



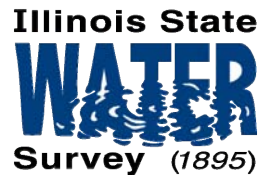
# Field Testing and Modeling of the Fenton-Filtration Process for Arsenic Removal

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## **Disclaimer**

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## Abstract

The Fenton-filtration process has been found to lower the arsenic (As) concentration in groundwater below the maximum contaminant level (MCL) of 10 micrograms per liter ( $\mu\text{g/L}$ ). Oxidation of As(III) to As(V) and the addition of supplemental iron (Fe) to improve sorption were both essential for effective treatment. In the present work, Fenton-filtration was compared with chemical oxidation using conventional treatment chemicals. Both sodium hypochlorite and potassium permanganate were more effective than Fenton filtration at oxidizing As(III). Therefore, the choice of treatment method may depend on economic factors. The effect of natural organic matter (NOM) on the Fenton-filtration process was unclear. Laboratory experiments using groundwater and synthetic solutions showed that reactions involving NOM are significant, that hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is produced in these reactions, and that there is no benefit in adding  $\text{H}_2\text{O}_2$  in excess of the Fe(II) concentration. Earlier research on As sorption used a double-layer model that generally under-predicted As removal. A more recent triple-plane model was applied to the data from a series of Fenton-filtration tests and was found to give better predictions of soluble As in treated water than the double-layer model, although it still under-predicted As removal.

## Table of Abbreviations and Symbols

ADW	Aerated Danvers groundwater
As(III)	The sum of all arsenic species in the +3 oxidation state
As(V)	The sum of all arsenic species in the +5 oxidation state
CFDW	Carbonate-free Danvers groundwater
CO <sub>3</sub>	Carbonate buffer
DF	Dose of ferrous ion, the initial concentration of Fe(II)
DIW	Deionized water
DLM	Double-layer model
DO	Dissolved oxygen
DP	Dose of hydrogen peroxide, the initial concentration of H <sub>2</sub> O <sub>2</sub>
EDTA	Ethylenediamine tetraacetic acid
Fe(II)	The sum of all ferrous iron species
Fe(III)	The sum of all ferric iron species
FeCl <sub>3</sub>	Ferric chloride, iron (III) chloride
FeO <sup>2+</sup>	Ferryl ion
ΔF	Change in Fe(II), initial minus final Fe(II) concentration
ΔFe	Change in iron concentration
ΔH <sub>2</sub> O <sub>2</sub>	Change in hydrogen peroxide concentration, initial minus final concentration
ΔP	Change in hydrogen peroxide, initial minus final H <sub>2</sub> O <sub>2</sub> concentration
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
H <sub>3</sub> AsO <sub>3</sub>	Arsenious acid
H <sub>3</sub> AsO <sub>4</sub>	Arsenic acid
HFO	Hydrous ferric oxide
HNO <sub>3</sub>	Nitric acid
JT1	Jar Test 1
KMnO <sub>4</sub>	Potassium permanganate
L	Liter
MCL	Maximum contaminant level
mg/L	Milligrams per liter
mL	Milliliter
mM	Millimoles per liter
MnO <sub>4</sub> <sup>-</sup>	Permanganate ion
μg/L	Micrograms per liter
μM	Micromoles per liter
NaOCl	Sodium hypochlorite
NH <sub>3</sub> -N	Ammonia nitrogen
NOM	Natural organic matter
OCl <sup>-</sup>	Hypochlorite ion
·OH	Hydroxyl radical
PO <sub>4</sub>	Phosphate buffer
TPM	Triple-plane model



## Introduction

Arsenic (As), an element that occurs naturally in groundwater, causes several chronic health effects in elevated doses (Jain and Ali, 2000). Because As in drinking water has been associated with increased risk of cancer (Smith et al., 1992), the U.S. Environmental Protection Agency lowered the maximum contaminant level (MCL) from 50 micrograms per liter ( $\mu\text{g/L}$ ) to  $10 \mu\text{g/L}$  (0.13 micromoles per liter or  $\mu\text{M}$ ), effective February 2006. Almost all Illinois water utilities satisfied the old MCL, but approximately 50 out of 1030 active groundwater systems were out of compliance when the MCL was lowered.

Arsenic occurs in two chemical forms, which are commonly denoted by their oxidation states. As(V) consists of arsenic acid ( $\text{H}_3\text{AsO}_4$ ) and its conjugate bases. In the pH range of most natural waters, the predominant As(V) species are the anions  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ . In the same pH range, As(III) consists of mostly arsenious acid ( $\text{H}_3\text{AsO}_3$ ) with a minor amount (<10%) of the anion  $\text{H}_2\text{AsO}_3^-$ . The predominant form of As in Midwest groundwater is As(III) (Kelly et al., 2005; Kim et al., 2002; Warner, 2001). Most groundwater with As levels above the MCL also has soluble iron (Fe) at a concentration high enough to require treatment to deal with aesthetic problems such as taste and laundry staining. Iron removal from groundwater consists of the oxidation of soluble ferrous iron (Fe[II]), to insoluble hydrous ferric oxide (HFO) and filtration to remove the particulate HFO. Both As(V) and As(III) adsorb to HFO (Dzombak and Morel, 1990), so Fe removal also removes some As, although As removal efficiency is highly variable (McNeill and Edwards, 1995; Wilson et al., 2004). Illinois water treatment plants were designed for Fe removal, not As removal. Therefore, some facilities need to be upgraded to satisfy the new As MCL.

An important factor in As removal by Fe-removal plants is the Fe concentration. Wilson et al. (2004) found that Illinois facilities with Fe:As molar ratios greater than 150 had the best As removal, while facilities with lower ratios had variable success. Another factor in As removal is As speciation. As(V) is more effectively removed from surface water by ferric chloride ( $\text{FeCl}_3$ ) coagulation than is As(III) for all groundwater pH values and practical coagulant doses (Hering et al., 1997; Hering and Elimelech, 1996), which suggests that As(V) would be more effectively removed than As(III) at Fe-removal plants. Therefore, both oxidation and sorption are likely to be important factors in As removal from groundwater.

In Fenton's reaction (Walling, 1975), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) reacts with Fe(II) to produce a very reactive species that readily oxidizes As(III) to As(V) (Hug and Leupin, 2003). (See Peyton et al. [2006b] for a description of the Fenton reaction.) Because As-contaminated groundwater also contains Fe(II), it was hypothesized that adding  $\text{H}_2\text{O}_2$ , an inexpensive chemical, might result in As(III) oxidation and improved As removal. Laboratory- and pilot-scale experiments were conducted in which Fenton oxidation was combined with sand filtration, a common process at water treatment plants. The process (dubbed Fenton-filtration) was tested at a central Illinois water treatment plant and was found to lower As below the MCL when supplemental Fe was added (Peyton et al., 2006b). Further testing of the process was conducted at two other facilities where the MCL was also satisfied (Peyton et al., 2006a).

The present work is a follow-up to previous research. One objective was to compare Fenton-filtration with conventional chemical oxidation by conducting on-site experiments using conditions as near constant as feasible. The second objective was to characterize the reaction pathway of the Fenton-filtration process. There was some question about the stoichiometry of the process (i.e., how much  $\text{H}_2\text{O}_2$  was consumed per  $\text{Fe}^{2+}$  ion oxidized). Laboratory experiments

using groundwater and synthetic solutions were conducted to characterize the reaction stoichiometry. The third objective was to develop a chemical equilibrium model of As removal by Fenton-filtration. The As sorption model used in previous research was believed to be inadequate. In the present work, a recently developed model was applied to the data from the pilot-scale tests. A fourth objective was to conduct a full-scale test of the Fenton-filtration process at a water treatment plant. This was not feasible, however, so sampling and analyses were performed in support of conventional chemical oxidation.

## Jar Tests

Fenton-filtration was compared with oxidation of Fe(II) and As(III) by sodium hypochlorite (NaOCl) and potassium permanganate (KMnO<sub>4</sub>), two common water treatment chemicals. The experiments were conducted in batch mode, commonly referred to as jar tests.

### Methods and Materials for Jar Tests

Jar tests were conducted in Danvers, Illinois, which is located in McLean County approximately 10 miles west of the Bloomington-Normal area. The Danvers water treatment plant receives water from three wells that are screened in the Mahomet Aquifer and numbered 3, 4, and 5. (Wells 1 and 2 were abandoned when the newer wells were finished.) The plant (Figure 1) was designed for Fe removal. Raw water is aerated, sand filtered, softened (33% of flow), and then chlorinated and fluoridated.

Jar tests were conducted at the well head of well 3. Groundwater was analyzed on-site for Fe and ammonia nitrogen (NH<sub>3</sub>-N) using a portable colorimeter (CheMetrics). Dissolved oxygen (DO) levels were determined using a luminescent DO meter (Hach LDO). Doses of H<sub>2</sub>O<sub>2</sub> and KMnO<sub>4</sub> were based on the on-site measurements of Fe(II). Doses of NaOCl were based on measurements of Fe(II) and NH<sub>3</sub>-N. A paddle stirrer (Hach) with 2L Wagner flocc jars was used. For each experiment, the vessel was filled and allowed to overflow by at least 3 volumes to minimize contact with air and the resulting oxidation of Fe<sup>2+</sup> by O<sub>2</sub>. The flow rate was approximately 500 milliliters per minute.

The general procedure was to add the oxidant and any FeCl<sub>3</sub>, stir manually to mix, aerate, and then turn on the paddle stirrer for 30 minutes, the approximate residence time in the Danvers detention tank and sand filter. The oxidant and FeCl<sub>3</sub> doses used in jar tests are given in Appendix 1. Immediately after the 30-minute reaction period, filtered and unfiltered water samples were collected. Because of time limitations, each jar test involved six combinations of oxidant and FeCl<sub>3</sub>. For Fe samples, ferrozine reagent (Viollier et al., 2000) was immediately added. The color was stable for several hours. Samples for Fe determination were analyzed after they were returned to the lab (within four hours after sample collection). The ferrozine reagent forms a colored complex with Fe(II), but not Fe(III). Filtered and unfiltered samples were first analyzed for Fe(II). Hydroxylamine hydrochloride, a reducing reagent, was then added to reduce any Fe(III) to Fe(II) and the sample absorbances were measured again. Any increase in absorbance was attributed to Fe(III). Any difference between filtered and unfiltered Fe concentrations was attributed to particulate Fe.

Filtered (0.2 µm) and unfiltered samples for determining dissolved and total As were preserved with 0.2% nitric acid (HNO<sub>3</sub>). Filtered samples for As speciation were acidified with 0.05% sulfuric acid and immediately poured through anion exchange columns. The columns

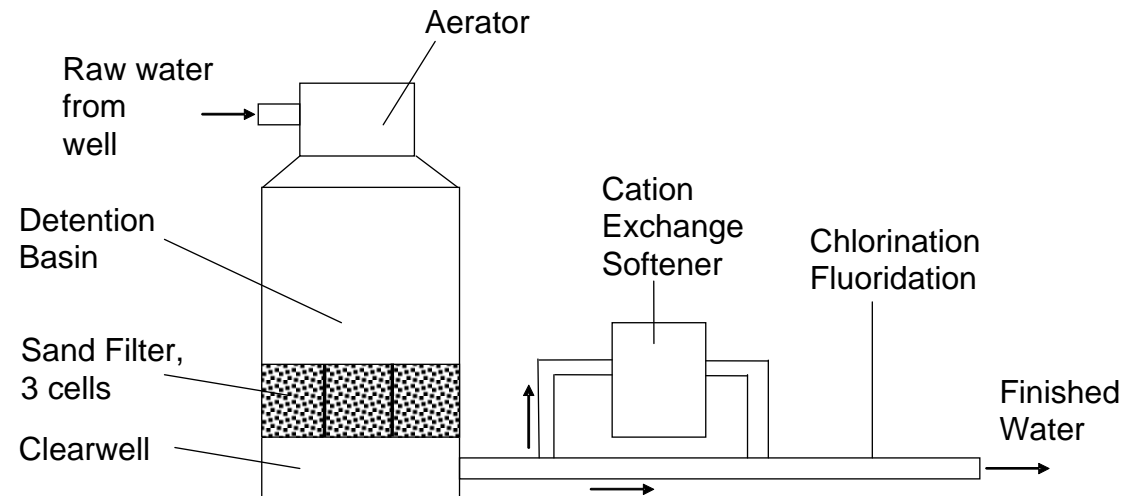


Figure 1. Schematic of the Danvers, IL water treatment plant. 33% of the flow goes through the softener.

retained As(V) but allowed As(III) to pass through (Chen et al., 2002; Edwards et al., 1998). Arsenic concentrations were determined by graphite furnace atomic absorption with Zeeman background correction (Varian). A palladium matrix modifier was used to inhibit As loss through volatilization (Welz et al., 1988).

For full-scale tests at the Danvers plant, Mr. Scott Seniff, the plant operator, collected water samples from a raw water tap in the plant, a tap downstream from the sand filter, and a finished water tap in the plant. Samples were preserved with acetic acid and ethylenediaminetetraacetic acid. This preservative stabilizes As speciation for at least one month (Karori et al., 2006; Samanta and Clifford, 2005; Samanta and Clifford, 2006). Samples were sent via overnight delivery to the ISWS laboratory and analyzed the next day by atomic absorption as described above. Mr. Seniff determined Fe levels by phenanthroline colorimetry when he collected the samples.

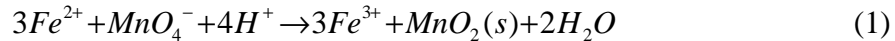
### Results of Jar Tests

In the first jar test (JT1) the oxidant was H<sub>2</sub>O<sub>2</sub>. The raw groundwater Fe concentration measured on-site was 1.8 milligrams per liter (mg/L) (32 μM). The H<sub>2</sub>O<sub>2</sub> doses were multiples of

the molar Fe concentration, and FeCl<sub>3</sub> doses provided a total Fe concentration that had lowered As concentrations to the MCL in the Fenton-filtration pilot-scale experiments (Peyton et al., 2006b). Figure 2 presents the Fe speciation in JT1 with the H<sub>2</sub>O<sub>2</sub> and Fe doses given below the x-axis for reference. As expected, the only Fe species detected in the raw water was dissolved Fe(II) at the same concentration as measured before the experiment. Oxidation was essentially complete for all H<sub>2</sub>O<sub>2</sub> doses; the only significant Fe species in all cases was particulate Fe(III). (Only three unfiltered samples were collected.) There was very little dissolved Fe(II), and Fe(III) is insoluble at neutral pH values (Stumm and Morgan, 1996).

The As concentration in the raw water was 34.5 µg/L (0.43 µM). Most of the As was As(III), which was consistent with previous measurements (Figure 3) (Holm et al., 2005; Peyton et al., 2006b). No unfiltered samples for As were collected in JT1. Aeration alone caused little oxidation of As(III). This is similar to As speciation changes in the Danvers plant (Wilson et al., 2004). The addition of H<sub>2</sub>O<sub>2</sub> without FeCl<sub>3</sub> had little effect on dissolved As but lowered As(III) by ~50%. Although there was some As(III) oxidation, Fe levels were insufficient to lower the dissolved As by sorption. The addition of H<sub>2</sub>O<sub>2</sub> and FeCl<sub>3</sub> lowered both dissolved As and As(III) concentrations to near the MCL. The addition of FeCl<sub>3</sub> without H<sub>2</sub>O<sub>2</sub> lowered dissolved As and As(III) concentrations by 30-35%, probably by sorption and not oxidation. Therefore, both oxidation of As(III) and sorption were important for As removal using Fenton-filtration.

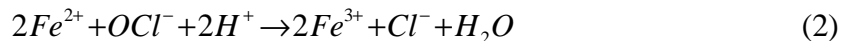
The oxidant in the second jar test (JT2) was KMnO<sub>4</sub>. Every permanganate (MnO<sub>4</sub><sup>-</sup>) ion oxidizes three Fe<sup>2+</sup> ions (equation 1) so the molar Fe:KMnO<sub>4</sub> ratio must be 1:3 for complete Fe(II) oxidation.



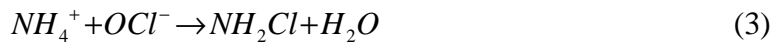
The on-site Fe analysis of raw water gave a value of 1.8 mg/L (32 µM). Essentially all Fe in the raw water was dissolved Fe(II) as in JT1 (Figure 4). The KMnO<sub>4</sub> oxidized the Fe(II) completely in all jars. There was some fluctuation in total Fe concentrations, probably due to settling of particles during sampling, especially for jars with no KMnO<sub>4</sub> or FeCl<sub>3</sub> addition.

As in JT1, nearly all of the As in the raw water of JT2 was As(III) (Figure 5). In the jar with only 1.6 mg/L KMnO<sub>4</sub> added and no Fe, As(III) was mostly oxidized and As removal was better than for the Danvers plant but still above the MCL. For the jar with only Fe added and no KMnO<sub>4</sub>, there was little As removal. For the jar with 0.8 mg/L KMnO<sub>4</sub> (half dose), approximately two-thirds of the As(III) was oxidized and the dissolved As concentration was just slightly above the MCL. For jars with both Fe and the higher doses of KMnO<sub>4</sub>, As(III) was completely oxidized, and dissolved As concentrations were well below the MCL. Clearly, oxidation and sorption are both important factors in As removal.

The oxidant in jar test 3 (JT3) was NaOCl. On-site analyses revealed Fe and NH<sub>3</sub>-N concentrations of 1.7 and 7.6 mg/L (30 and 543 µM), respectively. Every OCl<sup>-</sup> ion oxidizes two Fe<sup>2+</sup> ions (equation 2), so the Fe:NaOCl ratio must be at least 0.5 for complete Fe(II) oxidation.



However, OCl<sup>-</sup> also reacts with aqueous NH<sub>4</sub><sup>+</sup> to produce chloramine (equation 3).



The NaOCl doses took both Fe and NH<sub>3</sub>-N into account.

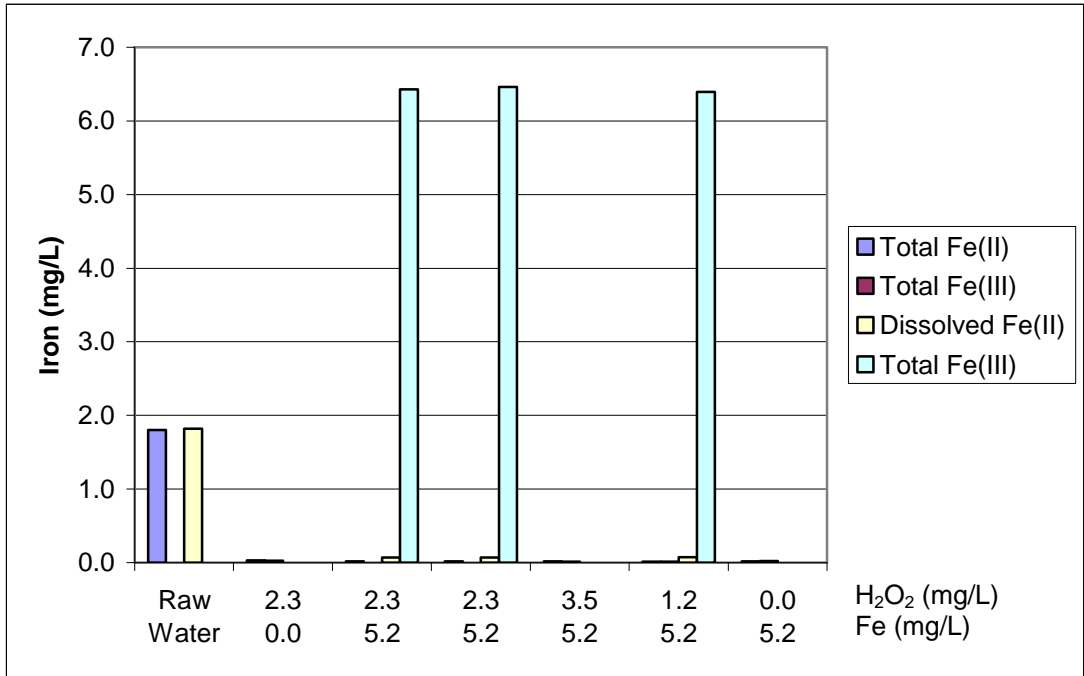


Figure 2. Iron speciation in Jar Test 1, Fenton-filtration. Raw water Fe species are shown for comparison. Doses of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ferric chloride (as Fe) are given below the x-axis. Note: Unfiltered samples were only collected for H<sub>2</sub>O<sub>2</sub>/Fe doses of 2.3/5.2 and 1.2/5.2 mg/L.

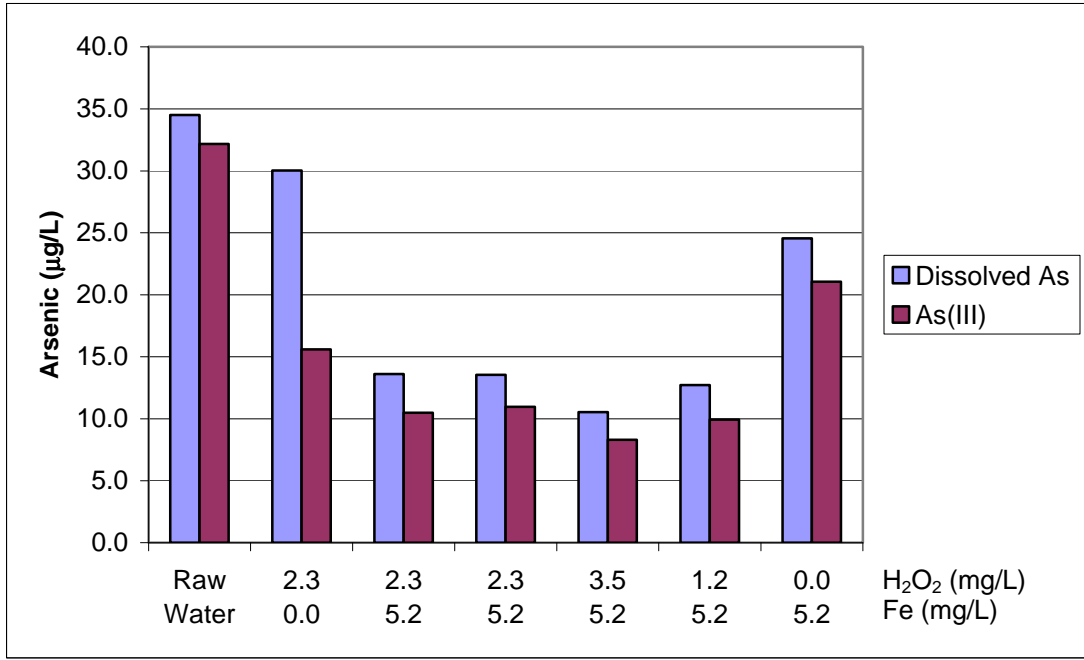


Figure 3. Arsenic speciation in Jar Test 1. Note: no unfiltered (total) As samples were collected. Raw water As species are shown for comparison. Doses of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ferric chloride (as Fe) are given below the x-axis.

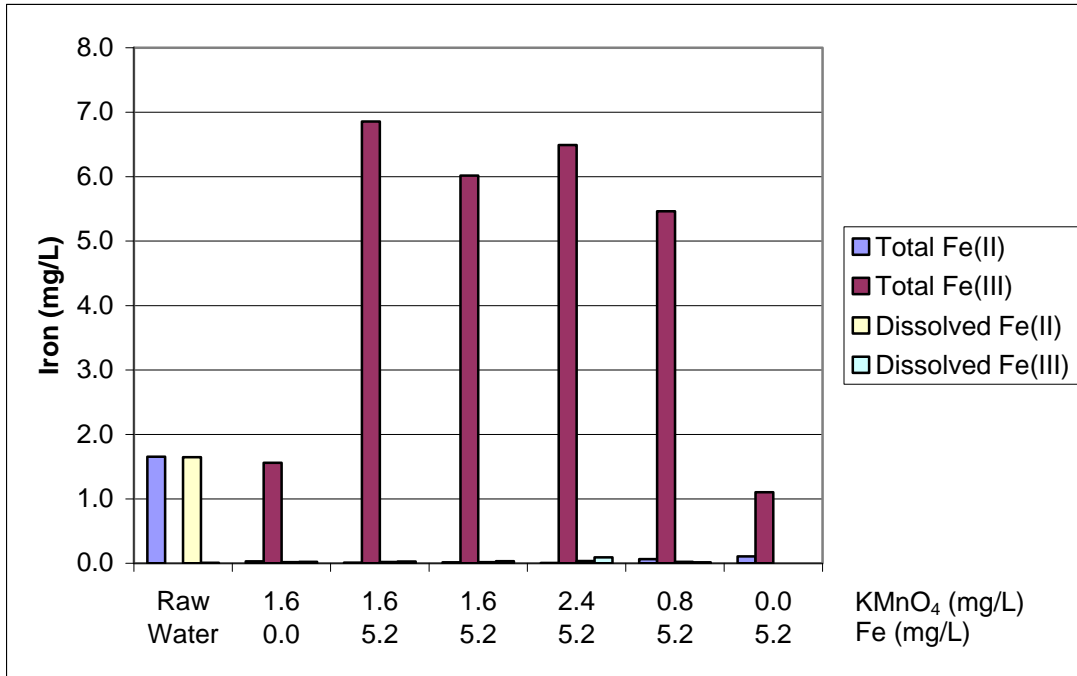


Figure 4. Iron (Fe) speciation in Jar Test 2, KMnO<sub>4</sub>. Raw water Fe species are shown for comparison. Doses of potassium permanganate (KMnO<sub>4</sub>) and ferric chloride (as Fe) are given below the x-axis.

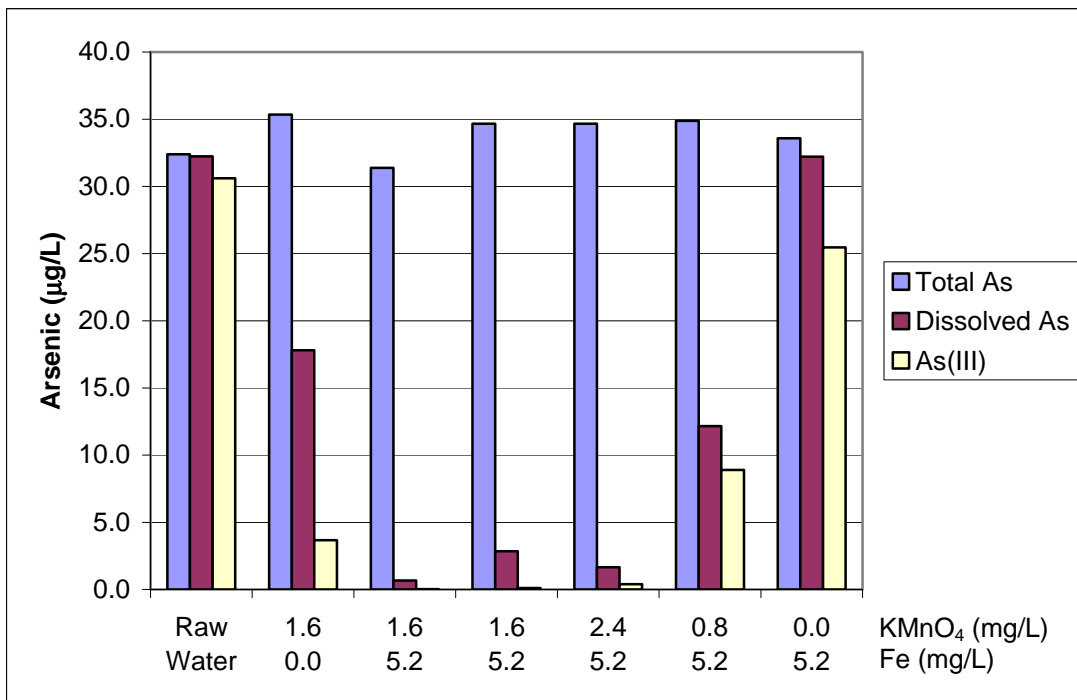


Figure 5. Arsenic (As) speciation in Jar Test 2. Raw water As species are shown for comparison. Doses of potassium permanganate (KMnO<sub>4</sub>) and ferric chloride (as Fe) are given below the x-axis.

For jar test 3 (JT3), all the Fe in the raw water was dissolved Fe(II), as in JT1 and JT2 (Figure 6). All NaOCl doses were sufficient to oxidize all the Fe(II). No Fe(II) was detected in any jar with added NaOCl. Stirring during sampling produced more uniform results between jars with respect to total Fe than in JT1. In the two jars with no added Fe, the total Fe concentration was the same as in the raw water. In the four jars with added Fe, the total Fe concentration was the same.

As in JT1 and JT2, essentially all the As in the raw water of JT3 was dissolved As(III) (Figure 7). Because of small random fluctuations in analyses, the dissolved and As(III) concentrations in raw water appeared slightly higher than did the total As concentration. The higher NaOCl doses were sufficient to completely oxidize the As(III). For the jar to which only NaOCl was added, the resulting dissolved As concentration was well above the MCL due to inadequate sorption. For all jars with added NaOCl and FeCl<sub>3</sub>, dissolved As was well below the MCL. For the lowest NaOCl dose and no added FeCl<sub>3</sub>, As(III) oxidation was incomplete. This is consistent with previous MTAC-sponsored research (Holm, 2006). The jar with 5.2 mg/L Fe plus 9.6 mg/L NaOCl had less than 5 µg/L dissolved As, whereas the jar with only 9.6 mg/L NaOCl had over 20 µg/L dissolved As. As in JT2, this shows the importance of both oxidation and sorption to As removal.

The oxidant in jar test 4 (JT4) was H<sub>2</sub>O<sub>2</sub>, as in JT1. In JT4 a range of H<sub>2</sub>O<sub>2</sub> concentrations was used. Soluble Fe(II) was essentially completely oxidized to particulate Fe(III) for all H<sub>2</sub>O<sub>2</sub> doses (Figure 8). As in the other jar tests, essentially all As in the raw water was dissolved As(III) (Figure 9). (The unfiltered, filtered, and anion exchange As concentrations were the same within experimental uncertainty.) Aeration alone oxidized little As(III) and the Fe concentration in the raw water was inadequate to lower the dissolved As concentration to the MCL by sorption. H<sub>2</sub>O<sub>2</sub> incompletely oxidized As(III). The highest FeCl<sub>3</sub> dose lowered the As concentration below the MCL.

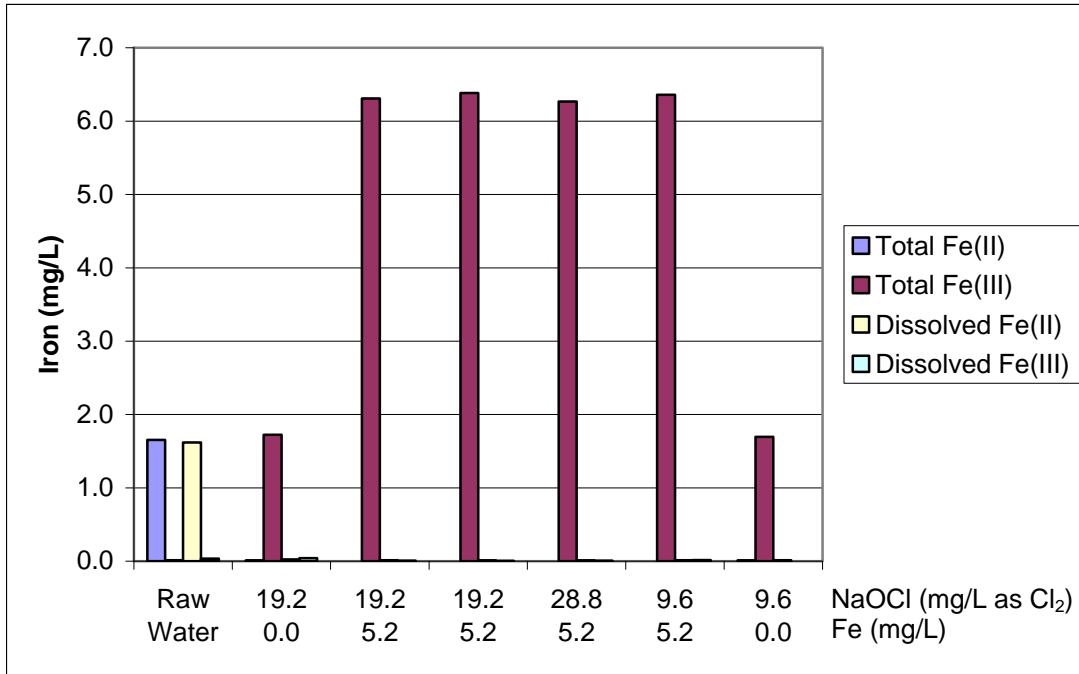


Figure 6. Iron (Fe) speciation in Jar Test 3, NaOCl. Raw water Fe speciation is shown for comparison. Doses of sodium hypochlorite (NaOCl) and ferric chloride (as Fe) are given below the x-axis.

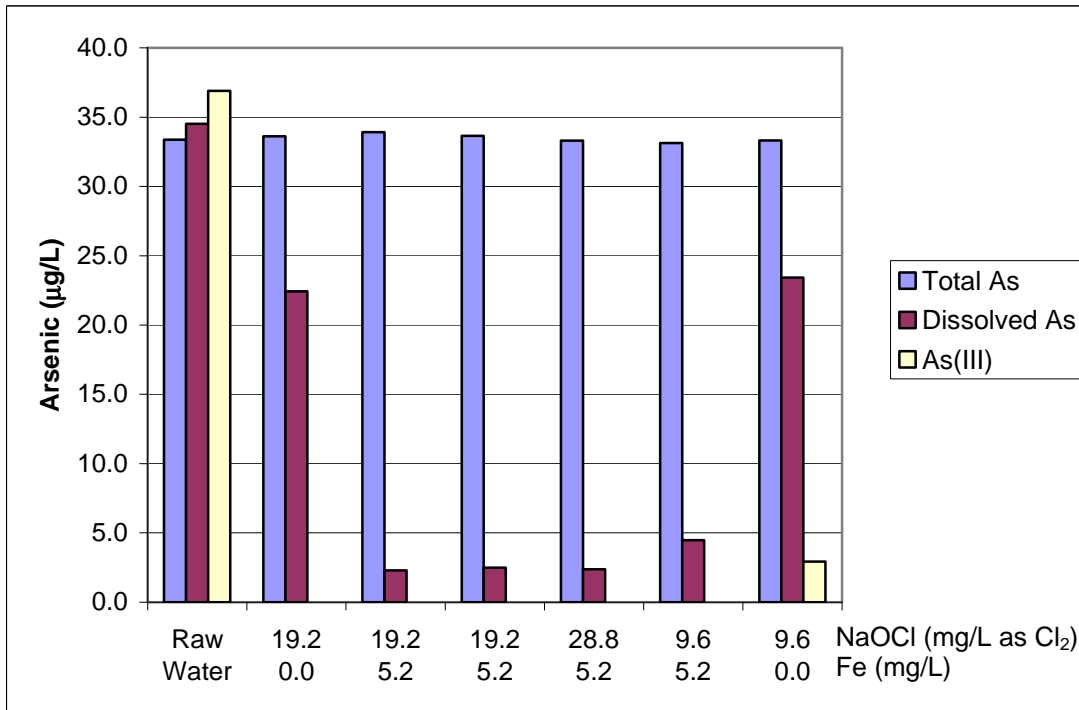


Figure 7. Arsenic (As) speciation in Jar Test 3. Raw water As speciation is shown for comparison. Doses of sodium hypochlorite (NaOCl) and ferric chloride (as Fe) are given below the x-axis.



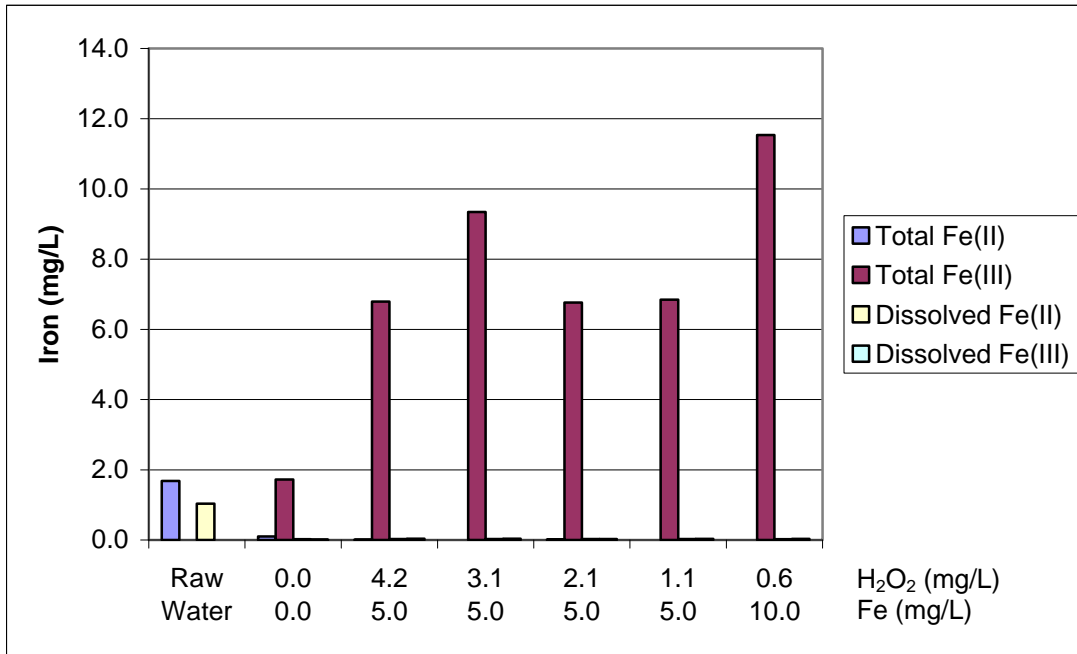


Figure 8. Iron (Fe) speciation in Jar Test 4, Fenton filtration. Raw water Fe speciation is shown for comparison. Doses of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ferric chloride (as Fe) are given below the x-axis.

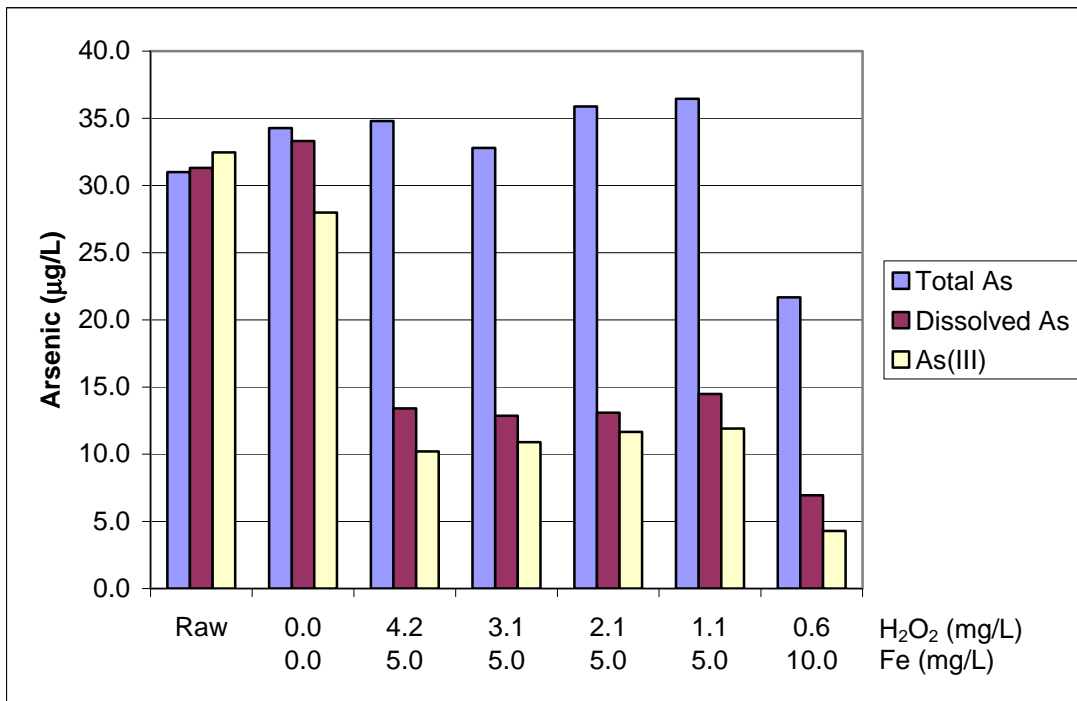
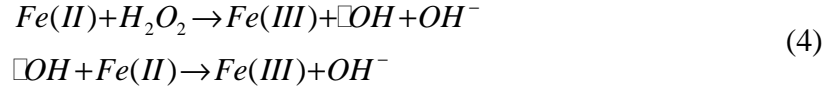


Figure 9. Arsenic speciation in Jar Test 4. Raw water Fe speciation is shown for comparison. Doses of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ferric chloride (as Fe) are given below the x-axis.

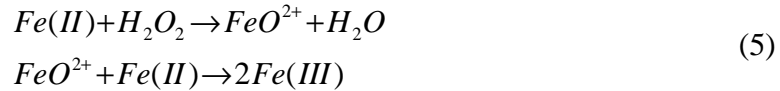


## Reaction Pathways of the Fenton-Filtration Process

In the absence of other species, the core Fenton mechanism consists of a reaction that produces a hydroxyl radical ( $\bullet\text{OH}$ ) (equation 4)



and/or a reaction that produces a ferryl ion ( $\text{FeO}^{2+}$ ) (equation 5).



In equations 4 and 5, Fe(II) refers to  $\text{Fe}^{2+}$  and all of its complexes. Similarly, Fe(III) refers to  $\text{Fe}^{3+}$  and all of its complexes. Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  form complexes with  $\text{OH}^-$  and NOM;  $\text{Fe}^{2+}$  also forms complexes with  $\text{HCO}_3^-/\text{CO}_3^{2-}$ . The Fe(III) formed by either reaction may precipitate as hydrous ferric oxide (King, 1998; King and Farlow, 2000; Rose and Waite, 2003a; Rose and Waite, 2003b; Stumm and Morgan, 1996). Although Fe speciation clearly depends on the pH, alkalinity, and NOM concentration, the basic Fenton reactions remain the same. Either reaction leads to a consumption of two Fe(II) for each  $\text{H}_2\text{O}_2$  that reacts with Fe(II). Therefore, the amounts of Fe(II) [ $\Delta\text{Fe(II)}$ ] and  $\text{H}_2\text{O}_2$  [ $\Delta\text{H}_2\text{O}_2$ ] consumed are related, as in equation 6.

$$\frac{\Delta\text{Fe(II)}}{\Delta\text{H}_2\text{O}_2} = 2 \quad (6)$$

There is no general agreement in the literature about which reactive species ( $\bullet\text{OH}$  or  $\text{FeO}^{2+}$ ) is prevalent in various solutions. Either is sufficiently reactive to oxidize As(III).

The presence of natural organic material (NOM), such as that which occurs in surface water and groundwater, results in scavenging of the reactive species, resulting in the formation of organic radicals. These radicals can be either oxidants or reductants, depending on the site within the NOM where the attack occurs. Oxidizing radicals can oxidize Fe(II) to Fe(III), and reducing radicals can reverse that reaction, both of which would affect the Fe(II)/ $\text{H}_2\text{O}_2$  stoichiometry. Furthermore, any oxygen present can be rapidly reduced to superoxide ( $\text{O}_2^-$ ) by organic-reducing radicals. Superoxide can react with Fe(II) or another superoxide (disproportionation) to yield  $\text{H}_2\text{O}_2$ , which also affects the stoichiometry. Thus, the presence of NOM may have a profound effect on reaction stoichiometry, and therefore, treatment efficiency.

### Methods and Materials for Fenton Stoichiometry Experiments

Experiments were performed to understand important pathways in the Fenton reaction system in groundwater. Previous experiments (Peyton et al., 2006a; Peyton et al., 2006b) were conducted to examine this stoichiometry, but in the calculations it was necessary to assume that all peroxide had been consumed because the levels were too low to be measured by our available methods. The results were similar among several cases for which different results were expected.

In the present study, an analytical method employing fluorescence was adapted from the literature and modified for the present reaction system, which lowered our quantitation limit by orders of magnitude. Iron speciation was determined by the same method as in the jar tests (Viollier et al., 2000). Solutions containing various Fe(II) concentrations (0-180  $\mu\text{M}$ ) were spiked with 30  $\mu\text{M}$   $\text{H}_2\text{O}_2$  and allowed to react for 5 minutes before the consumption of Fe(II) and  $\text{H}_2\text{O}_2$  was determined. Experiments were performed in aerated Danvers raw groundwater (ADW) (to oxidize Fe(II) that is initially present), deionized water (DIW), 1 millimolar (mM) phosphate buffer pH 7 ( $\text{PO}_4$ ), 1 mM carbonate buffer pH 7 ( $\text{CO}_3$ ), and carbonate-free Danvers raw groundwater (CFDW), which had previously been acidified to pH 3, sparged 30 minutes to remove  $\text{CO}_2$ , and adjusted to pH 7 with fresh sodium hydroxide. All solutions were equilibrated with air before iron addition.

## Results of Stoichiometry Experiments

The final concentrations of Fe(II) and  $\text{H}_2\text{O}_2$  are plotted versus the initial Fe(II) concentration for ADW, DIW,  $\text{PO}_4$ ,  $\text{CO}_3$ , and CFDW in Figures 10-14. For DIW,  $\text{PO}_4$ , and  $\text{CO}_3$ , there was a clear breakpoint where sufficient Fe(II) had been added to consume the initial peroxide dose. For  $\text{PO}_4$  and  $\text{CO}_3$  it falls at  $\text{DF}=2\text{DP}$  as expected (Figures 12, 13). However, for DIW it appears to fall at about  $\text{DF} = \text{DP}$  (Figure 11). Iron added beyond that required to reach the breakpoint was only 70, 50, and 60% recovered for DIW,  $\text{PO}_4$ , and  $\text{CO}_3$ , respectively. For CFDW the  $\text{H}_2\text{O}_2$  concentration decreased as the Fe dose increased, but  $\text{H}_2\text{O}_2$  was detectable in all samples (Figure 14). For ADW (Figure 10) it is clear that  $\text{H}_2\text{O}_2$  was produced and higher doses of Fe(II) were oxidized to very low levels. Both ADW and CFDW contained NOM.

The corresponding values of  $\Delta\text{Fe(II)}/\Delta\text{H}_2\text{O}_2$  are plotted versus the molar ratio of the Fe(II) dose to the peroxide dose,  $\text{DF}/\text{DP}$ , for ADW in Figure 15. The very high  $\Delta\text{Fe(II)}/\Delta\text{H}_2\text{O}_2$  values indicate low apparent peroxide consumption because of peroxide regeneration. This is consistent with results that indicate little increase in arsenic oxidation at higher peroxide doses, since, due to peroxide regeneration, Fe(II) is the limiting reactant.

The curves for DIW,  $\text{PO}_4$ ,  $\text{CO}_3$ , and CFDW (Figure 16) indicate a slight inflection at  $\Delta\text{Fe(II)}/\Delta\text{H}_2\text{O}_2 \sim 2$ , while increased values at higher iron doses probably reflect Fe(II) oxidation by oxygen during the 5-minute reaction time following the very rapid Fe(II)- $\text{H}_2\text{O}_2$  reaction. Phosphate is particularly known to catalyze that reaction. The low pH values used for  $\text{CO}_2$  sparging may have caused some NOM denaturation/precipitation in the CFDW samples.

It is concluded that the NOM in Danvers groundwater has an important effect on treatment due to the regeneration of hydrogen peroxide. Under these circumstances, addition of a higher peroxide dose would not be expected to increase arsenic oxidation.

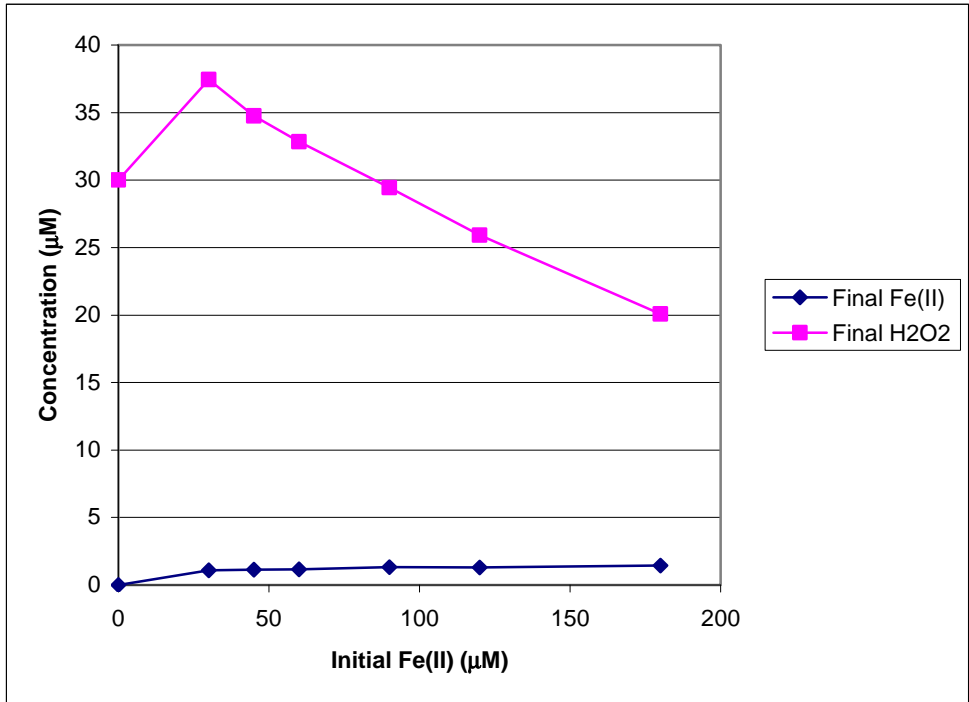


Figure 10. Concentrations of Fe(II) and H<sub>2</sub>O<sub>2</sub> remaining after 5-minute reaction time in aerated Danvers groundwater (ADW). Initial H<sub>2</sub>O<sub>2</sub> concentration was 30 μM. Initial Fe(II) concentration is indicated on x-axis.

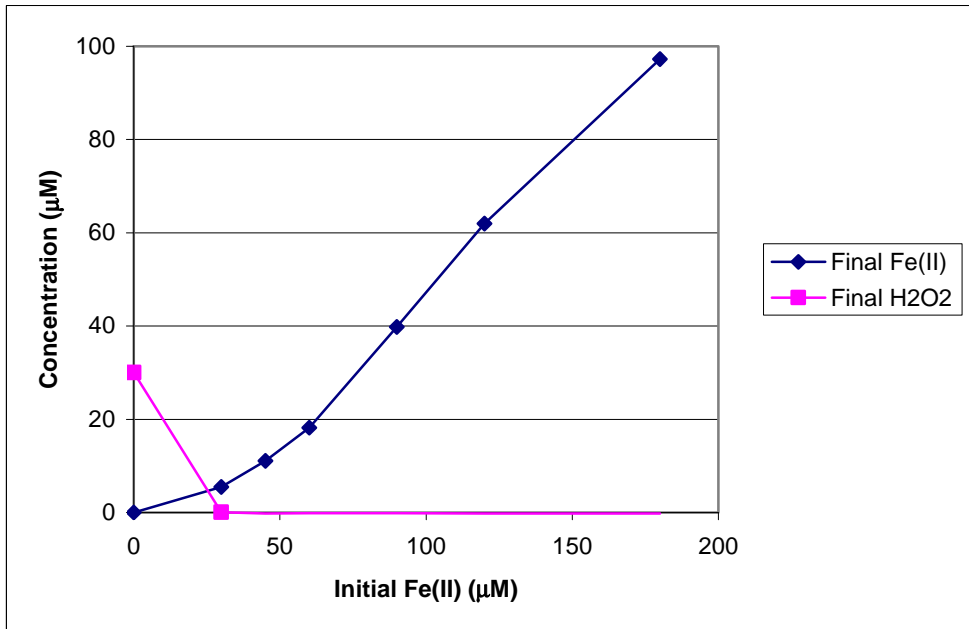


Figure 11. Concentrations of Fe(II) and H<sub>2</sub>O<sub>2</sub> remaining after 5-minute reaction time in deionized water (DIW). Initial H<sub>2</sub>O<sub>2</sub> concentration was 30 μM. Initial Fe(II) concentration is indicated on x-axis.

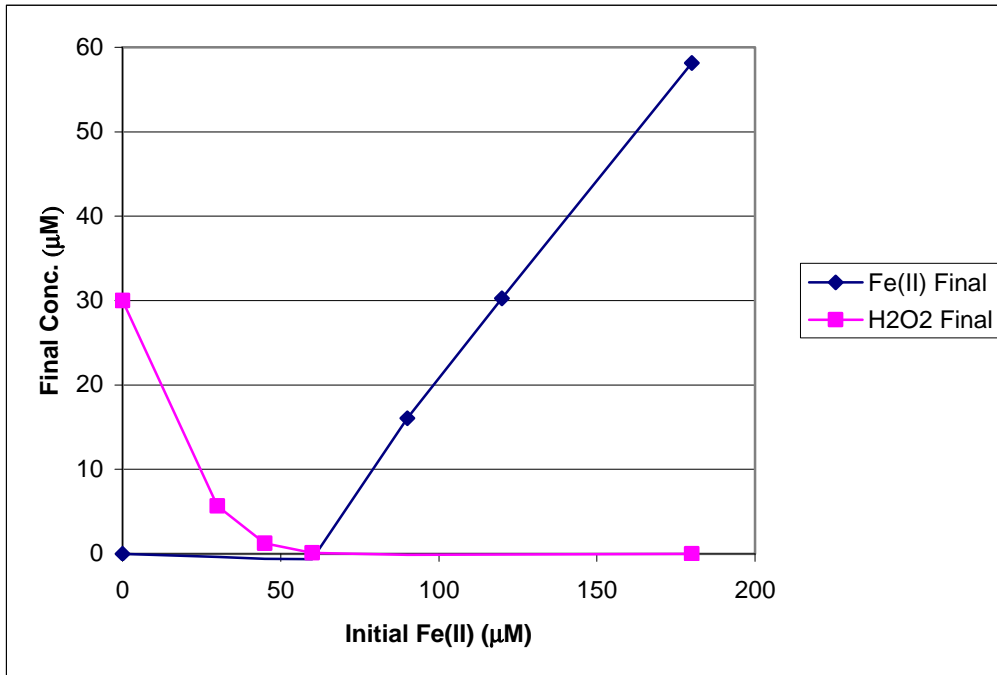


Figure 12. Concentrations of Fe(II) and H<sub>2</sub>O<sub>2</sub> remaining after 5-minute reaction time in phosphate buffer (PO<sub>4</sub>). Initial H<sub>2</sub>O<sub>2</sub> concentration was 30 µM. Initial Fe(II) concentration is indicated on x-axis.

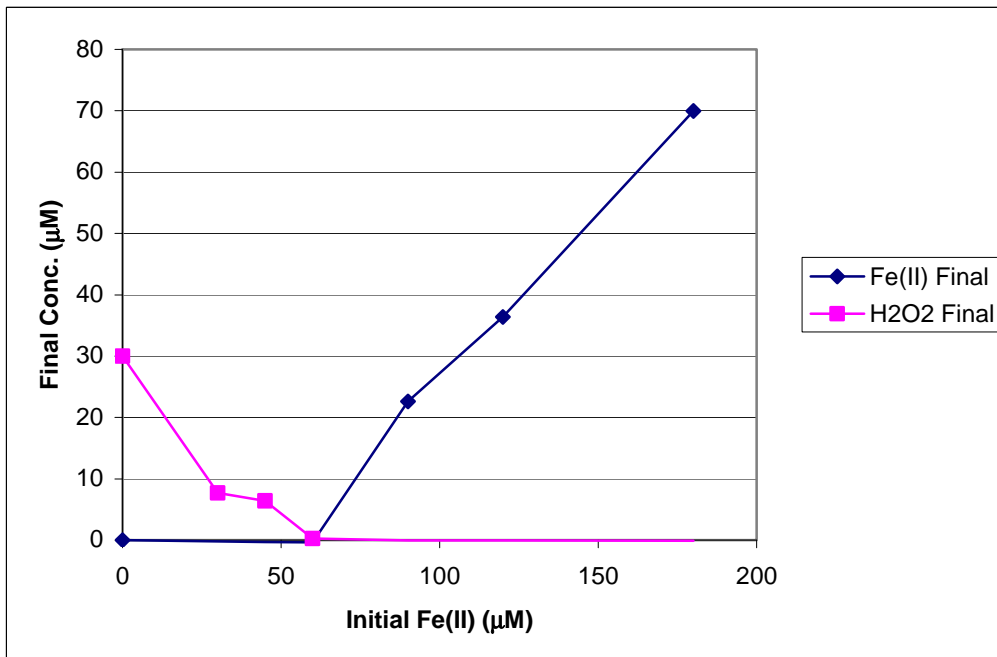


Figure 13. Concentrations of Fe(II) and H<sub>2</sub>O<sub>2</sub> remaining after 5-minute reaction time in carbonate buffer (CO<sub>3</sub>). Initial H<sub>2</sub>O<sub>2</sub> concentration was 30 µM. Initial Fe(II) concentration is indicated on x-axis.

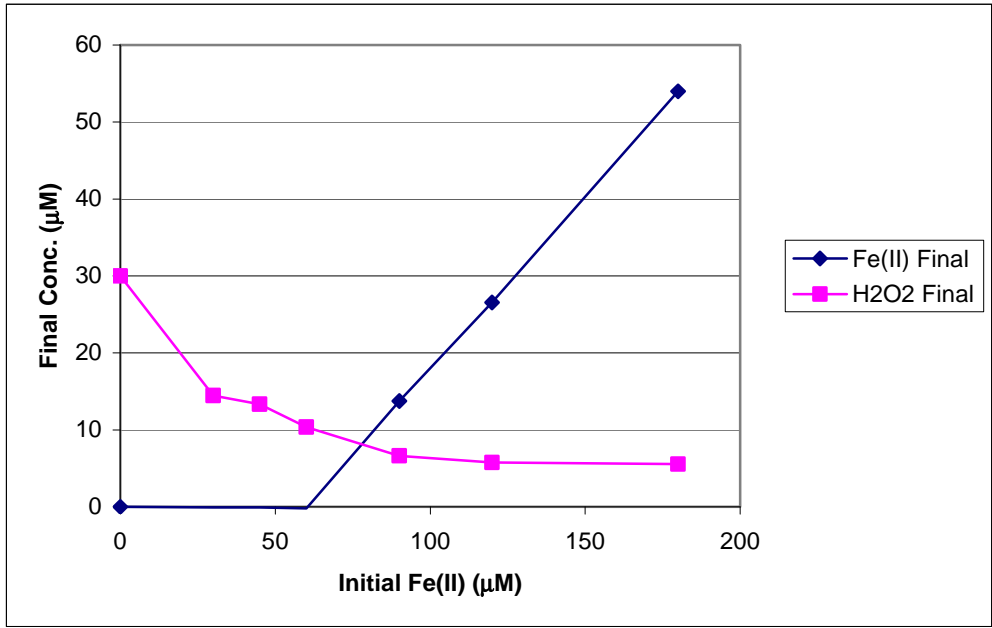


Figure 14. Concentrations of Fe(II) and H<sub>2</sub>O<sub>2</sub> remaining after 5-minute reaction time in carbonate-free Danvers groundwater (CFDW). Initial H<sub>2</sub>O<sub>2</sub> concentration was 30 µM. Initial Fe(II) concentration is indicated on x-axis.

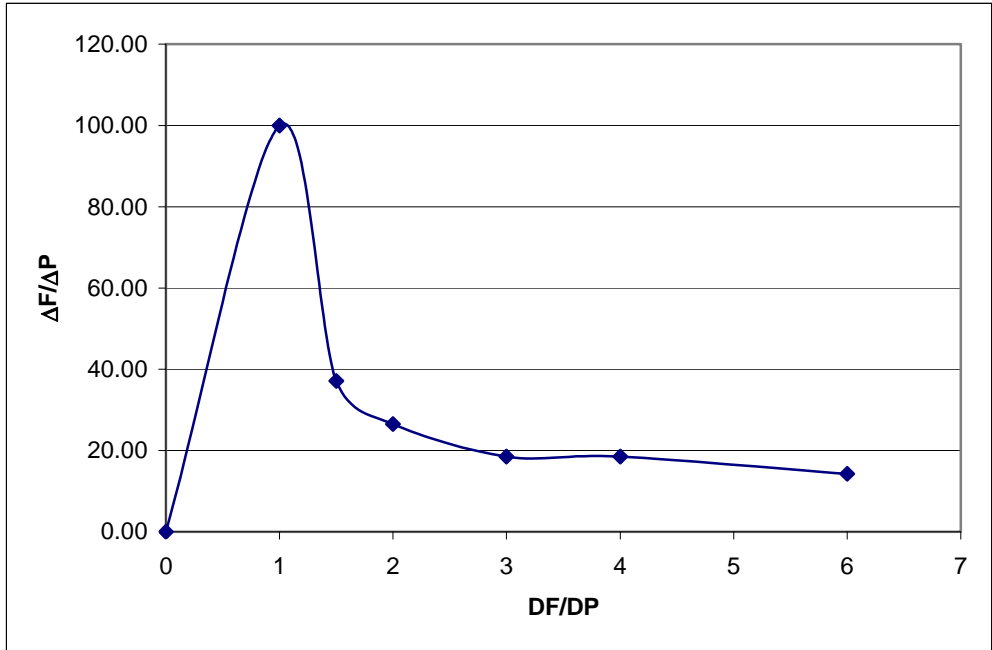


Figure 15. Ratio of change in Fe(II) to change in H<sub>2</sub>O<sub>2</sub> ( $\Delta F/\Delta P$ ) vs. ratio of initial concentrations (doses) of Fe(II) and H<sub>2</sub>O<sub>2</sub> ( $DF/DP$ ) for aerated Danvers groundwater.

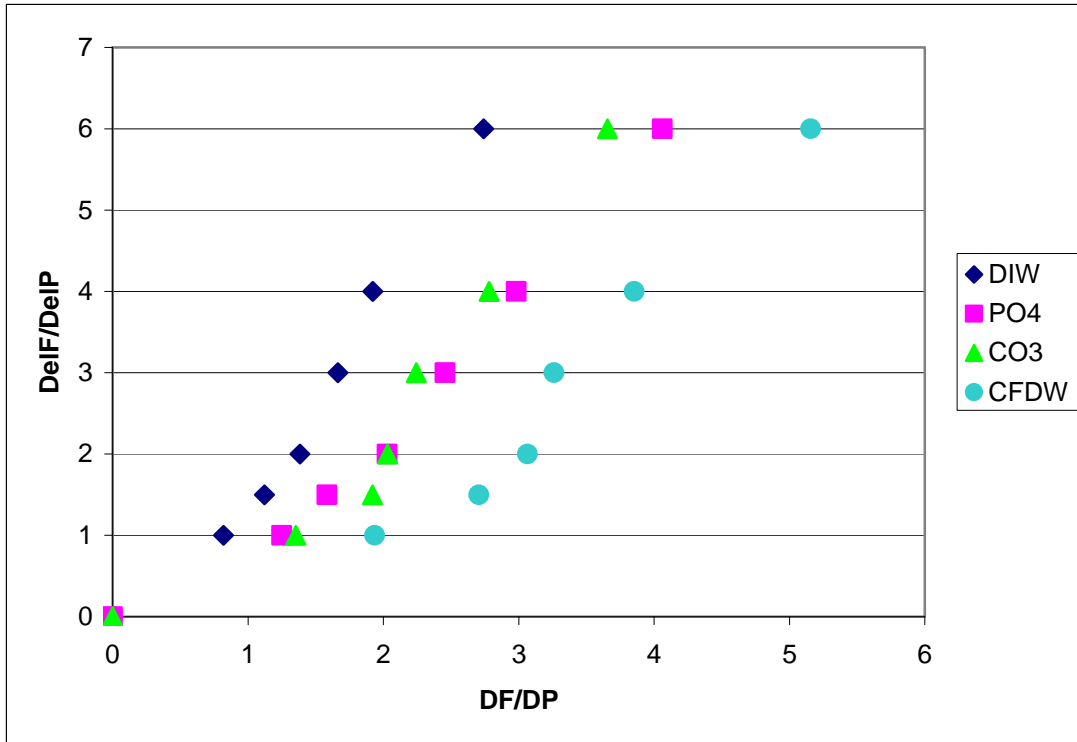


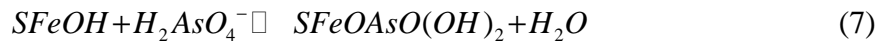
Figure 16. Ratio of change in Fe(II) to change in H<sub>2</sub>O<sub>2</sub> ( $\Delta F/\Delta P$ ) vs. ratio of initial concentrations (doses) of Fe(II) and H<sub>2</sub>O<sub>2</sub> (DF/DP) for deionized water (DIW), phosphate buffer (PO4), carbonate buffer (CO3), and carbonate-free Danvers water (CFDW).



## Sorption Modeling

A model of As sorption in the Fenton-filtration process was developed in previous work (Peyton et al., 2006b) based on the generalized double-layer model (DLM) developed by Dzombak and Morel (1987). The authors fit their model to published data on the sorption of many cations and anions to hydrous ferric oxide (HFO) (Dzombak and Morel, 1990). A brief summary of the DLM can be found in Peyton et al. (2006b). All papers cited by Dzombak and Morel (1990) were based on experiments using aged HFO for the sake of reproducibility. However, the degree of As sorption to freshly precipitated HFO is greater than to aged HFO, probably because of a greater surface area accessible to As(V) or As(III) (Edwards, 1994; Fuller et al., 1993). It was found that the DLM could be fit to data for As(V) sorption to fresh HFO using published equilibrium constants (Dzombak and Morel, 1990) supplemented with subsequently published parameters for carbonate and silica sorption (Appelo et al., 2002; Swedlund and Webster, 1999) and an “effective” Fe concentration 3.7 times the actual Fe concentration (Holm, 2002). The “adapted” DLM successfully modeled the effects of competition between As(V) and carbonate and silica in laboratory experiments. The adapted model reproduced the trend of decreasing dissolved As concentration with increasing Fe dose in Fenton-filtration, a result which is not surprising, but it under-estimated As removal (Peyton et al., 2006b).

The DLM assumes monodentate surface complexation, a single bond between a surface Fe(III) ion and an arsenate or arsenite ion. Equation 7 gives an example, in which SFeOH is a surface hydroxyl group and SFeOAsO(OH)<sub>2</sub> is a surface complex.



Recent research has found that As(V) and As(III) predominantly form bidentate surface complexes on HFO rather than the monodentate complexes assumed in the DLM (Manning et al., 1998; Waychunas et al., 1993). A model that includes bidentate surface complexes and also considers the distribution of charge in surface complexes has recently been developed (CD-MUSIC model for charge distribution multi-site complexation model) (Hiemstra and Van Riemsdijk, 1996; Hiemstra and Van Riemsdijk, 1999) and is implemented in the program Visual Minteq as the triple-plane model (TPM) (<http://www.lwr.kth.se/English/OurSoftware/vminteq/>). Sorption parameters for the TPM were obtained by fitting the TPM to data for As(V) and As(III) sorption to fresh HFO (Gustafsson, 2001; Gustafsson and Bhattacharya, 2007).

The TPM with the sorption database cited previously was used to model Fenton-filtration As removal data (Peyton et al., 2006b), and is compared with the DLM in Figure 17. For both models it was assumed that the raw water contained 1.8 mg/L Fe(II) and 37.5 µg/L As(III) (typical value for Well 3) and that the Fe(II) and As(III) were 100% and 90% oxidized, respectively (typical for Fenton-filtration). Both models correctly predicted a small amount of As removal for no added FeCl<sub>3</sub> (just the Fe in the raw water), but the TPM value was closer to the observed value. Both models converged to roughly the same value at very high FeCl<sub>3</sub> doses, which was also close to the observed value, which suggests that the limiting process may be incomplete As(III) sorption, which in turn suggests that As(III) oxidation is important to As removal. Although the TPM was somewhat closer to the observed values at intermediate FeCl<sub>3</sub> doses, it still under-predicted As removal. The under-prediction may have been due in part to

over-estimation of competition between silica and As(V). The only silica surface complex in the sorption database is  $SFeOSi(OH)_3$ , i.e., it has only a single silicic acid molecule. However, silica is known to polymerize on the HFO surface (Davis et al., 2002; Swedlund and Webster, 1999). Inclusion of a dimeric or polymeric silica surface complex may decrease competition between silica and As(V), and therefore increase modeled As(V) sorption (lower the modeled dissolved As concentration). Danvers groundwater has a relatively high DOC concentration and neither sorption model considers the effects of organic matter. However, NOM is expected to hinder As sorption, not enhance it. For both models, sorption is the only process for As removal. Other reactions, such as coprecipitation, may contribute to As removal.

The TPM sorption parameters could be optimized for good agreement with Fenton-filtration As removal for Danvers groundwater. However, the parameters would probably not apply to other systems. However, even with the available parameters, the TPM offers improved As sorption modeling compared with the DLM. The TPM will be useful in qualitatively predicting the effects of treatment variables like As(III) oxidation or Fe addition. However, it clearly cannot predict whether or not a specific process applied to a specific groundwater will satisfy the As MCL.

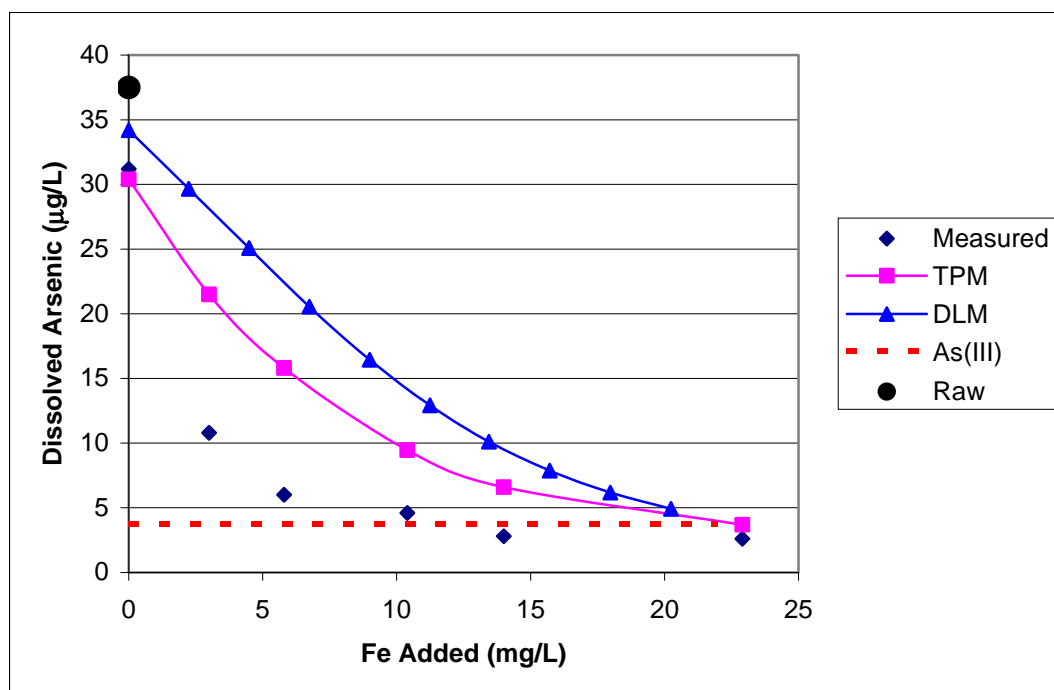


Figure 17. Comparison of sorption models and data from Fenton-filtration pilot-scale experiments (Peyton et al., 2006b). TPM and DLM stand for triple-plane model and diffuse layer model.

## Arsenic Removal During Full-Scale Treatment Plant Operation

The Danvers, Illinois water utility had planned to evaluate  $\text{KMnO}_4$  as an oxidant for improved As removal. Permission was granted to the authors to run a full-scale test of the Fenton-filtration process before the  $\text{KMnO}_4$  testing started. The doses of  $\text{H}_2\text{O}_2$  (1.2 mg/L) and  $\text{FeCl}_3$  (5 mg/L Fe) were the same as those that gave a total (unfiltered) As concentration below the MCL in the pilot-scale experiments (Peyton et al., 2006b). The test had to be aborted after a few hours because of excessive back pressure, or clogging, in the sand filter. No further full-scale  $\text{H}_2\text{O}_2$  testing was conducted. It was decided to support the  $\text{KMnO}_4$  testing by analyzing water samples for each oxidant dose.

### Results of Full-Scale Tests

The Danvers plant normally receives water from wells 3 and 4 simultaneously or well 5. Water quality is similar for all three wells (Table 1). Fe concentrations in the raw water generally fluctuated between 2.5 and 3.0 mg/L regardless of which wells were operating (Figure 17). Aeration and filtration had usually reduced Fe concentrations to below 0.2 mg/L (Wilson et al., 2004), but at the beginning of the tests for the present work, Fe concentrations in the clearwell were between 1.0 and 2.0 mg/L. It was discovered that one of the filter cells had lost all sand, probably during back washing. When the cell was closed off in early December 2007 and subsequently refilled, clearwell Fe concentrations dropped to below 1.0 mg/L. Fe concentrations in the finished water were almost always lower than in the clearwell, probably because the cation exchange resin acted as a filter and removed particulate HFO from the 33% of the water that went through the softener.

Arsenic concentrations in the raw water generally fluctuated between 35 and 40  $\mu\text{g/L}$  regardless of which wells were operating (Figure 18). Arsenic concentrations in the clearwell fluctuated between 20 and 40  $\mu\text{g/L}$  before the empty filter cell was closed off and between 10 and 20  $\mu\text{g/L}$  afterward. The finished-water As concentrations generally decreased as the  $\text{KMnO}_4$  dose increased; one might speculate that the degree of As(III) oxidation increased through the entire series of tests. However, the few As speciation determinations showed that As(III) was more than 90% oxidized at a relatively low  $\text{KMnO}_4$  dose of 1.25 mg/L (Table 2). Figure 19 shows the As concentration as a function of Fe in the clearwell. As expected, the lower the Fe concentration, the lower the As concentration. However, extrapolating the regression line to zero Fe (complete filtration) gives a dissolved As concentration that is greater than the MCL. Arsenic removal with  $\text{KMnO}_4$  oxidation was better than with aeration alone (20-25%). However, sorption was inadequate. It is probably necessary to add some  $\text{FeCl}_3$  along with  $\text{KMnO}_4$  to satisfy the MCL.

**Table 1. Water quality in Danvers, Illinois wells**

<i>Well #</i>	<i>Raw or Finished</i>	<i>As(III)</i>	<i>As(V)</i>	<i>Dissolved As</i>	<i>Total As</i>	<i>Fe</i>	<i>Mn</i>	
3	Raw	32.8	6.19	37.3	43	1.53	0.022	
4	Raw	37.4	3.76	42.4	32.1	2.99	0.034	
5	Raw	32.6	5.63	36.2	41.3	2.12	0.030	
5	Finished	< 2	24.5	25.2	28.1	0.07	0.032	

<i>Well #</i>	<i>Raw or Finished</i>	<i>Ca</i>	<i>Mg</i>	<i>Na</i>	<i>Si</i>	<i>Alkalinity</i>	<i>Al</i>	
3	Raw	52.4	22.7	220	6.88	495	0.001	
4	Raw	75.8	35.1	130	8.14	556	<0.001	
5	Raw	69.3	32.3	165	7.72	544	0.002	
5	Finished	57.5	37.1	160	7.91	531	0.001	

<i>Well #</i>	<i>Raw or Finished</i>	<i>NO<sub>3</sub>-N</i>	<i>SO<sub>4</sub></i>	<i>Cl</i>	<i>F</i>	<i>PO<sub>4</sub>-P</i>	<i>TOC</i>	<i>NH<sub>3</sub>-N</i>
3	Raw	< 0.02	< 0.1	48.9	0.32	1.12	13.2	7.12
4	Raw	< 0.02	< 0.1	29.1	0.33	0.37	13.2	9.4
5	Raw	< 0.02	< 0.1	41.0	0.31	0.35	13.4	8.29
5	Finished	< 0.02	< 0.1	39.3	0.84	0.38	12.8	8.35

**Notes:** Arsenic concentrations in µg/L. All other concentrations in mg/L. Data from Wilson et al. (2004).

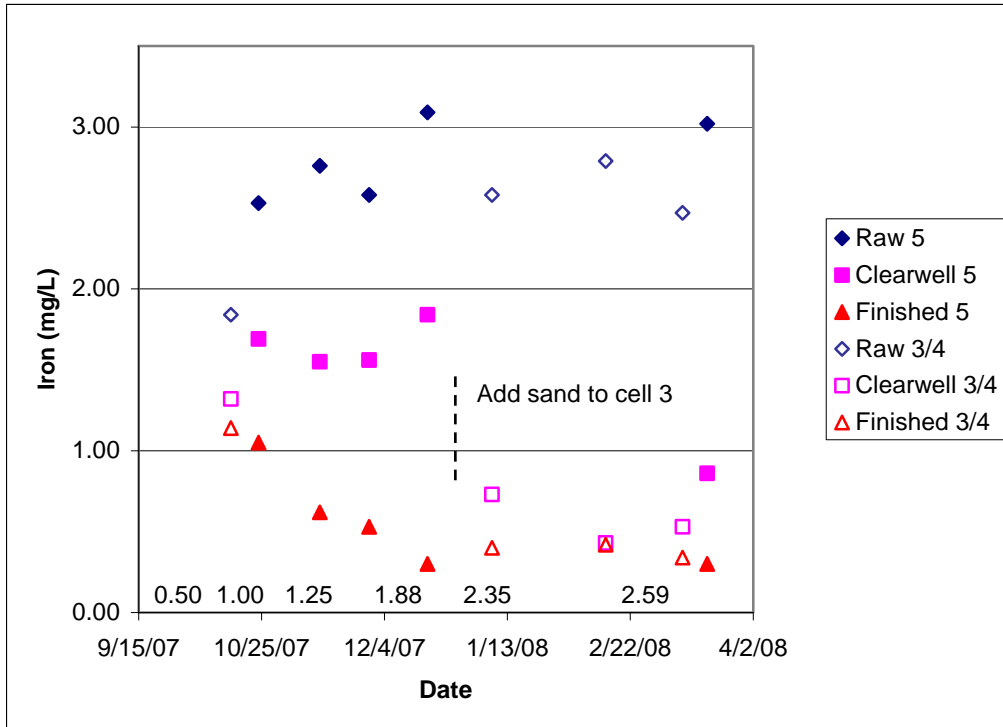


Figure 17. Total (unfiltered) iron concentrations in the Danvers water treatment plant during full-scale testing. Filled symbols indicate well 5, open symbols are wells 3 and 4. The numbers above the x-axis indicate the  $\text{KMnO}_4$  doses in mg/L.

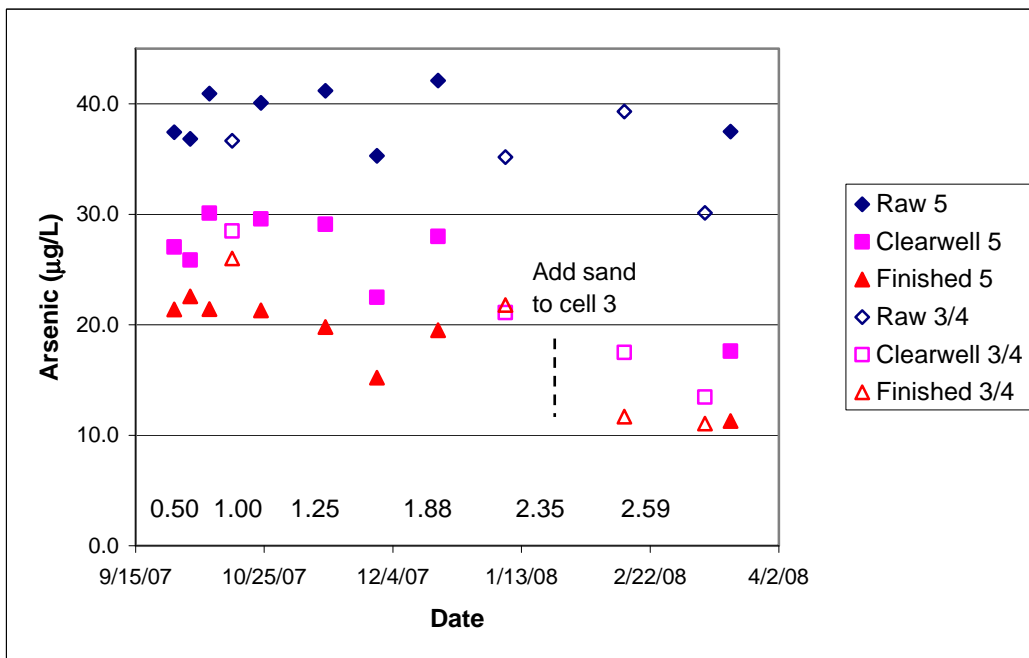


Figure 18. Arsenic concentrations in the Danvers, IL water treatment plant during full-scale testing. Symbols and numbers above the x-axis appear as in Figure 17.

**Table 2. Arsenic (As) speciation in full-scale tests**

Date	Raw Water As ( $\mu\text{g/L}$ )		$\text{KMnO}_4$ Dose (mg/L)	Clearwell As ( $\mu\text{g/L}$ )	
	Total	As(III)		Total	As(III)
10/02/07	36.8	30.1	0.50	25.9	12.6
10/08/07	40.9	46.6	0.50	30.1	10.1
10/15/07	36.7	36.2	1.00	28.5	5.7
10/24/07	40.1	40.6	1.25	29.6	2.9

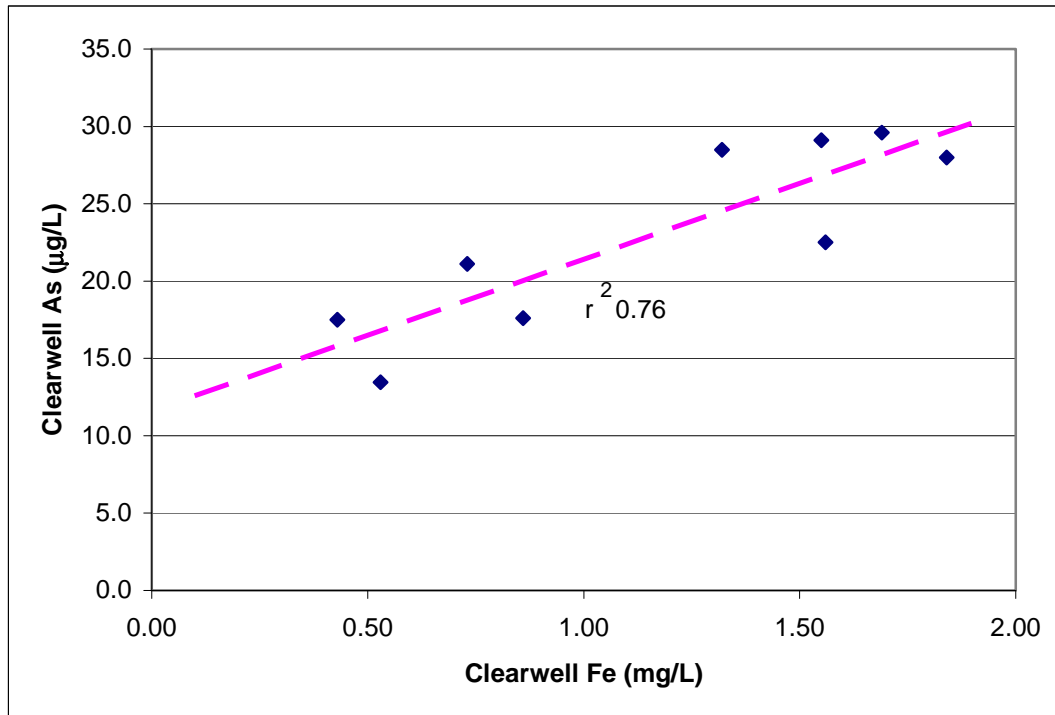


Figure 19. Arsenic concentrations in the Danvers clearwell as a function of the iron concentration.

## **Acknowledgments**

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## Appendix 1. Data from Jar Tests

Weight-based concentration units, such as mg/L or  $\mu\text{g/L}$ , may be more familiar to some people, but oxidant and adsorbent doses and all modeling are based on molar concentrations. The following tables give the oxidant and  $\text{FeCl}_3$  doses and final concentrations of Fe and As species in the jar tests.

Table 1.1. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferric chloride ( $\text{FeCl}_3$ ) doses in Jar Test 1

Jar	$\text{H}_2\text{O}_2$ dose		$\text{FeCl}_3$ dose	
	$\mu\text{mol/L}$	mg/L	$\mu\text{mol/L}$	mg/L as Fe
1	68	2.3	0	0
2	68	2.3	92	5.15
3	68	2.3	92	5.15
4	102	3.5	92	5.15
5	34	1.2	92	5.15
6	0	0.0	92	5.15

Table 1.2. Potassium permanganate ( $\text{KMnO}_4$ ) and ferric chloride ( $\text{FeCl}_3$ ) doses in Jar Test 2

Jar	$\text{KMnO}_4$ dose		$\text{FeCl}_3$ dose	
	$\mu\text{mol/L}$	mg/L	$\mu\text{mol/L}$	mg/L as Fe
1	10	1.6	0	0.0
2	10	1.6	92	5.2
3	10	1.6	92	5.2
4	15	2.4	92	5.2
5	5	0.8	92	5.2
6	0	0.0	0	0

Table 1.3. Sodium hypochlorite ( $\text{NaOCl}$ ) and ferric chloride ( $\text{FeCl}_3$ ) doses in Jar Test 3

Jar	$\text{NaOCl}$ dose		$\text{FeCl}_3$ dose	
	$\mu\text{mol/L}$	mg/L	$\mu\text{mol/L}$	mg/L
1	270	19.2	0	0.0
2	270	19.2	92	5.2
3	270	19.2	92	5.2
4	360	28.8	92	5.2
5	135	9.6	92	5.2
6	135	9.6	0	0.0

## Appendix 1 (cont.)

Table 1.4. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ferric chloride (FeCl<sub>3</sub>) doses in Jar Test 4

Jar	H <sub>2</sub> O <sub>2</sub> dose		FeCl <sub>3</sub> dose	
	μmol/L	mg/L	μmol/L	mg/L
1	0	0.0	0	0.0
2	123	4.2	90	5.0
3	91	3.1	90	5.0
4	61	2.1	90	5.0
5	32	1.1	90	5.0
6	18	0.6	179	10.0

Table 1.5. Iron (Fe) speciation in Jar Test 1

Jar	Filtered				Unfiltered			
	mg/L		μmol/L		mg/L		μmol/L	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Raw	1.80	ND	32.25	ND	1.82	ND	32.55	0.04
1	0.03	0.03	0.53	0.49				
2	0.02	ND	0.33	0.08	0.07	6.43	1.20	115.13
3	0.02	ND	0.30	0.05	0.07	6.46	1.24	115.73
4	0.02	0.01	0.28	0.19				
5	0.01	0.01	0.26	0.26	0.07	6.40	1.34	114.51
6	0.02	0.02	0.34	0.40				

Notes: Blank indicates no sample.  
ND indicates not detected.

Table 1.6. Arsenic (As) speciation in Jar Test 1

Jar	As concentration			
	μg/L		μmol/L	
	Dissolved	As(III)	Dissolved	As(III)
Raw	34.5	32.2	0.46	0.43
1	30.0	15.6	0.40	0.21
2	13.6	10.5	0.18	0.14
3	13.5	11.0	0.18	0.15
4	10.5	8.3	0.14	0.11
5	12.7	9.9	0.17	0.13
6	24.6	21.0	0.33	0.28

## Appendix 1 (cont.)

Table 1.7. Iron (Fe) speciation in Jar Test 2

	Filtered				Unfiltered			
	mg/L		µmol/L		mg/L		µmol/L	
Jar	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Raw	1.649	0.006	29.525	0.114	1.656	ND	29.644	ND
1	0.017	0.023	0.308	0.415	0.031	1.559	0.911	29.336
2	0.019	0.028	0.346	0.508	0.010	6.856	0.823	28.143
3	0.019	0.032	0.332	0.571	0.015	6.018	0.816	28.987
4	0.034	0.093	0.609	1.657	0.004	6.490	0.424	29.403
5	0.023	0.015	0.412	0.277	0.065	5.464	10.158	20.064
6	ND	ND	ND	ND	0.106	1.104	29.382	0.150

Table 1.8. Arsenic (As) speciation in Jar Test 2

	As concentration					
	µg/L			µmol/L		
Jar	Total	Dissolved	As(III)	Total	Dissolved	As(III)
Raw	32.4	32.2	30.6	0.43	0.43	0.41
1	35.3	17.8	3.7	0.47	0.24	0.05
2	31.4	0.7	ND	0.42	0.01	ND
3	34.7	2.8	0.1	0.46	0.04	0.00
4	34.7	1.7	0.4	0.46	0.02	0.01
5	34.9	12.2	8.9	0.47	0.16	0.12
6	33.6	32.2	25.5	0.45	0.43	0.34

Table 1.9. Iron (Fe) speciation in Jar Test 3

	Filtered				Unfiltered			
	mg/L		µmol/L		mg/L		µmol/L	
Jar	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Raw	1.620	0.034	29.0	0.6	1.655	0.013	29.6	0.2
1	0.023	0.042	0.4	0.8	0.010	1.724	0.2	30.9
2	0.013	0.007	0.2	0.1	ND	6.310	ND	113.0
3	0.012	0.004	0.2	0.1	ND	6.382	ND	114.3
4	0.010	0.008	0.2	0.1	ND	6.268	ND	112.2
5	0.013	0.014	0.2	0.3	ND	6.358	ND	113.8
6	0.014	ND	0.2	ND	0.012	1.696	0.2	30.4

## Appendix 1 (cont.)

Table 1.10. Arsenic (As) in Jar Test 3

Jar	As concentration					
	µg/L			µmol/L		
	Total	Dissolved	As(III)	Total	Dissolved	As(III)
Raw	33.4	34.5	36.9	0.45	0.46	0.49
1	33.6	22.4	0.0	0.45	0.30	0.00
2	33.9	2.3	0.0	0.45	0.03	0.00
3	33.7	2.5	0.0	0.45	0.03	0.00
4	33.3	2.4	0.0	0.44	0.03	0.00
5	33.1	4.5	0.0	0.44	0.06	0.00
6	33.3	23.4	2.9	0.44	0.31	0.04

Table 1.11. Iron (Fe) speciation in Jar Test 4

Jar	Filtered				Unfiltered			
	mg/L		µmol/L		mg/L		µmol/L	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Raw	1.037	ND	18.6	ND	1.683	ND	30.1	ND
1	0.023	0.010	0.4	0.2	0.099	1.724	1.8	30.9
2	0.027	0.038	0.5	0.7	0.007	6.793	0.1	121.6
3	0.029	0.037	0.5	0.7	ND	9.345	ND	167.3
4	0.026	0.028	0.5	0.5	0.011	6.766	0.2	121.1
5	0.026	0.031	0.5	0.5	ND	6.846	ND	122.6
6	0.021	0.034	0.4	0.6	ND	11.533	ND	206.5

Table 1.12. Arsenic (As) speciation in Jar Test 4

Jar	As concentration					
	µg/L			µmol/L		
	Total	Dissolved	As(III)	Total	Dissolved	As(III)
Raw	31.0	31.3	32.5	0.41	0.42	0.43
1	34.3	33.3	28.0	0.46	0.44	0.37
2	34.8	13.4	10.2	0.46	0.18	0.14
3	32.8	12.9	10.9	0.44	0.17	0.15
4	35.9	13.1	11.7	0.48	0.17	0.16
5	36.5	14.5	11.9	0.49	0.19	0.16
6	21.7	6.9	4.3	0.29	0.09	0.06