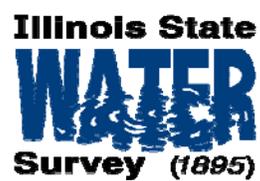SMALL PUBLIC WATER SYSTEMS

Chemical Oxidation for Arsenic Removal

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Introduction

All water utilities in Illinois that exceed the arsenic (As) maximum contaminant level also have high iron (Fe) concentrations in their source water. Some treatment plants remove Fe by oxidation of soluble ferrous iron to insoluble hydrous ferric oxide (HFO) and filtering to remove the HFO. Both As(III) and As(V) adsorb to HFO and, as a result, some As is removed in Fe-removal plants, although the As removal efficiency varies greatly (McNeill and Edwards 1995; Wilson 2004).

As one would intuitively expect, the fraction of As(III) and As(V) adsorbed to HFO increases as the Fe:As ratio increases. Therefore the ratio of Fe to As is a critical factor in As removal at Fe-removal plants. For example, Viraraghavan et al. (1999)found that a minimum Fe:As (wt:wt) ratio of 20:1 was necessary to lower the As concentration from 100 µg/L to < 20 µg/L by $KMnO_4$ oxidation and manganese greensand filtration. Wilson et al. (2004) found that As removal at Illinois water treatment plants was highly variable but generally less than 75% for Fe:As molar ratios less than ~100. For higher Fe:As values, As removal was generally better than 80% (Figure 1). These data suggest that adding Fe may improve As removal at Fe-removal plants.

Arsenic speciation affects As removal by enhanced coagulation, the addition of ferric or aluminum salts to improve particulate removal. Arsenic(V) is generally more effectively removed by coagulation than As(III) (Hering et al. 1996; Hering et al. 1997). Coagulation is generally used to treat surface water, not groundwater because turbidity is rarely an issue for groundwater. However, As(III) is usually the predominant As species in Midwestern glacial aquifers (Holm 2005; Kelly et al. 2005) and oxidation to As(V) may improve As removal at Fe-removal plants.

Oxidation of As(III) by air is a fairly slow process. For example, Hug et al. (2003) performed laboratory air oxidation experiments with As(III), Fe(II), and bicarbonate concentrations and pH values typical of groundwater and found that As(III) oxidation by air occurred on a time scale of tens of minutes. This is similar to the hydraulic residence time in an Fe-removal plant, so one would expect that As(III) might be incompletely oxidized by the time water passed through a sand filter. Arsenic(III) oxidation was found to be less than 20% in a central Illinois Fe-removal plant that uses air oxidation (Wilson 2004; Peyton et al. 2006).

In contrast to air oxidation, As(III) oxidation by $KMnO_4$ (Jekel 1994) and NaOCl (Meng et al. 2001), two common water treatment chemicals, is very rapid. Hydrogen peroxide in combination with Fe^{2+} found in As-containing groundwater also rapidly oxidizes As(III) (Peyton et al. 2006). Therefore, As removal in an Fe-removal plant may be improved by adding one of these strong oxidants. Lytle et al. (2005) found that chlorination improved arsenic removal by oxidizing

As(III). They also found that As removal was better when NaOCl was added to anoxic water than adding NaOCl to water that had already been aerated. The reason was formation of finer HFO particles with a higher specific surface area by chlorination than by aeration. As(III) is sometimes incompletely oxidized by prechlorination (NaOCl addition before aeration), probably because of a side reaction of OCl^- with NH_4-N (Ghurye and Clifford 2004; Holm 2004; Wilson 2004).

The goal of this research was to characterize the effects of added Fe(III) and two commonly used oxidants ($KMnO_4$ or NaOCl) on As removal at different Illinois water treatment plants.

Materials and Methods

Groundwater samples for laboratory experiments were collected from the water treatment plants at Kenney, Grand Ridge, and Waterman, IL in conjunction with another MTAC-sponsored project entitled "Time Series Sampling and Resampling Facilities with High Particulate Arsenic to Evaluate the Variability of Arsenic Concentration in Small Community Water Supplies." The Kenney plant uses aeration and sand filtration for Fe removal. The Grand Ridge and Waterman plants do not remove Fe but add polyphosphate to inhibit "red water" formation (ferrous iron oxidation and ferric oxide/hydroxide precipitation).

The water quality characteristics of the three groundwaters are presented in Table 1. Most of the As was in the form of As(III) for all wells. The sum of As(III) and As(V) was slightly greater than that of filtered As for two of the wells because separate samples were collected for As speciation and total dissolved As and there was some imprecision in the measurements. Waterman had the lowest As and highest Fe concentrations, which gave the most favorable Fe:As ratio.

Table 1. Water quality characteristics of Kenney, Grand Ridge, and Waterman groundwater.

	Grand Ridge[a]	Waterman[a]	Kenney[b]
As, unfiltered ($\mu g\ L^{-1}$)	47.4	17.0	35.3
As, filtered ($\mu g\ L^{-1}$)	49.9	18.2	35.0
As(III) ($\mu g\ L^{-1}$)	51.4	14.6	35.5
As(V) ($\mu g\ L^{-1}$)	2.4	1.4	2.0
Temperature (°C)	12.8	11.3	13.2
Conductivity ($\mu S\ cm^{-1}$)	598	711	878
pH	7.87	7.20	7.35
Oxidation-Reduction Potential (mV)	69	129	<95[c]
Total Organic Carbon	4.0	1.1	10.7
Fluoride	1.1	0.5	0.4
Chloride	3.6	15.7	48.2
Nitrate (as NO_3)	<0.25[d]	1.9	<0.02[d]
Sulfate (as SO_4)	<0.25[d]	47.9	<0.1[d]
Al	0.002	0.003	0.001
Na	96.2	13.6	84.5
Mg	14.3	47.1	36.1
Ca	22.7	73.3	66.8
Fe	0.69	1.66	0.66
Mn	0.03	0.02	0.02
Si	4.3	9.4	5.6
P	0.08	0.02	0.21
NH_3 (as N)	1.6	0.7	2.7
Alkalinity (as $CaCO_3$)	326	325	416

Notes: [a](Wilson 2004)
[b](Holm 2004)
[c]Potential was still decreasing after the pH, temperature, and conductivity readings had stabilized.
[d]Below detection limit.
Concentrations in mg L^{-1} except as noted.

The Kenney and Grand Ridge wells were finished in glacial aquifers and the groundwaters from these two wells generally had chemical compositions typical of glacial aquifers. Neither well had detectable sulfate or nitrate, which are usually not found with arsenic in such systems (Panno et al. 1994; Warner 2001; Holm 2005; Kelly et al. 2005). The Waterman well was finished in bedrock (sandstone). Unlike the Kenney and Grand Ridge wells, Waterman groundwater had detectable nitrate and sulfate. All three waters had moderately high NH_3-N, which may compete with As(III) for NaOCl (Ghurye and Clifford 2004).

Immediately before performing on-site experiments the Fe concentration was determined by the phenanthroline colorimetric method (Clesceri et al. 1998) using a portable colorimeter (CheMetrics). After the on-site experiments groundwater samples were collected for laboratory experiments. The sample collection procedure was designed to minimize exposure to air. A tube connected to a sample tap was used to fill glass bottles from the bottom. The bottles were allowed to overflow for 3 bottle volumes and then capped with minimal headspace. The samples were kept on ice for return to the laboratory and then kept in a cold room at 4°C.

Solutions of $FeCl_3$ (40% by wt) and $KMnO_4$ (0.01 M) were obtained from Fisher Scientific. A solution of Fe(II) (0.022M) was prepared on each day of use by dissolving $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 0.01M HCl. A solution of NaOCl (0.06M) was prepared by diluting Chlorox® bleach. The diluted NaOCl was standardized on the day of use by iodometric titration (Clesceri et al. 1998). The $FeCl_3$ stock solution (4% by wt) was standardized by titrating with standard EDTA using thiocyanate as an indicator (Butler 1964).

Sand filters were prepared by filling 60cc disposable syringes with quartz sand (0.15 – 0.35 mm, Global Drilling Suppliers). Water was pumped at a fixed rate of 45 mL min^{-1} using a peristaltic pump. The corresponding loading rate was 4.2 gal $min.^{-1} ft^{-2}$, which is typical of drinking water filtration (Cleasby 1972). Filtration efficiency improved with use (Figure 2). An HFO suspension was prepared by adding $FeCl_3$ to a $NaHCO_3$ solution (1 mM, 50 mg L^{-1} as $CaCO_3$, pH 8.3) to give a total Fe concentration of 1.8 mg L^{-1}, which is typical of Illinois groundwater. The HFO in effluent samples was reduced to Fe^{2+} for colorimetric measurement using thioglycollic acid (CheMetrics). After three or four bed volumes Fe removal was at least 95%, which is typical of Illinois Fe-removal plants. Thus, after a brief breaking in period the sand filters appeared to be representative of those in water treatment plants. A sand filter was used only once per set of experiments. The sand filters were back-washed with deionized water after each set of experiments.

Experiments involving either NaOCl or $KMnO_4$ were performed on-site at Kenney, Waterman, and Grand Ridge. The oxidant and $FeCl_3$ doses were based on the Fe concentration in the groundwater. One mole of NaOCl was assumed to be equivalent to 2 moles of Fe^{2+} (equation 1).

$$HOCl + 2Fe^{2+} + H^+ \rightarrow Cl^- + 2Fe^{3+} + H_2O$$
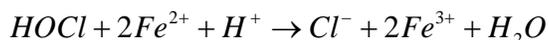
Equation 1

Similarly, one mole of $KMnO_4$ was assumed to be equivalent to 3 moles of Fe^{2+} (equation 2).

$$MnO_4^- + 3Fe^{2+} + 4H^+ \rightarrow MnO_2(s) + 3Fe^{3+} + 2H_2O$$
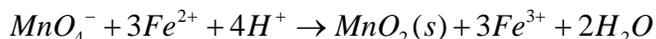
Equation 2

The molar Fe:As ratio, which was expected to be a major factor in As removal (Wilson 2004), ranged from 14 at Grand Ridge to 157 at Waterman.

For each experiment a groundwater sample was collected at the well head in a HDPE bottle and oxidant and $FeCl_3$ were added and mixed immediately (less than one minute delay). After 15 minutes (typical hydraulic residence time for an Fe-removal plant) the treated water was pumped through a sand filter. After allowing 100 mL of effluent to run to waste a 30 mL sample was collected. A syringe filter (25 mm, 0.2 μm) was then attached to the pump tubing and a filtered sample was collected.

For the laboratory experiments precautions were taken to minimize exposure of the water samples to air. A silicone stopper with a glass tube was inserted in the mouth of the sample bottle and the tube was flushed with N_2. Water was pumped from the sample bottle to HDPE bottles for treatment. The water flow rate was less than 20% of the N_2 flow rate to exclude air. As in the on-site experiments the time between chemical addition and filtration was 15 minutes. Because of sample volume limitations, only membrane filters were used in the laboratory experiments.

In addition to NaOCl and $KMnO_4$ addition, laboratory aeration experiments were performed to provide a basis for comparison. Filtered compressed air was bubbled through a groundwater sample for 15 minutes at 150 cm^3 min^{-1}. The dissolved O_2 concentration approached the saturation value after 8-10 minutes (Figure 3) so it was felt that the aeration experiments were at least a fair simulation of an aeration plant. The chemical doses used in the on-site and laboratory experiments are presented in Appendix A. As in the other experiments, the aeration time was 15 minutes. A filtered sample taken at the end of one aeration run had no detectable Fe, so the 15 minute aeration time appeared to be adequate.

In the laboratory experiments arsenic species were separated using arsenic speciation cartridges obtained from X. Meng, Stevens Institute of Technology (http://personal.stevens.edu/~xmeng/technologies%20developed.htm). Filtered (0.2 μm) water was pumped through the cartridges at the recommended flow rate of 20 mL min^{-1}. The cartridges retained As(V) and let As(III) pass through. The As(V) concentration is calculated by difference between total As and As(III). In each set of experiments at least one set of duplicate samples was collected to assess overall precision (sampling, storage, and analysis).

All water samples were preserved with 0.2% (v/v) HNO_3 (0.032M).

Arsenic concentrations were determined by graphite furnace atomic absorption spectrophotometry using Pd as a matrix modifier (Welz et al. 1988). The method detection limit (MDL) (Glaser et al. 1981) ranged from 0.5-1.0 μg L^{-1}. Concentrations below the MDL are considered not significantly different from zero. The corresponding practical quantitation level (PQL) of roughly five times the MDL (Clesceri et al. 1998) was 2.5 - 5.0 μg L^{-1}. Concentrations

between the MDL and PQL are considered highly uncertain. For each batch of samples (~20 samples) 4 samples were run in duplicate to assess analytical precision and 2 samples were spiked to assess any matrix effects. A calibration verification standard, which was from a different source than the calibration standards, was run after every calibration and at the end of every batch.

Results and Discussion

The Fe concentration measured on-site at Kenney was 1.85 mg L^{-1}, which was significantly higher than the concentration measured in an earlier study (Table 1) (Holm 2004). The reason for the difference is unknown. However, Fe concentrations greater than 1.5 mg L^{-1} were consistently measured in the laboratory experiments. Both KMnO$_4$ and NaOCl lowered As concentrations in the Kenney on-site experiments (Figure 4). For no added FeCl$_3$, a higher dose of either oxidant resulted in a lower As concentration. Adding ~2 mg L^{-1} Fe lowered the As concentration below the MCL for both oxidants. Increasing the Fe dose to ~4 mg L^{-1} produced a modest reduction in the As level. Samples filtered with a 0.2 μm membrane filter had somewhat lower As concentrations than for the sand filters (Figure 5). Therefore there appeared to be some particulate/colloidal As in the sand filter effluent.

Aeration caused only a modest lowering of As concentrations in the Kenney laboratory experiments (Figure 6). The filtered As concentrations for no added Fe were very close to that for the Kenney water treatment plant (Holm 2004). Adding FeCl$_3$ improved As removal somewhat but even for ~4 mg L^{-1} added Fe the As concentration was well over the MCL. Duplicate experiments were run for 0 and 2.2 mg L^{-1} added Fe. Reproducibility was good, particularly for 2.2 mg L^{-1} added Fe. Essentially all of the As in the raw water was As(III). Aeration oxidized less than 20% of the As(III) to As(V).

Two KMnO$_4$ doses were used in the Kenney laboratory experiments. The lower dose, 1.9 mg L^{-1}, was equivalent to 90% of the Fe concentration while the higher dose of 3.2 mg L^{-1} was in excess of the Fe(II) demand. For no added Fe, the filtered As concentration was lowered to the MCL (Figure 7). For 1 mg L^{-1} added Fe filtered As was well below the MCL and for 2 mg L^{-1} it was less than 5 μg L^{-1}. There were no significant differences in filtered As concentrations at any FeCl$_3$ dose for the two KMnO$_4$ doses. In all filtered/anion exchange samples As was below the MDL. Therefore, As(III) was essentially completely oxidized by both KMnO$_4$ doses.

Two sets of experiments were performed with Kenney groundwater and NaOCl as oxidant. In the first set most results were as expected (Figure 8). For no added FeCl$_3$, 1.9 mg L^{-1} NaOCl (equivalent to roughly twice the Fe(II)) removed ~40% of the As while 5.1 mg L^{-1} NaOCl removed ~70%. The As removal improved as more FeCl$_3$ was added; for every FeCl$_3$ dose the remaining filtered As concentration was lower for 5.1 mg L^{-1} NaOCl dose than for 1.9 mg L^{-1}. For every treatment the As(III) concentration was lower than the filtered As concentration. However, some results were unexpected. The filtered As concentrations for 5.1 mg L^{-1} NaOCland 0 and 1 mg L^{-1} added Fe were about the same. By comparison, for 0 and 2 mg L^{-1} added Fe the filtered As concentration for 5.1 mg L^{-1} NaOCl and 1 mg L^{-1} added Fe was considerable higher than for 0 and 2 mg L^{-1} added Fe. The unexpected results may have been caused by sampling or labeling errors.

Because of the ambiguities in the first set of Kenney NaOCl experiments a second set was performed. In these experiments filtered As decreased in a regular fashion as the FeCl$_3$ dose increased and filtered As was lower for 5.3 mg L^{-1} NaOCl than for 2.1 mg L^{-1} for both FeCl$_3$ doses (Figure 9). For 2.1 mg L^{-1} NaOCl As(III) decreased only slightly as the FeCl$_3$ dose

increased. As(III) was almost completely oxidized by 5.3 mg L^{-1} NaOCl. (It was below the GFAAS detection level in both samples.) There was generally good agreement between the two sets of Kenney NaOCl experiments for all combinations of NaOCl and FeCl$_3$ doses. Figures 10 and 11 show the suspected outliers for filtered As and As(III) (from the same experiment).

Despite the "excess" NaOCl (compared to Fe^{2+}), As(III) oxidation was incomplete for the lower NaOCl dose. The most likely reason is that the NaOCl dose calculation did not consider NH$_3$-N. It is widely known that OCl$^-$ reacts with aqueous NH$_3$ to form chloramine (equation 3) (Jafvert and Valentine 1987; Jafvert and Valentine 1992).

$$NH_3(aq) + HOCl \rightarrow NH_2Cl + H_2O$$
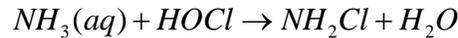
Equation 3

Incomplete oxidation of As(III) by NaOCl in the presence of NH$_3$-N has been observed in laboratory experiments (Ghurye and Clifford 2004) and in water treatment plants (Holm 2004; Wilson 2004). NaOCl also reacts with natural organic matter (NOM) to form chloroform and other disinfection by-products (Singer 1993; Trussell 1993; Richardson 1998). Reaction with NOM may be another reason for incomplete oxidation of As(III) by NaOCl.

The molar ratio of NH$_3$-N to Fe^{2+} for Kenney groundwater was approximately 6. Therefore, even though 5.1 mg L^{-1} NaOCl was equivalent to 5 times the Fe^{2+}, it was less than the sum of Fe^{2+} and NH$_3$-N. Figure 12 shows the percent reduction in As(III) concentration (equation 4) as a function of both the molar ratio of NaOCl to Fe^{2+} + NH$_3$-N (equation 5) and the molar ratio of total Fe (groundwater Fe^{2+} + added FeCl$_3$) to As in untreated groundwater (equation 6). The former ratio is expected to relate to oxidation while the latter ratio relates to adsorption. For the lower range of oxidant-to-reductant ratios As(III) removal increased with increasing Fe:As, probably because of adsorption of some of the residual As(III) to HFO. For the higher range of oxidant-to-reductant ratio, on the other hand, As(III) removal was nearly complete.

$$Percent\ change\ in\ As(III) = \frac{[As(III)]_{raw} - [As(III)]_{treated}}{[As(III)]_{raw}}$$

Equation 4

$$Ratio\ of\ NaOCl\ to\ Fe + NH_3 - N = \frac{2[NaOCl]_{added}}{[Fe]_{gndwtr} + 2[NH_3 - N]_{gdwtr}}$$

Equation 5

$$Ratio\ of\ Fe\ to\ As = \frac{[Fe]_{gdwtr} + [FeCl_3]_{added}}{[As]_{gdwtr}}$$

Equation 6

In equations 4-6 square brackets indicate molar concentrations. One mole of NaOCl oxidizes 2 moles of Fe^{2+} or 1 mole of NH$_3$-N (equations 1 and 3).

On-site and laboratory experiments with roughly the same $KMnO_4$ and $FeCl_3$ doses had similar remaining filtered As concentrations (Table 2). The differences between on-site and laboratory experiments were generally on the order of the differences between duplicate experiments (same symbol and same Fe dose on the same graph, Figures 6-9). Therefore, the groundwater samples were chemically stable during the storage time of 9-14 days and the on-site and laboratory experiments were comparable.

Table 2. Summary of Kenney on-site experiments.

Oxidant	Fe dose (mg L^{-1})	Oxidant Dose (mg L^{-1})[a]	Remaining Arsenic (μg L^{-1})	
			Sand Filter	Membrane Filter (0.2 μm)
$KMnO_4$	1.1	0.0	16.2	13.8
$KMnO_4$	1.6	0.0	10.6	7.9
$KMnO_4$	1.1	1.9	6.6	5.2
$KMnO_4$	1.6	1.9	5.5	2.1
NaOCl	2.5	0.0	19.7	15.8
NaOCl	5.1	0.0	14.0	9.2
NaOCl	5.1	1.9	4.6	2.4
NaOCl	5.1	3.8	3.2	1.5
—[b]	--	--	--	40.0

Notes: [a]Concentration units for oxidant doses are mg L^{-1} as $KMnO_4$ or as Cl_2.
      [b]Raw water.

The Grand Ridge groundwater had a similar As concentration to Kenney (47 μg L^{-1}) but a lower Fe concentration (0.5 mg L^{-1}). Four on-site experiments were run with a KMnO$_4$ dose equivalent to the Fe concentration. For no added Fe there was a modest reduction in the remaining As (Figure 12). Adding both KMnO$_4$ and FeCl$_3$ gave improved As removal. For ~2 mg L^{-1} added Fe the As concentration approached the MCL and the two runs had nearly equal As concentrations. Addition of NaOCl equivalent to the Fe in the raw groundwater had little effect on the As concentration. Excess NaOCl (three times the Fe equivalent) and FeCl$_3$ improved As removal somewhat, although KMnO$_4$ gave better As removals for the same FeCl$_3$ doses.

As for the Kenney on-site experiments, membrane-filtered (0.2 μm) Grand Ridge As concentrations were somewhat lower than those of sand filter effluents (Figure 13). Therefore, the effluent had a small amount of particulate/colloidal As.

Despite measures to exclude air, the dissolved (filtered) Fe concentration in the groundwater used in the laboratory aeration experiments dropped from 0.5 to 0.2 mg L^{-1}. Because the natural groundwater Fe concentration was so low, it was decided to run the aeration experiments with the partially oxidized water. Aeration caused only modest lowering of filtered As concentrations (Figure 14) which was similar to the Kenny aeration experiments. Even for a FeCl$_3$ dose of ~2 mg L^{-1} filtered As was well above the MCL. Aeration caused very little As(III) oxidation.

The As concentration in the groundwater used in the Grand Ridge KMnO$_4$ experiments was considerably higher than in the on-site experiments, possibly because of contamination. For no added FeCl$_3$, KMnO$_4$ gave only a modest reduction in filtered As in Grand Ridge water, probably because of the low Fe concentration (Figure 15). For a FeCl$_3$ dose of ~2 mg L^{-1}, filtered As was well below the MCL, despite the apparently "augmented" As concentration. As(III) was completely oxidized in all experimental runs.

As in the KMnO$_4$ experiments, the groundwater used for the Grand Ridge NaOCl experiments had a higher As concentration than in the on-site experiments, possibly because of contamination. For no added FeCl$_3$, 1 mg L^{-1} NaOCl (equivalent to 2 mg L^{-1} Fe(II)) lowered filtered As in Grand Ridge water by ~25% but did not oxidize As(III) significantly (Figure 16). For a FeCl$_3$ dose of ~ 4 mg L^{-1} the filtered As concentration approached the MCL and for ~6 mg L^{-1} it was well below the MCL. For 2 mg L^{-1} NaOCl the filtered As concentration was near the MCL for a FeCl$_3$ dose of ~2 mg L^{-1} and well below the MCL for a dose of ~4 mg L^{-1}. As(III) oxidation was more extensive for 2 mg L^{-1} NaOCl than for 1 mg L^{-1}, although As(III) was detectable in all samples.

The Waterman groundwater had 18 μg L^{-1} As, the lowest As concentration of all facilities studied, and 2 mg L^{-1} Fe. The on-site experiments used KMnO$_4$ doses of 1.0 and 1.9 mg L^{-1}, equivalent to 50% and 100% of the groundwater Fe(II). The NaOCl doses of 2.5 and 5.0 mg L^{-1} (as Cl$_2$) were equivalent to 100% and 200% of the Fe(II). The remaining As concentrations in sand filter effluent were well below the MCL for all oxidant doses and no added FeCl$_3$ (Figure 17). The As concentrations were somewhat lower for ~1 mg L^{-1} added Fe. Even though the As concentrations approached the PQL, the As concentrations were apparently lower for the higher oxidant doses.

The Waterman water sample used for the aeration experiments was partially oxidized. It had 1.6 mg L^{-1} Fe while the raw water had 2.0 mg L^{-1}. It was decided to run the experiments without added Fe(II). Aeration without added Fe and with 1.0 mg L^{-1} lowered the filtered As concentration somewhat (Figure 18). Higher doses of Fe (2-3 mg L^{-1}) produced filtered As concentrations near the MCL. There was little As(III) oxidation.

The Waterman groundwater samples that were used for the $KMnO_4$ and NaOCl experiments were more extensively oxidized than the sample used for aeration; neither sample had detectable Fe. Rather than delay the experiments until the groundwater could be analyzed it was decided to add Fe(II) and As(III) for the experiments. A Fe(II) solution was prepared daily from $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.0224 M) and H_2SO_4 (0.005M). A commercial As(III) solution (Spex) was used. Immediately before each experiment Fe(II) (2 mg L^{-1})and As(III) (30 μg L^{-1}) were added to groundwater and mixed before adding oxidant and any $FeCl_3$. One dose of $KMnO_4$, 1.9 mg L^{-1}, equivalent to 2 mg L^{-1} Fe(II), was used. Two doses of NaOCL, 2.5 mg L^{-1}, equivalent to the Fe(II), and 5.0 mg L^{-1} were used. The filtered As concentration was lowered well below the MCL for all $FeCl_3$ doses for both oxidants (Figures 19, 20). For the higher doses filtered As was below the GFAAS practical quantitation limit. As(III) was undetectable in all samples treated with either $KMnO_4$ or NaOCl.

The effect of oxidant dose on As removal is shown by the on-site experiments in which only NaOCl or $KMnO_4$ (no $FeCl_3$) was added. For these experiments there were no sample storage/stability issues. Figure 22 shows percent arsenic removal as a function of oxidant dose in these experiments. The independent variable is oxidant dose to total reductant concentration. For NaOCl this ratio is given by equation 5. For $KMnO_4$ the only reductant was Fe(II) (equation 7). One mole of $KMnO_4$ oxidizes 3 moles of Fe^{2+} (equation 2).

$$Ratio\, of\, KMnO_4\, to\, Fe = \frac{3[KMnO_4]_{added}}{[Fe]_{gdwtr}}$$

Equation 7

Arsenic was almost entirely in the As(III) form in all raw groundwaters. Two doses of both NaOCl and $KMnO_4$ were used at Kenney. For both oxidants the higher dose resulted in significantly better As removal. At Grand Ridge As removal was better with $KMnO_4$ than with NaOCl because of the better oxidant-to-reductant ratio. Arsenic removal at Grand Ridge was lower than at the other two facilities because of the low Fe concentration. The oxidant dose seemed to have little effect for the Waterman samples. However, this groundwater had the highest Fe:As ratio of the three facilities. In general, As removal asymptotically approached 100% as the oxidant-to-reductant ratio increased.

The Fe:As ratio seems to be a key parameter in As removal. Figure 23 shows As removal in the on-site and laboratory $KMnO_4$ experiments as a function of the Fe:As ratio (equation 6). Arsenic removal increased rapidly for Fe:As < 25 and asymptotically approached 100% for Fe:As > 50. For the range of Fe:As that was common to the three sets of experiments (50-125), As removal was similar. These results agree qualitatively with those of Wilson et al. (2004).

Some substances commonly found in groundwater such as phosphate, bicarbonate, silica, and organic matter interfere with As adsorption to HFO (Holm 2002; Simeoni et al. 2003). Therefore, these substances may reduce the efficiency of As removal in water treatment plants. For $KMnO_4$ addition and Fe:As values between 50 and 100 (Figure 23), As removals from Kenney groundwater were lower than for some of the Grand Ridge and Waterman tests.

Both chemical oxidation and adsorption seem to be important factors in As removal. Figure 24 shows As removal as a function of Fe:As in all on-site and laboratory experiments. Generally, adding $FeCl_3$ to increase the Fe:As ratio improved As removal for aeration, NaOCl, and $KMnO_4$. For Fe:As > 50 and the same Fe:As ratio, As removal was somewhat better with $KMnO_4$ than with NaOCl, which was considerably better than aeration. For Fe:As < 50, As removal by all three oxidants were comparable, although the data are limited. In contrast, Lytle et al. (2005) found that chlorination (1 mg L^{-1}) followed by aeration resulted in much better As removal than just aeration (Fe 1 mg L^{-1}, As(III) 100 µg L^{-1}, Fe:As 13.5). A likely reason for the disagreement is that their systems had no NH_3-N. Therefore, the NaOCl was sufficient to oxidize both the Fe(II) and As(III).

Because of the experimental design (or lack thereof) it is difficult to separate the effects of oxidation and adsorption on As removal. Figure 25 shows As removal as a function of both the NaOCl to Fe(II) + NH_3-N ratio (equation 5) and the Fe:As ratio (equation 6) for all on-site experiments. Although As removal generally increased as the oxidant-to-reductant ratio increased, which would indicate oxidation control, the Fe:As ratio also increased, which would indicate adsorption control. For a given oxidant-to-reductant ratio, As removal tended to increase as Fe:As increased. Figure 26 is similar to Figure 25. It shows As removal in on-site experiments as a function of the $KMnO_4$ to Fe(II) ratio (equation 7) and the Fe:As ratio. Unlike NaOCl, there is no apparent increase in As removal for increasing oxidant-to-reductant ratio. Even for a $KMnO_4$ dose sufficient to oxidize only ~50% of the groundwater Fe(II), As removal was better than 90%. On the other hand, As removal generally increased as Fe:As increased. Apparently the kinetics of As(III) oxidation by $KMnO_4$ are favorable.

Summary and Conclusions

Aeration with no added $FeCl_3$ removed 20-25% of the As from Kenney and Waterman groundwater. Water from these wells had moderately high Fe concentrations (1.8-2.1 mg L^{-1}). On the other hand, aeration hardly removed any As from Grand Ridge water, probably because of the low Fe concentration (0.5 mg L^{-1}). Adding $FeCl_3$ improved As removal by aeration in all cases but only satisfied the MCL for Waterman because of the relatively low As concentration (18 μg L^{-1}). Aeration had little effect on As speciation; As(III) made up a large fraction of filtered As in all aeration experiments. This is consistent with other observations (Wilson 2004; Peyton et al. 2006).

Chemical oxidation, addition of NaOCl or $KMnO_4$, improved As removal compared with aeration. However, in some cases addition of $FeCl_3$ was needed to meet the MCL.

$KMnO_4$ effectively oxidized As(III), even when the $KMnO_4$ dose was only ~50% of the dose required to oxidize the soluble Fe. In all $KMnO_4$ experiments As(III) was below the practical quantitation limit (2.5 - 5.0 μg L^{-1}) and was below the method detection limit (0.5 - 1.0 μg L^{-1}) in most experiments. $KMnO_4$ lowered the filtered As concentration below the MCL in Kenney and Waterman water, both of which had ~2 mg L^{-1} Fe, without supplementary $FeCl_3$. Grand Ridge water, which had low Fe, needed ~2 mg L^{-1} Fe to get below the MCL.

NaOCl only partially oxidized As(III), even when there was excess NaOCl relative to Fe^{2+}. The reason was the NaOCl dose did not account for the NH_3-N in the groundwater. A NaOCl dose equivalent to ~20% of Fe + NH_3-N and a total Fe concentration (natural Fe^{2+} plus added $FeCl_3$) of ~4 mg L^{-1} were needed to meet the As MCL with the Kenney and Grand Ridge groundwater. Waterman groundwater, on the other hand, had low NH_3-N and As concentrations and high Fe. A NaOCl dose of 2.5 mg L^{-1} reduced the filtered As concentration to 5 μg L^{-1}, which is well below the MCL.

Recommendations

The following recommendations are for bench-scale testing of chemical addition to improve arsenic removal at facilities that currently remove Fe by aeration and filtration. In a full-scale water treatment plant, NaOCl or $KMnO_4$ should be added before aeration, not after. The $FeCl_3$ addition point (before or after aeration) may be unimportant. Chemical addition would probably no major capital expenses, but only minor plumbing modifications. However, $FeCl_3$ addition will surely result in more-frequent filter back washing.

- Chemical analyses should include As, Fe, and NH_3-N.
- If possible, bench-scale testing should be done at the well head with minimal delay between sample collection and chemical addition to avoid ferrous Fe oxidation and ferric Fe precipitation.
- If testing must be done in a laboratory, sample bottles should be filled to overflowing and capped with no headspace. An analysis for Fe should be done on-site when samples are collected. Before testing sample bottles should be inspected for Fe oxide precipitate. The contents of each bottle should be analyzed for Fe before any testing.
- For NaOCl addition, calculate the dose from the Fe and NH_3-N concentrations.
- For $KMnO_4$ addition, the dose should be less than that required to completely oxidize the Fe. This assures complete reduction of the $KMnO_4$.

Acknowledgements

References

Butler, J. N. (1964). *Ionic Equilibrium a Mathematical Approach*. Reading, MA, Addison-Wesley.

Cleasby, J. L. (1972). "Filtration". *Physicochemical Processes for Water Quality Control*. W. J. Weber, Jr. New York, Wiley-Interscience**:** 139-198.

Clesceri, L. S., A. E. Greenberg and A. D. Eaton (1998). *Standard Methods for the Examination of Water and Wastewater, 20th ed.* Washington, D.C., A.P.H.A., A.W.W.A., W.E.F.

Ghurye, G. and D. Clifford (2004). "As(III) oxidation using chemical and solid-phase oxidants." *Journal American Water Works Association* **96**(1): 84-96.

Glaser, J. A., D. L. Foerst, G. D. McKee, S. A. Quave and W. L. Budde (1981). "Trace analyses for wastewaters." *Environ. Sci. & Technol.* **15**(12): 1426-1435.

Hering, J. G., P. Y. Chen, J. A. Wilkie and M. Elimelech (1997). "Arsenic Removal From Drinking Water During Coagulation." *Journal of Environmental Engineering-ASCE* **123**(8): 800-807.

Hering, J. G., P. Y. Chen, J. A. Wilkie, M. Elimelech and S. Liang (1996). "Arsenic Removal By Ferric Chloride." *Journal American Water Works Association* **88**(4): 155-167.

Holm, T. R. (2002). "Effects of carbonate/bicarbonate, silica, and phosphate on arsenic sorption to hydrous ferric oxide." *J. Am. Water Works Assoc.* **94**(4): 174-181.

Holm, T. R., Kelly, W. R., Wilson, S. D., Roadcap, G. R., Talbott, J. L., Scott, J. S. (2004). *Arsenic Geochemistry and Distribution in the Mahomet Aquifer, Illinois*. Champaign, IL, Waste Management and Research Center. http://www.wmrc.uiuc.edu/main_sections/info_services/library_docs/RR/RR-107.pdf.

Holm, T. R., Kelly, W. R., Wilson, S. D., Roadcap, G. R., Talbott, J. L., Scott, J. S. (2005). "Arsenic Distribution and Speciation in the Mahomet and Glasford Aquifers, Illinois". *Advances in Arsenic Research. Integration of Experimental and Observational Studies and Implications for Mitigation*. P. A. O'Day, D. Vlassopoulos, X. G. Meng and L. G. Benning. Washington, D. C., American Chemical Society. **ACS Symposium Series 915:** 148-160.

Hug, S. J. and O. Leupin (2003). "Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction." *Environmental Science & Technology* **37**(12): 2734-2742.

Jafvert, C. T. and R. L. Valentine (1987). "Dichloramine Decomposition in the Presence of Excess Ammonia." *Water Research* **21**(8): 967-973.

Jafvert, C. T. and R. L. Valentine (1992). "Reaction Scheme for the Chlorination of Ammoniacal Water." *Environmental Science & Technology* **26**(3): 577-586.

Jekel, M. R. (1994). "Removal of arsenic in drinking water treatment". *Arsenic in the Environment. Part 1: Cycling and Characterization*. J. O. Nriagu. New York, Wiley. **26:** 119-132.

Kelly, W. R., T. R. Holm, S. D. Wilson and G. S. Roadcap (2005). "Arsenic in glacial aquifers: Sources and geochemical controls." *Ground Water* **43**(4): 500-510.

Lytle, D. A., T. J. Sorg and V. L. Snoeyink (2005). "Optimizing arsenic removal during iron removal: Theoretical and practical considerations." *Journal of Water Supply Research & Technology - Aqua* **54**(8): 545-560.

McNeill, L. and M. Edwards (1995). "Soluble arsenic removal at water treatment plants." *Jour.*

AWWA **87**(4): 105-113.

Meng, Z. G., G. P. Korfiatis, C. Christodoulatos and S. Bang (2001). "Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system." *Water Research* **35**(12): 2805-2810.

Panno, S. V., K. C. Hackley, K. Cartwright and C. L. Liu (1994). "Hydrochemistry of the Mahomet Bedrock Valley Aquifer, East-Central Illinois - Indicators of Recharge and Ground-Water Flow." *Ground Water* **32**(4): 591-604.

Peyton, G. R., T. R. Holm and J. Shim (2006). *Development of Low Cost Treatment Options for Arsenic Removal in Water Treatment Facilities*. Champaign, IL, Midwest Technology Assistance Center for Small Public Water Systems. http://mtac.sws.uiuc.edu/mtacdocs/pubs/MTACTR06-03.pdf.

Richardson, S. D. (1998). "Drinking Water Disinfection Byproducts". *Encyclopedia of Environmental Analysis and Remediation*. R. A. Meyers. New York, Wiley.

Simeoni, M. A., B. D. Batts and C. McRae (2003). "Effect of groundwater fulvic acid on the adsorption of arsenate by ferrihydrite and gibbsite." *Applied Geochemistry* **18**(10): 1507-1515.

Singer, P. C. (1993). "Formation and characterization of disinfection by-products". *Safety of Water Disinfection: Balancing Chemical & Microbial Risks*. G. F. Craun. Washington, D. C., ILSI Press**:** 201.

Trussell, R. R. (1993). "Treatment for the control of disinfectant residuals and disinfection by-products". *Safety of Water Disinfection: Balancing Chemical & Microbial Risks*. G. F. Craun. Washington, D. C., ILSI Press**:** 319.

Viraraghavan, T., K. S. Subramanian and J. A. Aruldoss (1999). "Arsenic in drinking water - Problems and solutions." *Water Science & Technology* **40**(2): 69-76.

Warner, K. L. (2001). "Arsenic in glacial drift aquifers and the Implication for drinking water - lower Illinois River basin." *Ground Water* **39**(3): 433-442.

Welz, B., G. Schlemmer and J. R. Mudakavi (1988). "Palladium nitrate-magnesium nitrate modifier for graphite furnace atomic absorption spectrometry. Part 2. Determination of arsenic, cadmium, copper, manganese, lead, antimony, selenium, and thallium in water." *Journal of Analytical Atomic Spectrometry* **3**: 695-701.

Wilson, S. D., Holm, T. R., Kelly, W. R. (2004). *Arsenic Removal in Water Treatment Facilities: Survey of Geochemical Factors and Pilot Plant Experiments*. Champaign, IL, Midwest Technology Assistance Center. http://mtac.sws.uiuc.edu/mtacdocs/finalreports/ArsenicTreatmentMTACFinalReport.pdf.