Plots Showing Simulated Arsenic Curves for Each ASR Well at TRAP (left), and Asymptote Arsenic Concentration at Each ASR Well During Each Cycle (right). Arsenic Concentrations for Cycles 7 through 9 are Predicted Values

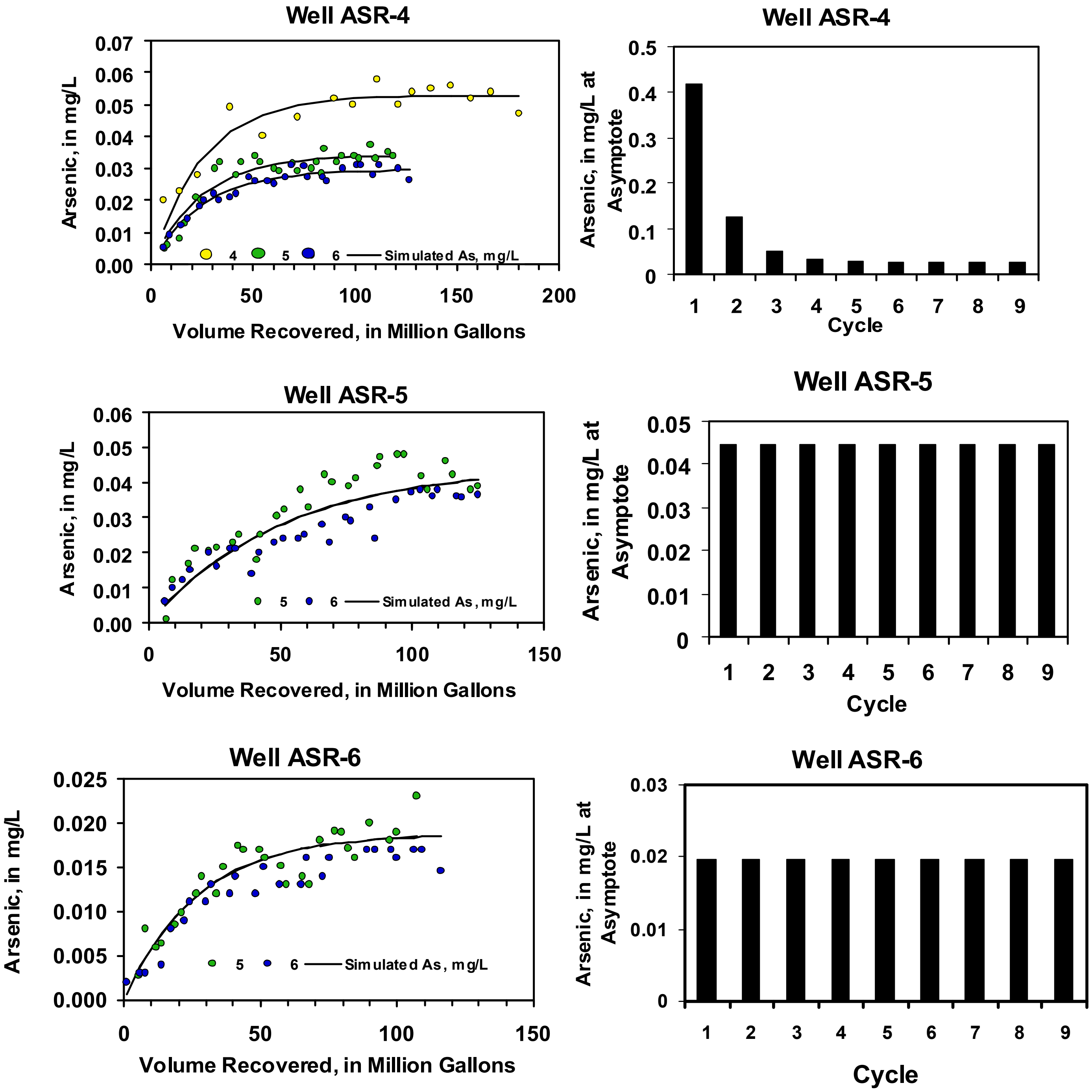

FIGURE 5 (*CONTINUED*)
Plots Showing Simulated Arsenic Curves for Each ASR Well at TRAP (left), and Asymptote Arsenic concentration at Each ASR Well During Each Cycle (right). Arsenic Concentrations for Cycles 7 through 9 are Predicted Values

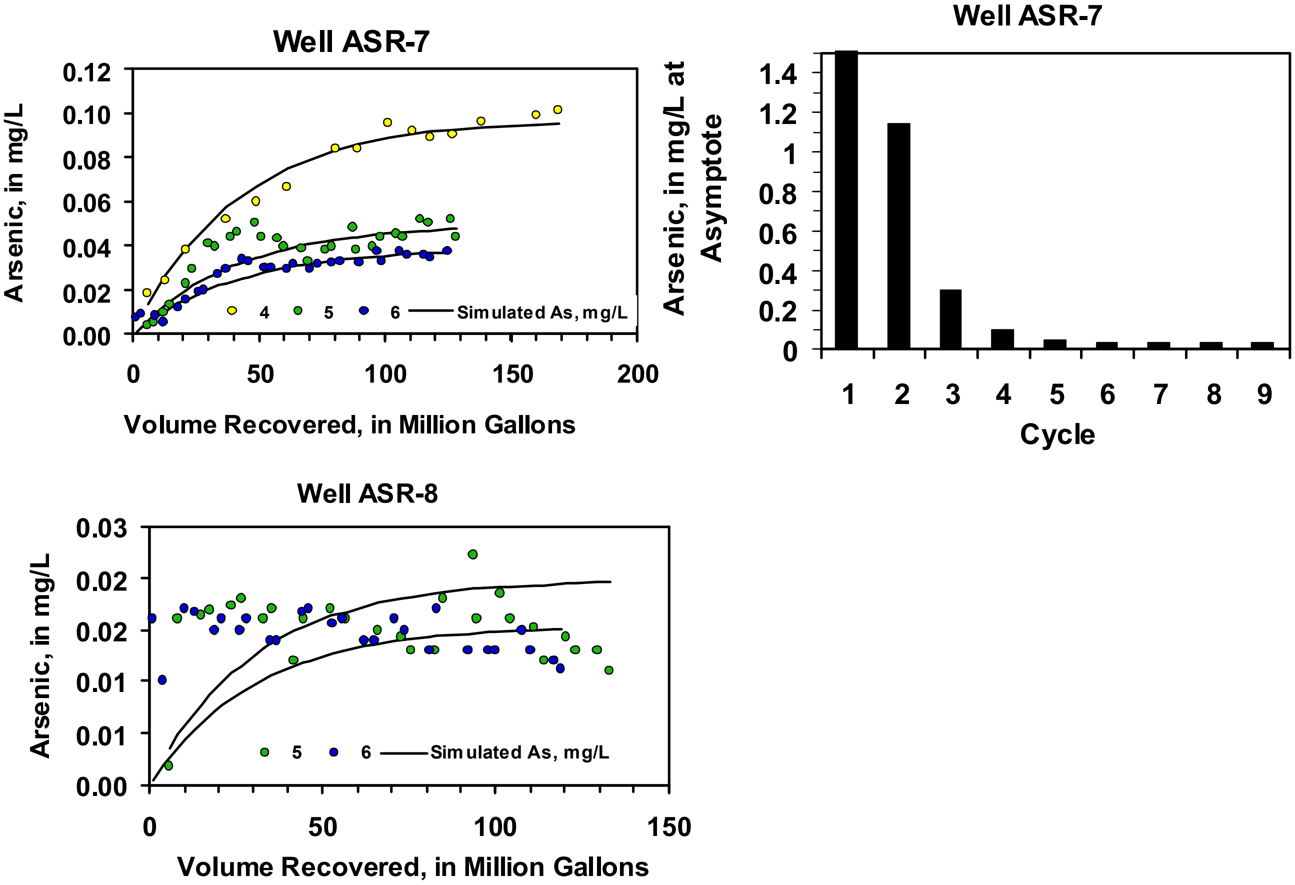

FIGURE 5 (*COMPLETED*)
Plots Showing Simulated Arsenic Curves for Each ASR Well at TRAP (left), and Asymptote Arsenic Concentration at Each ASR Well During Each Cycle (right). Arsenic Concentrations for Cycles 7 through 9 are predicted values

TABLE 1
Summary of Model Simulations Presented in Figure 5. Goodness-of-Fit Represented as r^2 Value for All Curves in the Plot. Simulated Arsenic Concentrations are Based on Measured Values for Cycles 4 through 6, and are Predicted for Cycles 7 Through 9

Well Number	Cycles Simulated	Goodness of Fit (r2)	Predicted Arsenic Concentration at Asymptote, in mg/L (MCL = 0.010 mg/L)					
			cycle 4	cycle 5	cycle 6	cycle 7	cycle 8	cycle 9
1	3 through 6	0.93	**0.032**	**0.022**	**0.015**	**0.010**	**0.006**	**0.004**
2	3 through 6	0.89	**0.015**	**0.010**	**0.008**	**0.008**	**0.007**	**0.007**
3	3 through 6	0.91	**0.050**	**0.035**	**0.029**	**0.027**	**0.026**	**0.025**
4	4 through 6	0.94	**0.034**	**0.030**	**0.028**	**0.028**	**0.028**	**0.028**
5	5 and 6	0.88	**no change**					
6	5 and 6	0.92	**no change**					
7	4 through 6	0.95	**0.097**	**0.050**	**0.038**	**0.036**	**0.035**	**0.035**
8	5 and 6	0.01	**no curve fit**					

1.5 Conceptual Geochemical Model of Arsenic Mobility During ASR Cycle Testing at TRAP

The sources, transport, and fate of arsenic in pumped aquifer systems have been detailed (for example, Harvey et al., 2002; Saaltink et al., 2003; Gotkowitz et al., 2004), and also under specific conditions of the upper Floridan Aquifer System (FAS; Williams et al, 2002; Pearce, 2006; Lazareva and Pichler, 2004; Price and Pichler, 2006; Mirecki, 2006; Haque and Johannesson, 2006; Jones and Pichler, 2007). Arsenic mobility during ASR is controlled by redox evolution of the aquifer system, as initially oxidizing recharge water reacts with minerals, under the sulfate-reducing conditions (Rye et al., 1981) that prevail in the upper FAS.

The source of arsenic in the Suwannee Limestone is euhedral and framboidal pyrite (Lazareva and Pichler, 2004; Price and Pichler, 2006). Arsenic is coprecipitated with syndepositional iron sulfide (euhedral pyrite), or during microbe-mediated sulfate reduction that proceeds in voids and fractures of the Suwannee Limestone. Representative examples of euhedral and framboidal pyrite from cores at the TRAP ASR system were identified (Figure 6, Appendix B), and analyzed for arsenic content by X-ray fluorescence (XRF). Both euhedral and framboidal pyrite are restricted to black organic phases in the limestone. The black organic phase occurs as small irregular lenses or clots within the limestone. This relationship suggests that limestones having these readily identifiable black organic phases may contain a pyrite source that may release arsenic during the ASR cycles. Unfortunately, arsenic occurs at trace concentrations in our bulk samples, well below the XRF detection limit of 20 milligrams per kilogram (mg/kg). Arsenic concentrations as great as 2 percent by weight in framboidal pyrite were reported by Price and Pichler (2002) or averaging 2,300 ppm (Price and Pichler, 2006), using more sensitive analytical methods.

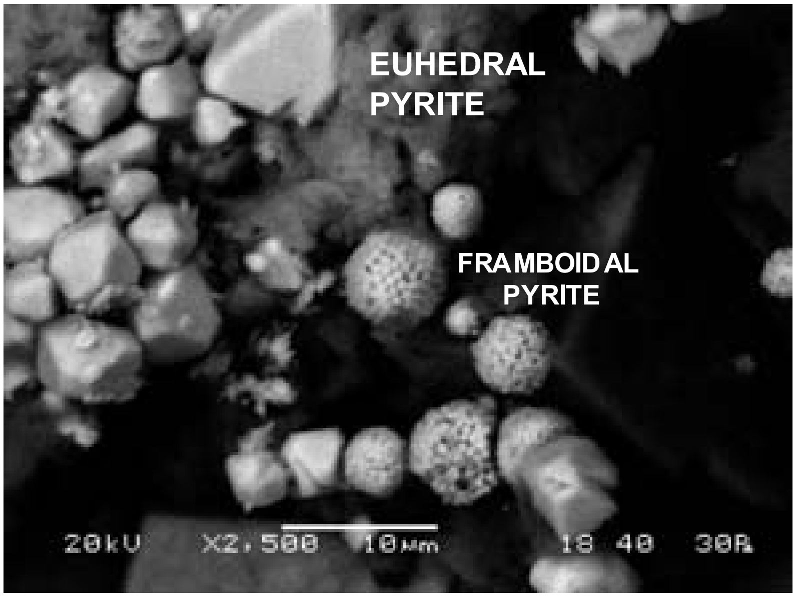

FIGURE 6
SEM Image of Sample from Boring SZMW-7, Suwannee Limestone, 320-330 ft bls (approximately 321 ft bls). Magnification is 2,500X, and Shows Detail of Eudhedral and Framboidal Pyrite. Additional SEM images are found in Appendix B.

When pyrite is exposed to oxic recharge water, the result is the release of sulfate, ferric iron, and co-precipitated metals such as arsenic (Jones and Pichler, 2007). Sulfate released by pyrite oxidation cannot be discerned from native sulfate (> 100 mg/L) in the upper FAS in this area. Ferric iron is unlikely to remain in solution due to extremely low solubility, and will return to the solid phase as ferric oxyhydroxide (ferrihydrite; $K_{sp} \approx 10^{-39}$; Brownlow, 1996). Arsenic can be transported after release, although it is readily complexed or sorbed by iron oxyhydroxide (for example, Tadanier et al., 2005). Dissolved arsenic exists as weakly acidic oxyanion (arsenite, with As(III); arsenate with As(V)), the speciation of which depends on pH, pE, and sulfide concentration (Helz, 2006). The speciation of arsenic in sulfide-rich waters is poorly understood, and speciation will determine the extent to which arsenic can be sorbed.

During ASR recharge and early storage, it is likely that dissolved arsenic is sorbed along the flowpath between the ASR and monitor wells by native and precipitated iron oxyhydroxide, minor clays, or other mineral surfaces in the aquifer matrix. Evidence to support arsenic sorption includes:

- Arsenic is detected infrequently at monitor wells throughout 6 cycles at TRAP (Sections 1.2 and 1.3), and monitor wells are located 150 to 350 feet away from ASR wells.
- Arsenic is detected infrequently at monitor wells at other ASR systems that store water in aquifers that include the Suwannee Limestone. These sites are Peace River (5 cycles; as discussed later in this report) and Olga – Lee County (4 cycles; Mirecki, 2006). The flowpath length between ASR and monitor wells at these sites is at least 250 feet.

Iron oxyhydroxide is not common in Suwannee Limestone samples. Our analyses of selected samples from TRAP cores in the storage zone interval show Fe_2O_3 concentrations that range between 0.03 and 0.12 weight percent (Appendix B). Price and Pichler (2006) report iron oxyhydroxide occurring in only 3 of 306 samples, but this solid was observed as a reaction halo around pyrite. Arsenic sorption by native or precipitated iron oxyhydroxides, or other uncharacterized mineral surface, must occur along the flowpath between ASR and monitor wells during recharge and early storage.

During late storage and recovery, the aquifer redox environment evolves from oxic (dissolved oxygen-rich), through anoxic (depleted in dissolved oxygen), to reducing (dissolved hydrogen sulfide present). This redox evolution results in the reproducible patterns of arsenic concentration on which the following conceptual model is based. Arsenic is sequestered when solid iron oxyhydroxide is stable, but if this mineral becomes unstable, arsenic will be released back into solution. The pE-pH stability field for amorphous iron oxyhydroxide is fairly well-defined. For example, at pH 7.0, the boundary between solid iron oxyhydroxide and ferrous iron occurs at an Eh value of +14 millivolts (mV) (Merkel and Planer-Friedrich, 2005), although the boundary between iron oxyhydroxide and ferrous (Fe^{2+}) iron stability fields is affected by solution composition. Generally, if the redox environment of the upper FAS shows more negative (reducing) redox potentials, iron oxyhydroxide will become unstable, undergo reductive dissolution, and release sorbed arsenic and ferrous iron. This is believed to be the process that causes elevated arsenic (by *Re*-mobilization) during recovery in ASR well samples.

The geochemical evidence that supports arsenic re-mobilization by reductive dissolution of iron oxyhydroxides includes:

- Dissolved iron concentrations increase in ASR well samples as recovery proceeds.
- Arsenic and iron both increase simultaneously during recovery.

Ideally, changing solution composition plus redox indicators can confirm reductive dissolution as the primary process that liberates iron and arsenic during recovery. Typical trends in arsenic and iron during cycles 5 and 6 recovery phases are consistent with arsenic release by reductive dissolution of iron oxyhydroxides (Figure 7). It is interesting to note that iron concentration increases gradually as recovery proceeds. Gradually increasing concentrations indicate that iron (and associated arsenic) is swept back to the ASR well, rather than moving with a geochemical redox boundary.

Aquifer redox environment is more difficult to characterize. Unfortunately, redox parameters show too much scatter to specify a numerical value for pE (Eh). There is no consistent trend in dissolved oxygen concentration or ORP value (Figure 7) in recovered water samples. Field factors probably account for the lack of correlation between ORP and dissolved oxygen concentration data. Maintaining stable dissolved oxygen probes with membranes are difficult without constant calibration. Also, the reference calibration for ORP probes used during TRAP cycle testing is not known. ORP probe reference calibration varies by manufacturer, and this can result in variation of 200 mV (Nordstrom and Wilde, 2005).

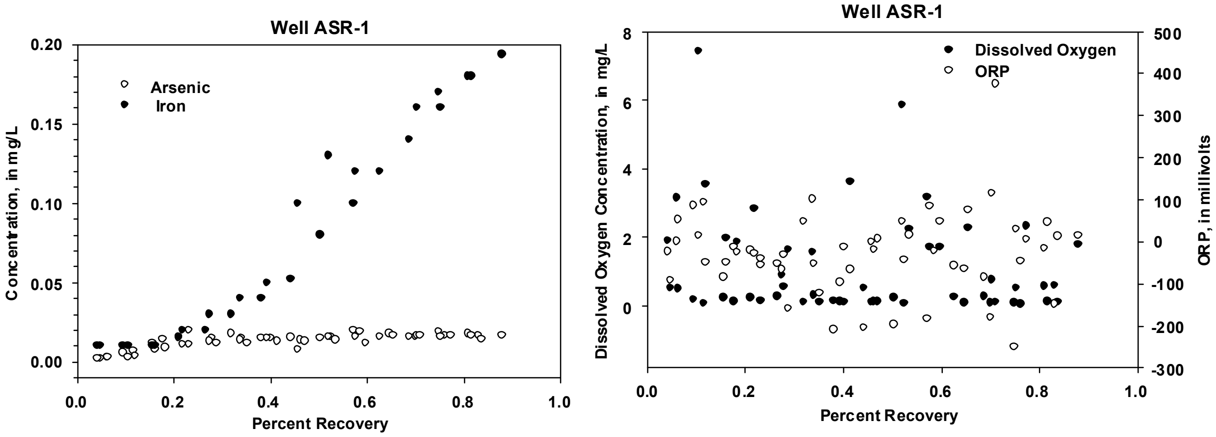

FIGURE 7
Graphs Showing Geochemical Trends of Arsenic, Iron (Left), and Dissolved Oxygen and Redox Potential (ORP; Right) During Recovery in ASR Well Samples. Data From Cycles 5 and 6 Recovery Phases at ASR-1 Are Shown

There are other geochemical species that enable characterization of the aquifer redox environment. Typically, the ratio between dissolved sulfate and sulfide concentrations measured throughout an ASR cycle would show the onset of reducing conditions in the aquifer. Unfortunately, sulfide is rarely measured at any ASR system in Florida, and these data are not available for TRAP ASR cycle tests. The odor of hydrogen sulfide in recovered water samples is anecdotal evidence of the presence of sulfide in the aquifer and the possibility of sulfate-reducing conditions in at least part of the aquifer.

In conclusion, the conceptual model for arsenic mobility during ASR cycle testing can be summarized as a three-step process:

- Release of arsenic by pyrite oxidation during recharge

- Sequestration of arsenic by mineral surfaces (iron oxyhydroxide) during recharge and storage
- Re-release of arsenic by reductive dissolution of iron oxyhydroxide during recovery

This three-step process is consistent with the geochemical data at the TRAP ASR system, and will serve as a basis for interpretation of the Peace River ASR system data in the following section. Geochemical models will be presented in Section 3 to support this conceptual model, and to quantify solute mass flux during recharge and recovery.

2.0 Arsenic Concentration Trends in Recovered Water at the Peace River Facility ASR System

2.1 Introduction

The Peace River/Manasota Regional Water Supply Authority operates the largest ASR system east of the Mississippi River. This site is challenging because of the large quantity of cycle test data available. Two ASR wellfields are in operation at the Peace River Regional Water Supply Facility (PRF). Wellfield 1 (WF1) is the older wellfield, consisting of nine ASR wells that have been in operation since the early 1980s. PRF ASR WF2 (WF2) is a newer wellfield that has been in operation since 2002. Few arsenic data are available for WF1; therefore, this report focuses on the substantial dataset that has been developed for WF2.

Water-quality data were compiled from cycle tests 2 (2003) through 5 (2006) at the PRF ASR WF2. Water-quality datasets consist of parameters (specific conductance, pH, temperature, and ORP), major constituents (alkalinity, calcium, magnesium, sodium, chloride, sulfate, fluoride), trace constituents (iron, manganese), plus species of regulatory concern (arsenic, total trihalomethanes, gross alpha, radium 226+228, uranium). Later cycles (4 and 5) have more complete analyses compared to earlier cycles. To evaluate water-quality changes as recovery proceeds, concentrations are plotted as a function of total volume recovered (in MG), or percent recovery. Percent recovery is calculated as the volume of water recovered at the sampling event/total volume of water recovered. Because arsenic mobilization and transport are of primary interest at this ASR system, arsenic is the only constituent considered in the following discussion. All water-quality data from WF2 appear in an Excel spreadsheet entitled "Peace River Wellfield2_Alldata" (CD).

The PRF ASR WF2 system (Figure 8) consists of 12 ASR (recharge/recovery) wells and 10 storage zone monitor wells (M-9, and M-11 through M-19). Prior to distribution in the ASR system, surface water from the Peace River is treated with a conventional alum coagulation process, then disinfected using chloramines prior to recharge. This use of chloramine disinfectant is a major difference between the Peace River and TRAP, where ozone is used for disinfection. Recharge water is stored at depths between approximately 560 and 900 feet bls (Figure 9) in permeable zones of the Suwannee Limestone. Recharge water quality is characterized by low concentrations of dissolved constituents (Appendix A), and shows dissolved oxygen concentrations ranging between 4 and 7 mg/L (median value 5.5 mg/L). The dissolved oxygen and disinfectant concentrations of PRF recharge water are less corrosive than those of the TRAP ASR system, and reflect differences between ozone and chloramine disinfection processes.

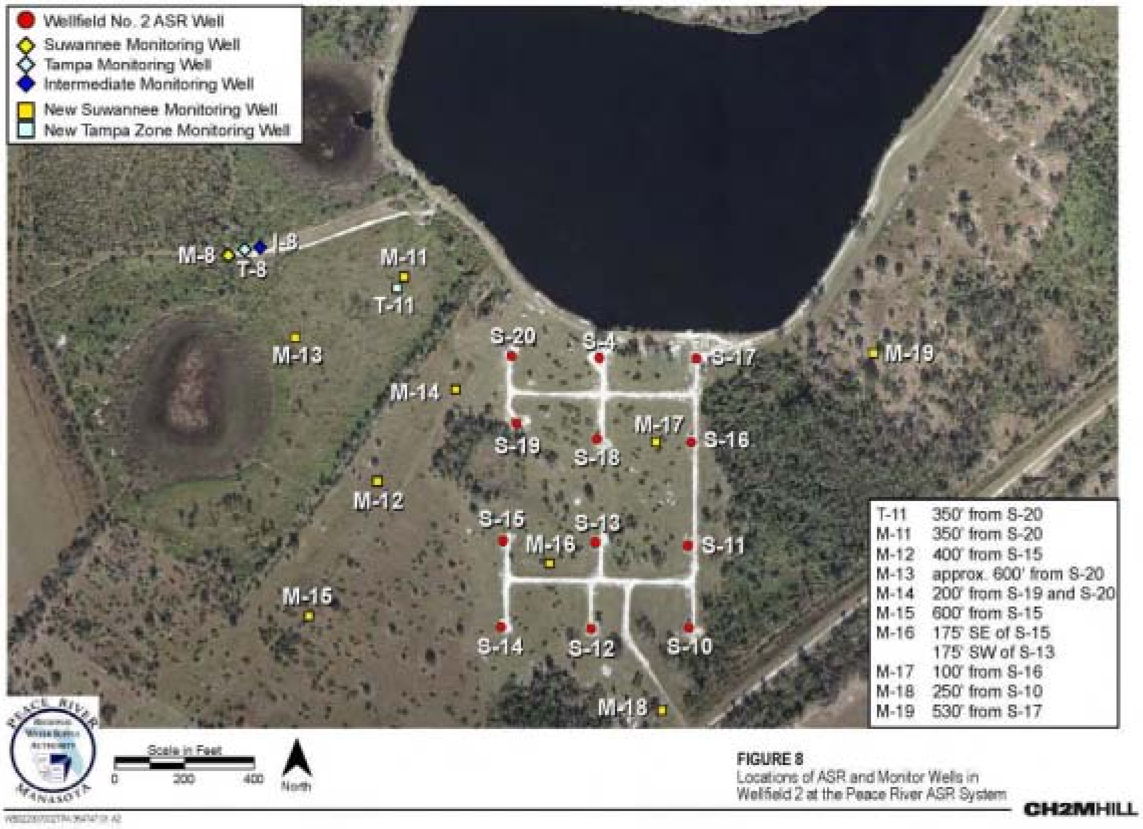

FIGURE 8
Locations of ASR and Monitor Wells in Wellfield 2 at the Peace River ASR System. Figure from CH2M HILL (2007)

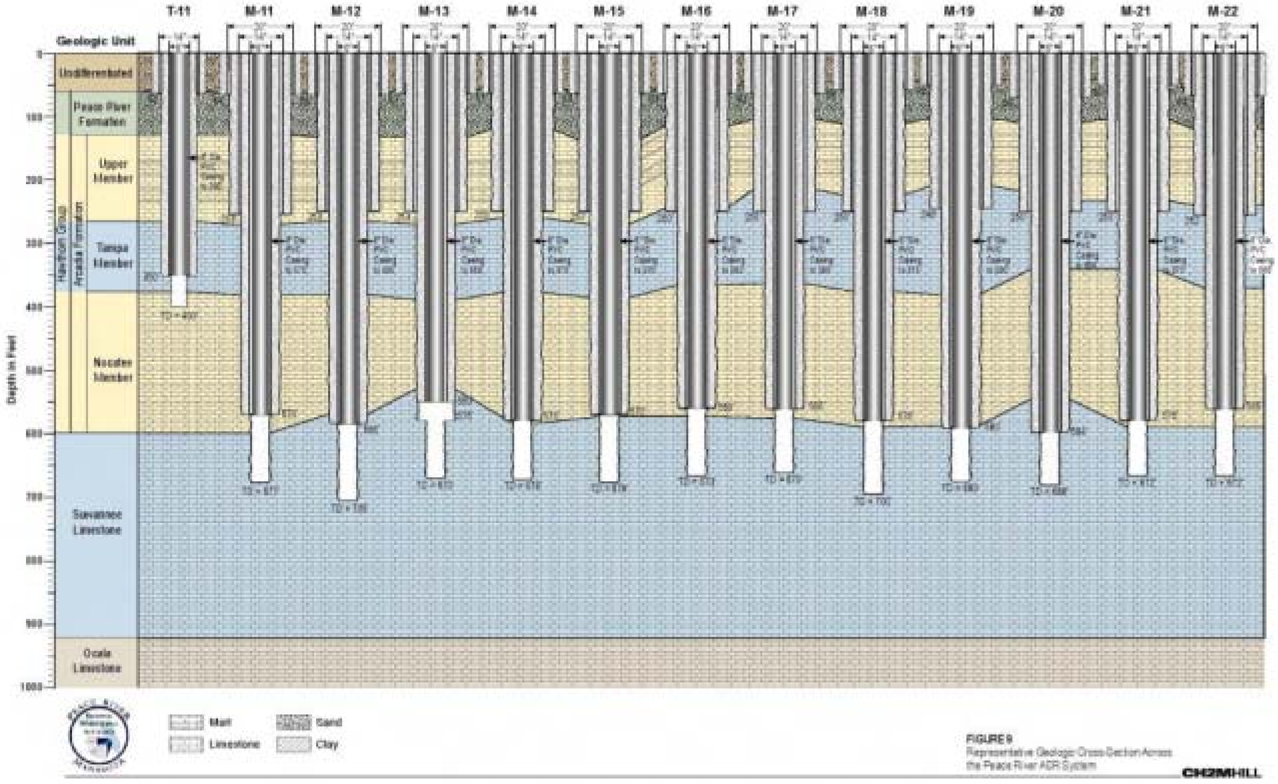

FIGURE 9
Representative Geologic Cross-Section Across the Peace River ASR System. Figure from CH2M HILL (2007)

Five ASR system cycle tests were completed at the PRF ASR system between 2003 and 2006. Cycle 6 is ongoing, but data were unavailable for interpretation in this report. During each cycle, approximately 1 billion gallons of treated surface water is recharged seasonally (July to January) in the wellfield, stored for periods ranging from 1 week to 3 months depending on need, then recovered (typically April through June). Volumes recovered at individual ASR wells typically range between 60 and 70 MG per cycle, with the exception of cycle 5 (2006). During cycle 5, approximately 100 MG was recovered from each ASR well, resulting in a 146 percent recovery for the entire WF2. Percent recoveries for ASR wells at PRF generally range between 70 and 80 percent. The cumulative pattern of recharge and recovered volumes for the entire PRF ASR WF2 shows this consistent recharge-recovery pattern (Figure 10). "Over-recovery" during cycle 5 showed a different pattern of arsenic concentration, for geochemical reasons that are discussed in the following sections.

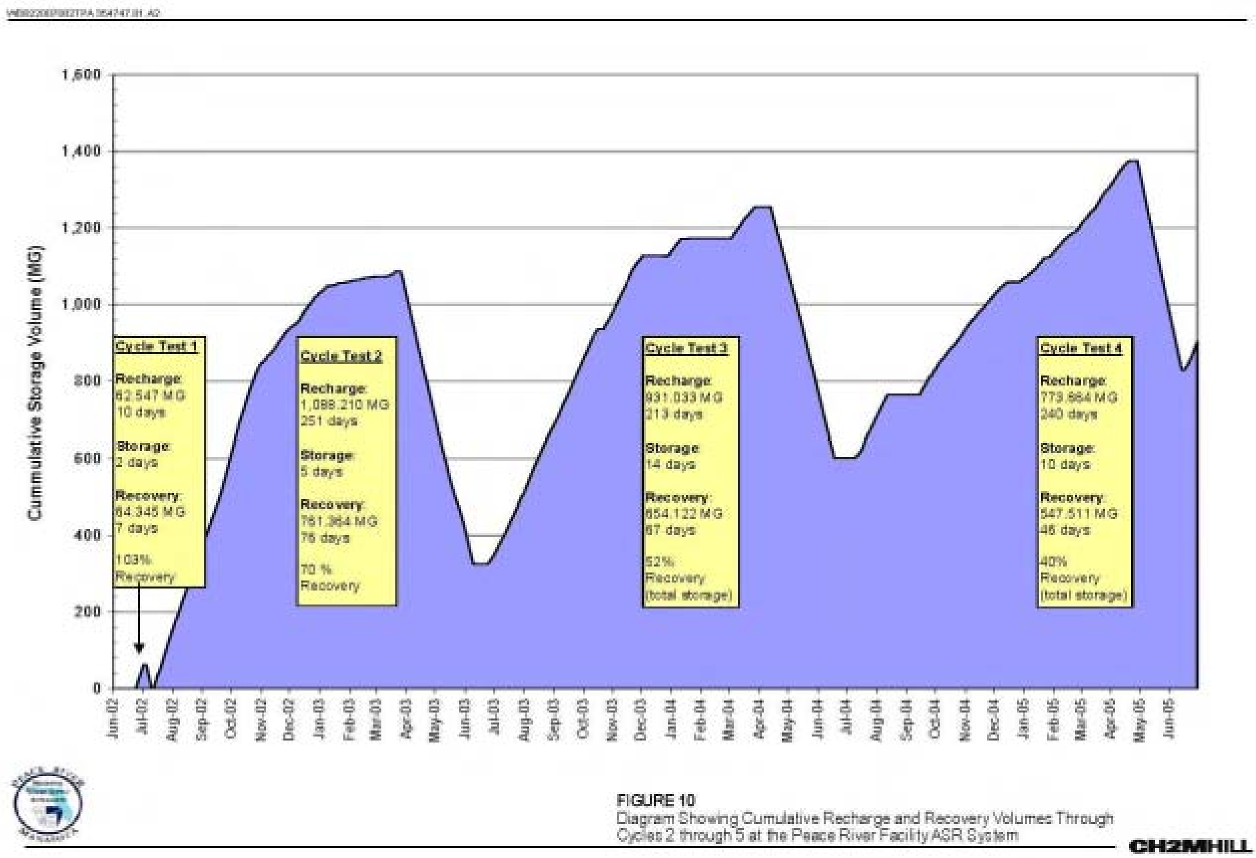

FIGURE 10
Diagram Showing Cumulative Recharge and Recovery Volumes Through Cycles 2 through 5 at the Peace River Facility ASR System

2.2 Arsenic Trends at PRF ASR WF2 During Successive ASR Cycle Tests

Arsenic concentrations were measured throughout each cycle test, in samples from both ASR and monitor wells at the PRF ASR WF2. At ASR wells, arsenic concentrations in recovered water regularly exceeded the Federal and State MCL (10 µg/L), often at concentrations approaching 190 µg/L during cycle 5. The patterns of measured arsenic concentration during recovery in successive cycles at each ASR well differ from those observed at TRAP, and this difference probably relates to hydraulic and geochemical factors near the wellbore and within the aquifer.

The patterns of arsenic concentrations observed during successive recovery phases are shown at each ASR well (Figure 11). Patterns observed at each well are similar regardless of the x-axis used (percent recovery versus volume recovered). During each cycle, arsenic concentrations increase nearly linearly, with maximum values occurring at the end of each cycle (typically 80 to 100 percent recovery, or approximately 60 MG). Arsenic concentration trends with successive cycles suggest gradually diminishing arsenic, although the patterns are not observed at all ASR wells. Consequently, arsenic concentrations measured in recovered water throughout WF2 cycle tests were interpreted using a statistical model, presented in Section 2.3.

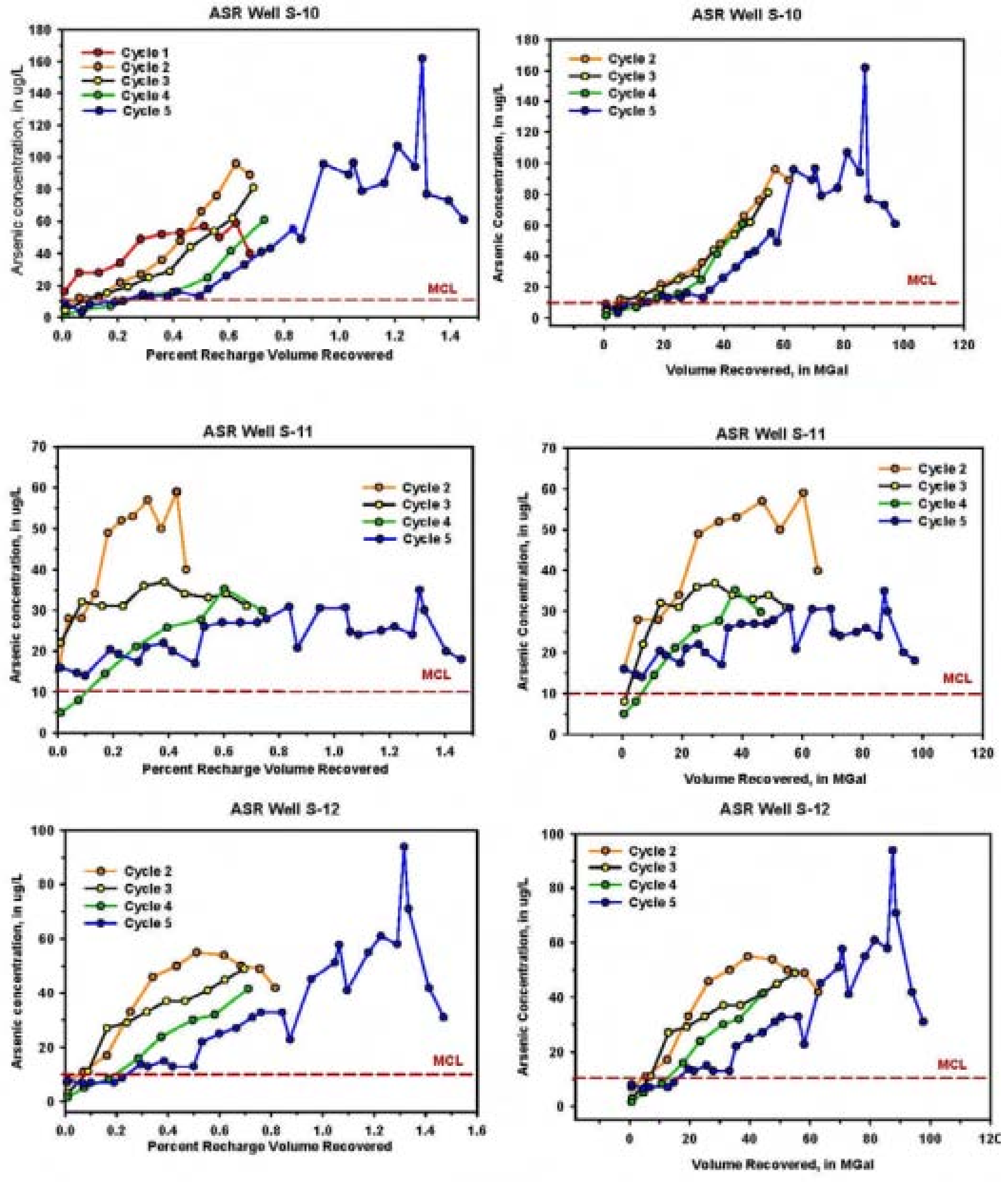

FIGURE 11

Plots Showing Arsenic Concentration Versus Percent Recovery (left) or Volume Recovered (right) During Recovery, as Measured in ASR Well Samples at the Peace River Facility Wellfield 2 ASR System

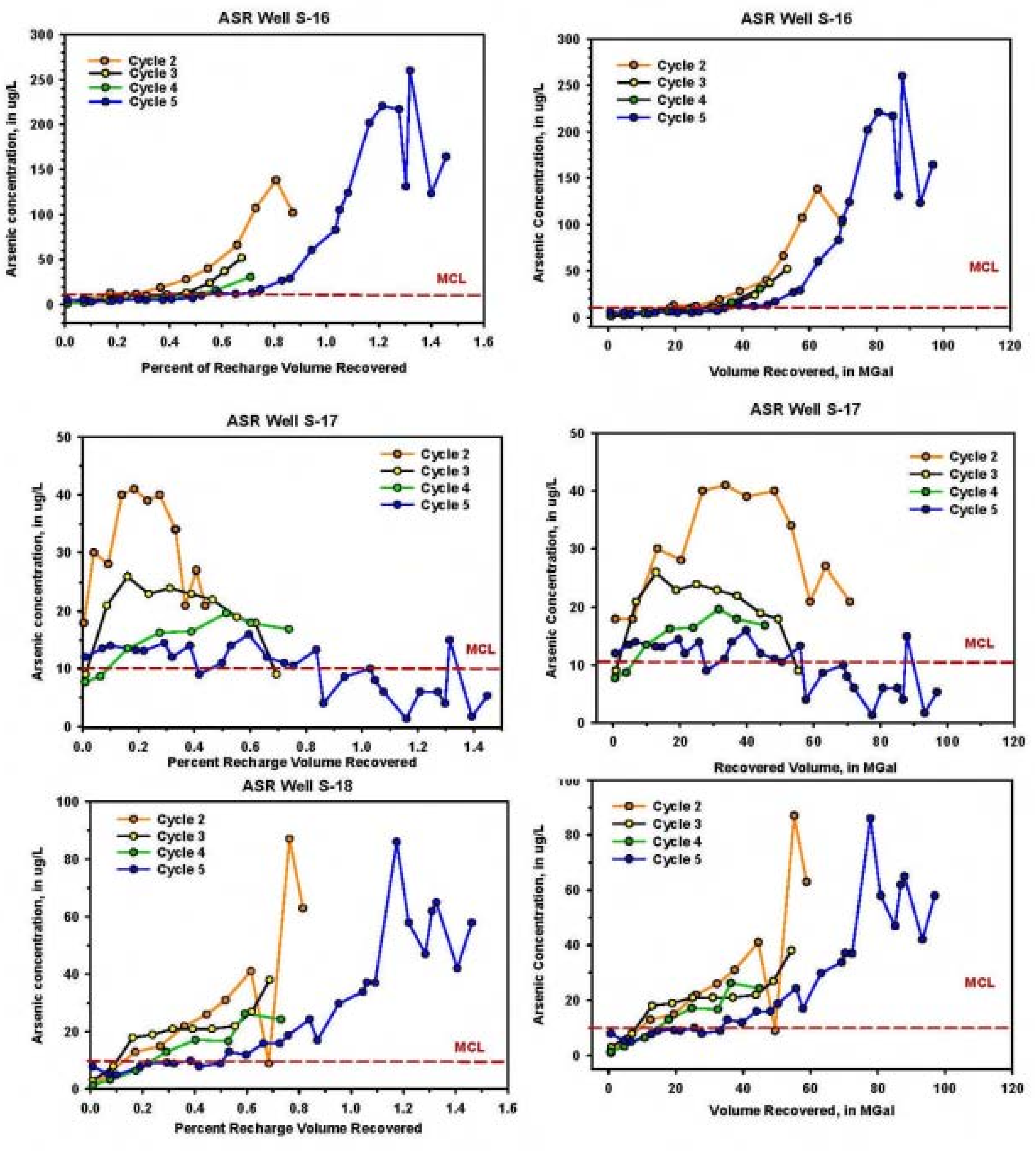

FIGURE 11 (*CONTINUED*)
Plots Showing Arsenic Concentration Versus Percent Recovery (left) or Volume Recovered (right) During Recovery, as Measured in ASR Well Samples at the Peace River Facility Wellfield 2 ASR System
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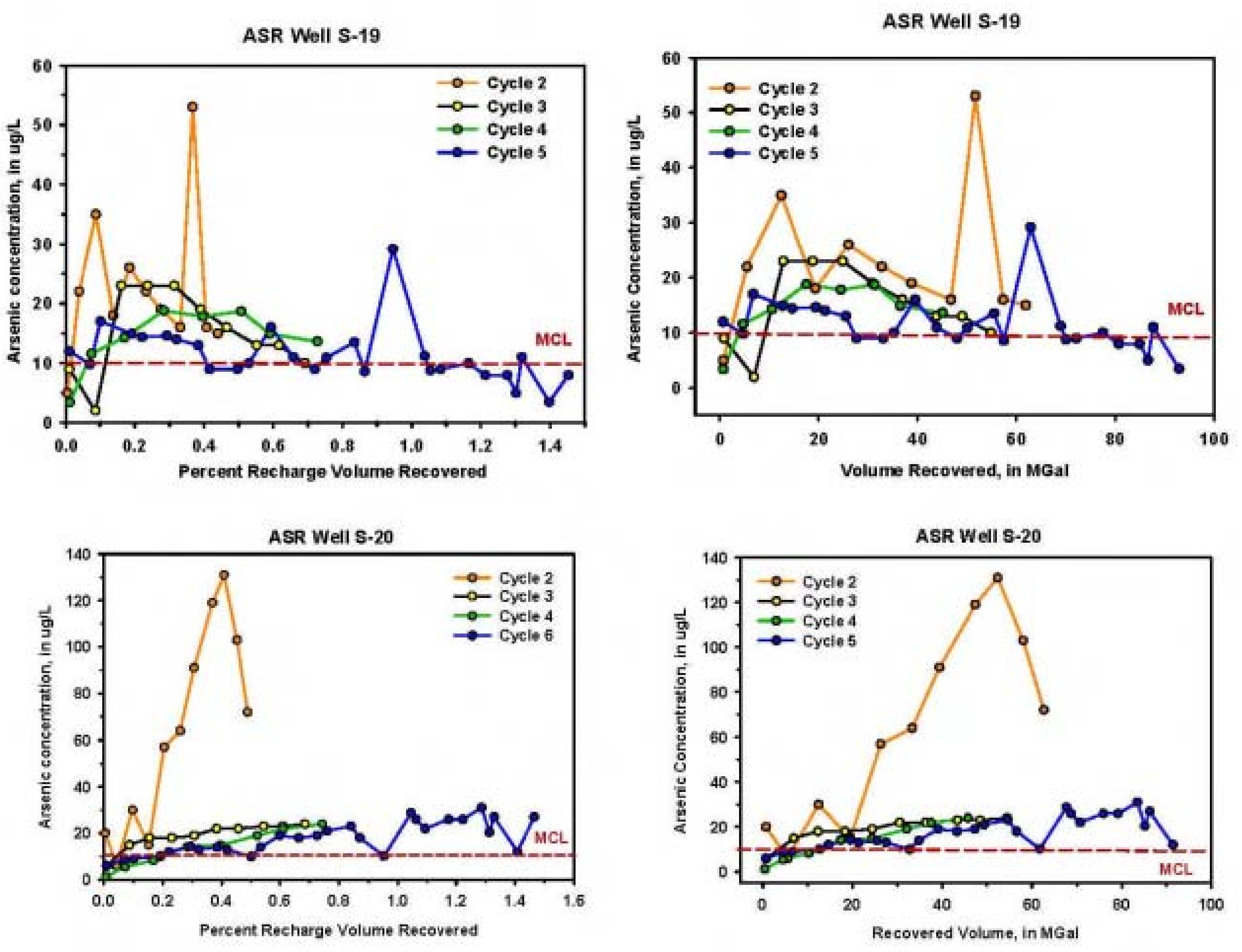

FIGURE 11 (*COMPLETED*)
Plots Showing Arsenic Concentration Versus Percent Recovery (left) or Volume Recovered (right) During Recovery, as Measured in ASR Well Samples at the Peace River Facility Wellfield 2 ASR System

Cycle test operation during cycle 5 differed from the previous cycles, in that approximately 150 percent of recharged water was recovered. A pulse of arsenic appears in all but three ASR wells (S-17, S-19, and S20; Figure 11) during this "over-recovery" event. The arsenic pulse commonly exceeds the MCL, with concentrations in some ASR wells ranging between 150 and 250 µg/L. It is likely that geochemical redox controls the occurrence of elevated arsenic concentrations during recovery in PRF ASR WF2 wells, in a manner identical to that proposed for TRAP. Similarities in ASR system geochemistry are discussed in Section 2.4.

Arsenic concentrations at PRF storage zone monitor wells rarely show arsenic concentrations above the MCL. Ten monitor wells are located near WF2, at distances of approximately 100 feet to 900 feet from the nearest ASR wells. One of these wells (M-8) has a period of record that extends through 3.5 years of cycle testing; the remaining 9 wells have periods of record that began in June 2005. Water-quality data from monitor well samples are tabulated in Peace River_Wellfield_AllData.xls (CD). Only 5 of 538 monitor well samples collected between June 2002 and September 2005 show arsenic in excess of 10 µg/L (Table 2).

Interpretations of arsenic transport at the PRF are similar to those drawn at TRAP. Arsenic transport at distances of approximately 200 ft from WF2 is insignificant. Monitor well M-14, located approximately 200 feet from WF2, is the only monitor well with sustained concentrations above 10 µg/L. This pattern was observed during the cycle 5 recovery event. Arsenic that is mobilized during recharge appears in ASR wells only during recovery. It is likely that the geochemical redox controls on arsenic mobility (or lack of mobility) are identical at PRF and TRAP.

TABLE 2
Summary of Arsenic Exceedances in Monitor Wells at WF2 of the Peace River Facility. Data Tabulated from the "Peace River Wellfield2_Alldata.xls" file on the Report CD

Well	Period of Record	Number of Samples	Number of Samples > 10 µg/L	Minimum As (µg/L)	Maximum As (µg/L)
M-7	01-2002 to 09-2005	194	0	0.9	7.2
M-8	01-2002 to 09-2005	167	0	0.2	3.46
M-11	06-2005 to 09-2005	15	0	<1	3
M-12	06-2005 to 09-2005	15	0	< 7	10
M-13	06-2005 to 09-2005	15	0	< 1	1
M-14	06-2005 to 09-2005	13	0	< 1	2
M-15	06-2005 to 09-2005	15	0	< 1	3
M-16	06-2005 to 09-2005	13	5	1	17
M-17	06-2005 to 09-2005	15	0	< 1	5
M-18	06-2005 to 09-2005	16	0	< 1	2
M-19	06-2005 to 09-2005	15	0	< 1	2
M-20	06-2005 to 09-2005	15	0	< 1	2
M-21	06-2005 to 09-2005	15	0	< 1	3
M-22	06-2005 to 09-2005	15	0	1	6

2.3 Linear Least-Squares Regression Model of Arsenic Mobility During Cycle Testing at the PRF: Model Interpretations

A pattern of declining arsenic concentration is shown in successive recovery phases during cycles 2 through 4 at the PRF ASR WF2. This pattern is evident in 6 of 12 ASR wells (Figure 11). Specifically, declining arsenic is characterized at a recovered volume of 50 MG, or at approximately 80 percent recovery in cycles 2 through 4.

Declining maximum arsenic concentrations in successive cycles are quantified using a linear least-squares regression model (Table 3). By calculating the magnitude of arsenic decline during cycles 2 through 4, it is possible to estimate the cycle number when arsenic concentration will remain below 10 µg/L. Arsenic maxima in recovered water from wells S-4 and S-14 are predicted to decline below 10 µg/L in cycle 5—this decline is confirmed in measured arsenic concentrations from S-14 during cycle 5. A summary of model output and goodness-of-fit is presented in Table 3.

TABLE 3
Linear Least-Squares Fit Equations for Cycles 2 through 4 for Selected Peace River ASR Wells and Statistical Summary for the Equation Arsenic (µg/L) = A + (B X Recovered Water Volume in MG

ASR Well	Cycle Number	Number of Samples	Constant A	Slope B	R	R^2	As @ 50 MG (in µg/L)	Percent Reduction	# Cycles for As ≤10µg/L
S-4	2	6	7.8355	1.1679	0.89	0.8	66.2	100	
S-4	3	8	4.8141	0.6189	0.93	0.87	35.8	54	
S-4	4	17	8.1306	0.2493	0.91	0.84	20.6	31	5
S-10	2	9	-0.277	1.187	0.98	0.96	59.1	100	
S-10	3	23	-1.19	0.836	0.87	0.75	40.6	67	
S-10	4	21	0.581	0.685	0.92	0.85	34.8	58.9	6
S-12	2	10	10.0727	0.7532	0.95	0.9	47.7	100	
S-12	3	8	0.4257	0.9162	1	0.99	46.2	97	
S-12	4	15	2.5642	0.5307	0.94	0.88	29.1	61	7
S-14	2	9	-4.6336	1.7762	0.99	0.97	84.2	100	
S-14	3	8	-5.4392	1.2931	0.96	0.93	59.2	70	
S-14	4	15	0.3837	0.5616	0.81	0.66	28.5	34	5
S-15	2	10	1.819	1.625	0.96	0.92	83.1	100	
S-15	3	8	-2.51	0.675	0.98	0.95	31.2	38	
S-15	4	15	2.078	0.31	0.94	0.88	17.6	21	5
S-16	2	10	-4.976	0.792	0.88	0.78	34.6	100	
S-16	3	7	-3.803	0.615	0.91	0.83	26.9	78	
S-16	4	30	0.779	0.349	0.8	0.64	18.2	22	6
S-18	2	9	7.744	0.401	0.89	0.79	27.8	100	
S-18	3	8	1.3124	0.5693	0.97	0.93	29.8	107	
S-18	4	15	4.6589	0.2245	0.9	0.8	15.9	57	6
Statistical Summary									
	2	7	2.512	1.1	0.93	0.87	57.5		
	3	7	-0.913	0.789	0.95	0.89	38.5	73	
	4	7	2.739	0.416	0.89	0.79	23.5	41	5

Notes:

r = Correlation Coefficient

R^2 = Distribution Coefficient. The fraction of the variance accounted for by the equation

As @ 50 MG, µg/L. The arsenic concentration calculated from the equation at 50 MG volume of water recovered.

Percent reduction. The percent reduction in arsenic concentration for cycles 3 and 4 using cycle 2 is 100 percent.

 # Cycles for As ≤ 10µg/L. The number of cycles estimated to be needed for each ASR well to produce recovered water with an arsenic concentration equal to or less than **10 µg/L** at 50 MG volume of water recovered

2.4 Conceptual Geochemical Model of Arsenic Mobility During ASR Cycle Testing at PRF

A three-step process was proposed to explain arsenic mobilization during cycle testing at the TRAP ASR system (Section 1.5). Specifically, arsenic is released, sequestered, then remobilized under a condition of increasingly reducing (or anoxic) conditions that prevail in the recharged aquifer. As noted in Section 1, the three-step process is:

- Release of arsenic by pyrite oxidation during recharge
- Sequestration of arsenic by mineral surfaces (iron oxyhydroxide) during recharge and storage
- Re-release of arsenic by reductive dissolution of iron oxyhydroxide during recovery

An identical process is supported by water-quality data at the PRF ASR WF2. The water-quality dataset at PRF shows assests and deficiencies similar to those at TRAP. The number of samples collected during a cycle test is large, particularly for cycles 4 and 5. There are also abundant arsenic and iron concentration data from all wells, on which much of the conceptual geochemical model is based. However, the PRF dataset lacks accurate redox indicators. Those data that are reported (dissolved oxygen, ORP) are too variable to interpret in the context of aquifer redox evolution.

During recovery at the PRF ASR WF2, all ASR wells show a coincident pattern of increasing dissolved iron concentrations. This dissolved iron pulse is accompanied by increasing arsenic in all wells except S-17, S-19, and S-20 (Figure 12). Dissolved (ferrous) iron and arsenic concentrations increase simultaneously during recovery. This characteristic supports reductive dissolution of iron oxyhydroxide sorption surfaces as the primary mechanism for arsenic mobilization during recovery.

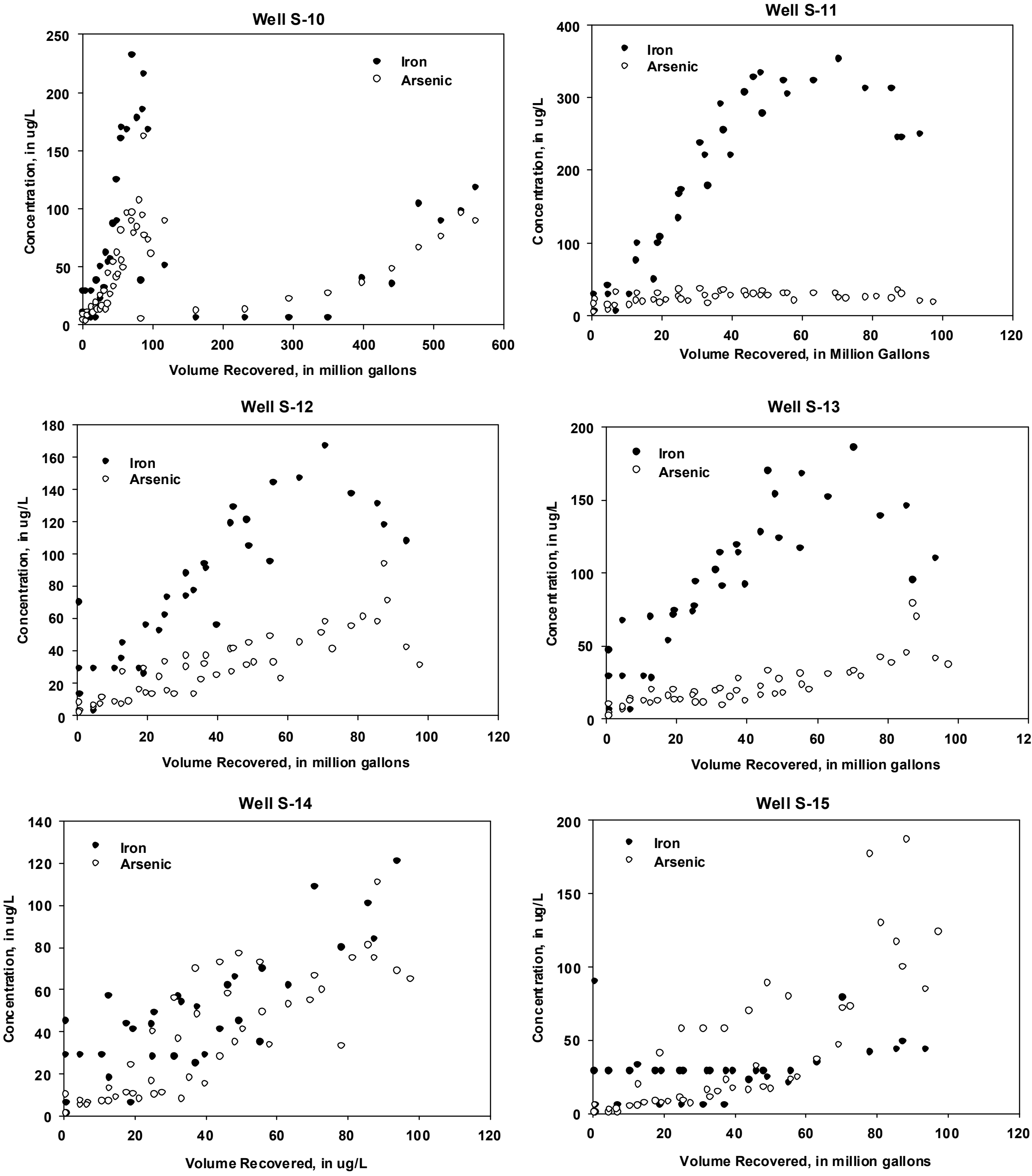

FIGURE 12

Graphs Showing Arsenic and Iron Concentrations Versus Volume Recovered from ASR Wells During Cycles 3, 4, and 5 at the Peace River Facility

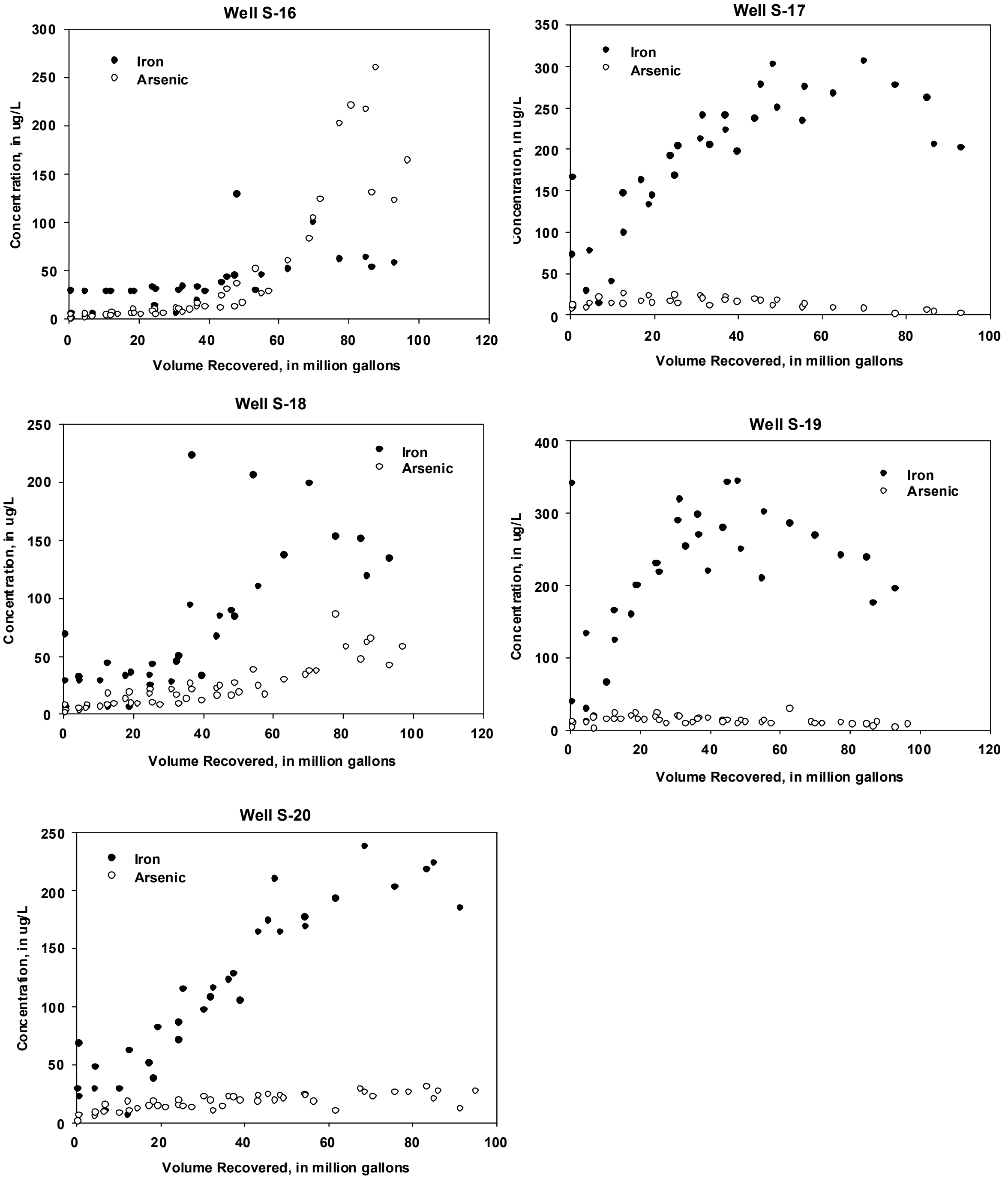

FIGURE 12 *(COMPLETED)*
Graphs Showing Arsenic and Iron Concentrations Versus Volume Recovered from ASR Wells During Cycles 3, 4, and 5 at the Peace River Facility

3.0 Geochemical Models of Major Controls on Arsenic Mobility in ASR Systems

3.1 Inverse Geochemical Models of Recovery Trends

Geochemical models are useful to quantify mass changes in solution composition as ground water travels along a flowpath. The most detailed geochemical models can simulate solution composition that results from simultaneous geochemical reactions that include mineral and gas solubility, redox evolution, sorption-desorption on mineral surfaces, and metal complexation. However, these detailed models also require significant data input, including complete water-chemical analyses, accurate estimation of the redox conditions, and quantitative information on solid phase mineralogy and composition. In the context of ASR, geochemical models have been developed to simulate water-quality changes during ASR in carbonate aquifers in South Carolina (Mirecki et al., 1998; Petkewich et al., 2004), Florida (Jones and Pichler, 2007; Mirecki, 2006), Australia (Vanderzalm et al., 2006), and Great Britain (Gale et al., 2002).

The water-quality datasets collected during successive cycle tests at TRAP and PRF ASR WF2 systems fulfill regulatory requirements and allow evaluation of the spatial and temporal distribution of important elements, such as arsenic and chloride, throughout the wellfields. However, these datasets are not sufficient for construction of detailed geochemical models that simulate arsenic transport. Specifically, there is insufficient information about the aquifer redox environment, and water-chemistry datasets lack complete elemental analyses. As shown in Figure 7, ORP values are too variable to adequately describe the aquifer redox environment. Additional analytes that are necessary for geochemical model simulations are calcium, magnesium, and sodium, for example. Additional analytes that would enable redox characterization include dissolved sulfide and sulfate.

A geochemical model that simulates reductive dissolution of iron oxyhydroxide can be developed using existing data, supplemented by redox data (specifically, dissolved sulfide concentrations) measured during cycle test 4 at the Olga ASR system in Lee County, Florida. Trends in major elements at the Olga ASR system are shown in Figure 13. Water is stored in the Suwannee Limestone at this ASR system. Solute concentrations measured during cycle 4 recovery are: iron, 0.04 mg/L; sulfide, 0.1 to 0.4 mg/L; sulfate, 93 to 156 mg/L; chloride, 60 to 238; and arsenic, 33 to 69 µg/L. These concentration ranges are similar to those measured at TRAP. Calculation of Eh (in millivolts) from the sulfide/sulfate redox couple defines the aquifer redox environment more reliably than do ORP values measured at the wellhead.

This simple geochemical model tests the hypothesis that reductive dissolution of iron oxyhydroxide under sulfate-reducing conditions can occur, as shown by recovered water-chemistry data. Geochemical model output (Appendix F) shows positive phase mole transfers for $H_2S(g)$ (dissolved hydrogen sulfide) and $Fe(OH)_3$ (amorphous iron oxyhydroxide). Micromolar quantities of dissolved hydrogen sulfide (22.5 micromoles/L) accumulate, as sulfate is reduced. Micromolar quantities of iron oxyhydroxide dissolve (5.6 micromoles/L) as Eh becomes more negative. Eh values of approximately -250 millivolts were calculated from dissolved sulfide and sulfate concentrations in recovered water samples. This simple model indicates that reductive dissolution of oxyhydroxide is feasible during recovery, and therefore could exert a significant control on arsenic mobility.

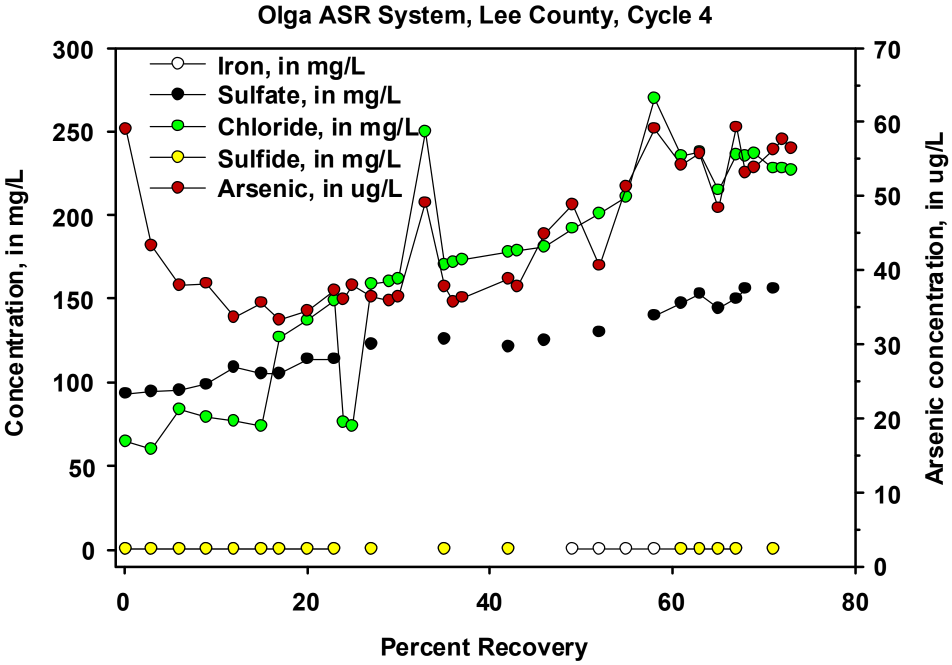

FIGURE 13
Trends in Iron, Sulfate, Dissolved Sulfide, Chloride, and Arsenic during Cycle 4 Recovery at the Olga ASR System in Lee County, FL

3.2 Native Microbiological Responses in Native: Recharge Water Microcosms

Very little is known about either the native microbial community in the FAS or the responses of the microbes to water-quality changes that occur during ASR cycle testing. Microbes affect, and possibly control, the redox environment in aquifers. Therefore, investigations that relate microbe composition, biomass, and physiology with water-chemistry can indicate some control on metal mobility. Laboratory experiments were conducted by Dr. John Lisle (U.S. Geological Survey) as part of this investigation. The overall objective is to quantify certain characteristics of the native microbial community physiology during changing conditions that represent mixing of recharge and native FAS waters during ASR cycle testing. The full text of this work is presented in Appendix D; the context and summary conclusions are presented in this section.

Laboratory microcosm experiments were designed to quantify trends in 5 measures of native microbe physiology and community structure during 2-week incubations. Microcosms consisted of mixtures of recharge water (ozone-treated TRAP ASR system) and native FAS water, plus pure end members. Microcosms consisted only of solutions. No aquifer matrix material was included in these experiments, to reduce the number of geochemical variables in these systems. Native microbes from the FAS responded to nutrients (organic carbon) and electron acceptors (such as dissolved oxygen) that result in the water mixtures. The 5 measures of native microbe physiology and community structure are: (1) total direct counts of bacteria (TDC); (2) dissolved oxygen utilization rates; (3) CLPP; (4) bacterial community productivity; and (5) bacterial community diversity.

Some results from this investigation were surprising. First, ORP measurements became more positive during the 2-week incubation period, even though dissolved oxygen (from the recharge water) was consumed. It is possible that ferrous iron may serve as an electron donor in these systems, although iron was not measured. Microbe metabolism clearly occurs in these systems, as shown by increased total direct counts of bacteria, particularly in recharge water:native FAS water mixtures. Increased microbial biomass is not concomitant with declining concentrations of organic carbon (total or dissolved). It is likely that concentrations of total and dissolved organic carbon in recharge water (ranging between 1.7 and 3.3 mg/L) are more than sufficient to support increased biomass in these microcosms, without ppm-level changes in concentration.

Experimental parameters showed consistent changes in the microcosms over a 2-week duration. Specifically, these microcosms showed increased dissolved oxygen consumption rates, changes in bacterial CLPP that differed from those of the end-member microcosms, greater bacterial community productivity, and changing bacterial community diversity compared to that in pure end-member microcosms. Specifically, these microcosms showed increased dissolved oxygen consumption rates, changes in bacterial CLPP that differed from those of the end-member microcosms, greater bacterial community productivity, and changing bacterial community diversity compared to that in pure end-member microcosms. The overall conclusion from these data is that mixing between recharge and native FAS waters stimulates microbial growth and replication, while the redox environment is still largely under oxic conditions.

Specific conclusions are as follows:

1. Treated recharge water in this study was stimulatory to native bacteria from the upper FAS.
2. The native bacterial communities responded to relative increases in organic carbon, oxygen, and other nutrients in the treated recharge water by increasing their physiological activity.
3. Increases in bacterial community physiological activity resulted in increased rates of oxygen utilization (i.e., bacterial respiration) and biomass production (productivity data) and changes in the community's carbon substrate preferences (Biolog Eco Plate data) and numerically dominant species (denaturing-gradient gel electrophoresis [DGGE]) and dioxyribonucleaic acid [DNA] fingerprint data).
4. The changes in the native bacterial community physiological activity and structure, which were driven by the introduction of treated recharge water into the native aquifer water, may promote and enhance geochemical processes, such as metal mobilization.

Bacterial cells in the treated recharge waters exhibited growth responses that indicate these cells become injured during the disinfection process and are able to recover during storage in the native ground water. This phenomenon of recovery of physiological capacity following exposure to disinfectants and during storage has regulatory significance with regard to the monitoring of the microbiological quality of ASR recharge and recovered waters.

4.0 Major Conclusions and Recommendations

This report summarizes and synthesizes ASR water-quality datasets, modeling efforts, and microbial experiments, to better understand the major controls on arsenic mobility during ASR system operation. This investigation focuses on the Tampa-Rome Avenue Park (TRAP) ASR system and Wellfield 2 at the Peace River Facility (PRF ASR WF2). At TRAP, ozone-treated recharge water is stored in permeable zones of the Suwannee Limestone. At the PRF-WF2 site, chloramine-treated recharge water is stored in permeable zones of the Suwannee Limestone. Arsenic mobilization is a significant challenge to ASR feasibility for many systems that store water in the Suwannee Limestone.

The objectives of this investigation are to:

- Characterize and quantify arsenic trends during successive ASR cycle tests at both systems.
- Define the major geochemical controls on arsenic mobility at these two systems, which share similar aquifer matrix but differ in water treatment methodology.
- Integrate interpretations from microbial microcosm experiments.

4.1 Trends in Arsenic during ASR Recovery at Tampa-Rome Avenue Park

At the TRAP ASR system, water-quality data from 6 cycle tests (2002 through 2006) were analyzed to define patterns in arsenic occurrence and mobility during recovery. Water-chemistry datasets consist of field parameters (specific conductance, pH, temperature, dissolved oxygen, ORP), major constituents (alkalinity, chloride, sulfate, fluoride), trace constituents (iron, manganese), plus species of regulatory concern (arsenic, total trihalomethanes, gross alpha, radium 226+228). Samples were collected from eight ASR wells and five storage zone monitor wells. Reproducible trends in arsenic concentrations were interpreted from recovered water chemistry data, which define a family of exponential curves that reach an asymptote during each cycle. This asymptote, or plateau of arsenic concentration, declines with each successive recovery in five of eight ASR wells at TRAP. Using this pattern of arsenic occurrence, a model was developed to simulate and quantify the pattern during successive cycles 2 through 6. Based on the pattern through successive cycles, this model also predicts maximum arsenic concentrations that can be expected during recovery in cycles 7 through 9.

Predicted asymptote arsenic concentrations at TRAP will be at or below the MCL during cycle 7 at wells ASR-1 and ASR-2. Although significant declines have occurred in wells ASR-3, ASR-4, and ASR-7, the predicted asymptote arsenic concentration remains in excess of the MCL through cycle 9, ranging between 0.025 and 0.035 mg/L. More data are required to quantify the pattern of arsenic during recovery at wells ASR-5 and ASR-6.

4.2 Trends in Arsenic during ASR Recovery at Wellfield 2 at the Peace River Facility

At the PRF ASR WF2, water-quality data were compiled from cycle tests 2 (2003) through 4 (2006). Water-quality datasets consist of field parameters (specific conductance, pH, temperature, and ORP), major constituents (alkalinity, calcium, magnesium, sodium, chloride, sulfate, fluoride), trace constituents (iron, manganese), plus species of regulatory concern (arsenic, total trihalomethanes, gross alpha, radium 226+228, uranium). Later cycles have more complete analyses compared to earlier cycles. The PRF ASR WF2 system consists of 12 ASR wells and 10 storage zone monitor wells.

Reproducible trends in arsenic concentrations were interpreted from recovered sample data, defined as a linear relationship between arsenic and volume recovered. Successive cycles show lines having progressively lower slope. Maximum arsenic concentrations were calculated at a fixed point in each cycle (50 MG recovered volume, or approximately 80 percent recovery). Maximum arsenic concentrations decline during recovery in 7 of 12 ASR wells, by 21 to 59 percent between cycles 2 and 4. Maximum arsenic concentrations are predicted to decline below 10 µg/L during cycles 5 through 7 in these same ASR wells.

4.3 Comparison of Arsenic Trends at Tampa-Rome Avenue Park and the Peace River Facility

Reproducible patterns of arsenic concentrations can be defined in recovered water during successive ASR cycles at each system examined in this study. However, the asymptote pattern observed at TRAP differs from the linear pattern observed at PRF ASR WF2. This difference results from a combination of water disinfectant, geochemical, possibly microbial, and hydraulic factors. It is likely that redox evolution of the aquifer environment throughout the ASR cycle test controls arsenic mobility and the stability of the mineral phase(s) that release and sorb arsenic (and likely other trace elements). Data to support redox evolution as the major control are equivocal at present. Ground water ORP values at both ASR systems, although abundant, are too variable to characterize the redox environment of the aquifer. Neither system has measured dominant redox couple concentrations (specifically sulfate/sulfide) with regularity to calculate Eh through the ASR cycle. Therefore, our conclusions on redox controls are based on the concentration trends observed in the datasets, supplemented by limited modeling and reasoned geochemical intuition. Specifically, the aquifer redox environment becomes significantly less oxidized to reducing as the ASR cycle proceeds through storage and recovery. More reducing conditions are indicated by detectable sulfide and increasing dissolved (presumably ferrous) iron in recovered water. Arsenic, iron, and sulfide are all mobile under low oxidizing to reducing redox conditions.

Different patterns in arsenic concentrations between TRAP and PRF ASR WF2 during recovery result (in part) from different redox conditions during recharge. Elevated dissolved oxygen concentrations (exceeding saturation) in TRAP recharge water oxidize more pyrite per cycle, releasing more arsenic from voids and fractures. Apparently, oxic recharge water reacts with available pyrite along flowpaths, such that arsenic is progressively removed with each successive cycle. To determine whether all TRAP wells will show consistent declining arsenic concentrations in recovered water during future cycles, continued monitoring would be required. In comparison, PRF ASR WF2 recharge water has dissolved oxygen concentrations at or near saturation. Progressive removal of arsenic is suggested by declining slopes. A consistent pattern of declining arsenic was documented in both the TRAP and PRF wellfields with each additional ASR cycle.

Future investigations that quantify the relationship between dissolved oxygen with arsenic release during recharge will likely be fruitful. Dissolved oxygen is the principal electron acceptor in recharge water, so removing dissolved oxygen from recharge water should ameliorate high arsenic concentrations during ASR cycle testing. Technologies that remove dissolved oxygen as part of industrial water treatment processes are described in Appendix C.

4.4 Significance of Changes in Microbe Physiology and Community Structure

The changes observed in microcosm experiments are most applicable to oxic, recharge conditions. Native FAS:recharge water microcosms show increased biomass and respiration activity while oxic conditions are maintained. This condition indicates that mixing stimulates microbial growth, presumably due to increased nutrient or organic carbon content in recharge water. What remains unknown is whether microbe community structure changes as lower Eh (possibly sulfate-reducing) conditions ensue during storage and recovery. The relationship between microbe community structure in the FAS and redox evolution of the aquifer environment remains elusive.

4.5 Recommendations

Future investigations should focus on the following approaches to understand arsenic behavior in ASR applications in Florida:

- Confirm the evolution of aquifer redox environment during ASR cycle tests. The least costly and most useful way to quantify redox environment is to measure concentrations of dissolved sulfide and sulfate in ASR well samples through a complete cycle and add calibrated ORP measurements to the field parameters.
- Construct geochemical models to simulate arsenic sorption and desorption using measured concentrations of redox couples (sulfide/sulfate) supplemented by existing mineralogical and bulk chemical data from the Suwannee Limestone lithologies.
- Support ongoing microbial-geochemical investigations (Florida Geological Survey, US Geological Survey) that determine the mechanisms of microbe-mediated metals mobilization.
- Incorporate cycle 7 and later ASR cycle data from TRAP into the existing exponential model, to document the clear trend of continuing arsenic concentration decline with successive ASR cycles at this site at a predictable site-specific rate.
- Evaluate operational strategies at TRAP and PRF ASR WF2 sites to minimize upconing and arsenic mobility during ASR cycle tests.
- Utilize the above investigations actions to develop a stoichiometric model to relate dissolved oxygen concentrations in recharge water to arsenic concentrations in recovered water.

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Appendix A

Technical Memorandum TM-1

TECHNICAL MEMORANDUM

Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage and Recovery Activities for SWFWMD

TO:	Southwest Florida Water Management District
FROM:	CH2M HILL U.S. Army Engineer Research and Development Center U.S. Geological Survey ASRus
DATE:	June 6, 2006

Contents

Executive Summary

This technical memorandum will summarize progress of the CH2M HILL/U.S. Geological Survey/U.S. Army ERDC team project entitled, “Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage and Recovery Activities” for the Southwest Florida Water Management District (SWFWMD). As outlined in the Scope of Work, the focus of Technical Memorandum 1 was to assess the completeness and quality of water-quality data sets of two ASR systems within the focus area of SWFWMD. A progress report on experiments to quantify effects of native microbe respiration on water-quality also will be presented.

The overall objective of this project is to use geochemical modeling methods to interpret arsenic mobility as redox environment changes during ASR cycle tests. To complete this objective, water-quality data were compiled for two ASR systems: The Rome Avenue Park ASR system, and the Peace River Wellfield 2 ASR system. Ideally, water-quality data sets include the following:

1. Complete analyses of recharge water quality characteristics
2. Complete analyses of native water quality from permeable zones of the Suwannee Limestone
3. Complete analyses of water quality samples from ASR and monitor wells obtained during successive cycle tests

Complete water-quality analyses are those in which at least 90 percent of the dissolved mass is measured. Ideally, measurements of reactive trace element concentrations (for example, dissolved iron and sulfide) are also important, even though they comprise a small fraction of the solute mass. The extent to which these data set requirements are satisfied is the primary focus of this memorandum.

Data gaps exist in data sets from the Rome Avenue Park and Peace River ASR systems. The following data are needed to complete the Rome Avenue Park ASR system data set:

- Recharge water samples in which calcium, magnesium, and sodium are measured in addition to typical analytes. These may be available from the archives at David L. Tippin Water Treatment Plant.
- Native groundwater samples in which dissolved sulfide and iron are measured in addition to typical analytes. Existing water quality analyses from nearby SWFWMD ROMP wells may satisfy this requirement.

The following data are needed to complete the Peace River ASR system data set:

- Recharge water samples in which calcium, magnesium, sodium and total organic carbon are measured in addition to typical analytes.
- Existing water quality analyses from nearby SWFWMD ROMP wells to supplement native groundwater quality data from nearby monitor well M-6.

Microbial ecology of the Upper Floridan Aquifer system likely exerts an effect on arsenic mobilization. Unfortunately, few investigations have been performed to define this relationship. As part of this project, bench-top experiments have been defined to quantify the relationship between microbial respiration rate and redox condition. These experiments are in progress.

Two data sets are available now that complement this technical memorandum. All available recharge and groundwater quality data have been assembled into two Excel spreadsheets for future use. Data include water quality parameters, concentrations of major and trace dissolved inorganics, trace organics, and radionuclides for all ASR and monitor wells at the Rome Avenue Park and Peace River Wellfield 2 ASR systems from 2000 to present. Water quality data were compiled to represent native groundwater composition, recharge-water composition, and samples from ASR and monitor wells throughout the recharge, storage, and recovery stages of successive cycle tests.

Water Quality Characteristics at the City of Tampa - Rome Avenue Park ASR System

Recharge Water Quality

The Rome Avenue Park ASR system consists of 8 recharge/recovery (or ASR) wells that are completed in permeable zones of the lower Suwannee Limestone. The wells are completed with total depths between 375 and 430 feet below land surface (bls). The City of Tampa Water Department stores and recovers approximately 10 million gallons per day (mgd) of potable water for a period of approximately 100 days, resulting in approximately 1 billion gallons of water stored each year at its Rome Avenue Park ASR system. The water is stored until the following dry season (typically 4 to 6 months of storage) when the water is recovered as a supplemental drinking water supply.

Surface water from the Hillsborough River is treated at the David L. Tippin Water Treatment Plant (DLTWTP). Approximately 90 million gallons of this source water is treated daily by the conventional coagulation treatment processes plus ozonation and biofiltration. To ensure the quality of the recovered water, the system was designed to bring the recovered water to the head of the treatment plant to be mixed with the source water to be fully re-treated. This resolved concerns regarding the mobilization of arsenic and other metals in the recovered water. The ferric sulfate coagulation process has been shown to be very effective at removing arsenic concentrations with less than 1 part per billion (ppb) consistently delivered to the customers. Full volumetric recovery of the water from the outset of this project, however, has been used to minimize arsenic levels in the aquifer, and this practice has resulted in elevated chloride and bromide concentrations in the recovered water indicating upconing from below (brackish water intrusion). Following coagulation with ferric sulfate, the water undergoes ozonation which is the City’s primary disinfectant utilized for its drinking water supply. Biofiltration treatment and chloramination follow the ozone process to maintain a chlorine residual in the distribution system.

Treated water then flows through the City’s potable water transmission system to the Rome Avenue Park ASR system for cycle testing. During the storage cycle, up to 10 mgd of this treated water is delivered to the ASR site. Treated recharge water-quality was measured at two points:

1. At the DLTWTP (n = 1044 for most analytes, time span 2000 through 2004)
2. At the common distribution point at the Rome Avenue Park ASR system (n = 60-65 for most analytes, time span 2000 through mid-2005)

Travel time for recharge water from the DLTWTP to the Rome Avenue Park ASR system is not known, but is estimated at 1 to 2 hours. Data gaps are identified in a subsequent section.

Different analytes are measured in samples from DLTWTP versus Rome Avenue Park ASR system (Table 1). In order to use recharge water quality data for geochemical modeling, analytes from both data sets will be combined, and uncertainty estimated for each median concentration. Of particular importance will be examination of redox-sensitive species and indicators, namely dissolved oxygen (DO) and oxidation-reduction potential (ORP). Similar to water quality data sets at ASR systems throughout south Florida (Mirecki, in review), these analytical data sets are incomplete for geochemical modeling. Both recharge water quality data sets lack measurement of all major dissolved inorganic constituents (sodium, calcium, magnesium, potassium) plus carbonate alkalinity in each sample. Calculation of calcium and magnesium concentrations from total, non-carbonate, and calcium and magnesium hardness values result in unacceptably large errors, which are discussed in a subsequent section. The following discussion will focus on those analytes that affect arsenic mobility during ASR cycle testing.

TABLE 1
Analytes Measured in Treated Surface Water Samples at the Common Distribution Point at the Rome Avenue Park ASR System and the David L. Tippin WTP

Rome Avenue Park ASR System			**David L. Tippin WTP**		
Water Quality Parameters	Major and Trace Inorganics	Other	Water Quality Parameters	Major and Trace Inorganics	Other
Temperature	Chloride	Total Dissolved Solids	Temperature	Chloride	Turbidity
pH	Iron	Gross Alpha	pH	Iron	Chlorine Residual
Specific Conductance	Manganese	Ra^{226}	Specific Conductance	Manganese	Trihalo methanes
ORP	Total Alkalinity	Ra^{228}	--	Total Alkalinity	--
--	Sulfate	Chlorine Residual	--	Total Hardness	--
--	Fluoride	Trihalo methanes	--	Calcium and Magnesium Hardness	--
--	Arsenic	DO	--	Total Organic Carbon	--

Trends in DO and ORP. Oxidation of minerals in the Suwannee Limestone by ozone and its decomposition products in recharge water is the most likely mechanism for arsenic mobilization at the Rome Avenue Park ASR system. Ozone (O_3) is used for disinfection and oxidation of organics during treatment (VonGunten, 2003). Ozone is unstable in water, and decomposes rapidly to form hydroxyl free radicals, which are strong oxidants. The rates of free radical formation depend on the pH, alkalinity, and the nature of organic carbon in the water (VonGunten, 2003). Ozone also will decompose to yield other free radicals and dissolved oxygen (DO, as O_2 in mg/L) at rates that vary with water composition. Variations in these complex redox reactions obscure the relationship between ORP (in millivolts, mV) and DO concentration at the common distribution point at the Rome Avenue Park ASR system (Figure1). Linear regression of DO and ORP was not significant ($r^2 = <0.01$), even when only positive ORP values are used. Lack of significance results from two factors:

1. Recharge water has not equilibrated with respect to ozone and its products of decomposition during transport from the DLTWTP and the ASR system
2. DO probes are not stable in the oxidizing redox condition of these waters

However, DO measurements at the ASR system provide a range of oxidant concentrations and uncertainty for geochemical model input (Table 2).

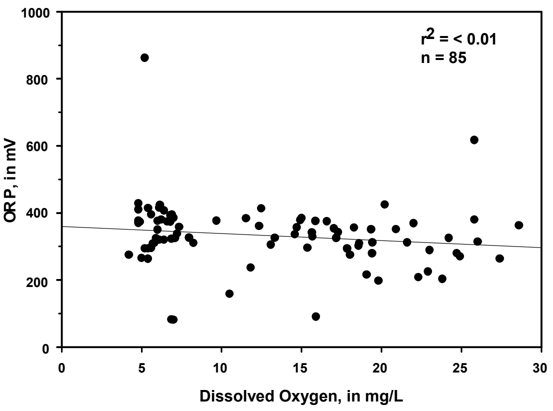

FIGURE 1 . Linear Regression of Dissolved Oxygen Concentration and ORP Value, as Measured at the Common Distribution Point at the Rome Avenue Park ASR System. Data Measured During Recharge, from November 2000 Through May 2005.

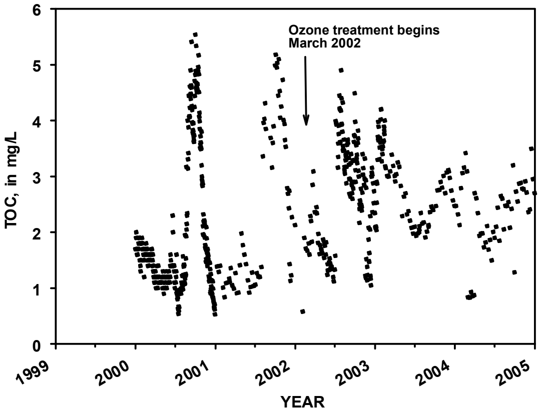

FIGURE 2. Time-Series Plot of Total Organic Carbon (TOC) Concentrations Measured in Treated Water Samples from DLTWTP. TOC Concentrations Measured after March 2002 are used for Geochemical Model Input.

Trends in Organic Carbon Concentration. Organic carbon is necessary for microbial metabolism, and therefore is an important water-quality constituent to understand biogeochemistry of the Upper Floridan aquifer system. TOC values were measured frequently after treatment at DLTWTP (Figure 2). TOC shows a pronounced seasonality, with highest values coincident with late summer-fall rainfall or algal biomass accumulation. Maximum values of TOC during the wet season roughly coincide with recharge periods. It is presumed that TOC degradation is not significant during transport from DLTWTP to the ASR system because carbonate alkalinity does not increase significantly (discussed in a subsequent section). Additional TOC and DOC analyses (ongoing) at the ASR site will quantify whether organic carbon concentration changes significantly between the DLTWTP and the Rome Avenue Park ASR system. TOC data from March 2002 through 2005 (after ozone treatment begins) are used to establish the range of TOC concentrations and uncertainty for geochemical model input (Table 2).

Trends in Chloride and Specific Conductance. Chloride and specific conductance were measured at DLTWTP and the Rome Avenue Park ASR system. Seasonal trends in chloride are evident, with higher chloride concentrations corresponding to dry winter-spring months (Figure 3) when supplemental sources such as ASR and Sulphur Springs are utilized. Chloride concentrations have declined overall since 2000, which was one of the worst droughts on record in the City. Chloride measurements from the DLTWTP are not available after mid-2002, but measurements continue at the ASR system. ASR system values (Sept 2001 through May 2005) are considered representative for geochemical model input (Table 2). Specific conductance values follow similar seasonal trends, although fewer data are available at the ASR system (Figure 4). Linear regression of specific conductance values measured at both sites on the same day show an r^2 of 0.4.

Trends in Other Major and Trace Dissolved Constituents. Carbonate alkalinity was measured at the DLTWTP and the Rome Avenue Park ASR system, and both data sets show similar trends (Figure 5). Linear regression of total alkalinity values measured at both sites on the same day show an r^2 of 0.70, which suggests that limited oxidation of TOC occurs (by all oxidants, to form bicarbonate) during conveyance to the Rome Avenue Park ASR system. ASR system values (Sept 2001 through May 2005) are considered representative for geochemical model input (Table 2).

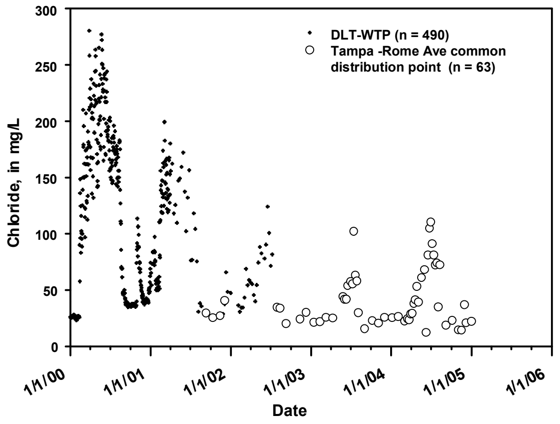

FIGURE 3. Time-Series Plot of Chloride Concentrations Measured in Samples from DLTWTP and Rome Avenue Park ASR System. The Latter Data will be used for Geochemical Model Input.

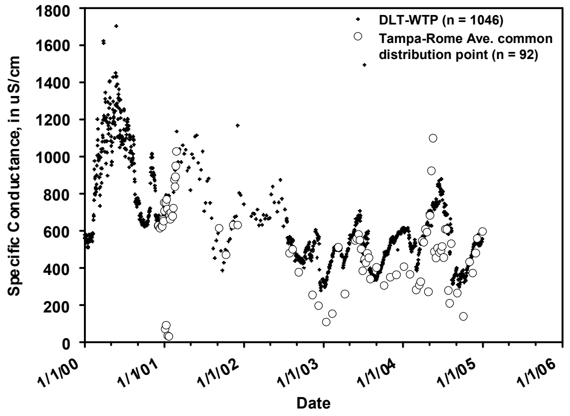

FIGURE 4. Time-Series Plot of Specific Conductance Values Measured in Samples from DLTWTP and Rome Avenue Park ASR System.

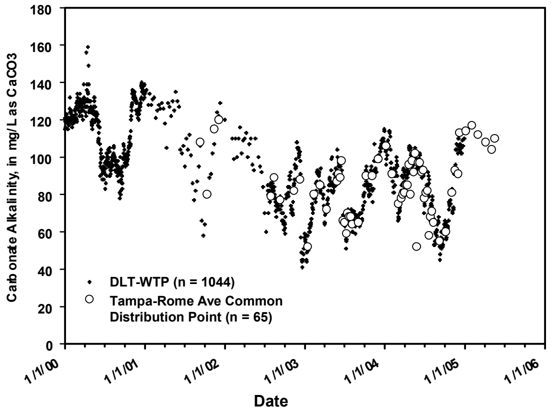

FIGURE 5. Time-Series Plot of Carbonate Alkalinity Concentrations Measured in Samples from DLTWTP and the Rome Avenue Park ASR System. The latter data will be used for Geochemical Model Input

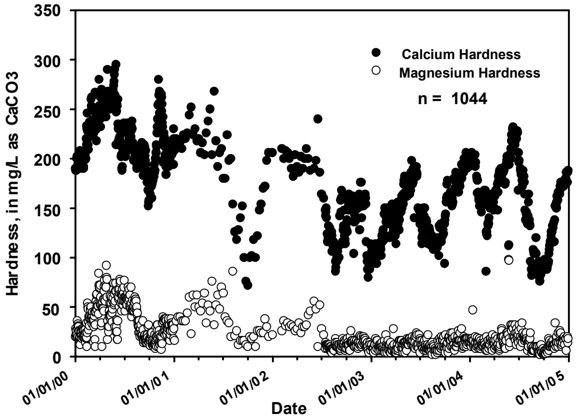

FIGURE 6. Time-Series Plot of Calcium and Magnesium Hardness Values Measured in Samples from DLTWTP Only. Calcium and Magnesium Concentrations can be estimated from hardness for Geochemical Model Input

Calcium and magnesium hardness values were calculated from measured calcium and magnesium concentrations (standard method 2340B; APHA, 1998a) in samples from DLTWTP only. Observed hardness trends mimic those for carbonate alkalinity because calcium and magnesium stoichiometries are related to carbonate alkalinity. Unfortunately, the original calcium and magnesium concentrations were not reported in the DLTWTP data set. Calcium and magnesium concentrations are back-calculated from calcium and magnesium hardness values, possibly resulting in significant error due to the presence of non-carbonate hardness in these samples. Errors from these calculations are discussed in detail in the "data gaps" section. It is important to report measured calcium and magnesium concentrations so that carbonate equilibria can be simulated accurately in geochemical models. Calculated calcium and magnesium concentrations will be used initially for geochemical model input (Table 2).

Dissolved iron concentrations were measured at DLTWTP and the Rome Avenue Park ASR system, and both data sets show a similar range of values (Figure 7). Also, there are hundreds of analyses that are below detection (less than 0.01 mg/L) in both data sets. Total dissolved iron concentrations typically are low, ranging between 0.01 and 0.03 mg/L (10 and 30 µg/L). Addition of ferric sulfate during the treatment process does not significantly increase iron concentration in the recharge water. These values will be used for geochemical model input (Table 2). Dissolved manganese concentrations were measured at both sites between 2002 and 2005. Of 1,044 analyses at the DLTWTP, all but 46 analyses were below detection (less than 10 µg/L). When manganese was detected, the median concentration was 20 µg/L. Of 65 analyses at the Rome Avenue Park ASR system, all but 6 analyses were below detection (less than 10 µg/L); when detected, the median concentration also was 10 µg/L.

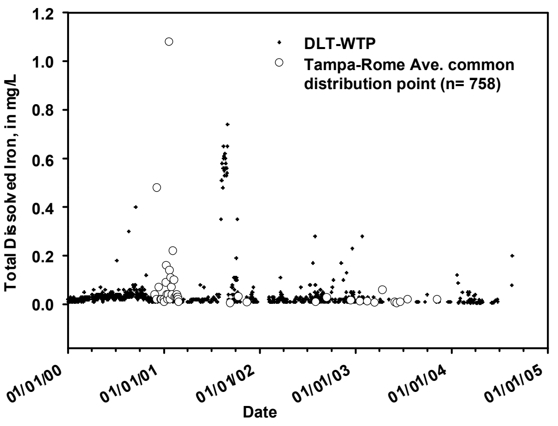

FIGURE 7. Time-Series Plot of Total Dissolved Iron Concentrations Measured in Samples from DLTWTP and Rome Avenue Park ASR System. Both datasets provide a range of values for Geochemical Model Input.

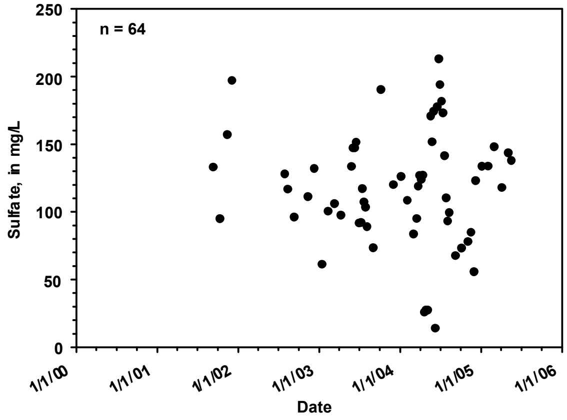

FIGURE 8. Time-Series Plot of Sulfate Concentrations Measured in samples from Rome Avenue Park ASR System Only. These data will be used for Geochemical Model Input

Sulfate concentrations were measured only at the common distribution point at the Rome Avenue Park ASR system (Figure 8). These data are normally distributed (one of few analytes that show this distribution), and, thus, do not show seasonal patterns as do other analytes. Sulfate concentrations are significantly higher in recharge water compared to native groundwater, most likely due to the addition of ferric sulfate. Median values of sulfate will be used for geochemical model input (Table 2).

Arsenic concentrations were measured in samples (n = 60) from the Rome Avenue Park ASR system common distribution point between 2002 and 2005. All arsenic concentrations were below the detection limit (less than 1 μg/L) in recharge water. This is consistent with arsenic concentrations measured leaving the DLTWTP, which have all been less than 1 μg/L.

Native Groundwater Quality

Native groundwater quality in the permeable zones of the Suwannee Limestone at the Rome Avenue Park ASR system is best characterized by samples from SZMW-2 (storage zone monitor well; Table 3). This storage zone monitor well is located approximately one-half mile west of the Armenia Avenue site boundary, and has not been affected by ASR operations at this site. Approximately 90 samples were collected from this well during the period of September 2001 through January 2006. Unfortunately, most major dissolved constituents were not measured in these samples. Descriptive statistics for all available analytes are presented in Table 3.

Native groundwater quality in the permeable zones of the Avon Park Formation at the Rome Avenue Park ASR system is characterized by samples from Well 2D. This monitor well is located approximately 600 feet south of Sligh Avenue. Approximately 75 samples were collected from this well during the period between September 2001 and January 2006. Most major dissolved constituents were not measured in these samples. Descriptive statistics for all available analytes are presented in Table 4.

Trends in Dissolved Oxygen and ORP. Native groundwater should be anoxic in all samples, and, therefore, show strongly negative (less than -200 mV) ORP values. Hydrogen sulfide was detected in native groundwater from the lower Suwannee Limestone permeable unit, which generally is consistent with strongly negative ORP. DO is not stable under these reducing conditions. DO concentrations should only be a few tenths of mg/L at most, and would reflect aeration during sampling. There are a few DO measurements that are near saturation (Figure 9). These DO values do not accurately reflect redox conditions in the Suwannee Limestone permeable zone. There is no significant relationship observed between DO and ORP in these samples because ORP reflects the abundance of redox pairs (for example, ferrous and ferric iron, as well as hydrogen sulfide and sulfur oxidation products) in the aquifer.

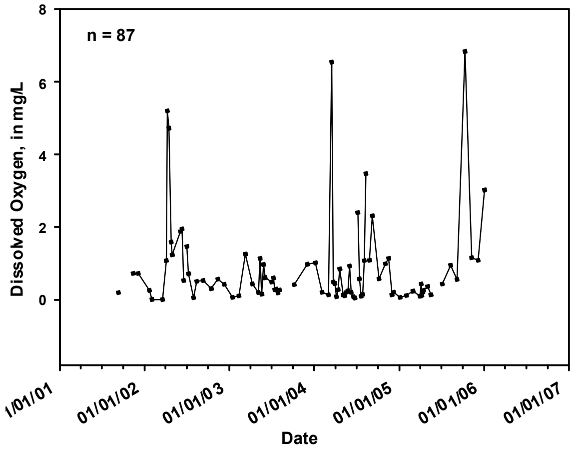

FIGURE 9. Time-series plot of DO concentrations in native groundwater from the Lower Suwannee Limestone near the Rome Avenue Park ASR system between September 2001 and January 2006.

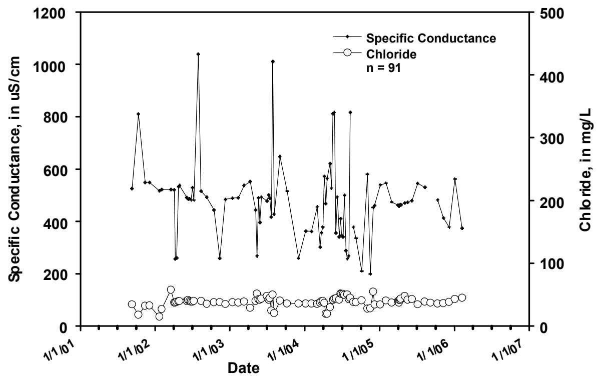

FIGURE 10. Time-series plot of chloride and specific conductance values in native groundwater near the Rome Avenue Park ASR system, between September 2001 and January 2006.

Dissolved oxygen was measured in samples from the permeable unit of the Avon Park Formation (Table 4). The median DO concentration was 1.72 mg/L, and DO values ranged between 0.2 mg/L (generally, the detection level of a DO probe) to 8.0 mg/L. There were a few erroneous DO measurements that were greater than 8.0 mg/L. Native groundwater in the Avon Park Formation should be anoxic, so DO values greater than 0.2 mg/L indicate aeration during sampling.

Trends in Chloride and Specific Conductance. Chloride concentrations are generally low (less than 100 mg/L; Figure 10) in native groundwater from the lower Suwannee Limestone permeable unit and are similar to recharge water concentrations. Specific conductance values generally are less than 800 µS/cm, and are not significantly correlated with chloride concentration ($r^2 < 0.1$).

Chloride concentrations in the permeable zone of the Avon Park Formation are considerably higher than those measured in the recharge water and Suwannee Limestone permeable zone (Table 4). The median chloride concentration was 870 mg/L, and chloride values ranged between 21.8 and 1626 mg/L. Low chloride concentrations (less than 100 mg/L) are suspect. The median specific conductance value is 2720 µS/cm, with values ranging between 1,162 and 5,800 µS/cm. There are 14 samples with spurious values less than 500 µS/cm. Low specific conductance values do not correlate with low chloride concentrations.

Trends in Other Major and Trace Dissolved Constituents. Total alkalinity, sulfate, and total dissolved iron were the only other major and trace dissolved constituents measured in native groundwater from the lower Suwannee Limestone permeable zone. Total alkalinity concentrations are significantly greater (almost double) in native groundwater when compared to recharge water (Mann-Whitney rank sum test P< 0.001). Sulfate is significantly lower (approximately one-third) in the native groundwater when compared to recharge water, possibly due to the addition of ferric sulfate coagulant during the treatment process. Sulfate in recharge water may serve as an electron acceptor for native sulfate-reducing bacteria in the aquifer. Concentrations of total dissolved iron and manganese are similar in native groundwater from the Suwannee Limestone permeable zone and recharge water.

Total alkalinity, sulfate, and total dissolved iron also were measured in samples from Avon Park permeable zone (Table 4). Sulfate and iron concentrations in native groundwater from the Avon Park Formation are significantly higher than those measured in recharge water or the Suwannee Limestone permeable zone. Sulfate and iron may be useful indicators of upconing in recovered water.

Data for Geochemical Model Input

Recharge water quality data sets from the DLTWTP and from the Rome Avenue Park ASR system were characterized using standard statistical methods (descriptive methods, time-series analysis, linear regression). Concentrations of individual analytes (except sulfate) typically are not normally distributed. Water quality characteristics are reported as median values, and values that represent the 25th and 75th percentiles of the population (Table 2). Native groundwater quality in the permeable zone of the lower Suwannee Limestone at the Rome Avenue Park ASR system is best characterized by samples from offsite storage zone monitor well SZMW-2 (Table 3).

TABLE 2

Recharge Water Quality Characteristics for Geochemical Model Input

Data sets consist of analyses of treated water from the David L. Tippin WTP and also the common distribution point samples at the Rome Avenue Park ASR system

Composite Recharge Water Quality Data: Rome Avenue Park ASR System

Analyte	Median value	Uncertainty: 25th percentile	Uncertainty: 75th percentile	Number of Analyses
Dissolved Oxygen, in mg/L	12.4	6.1	19.4	90
Total Organic Carbon, in mg/L	2.7	2.1	3.3	292
Chloride, in mg/L	31.2	24.2	57	63
Sulfate, in mg/L	118	93	144	64
Carbonate Alkalinity, in mg/L as $CaCO_3$	85	71.8	97	65
Total Dissolved Iron, in µg/L	20	10	50	801
Total Dissolved Manganese, in µg/L	10	< 10	30	52
Calculated calcium, in mg/L	71.3	55.3	83.3	1046
Calculated magnesium, in mg/L	3.9	2.4	7.3	1044
Arsenic in µg/L	< 1	--	--	60
pH	7.9	7.6	8.2	1044

TABLE 3
Native Water Quality Characteristics of the Lower Suwannee Limestone Permeable Zone for Geochemical Model Input
Data set consists of analyses from SZMW-2, located approximately one-half mile west of the Rome Avenue Park ASR system

Composite Native Water-Quality Data, Suwannee Limestone permeable zone (SZMW-2): Rome Avenue Park ASR System

Analyte	Median value	Uncertainty: 25th percentile	Uncertainty: 75th percentile	Number of Analyses
Dissolved Oxygen, in mg/L	0.45	0.2	1.05	87
Total Organic Carbon, in mg/L	--	--	--	--
Chloride, in mg/L	39.1	35.7	42.8	91
Sulfate, in mg/L	31.5	25.1	39.2	88
Total Alkalinity, in mg/L as $CaCO_3$	193	188	197	89
Total Dissolved Iron, in µg/L	20	10	30	44 detects, 45<10 µg/L
Total Dissolved Manganese, in µg/L	10	--	--	3 detects, 68 < 10 µg/L
Calcium, in mg/L	--	--	--	--
Magnesium, in mg/L	--	--	--	--
Sodium, in mg/L	--	--	--	--
Arsenic in µg/L	4	2	6	4 detects, 88 < 1 µg/L
Oxidation-Reduction Potential, in mV	-290	-325	-231	91
pH	7.5	7.3	7.6	91

TABLE 4
Native Water Quality Characteristics of the Avon Park Formation Permeable Zone for geochemical Model Input
Data set consists of analyses from Well 2D located approximately 600 ft south of Sligh Avenue.

Composite Native Water-Quality Data, Avon Park Formation Permeable Zone (Well 2D): Rome Avenue Park ASR System

Analyte	Median value	Uncertainty: 25th percentile	Uncertainty: 75th percentile	Number of Analyses
Dissolved Oxygen, in mg/L	1.72	1.0	2.6	81
Total Organic Carbon, in mg/L	--	--	--	--
Chloride, in mg/L	870	663	1164	75
Sulfate, in mg/L	191	145	267	74
Total Alkalinity, in mg/L as $CaCO_3$	98	69	129	76
Total Dissolved Iron, in µg/L	1470	990	2113	77
Total Dissolved Manganese, in mg/L	60	40	78	68 detects, 2 < 10 µg/L
Calcium, in mg/L	--	--	--	--
Magnesium, in mg/L	--	--	--	--
Sodium, in mg/L	--	--	--	--
Arsenic in µg/L	--	--	--	76 below detect (< 1 µg/L)
Oxidation-Reduction Potential, in mV	-195	-289	-147	77
pH	7.9	7.5	8.2	87

Water-Quality Characteristics at the Peace River/Manasota Regional Water Supply Authority (PRMRWSA) ASR System

Recharge Water Quality

The PRMRWSA (Peace River) ASR system consists of two wellfields. Wellfield 1 is located near the Peace River Facility (PRF) and consists of 9 recharge/recovery (ASR) wells, of which 8 are completed in permeable zones of the Suwannee Limestone (total depths 623 to 955 feet bls). One additional well is completed in the Tampa Member of the Hawthorn Group, at a total depth of 482 feet (CH2M HILL, 2003a). Wellfield 1 was is the older of the two wellfields, developed and expanded during the period of 1984 through 1995. Wellfield 2 consists of 12 ASR wells completed in permeable zones of the Suwannee Limestone (total depths 883 to 905 feet bls). Wellfield 2 began operation in 2002 (CH2M HILL, 2003a). The data set from Wellfield 2 is more complete, and, thus, provides a better characterization of native groundwater quality for use in geochemical models.

Surface water from the Peace River is treated at the PRF and recharged through ASR wells, or stored for future treatment in an adjacent off-stream reservoir, depending on stage of the river and available capacity in the reservoir. The surface-water treatment process consists of coagulation with alum, filtration, and chloramine disinfection to meet drinking water standards. Recharge water has undergone full treatment at the PRF, whereas water sent directly to the surface reservoir is untreated. Recharge water-quality (as indicated by Total Dissolved Solids (TDS) concentrations) for the period 1987-2002 was summarized previously (CH2M HILL, 2003b). Major and trace element concentrations obtained from treated surface water during 2002 and 2003, and 2005 are summarized here for input into geochemical models. Compared to the Rome Avenue Park ASR system data set, fewer recharge water-quality data are available for the Peace River ASR Wellfield 2. The only major dissolved constituent concentrations that have large populations are: dissolved oxygen, sulfate, chloride, and total alkalinity. A few (less than 5) calcium, magnesium, and sodium analyses are available. Trace dissolved constituent concentrations having large data populations are: arsenic and iron. At least half of the analyses are below their respective minimum detection limit for arsenic and iron. Water-quality parameters pH, ORP, and specific conductance are measured in the field and are abundant for ASR Wellfield 2. Data gaps for the Peace River ASR Wellfield 2 are identified in a subsequent section.

Trends in Dissolved Oxygen and ORP. Ozonation is not part of the surface water treatment process at the Peace River ASR system; therefore, DO concentration depends primarily on recharge water temperature. Recharge water temperature ranges between 16 and 35 degrees, and varies seasonally with surface water temperature. In pure water, the concentrations of DO saturation at these temperatures range between 9.87 and 6.85 mg/L, respectively (APHA, 1998b). The observed range of DO values in the Peace River ASR Wellfield 2 recharge water-quality data set is 9.86 to 2.72 mg/L, with a median value of 5.5 mg/L (Table 5). ORP values are consistent with water that is near-saturation with DO (approximately +450 mV). Linear regression of DO and ORP values are not significantly correlated, with an r2 value of 0.28 (Figure 11). Lack of significance between DO and ORP probably results from a disequilibrated or incompletely calibrated DO meter, and waters in redox disequilibrium.

Trends in Chloride and Specific Conductance. Chloride concentrations and specific conductance values show similar trends over time (Figure 12). Linear regression of chloride and specific conductance shows moderate significance ($r^2 = 0.79$). There is some suggestion for seasonality to chloride and specific conductance, with greater values measured during late spring-summer dry period of 2005. More data are needed to confirm a seasonal trend. Since no dam is present on the Peace River, minor tidal influence may affect the recharge water quality during low river flow periods. Chloride values measured here represent a range of expected recharge water concentrations for geochemical model input, compiled in Table 5.

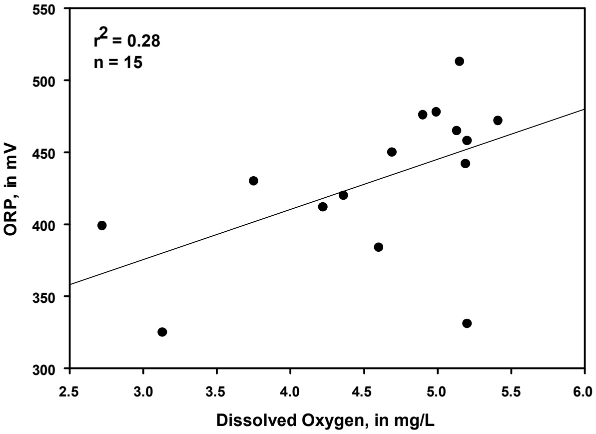

FIGURE 11. Linear Regression of Dissolved Oxygen Concentration and ORP Value at the Peace River ASR System.

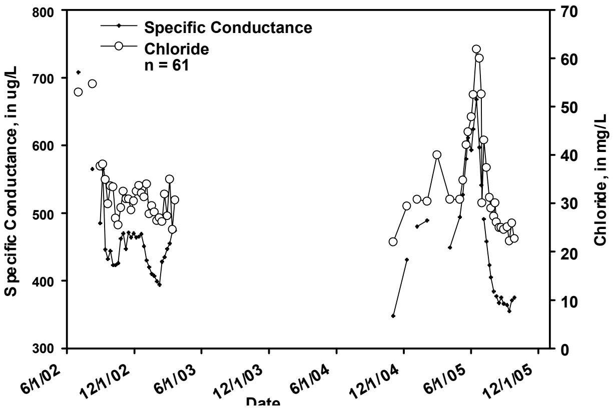

FIGURE 12. Time-Series Plot of Specific Conductance and Chloride Concentration in Recharge Water at the Peace River ASR System.

Trends in Other Major and Trace Dissolved Constituents. Total alkalinity, sulfate, iron, and arsenic concentrations were measured in recharge-water samples at the Peace River ASR system. Concentrations of total alkalinity and sulfate represent the ranges of expected recharge water concentrations for geochemical model input (Fig. 13, Table 5). All sulfate concentrations were below the secondary drinking water standard (DWS) maximum contaminant level (MCL) of 250 mg/L.

Few data (n < 6) are available to characterize calcium, magnesium, and sodium concentrations. Although few in number, these analyses will serve as geochemical model input (Table 5). Considering dissolved iron, more than half of the samples were below the detection level (typically 30 µg/L). When detected, iron concentrations ranged between 25 and 132 µg/L. Considering arsenic, approximately two-thirds of the samples were below the detection level (typically 1.32 µg/L). When detected, arsenic concentrations ranged between 0.8 and 3.7 µg/L. All arsenic analyses are below the primary DWS MCL of 10 µg/L.

Native Groundwater Quality

Water quality characteristics of the Suwannee Limestone producing zone at the Peace River ASR system are defined from data obtained from background monitor well M-6.Few data were available for the nearby ROMP well 9.5 although native groundwater characterization can be expanded if these data can be acquired.

Trends in Dissolved Oxygen, Dissolved Sulfide, and ORP. DO and sulfide were measured during 2005 (n=20) in native groundwater at the Peace River ASR system (Figure 14, Table 6). These data are critical for redox state assessment, and show values common to anoxic aquifers where sulfate reduction occurs. DO concentrations generally range less than 1 mg/L, with trace DO ingassing likely during sampling. Dissolved sulfide concentrations range from 1.4 to 4.4 mg/L. ORP values range from -110 to -257 mV (3 positive values deleted). The ranges of dissolved sulfide and ORP values are consistent with sulfate-reducing conditions in the aquifer.

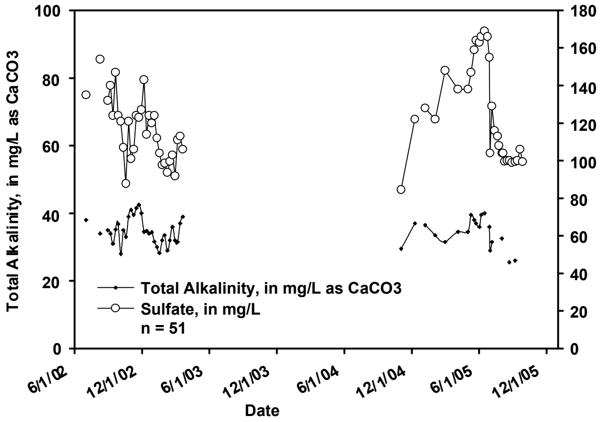

FIGURE 13. Time-Series Plot of Total Alkalinity and Sulfate Concentrations Measured in Treated Surface Water at the Peace River ASR System.

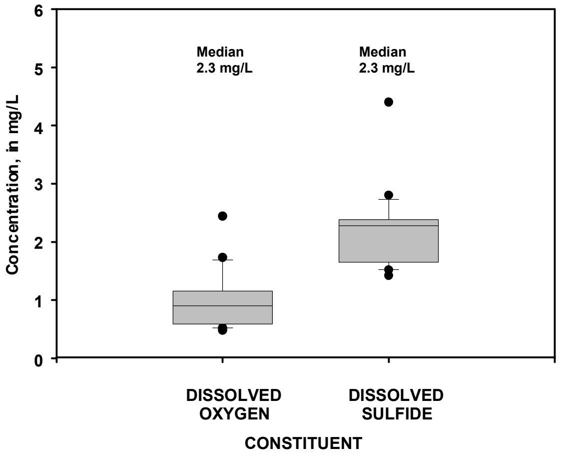

FIGURE 14 . Box-Plots Showing Concentration Ranges of Dissolved Oxygen and Dissolved Sulfide in Native Ground-Water from M-6 At the Peace River ASR System.

Trends in Chloride and Specific Conductance. Chloride and specific conductance were measured monthly in native groundwater from 2002 through 2005 (Figure 15, Table 6). The median chloride concentration was 224 mg/L, and ranged between 85 and 279 mg/L. The median specific conductance value was 1460 µS/cm, and ranged between 862 and 1809 µS/cm. Linear regression of chloride and specific conductance is not significant (r^2 = 0.20). Chloride concentrations and specific conductance values differ significantly when recharge and native groundwater are compared (Mann-Whitney rank sum test $P < 0.001$). Therefore, chloride can be used as a tracer of native groundwater at the Peace River ASR system.

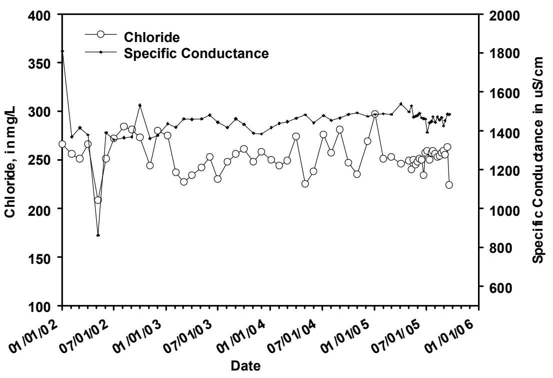

FIGURE 15. Time-Series Plot of Chloride and Specific Conductance Values from Background Monitor Well M-6 at the Peace River ASR System

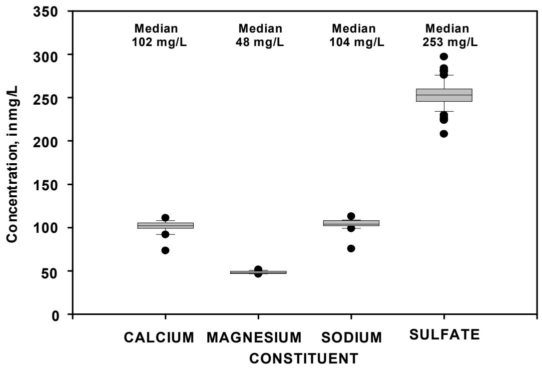

FIGURE 16. Box Plot Showing Concentration Ranges of Calcium, Magnesium, Sodium, and Sulfate from Background Monitor Well M-6 at the Peace River ASR System

Trends in Other Major and Trace Dissolved Constituents. Calcium, magnesium, and sodium were measured during 2005 (n=20) in native groundwater at M-6 (Figure 16, Table 6). Sulfate concentrations were measured monthly between 2002 and 2005 (n=61). These data will be incorporated into geochemical models. Measurement of sulfate and dissolved sulfide in M-6 is a rigorous way to define redox environment of native groundwater in the Suwannee Limestone producing zone at the Peace River ASR system, and this will benefit subsequent geochemical model development. Iron was below method detection limits in all native groundwater samples (< 29 µg/L). Arsenic and total organic carbon concentrations were not measured in native groundwater at the Peace River ASR system.

Data for Geochemical Model Input

Recharge water-quality data sets from the Peace River ASR Wellfield 2 were characterized using standard statistical methods (descriptive methods, time-series analysis, linear regression). Concentration data for individual analytes typically are not normally distributed. Median values and 25th and 75th percentiles of each constituent or parameter are shown on Table 5.

Native groundwater quality data sets at the Peace River ASR Wellfield 2 were characterized using standard statistical methods, similar to that for the recharge water. Monitor well M-6 was sampled monthly during the period of record between June 2002 and January 2006. Median values and 25th and 75th percentiles of each constituent or parameter are shown in Table 6.

TABLE 5

Recharge Water Quality Characteristics for Geochemical Model Input

Data sets consist of analyses of treated water from the Peace River Facility during the periods of 2002-2003 and 2005

Composite Recharge Water Quality Data: Peace River Facility

Analyte	Median value	Uncertainty: 25th percentile	Uncertainty: 75th percentile	Number of Analyses
Dissolved Oxygen, in mg/L	5.5	5.0	7	55
Total Organic Carbon, in mg/L	--	--	--	--
Chloride, in mg/L	30.8	27.2	34.9	61
Sulfate, in mg/L	120	102.5	135.7	61
Carbonate Alkalinity, in mg/L as $CaCO_3$	34.5	31.7	37	51
Total Dissolved Iron, in µg/L	59	42	80	26 detects, 34 < 30 µg/L
Total Dissolved Manganese, in mg/L	0.006	--	--	2
Calcium, in mg/L	19.9	18.3	29.2	3
Magnesium, in mg/L	8.4, 11.9			2
Sodium, in mg/L	34.8	35.6	43.9	5
Arsenic in µg/L	1.79	1.58	2.47	19 detects, 42 < 1.3 µg/L
Oxidation-Reduction Potential, in mV	442	402	470	15
pH	8.2	8.1	8.3	61

TABLE 6

Native Groundwater Quality Characteristics of the Suwannee Limestone Producing Zone for Geochemical Model Input

Data set consist of analyses from distal monitor well M-6, obtained during the period of June 2002 through January 2006

Native Groundwater Quality Data from the Suwannee Limestone Producing Zone (M-6): Peace River Facility

Analyte	Median value	Uncertainty: 25th percentile	Uncertainty: 75th percentile	Number of Analyses
Dissolved Oxygen, in mg/L	0.9	0.6	1.15	20
Dissolved Sulfide, in mg/L	2.3	1.7	2.4	21
Chloride, in mg/L	224	217	231	61
Sulfate, in mg/L	253	246	260	61
Total Alkalinity, in mg/L as $CaCO_3$	142	140	143	61
Total Dissolved Iron, in µg/L	<29	--	--	20
Calcium, in mg/L	102	99.4	105	21
Magnesium, in mg/L	47.8	47.1	49.4	20
Sodium, in mg/L	104	102	108	21
Oxidation-Reduction Potential, in mV	-197	-213	-137	20
pH	7.4	7.36	7.49	61

Data Gaps in Water-Quality Data Sets

City of Tampa Rome Avenue Park ASR System

Summary water quality characteristics presented in Tables 2 through 4 provide a basis for geochemical model construction, and estimation of model uncertainty. Inverse and reaction path geochemical models simulate mass flux (mole transfer) between water and rock, under either static of dynamic (flowing) conditions. Concentration ranges of individual solutes, along with rock composition, are necessary to quantify water-quality changes that occur along a flow path (for example, Parkhurst, 1997).

The recharge water quality data set for the Rome Avenue Park ASR system is fairly complete. Most analytes have a large population of data, from which 25th, 50th (median) and 75th percentiles can be extracted so that uncertainty (variation) is quantified. The greatest source of uncertainty is the use of calcium and magnesium concentrations calculated from total and calcium hardness values. Because there is a significantly large non-carbonate hardness component in groundwaters of the Upper Floridan Aquifer system, back-calculation of calcium and magnesium from total hardness values often results in variable degrees of error. Comparison of calculated and measured calcium and magnesium concentrations in single samples (n=5) elsewhere from the Upper Floridan Aquifer system (Mirecki, in review) showed that calculated calcium was 17 to 38 percent greater than measured calcium; and calculated magnesium was 62 to 76 percent lower than measured magnesium. Measured calcium and magnesium concentrations (possibly available in archived data from DLTWTP) would eliminate this data gap.

Another source of uncertainty is the lack of sodium analyses measured in Rome Avenue Park recharge water samples. Sodium values are estimated so that resultant charge balance errors for each sample will be less than 5 percent. Estimated sodium concentrations for recharge water at the Rome Avenue Park ASR system are 20 to 30 mg/L. The City of Tampa Annual Water Quality Report listed the range of sodium concentration during 2005 at 57 to 58 mg/L (City of Tampa, 2006); therefore, this assumption may be on the low side and should be confirmed. Measurements of sodium concentration are necessary to reduce uncertainty in geochemical models.

The lack of correlation between ORP and DO in these oxic water samples limits the ability to quantify redox environment in ASR cycle tests. Membrane-equipped DO probes are not stable over long periods (hours or days), have slow response times for field application (many minutes), and are susceptible to degradation through continued use (Mitchell, 2006). Use of new optical technology for field and laboratory DO measurements may improve precision and accuracy of DO measurements, and thus, assessment of the redox environment of oxic waters.

Peace River ASR System

Fewer recharge water quality data were available from the Peace River ASR system, and these data were intermittent rather than continuous. Available data do include direct measurement of all major dissolved species, although the sample population size differs for each analyte (n = 2 to 61; Table 5). The charge balance error calculated from median concentrations listed on Table 3 is -10.9 percent. Calculated charge balance errors in single samples are lower. Additional analyses of major dissolved constituents, if available, can be incorporated into this recharge water-quality data set to reduce uncertainty. Total organic carbon analyses are need.

Native groundwater quality data are mostly complete. All major and trace dissolved concentrations except total organic carbon were measured in background monitor well M-6. Redox condition of the Suwannee Limestone producing zone can be assessed using dissolved sulfate and sulfide concentrations from M-6.

Microbial Ecology of the Suwannee Limestone Aquifer During ASR Cycle Testing

Introduction

Microbially mediated mobilization of arsenic is possibly enhanced in the presence of organic carbon that is readily assimilated by native and/or introduced bacteria. The oxidation of these carbon constituents is dependent upon a series of redox reactions from which energy and/or electrons are cycled. These reactions may promote the mobilization of absorbed or complexed arsenic. Currently, there are no data on the influence that injected waters, which contain relatively high concentrations of carbon, nitrogen, phosphorus and oxygen has on the native bacterial populations. It is assumed that the injected waters will stimulate bacterial activity and biomass production due to these elevated concentrations of nutrients and oxygen.

Measuring biological oxygen demand (BOD) is a general approach to estimating the rates of bacterial respiration, carbon assimilation and biomass production. The objective of this phase of the project is to measure the oxygen utilization rates in native, recharge, and native/recharge mixtures at in situ temperatures during a time periods that simulates typical ASR storage periods.

Research Approach

The following approach will be used to quantify oxygen utilization by native microbial populations under changing water compositions.

1. Ratios of native groundwater and recharge water will be added to serum bottles and sealed with no head space using rubber septa. The different mixing ratios, in addition to strictly native and recharge water samples, and incubation times will be determined.
2. DO concentrations will be determined from the same bottles during the incubation time using a fiber optic oxygen microprobe that is designed to pierce the bottle septa. This method allows us to sample the same bottle repeatedly during the incubation period without removing any volume for analysis.
3. The following assays will be performed for each water type and water mix ratio at time zero: DO (oxygen probe), total direct counts (epifluorescent microscopy), community level physiological profiles (BioLog EcoPlates), secondary productivity (tritiated leucine).

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Appendix B

Scanning Electron Microscopy and Bulk Rock Geochemical Data from Tampa-Rome Avenue Park Core Samples

Figure B1. Scanning Electron Micrograph (SEM) image of sample from boring SZMW-9, Suwannee Limestone, 301-303 ft below land surface (bls). Boring obtained at the Tampa-Rome Avenue Park ASR system. Image is 95X. Image shows texture of bulk limestone.

Figure B2. SEM image of sample from boring SZMW-9, Suwannee Limestone, 301-303 ft bls. Boring obtained at the Tampa-Rome Avenue Park ASR system. Image is 200X. Image shows recrystallized calcite crystals, which appear as hexagonal dipyramids.

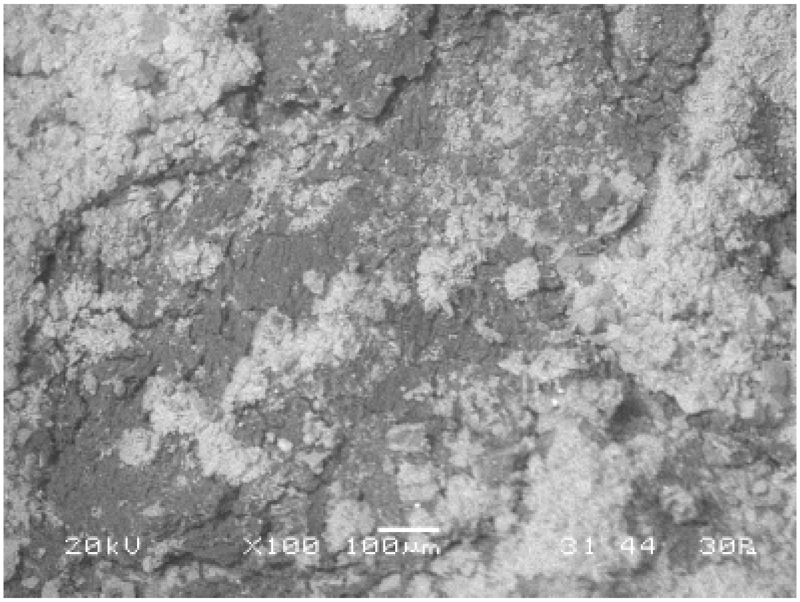

Figure B3. SEM image of sample from boring SZMW-7, Suwannee Limestone, 318 ft bls. Boring obtained at the Tampa-Rome Avenue Park ASR system. Image is 100X. Image shows bulk mineralogical texture of limestone.

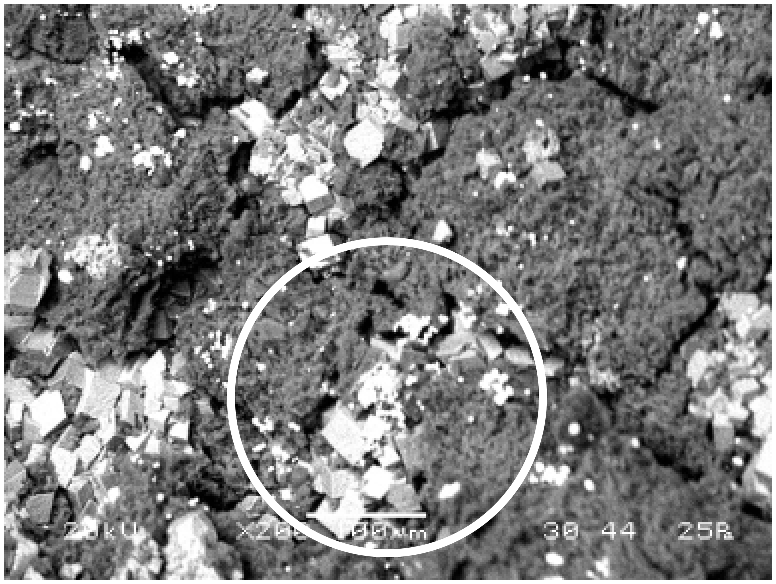

Figure B4. SEM image of sample from boring SZMW-7, Suwannee Limestone, 320-330 ft bls (approximately 321 ft bls). Image is 200X. White crystals are euhedral pyrite embedded in limestone matrix. Area in circle is shown in Figure B5.

Figure B5. SEM image of sample from boring SZMW-7, Suwannee Limestone, 320-330 ft bls (approximately 321 ft bls). Image is 370X, a detail from Figure B4. Large euhedral cubic pyrite crystals occur with framboidal pyrite. Framboidal pyrite appears as white spots. Area in circle is shown in Figure B6.

Figure B6. SEM image of sample from boring SZMW-7, Suwannee Limestone, 320-330 ft bls (approximately 321 ft bls). Image is 850X, a detail from Figure B5. Large euhedral cubic pyrite crystals occur with framboidal pyrite. Framboidal pyrite appears as white spots. Area in circle is shown in Figure B7.

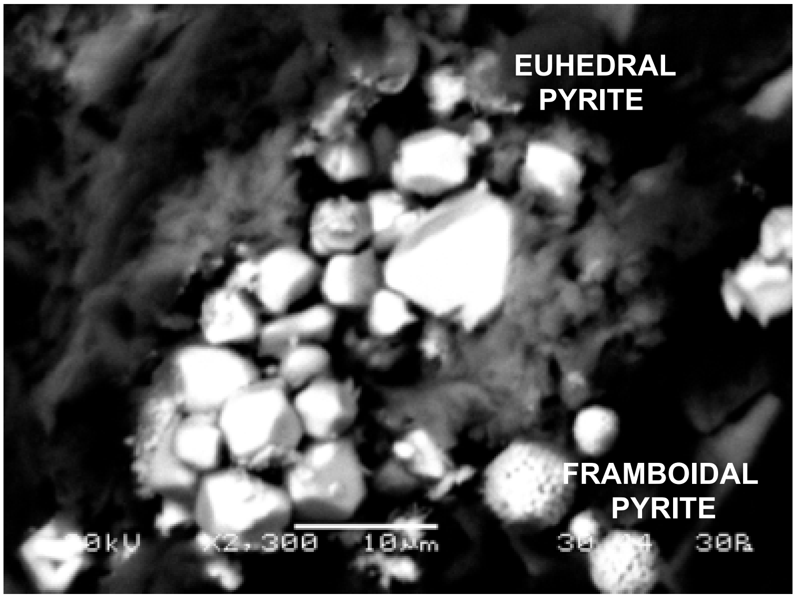

Figure B7. SEM image of sample from boring SZMW-7, Suwannee Limestone, 320-330 ft bls (approximately 321 ft bls). Image is 2,300X, a detail from Figure B6. Image shows small euhedral cubic pyrite crystals with framboidal pyrite.

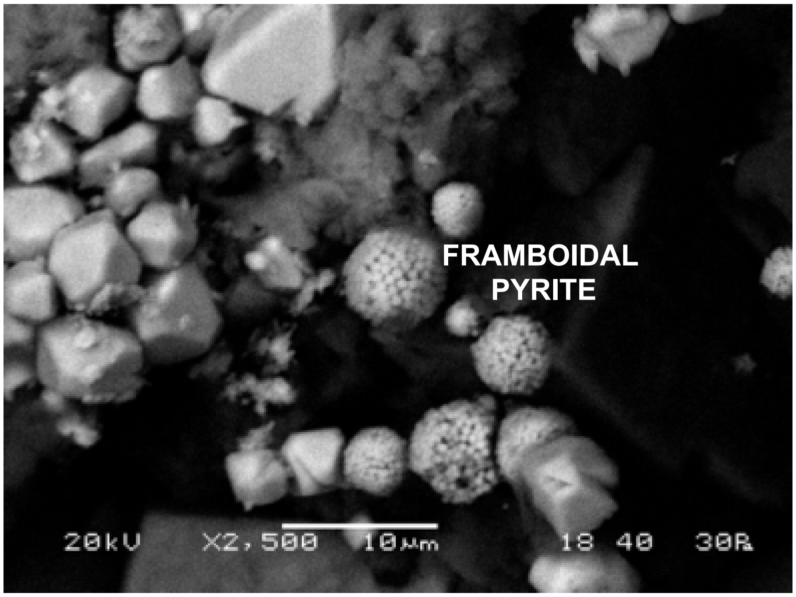

Figure B8. SEM image of sample from boring SZMW-7, Suwannee Limestone, 320-330 ft bls (approximately 321 ft bls). Image is 2,500X, and shows detail of euhedral and framboidal pyrite, similar to Figure B7.

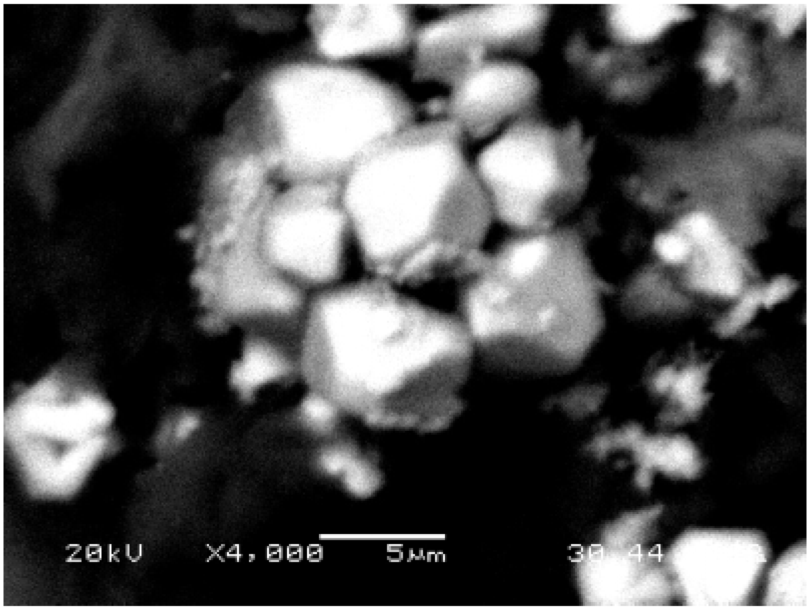

Figure B9. SEM image of sample from boring SZMW-7, Suwannee Limestone, 320-330 ft bls (approximately 321 ft bls). Image is 4,000X and shows detail of euhedral pyrite crystals.

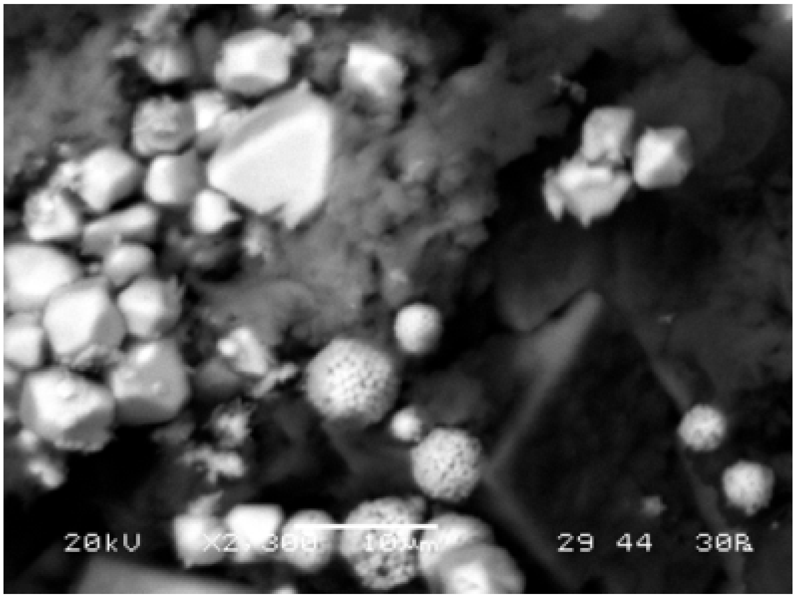

Figure B10. SEM image of sample from boring SZMW-7, Suwannee Limestone, 320-330 ft bls (approximately 321 ft bls). Image is 2,300X and shows detail of euhedral and framboidal pyrite crystals.

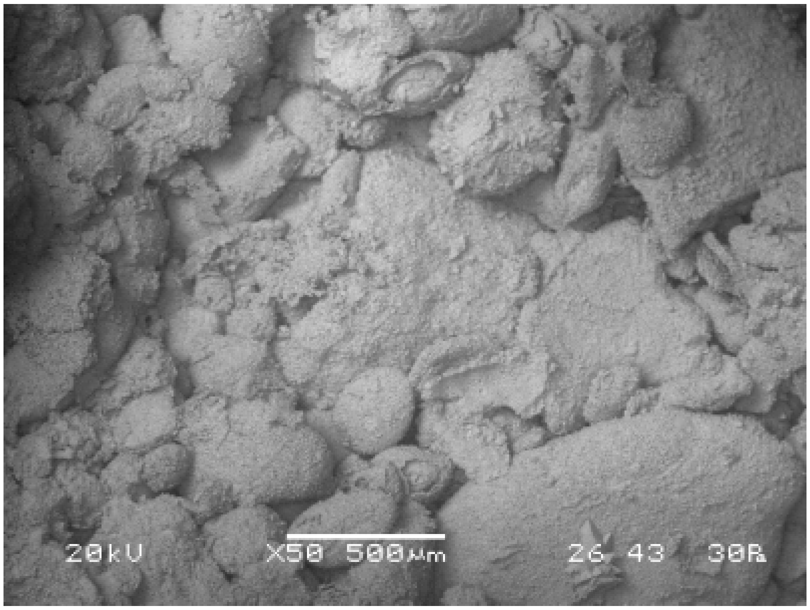

Figure B11. SEM image of sample from boring SZMW-10, Suwannee Limestone, approximately 306-325 ft bls. Image is 50X and shows detail of fossiliferous limestone matrix.

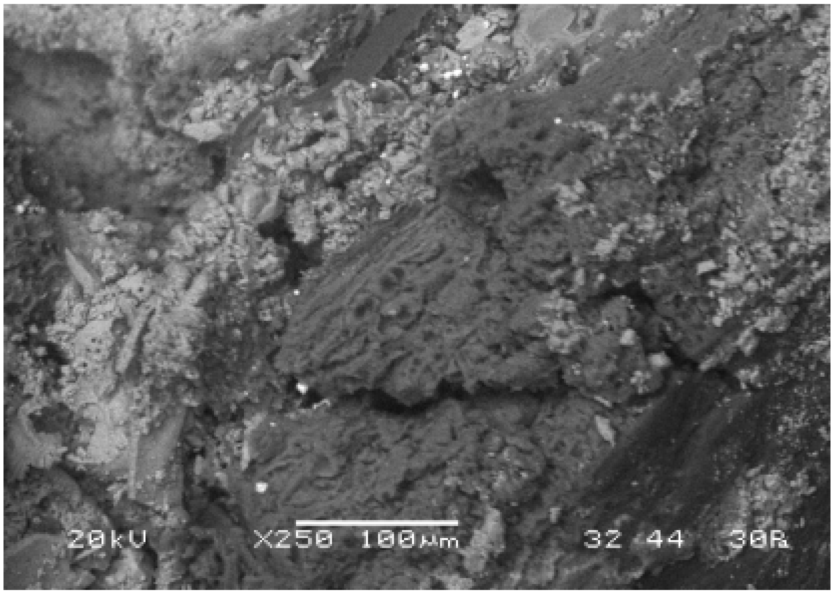

Figure B12. SEM image of sample from boring SZMW-10, Suwannee Limestone, approximately 333.5-334 ft bls. Image is 250X and shows detail of fossiliferous limestone matrix.

Appendix C

Technical Memorandum TM-2

TECHNICAL MEMORANDUM CH2MHILL

Dissolved Oxygen Removal

PREPARED FOR: Southwest Florida Water Management District

PREPARED BY: CH2M HILL

DATE: June 11, 2007

This Technical Memorandum provides a brief introduction to some of the issues related to dissolved oxygen removal from groundwater. Topics covered include:

- Overview of Deoxygenation Technologies;
- Comparison of Available Deoxygenation Technologies;
- Cost Estimates for Feasible Deoxygenation Technologies;
- Equipment Suppliers; and
- Recommendations and Conclusions.

Overview of Deoxygenation Technologies

Dissolved oxygen (DO) is a measure of the amount of oxygen in water that is available for chemical reactions and for use by aquatic organisms. Levels of DO in water vary and are dependent on interactions with the atmosphere, turbulence and other flow patterns, aquatic vegetation, and chemical reactions that may take place. DO levels in surface water typically range between 5 and 15 milligrams per liter (mg/L), with the optimal range for aquatic life between 5 and 6 mg/L. DO levels in groundwater are usually well below 5 mg/L, unless water with higher DO levels is introduced (infiltration, recharge, interaction with surface water, etc.) into the aquifer.

Higher DO levels in groundwater are associated with the potential release of arsenic into the groundwater via oxidation of the porous media within the aquifer. In such cases, removal of excess DO is recommended.

Deoxygenation methods and chemicals include: a) stripping, b) chemical addition (sulfur dioxide, sodium bisulfite, sodium sulfite and sodium metabisulfite), c) gas transfer membranes, d) gas displacement technology, e) activated carbon; and f) catalytic oxygen removal systems. A preliminary evaluation of the aforementioned methods and chemicals was performed against the following criteria:

- Time to implement;
- Space required for its implementation;
- Ability to be implemented in-line without having to repump the water;
- Ability to meet desired DO concentration goal;

- Capital cost; and
- Annual operation and maintenance cost.

The goal of the evaluation was to identify a method or chemical that could deoxygenate the water cost-effectively. Depending on the desired final DO concentration for the water being pumped into or extracted from the aquifer, a cost-effective combination of methods or chemicals was acceptable. Unacceptable options included those options that would have a detrimental effect on deoxygenation, equipment life time and high annual operating and maintenance costs.

Comparison of Available Deoxygenation Technologies

Common technologies for dissolved oxygen removal from drinking water include:

- Chemical addition (Sulfur dioxide (SO_2), Sodium bisulfite ($NaHSO_3$), Sodium metabisulfite ($Na_2O_5S_2$), Sodium sulfite (Na_2SO_3))
- Gas transfer membranes (GTM)
- Activated carbon deoxygenation (DEOX)
- Catalytic oxygen removal systems (CORS)
- Gas displacement technology (GDT™ Process)
- Hydrogen Injection
- Minox Deoxygenation Systems

Deoxygenation is an expensive process that often requires extended reaction times. Sulfur dioxide requires expensive capital equipment and ongoing maintenance. Sodium sulfite and sodium metabisulfite both require hydration. Hydrogen injection is not a proven process. Activated carbon deoxygenation (DEOX) produces water with less than 1 ppb of dissolved oxygen but it requires the addition of hydrazine (a carcinogen) and an ion exchange bed, making the process expensive and relatively more complicated than other available technologies. The catalytic oxygen removal system (CORS) also produces water with DO levels below one part per billion (ppb). It utilizes a palladium-doped catalytic resin in combination with either hydrogen (H_2) or hydrazine (N_2H_4). It is expensive and fairly complicated.

Effective Technologies

Sodium bisulfite is a liquid and is effective at deoxygenation. Gas transfer membranes are effective to very low dissolved oxygen concentrations (0.1 mg/L). Stripping (GDT™ and GDT™ nitrogen assisted process) is also an effective means of deoxygenation. The Minox™ process can produce water with residual oxygen content of less than 10 ppb without the use of an oxygen scavenger. These technologies were further evaluated for deoxygenation.

Table 1 presents the advantages and disadvantages of the technologies considered for evaluation.

TABLE 1
Comparison of Technologies
ASR Well Field Deoxygenation

Technology	**Advantages**	**Disadvantages**
Sodium bisulfite	- The required reaction time for deoxygenation is water specific and must be determined, but the reaction will continue in the subsurface - Simple process and equipment layout - Low operation and maintenance costs - Small footprint - Does not require repumping of treated water	- Must be NSF 60 approved in order to be added to drinking water - The deoxygenation reaction is a slow process - The dose limit of 46 mg/L under NSF 60 restricts the amount of oxygen that may be removed by sodium bisulfite (Assuming a 20% over theoretical dose, the maximum concentration of dissolved oxygen that may be removed with 40% sodium bisulfite without exceeding NSF 60 is about 4.5 mg/L) - Sodium bisulfite is not an option in and of itself to deoxygenate the recharge water - Requires a building for storage of the chemical and feed supply equipment - Potential corrosion problems
Gas transfer membranes	- Cost effectiveness (or efficiencies) of redundant units - Lower installation cost - Lowest total cost of ownership - Performance equal to or better than other technologies - Smaller footprint compared to degasifier towers - Does not require repumping of treated water	- Chlorine and ozone affect membrane performance - Excess ozone needs to be removed from the water - High pressure drop through membrane train (28 psi for 1 mgd of treatment) - Requires a vacuum pump - Operating under vacuum only condition - Requires modifications to the existing building to house GTM equipment
GDT^{TM} Process	- Uses high-efficiency Mazzei® injectors to infuse the pressurized water with the gas - The GDT™ process dynamically captures and removes the gas in an efficient inline system - Small footprint - Design flexibility for any flow rate - Low installation and operating costs - Low maintenance requirements - Does not require a building to house the equipment	- High equipment cost - May require ozone destruction for additional cost savings - Requires nitrogen addition to reach DO levels below saturation (8 to 9 mg/L) - Requires repumping of water before being injected into the aquifer
Minox^{TM} Process	- Small footprint - The Compact Minox^{TM} Deoxygenation process can be delivered in a wide range of capacities and for almost any process environment with regard to pressure, temperature etc. - Dry, robust catalyst	- Requires nitrogen as the stripping agent - Requies fuel and a reactor tank for the regeneration process - Catalyst needs to be replaced every six years - Higher operating costs than the other alternatives - System is more complicated

	- No need for fine filtration of water - No need for booster pumps - Effective mass transfer - Stripping gas is regenerated using a patented process	- Gas to water ratio is critical for optimum oxygen removal - Technology mostly utilized in the oil industry

Description and Design Parameters for Available Deoxygenation Technologies

This section summarizes design parameters for the four technologies being evaluated.

Sodium Bisulfite

Sodium bisulfite is a readily available product. However, sodium bisulfite must be National Science Foundation (NSF) NSF 60 (drinking water additives guidance document) approved in order to be added to drinking water. This requirement limits the available suppliers of sodium bisulfite. Hydrite Chemical Company operates a plant in Waterloo, Iowa that manufactures NSF 60 approved sodium bisulfite. Sodium bisulfite is typically available in concentration between 38% and 40%. Sodium bisulfite is available in drums, totes (portable chemical storage tanks) or bulk. Sodium bisulfite neutralizes chlorine and deoxygenates according to the following reactions:

$$NaHSO_3 + Cl_2 + H_2O = NaHSO_4 + 2HCl$$

$$NaHSO_3 + O_2 + H_2O = NaHSO_4 + 2OH^-$$

Sodium bisulfite is effective at deoxygenation. However, the deoxygenation reaction is much slower than the dechlorination reaction. The required reaction time is water specific and must be determined, but the reaction will continue well after chemical injection meaning a reaction vessel is not required. Therefore, time is not an issue. The allowable sodium bisulfite dosage is an issue. The dose limit of 46 mg/L under NSF 60 restricts the amount of oxygen that may be removed by sodium bisulfite. Assuming a 20% over theoretical dose, the maximum concentration of dissolved oxygen that may be removed with 40% sodium bisulfite without exceeding NSF 60 is about 4.5 mg/L. Therefore, sodium bisulfite may not be an option in and of itself. Sodium bisulfite can be used in conjunction with other treatment processes.

Key design parameters include:

- Influent DO level (mg/L)
- Desired effluent DO level (mg/L)
- Water temperature
- Flow rate

Gas Transfer Membranes (Liqui-Cel)

Membrane contactors allow a gaseous phase and a liquid phase to come into direct contact with each other, for the purposes of mass transfer between phases, without dispersing one phase into the other such as in the removal or dissolution of gases in water.

For removal of dissolved gases, membrane contactors are operated with the aqueous phase on one side of a hydrophobic membrane and a sweep gas and/or vacuum applied to the other side of the membrane. The membrane will not allow liquid water to pass through the pores into the gas side of the membrane.

Membranes are hollow-fiber (hydrophobic polypropylene material) with a pore size of 0.05 micron with a breakthrough pressure that exceeds 150 pounds per square inch (psi). Water will not pass through the membrane at pressures below 150 psig.

Key design parameters include:

- Influent DO level (mg/L)
- Desired effluent DO level (mg/L)
- Flow rate
- Operating pressure
- Influent water pH

GDT™ Process

The GDT Water Process Corporation manufactures equipment that strips contaminants from water using air or other gases. The equipment includes a reaction gas injector, degassing separator, back pressure control valve, degas relief valve, booster pump, and vacuum pump. The GDT process allows for stripping at high flow rates eliminating the need for a large reaction vessel. It also allows for lower consumption of reaction gases.

Air and sodium bisulfite can be used as reaction gases. However, those two gases cannot achieve low enough levels in most cases. The GDT process with nitrogen as a reaction gas has two alternatives: GDT process and VacGDT process. The VacGDT process occurs under vacuum and requires a vacuum pump but uses less nitrogen. The GDT process requires about 21 cubic feet per minute (cfm) of nitrogen while the VacGDT process requires about 6 cfm of nitrogen. The GDT process requires too much nitrogen to make it a cost effective alternative. The VacGDT process will not achieve a 1 mg/L DO, but the GDT process followed by sodium bisulfite addition will achieve a 1 mg/L DO. A pilot test is necessary to determine the exact performance results.

It is possible to use the GDT process to treat the water to a higher dissolved oxygen concentration (e.g. 5.5 mg/L) and use sodium bisulfite to treat the remaining DO. However, it is best to minimize the amount of chemical added to the water.

Key design parameters include:

- Influent DO level (mg/L)
- Desired effluent DO level (mg/L)
- Flow rate
- Operating pressure
- Influent water pH

Minox™ Process

The Minox systems are based on a patented technology for nitrogen gas stripping. The nitrogen gas is effectively mixed with the water in static mixers (2-stage system) or in a packing (compact tower system). This results in an extremely effective mass transfer and residual oxygen content of less than 10 ppb in the water is achieved without the use of oxygen scavenger.

The oxygen is stripped from the water by the nitrogen. The nitrogen is then catalytically purified and recycled.

Key design parameters include:

- Influent DO level (mg/L)
- Desired effluent DO level (mg/L)
- Flow rate
- Gas to water ratio
- Oxygen content in purified cycling gas
- Number of stripping stages

Cost Estimates for Feasible Technologies

Table 2 presents capital and annual operation and maintenance costs for technologies evaluated.

TABLE 2
Capital and Annual O&M Costs
ASR Well Field Deoxygenation

Technology	**Capital Cost**	**Annual O&M Cost**
Sodium bisulfite	\$482,000[1]	\$124,000
Liqui-Cel (GTM)	\$244,000[2]	\$28,000
GDT™ Process	\$202,000	\$15,000[3]
Minox		

[1] the cost of this technology could be \$112,000 if a building is not required. Dissolved oxygen levels are decreased by approximately 5 mg/L.
[2] this cost includes a canopy over the equipment. Dissolved oxygen concentration is decreased to 1 mg/L. This cost does not include the cost of the nitrogen generator producing 1.2 scfm.
[3] this cost does not include the cost of the nitrogen generator producing 50 to 80 scfm of nitrogen. However, nitrogen dosage needs to be determined at the site. This process does not require a building.

Assumptions made to prepare the cost estimates presented in Table 2 include:

- Design flow of 1.5 million gallons per day (mgd)
- Initial dissolved oxygen concentration of 25 mg/L
- Final dissolved oxygen levels vary for each technology
- Removal of excess chlorine and ozone may be required to optimize deoxygenation
- Cost of removing excess chlorine and ozone was not included
- The system operates 365 days per year

Table 3 presents the capital and annual O&M for a typical nitrogen generation system.

TABLE 3
Capital and Annual O&M Costs for Nitrogen Generation System
ASR Well Field Deoxygenation

Capacity	Capital Cost	Annual O&M Cost
Co-Current Deaeration		
1.0 mgd		\$71,000[1]
1.5 mgd		\$87,000[1]
Counter Current Deaeration		
1.0 mgd		\$43,000[2]
1.5 mgd		\$55,000[2]

[1] this assumes an effluent concentration of 100 micrograms per liter (µg/L).
[2] this assumes an effluent concentration of 50 µg/L.

Equipment Suppliers

Liqui-Cel
704-588-5310
Contact Person: Jorge Munoz
http://www.liqui-cel.com

Ionics
281-558-6655
Contact Person: John Herring
The GTM™ process from Ionics uses Liqui-Cel membranes.
http://www.gewater.com

GDT™ Process
480-247-2305
Contact Person: James Jackson
http://www.mazzei.net

Minox Deoxygenation System
281-935-9472
Contact Person: Jason Matsumoto
http://www.greenlandgroup.com

Recommendations and Conclusions

- The GTM membranes (Liqui-Cel) seem to be the most cost-effective solution for deoxygenation of Tampa water. A demonstration site should be implemented to confirm the effectiveness of the treatment technology and its effect on the aquifer's ability to release arsenic when treated water is injected. Necessary equipment can be obtained directly from Liqui-Cel without having to go through Ionics.

- Changes to existing well sites are required in order to implement any of these technologies.
- The GDT Process and addition of sodium bisulfite are competitive options depending on the dissolved oxygen concentration goal.
- A thorough evaluation of water quality and other site-specific factors should be performed before selecting a technology to be implemented.

Appendix D

The Effects of Mixing Treated Recharge and Native Ground Waters on the Microbial Ecology of Native Bacterial Communities, Dr. John Lisle, US Geological Survey

The Effects of Mixing Treated Recharge and Native Ground Waters on the Microbial Ecology of Native Bacterial Communities

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U.S. Geological Survey
Center for Watershed & Coastal Research
St. Petersburg, FL

Introduction

One of the critical components in the development and conservation of water resources is the development of technologies that conserve and provide water of high quality, while sustaining current and future increases in population and agricultural activities in the state. One of these technologies is aquifer storage and recovery (ASR), where waters from streams, reservoirs, lakes and wastewater reuse facilities are injected into aquifer systems and subsequently recovered for above ground use when water supplies are diminished.

One of the concerns associated with ASR is the potential for contamination of the native aquifer waters with chemical and microbiological constituents from the injected waters. Accordingly, current regulations require that all waters injected into ASR wells located in aquifers with high-quality native water be treated to meet or surpass safe drinking water regulations. This treatment approach addresses regulatory-associated public health concerns by minimizing the probability of pathogenic microorganisms being introduced into the native aquifer and present in the recovered water. However, this approach to treatment and monitoring of ASR waters ignores the effects that injected waters may have on the indigenous microbial populations and how these effects may alter existing microbial and geochemical equilibria. Constituents of injected waters that have been shown to greater than those of native Floridan aquifer waters include: dissolved oxygen, redox potential, total phosphates, ammonia-nitrogen, nitrates and total organic carbon (20).

A recurring issue with waters recovered from ASR systems in specific areas of Florida is elevated arsenic levels that may pose a risk to public health. The water that has been treated prior to injection into ASR wells has been shown to be a contributor to this increase as arsenic levels in the native ground waters are substantially lower if not absent (3). To date, water treatment and transportation processes that increase dissolved oxygen concentrations in injectates, such as ozonation and pumping, have been implicated. The presence of dissolved oxygen in groundwaters is not an issue until it comes into contact with geologic material that contains arsenopyrite. Recent studies have shown that geologic features within ASR storage zones contain arsenopyrite and oxygen-containing waters that interact with these materials enhance rates of arsenic release and mobilization (3,25,31,32). In addition to geochemical interactions that mobilize arsenic from arsenopyrite, microbial interactions with the surfaces of these and other arsenic containing materials have also been shown to effectively mobilize arsenic into the overlying water (14,16,28,29).

This study investigates the effects of mixing recharge and native water end members on native bacterial community physiological activity and diversity. The recharge water end-members are either ozone-treated drinking water from the Tampa-Rome Avenue Park ASR system.. The native water end-member is water from the upper Floridan Aquifer System, obtained from the Tampa-Rome Avenue Park ASR system.

Materials and Methods

Sample collection and processing. Samples were collected from sites designated as being the most representative of the treated recharge and native waters at the City of Tampa- Rome Avenue ASR site. The treated recharge water samples were collected from a residential hose faucet at the City of Tampa Police Athletic League (PAL) facility. The faucet was opened completely and allowed to flush for 15-20 min. After the flushing period was complete, an adapter was connected to the faucet that allowed a direct connection to the sterile sample collection carboy. The flow was reduced until laminar flow was maintained and a 10.0 L sample was collected through the closure (Fisher Scientific #02-923-15) of the carboy that had been adapted for filling the carboy from the bottom.

The native water samples were collected from a monitoring well SZMW2 (storage zone monitor well 2) located approximately 1.5 miles southeast of the ASR system facility. SZMW2 has a 6-in.casing, and was completed to a total depth of 375 ft. below land surface (bls) with an open interval extending from 300 to 375 ft bls, completed in the lower permeable zone of the Suwannee Limestone (2). Prior to collecting the native water samples, the well was flushed approximately three casing volumes (approximately 1650 gallons). Following a proper flushing period, the discharge was reduced to maintain laminar flow and the samples were collected as described for the recharge water. All samples were either delivered to a commercial laboratory or processed in the U.S. Geological Survey (USGS) laboratory within three hrs of collection.

In addition to the 10.0L samples collected at both site, dissolved oxygen (DO) samples were also collected on site. Overflow from the carboys was used to filled 250ml serum bottles. These bottles were immediately sealed with a silicon stopper that was held in place by a crimped aluminum cap. No air was retained in the bottles. These samples were also immediately stored on ice and in the dark and processed upon arrival to the USGS laboratory.

Field data. The following data were collected at each site immediately following sample collection: temperature, pH, specific conductance, total dissolved solids (TDS) and oxidation/reduction potential (ORP). These data were obtained from a 5.0 mL sample from each site and microcosm that was analyzed with a model 6P Ultrameter (Myron L. Company).

Laboratory microcosm study design. Recharge and native water samples returned to the USGS laboratory were set up in 500 mL serum bottles that were sealed with a silicon stopper and held in place with an aluminum crimped cap. Two sets of microcosms were set up, with the first set being processed one (1.0) hr after set up and the second set being processed 14 days following set up. All samples were incubated at ~24°C and in the dark.

Five (5) types of microcosms were set up based on mixing ratios of treated recharge (R) and native groundwater (GW) as follows: 100% recharge (R100), 100% native groundwater (GW100), 25% recharge: 75% native groundwater (R25:GW75), 50% recharge: 50% native groundwater (R50:GW50) and 75% recharge: 25% native groundwater (R75:GW25). Each microcosm was filled so no headspace was retained in the bottle.

In addition to the 500 mL microcosms, 26.0 mL serum bottles were also setup for each of the five sample types for DO analysis. These samples were incubated in a temperature-controlled water bath set to ~24°C and protected from light.

Total and dissolved organic carbon analyses. Samples for total organic carbon (TOC) and dissolved organic carbon (DOC) analyses were collected in pre-cleaned, brown glass bottles that were supplied by Severn Trent Laboratories (STL) (Tampa, FL). All TOC bottles were preloaded with the appropriate amount and concentration of sulfuric acid. The DOC samples were not filtered in the field. Following collection all samples were immediately placed on ice and protected from sunlight. All TOC and DOC analyses were performed by STL.

Total direct counts of bacteria. Predetermined volumes (1.0 and 5.0 ml) of each sample were filtered through separate, sterile, 25-mm-diameter, 0.2-µm pore-size black polycarbonate filters (Millipore; GTBP02500) by applying gentle vacuum (50-70 mm Hg). Each filter was stained with the nucleic acid stain SYBR Gold following established protocols (22).

Prepared slides were counted under a fluorescent microscope (Olympus BX51) that was equipped with a ×100 oil-immersion objective (UPlanApo) and a 10× ocular, providing a total magnification of ×1000. All counts were performed using a DAPI filter cube (Ex λ: 360nm; Em λ: 460nm). A calibrated ocular reticle permitted the counting of 20 systematically selected fields and calculation of the number of cells ml^{-1} (23). The volumes selected for calculation of cell abundances contained a minimum of 20 cells per reticle grid (23).

Dissolved oxygen utilization rates. Dissolved oxygen (DO) concentrations in each sample were determined using the FOXY-R oxygen probe (Ocean Optics, Inc.). The probe was connected to a UV-light source (Ocean Optics, Inc.; USB2000) and spectrophotometer (Ocean Optics, Inc.; USB-LS-450). The probe was zeroed by placing the entire probe in a stream of nitrogen gas and waiting until the reading stabilized at 0.0 ppm oxygen. Temperature compensation was achieved by placing a temperature probe in the water bath.

Once these settings had been loaded into the accompanying software program, the standard curve data generated by the manufacturer and specific to the probe were loaded, which calibrated the probe. DO readings were taken by first inserting a stainless steel cannula (13 gauge) through the bottle's stopper and then gently inserting the oxygen probe into the cannula until the tip of the probe was visible and beyond the tip of the cannula. Temperature adjusted DO values were recorded until the readings stabilized. DO data were recorded immediately after setting up the mixed samples in the USGS laboratory and periodically during an eight (8) day incubation period, after which the readings stabilized. DO values per unit time were used to calculate oxygen utilization rates using linear regression.

Bacterial community level physiological profiles. Approximately 50.0 ml of each sample were transferred to a sterile sample transfer trough, from which 150 µl was pipetted to each of the 96 wells in an EcoPlate (Biolog, Inc.) (7). After inoculation, each plate was immediately scanned with a microtiter plate reader, set at 590 nm, to establish time-zero baselines. Each plate was sealed with Parafilm and incubated in the dark and at room temperature (22-25°C). Periodically, each plate was scanned to monitor the color development in each well. All data were normalized to the baseline data, and the normalized data were analyzed for relatedness using principle component analysis (12). Statistical analyses were performed with Minitab, Release 14 (Minitab, Inc.).

Bacterial community productivity. Once each microcosm had been setup, all were allowed to incubate for 1.0 hr prior to taking the respective samples. For each sample, 1.7 ml volumes were transferred to four separate, sterile 2.0 mL screw-cap tubes. Each tube was supplemented with 20 nM ^{3}H-leucine (59.5 Ci $mmol^{-1}$) and gently mixed. The negative control tube for each series had 89 µL of 100% (w/v) trichloroacetic acid (TCA) immediately added and was gently mixed. All samples were incubated at room temperature (22-25°C) for 1.0 hr. Following the incubation period all samples were processed using the microcentrifuge method (15). Prior to counting on a scintillation counter, 1.0 ml of ULTRA Gold scintillation cocktail (Packard BioScience) was added to each tube and the contents vortexed. All samples were stored at room temperature (22-25°C) overnight, and then read on a scintillation counter. The scintillation count data (counts per minute; CPM) were used to calculate bacterial-community productivity values (μg C l^{-1} d^{-1}) for each sample (15).

Bacterial community diversity. Bacterial community diversity was determined by first concentrating the bacteria in each microcosm water sample (20 mL per filter) onto a 25 mm diameter, 0.2 µm pore size, cellulose acetate filter (Millipore Corp.; GTTP02500). Each filter was then placed into a UltraClean Soil DNA extraction tube (MoBio Laboratories, Inc.), 0.5 ml of sterile glass beads (0.1 mm diameter) was added and the bacterial community DNA extracted using the FastPrep system (Q BIOgene) set at a speed setting of 3.5 for 30 sec. The extracted DNA was collected and concentrated from the spin column systems included in the UltraClean Soil DNA kit, per the manufacturer's recommendations.

Community DNA from each sample was initially amplified using PCR and primers 8F (5'-AGAGTTTGATCMTGGCTCAG-3') and 1492R (5'-GGTTACCTTGTTACGACTT-3') which target the majority of the 16S rRNA gene (1). The hot start tempcycler program 94°C for 5 min, 25 cycles of 94°C for 30 sec., 50°C for 30 sec. 72°C for 2 min. and a final extension at 72°C for 5 min.(9). PCR products (1485 bp) were semi-quantified from 2% (w/v) agarose, ethidium bromide gels using a standard molecular marker with known DNA concentrations per band and the Kodak EDAS 290 documentation and analysis system (Eastman Kodak).

A nested PCR, using 1.0 µL of the primary PCR products, using primers 1070F (5'-ATGGCTGTCGTCAGCT-3') and 1392gc (5'-CGCCCGCCGCGCCCCGCGCCCGGCCCGCCGCCCCCGCCCCACGGGCGGTGTGTAC-3') (the underlined bases represent the GC-clamp) which target a specific region of the 16S rRNA gene (10,11). The tempcycler program was 94°C for 5 min, 30 cycles of 94°C for 45 sec., 55°C for 45 sec., 72°C for 45 sec. and a final extension at 72°C for 10 min. PCR products (323 bp) were semi-quantified as described above.

Denaturing-gradient gel electrophoresis (DGGE) (26,27) was performed on all samples by transferring equal concentrations of PCR product into wells of a double gradient gel (8) that had a 6-12% PAGE concentration and a 40-80% denaturant concentration [100% denaturant considered 40% (v/v) formamide and 7 M urea]. Samples were run for 16 hr at approximately 60 V. The gels were stained with ethidium bromide and digitally imaged using the system described above. The digital images were analyzed using Bionumerics (Applied Maths, Inc) to determine if the "fingerprints" created by the different DNA banding patterns per sample were significantly different among samples. Cluster analysis, using the unweighted pair group method with arithmetic mean (UPGMA) method (34), was used to generate the distance tree dendrogram. The Pearson Product Moment correlation coefficients (hereafter referred to as correlation coefficient), as described within the Bionumerics program, were used as similarity coefficients to provide an estimate of the degree of relatedness between the different clades within the distance tree.

Results and Discussion

Field data. Most often field data collection for ASR systems includes temperature, pH, specific conductance, and total dissolved solids (TDS). Though there were some changes in these parameters in the mixed microcosm samples, these differences are not considered significant as similar magnitudes of change occurred in the unmixed Recharge and GW samples over time (Table 1). This conclusion does not preclude the possibility of significant changes occurring in specific conductance and TDS during longer incubation periods that more realistically model storage times in operating ASR systems.

Table 1. Temperature, pH, specific conductance & total dissolved solids (TDS) data

Sample Type	Temperature (°C)		pH		Specific Conductance ($\mu S\ cm^{-1}$)		TDS ($mg\ L^{-1}$)	
	T_0	T_{14}	T_0	T_{14}	T_0	T_{14}	T_0	T_{14}
Recharge	25.0	22.1	7.3	7.7	835.5	804.1	387	397
GW	24.9	22.3	7.4	7.5	516.2	552.4	272	270
R25:GW75	24.1	20.7	7.4	7.6	636.1	613.8	306	306
R50:GW50	24.1	22.3	7.4	7.4	694.2	670.5	334	329
R75:GW25	24.1	23.1	7.3	7.6	759.7	755.2	367	368

Though the temperature, pH, specific conductance and TDS data did not change significantly during the two-week incubation period, the oxidation/reduction potential (ORP) did change significantly in the mixed samples (Table 2). The unmixed Recharge and GW sample ORP values did not change significantly during the incubation period. The relatively high ORP values for the Recharge samples are due to the supersaturated concentrations of oxygen in these waters that result from the use of ozone in the drinking water treatment process. The reduced ORP values of the GW samples are typical of Upper Floridan aquifer waters in the Tampa Bay area and are within the range that favors bacterial reduction of sulfate (5,30). However, in the mixed samples the ORP values at T_0 follow a somewhat predictable trend of an increasing ORP with increasing ratios of Recharge waters (Table 2). Interestingly, the ORP values for all of the mixed samples are positive following the two-week incubation period, indicating that the oxidation potential of the Recharge water has a significant influence on the eventual ORP of the system. This change in ORP has important implications to geochemical and microbial processes and modeling of those processes, as both are significantly influenced by ORP. For example, the positive ORP values do not favor sulfate reduction by bacterial communities. These conditions may influence arsenic mobility as active sulfate-reducing bacteria produce sulfide that reacts to precipitate arsenic, or coprecipitates arsenic with iron, thereby removing it from solution (16).

Table 2. Oxidation/Reduction Potential (ORP)

Sample Type	ORP (mV)	
	T_0	T_{14}
Recharge	318	304
GW	-240	-215
R25:GW75	-206	9
R50:GW50	-175	34
R75:GW25	62	139

Total organic carbon (TOC), dissolved organic carbon (DOC) and bacterial abundance. The total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations did not change significantly during the incubation period (Table 3). However, there were increases in the total direct counts (TDC) or bacterial abundances in all of the samples (Table 3). The increases in bacterial abundances and biomass without a concomitant decrease in TOC or DOC may appear as contradictory. This is not the case, however, when taking into consideration the general carbon requirements of native bacterial populations. Using the general assumptions that native bacteria have a biovolume between 0.2-0.6 µm^{-3} and average specific carbon content per bacterial cell of 5.60×10^{-13} g carbon µm^{-3} (4), an estimation of organic carbon demand by the native bacterial community can be calculated (Table 4). The data in Table 4 shows that regardless of whether estimations on the quantity of carbon required for the net or total increases in cell abundances following incubation, the amount of carbon required is in the range of µg L^{-1}. In regard to carbon concentrations, the most obvious conclusion that can be derived from comparing the carbon data in Tables 3 and 4 is that there is more than enough carbon present in the native and recharge waters to support a physiologically active bacterial population. The absence of a negative correlation between increases in bacterial biomass and organic carbon concentrations is most likely an artifact of the analytical methods used to quantify TOC and DOC, as the detection limit for the methods used during this study was approximately 2.0 mg L^{-1}.

Table 3. Total (TOC) & dissolved (DOC) organic carbon & bacterial abundance (TDC) data

Sample Type	TDC (cells mL^{-1})		TOC (mg L^{-1})		DOC (mg L^{-1})	
	T_0	T_{14}	T_0	T_{14}	T_0	T_{14}
Recharge	2.35×10^5	3.10×10^5	2.0	2.0	1.7	1.8
GW	1.04×10^4	1.29×10^4	3.2	3.3	2.7	3.2
R25:GW75	7.41×10^4	3.50×10^5	2.9	2.7	2.8	2.5
R50:GW50	5.73×10^4	1.07×10^5	2.1	2.0	2.1	2.0
R75:GW25	1.52×10^5	3.14×10^5	2.0	1.8	1.8	1.8

Table 4. Carbon demand for native bacterial populations.

Sample Type	Carbon Requirement for Net Increase in Cell Abundance (mg L^{-1})	Carbon Requirement for Total Increase in Cell Abundance (mg L^{-1})
Recharge	0.00840 - 0.02520	0.03472 - 0.10416
GW	0.00028 - 0.00084	0.00144 - 0.00433
R25:GW75	0.03090 - 0.09270	0.03920 - 0.11760
R50:GW50	0.00557 - 0.01670	0.01198 - 0.03595
R75:GW25	0.01814 - 0.05443	0.03517 - 0.10550

One of the objectives of this study was to determine if recharge waters inhibited or enhanced the activity of native bacterial populations. The abundance data in Table 3 show that following the incubation period, respective to the non-mixed samples (i.e., Recharge and GW), the R25:GW75 (3.6-3.8 fold increase), R50:GW50 (1.4-1.5 fold increase) and R75:GW25 (1.6-1.7 fold increase) microcosms all had relatively significant increases in bacterial biomass. These data indicate that the mixing of these water types does stimulate bacterial growth and replication.

Bacterial respiration rates. Data for dissolved oxygen (DO) utilization or bacterial respiration were collected over an eight-day period. Table 5 lists the dissolved oxygen concentrations in each of the DO bottles at the beginning and end of the experiment. The data for the intermediate time samples are not provided. The data from the linear segment of each data set were used to calculate the respective respiration rates (i.e., slopes) using linear regression (Figure 1). The slopes of the regression lines are listed as negative values at the end of the regression lines (Figure 1).

Table 5. Dissolved oxygen (DO) data

Sample Type	DO (mg L^{-1}) T_0	T_8
Recharge	9.00	8.18
GW	0.29	0.18
R25:GW75	2.77	0.25
R50:GW50	3.59	2.46
R75:GW25	6.30	4.63

The respiration rate (0.013 mg O_2 L^{-1} d^{-1}) for the GW microcosm is significantly lower than that for the Recharge water, which was unexpected considering the use of residual disinfectant as part of the treatment and distribution process. However, the respiration rate in the Recharge water (0.166 mg O_2 L^{-1} d^{-1}) is considered an artifact of the sample as the oxygen super saturation of this water resulted in obvious out gassing when the bottle septum was punctured to take the DO readings. The release of this internal pressure did not occur or was not noticeable when taking reading from the mixed water microcosms.

When comparing the respiration rates of the R25:GW75 (0.327 mg O_2 L^{-1} d^{-1}), R50:GW50 (0.158 mg O_2 L^{-1} d^{-1}) and R75:GW25 (0.227 mg O_2 L^{-1} d^{-1}) microcosms, a trend of decreasing respiration rates with increasing ratios of Recharge water is not apparent. However, if these respiration rates are evaluated with respect to the bacterial cell abundances within each microcosm (Table 4), a more predictable trend based on the number of cells per microcosm is obvious. Ranking the microcosms (but omitting the Recharge data) based on the net increase in bacterial abundances and respiration rates gives the same sequence, as follows: GW < R50:GW50 < R75:GW25 < R25:GW75. Another approach for evaluating these data is to put them in context of oxygen consumption per cell. Using an average oxygen consumption rate of 3.20×10^{-13} mg O_2 $cell^{-1}$ hr^{-1} (35) and the cell abundances from the end of the experiment (Table 3), the predicted respiration rates range between 0.0021 (GW) to 0.0559 (R25:GW75) mg O_2 per microcosm per eight day experiment. These estimates should be considered overestimations as the cell abundances from the end of the experiment were used in the calculations. When comparing these empirical values to those actually measured (Table 5),

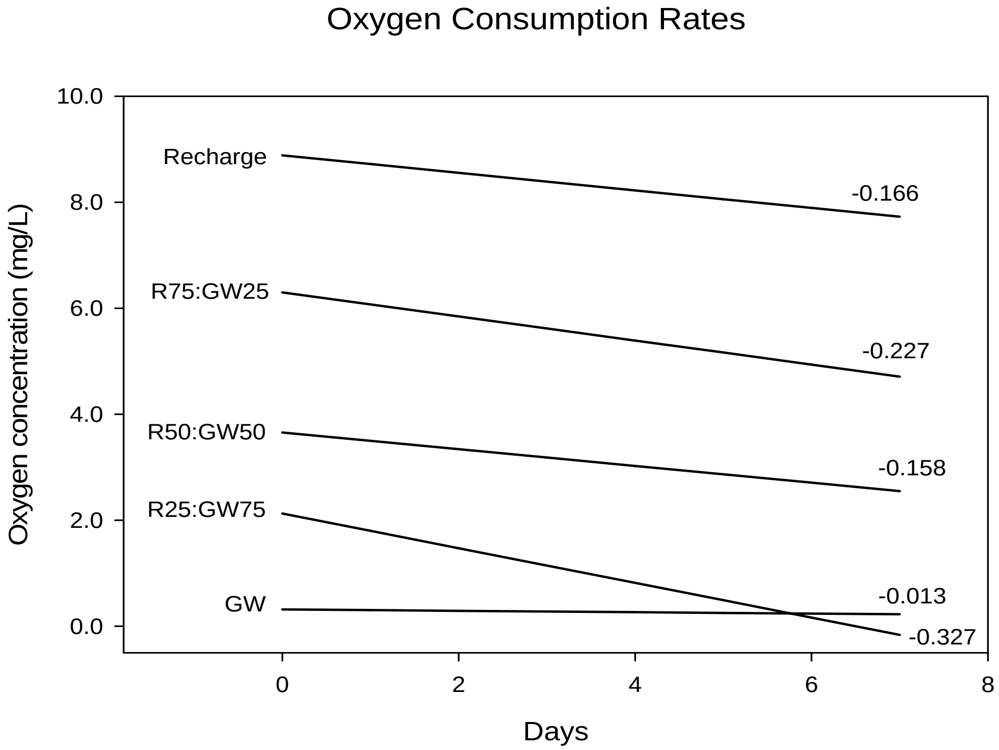

Figure 1

the estimates are significantly lower. There are several factors that could contribute to these discrepancies that include, but are not limited to (1) undetected out gassing from all of the microcosms during repeated sampling and (2) presence of sulfides and other reduced metals that consume oxygen. Though there are methods with which these issues can be minimized or avoided, they were not part of this experimental design.

When comparing the data in Table 5 and Figure 1, there are significant differences between the GW respiration rate and those from the mixed microcosms. These data corroborate the TDC data in Table 3 in that increased cell numbers would result in increased oxygen consumption and respiration rates. As with the TDC data, it can be generally stated that the mixing of recharge water with native ground water stimulates the physiological activity of the associated aerobic and facultative anaerobic bacterial populations.

Community level physiological profiles (CLPP). The Biolog EcoPlates were used to assess the physiological capacity of the bacterial populations from the respective microcosms to metabolize (i.e., reduce) a range of nutrient substrates. The data from each plate was summarized into a two-dimensional graph that provides insight into how related the bacterial populations are to each other in regard to how they metabolize the nutrient substrates. Figure 2 shows that, based upon similar utilization rates of specific substrates, how similar the bacterial populations in the respective microcosms are at the beginning and end of the experiments. The closer the data points are to each other the more similar the bacterial populations in regard to which substrates are metabolized and the rates at which those substrates are oxidized.

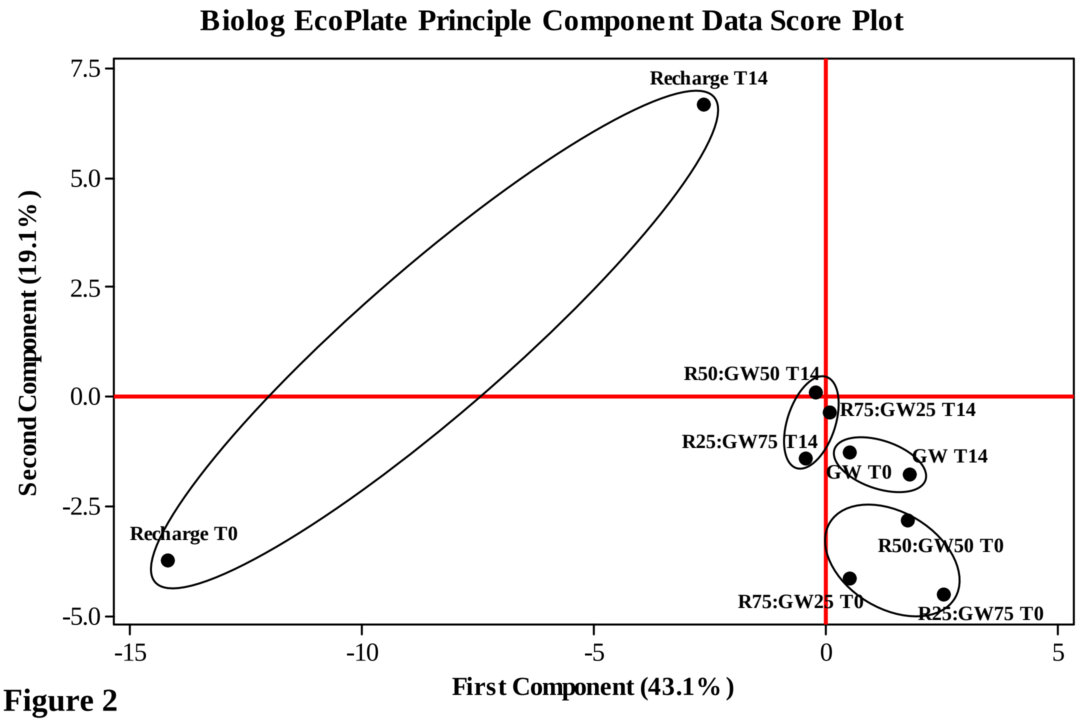

Figure 2

The GW bacterial populations show little difference in the substrate utilization patterns when comparing the data from the beginning (GW T_0) to that from the end (GW T_{14}) of the incubation period. Similarly, the mixed samples from the beginning of the experiment (T_0 data points) cluster together, but are distinctly different from the GW data. The mixed sample data show moderate differences due to the unequal mixing of the bacterial populations in the two types of samples. Following the incubation period, the mixed sample data (T14) clusters again, but these data points are significantly different from the T0 data and GW data. Collectively these data suggest that the mixing of the recharge water with the native ground waters significantly alters the substrate responsiveness of the bacterial populations. Additionally, the rate at which all of the mixed microcosm samples from the end of the experiment achieved an equivalent substrate reduction level when compared to the samples from the beginning of the experiment was significantly faster (data not shown). This indicates that the bacterial populations in these samples were able to respond more rapidly to the presence of these substrates, which may be of interest in regard to bacterial populations in the subsurface being "primed" for specific types of carbon that may be unique to the recharge waters.

An interesting data set is provided by the Recharge T0 and T14 data points. Unlike the GW data, there is a very significant difference in the substrate utilization patterns for the bacterial populations in this microcosm. This dramatic alteration in substrate responsiveness is most likely the result of repair and recovery from oxidative stress to the bacterial populations from exposure to ozone and oxygen free radicals, and chloramines during the treatment and distribution of the recharge water. This physiological response to oxidative stress has been characterized and is common in systems that use chemical oxidants and ultra violet light for disinfection (19,21,24). The most common response of oxidation-stressed bacterial populations is their inability to grow on or in media, especially those routinely used for regulatory monitoring (18,21). The recovery of bacteria from oxidative stressors has important implication for monitoring the microbiological quality of treated recharge waters as initial attempts to culture the injured cells will be unsuccessful, even though the cells are still viable. This phenomenon is evident in the TDC data (Table 3) as the total bacterial population in the Recharge microcosm increased by 7.50×10^4 cells during the two-week incubation period.

Bacterial productivity. The incorporation of tritium-labeled leucine into bacterial proteins and thereby biomass is a very sensitive method of quantifying bacterial productivity (i.e., biomass production)(6,15). This assay is fundamentally different from the CLPP assay in that it is not dependent upon substrate responsiveness. The objective of this experiment was to assess whether there was an inhibition or enhancement of bacterial productivity immediately after the mixing of native ground water with recharge water. The data in Table 6 indicate that the bacterial population in the Recharge water had a very low productivity rate, which approaches the detection limit of this assay. These data corroborate the TDC (Table 3) and CLPP (Figure 2) data and hypothesis that the bacterial population was possibly oxidatively stressed resulting in an inhibition of physiological activity.

Table 6. Bacterial productivity data

Sample Type	Productivity (µg C L^{-1} d^{-1}) T_0	Productivity (Cells L^{-1} d^{-1}) T_0
Recharge	0.01	1.00×10^5
GW	0.81	4.10×10^7
R25:GW75	0.53	2.31×10^7
R50:GW50	0.23	1.20×10^7
R75:GW25	0.10	5.00×10^6

The productivity data for the mixed microcosms follows a regressive trend, with lower productivity in samples with lower proportions of GW. Converting the carbon equivalents to cell production, it is evident that the native ground water supports a relatively productive bacterial community, though these estimates when compared to the TDC data (Table 3) appear to be overestimations. One of the caveats of this method for calculating the number of cells produced per unit carbon is that bacterial cells that have uncoupled cellular replication processes from other physiological activities (i.e., cellular maintenance and repair, basal level metabolism, starvation response) are not accounted for. These types of physiological responses are normal in environments such as ground water systems (17,33).

These data, unfortunately, provide only a snapshot of how the mixing of the two water types influences the productivity of the respective bacterial populations. A more rigorous study needs to be performed where longer incubation times are used, during which samples are collected from each microcosm at different time points. The incubation period used in this study was too short.

Bacterial community diversity. Assessment of the changes in the bacterial community structure or diversity in the respective microcosms was one of the central objectives of this study. Denaturing gradient gel electrophoresis (DGGE) was used to acquire a representative “fingerprint” of each microcosm’s bacterial population at the beginning (T_0) and end of the experiment (T_{14}). Figure 3 is a DGGE gel that presents the “fingerprint for each of the microcosm samples. Each band theoretically represents a different species, though this interpretation should be used with extreme caution. The more appropriate interpretation is to take each “fingerprint” in toto and look for bands that appear or do not appear in one “fingerprint” when compared to another and assume that each band represents one of the numerically dominant species in the sample. All species within the sample will not be represented in each “fingerprint”.

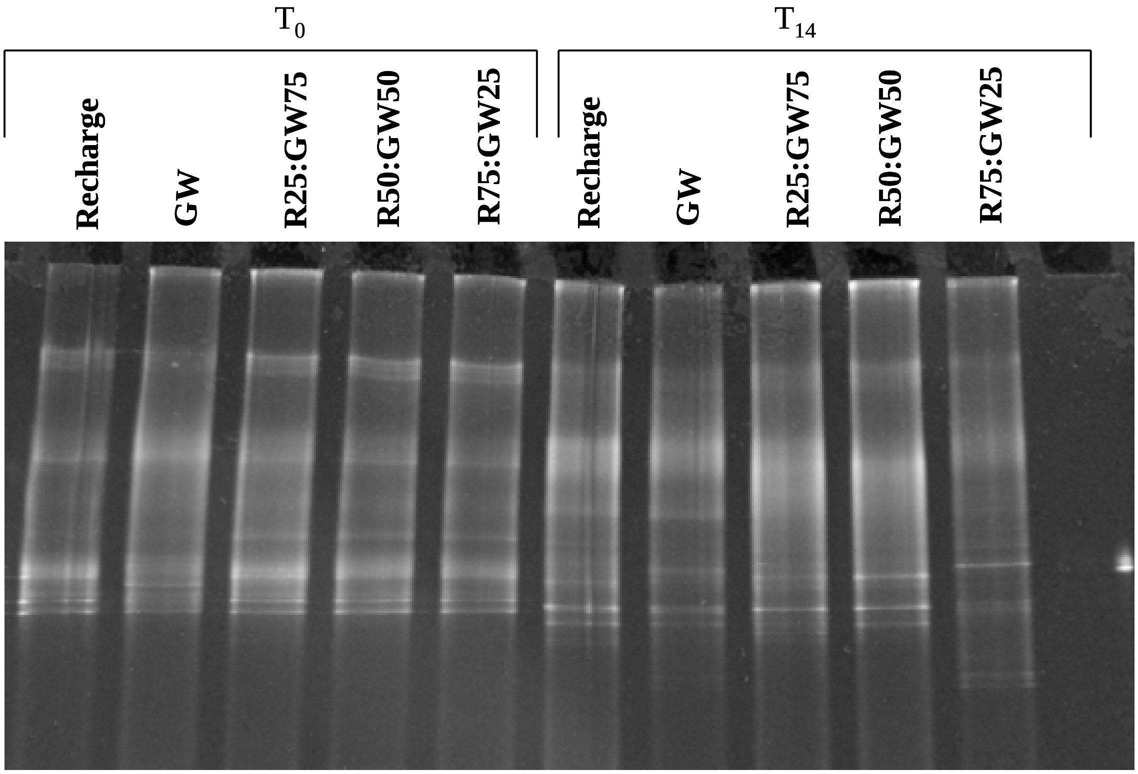

Figure 3

There are obvious differences in the DGGE profiles for each sample when comparing the respective T_0 and T_{14} lanes (Figure 3). These differences were compared using software that estimates the relatedness or similarity of each “fingerprint”. Figure 4 is the dendogram produced from the “fingerprint” image data in Figure 2. The Recharge samples are practically identical in their diversity, even after the two week incubation period. These data again corroborate previous data and the hypothesis that the bacterial populations in these samples were physiologically compromised due to the treatment and distribution processes and unable to replicate as efficiently as those populations in the other microcosms. Interestingly, the T_{14} sample from the

R50:GW50 microcosm is more similar to the Recharge samples than the rest of the microcosm samples. This may be the effect of recovery of the oxidatively stressed cells following an incubation period that was long enough for the cells to repair the damage and re-establish normal physiological activity. Oxidative stress recovery may also explain the low correlation of the T_{14} sample from the R75:GW25 microcosm with the rest of the T_{14} samples. This sample contained the most unique bacterial population in this study.

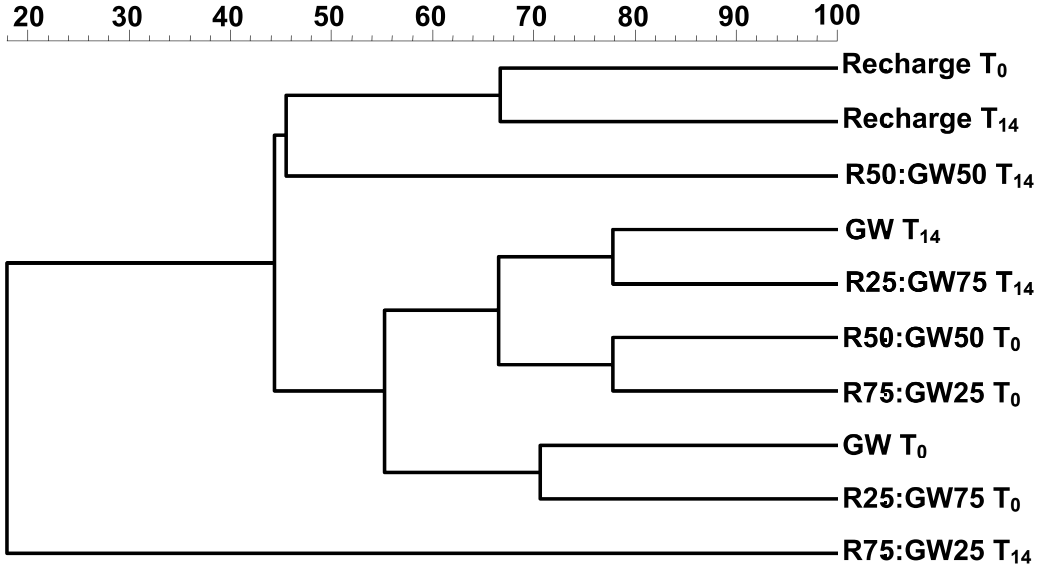

Figure 4

Unlike the Recharge samples, the GW samples were altered during the incubation period. This change in dominant bacterial groups is most likely due to the “bottle effect” (13), which occurs in all samples that are exposed to solid surfaces for prolonged periods of time.

The bacterial populations in the T_0 samples, except for the Recharge sample, do cluster somewhat together and follow a trend that would be predicted based on the simple mixing ratios of the respective bacterial populations from the two sample types. This same trend of the GW population dominating the Recharge population is maintained as the T_{14} sample for GW and R25:GW75 as both are highly correlated.

Sequencing the DNA from each of the unique bands in each lane would provide insight into which bacterial species become dominant or repressed during the incubation period. Sequencing was not included in this study design.

Collectively, the DGGE data support the previously stated conclusion that the mixing of recharge and native ground waters promotes the alteration of bacterial community diversity in conjunction with enhancement in nutrient responsiveness and productivity. Additional studies need to be designed and conducted to determine if these same physiological enhancements promote the mobilization of arsenic species in the subsurface.

Summary

1. Treated recharge water in this study was stimulatory to native bacteria from the Upper Floridan aquifer.

2. The native bacterial communities responded to relative increases in organic carbon, oxygen and other nutrients in the treated recharge water by increasing their physiological activity.

3. Increases in bacterial community physiological activity resulted in increased rates of oxygen utilization (i.e., bacterial respiration) and biomass production (productivity data) and changes in the community's carbon substrate preferences (Biolog Eco Plate data) and numerically dominant species (DGGE and DNA fingerprint data).

4. The changes in the native bacterial community physiological activity and structure, which were driven by the introduction of treated recharge water into the native aquifer, may promote and enhance geochemical processes, such as metal mobilization.

5. Bacterial cells in the treated recharge waters exhibited growth responses that indicate these cells become injured during the disinfection process and are able to recover during storage in the native ground water. This phenomenon of recovery of physiological capacity following exposure to disinfectants and during storage has regulatory significance in regard to the monitoring of the microbiological quality of ASR recharge and recovered waters.

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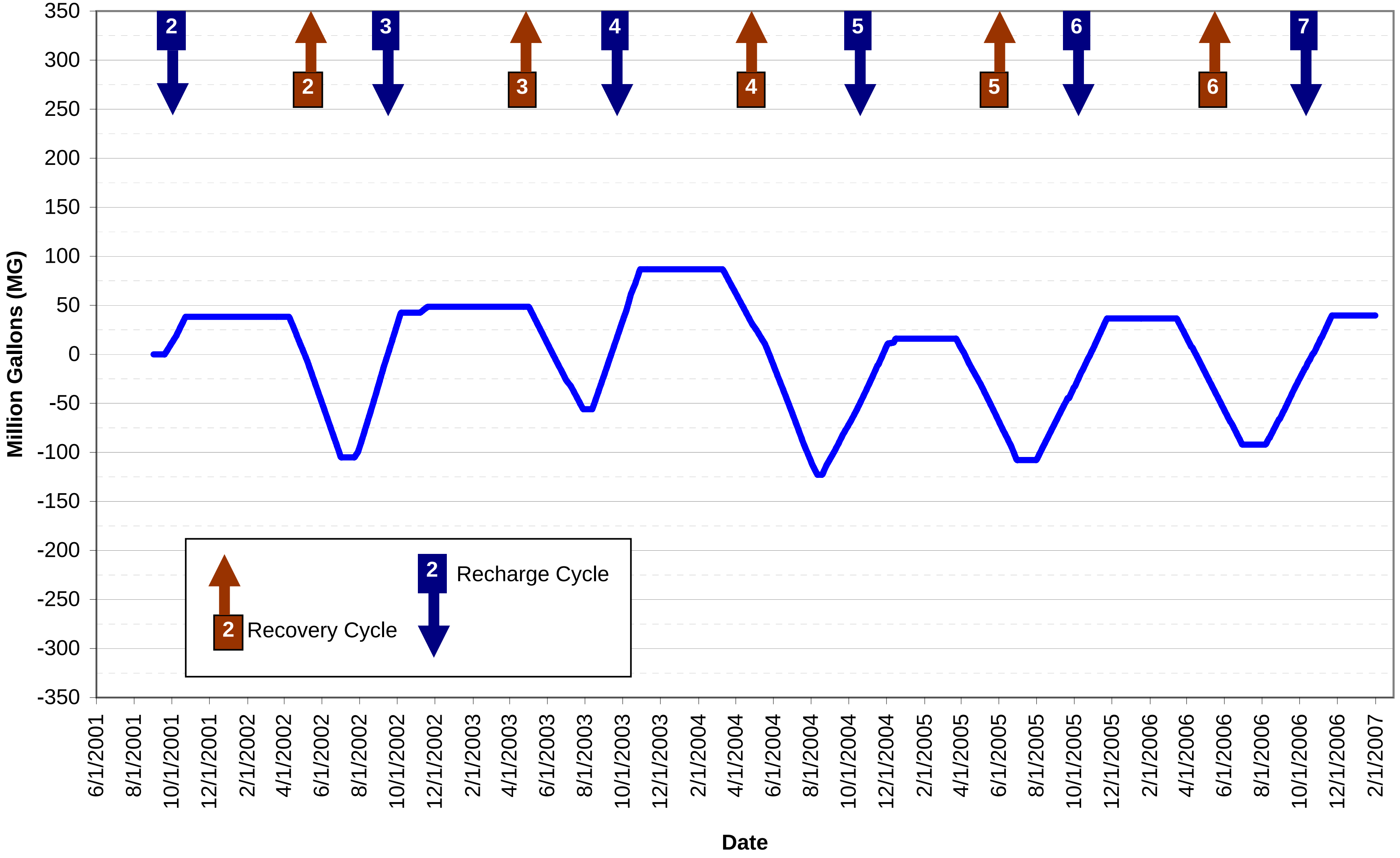
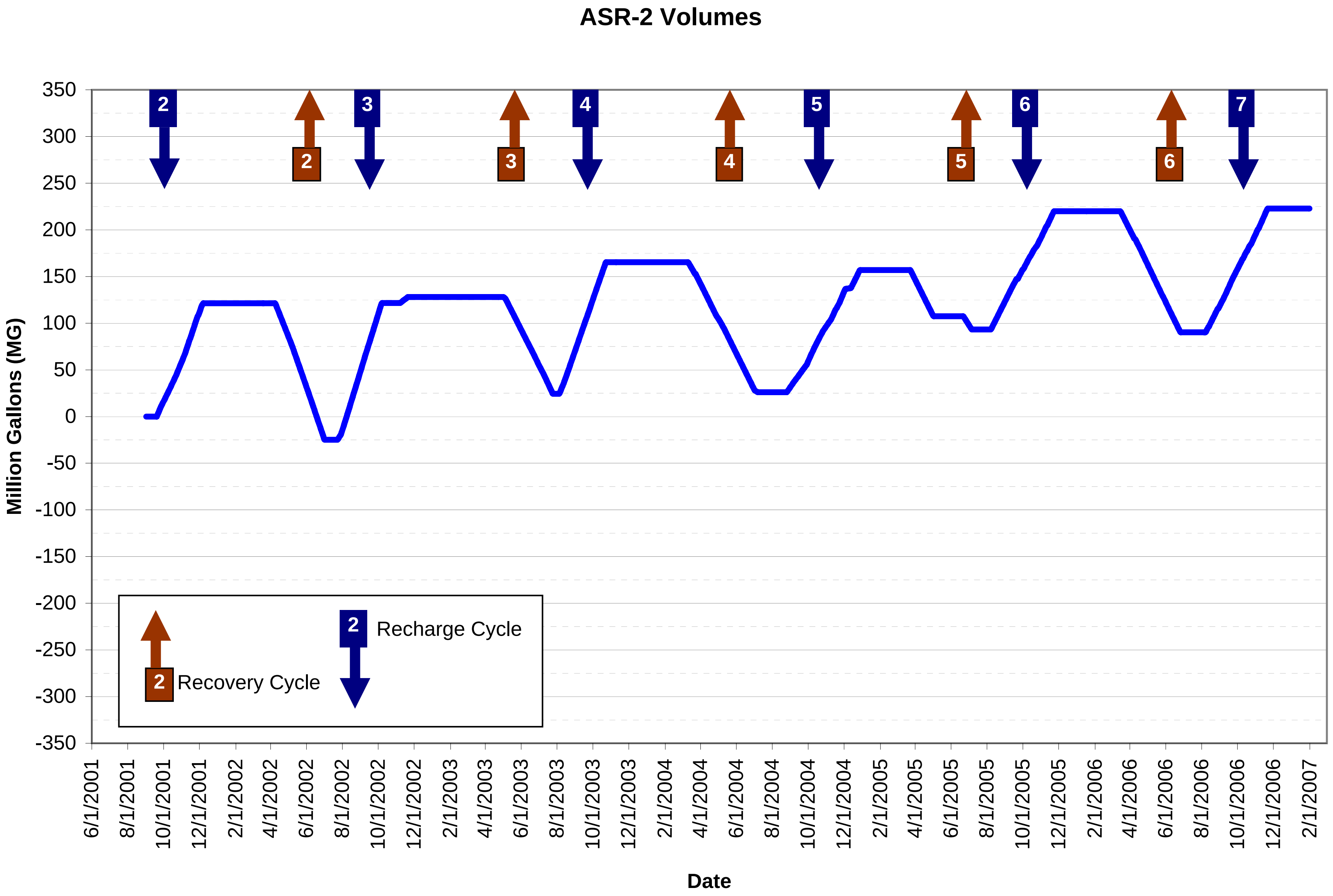
Appendix E

Graphs of Arsenic Concentrations in Monitor Wells at the TRAP and PRF WF2 ASR Wellfields

Tampa Rome Avenue Park
Enhanced Groundwater Monitoring Program

ASR-1 Volumes





ASR-2 Volumes
Million Gallons (MG)
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
Date
6/1/2001
8/1/2001
10/1/2001
12/1/2001
2/1/2002
4/1/2002
6/1/2002
8/1/2002
10/1/2002
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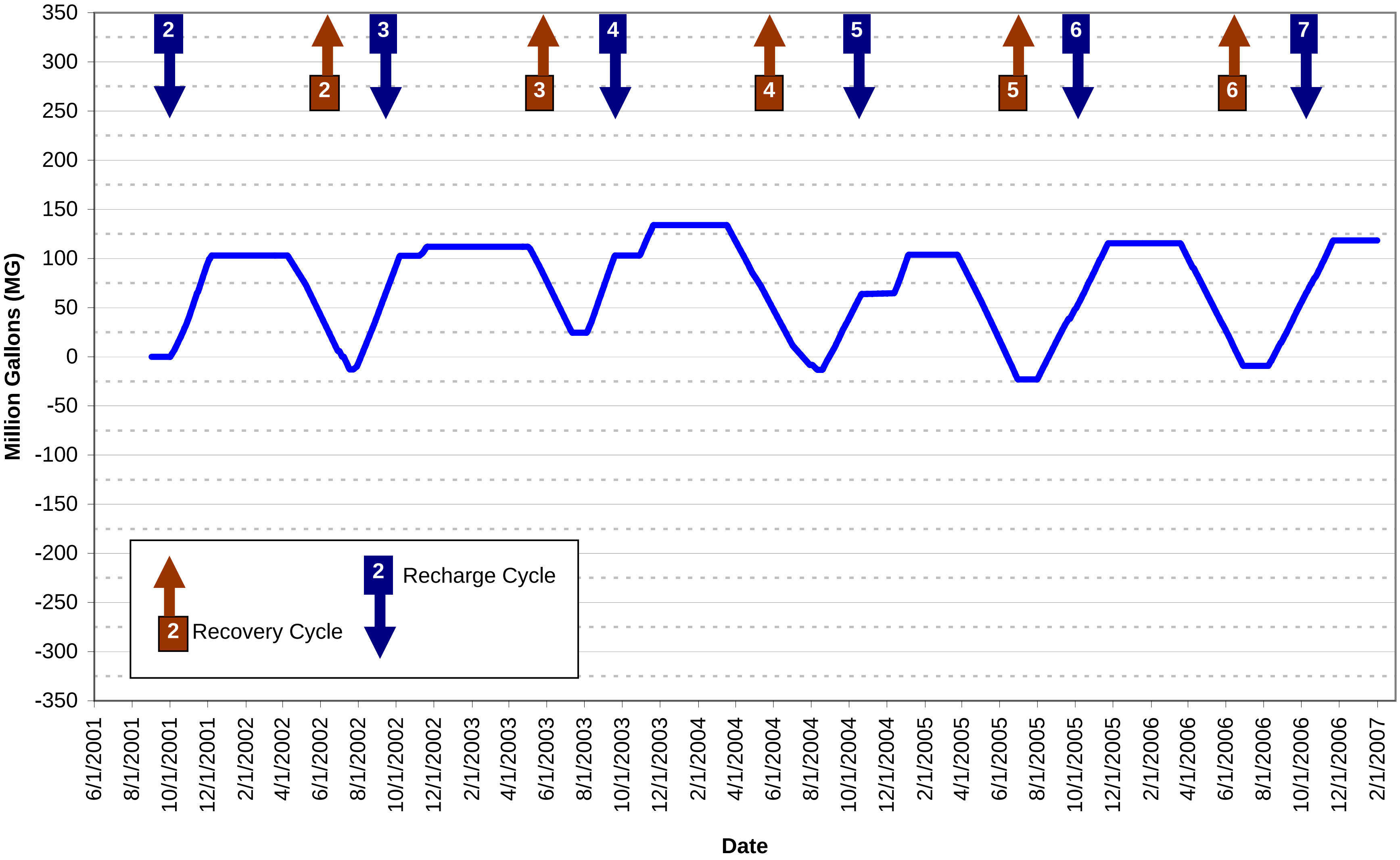
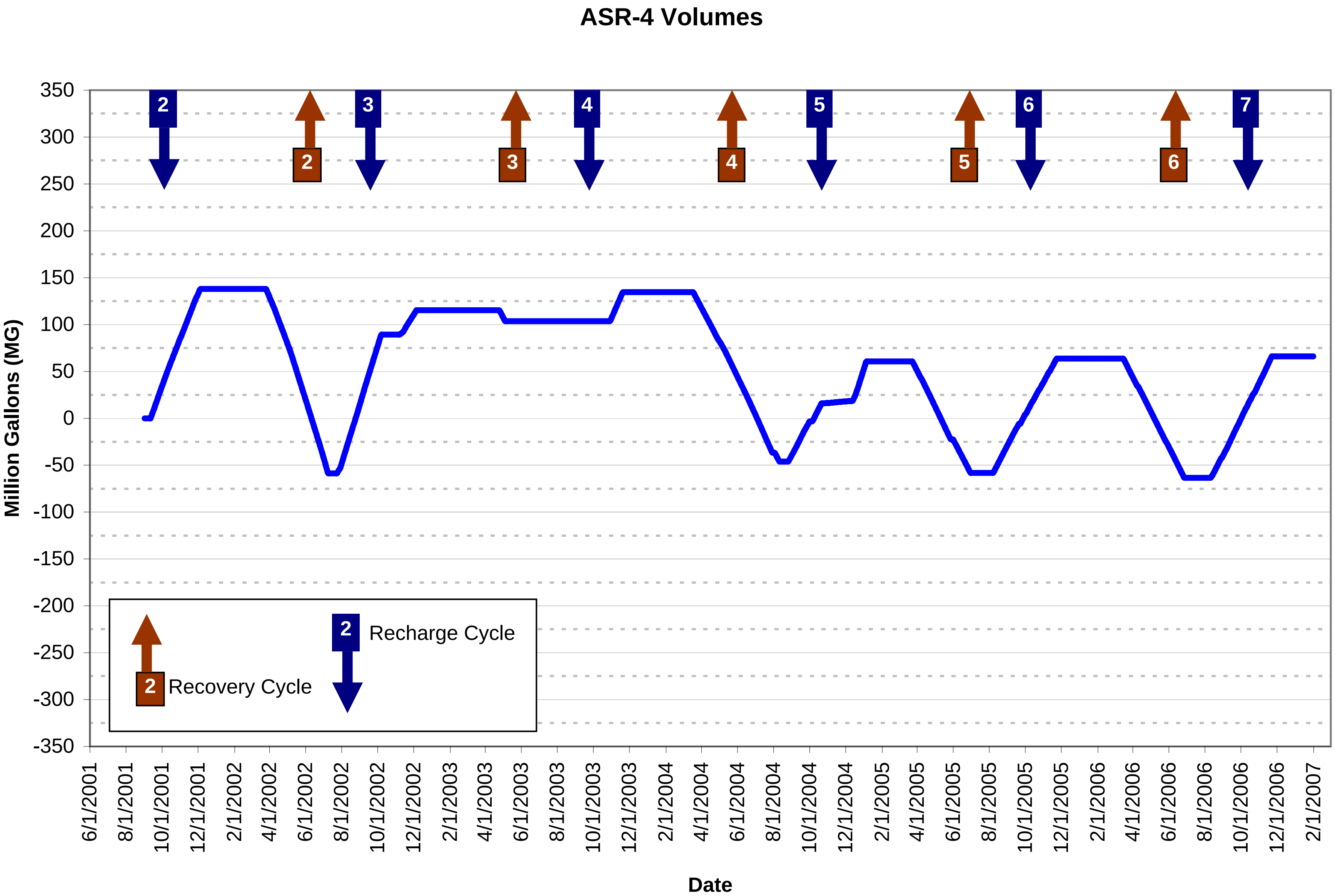
8/1/2006
10/1/2006
12/1/2006
2/1/2007
2
2
3
3
4
4
5
5
6
6
7
2 Recovery Cycle
2 Recharge Cycle

ASR-3 Volumes



ASR-4 Volumes
Million Gallons (MG)
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
Date
6/1/2001
8/1/2001
10/1/2001
12/1/2001
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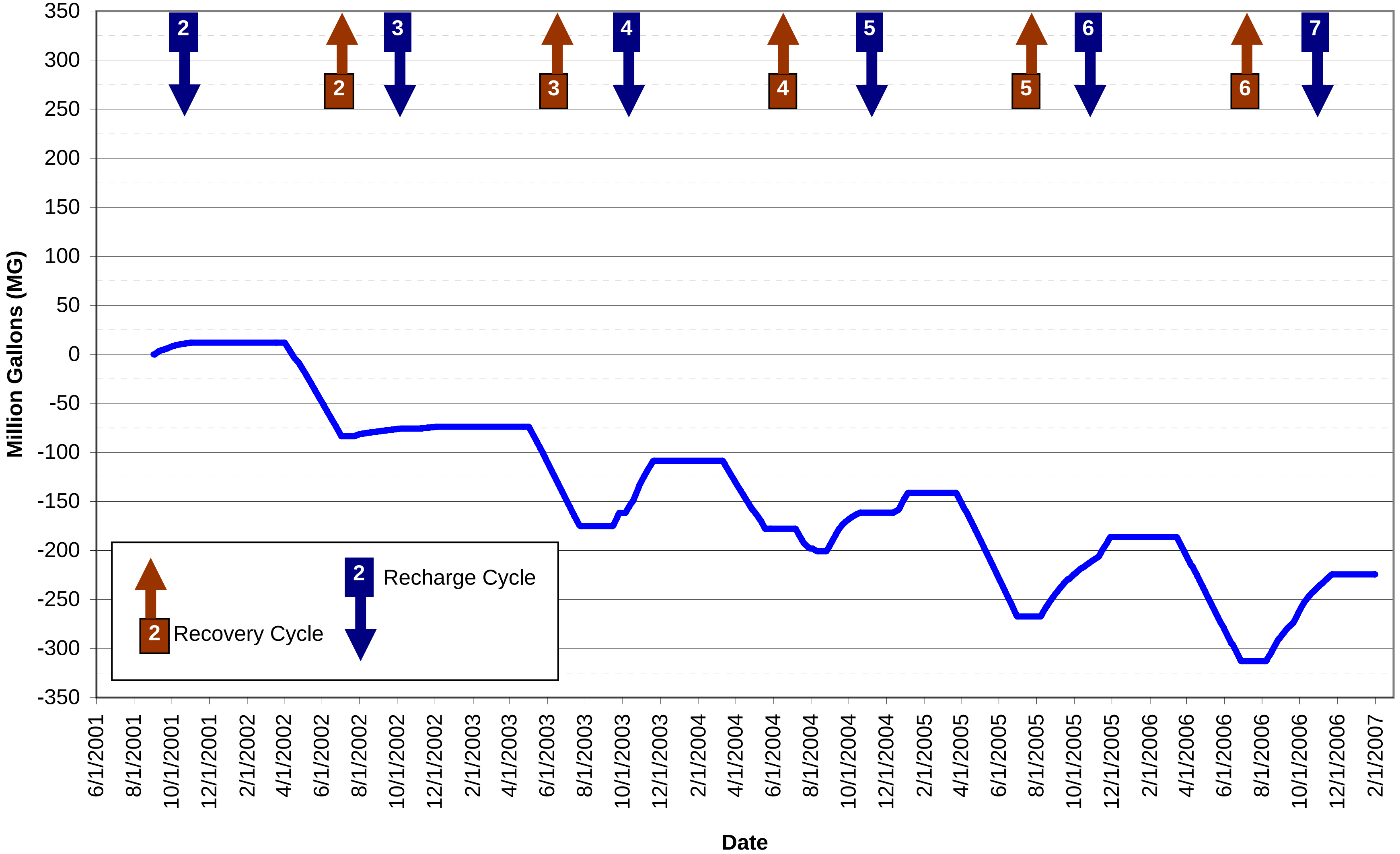
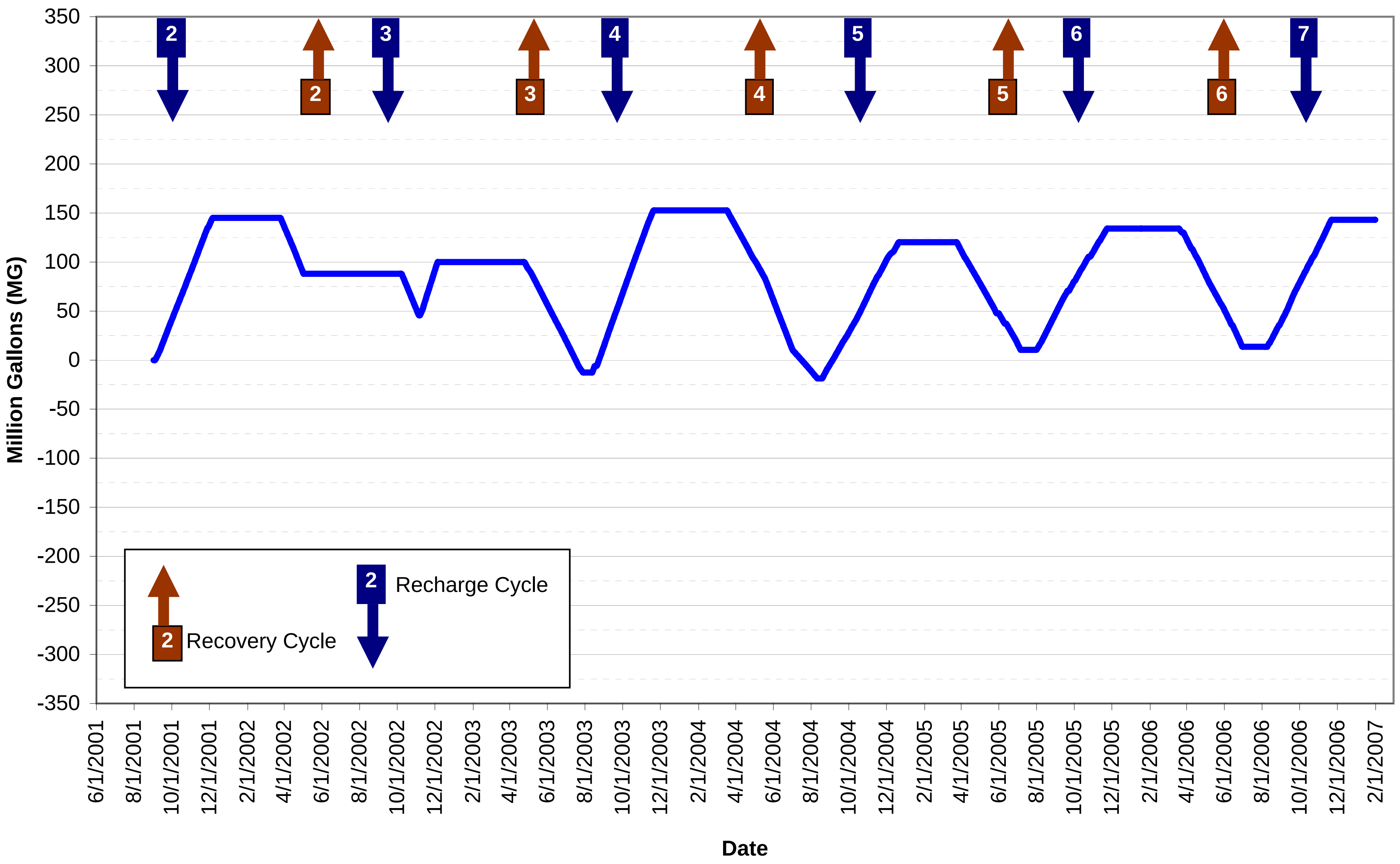
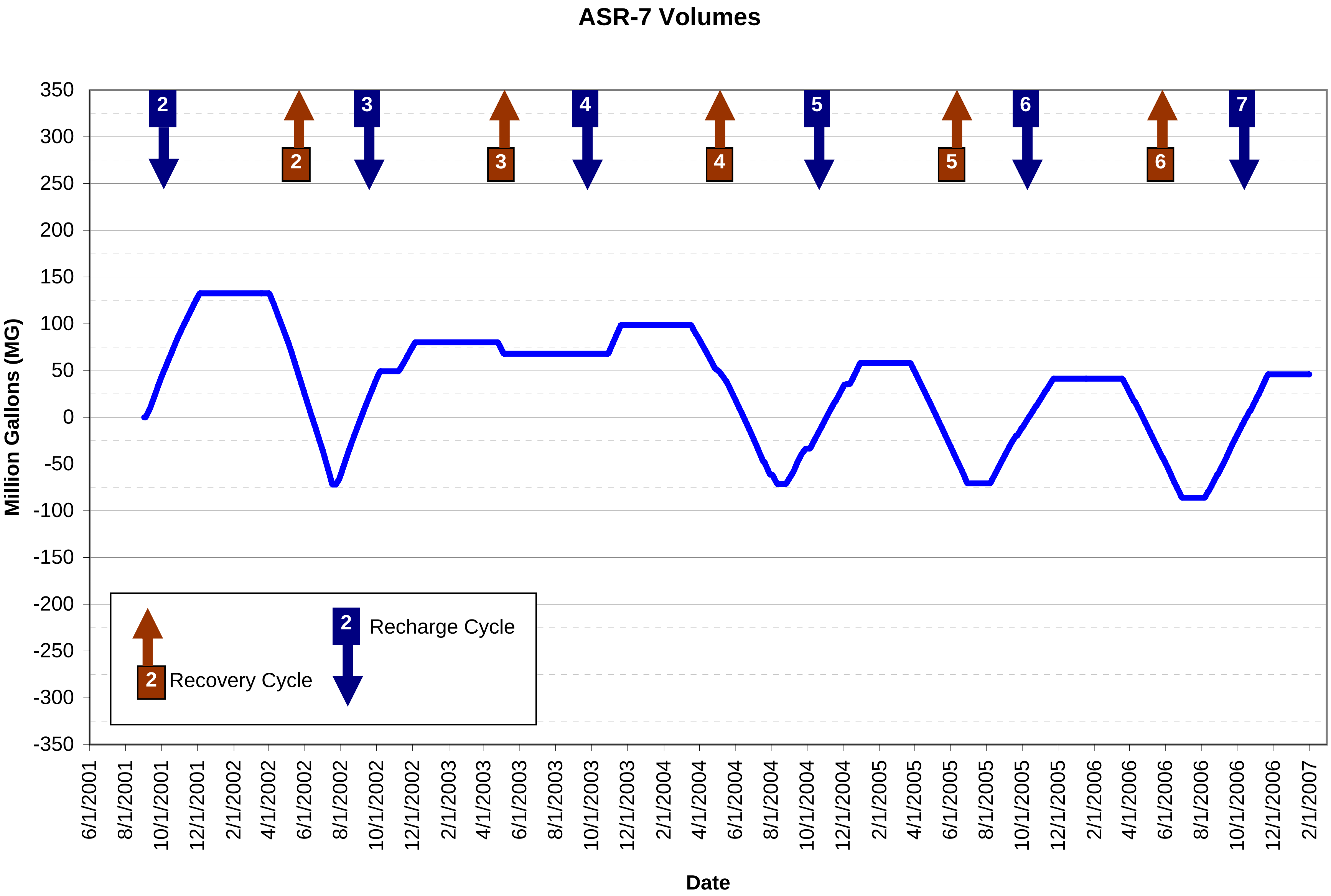
6/1/2005
8/1/2005
10/1/2005
12/1/2005
2/1/2006
4/1/2006
6/1/2006
8/1/2006
10/1/2006
12/1/2006
2/1/2007
2
2
3
3
4
4
5
5
6
6
7
2 Recovery Cycle
2 Recharge Cycle

ASR-5 Volumes

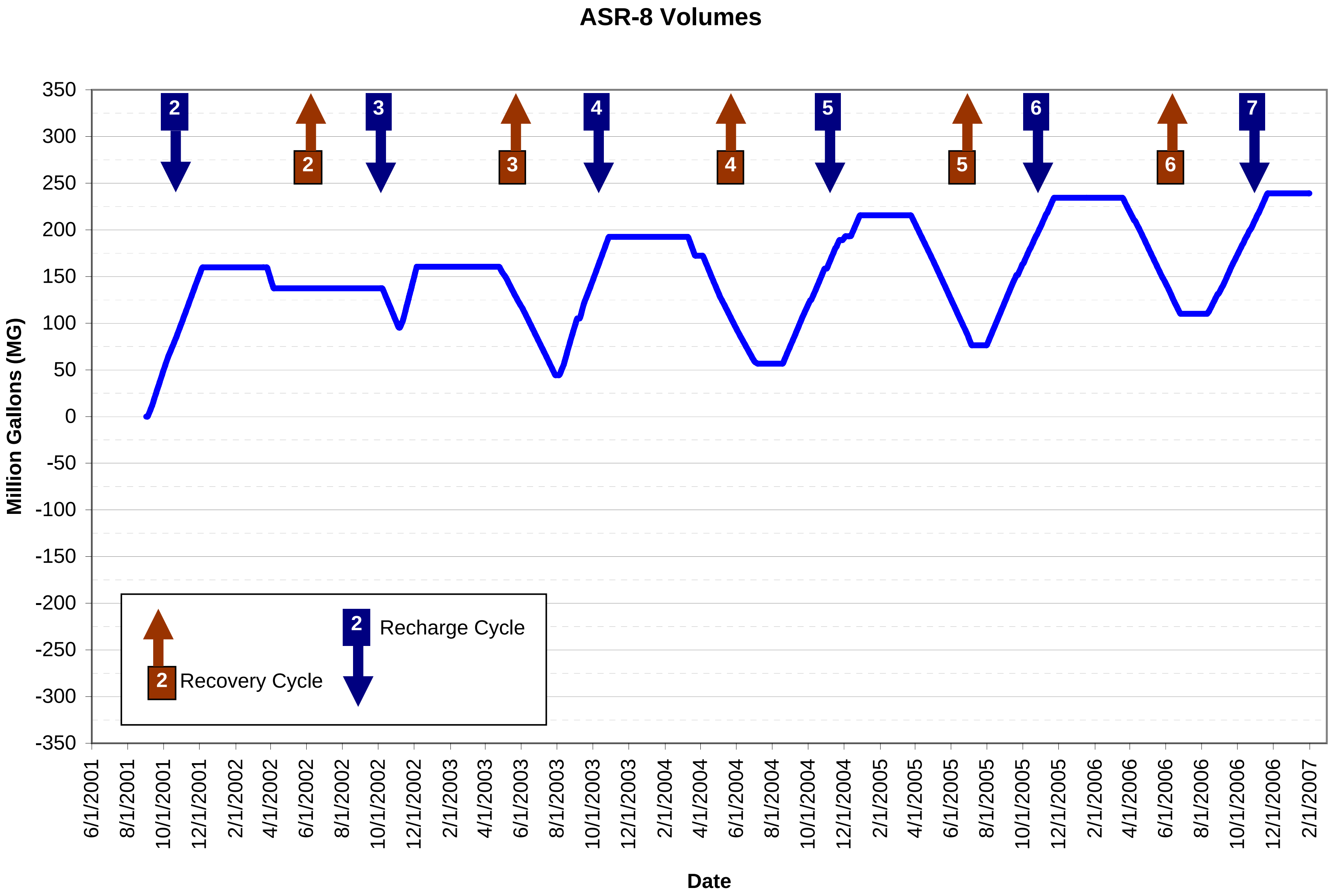


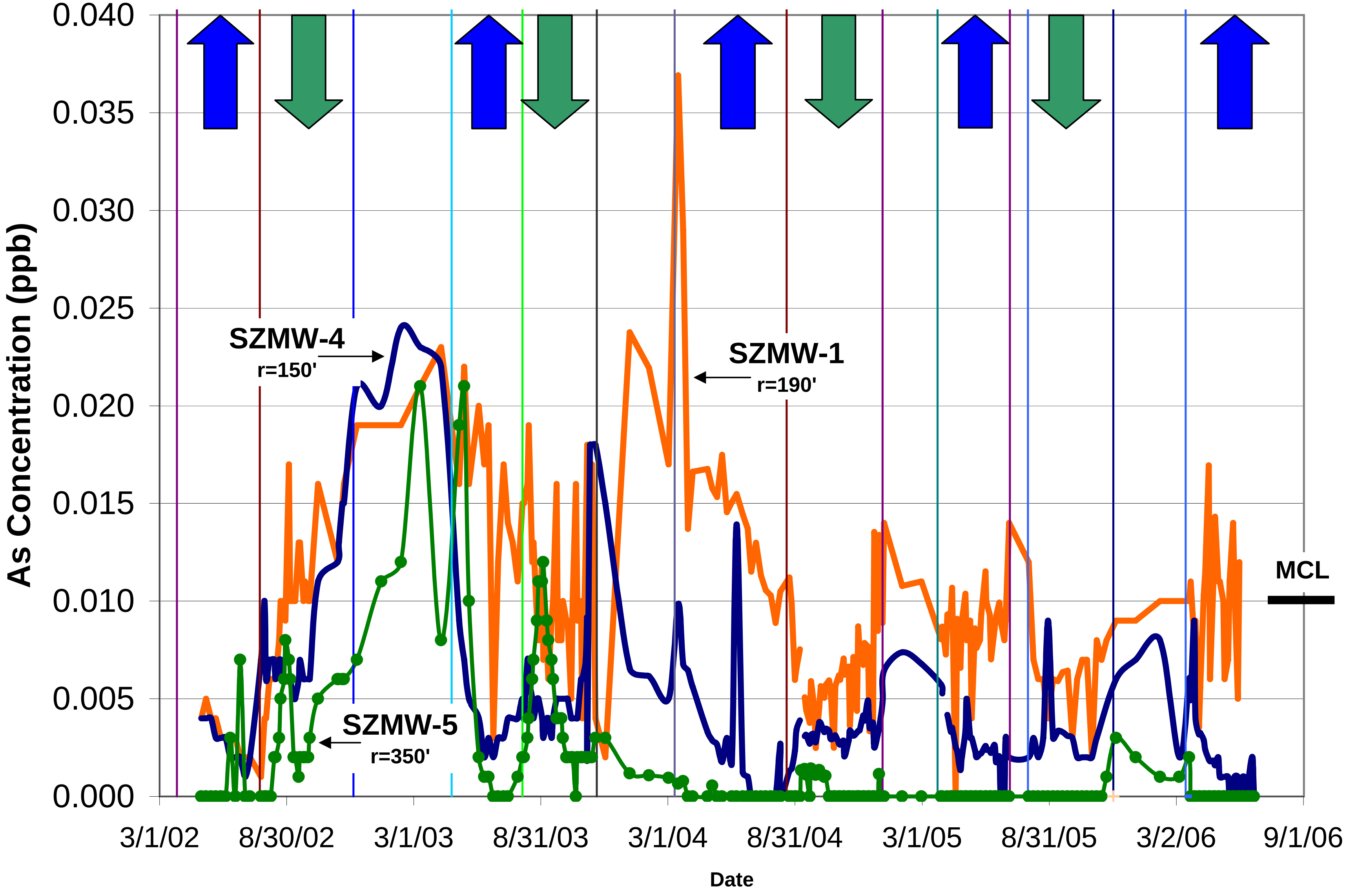
ASR-6 Volumes





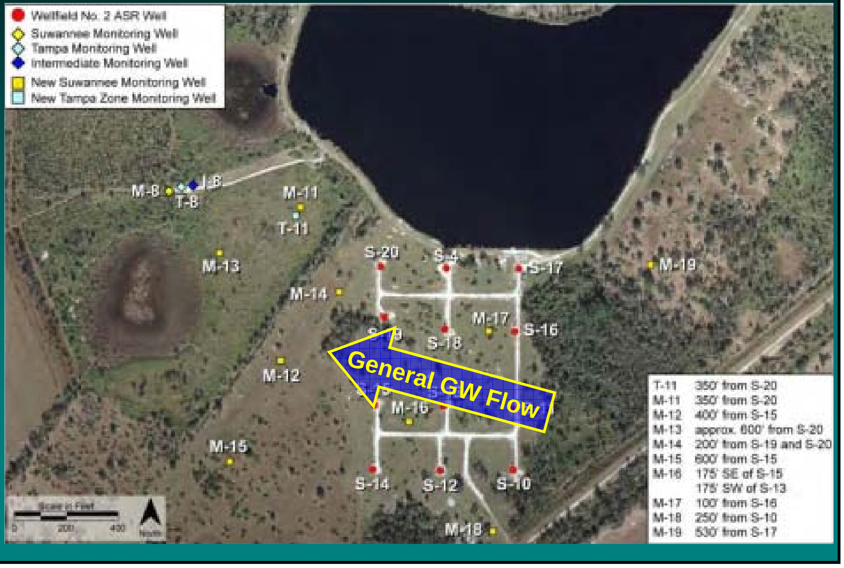
ASR-7 Volumes
Million Gallons (MG)
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
Date
6/1/2001
8/1/2001
10/1/2001
12/1/2001
2/1/2002
4/1/2002
6/1/2002
8/1/2002
10/1/2002
12/1/2002
2/1/2003
4/1/2003
6/1/2003
8/1/2003
10/1/2003
12/1/2003
2/1/2004
4/1/2004
6/1/2004
8/1/2004
10/1/2004
12/1/2004
2/1/2005
4/1/2005
6/1/2005
8/1/2005
10/1/2005
12/1/2005
2/1/2006
4/1/2006
6/1/2006
8/1/2006
10/1/2006
12/1/2006
2/1/2007
2
2
3
3
4
4
5
5
6
6
7
2 Recovery Cycle
2 Recharge Cycle


ASR-8 Volumes
Million Gallons (MG)
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
Date
6/1/2001
8/1/2001
10/1/2001
12/1/2001
2/1/2002
4/1/2002
6/1/2002
8/1/2002
10/1/2002
12/1/2002
2/1/2003
4/1/2003
6/1/2003
8/1/2003
10/1/2003
12/1/2003
2/1/2004
4/1/2004
6/1/2004
8/1/2004
10/1/2004
12/1/2004
2/1/2005
4/1/2005
6/1/2005
8/1/2005
10/1/2005
12/1/2005
2/1/2006
4/1/2006
6/1/2006
8/1/2006
10/1/2006
12/1/2006
2/1/2007
2
2
3
3
4
4
5
5
6
6
7
2 Recovery Cycle
2 Recharge Cycle


As Concentration (ppb)
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
3/1/02
8/30/02
3/1/03
8/31/03
3/1/04
8/31/04
3/1/05
8/31/05
3/2/06
9/1/06
Date
SZMW-4
r=150'
SZMW-1
r=190'
SZMW-5
r=350'
MCL

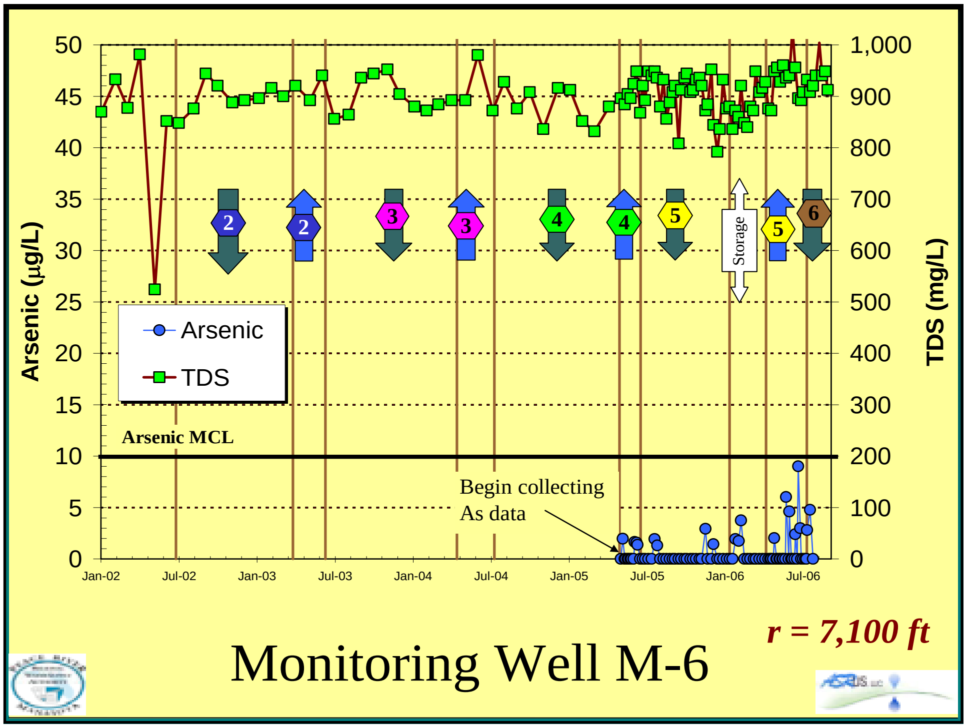
Peace River Facility ASR Wellfield 2
Enhanced Groundwater Monitoring Program

Monitoring Well Locations – ASR Wellfield 2



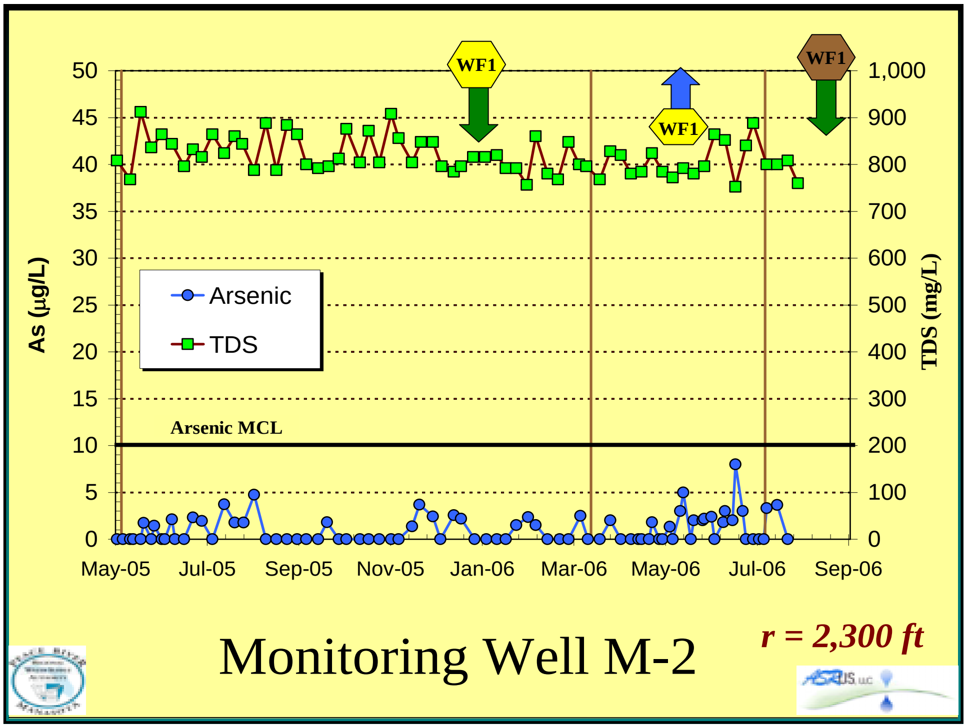
T-11	350' from S-20
M-11	350' from S-20
M-12	400' from S-15
M-13	approx. 600' from S-20
M-14	200' from S-19 and S-20
M-15	600' from S-15
M-16	175' SE of S-15 175' SW of S-13
M-17	100' from S-16
M-18	250' from S-10
M-19	530' from S-17

Well	Closest ASR Well	ASR Well	Well-field	Max As (ppb)	No. of Samples
M-2	2300'	S-1	WF1	8.0	89
M-6	7100'	S-14	WF2	9.0	89
M-7	320'	S-6	WF1	10.0	263
M-8	870'	S-20	WF2	**12***	234
M-11	350'	S-20	WF2	3.0	61
M-12	400'	S-15	WF2	2.0	60
M-13	600'	S-20	WF2	2.0	60
M-14	200'	S-19	WF2	**31**	74
M-15	600'	S-15	WF2	**22****	60
M-16	175'	S-13	WF2	**20****	74
M-17	100'	S-16	WF2	**17****	74
M-18	250'	S-10	WF2	2.0	60
M-19	530'	S-17	WF2	3.0	60
M-20	460'	S-5R	WF1	2.0	60
M-21	200'	S-7	WF1	4.0	60
M-22	83'	S-2	WF1	**38****	60
*** Single Sample**		**** ≤6 Samples**		**38**	1438



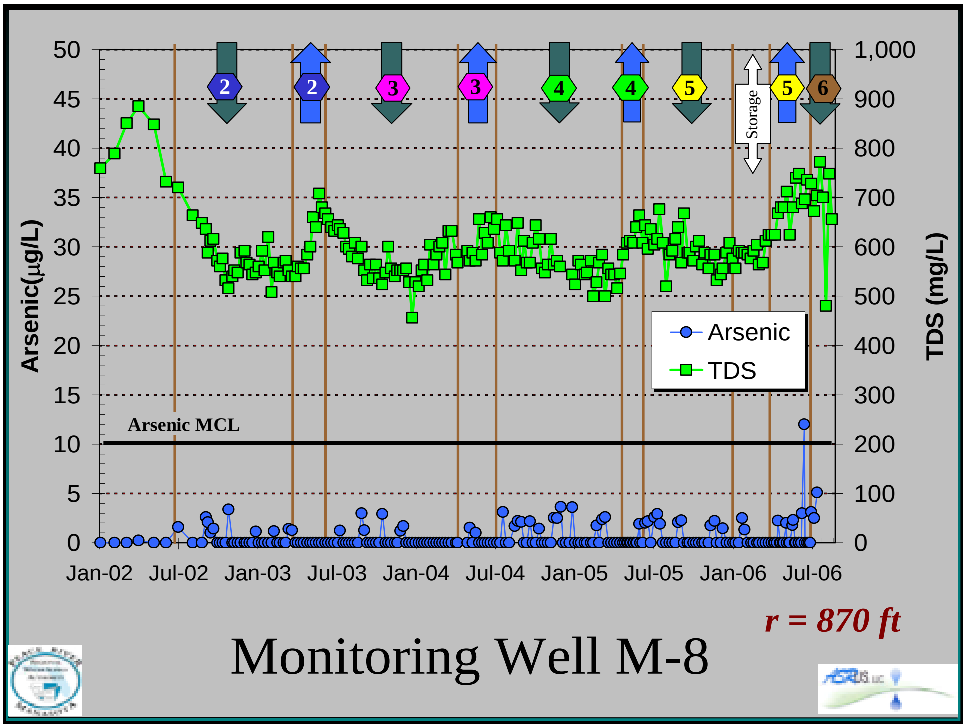
r = 7,100 ft

Monitoring Well M-6



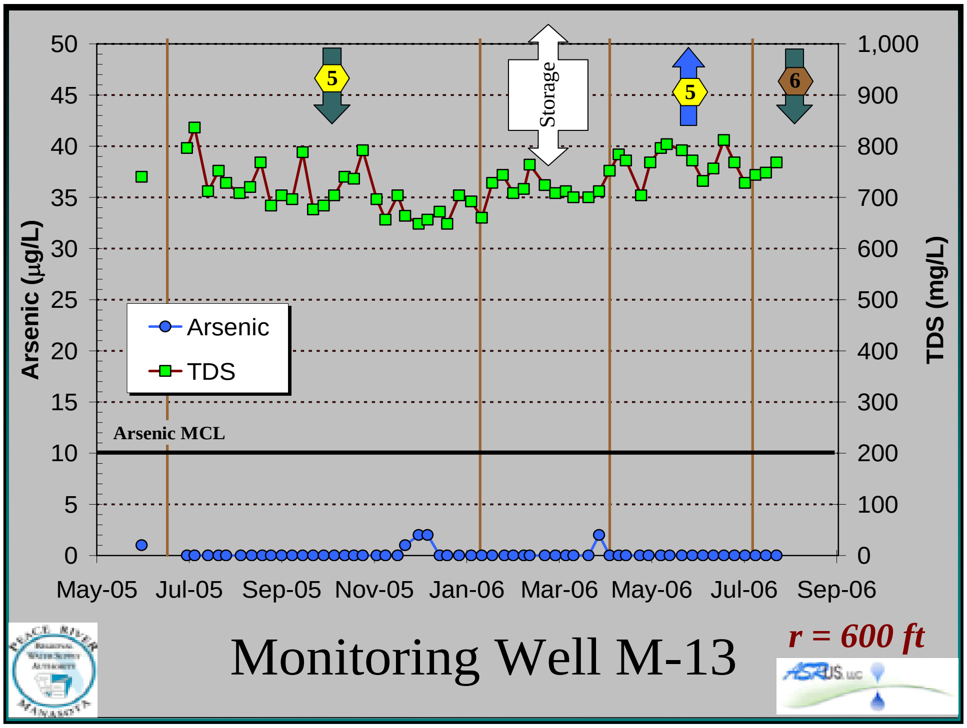
r = 2,300 ft

Monitoring Well M-2



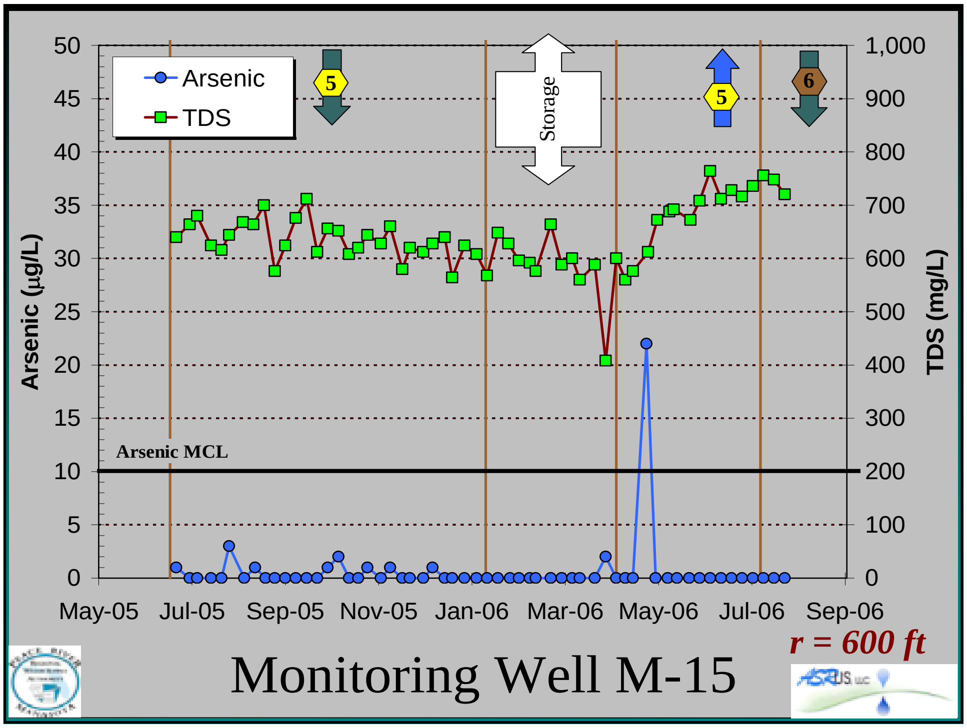
r = 870 ft

Monitoring Well M-8



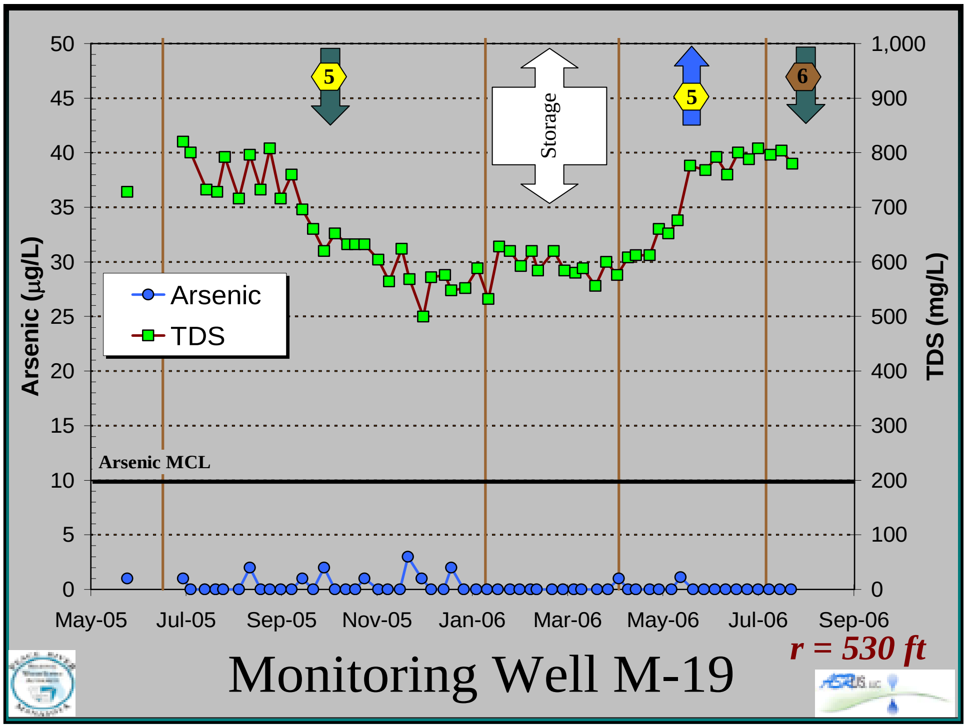
r = 600 ft

Monitoring Well M-13



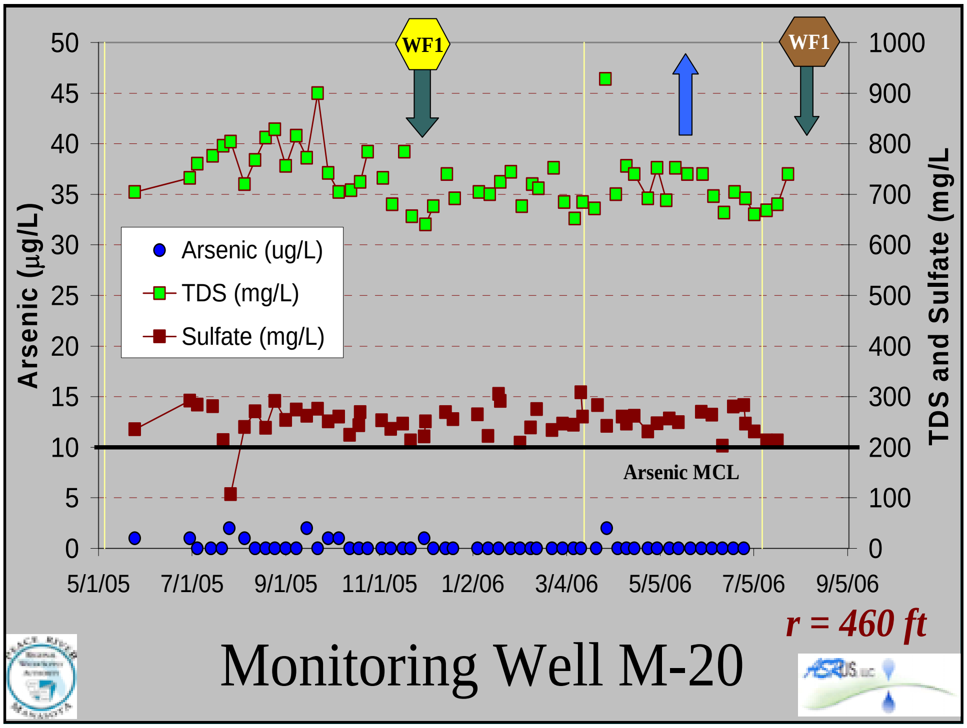
r = 600 ft

Monitoring Well M-15



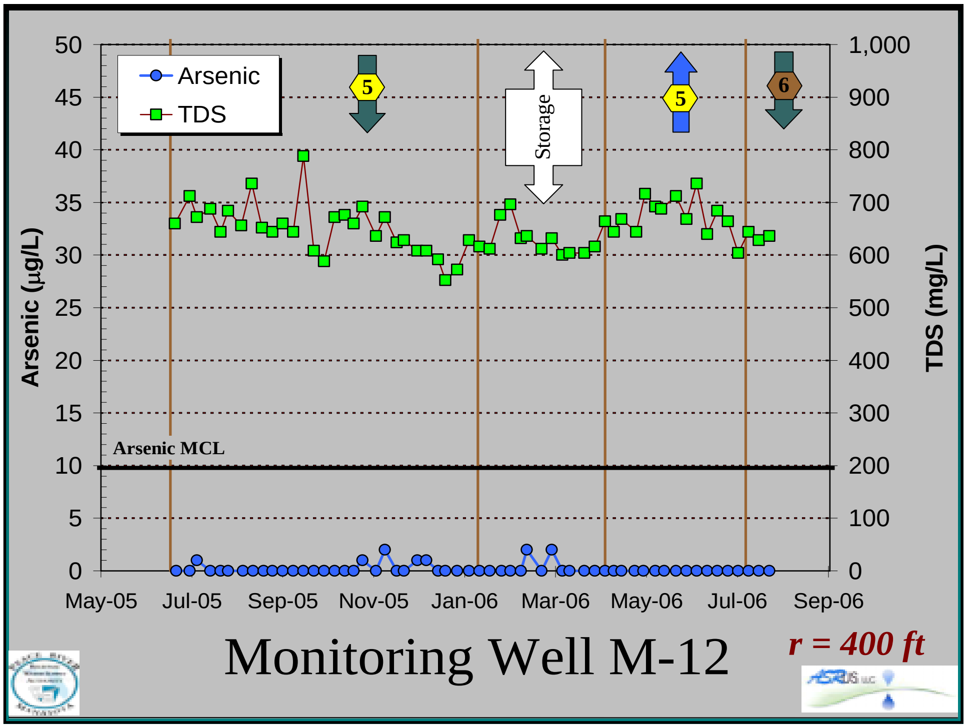
r = 530 ft

Monitoring Well M-19



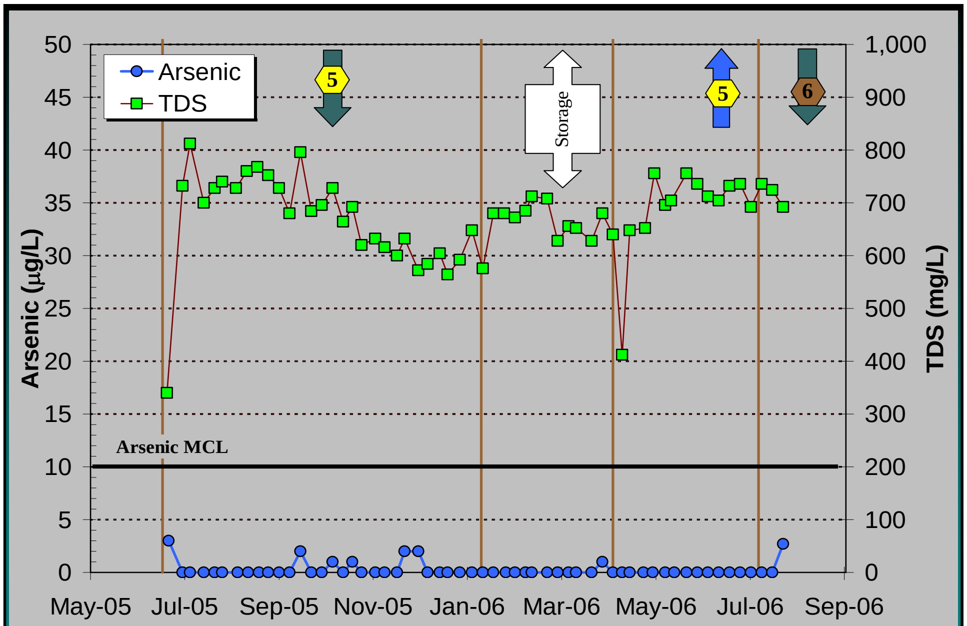
r = 460 ft

Monitoring Well M-20



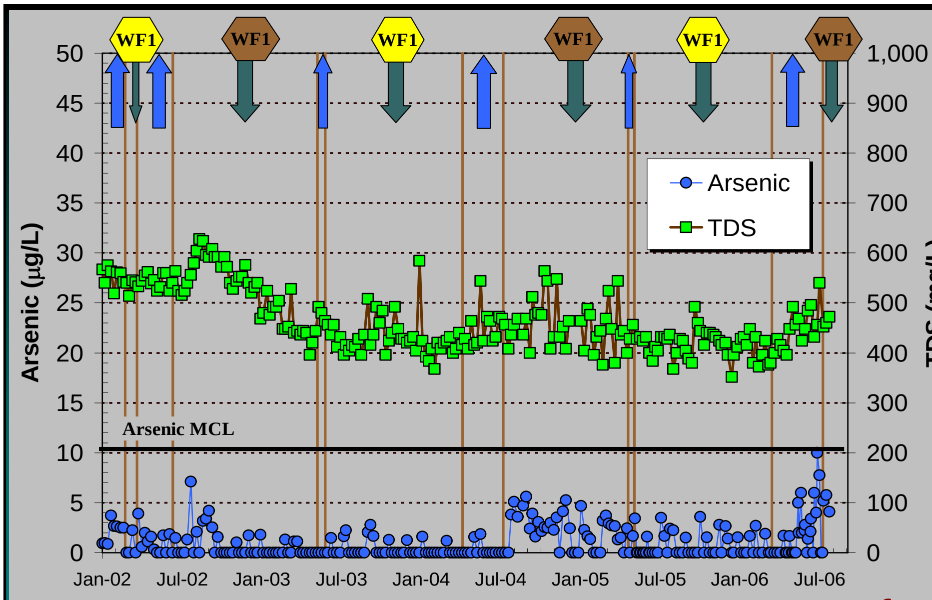
r = 400 ft

Monitoring Well M-12



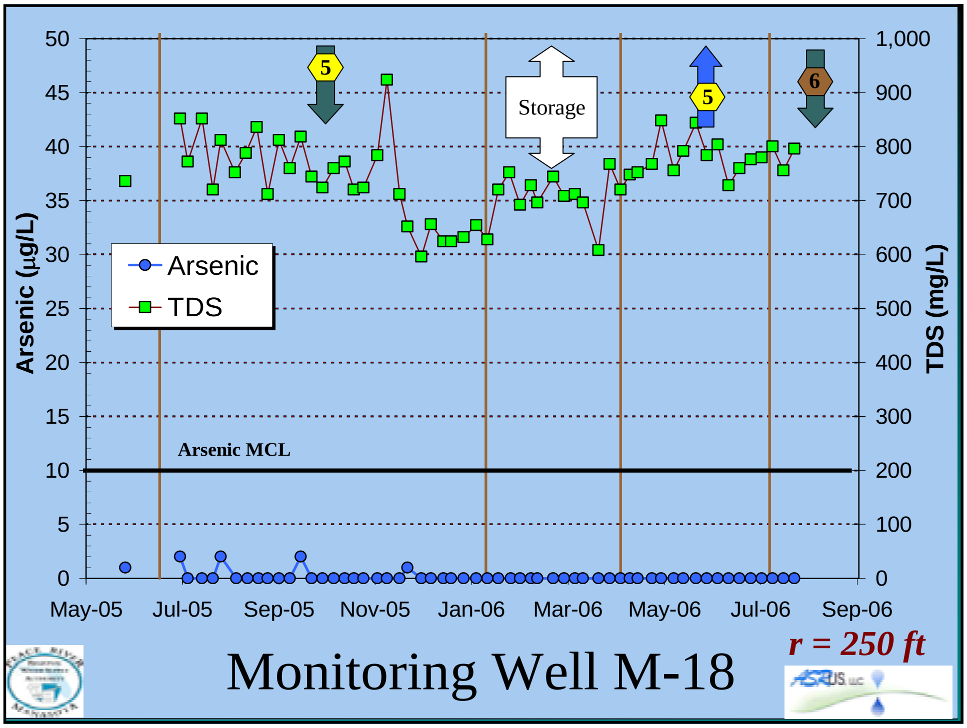
r = 350 ft

Monitoring Well M-11



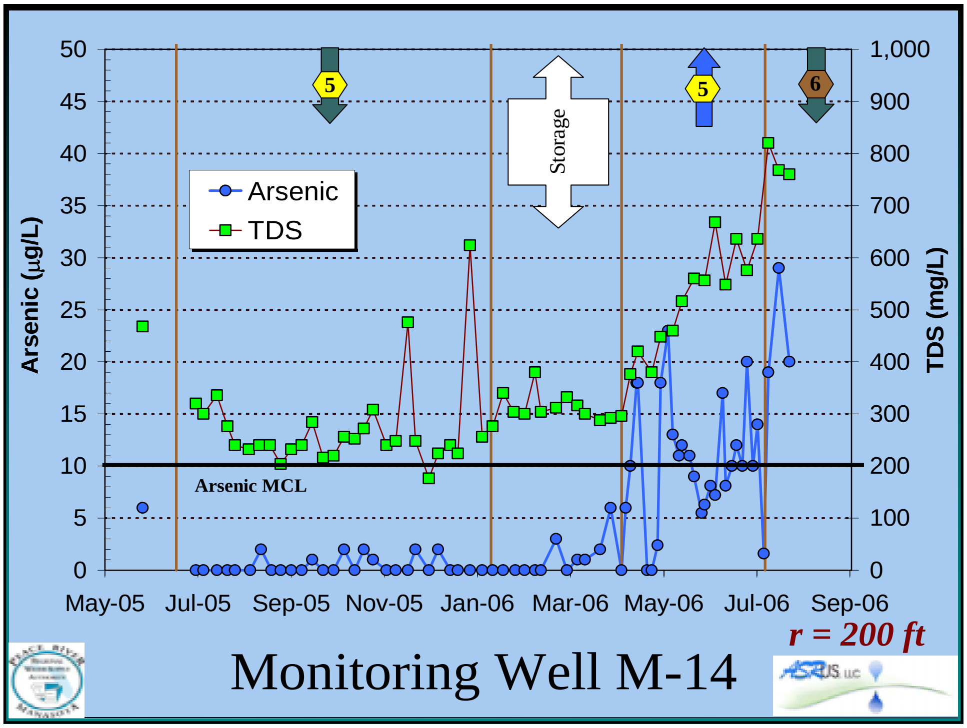
r = 320 ft

Monitoring Well M-7



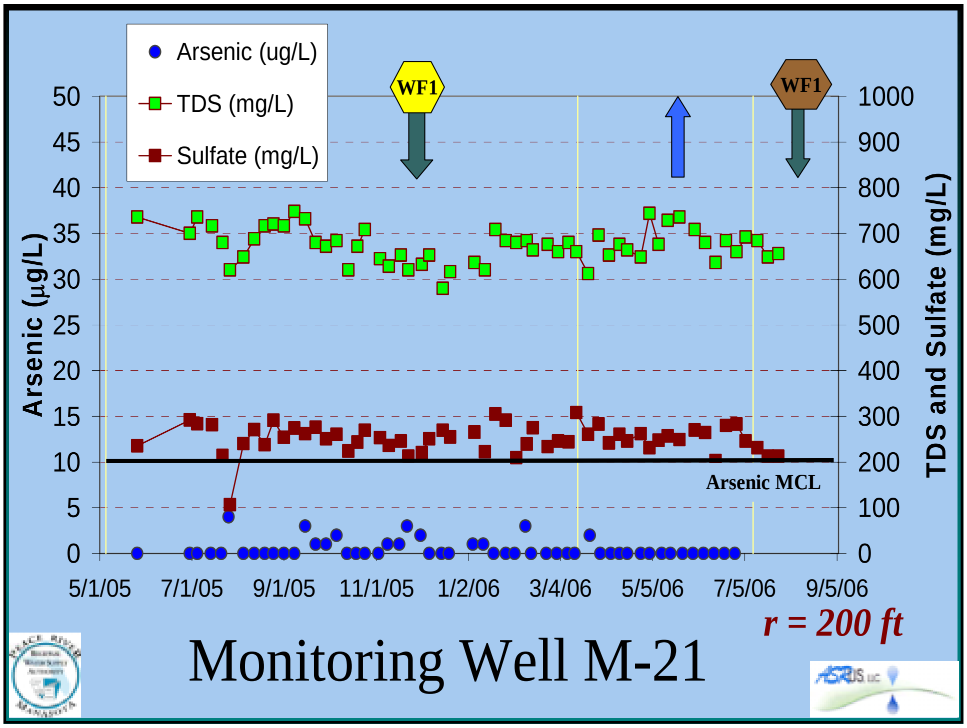
r = 250 ft

Monitoring Well M-18



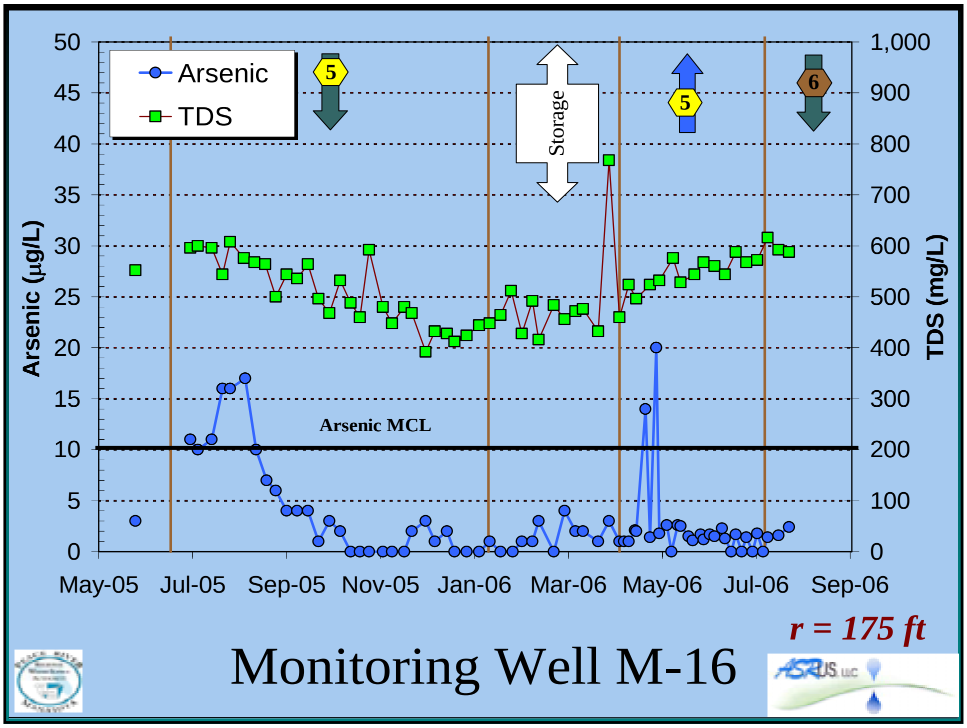
r = 200 ft

Monitoring Well M-14



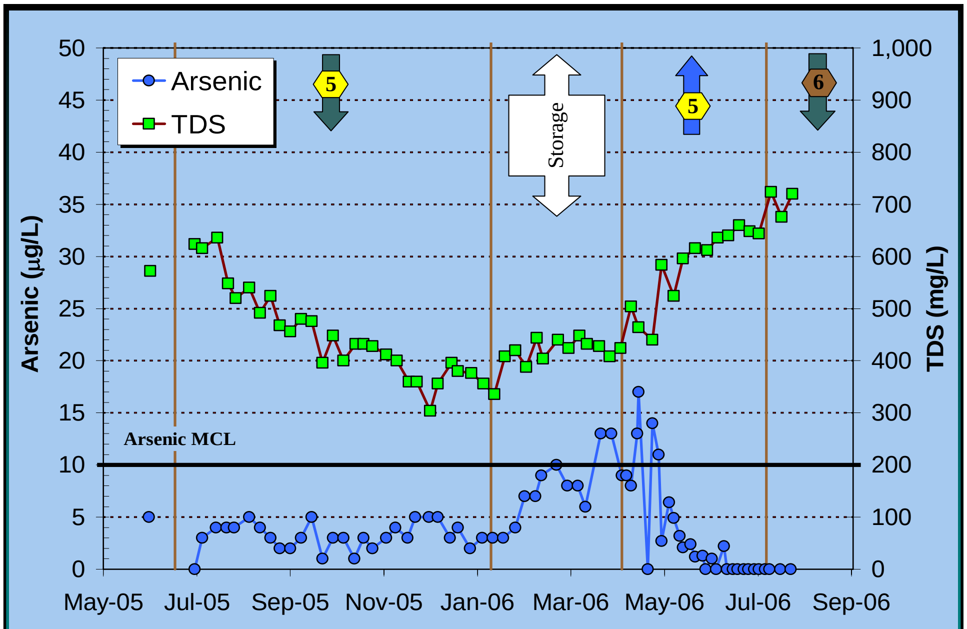
r = 200 ft

Monitoring Well M-21



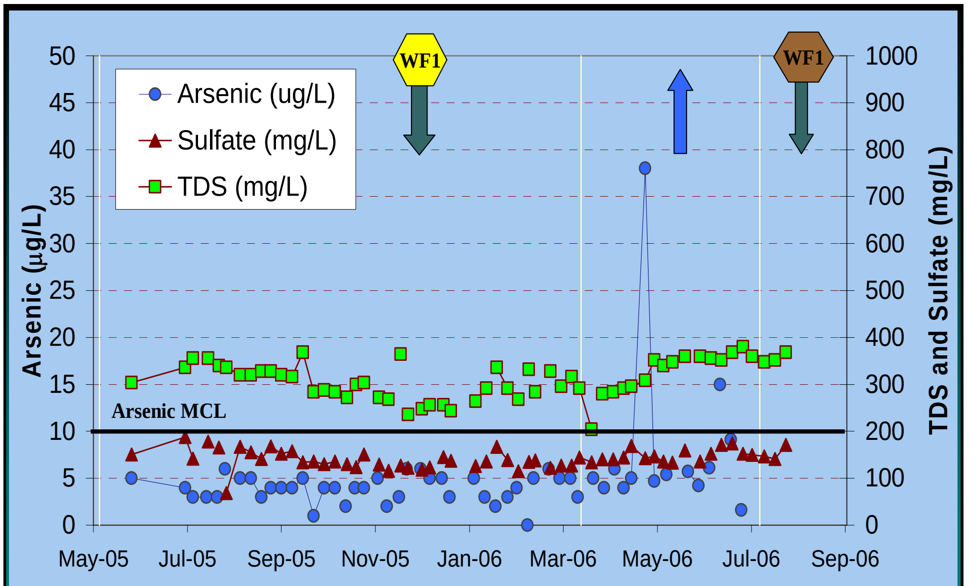
r = 175 ft

Monitoring Well M-16



r = 100 ft

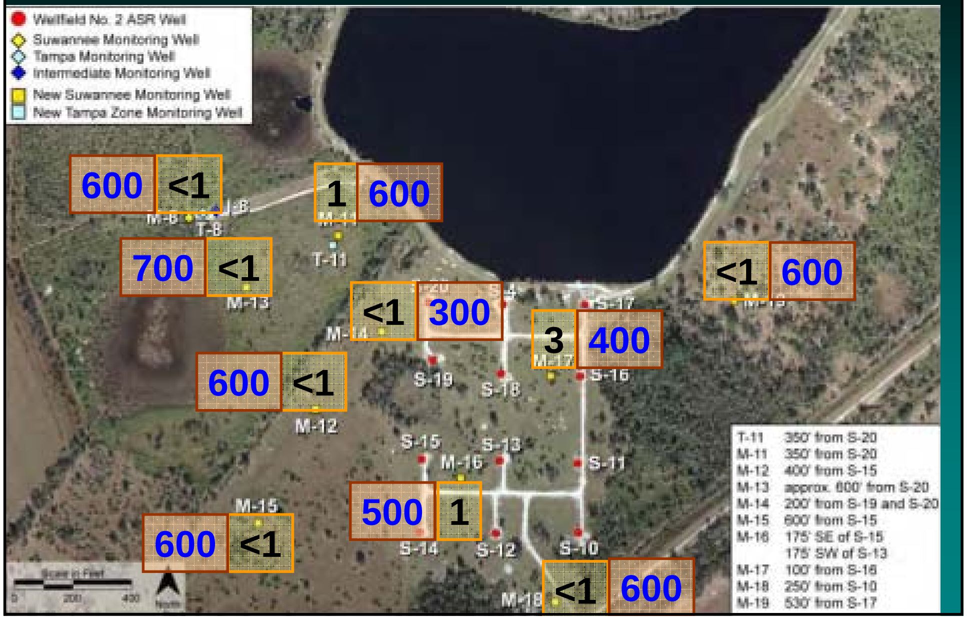
Monitoring Well M-17



r = 83 ft

Monitoring Well M-22

Approximate Suwannee Limestone As ($\mu g/L$) & TDS (mg/L) concentrations after Cycle 5 Recharge (Jan 2006)



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M-11	350' from S-20
M-12	400' from S-15
M-13	approx. 600' from S-20
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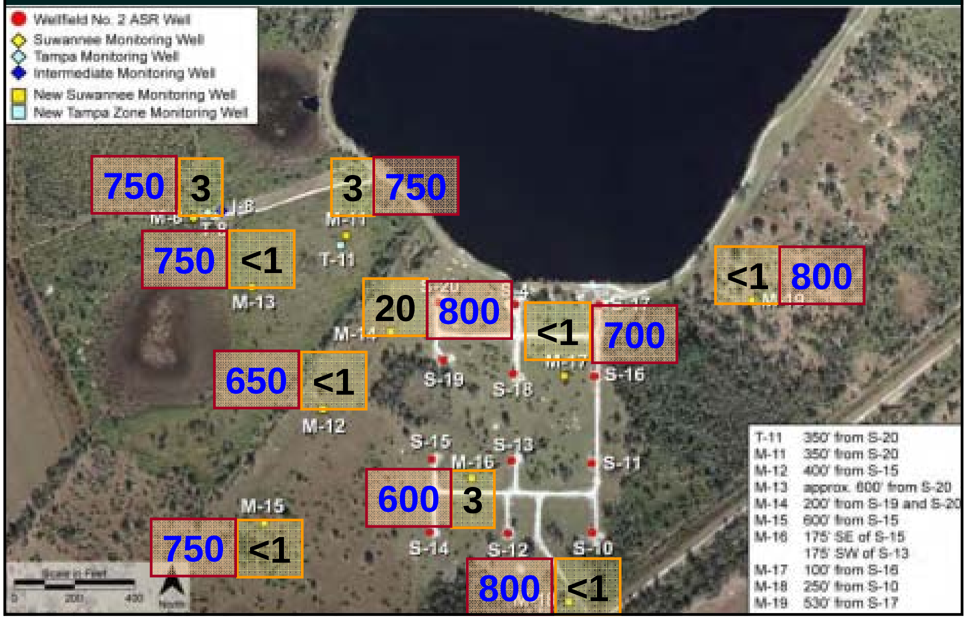
M-15	600' from S-15
M-16	175' SE of S-15 175' SW of S-13
M-17	100' from S-16
M-18	250' from S-10
M-19	530' from S-17

Approximate Suwannee Limestone As ($\mu g/L$) and TDS (mg/L) concentrations after Cycle 5 Recovery (July 2006)



T-11	350' from S-20
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M-19	530' from S-17

Appendix F

Script for PHREEQC Inverse Geochemical Model to Simulate Reductive Dissolution of Iron Oxyhydroxide

PHREEQC input file for inverse geochemical model. This model simulates geochemical evolution as recovery proceeds. Solution 1 (initial recovered water) reflects water quality closer to the ASR well; solution 2 (final recovered water) reflects conditions away from the ASR well. The PHREEQC version used is v. 2.1.3, available at

http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html

```
TITLE TRAP C6 Inverse Model_Recovery
SOLUTION 1 Initial Recovered Water from ASR well
units mg/L
temp 25
redox S(-2)/S(6)
pH   7.8
Fe(+2)  0.029
S(6)   127
S(-2)   0.1
Alkalinity 135
SAVE SOLUTION 1

SOLUTION 2 Final Recovered Water from ASR Well
units mg/L
temp 25
redox S(-2)/S(6)
pH 7.8
Fe(+2)  0.2
S(6)  111
S(-2)   0.8
Alkalinity  130
SAVE SOLUTION 2


INVERSE_MODELING 1
-solutions 1 2
-phases
   calcite
   H2S(g)
   Fe(OH)3(a)
-uncertainty 1
END
```