Arsenic behavior in SW Florida ASR systems and its expert modeling

Pieter J. Stuyfzand[1,2] and R. David G. Pyne[3]
[1]KWR Watercycle Research Institute, PO Box 1072, 3430 BB Nieuwegein, Netherlands
Email: pieter.stuyfzand@kwrwater.nl.
[2]VU University, Amsterdam, Netherlands
[3]ASR Systems LLC, Gainesville, Florida USA, Email: dpyne@asrsystems.ws

Abstract

Aquifer Storage Recovery (ASR) wellfields in karstified limestone have been operating at many locations in Florida since 1983. When in 2005 the water quality standard for As was lowered from 50 to 10 ug/L and elevated As concentrations showed up at some sites, ASR became a much disputed water storage technique. Pyrite oxidation during injection and storage was identified as the main driver behind the As problem, with subsequent As desorption from neoformed ferric (hydr)oxides (HFO) and reductive dissolution of HFO especially during recovery.

Data analysis revealed many complications in trying to simulate and predict As behavior with reactive transport models, due to scarcity of specific or high quality data. Therefore, considering the vast amount of hydrochemical data that have been collected on a routine basis on Floridan ASR sites, it was decided to construct an expert model for predicting As behavior in SW Florida ASR systems. This model is presented and tested against field data (from 6 ASR well fields with a total of 53 wells, each with 3-17 ASR cycles). It consists of an analytical model which calculates the As concentration by a sine function with decreasing amplitude during subsequent ASR cycles. The initial amplitude is determined by the As peak calculated via a mass balance equation which multiplies the average As content of pyrite with the total amount of pyrite oxidants in the recharge water.

The model predicts trends in As concentrations on any site, old or new, and the effects of changes in ASR operation, like reducing the oxidant input or recovery efficiency.

Key words:
ASR, arsenic, pyrite, limestone, expert modeling

INTRODUCTION

Aquifer Storage & Recovery (ASR) is a water management technique, in which water is stored in an aquifer during periods of water excess, and recovered by the same (injection) well from the groundwater reservoir during periods of water shortage (Pyne, 2005).

In Florida, ASR wellfields in karstified limestone have been operating at many locations since 1983. Initial indications of elevated As concentrations at some ASR wellfields (up to 220 ug/L) in SW Florida became evident in 2001. In 2005 the water quality standard for As was lowered in USA from 50 to 10 ug/L. Since then, ASR became a much disputed water storage technique, instigating several investigations (Pyne et al., 2004, 2008; Mirecki, 2004; Price & Pichler, 2006; CH2M Hill, 2007; ASR Systems, 2007; Arthur et al., 2007; Jones & Pichler, 2007), to better define the nature and extent of the problem, to advance understanding of the science of As mobilization and attenuation in the Floridan limestone aquifer and to seek potential solutions. Most investigations relied upon extensive operating and monitoring data from many ASR wells and a steadily increasing number of storage zone monitor wells.

Pyrite oxidation during injection and storage was identified as the main driver behind the As problem, with subsequent As desorption from neoformed hydrous ferric oxides (HFO) and reductive dissolution of HFO especially during recovery.

Nevertheless, many uncertainties remained due to the complexity of As behavior, heterogeneity of karstic limestones, and doubts about the quality or representativity of the hydrochemical data collected (Stuyfzand, 2008). Despite these and other important areas of uncertainty, clear patterns have become evident regarding arsenic mobilization and attenuation at Florida ASR wellfields (Pyne et al., 2008):

- Peak arsenic concentrations in the recovered water from ASR wells tend to decline with successive operating cycles, when the volumes for recharge and recovery are kept rather constant;
- Arsenic concentrations tend to decline during extended storage periods;

- Elevated arsenic concentrations do not extend very far from ASR wells, typically reaching acceptable concentrations within a radius of about 120 m;
- Formation and maintenance of an adequate buffer zone around an ASR well, separating the stored water from the surrounding ambient groundwater, tends to control arsenic concentrations within acceptable levels; and
- During ASR recovery, if over-recovery is allowed to occur and all or a portion of the buffer zone is recovered, the change in groundwater quality destabilizes arsenic sorbed onto ferric hydroxide floc and on other surfaces near the well, releasing the desorbed arsenic.

The improved insights stimulated to construct an expert model for predicting As behavior in SW Florida ASR systems (Stuyfzand et al., 2008). This model is presented here and tested against field data from 6 ASR well fields with a total of 53 wells (each with 3-17 ASR cycles). It constitutes a fast, easy to handle, predictive tool with a very low data hunger.

As future research will probably yield more detailed and better field data, the use of more sophisticated reactive transport models like PHT3D (Prommer et al, 2003) will become a better alternative.

MATERIAL AND METHODS

Field sites

The 5 studied ASR field sites are situated in SW Florida (Fig.1) and are composed of either a single ASR pilot well (Bradenton, North Port) or a set of 4-12 active ASR wells (Tampa, Peace River with 2 separate ASR well fields, and Punta Gorda). All ASR wells are open hole in the (semi)confined Floridan limestone aquifer system, at depths varying between 60 and 430 m below land surface (BLS). Characteristics of the field sites and wells are summarized in Table 1. Most ASR wells inject in the period July – December (some years continuing till March), when high quality surface water is available, and they recover the stored water in the period March – July. Injection and recovery rates are typically 40-260 m^3/h, with a recovery efficiency of 50-150%. On most sites there is 0.5-1 monitor well for each ASR well, at a distance of 25-162 m. These wells are open hole over about the same depth interval as their respective ASR wells (Table 1).

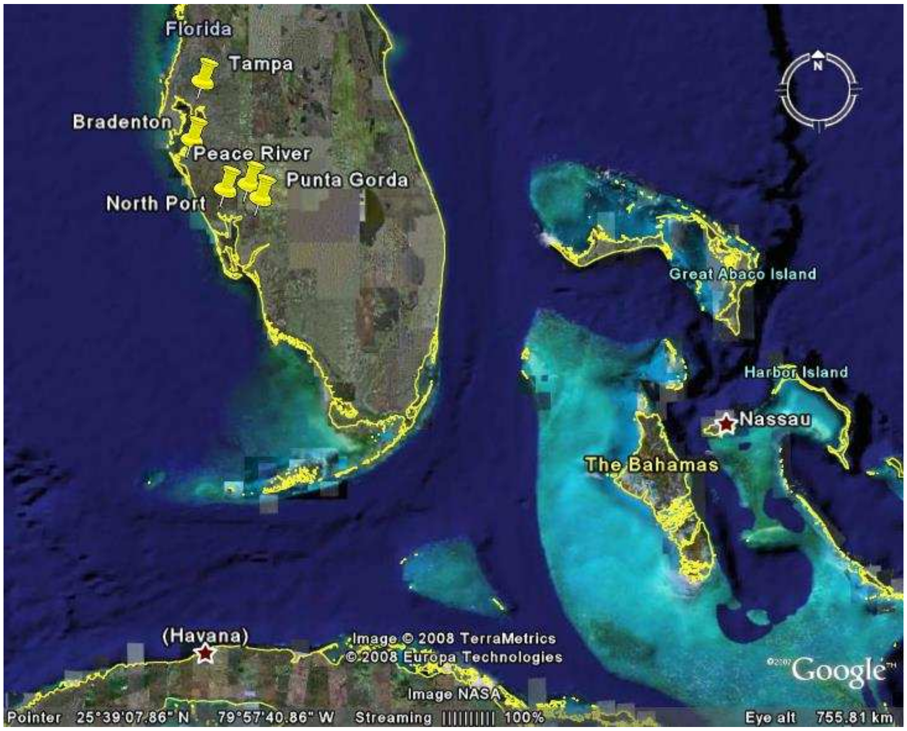

FIG.1. Location of the 5 studied ASR sites, with 2 separate ASR well fields at Peace River.

TABLE 1. Data on the target aquifer, the studied ASR and monitor wells, and the availability of water quality data.

ASR Site		Target aquifer			ASR well			Monitor well				Chem data	
		Name	Top	Base	No.	Top	Base	No.	Dist	Top	Base	for	since
			m BLS		n	m BLS		n	m	m BLS		Cycles	
1	Bradenton	Suwannee	122	183	1	127	154	1	68	123	168	1-7	2004
2	North Port	Suwannee	178	198	1	178	198	1	138	178 #	198 #	1-3	2002
3	Peace River #1	Suwannee	180	277	8	190	291	4	25-140	177	204	7-16	2004
4	Peace River #2	Suwannee	180	277	12	180	276	8	53-162	174	207	1-7	2002
5	Tampa RAP	Suwannee	91	131	8	91	122	3	46-107	91 #	122 #	1-9	1999
6	Punta Gorda	Suwannee	233	284	4	213	233	2	50-142	213 #	233 #	1-6	2002

 # = estimated

TABLE 2. Modal quality of the ambient groundwater in the UFA prior to ASR application, and of the infiltration water.

Par	Unit	Bradenton		North Port		Peace River WF#1		Peace River WF#2		Tampa RAP		Punta Gorda	
		ambient	input	ambient	input	ambient	input	ambient	input	ambient	input	ambient	input
EC	uS/cm	1400	529	2750	446	1428	469		469				673
TDS	mg/L	1200	330	3396	315	905	299	922	299			1959	429
pH		7.25	7.75	7.6	7.29	7.4	8.22	7.6	8.22	7.5	7.9	7.2	7.08
temp	oC	26.5	22.4	29.7	24.9	27.7	23.9		23.9				
ORP	mV	-330	385	-310		-300	448		448	-290			
O2	mg/L	0.02	9	0.1	6.9	0.9	5.7		5.7	0.45	20		
Oxidant			NH2Cl				NH2Cl		NH2Cl		O3		
H2S	mg/L	2.3		2.8	0.1	2.3							
As	ug/L	6.2	0.8	<8	<1	1	<1.3	<1	<1.3	4	<1	<2.2	3
Cl	mg/L	36	32	1490	43	224	32	167	32	39	31	865	98
SO4	mg/L	650	157	430	134	253	130	264	130	31.5	118	336	124
HCO3	mg/L	130	61	120	66	142	21		21	118	52	100	24
F	mg/L	1.8	1.0	1.8	1.0		1.0		1.0		1.0		
Na	mg/L	28	51	671	53	104	35		35				
Ca	mg/L	210	45	161	41	102	20		20		71		
Mg	mg/L	79	10	105	10	48	12		12		4		
Fe	mg/L	0.03	0.02	<0.1	0.03	<0.03	0.059	<0.012	0.059	0.02	0.02	0.137	
Mn	mg/L	0.0017		<0.01			0.006		0.006	0.01	0.01		
TOC	mg/L	1.4	2.9								2.7		

Hydrogeological and hydrochemical setting

On all 5 sites, ASR utilizes the Upper Floridan Aquifer (UFA), which is mainly composed of a (semi)confined, highly karstified limestone of middle Tertiary age, with some dolostone in the lower parts. Data on the geochemical composition of the ASR target aquifer indicate that arseniferous pyrite is abundant, especially along bedding planes, with an average content of 2,300 ppm As for pyrite, with extremes from 100 to 11,200 ppm (Price & Pichler, 2006).
Arthur et al. (2007) mention that the pyrite contains on average 1,300 ppm As, together with several other trace elements (notably Mo, Co, Ni, Sb and U).
The quality of the ambient groundwater in the UFA and of the infiltration water are shown in Table 2. The ambient groundwaters are (deeply) anoxic, in many cases with high SO_4 due to dissolution of gypsum, and with low Fe and As but high H_2S concentrations testifying of active pyrite formation. The infiltration waters are mostly composed of drinking water prepared from surface water, with additions of a disinfectant (extra oxidant) and sometimes F and/or $ZnHPO_4$. They are (sub)oxic and contain less TDS than the ambient groundwaters.

Hydrochemical monitoring during ASR operations

Hydraulic and hydrochemical data have been collected at all sites following regulatory requirements by the Florida Department of Environmental Protection (FDEP). Measurements of pH, O_2, ORP (Oxidation Reduction Potential) and temperature were done in the field, all other components in certified laboratories. Cations (including Fe) and As were analyzed in samples that were acidified to pH 1.5 by adding suprapure HNO_3 without prior filtration. Thus, some suspended fines may have contributed to the concentrations of especially Fe-total and As-total.
In most cases the analytical programme consisted of weekly samples of the injection water and half-weekly samples of the recovered water from each ASR-well, with analysis on Total Dissolved Solids (TDS), Electrical conductivity (EC), O_2, ORP, pH, temperature, Cl, SO_4, HCO_3, Fe and As. On some sites Fe-dissolved, Na, Ca, Mg, U, F, total sulfur, TOC, TTHMs, HAAs, $^{226/228}$Ra and gross alpha were measured as well. In the open source FDEP data files it

is mentioned for each sample, under which ASR setting it was taken (during injection, storage or recovery), during which cycle number and at which total injection or total recovery volume.

OBSERVATIONS

Observations on EC and As are shown for Bradenton's ASR and monitor well in Fig.2. They show simultaneous As and EC peaking some time after the start of pumping, in both the ASR and monitor well. This indicates that the arrival of higher salinity water (with raised SO_4, Cl and H_2S concentrations) from the mixing zone and beyond, triggers the As mobilization, because the ambient groundwater contains much less As (6 ug/L).

Only during the longer injection periods 5-7 the infiltration water with lower EC clearly arrived in the monitor well, after about 15 days. Arsenic peaking is relatively small in the ASR well during recovery phase of the very short cycles 1-4, but much higher during recovery phase of cycle 6 when it also showed up in the monitor well, although at a lower level. This lower peak in the monitor well (20 ug/L) during recovery phase of cycle 6 indicates that As is mobilizing most in between the monitor and ASR well. The peak in the monitor well shows, however, that the As mobilization front extends beyond 68 m. Another important observation is that the As concentration declined during the long storage phase of cycle 6. This shows that mobilized As needs time to sorb to neoformed HFO or to settle as a particle suspended in the infiltration water.

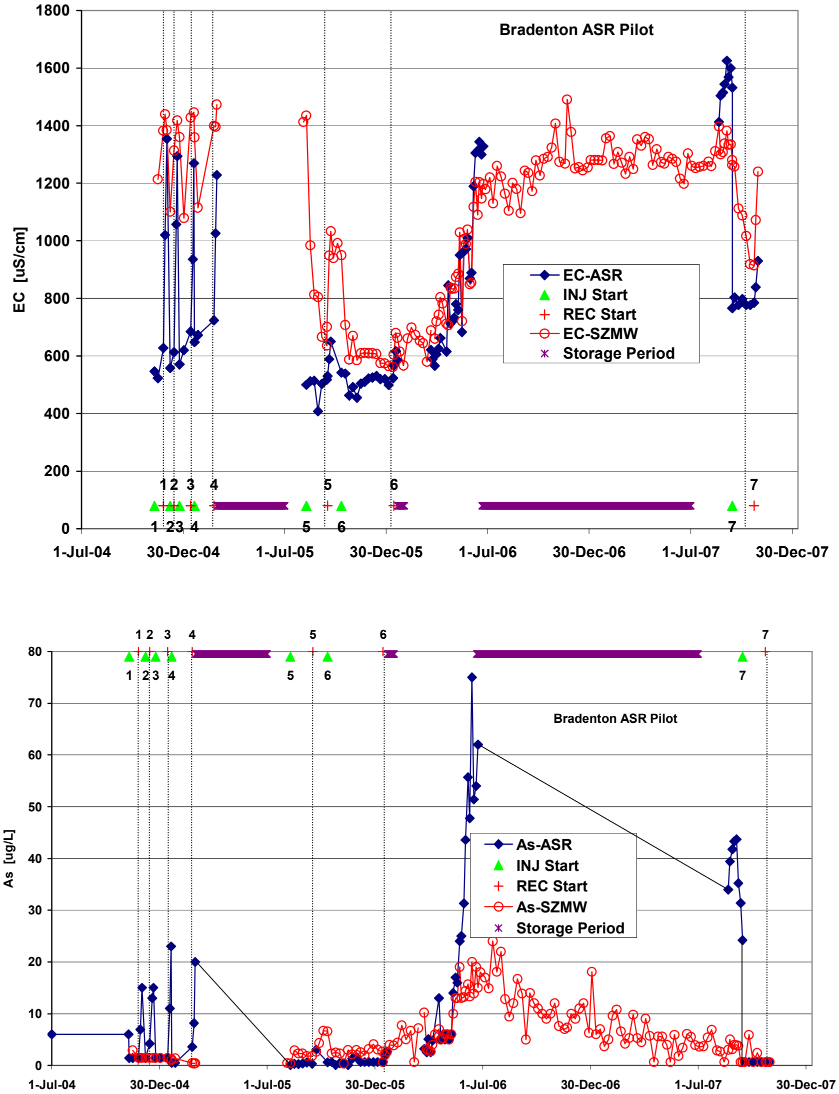

FIG. 2. *Electrical Concuctivity (EC) and As concentration in the ASR well and monitor well SZMW, during cycles 1-7 on ASR site Bradenton. The vertical lines indicate the start of the recovery phase of the numbered ASR cycle.*

The observations on 6 ASR well fields, with a total of 53 wells (ASR and monitor wells), each with 3-17 ASR-cycles, show a general tendency of declining maximum As concentrations during recovery, with increasing ASR cycle number (Fig.3). This corresponds with world-wide observations and accepted theory that arsenic becomes less mobile in increasingly more oxygenated environments when depleted in pyrite, due to decreasing chances on reductive dissolution of hydrous ferric oxides (HFO) that captured the mobilized As, and due to oxidation of uncharged, more mobile arsenite (H_3AsO_3) into charged, less mobile arsenate ($HAsO_4^{2-}$ + $H_2AsO_4^-$).

As can be seen in Fig.3, there are rather wide 'optical' confidence limits flanking the general trend (see ad discussion). Bradenton and Punta Gorda fit reasonably well within the pattern of Peace River, and the mean trends of Peace River and Tampa do not deviate much.

The ASR well in North Port did not follow the general trend at all. During the 3 investigated cycles there was a steady increase in As peak value, and the peak started in the first backflush during recovery. We suspect that arseniferous pyrite particles detach from the aquifer matrix (limestone or dolostone) upon its dissolution in rather aggressive infiltration water, and that these particles are thus included during sampling (which is without filtration) and dissolve in nitric acid added for sample conservation and total extraction. It is well known that the amount of suspended matter is highest during the first flush of a new pumping cycle (Stuyfzand et al., 2002).

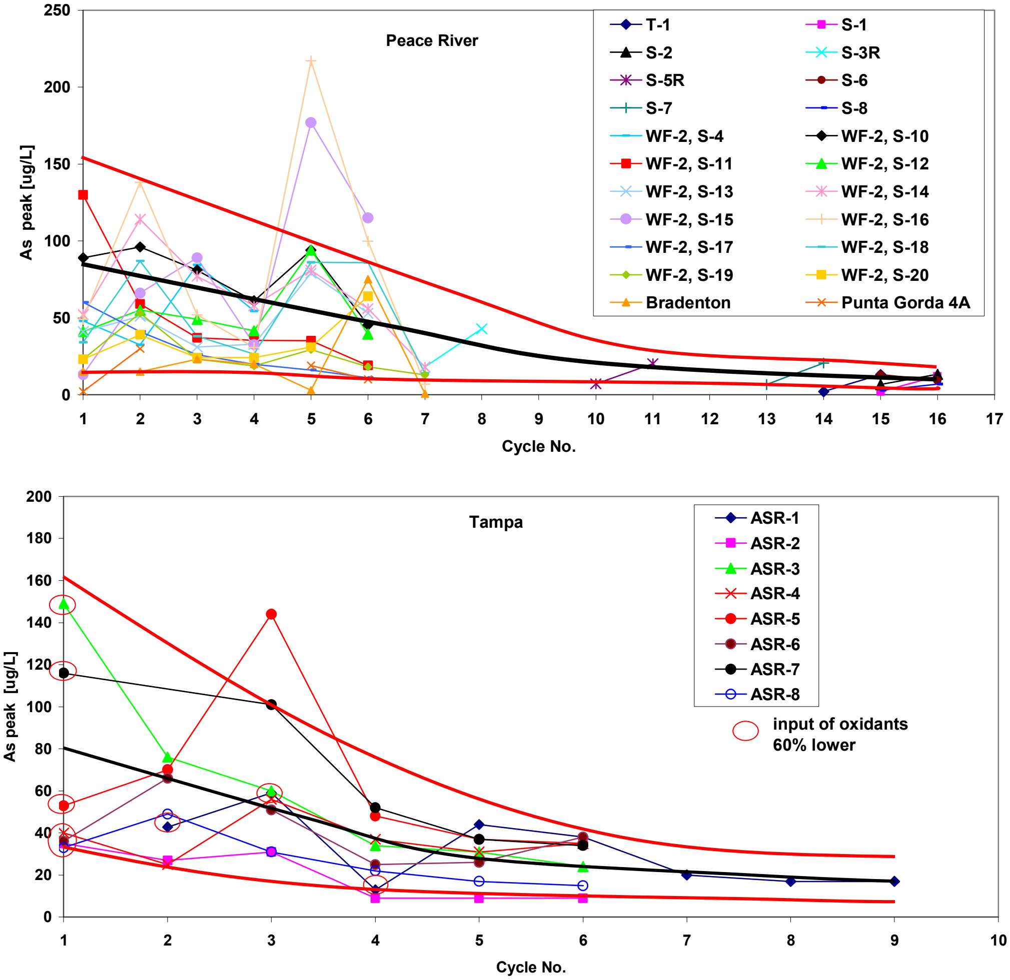

FIG. 3. Trends in As peak concentrations during ASR cycles 1-16 at Peace River (both well fields), Bradenton and Punta Gorda (above), and during ASR cycles 1-9 at Tampa (below). Heavy black line = mean trend; heavy red lines = resp. upper and lower 'optical' confidence limits.

There was a ca. 60% lower input of oxidants during cycles 1-2 for ASR-wells 2-8, and during cycles 1-4 for ASR-well 1, on well field Tampa.

TABLE 3. Spread sheet mass balance model for calculating the composition of the water injected after full reaction with pyrite, carbonate minerals (calcite and dolomite) and organic material (either dissolved as TOC or in solid aquifer phase as CH_2O; here O_2 assumed to be the only oxidant). Example is Bradenton's ASR well.

												0.0037					
	INFILTRATION WATER QUALITY + MAXIMUM PYRITE REACTION			48	70.906	51.453	32	35.45	96.06	61.02	62	74.922	40.08	24.31	18.0	12.0	44.0
	Reaction equation		Fraction	O3	Cl2	NH2Cl	O2	Cl	SO4	HCO3	NO3	As	Ca	Mg	NH4	TOC	CO2
			reacting	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L
						4	8.5	32	157	61	1	1	45.4	9.5	0.02	2.9	
	mmol/L			0.000	0.000	0.078	0.266	0.903	1.634	1.000	0.016	0.00001	1.133	0.391	0.001	0.242	0.000
Org.	O2 + [TOC or CH2O] --> CO2 + H2O	TOC-fraction	0.2				-0.048									-0.048	0.048
Pyrite	3.75O2+FeS2+4HCO3 --> Fe(OH)3+2SO4+4CO2+0,5H2O						-0.108		0.058	-0.116		0.00011					0.116
	3NO3+FeS2+HCO3+H2O --> Fe(OH)3+2SO4+CO2+1,5N2								0.047	-0.024	-0.071	0.00009					0.024
	2O3+FeS2+4HCO3 --> Fe(OH)3+2SO4+4CO2+0,5H2O			0.000					0.000	0		0.00000					0.000
	7.5Cl2+FeS2+19HCO3 --> Fe(OH)3+2SO4+15Cl+19CO2+8H2O				0.000			0.000	0.000	0.000		0.00000					0.000
	7.5NH2Cl+FeS2+4HCO3+7H2O --> Fe(OH)3+2SO4+7.5NH4+7.5Cl+4CO2					-0.078		0.078	0.021	-0.041		0.00004			0.078		0.041
	2O2 + NH4 + 2HCO3 --> NO3 + 2CO2 + 3H2O	NH4-fraction	0.7				-0.109			-0.109	0.054				-0.054		0.109
Carb	CO2 + H2O + CaCO3 <--> Ca + 2HCO3	CO2-fraction	0.5							0.338			0.169				-0.169
	2CO2 + 2H2O + CaMg(CO3)2 <--> Ca + Mg + 4HCO3	CO2-fraction	0.5							0.338			0.084	0.084			-0.169
	Output, after reaction of infiltration water with aquifer matrix		mmol/L	0	0	0	0	0.980	1.760	1.386	0.000	0.00025	1.386	0.475	0.024	0.193	0.000
			mg/L	0.0	0.0	0.0	0.0	34.8	169.1	84.6	0.0	18.4	55.6	11.6	0.4	2.3	0.0

MODELING

The analytical, semi-empirical formula

The following semi-empirical formula describes both the general trend of declining As peaks during successive cycles in the ASR well during recovery (as shown in Fig.3; sin() = 1), and the As concentration over time within each recovery cycle (Fig.4):

$$As = f\ As_{MAX}\ e^{-N/Y} \sin(0.9\ \pi/180\ [\alpha\ \%REC_{t,C\#X} + b]) \qquad (1)$$

With: As_{MAX} = Maximum As concentration as calculated with the mass balance approach [μg/L]; N = Cycle No.; $\%REC_{t,C\#X}$ = percentage of water recovered at time t = t during cycle N, of water infiltrated during cycle N [%]. Value can become >100%; f = fit factor for As peak level (3.5 on average); Y = fit factor for As peak decline with increasing cycle number (5 on average); $\alpha = a/\sqrt{(2N)}$; a = fit factor to regulate the sine frequency (3 on average); b = fit factor to regulate sine phase shift (often 0).

In Eq.1 the factor 0.9 π / 180 is needed to make sin( ) = 1 when %Rec = 100% (and α = 1, and b = 0).

If sin() ≤ 0, then the As concentration equals the natural background (ca 1 ug/L) or concentration in infiltration water (ca 1 ug/L).

By taking the best fit factors for the average situation, Eq.1 reduces to:

$$As = 3.5\ As_{MAX}\ e^{-0.2N} \sin(0.06664\ \sqrt{(N)}\ \%REC_{t,C\#X}) \qquad (2)$$

And when only the peak value during each cycle is needed, Eq.1 simplifies further to:

$$As = f\ As_{MAX}\ e^{-N/Y} \qquad (3)$$

Calculating As_{MAX} by a mass balancing

The mass balance calculation method of As_{MAX} is indicated in Table 3. It is assumed that all oxidants (O_2, NO_3 and the added disinfectant: O_3, NH_2Cl or Cl_2) react with pyrite, after subtracting a part for internal oxidation of injected NH_4 and TOC. The oxidation of organic material in the aquifer matrix has been neglected (which is reasonable in a limestone aquifer). The part of NH_4 and TOC oxidized is based on observations in the water recovered in various systems.

It is also assumed that the fraction of As in pyrite is known and released stoichiometrically without losses due to As sorption, coprecipitation with neoforming $Fe(OH)_3$ or other reactions. Thus, for pyrite the following average composition has been fixed: $FeS_{1.9963}As_{0.0037}$. This corresponds with an average arsenic content of pyrite in the Suwannee limestone aquifer of 2,300 ppm as observed by Price and Pichler (2006). However, this value may need adjustment, by changing either the coefficient 0.0037 or the value of f.

In a simplified form, As_{MAX} [in ug/L] can be directly calculated (without using a spread sheet mass balance calculation as shown in Table 3), namely as follows:

$$As_{MAX} = 74922\ [As_{IN} + As_{FeS2}\ \{(O_2 - c\ TOC - 2d\ NH_4 - 2e\ NH_2Cl)/3.75 + O_3/2 + Cl_2/7.5 + NH_2Cl/7.5 + (NO_3 + d\ NH_4 + e\ NH_2Cl)/3\}] \tag{4}$$

Where: all concentrations (except for As_{MAX} and As_{FeS2}) refer to the infiltration water [mmol/L]; As_{MAX} [ug/L]; As_{IN} = As in infiltration water [mmol/L]; As_{FeS2} = As content of pyrite on a mol basis, here fixed at 0.0037; c,d,e = fractions of input concentration [0 - 1], with standard setting as shown in Table 3.
In Eq.4 it is assumed that TOC and NH_4 (also deriving from NH_2Cl) are oxidized exclusively by O_2. This is not realistic as the disinfectants will be partly involved in their oxidation as well, but it yields a practical approximation of the loss of oxidative strength of the input. It is also assumed that NH_4 deriving from input NH_4 and NH_2Cl (if present) is first partly nitrified, and thus generated NO_3 is subsequently denitrified by pyrite.
Data of recovered water suggest that the following values can be maintained in the FAS: c = 0.2, and d = e = 0.7.
Now there still are 4 fit factors to deal with: f ,Y, a and b. The factors f and Y determine the As peak concentration trend during successive ASR cycles. They are more important than a and b which are needed to get the sine wave in place within the recovery phase of an ASR cycle. Factor b can even be skipped in most cases, but a value of 50 is performing best for Bradenton.

Arsenic during storage
During storage As concentrations generally decline (Fig.2). The following relation is used:

$$As_t = As_0\ e^{-Z\,t} \tag{5}$$

With: t = storage time [d]; Z = rate of concentration decline [1/d]; As_0 = As concentration at the end of injection or recovery, prior to storage [ug/L];
At the Bradenton site Z is about 0.006, at Peace River 0.012. When recovery is resumed after an intermittent storage phase (separating 2 recovery phases within the same cycle), then Eq.2 is applied again, continuing with the earlier %Rec, however, subtracting ΔAs from each calculated value within that remaining cycle, where

$$\Delta As = As_0\ (1 - e^{-Z\,t}) \tag{6}$$

Results of application
The arsenic behavior of various ASR wells has been successfully modeled with Eq.1. An example is shown in Fig.4. Such a good fit could not be realized for all ASR wells, which is not a big surprise (see discussion).

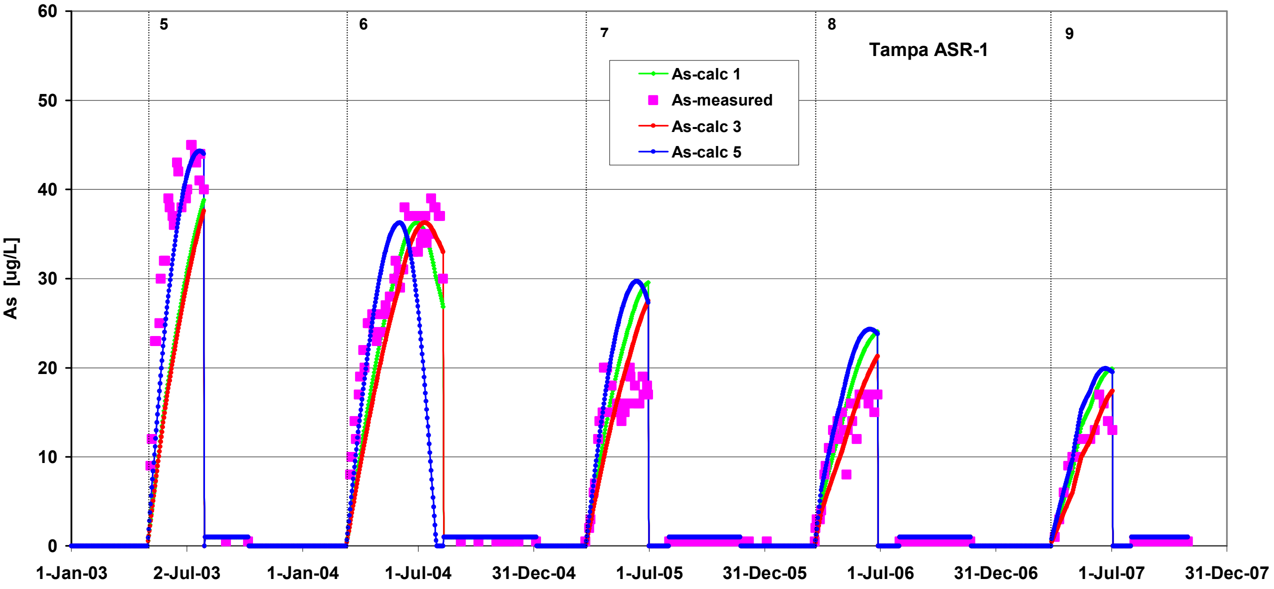

FIG. 4. Arsenic modeling results for Tampa ASR well No.1. using Eq.1 with f = 3.5, As_{MAX} = 34.3 ug/L, b = 0. $\alpha = 1$ for calc 1; $\alpha = 3\sqrt{(2N)}$ for calc 3; $\alpha = 5\sqrt{(2N)}$ for calc 5. Best simulation for calc 3.

DISCUSSION

The expert model here presented yields satisfactory results ($0.5\ As_{MEAS} < As_{CALC} < 1.5\ As_{MEAS}$) in about 50% of all 144 cases (Stuyfzand et al., 2008). Much better is, of course, the prediction of the general trend of declining peak arsenic concentrations in the recovered water from ASR wells with successive cycles (Fig.3).

A better performance is logically handicapped by the following:

- The pyrite content of the limestone and the As content of pyrite vary in space. Subsequent ASR cycles will normally address an increasing aquifer volume, which may therefore show different contents;
- The As content of pyrite varies also with time because the most reactive pyrite, the composition of which may differ from the average pyrite, will oxidize first;
- Water samples have not been filtered, so that suspended arseniferous pyrite particles or arseniferous iron(hydr)oxide flocs will dissolve upon addition of HNO_3 for analysis on total concentrations. In all cases the infiltration water is dissolving limestone, which contains very finely dispersed pyrite particles, and may thereby mobilize particles containing As;
- The amount of participating suspended arseniferous pyrite particles is probably subject to fluctuations during pumping, thereby causing significant noise in the As data;
- Effects of upconing or buoyancy of the injected ASR-water body cannot in all cases be distinguished from the effects of lateral flow of ambient groundwater;
- Total arsenic analytical methods may be biased by matrix effects (Cl, SO_4) and incomplete conversion of arsenate into arsenite (Van der Jagt & Stuyfzand, 1996). Results can be positively and negatively biased.
- Water quality of the input is ill defined because of lack of data on its total oxidation capacity (O_2, NO_3, O_3, Cl_2, NH_2Cl), internal consumption of oxidation capacity (NH_4, TOC) and anion desorptive strength (DOC, PO_4, F, SO_4, HCO_3, SiO_2);
- Not all oxidants in the water infiltrated react with pyrite; a yet unknown part will be consumed by organic matter in the UFA;
- Use of HCl or CO_2 for improving well yield or infiltration capacity. This may have 2 important consequences: (a) the carbonate rock is dissolving while pyrite grains detach from their matrix and become either suspended and transported away, or they sediment; and (b) iron monosulfide may dissolve as follows: $2HCl + FeS \leftrightarrow H_2S + Fe^{2+} + 2Cl^-$. The latter does not happen with CO_2 additions, which appears to be more common practice.
- Heterogeneity of the limestone, both in hydraulic conductivity and geochemistry.
- Mixing of different water qualities due to too long well screens; and
- Effects of neighbouring wells (especially Peace River WF#2) and bubble drift are not included.

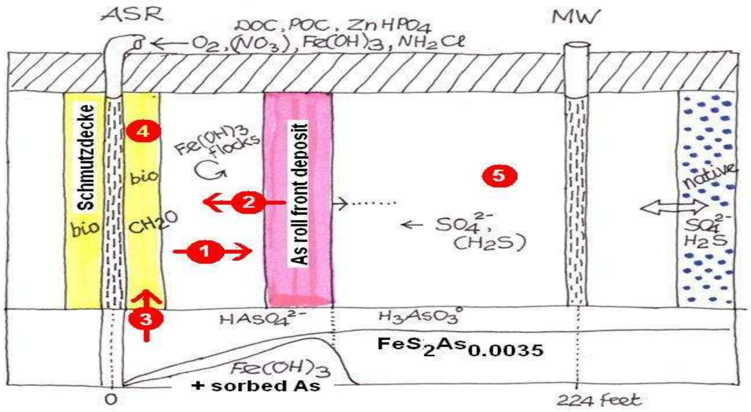

FIG. 5. Conceptual model of arsenic peaking during backpumping (example Bradenton), with zonation of various processes that mobilize and immobilize As during ASR-operations in Florida.

1: pyrite oxidation during injection, with mobilization of As (and SO_4);

2: As remobilization during recovery, by either reductive dissolution of $Fe(OH)_3$ or desorption;

3: upconing of brackish groundwater with high Cl, SO_4 and H_2S concentrations, of which SO_4 could desorb arsenate and H_2S could redissolve $Fe(OH)_3$ or convert As(V) into As(III);

4: during storage lack of nutrients may lead to anoxic conditions, remobilizing As;

5: In the anoxic buffer zone mixing with ambient groundwater may lead to supply of H_2S and SO_4 which favor As remobilization during pumping.

The expert model can be used to predict the effects of changes in ASR operation in order to bring the As concentrations back into an acceptable range. Changes like reducing the oxidant input (which reduces the parameter As_{MAX} in Eqs 1-4) or reducing the recovery efficiency (which lowers the sine value) have a direct impact on the calculated As output via Eqs 1-4.

CONCLUSIONS

With the analytical solutions presented, the arsenic peak concentration in the water recovered during each ASR cycle can be predicted. However, it should be realized that the resulting information has a rather high inaccuracy when local hydrogeochemical test data are lacking.

Further research is needed to provide better data that are unbiased by among others analytical errors (O_2, As), problems associated with observation wells having long open hole sections, and suspended particles (like arseniferous pyrite grains and ferrihydrite flocks). Also, a broader scan of water quality is needed, including all oxidants (also those added for disinfection) and important As desorbents (like PO_4, HCO_3, F and SiO_2).

Better data are a prerequisite for evolving from the expert model given here, to a well calibrated, true reactive transport model also for arsenic, like PHREEQC-2 or PhT3D. The success of the latter model has been demonstrated by Wallis et al. (in press), in simulating As behavior during Aquifer Storage Transfer Recovery (ASTR, using injection and remote recovery wells) in the Netherlands. In preparing reactive transport models the many processes acting in different zones indicated in Fig.5 need to be considered.

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