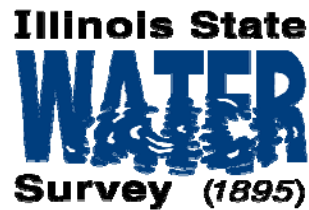




Demonstration of Low-Cost Arsenic Removal from a Variety of Illinois Drinking Waters

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A VARIETY OF ILLINOIS DRINKING WATERS**

by

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TABLE OF CONTENTS

Abstract.....	3
Introduction.....	3
Materials and Methods.....	5
Water sources.....	5
Chemicals.....	5
Analytical Methods.....	5
Experimental Procedures.....	6
Results and Discussion.....	7
Pilot Experiments using Monticello Groundwater.....	7
Laboratory Batch Experiments using Dwight Groundwater.....	8
Pilot Experiments using Danvers Groundwater... ..	9
Comparison of Treatability of Danvers, Monticello, and Dwight Waters.....	9
Interpretation of Treatment Results.....	11
Conclusions.....	13
Future Work.....	14
Acknowledgements.....	14
Appendix.....	15
References.....	17

ABSTRACT

Four groundwater sources used as drinking water in Illinois were treated using the Fenton reaction (hydrogen peroxide + Fe(II)) to oxidize As(III) to As(V) before adsorption of the arsenic to the iron precipitate produced during iron removal by aeration/filtration. For all four waters used, the arsenic concentration could be reduced to below the 10 microgram/liter maximum contaminant level using relatively inexpensive doses of iron and peroxide, despite the need to add iron (Fe(II) or Fe(III) were both tried) in all cases to completely adsorb the arsenic. The waters differed in their treatability, but in each case, the least expensive configuration used Fe(III) rather than Fe(II). It was shown that consumption of reactive species by reaction with Fe(II) was a very significant sink for Fe(II) at higher iron concentrations, and was primarily responsible for the difference in efficiency using Fe(II) and Fe(III). Peroxide doses greater than 20-27 micromolar improved arsenic removal in Monticello and Dwight water, but not in Danvers water. In most cases, the treatability of the waters did not appear to correlate negatively with the alkalinity, phosphate, silicate, or organic content of the waters. A correlation was expected because of the known competition between arsenic and the other natural solutes for both sorption sites and reactive species generated during the Fenton reaction. Chemical addition in the range of 3-6.4 milligrams per liter Fe(III) and 20-45 micromolar (0.68-1.5 milligrams/liter) peroxide was adequate to reduce the total arsenic to the maximum contaminant level in all four waters. The estimated chemical cost was \$0.04 to \$0.07 per thousand gallons in the most favorable cases for each water.

INTRODUCTION

Because chronic exposure to high concentrations of arsenic in drinking water has been linked to serious health problems, the United States Environmental Protection Agency (USEPA) lowered the maximum contaminant level (MCL) for arsenic to 10 micrograms/liter ($\mu\text{g/L}$) in early 2006. It is estimated (Wilson et al., 2004) that 30-50 water utilities in Illinois that had met the previously established 50 $\mu\text{g/L}$ MCL, would not meet the 10 $\mu\text{g/L}$ level without an upgrade of the existing drinking water treatment plant. Most of these facilities serve communities of fewer than 10,000 residents, for which the per capita cost of upgrading treatment systems can be particularly high (Frost et al., 2002).

Many arsenic-containing groundwaters in Illinois also contain a significant quantity of iron (Kelly et al., 2005), which often is removed during treatment because of aesthetic issues such as taste and staining. The most common method for iron removal is oxidation of the soluble iron [ferrous iron or Fe(II)] to the ferric form [Fe(III)], which precipitates as hydrous ferric oxides (HFO) and can be removed from water by filtration. Some arsenic adsorbs to the HFO precipitate and is removed during filtration, but the success of this removal varies widely. Arsenic in groundwater occurs almost entirely in two forms, As(III) and As(V) (see Appendix A, Peyton et al., 2006, for a more complete discussion of arsenic speciation). Because As(V) is less toxic than As(III) and is also adsorbed more completely to HFO in the typical near-neutral pH range of groundwater, it is desirable to convert As(III) to As(V) before iron filtration.

In a previous project (Peyton et al., 2006), a treatment method was developed, which utilized the existing Fe(II) present in groundwater, in combination with a relatively inexpensive oxidant, hydrogen peroxide (H_2O_2), to oxidize As(III) to As(V) prior to adsorption to HFO and filtration. The combination of Fe(II) and hydrogen peroxide, known as the Fenton reaction, is among the set of the chemical reactions that occur during the oxidation of Fe(II) by air. This process consumes two moles of Fe(II) to produce one mole of peroxide. The direct addition of hydrogen peroxide maximizes the radical-producing step in the oxidation process. This step is usually written as



where the dot signifies a radical (in this case, hydroxyl radical), but the reaction may also produce a very reactive “high-valence” iron species under some conditions (see below). More details of the chemistry and kinetics of this process can be found in Appendix B of Peyton et al. (2006). Following this oxidation step, the water is aerated to oxidize the remaining Fe(II) to Fe(III), then filtered to remove the HFO precipitate along with the adsorbed arsenic. Accordingly, this treatment is a type of oxidation/filtration (USEPA, 2003).

When this treatment method was evaluated using Danvers, Illinois, groundwater, it was found that oxidation of As(III) to As(V) could be achieved with a relatively low hydrogen peroxide dose [27 micromolar (μM) or 0.9 milligrams/liter (mg/L)], but little of the total

arsenic was removed by adsorption to the HFO that was formed when the iron was oxidized. It is known that other solutes in groundwater, such as bicarbonate, phosphate, silicate (Appelo et al., 2002; Manning and Goldberg, 1996; Swedlund and Webster, 1999) and natural organic material (NOM) (Simeoni et al., 2003), compete with arsenic for adsorption sites, thereby decreasing arsenic adsorption (see Peyton et al., 2006, Appendix A for a more detailed discussion). It was found in the previous project that addition of Fe(III) to the water greatly improved arsenic removal by oxidation followed by filtration, most likely by providing more adsorption sites to accommodate the more weakly adsorbed arsenic. It also was found that while the arsenic could be removed to below the 10 µg/L MCL just by adding more iron before aeration/filtration (i.e., no addition of hydrogen peroxide), this method required more iron and consequently had a higher chemical cost than when peroxide was added as well. Chemical costs for peroxide and iron addition to reduce the arsenic concentration to 6 µg/L (well below the MCL) were estimated to be about \$0.07/thousand gallons (kgal). In addition, the use of iron and hydrogen peroxide does not involve major modification of existing water treatment plants that already remove iron.

Because of the success of this treatment for Danvers water during the pilot experiments, it was desirable to determine whether the process was also effective in treating water from other drinking water sources, and to determine whether, why, and to what extent treatment success correlated with various water quality parameters. In the present work, raw waters from two other drinking water treatment plants, as well as from the Danvers plant after the water was apparently exposed to air were used to evaluate the effectiveness of the Fenton/filtration process for arsenic removal.

MATERIALS AND METHODS

Water Sources

Raw groundwater was obtained from the well heads at water treatment plants located at Danvers, Monticello, and Dwight, Illinois. One goal of the project was to determine which water quality characteristics had positive or negative effects on arsenic removal using the Fenton/filtration process. These three waters were chosen because they had significantly different dissolved organic carbon (DOC) content, one (Dwight) had a lower silicon (i.e., silicate) content, and one (Danvers) had higher alkalinity, while all three contained similar phosphate concentrations (Table 1). Both DOC and bicarbonate may be important because they can serve as scavengers for any reactive oxidizing species produced by the Fenton reaction, in competition with As(III), thereby reducing the efficiency of its oxidation to As(V). Silicate, bicarbonate, and phosphate are known to reduce the adsorption efficiency of arsenic. The experiments using Danvers and Monticello waters were performed on a side stream at the well head in the water treatment plants, while the experiments using Dwight water were performed in the laboratory on water samples that were collected anoxically (air excluded) and brought back from the treatment plant.

Table 1. Composition of Waters Used in Experiments.

Sample		pH (in lab)	NVOC, mg/L	Alkalinity, mg/L, as CaCO ₃	Iron by ICP ^a , mg/L	Ortho- phosphate, mg P/L	P by ICP, mg P/L	Si by ICP, mg/L
	MDL:		0.21	4	0.015	0.02	0.13	0.086
Danvers A	raw	7.65	13.4	490	1.45	n/a ^b	0.47	6.79
	treated	8.09	12.1	431	0.03	n/a	<0.13	6.05
	finished ^c	7.78	12.6	544	0.098	n/a	<0.13	8.18
Danvers B		7.9	14.1	467	0.48	0.40	0.49	6.37
Monticello	raw	7.91	2.70	357	2.38	0.14	<0.13	6.26
	treated	8.17	2.31	319	0.035	<0.02	<0.13	5.47
Dwight	raw	8.07	10.22	355	1.65	0.46	0.31	3.96
Notes: ^a ICP = inductively-coupled plasma, ^b n/a=no sample analyzed, ^c Danvers finished water from the treatment plant,								

Chemicals

All chemicals used were of reagent grade unless otherwise mentioned, and were used as received without further purification. Ferric chloride solution (40% w/v), ferrous sulfate heptahydrate (101.5%), glacial acetic acid (99.5%), hydrogen peroxide (30%), concentrated hydrochloric acid (37%), concentrated sulfuric acid (95-98%), and concentrated nitric acid (69-71%) were obtained from Fisher Scientific. Ferrous ammonium sulfate hexahydrate (98.5-101.5%) and sodium hydroxide (97%) were obtained from EM Science. Ammonium acetate (98.4%) was obtained from Acros. Laboratory water was from a Milli-Q system with ion exchange and a carbon canister.

Analytical Methods

Analytical methods and sample preservation are described in detail in the previous report (Peyton et al., 2006). Arsenic was determined by graphite furnace atomic absorption spectrophotometry (GFAAS) using Palladium as a matrix modifier (Welz and Schlemmer, 1988). As(III) and As(V) were separated by an ion exchange procedure (Edwards et al., 1988). Dissolved and total iron (II) and (III) were determined by the ferrozine method of Viollier et al., (2000). This method was shown to give more reliable measurement than the phenanthroline method, which suffered from Fe(III) reduction to Fe(II) on a time scale of minutes after the color was developed in some samples. Stock solutions of hydrogen peroxide for dosing during an experiment were assayed by a modification of the titanium (IV) method of Parker (1928). Dissolved oxygen (DO) was measured using an Orion Oxygen Meter model 820. The pH of aqueous solutions was measured using an Orion pH Meter model 920A, with calibration at two points.

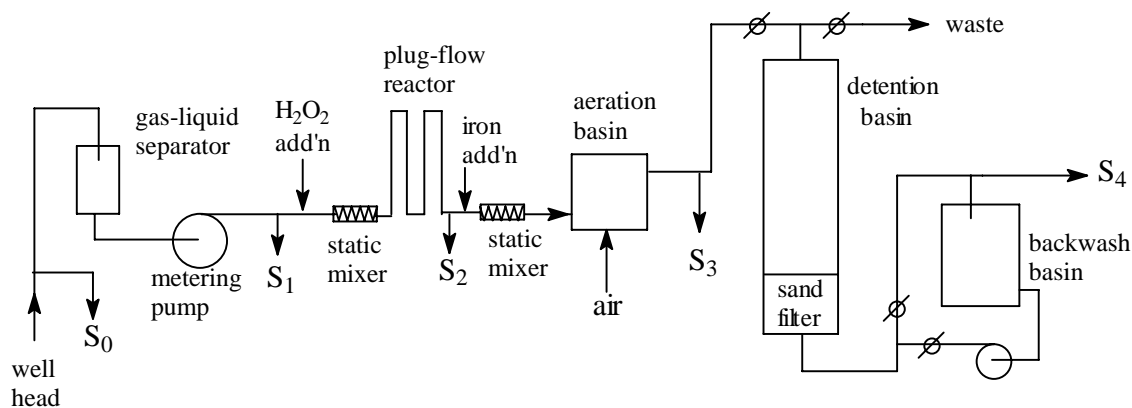


Figure 1. Schematic of the pilot plant used on-site for these studies. S₀ through S₄ are sampling points.

Experimental Procedures

Pilot experiments were conducted out at the Danvers and Monticello water treatment plants. The pilot plant and procedures are described in detail elsewhere (Peyton et al., 2006). The configuration of the pilot plant is shown in Figure 1. Raw water was sampled at sampling point S₁ before hydrogen peroxide addition. The water was passed through a static mixer and PVC plug-flow reactor to allow time (about 1.5 minutes) for the peroxide and Fe(II) to react. The pilot plant was operated for a length of time equal to at least the sum of three times the average hydraulic residence times (volume/flow) for each unit process (approximately 1.5-2 hours) before samples were taken at all sampling points. Iron samples were withdrawn by syringe and placed (or 0.22 μ m-filtered, in the case of dissolved iron analysis) directly into polyethylene bottles containing the Ferrozine reagent A and returned to the laboratory for analysis. Arsenic speciation by ion exchange was performed at the water plant, either immediately after sample collection or at the conclusion of the experiment, to eliminate concerns about changes in speciation during the time between sampling and analysis. Separated samples were returned to the laboratory for total arsenic analysis by GFAAS.

Batch experiments using water from the Dwight municipal drinking water treatment plant were carried out in the laboratory. These experiments were performed under anoxic conditions (under nitrogen) to avoid oxidation of the Fe(II) by air, because the Fenton reaction relies on the presence of Fe(II) to react with hydrogen peroxide. A nitrogen-filled glove bag proved unsuitable for this purpose. Therefore, an experimental procedure was devised in which liquid was transferred through tubing between nitrogen-preflushed vessels (bottles and syringes) by applying a slight nitrogen pressure (1-3 psi). Acid-cleaned amber bottles with septum caps were used as reactors. A water bubbler was incorporated into the nitrogen line to avoid overpressurizing the reaction vessels.

Samples of the raw water for the batch experiments were collected at the well head in 250-mL, 1-L, and 4-L bottles, depending on their intended use, by placing the end of the tygon sampling tube in the bottom of the bottle and overflowing the sample bottles by several bottle volumes, to ensure an anoxic sample. Samples for use in batch experiments were collected in septum-capped bottles that already contained magnetic stirring bars to avoid having to open the bottle before an experiment. The occasional sample into which air had leaked or diffused (as determined by depletion of Fe(II) identified at the time of an experiment) was discarded. A great variation in the suitability of various septa and bottles for this purpose was noted, and polyethylene caps with silicone septa were found not to be suitable for storage longer than a few days. No preservatives of any kind were used in the water samples to be returned to the laboratory for experiments because of the changes in water chemistry which would result, from the point of both iron complexation and reactive species scavenging. Even relatively stable anions such as phosphate, sulfate, and chloride can react with hydroxyl radicals to produce radical ions. Samples were stored at 4°C and discarded when significant changes were observed.

A few months after the results presented in Peyton et al., (2006) were obtained, additional raw water samples were taken from the well head at the Danvers plant. Chemical analysis showed very little Fe(II) present in the water (0.23 ± 0.20 mg/L average) and DO concentrations of a few tenths of a mg/L. Previous samples had contained about 2 mg/L Fe(II) and no measurable DO. The most likely reason for these changes was a leak in the pump discharge pipe, a common problem in high-capacity wells. Because it was reasonable to think that other treatment plants could experience the same conditions, another series of experiments was conducted using this “preoxidized” raw groundwater. Because the Fe(II) was already depleted in the water, Fe(II) was added during the treatment experiments, instead of Fe(III) as in the earlier tests using anoxic Danvers water, to enable the Fenton reaction. This set of experiments is referred to as Set B of the Danvers experiments, and the previous set is called Set A when shown for comparison in this report.

RESULTS AND DISCUSSION

Pilot Experiments using Monticello Groundwater

A series of 20 experiments was conducted at the Municipal Drinking Water Treatment Plant in Monticello from October 2005 to June 2006. The DOC content in Monticello groundwater was considerably lower (2.7 mg/L) than in either Danvers (13.4 mg/L) or Dwight (10.2 mg/L) groundwater, so it was expected that less peroxide would be required for As(III) oxidation in Monticello water due to less competition for the reactive species. In addition, less competition from DOC, alkalinity, or phosphate for adsorption sites on the HFO precipitate was anticipated. Due to the results from the Danvers waters (discussed below), both Fe(II) and Fe(III) addition were investigated. As before, when Fe(III) was added, it was introduced after sampling point S₂ while peroxide was added between S₁ and S₂. When Fe(II) was used, however, it was added between S₁ and the

peroxide addition point, so that it would be present in the water when the peroxide was added. Fe(III) was added as ferric chloride solution and Fe(II) was added as ferrous sulfate solution.

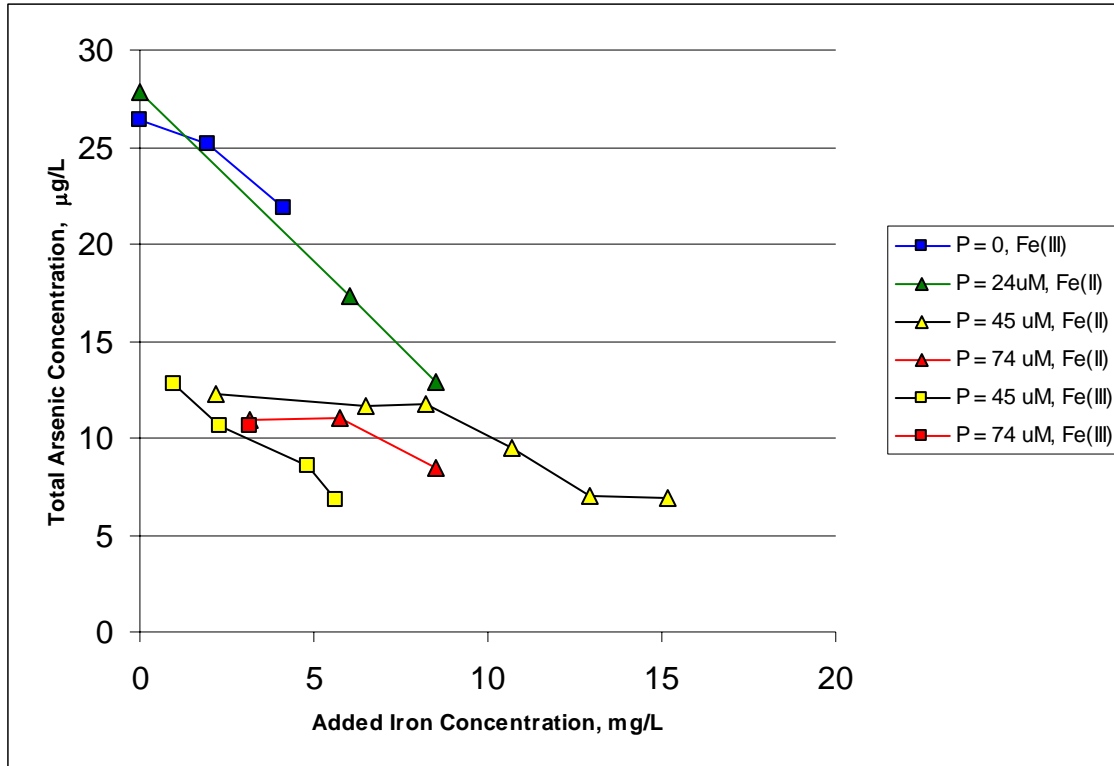


Figure 2. Total arsenic remaining after treatment of Monticello raw water with various peroxide (P) and iron Fe(II) or Fe(III) doses. Peroxide doses in legend are nominal.

Results of pilot experiments performed using Monticello water are shown in Figure 2, where remaining total (unfiltered) arsenic in the effluent is plotted versus the amount of iron added. Total arsenic concentrations in the influent raw water averaged 48.8 ± 7.0 $\mu\text{g/L}$ over the course of these experiments (8 months). The point plotted at zero added iron concentration with a peroxide dose of zero is for water that passed through the pilot plant and underwent aeration and iron removal with no addition of chemicals. This served as the control experiment. A peroxide dose of $20 \mu\text{M}$ (0.7 mg/L) was used as the starting point in early experiments, based on the results obtained using Danvers water. Remaining arsenic was about $13 \mu\text{g/L}$ after an Fe(II) dose of about 8 mg/L was used with this peroxide concentration. When the peroxide dose was increased to $45 \mu\text{M}$ (1.5 mg/L), an Fe(II) dose of about 11 mg/L was adequate to reach the $10 \mu\text{g/L}$ MCL. Interestingly, a 2 mg/L iron dose was almost as effective as the 11 mg/L iron dose using a $45 \mu\text{M}$ peroxide dose. Similar behavior was noted with a higher dose of $70 \mu\text{M}$ (2.4 mg/L) peroxide, which required an Fe(II) dose of about 7 mg/L to reach the MCL of $10 \mu\text{g/L}$, but iron doses of 3.2 and 5.8 mg/L left only $11 \mu\text{g/L}$ of arsenic. The appearance of this plateau just above $10 \mu\text{g/L}$ in the data for the 45 and $70 \mu\text{M}$ peroxide points is noteworthy.

When a 45 μM peroxide dose was tried with Fe(III) addition instead of Fe(II), only about 3 mg/L of Fe(III) was required to reach the MCL. Thus, addition of Fe(III) results in more efficient arsenic removal than does the use of Fe(II). This is in contrast to the findings of Roberts et al., (2004), who reported better adsorption of arsenic to HFO when the HFO was generated from Fe(II) than from Fe(III). However, the synthetic groundwater used by those investigators contained no organic matter. The single $P=70$ μM point falls close to that for $P=45$ μM and 3 mg/L added iron.

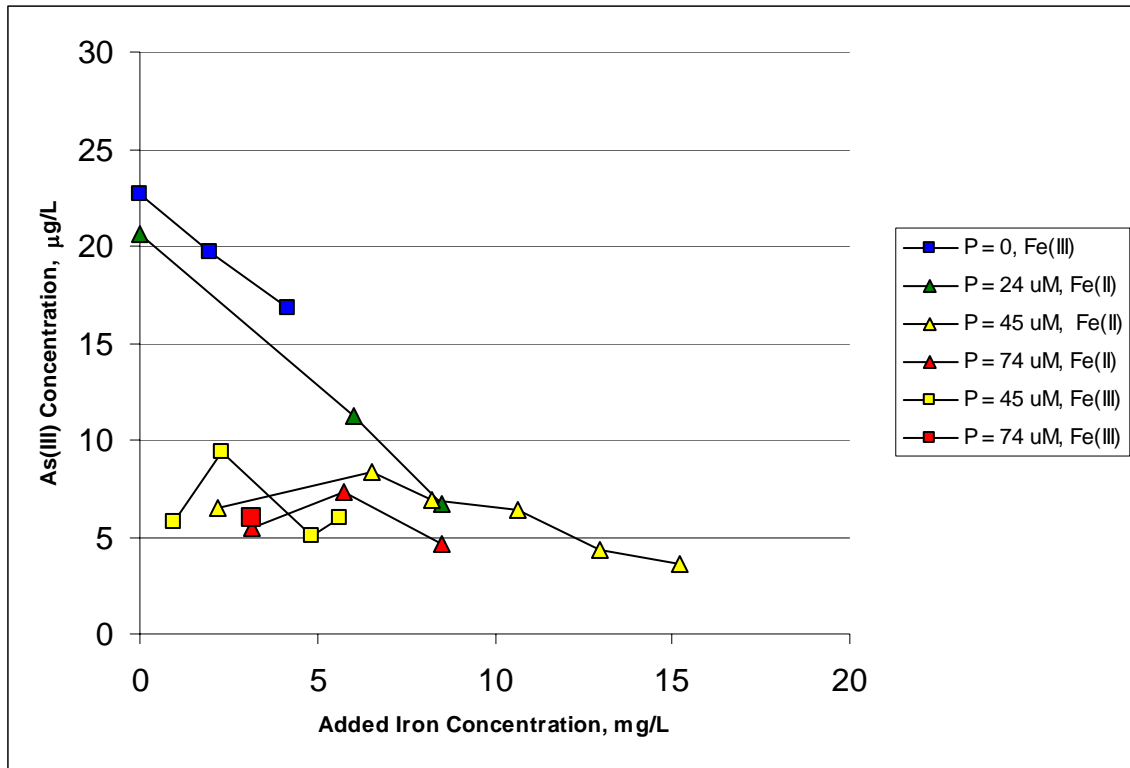


Figure 3. As(III) remaining in effluent (sampling point S₄) after treatment of Monticello raw water with various peroxide and Fe(II) or Fe(III) doses. Peroxide concentrations in legend are nominal.

Figure 3 shows a similar plot for As(III) remaining in the effluent, as a function of added iron dose. This plot shows a correlation between As(III) removal (i.e., oxidation) and peroxide dose, and may be expected to favor Fe(II) addition over that of Fe(III) because Fe(II) participates in the Fenton reaction. However, Fe(III) appears to do as well as, or better than Fe(II). In order to separate the influence of various possible effects, As(III) removal between sampling points S₁ and S₂ (where most of the rapid Fenton reaction is expected to occur) was plotted four different ways: As(III) remaining at sampling point S₂; As(III) removed across S₁ to S₂ (because peroxide was added between S₁ and S₂); the fraction of the As(III) concentration at S₁, that still remained at S₂; and the natural logarithm (ln) of the fraction remaining. All plots gave reasonable linear correlations, but the curves with the lowest residuals were the fraction of As(III) remaining, as shown in Figure 4 (a similar curve for the Danvers Set A data is shown in Figure 14, Peyton et al.,

2006), and the natural log of the fraction (not shown). Linear correlation with the log plot would be expected if the As(III) were competing with other solutes such as DOC and bicarbonate for reactive species. Because the concentrations of DOC and bicarbonate are high, compared to that of arsenic, the As(III) removal would be expected to exhibit approximately first-order behavior.

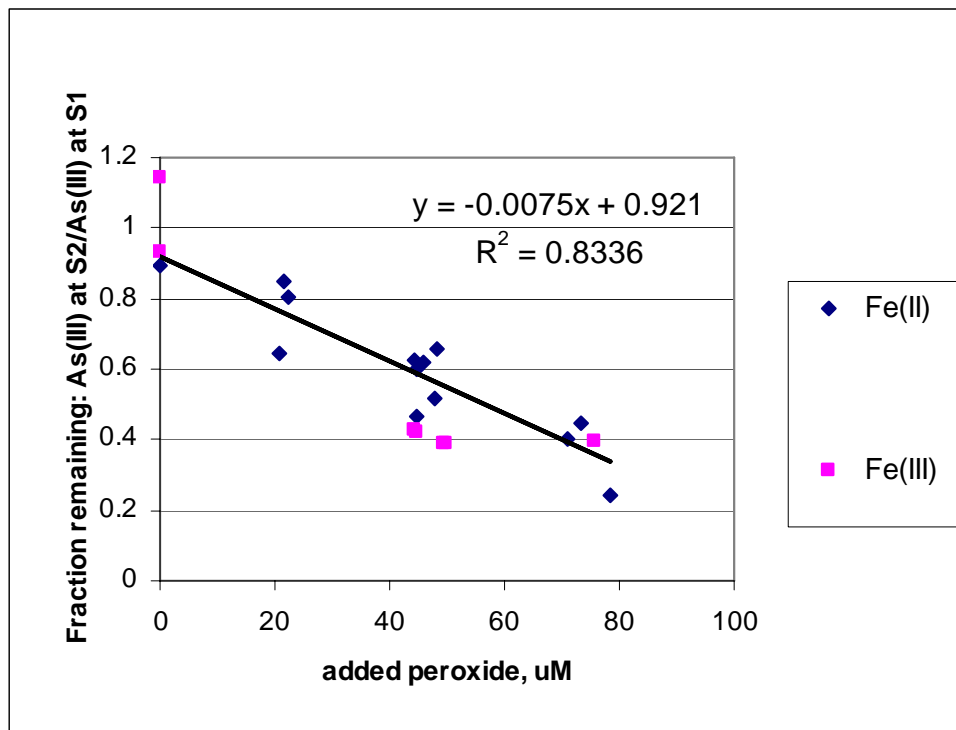


Figure 4. Fraction of As(III) remaining at sampling point S₂ after Fe(II)/H₂O₂ treatment of Monticello raw water. Linear regression line for Fe(II) is shown.

In summary, Monticello groundwater containing 2.7 mg/L of DOC required higher peroxide and iron doses than did the original Danvers water that contained 13 mg/L DOC, when Fe(II) was used in the Monticello water. In contrast, when Fe(III) was used, an iron dose of 5.5 mg/L and a 45 μ M peroxide dose reduced the total arsenic concentration to 6.8 μ g/L, and only about 3 mg/L of Fe(III) was required to reach the MCL. The reason for more efficient arsenic removal when Fe(III) is used rather than Fe(II) is discussed below.

Laboratory batch Experiments using Dwight Groundwater

A set of 20 laboratory batch experiments was performed using various iron and peroxide doses. Preparations for the experiments were conducted under anoxic conditions using nitrogen gas to move water and reagents between nitrogen-flushed vessels, to avoid any oxidation of Fe(II) in the samples until the peroxide was added.

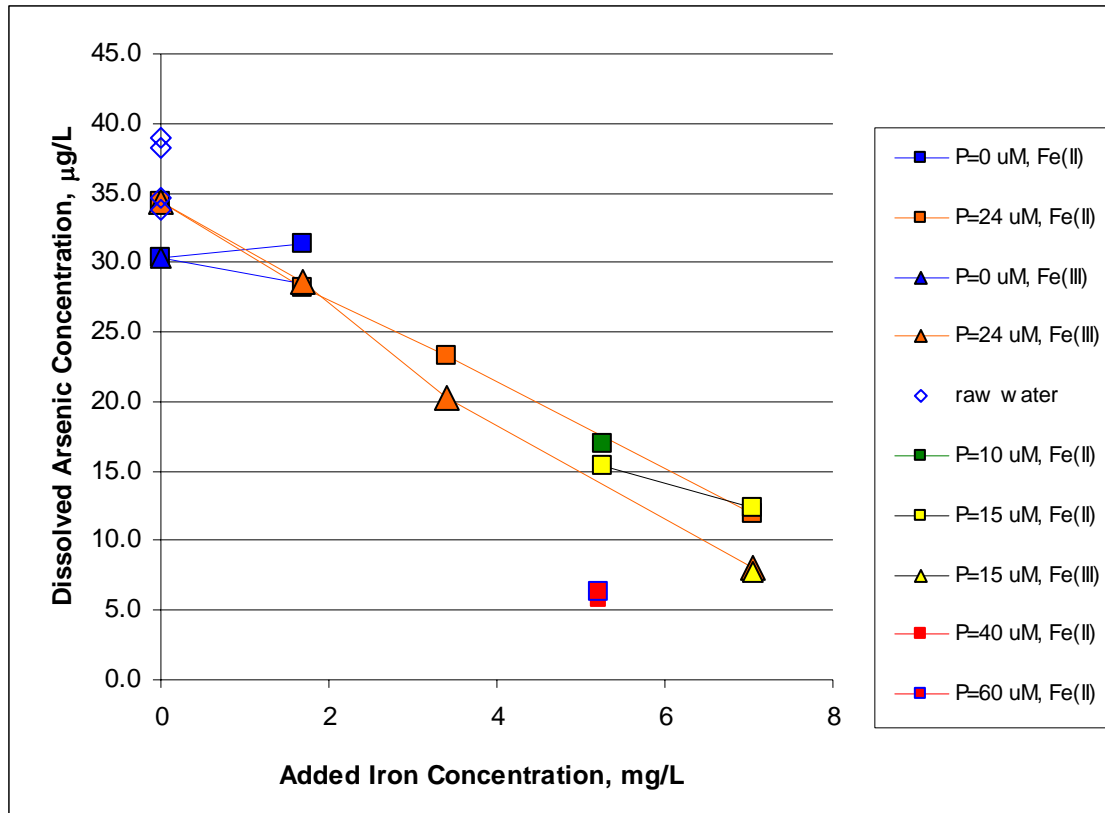


Figure 5. Dissolved arsenic remaining in Dwight ground water after treatment. Peroxide dose (P) and iron form [Fe(II) or Fe(III)] are listed in legend.

The results of these experiments are shown in Figure 5. The starting point for these experiments was a peroxide dose of 20 μM , in combination with Fe(II) and Fe(III) doses spanning the range of 0 to 7 mg/L. Arsenic removal was similar for Fe(II) and Fe(III) at low iron doses, but Fe(III) achieved somewhat greater arsenic removal at higher doses, reducing the dissolved arsenic concentration to about 8 $\mu\text{g/L}$ using 7 mg/L of added Fe(III) and either 15 or 20 μM peroxide. Dissolved arsenic (0.2 μm filtered) was used as the laboratory surrogate measurement to represent total arsenic after sand filtration. Under the same conditions but using Fe(II), dissolved arsenic was brought down to about 12 $\mu\text{g/L}$. Higher peroxide doses were effective using Fe(II), and dissolved arsenic was reduced to about 6 $\mu\text{g/L}$ by either 40 or 60 μM (1.4 and 2.0 mg/L) peroxide and 5.2 mg/L of added Fe(II).

Pilot Experiments using Danvers Groundwater

The results of treatment of Danvers groundwater in the previous project (Set A) and after apparent preoxidation in this project (Set B) are compared in Figure 6, which is a plot of the concentration of total arsenic remaining after treatment versus the amount of iron

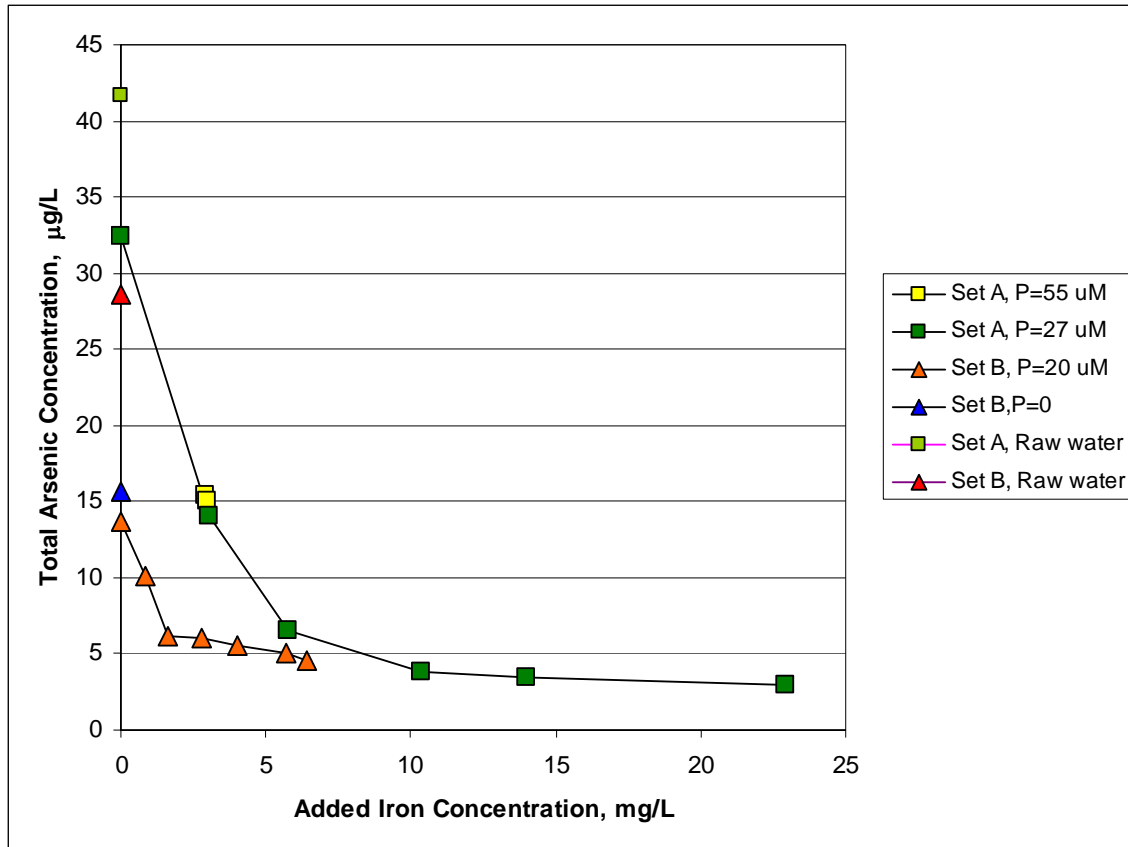


Figure 6. Comparison of Danvers Set A and Set B experiments.

added to the water. The peroxide dose used was 20 μM nominal ($21.6 \pm 1.3 \mu\text{M}$) in all Set B experiments except the control ($\text{Fe}=0$, $\text{H}_2\text{O}_2=0$), and the iron was added as Fe(II). Set A results are shown for nominal peroxide doses of 27 μM and 55 μM , using Fe(III). Use of a higher peroxide dose (55 μM) in the Danvers Set A water gave no improvement over the lower dose, in contrast to the Monticello and Dwight waters. The initial arsenic concentration in the Set B water ($28.6 \pm 6.8 \mu\text{g/L}$) was only about 70% of that found in the anoxic water used for Set A (41.7 ± 2.7). This is approximately the ratio of arsenic in treated water to that in the raw water during normal operation of this treatment plant. The concentration of Fe(II) remaining in Set B water was between 6% and 19% of the average for Set A water, except for one sample, in which 49% remained. These results are consistent with the water having come in contact with air that oxidized most of the Fe(II) to Fe(III), and as a result, removed a significant amount of the arsenic by sorption to the resulting HFO. In the course of this reaction, some phosphate and other competing anions also would be removed by adsorption to the HFO (e.g., Roberts et al., 2004), so that when iron was added during the Set B experiments, there was considerably less competition for sorption sites, and the remaining arsenic was removed more efficiently than in Set A. In summary, while in-depth interpretation of this data set is not possible because of uncertainty about what actually occurred in the water prior to these experiments, these results demonstrate that when groundwater has been exposed to air,

addition of small quantities of Fe(II) and peroxide may be sufficient to reduce the remaining arsenic below the MCL.

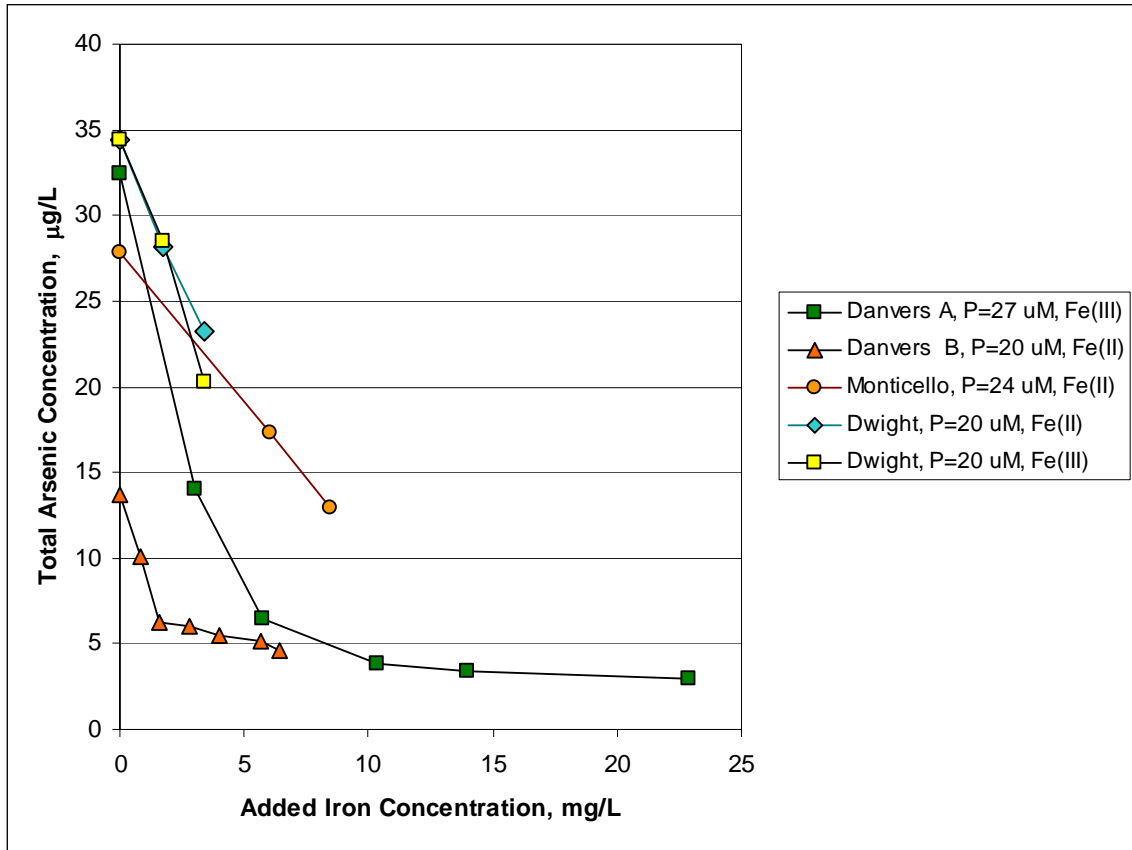


Figure 7. Comparison of arsenic removal in Dwight and Monticello water with Danvers Set A and B.

Comparison of Treatability of Danvers, Monticello, and Dwight Waters

Figure 7 shows the total arsenic concentrations (or dissolved arsenic, using Dwight water) remaining after treatment with 20-27 μM peroxide, as a function of added iron concentration, for all four experiment sets (including Danvers Set A). Iron was added as Fe(III) in the Danvers Set A waters and in some experiments that used samples from Dwight, and as Fe(II) in the Monticello, Danvers Set B, and some Dwight samples shown in this plot. Both Monticello and Dwight waters appear to be more difficult to treat using this peroxide dose than Danvers water, requiring more iron to attain the same extent of arsenic removal. Extrapolation indicates that a considerably higher iron dose would be required to reach the MCL than in Danvers water. Fe(III) appears to perform slightly better than Fe(II) in Dwight water at the higher iron concentration.

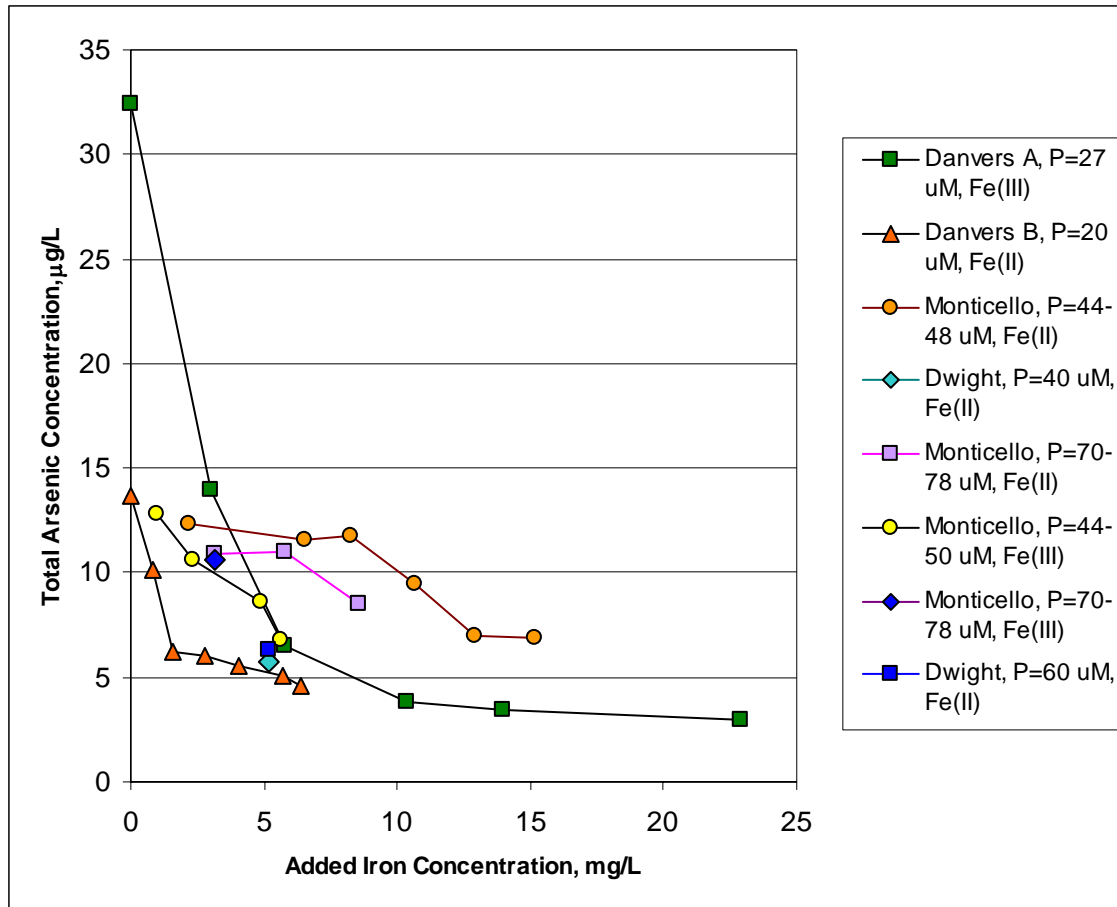


Figure 8. Arsenic removal from test waters using higher peroxide doses (40-50 μM and 70-78 μM), compared to Danvers A and B (27 μM and 20 μM , respectively).

Several experiments were performed at higher peroxide concentrations to determine whether the required iron dose could be lowered. Figure 8 shows results of experiments performed using peroxide in the 40-50 μM and 70-78 μM range in Monticello and Dwight waters, superimposed on the results obtained using Danvers waters. Very significant improvement in arsenic removal from Monticello water was achieved by using 46 or 74 (nominal) μM peroxide along with only 2-3 mg/L of Fe(II), but the removal appeared to reach a plateau just above the 10 $\mu\text{g/L}$ and the MCL was not reached until about 6.5 mg/L Fe(II) was added. This plateau might appear to be due to data scatter, had it not been present in more than one series of experiments using Monticello water (see Figure 2). It is also notable that the P=45 curve seems to merge with the P=20 curve at the point where the plateau ends (compare Figures 7 and 8). Using Fe(III) instead of Fe(II) in Monticello water, the MCL was reached with an iron dose of only about 3 mg/L (interpolated result from Figure 8) and 45-50 μM peroxide. Similarly, using 40 or 60 μM peroxide in Dwight water increased arsenic removal drastically over that obtained using 20 μM peroxide, leaving only 6 $\mu\text{g/L}$ arsenic with a 5 mg/L Fe(II) dose (see also Figure 5). These results demonstrate clear differences between the waters in their response to Fenton/filtration treatment. Peroxide concentrations higher than 20-27

μM improved arsenic removal in Monticello and Dwight water, but not in Danvers Set A water.

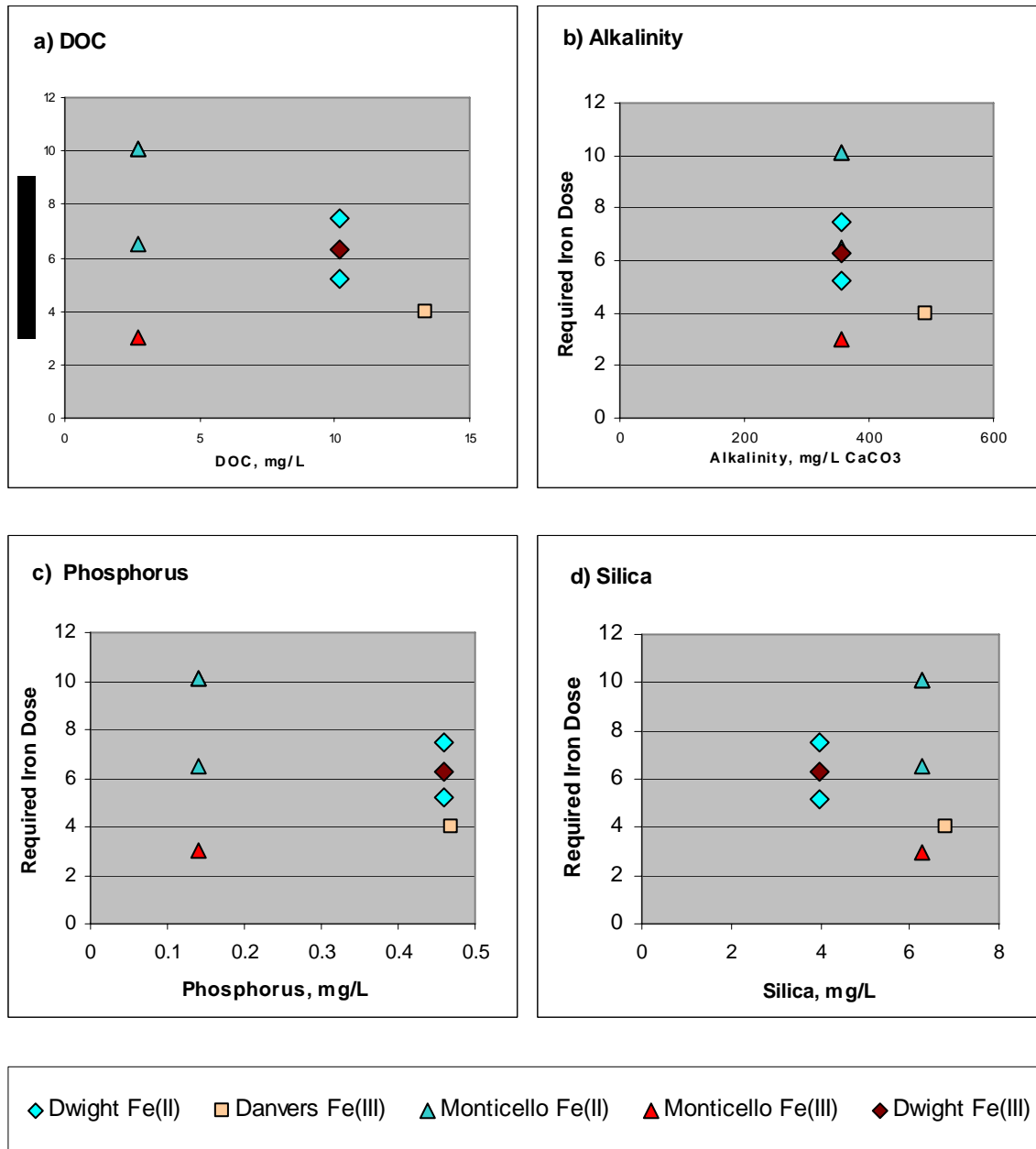


Figure 9. Effect of water composition on treatability by Fenton/filtration. DOC (a), alkalinity (b), phosphorus (c) and silica (d) may compete with arsenic for sorption sites.

It may be anticipated that because DOC and bicarbonate are known radical scavengers, As(III) oxidation may be more difficult in waters higher in DOC and/or bicarbonate. Similarly, because bicarbonate, phosphate, silicate, and DOC can interfere with arsenic adsorption to the HFO, total arsenic may be expected to be more difficult to remove from

waters high in these solutes. Waters selected for these studies were chosen using similar reasoning, with one of the three waters having a significantly different value of each water quality parameter. Danvers water was high in DOC and alkalinity, Monticello water was low in DOC and phosphorus, and Dwight water was low in silica.

In order to investigate the relationship between water composition and treatability, the iron dose required to remove total arsenic to the MCL was obtained from the figures by interpolation (or in one case, a short extrapolation) and plotted versus the four water quality parameters listed above as potential interferences with Fenton/filtration treatment. Iron doses are given in Table 2 and the plots are shown in Figure 9. The treatment of Monticello water stands out as unique, requiring the lowest iron dose of all samples when Fe(III) was used, and the highest dose when Fe(II) was used. Except for Fe(III) in Monticello water, however, Figure 9 shows a lower iron dose requirement at higher DOC, the opposite of what was expected. Similarly, except for the Fe(III) Monticello experiment, the lowest iron doses required were for the waters with the highest alkalinity (Danvers) and phosphorus (Danvers). The water with the lowest silica (Dwight) had an iron requirement about equal to the averages of the other values. The reasons for this behavior are not known, even though competition for reactive species and/or adsorption sites are well-established concepts. The results imply that more complex interactions occur between solutes and reactive species than can be accounted for by considering one solute at a time.

Table 2. Estimated Chemical Cost for Fenton/Filtration Treatment of Groundwaters Used in this Study

Water	H ₂ O ₂ Dose, mg/L (μM)	Fe(II) added, mg/L	Fe(III) added, mg/L	Estimated chemical cost, \$/(mg/L)/kgal ^a
Danvers (Set A)	0.92 (27)		4.0	0.05
Dwight	0.68 (20)	7.5		0.15
	1.36 (40)	5.2		0.11
	0.68 (20)		6.4	0.07
Monticello	0.68 (20)	10.1		0.20
	1.53 (45)	10.1		0.20
	2.38 (70)	6.5		0.14
	1.53 (45)		3.0	0.04

Notes: ^a kgal = thousand gallons

Treatment results for these waters can also be compared on an economic basis. Calculated chemical costs for treatment to the 10 μg/L MCL are also shown in Table 2, using prices from a regional supplier at the time of this report. The price of chemicals undoubtedly will change, but the estimated costs are a convenient way to compare the effectiveness of processes on the different waters. These values do not necessarily represent the best configurations for each water, but are simply configurations from which iron consumption required to reach the MCL can be determined by interpolation or short extrapolation in the figures. The cost calculated for Dwight water using 40 μM

peroxide is undoubtedly too high, because only a single point was available, at which the arsenic concentration was reduced to 6 µg/L instead of the MCL of 10 µg/L. A treatment configuration with estimated chemical costs between \$0.04 and 0.07 per thousand gallons was found for all three waters. Furthermore, all three treatments in this cost range used Fe(III) instead of Fe(II), but one used elevated peroxide doses, while the other two used higher iron doses.

Interpretation of Treatment Results

As a first approximation, Fenton/filtration can be thought of as consisting of three processes. An oxidation step converts As(III) to As(V); coprecipitation/adsorption/coagulation traps the arsenic on/in the HFO precipitate; and filtration removes iron, arsenic, and some phosphate, silicate, and NOM (natural organic material). The anions present in groundwater form complexes with iron, and the various complexes react with hydrogen peroxide at different rates to generate active species that can oxidize arsenic, iron, NOM and other solutes. Although the Fenton reaction generally has been thought to produce hydroxyl radicals (OH), there is considerable evidence (e.g., Hug and Leupin, 2003, and references therein) that other oxidants such as the Fe(IV) species ferryl (FeO^{2+}) are formed under some conditions. The ligand complexed with the iron and the pH value of the solution both appear to affect whether OH or ferryl is formed. Because these two reactive species have different reactivities, the composition of the water being treated will affect the course and efficiency of each reaction differently. Little is currently known about the Fe(IV) reactions that occur in natural waters, and very few rate constants have been measured for the reaction of ferryl with other substances, which makes kinetic modeling of potential ferryl reactions difficult and speculative. A great deal of work, however, has been done on the hydroxyl radical, including measurements of the reaction rate constants with NOM from various sources, and thousands of rate constants have been measured for the OH radical, compared to probably fewer than 100 measured rate constants for Fe(IV).

Comparison of Figures 2 and 3 indicates that total arsenic removal tracks As(III) oxidation, and that most of the arsenic remaining after treatment is As(III), which points to the need for As(III) oxidation to achieve better arsenic removal. It would be helpful to have a mathematical model based on fundamental kinetics of the system to aid in selecting efficient oxidation conditions, rather than using trial-and-error methods at the full plant scale, which can be time consuming and expensive. The As(III) is oxidized in competition with other solution components present at concentrations in the range of 0.1-1 millimolar (mM). This is considerably higher than the dose of reactive species that will be produced, which is on the same order of magnitude as the concentration of peroxide added, or 15-80 µM. Therefore, adding more peroxide will at some point yield diminishing returns with regard to As(III) oxidation, because As(III) captures a smaller fraction of the reactive species as its concentration drops. However, when a high Fe(II) dose is used, a higher peroxide dose helps by producing more reactive species. Use of a higher peroxide dose in Danvers Set A did not improve arsenic removal efficiency because there was already adequate peroxide to react with the amount of Fe(II) present [Fe(III) was added instead of Fe(II)].

Figure 4 shows that for Monticello water, the oxidation process successfully oxidizes As(III) between sampling points S₁ and S₂, with an extent of oxidation that increases with increased peroxide. A similar relationship is found for Danvers water (Figure 14, Peyton et al., 2006). More complete removal of arsenic and oxidation of As(III) was achieved when Fe(III) was used rather than Fe(II), suggesting that Fe(II) may be present in sufficient concentrations to compete for the reactive species. The As(III) is oxidized proportionately to the amount (rate x time) of reactive species generated and the fraction of those species that react with (i.e., are captured by) As(III). Using the method described in the Appendix and in more detail in Peyton et al., (1998), the fraction of hydroxyl radical captured by As(III) was calculated using the composition of Monticello water and literature values of the rate constants that are needed to calculate the fraction for various

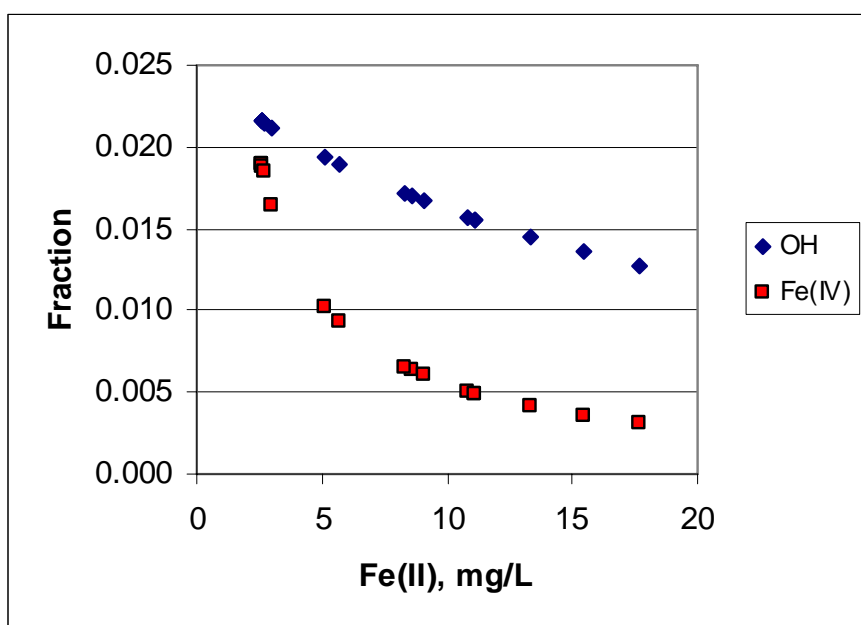


Figure 10. Fraction of reactive species captured by As(III), calculated for hydroxyl radical (OH) and ferryl [Fe(IV)].

initial Fe(II) concentrations found in the experiments (Figure 10). At higher Fe(II) concentrations, a smaller fraction of OH radical is captured by As(III) due to competition by Fe(II). A similar plot is obtained for Fe(IV) using literature values for the known rate constants and reasonable estimates for those not known. It is clear from this plot that higher Fe(II) concentrations can be detrimental to As(III) oxidation, especially in the case of Fe(IV). It should be noted that even under the best conditions shown, only about 2% of the reactive species generated goes toward oxidizing As(III).

The simplest mechanistic model (see Appendix) that could account for this competition was used to construct the three differential rate equations for Fe(II), As(III), and H₂O₂ this system, which were integrated to give the expression

$$\ln \frac{A}{A_o} = \frac{k_{XA}}{2k_{XF}} \ln \frac{\Sigma_X + 2k_{XF}F}{\Sigma_X + 2k_{XF}F_o}$$

where A_o and A and F_o and F are the As(III) and Fe(II) concentrations before and after peroxide addition, respectively; k_{XA} and k_{XF} are the reaction rate constants for the reaction of reactive species X with As(III) and Fe(II); and Σ_X is the sum of rate constant x concentration terms for each solute, except Fe(II), that competes with A for reactive species. When the hydroxyl radical or ferryl cases are being discussed, the X subscript is replaced by O or by a subscript representing Fe(IV), respectively. In the present case, Σ_X contains only DOC and bicarbonate (alkalinity) terms:

$$\Sigma_X = k_{XD}D + k_{XB}B$$

where D is DOC and B is bicarbonate. This equation predicts that a plot of $\ln(A/A_o)$ versus the log term on the right side of the equation should give a straight line through the origin. This equation should be valid for either the OH or Fe(IV) case, provided the appropriate rate constants are entered.

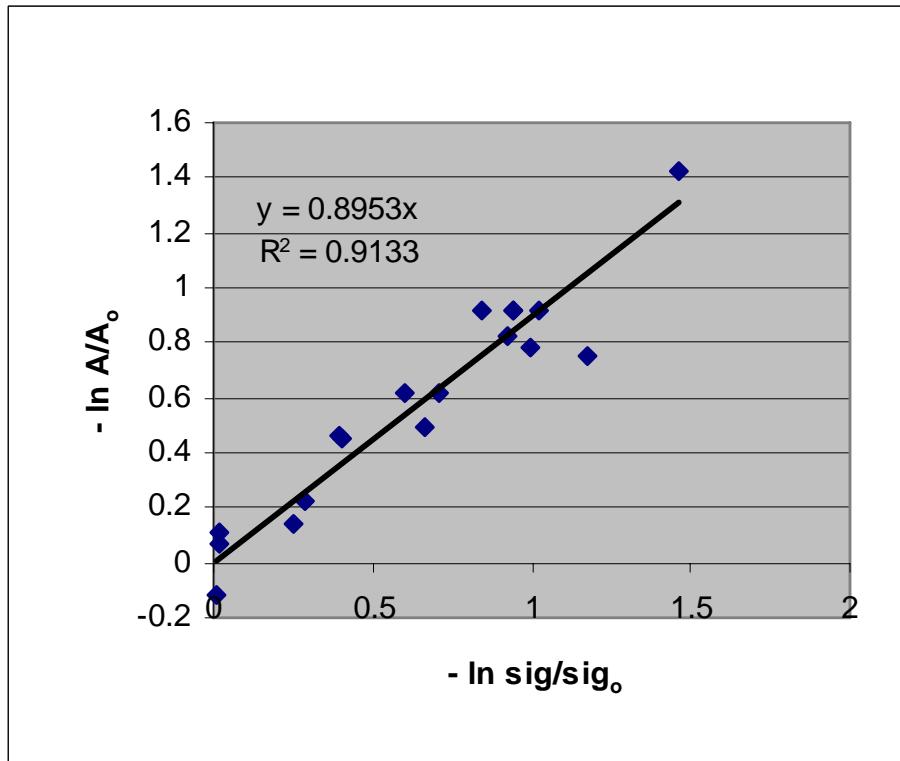


Figure 11. Monticello data plotted according to model equation. Functions sig and sig_o correspond to $\Sigma_X + 2k_{OF}F$ and $\Sigma_X + 2k_{OF}F_o$ respectively.

This plot is shown in Figure 11 for the Monticello data set assuming that the reactive species is OH radical. Variation of the Fe(II)+OH reaction rate constant to minimize the

R^2 value (0.9133) in the linear regression gave $k_{OF}=2.3 \times 10^9$ for the optimum value, compared to 3.3×10^8 for the literature value for Fe^{2+} . However, instead of being free Fe^{2+} , most of the iron in Monticello water would be complexed with inorganic anions or NOM. Since many organic complexes of iron have higher OH rate constants than that of the uncomplexed Fe^{2+} , the value determined by variation is not unreasonable. However, the slope (0.8953) is different than $k_{OA}/2k_{OF}$ (0.391) by a factor of 2.3. Iterating until the slope matched the rate constant ratio gave $k_{OF}=4.5 \times 10^8$, closer to the literature value, but a poorer R^2 value of 0.6949. Of these two cases, the minimization of R^2 giving a higher k_{OF} is considered preferable, because of the better fit to the experimental data.

A similar analysis of the data assuming Fe(IV) as the reactive species showed that this case also fits the data, using reasonable values for any unknown rate constants (data not shown), and thus this analysis does not support the assignment of one reactive species over the other. The identity will have to be determined in separate experiments.

CONCLUSIONS

1. For all four waters used, the arsenic concentration could be lowered below the 10 $\mu\text{g/L}$ MCL by treatment with hydrogen peroxide and iron, followed by filtration.
2. Estimated chemical costs to reduce total arsenic concentration to 10 $\mu\text{g/L}$ (i.e., not including any safety factor) were between \$0.04 and \$0.07 per thousand gallons of water treated for the best performing configurations for each water.
3. The use of ferric chloride and hydrogen peroxide does not involve major modification of existing water treatment plants that already perform iron removal.
4. As(V) appeared to be removed more easily than As(III). At higher removal extents, most of the remaining arsenic was As(III), supporting the need to better oxidize As(III) to achieve better arsenic removal.
5. For selecting treatment conditions, a model would be useful and preferable over trial and error, particularly at full plant scale.
6. A simple kinetic model was developed that included Fe(II) as a competitor for reactive species. The model provided a good fit to a relationship between starting and final iron and arsenic concentrations for all Monticello data, using literature values of the rate constants for OH radical. The same model also gave a good fit for the Fe(IV) case using literature values where available and reasonable estimates for the unavailable rate constants.
7. Because the model gave a good fit for both the OH and Fe(IV) cases, it could not be used to determine the identity of the reactive species, and other methods must be used.
8. The waters used differed in their ease of treatability, but in each case the least expensive configuration used Fe(III) rather than Fe(II).
9. Using an Fe(II) dose that is too high can be detrimental to As(III) oxidation. Using a peroxide dose higher than is necessary to react with all the Fe(II) present will not improve As(III) oxidation.
10. Use of peroxide doses greater than 20-27 μM (0.7-0.9 mg/L) improved arsenic removal in Monticello and Dwight water, but not in Danvers Set A water.

11. In most cases, treatability of waters did not appear to negatively correlate with NOM, alkalinity, phosphate, or silicate content of the waters. A negative correlation with treatability (i.e., a positive correlation between required iron dose and solute concentrations) was expected because of the known competition for sorption sites.

FUTURE WORK

It is clear that development of a mechanism-based kinetic model of the oxidation portion of the Fenton/filtration process can aid in its understanding and in selecting the proper chemical dosage. An essential part of that improvement would be 1) establishing whether (or under what conditions) the reactive species is hydroxyl radical and/or Fe(IV), and 2) the measurement of a few critical rate constants for use in the modeling. Similarly, development of an adsorption model would allow coupling of the two models for prediction of arsenic removals and chemical dose selection, allowing a further decrease in start-up and treatment costs.

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APPENDIX

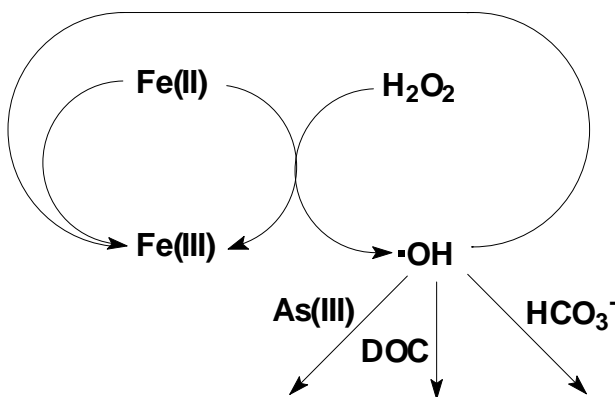
COMPETITION BETWEEN SOLUTES FOR REACTIVE SPECIES

The reactive species formed by the Fenton reaction are very reactive and are consumed almost immediately (e.g., less than a millisecond for hydroxyl radical, slower for ferryl). When solution components compete for reactive species, the fraction of reactive species consumed by each component is proportional to its concentration and rate constant for reaction. For example, the fraction of hydroxyl radical that reacts with As(III) in a solution also containing DOC, bicarbonate, and Fe(II) is

$$f_{OA} = \frac{k_{OA}A}{\sum_i k_{OM_i}M_i} = \frac{k_{OA}A}{k_{OA}A + k_{OD}D + k_{OB}B + k_{OF}F} = \frac{k_{OA}A}{\sum_i k_{OM_i}M_i} = \frac{k_{OA}A}{k'_O}$$

where k is a rate constant for the reaction of hydroxyl radical (subscript O) with As(III) (A), DOC (D), bicarbonate (B), or Fe(II) (F). Using the concentrations $A=40 \mu\text{g/L}$, $F=2 \text{ mg/L}$, $B=10 \text{ mM}$ (500 mg/L as CaCO_3), and $\text{DOC}=13 \text{ mg/L}$, along with $k_{OA}=8.5 \times 10^9$, $k_{OF}=3 \times 10^8$, $k_{OB}=8.5 \times 10^6$, and $k_{OD}=2 \times 10^4$, yields the following fractions of hydroxyl radical reaction with the various solutes at the beginning of the reaction: As(III) 1.2%, Fe(II) 3.1%, bicarbonate 23.6%, and DOC 72.1%. The symbol k'_O is a pseudo-first-order rate constant that represents the scavenging power of the water, and can be calculated if the rate constants and concentrations of the scavengers are known, as in this example.

Several observations during this project pointed to the possibility that Fe(II) could be an important competitor for reactive species in the experiments in which rather high amounts of Fe(II) were added, even though it is not particularly important in the above example. The simplest system of reactions that takes these features into account is shown in the scheme below, where the dot on OH signifies a radical species:



In this model, hydrogen peroxide reacts with Fe(II) to give the reactive species, which is shown as OH in this diagram, but could also be Fe(IV). In that case, the Fe(III) would be

generated when Fe(IV) reacted with solutes, rather than immediately upon reaction of H₂O₂ with Fe(II). Reactive species can react with DOC and bicarbonate, which capture a large portion of hydroxyl radical and are not destroyed, but reactive species can also react with As(III) and Fe(II), which are oxidized to a higher state. The rate equations for this system, ignoring secondary reactions of the products, are:

$$\frac{dA}{dt} = -f_{XA}k_{PF}PF$$

$$\frac{dF}{dt} = -(1 + f_{XF})k_{PF}PF$$

$$\frac{dP}{dt} = -k_{PF}PF$$

In these equations, A, F, and P are the molar concentrations of As(III), Fe(II), and H₂O₂, and subscripts indicate which species are reacting. The reaction P+F is the initiation reaction that forms reactive species X, and reaction of X+P can be shown to be relatively slow. These equations are easily integrated to yield the relationship

$$\ln \frac{A}{A_o} = \frac{k_{XA}}{2k_{XF}} \ln \frac{\Sigma_X + 2k_{XF}F}{\Sigma_X + 2k_{XF}F_o}$$

As(III) consumes such a small fraction of hydroxyl radical that its term in the denominator of the fractions f_{XA} and f_{XF} can be ignored. In the present case, only DOC and bicarbonate (alkalinity) terms appear in $\Sigma_X = k'_O - k_{OF}F$:

$$\Sigma_X = k_{XD}D + k_{XB}B$$

This term is constant because neither DOC nor bicarbonate are destroyed at the reactive species doses used in this work, which are small (20-70 μM, compared to 0.2-1 mM organic carbon and 6-10 mM bicarbonate).

The resulting integrated equation states that if $\ln(A/A_o)$ is plotted versus the log term on the right side, the result should be a straight line that passes through the origin and has slope = $k_{XA}/2k_{XF}$.