Removing the Stink: Advanced Treatment Processes for Hydrogen Sulfide

Clayton Johnson, Christine Owen, Luke Mulford, Shahnawaz Sinha, Zaid Chowdhury, Andre Dieffenthaller, and Andrew Coleman

Tampa Bay Water supplies drinking water to more than 2 million people in the greater Tampa Bay and adjacent areas. Approximately 60 percent of its source water comes from groundwater supplies. Groundwater in some portions of the region has a moderate amount (about 2 mg/L as total sulfides) of hydrogen sulfide. Tampa Bay Water currently provides water to a water treatment facility that utilizes aeration followed by biological oxidation to remove hydrogen sulfide.

This combined practice (Figure 1) is effective, but there are occasional reductions in the treatment efficiencies, resulting in customer complaints of odor and black water. In order to ensure the highest-quality drinking water to its customers, Tampa Bay Water is currently evaluating three alternative methods of hydrogen sulfide removal: (1) ozone with biological filtration, (2) chlorine oxidation followed by ultrafiltration (UF), and (3) biological oxidation followed by ultrafiltration.

A pilot study is currently underway at the Lithia Water Treatment Plant. In one of the pilot-scale treatment trains, ozone is used to fully oxidize the ambient levels of hydrogen sulfide. The ozonated water then passes through a biologically active granular carbon (BAC) filter to improve its biological stability by minimizing the biodegradable fraction of the natural organic matter. The effectiveness of naturally occurring sulfur-fixing bacteria on the GAC surface to remove sulfides is also monitored.

Oxidation of hydrogen sulfide with ozone to sulfate is not a primary health concern and would not approach the sulfate secondary maximum contaminant level (SMCL) at sulfide levels found in these regional groundwaters.

The other alternative evaluated in parallel to ozonation/BAC is oxidation followed by membrane filtration. Application of chlorine alone or chlorine in combination with a metal coagulant can partially or fully oxidize hydrogen sulfide to elemental (i.e., particulate) sulfur and dissolved sulfate, respectively.

The filtration process utilized in this pilot effort is the submerged UF membrane following oxidation for removing the elemental sulfur particles. The current process utilizes biological oxidation of sulfide without filtration prior to disinfection and distribution.

The final alternative under consideration is biological oxidation followed by chlorination and ultrafiltration following biological oxidation prior to distribution.

This article will discuss preliminary findings of this ongoing pilot study, including operational variables and effectiveness of the proposed treatment processes for hydrogen sulfide removal. As many Florida utilities are faced with the challenge of removing hydrogen sulfide from their groundwater, preliminary results of this study will be broadly applicable. Results from this study will provide useful information to water utilities that are contemplating removal of hydrogen sulfide using alternative treatment strategies.

Clayton Johnson is a project engineer in the Tampa office of the environmental engineering firm Malcolm Pirnie Inc. Christine Owen is a water quality assurance officer with Tampa Bay Water. Luke Mulford is a water quality engineer with Hillsborough County Water Resource Services. Shahnawaz Sinha is a project engineer with Malcolm Pirnie in Phoenix, Arizona. Zaid Chowdhury is a senior associate with Malcolm Pirnie in Phoenix. Andre Dieffenthaller is a senior associate with Malcolm Pirnie in Schaumburg, Illinois. Andrew Coleman is a project engineer with Malcolm Pirnie in Tampa.

Objectives

Key objectives of the Lithia pilot testing are to determine:

1) If ozonation of groundwater followed by biological filtration is an effective means for removing hydrogen sulfide;
2) If chlorination of groundwater or plant bio-treated water followed by membrane filtration (UF) is an effective means of removing hydrogen sulfide;
3) Effective operating criteria for ozone-BAC and chlorine-membrane filtration processes;
4) If treated water quality goals can be achieved (hydrogen sulfide target < 0.1 mg/L and turbidity less than 1 NTU) using these technologies;

Pilot Description

The pilot system consists of several process units, including an ozonation unit housed within an air-conditioned trailer, one

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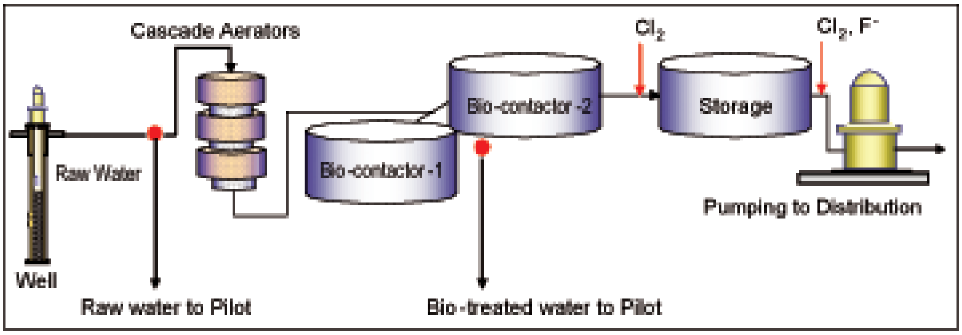

Figure 1

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biologically active granular carbon filter, and a submerged UF membrane filtration unit. Figure 1 shows the full-scale treatment process and the location of raw and bio-treated water intakes for the pilot system. The ozonation unit receives only plant raw water, whereas the membrane unit receives both raw water and bio-treated water prior to membrane filtration.

Ozone System

The ozone system is provided water from a 42-inch raw-water line at the Lithia Water Treatment Plant prior to the cascade aerators (Figure 1). Raw water is ozonated using an ozone generator, which produces ozone from ambient air. The ozone generation system is equipped with both gas and aqueous-phase monitors.

Ozone is introduced into the water by an in-line injection system using a venturi (Mazzei) injector. The flow rate through the pilot unit is approximately 9 gpm. The unit is capable of producing an ozone dose up to 7 mg/L.

After ozonation, the water flows into a 8-gallon contact tank and then passes through a 100-gallon dissipation tank, where residual ozone is dissipated prior to sending it to the BAC filter. Hydrochloric acid and hydrogen peroxide may also be added to the water prior to ozonation to determine the effects of reduced pH and advanced oxidation processes, respectively.

Biologically Active Carbon Filter

The BAC pilot system consists of a 3-inch diameter clear PVC pipe filled with 60 inches of GAC. The filter is operated under a constant head and declining flow rate. The filter has an EBCT of 9 minutes and was loaded with virgin GAC (Calgon) media.

The filter was run with ozonated water for 30 days in order to biologically activate the GAC. It is backwashed every 48 hours using non-chlorinated filtered water stored in a HDPE tank.

The filter is equipped with a flow meter and pressure gauges for monitoring flow and head loss, respectively. It is also equipped with an on-line turbidity meter for monitoring filtered water turbidity. The filter is mounted outside on (a 4 by 5 feet) a pallet with the filter column covered to protect it from sunlight.

Submerged Membrane

A submerged UF membrane is used in the alternative process train for this study. The UF system operates under negative (vacuum) pressure and consists of hollow fiber membranes submerged within the fluid.

The membrane system is cleaned every 60 minutes by an automatic backwashing system using water and air to dislodge solids. Chemical cleanings, also known as maintenance and recovery cleanings, are performed at the end of each experiment. Chlorine and/or citric acid are used during the maintenance and recovery cleanings.

Experimental Plan

Ozone-BAC System

In one process configuration, ozone and BAC treat raw water only. The ozonation pilot train receives raw water before the cascade aeration unit in the full-scale water treatment plant (Figure 1). Figure 2 shows how the ozone pilot unit fit into the overall system.

The ozonation train is equipped with a hydrogen peroxide feed system to evaluate if advanced oxidation processes (AOP) can reduce ozone dosages. Hydrogen peroxide addition to ozone enhances the formation of the hydroxyl radical (OH•), which is a more powerful oxidant than molecular ozone (O3)

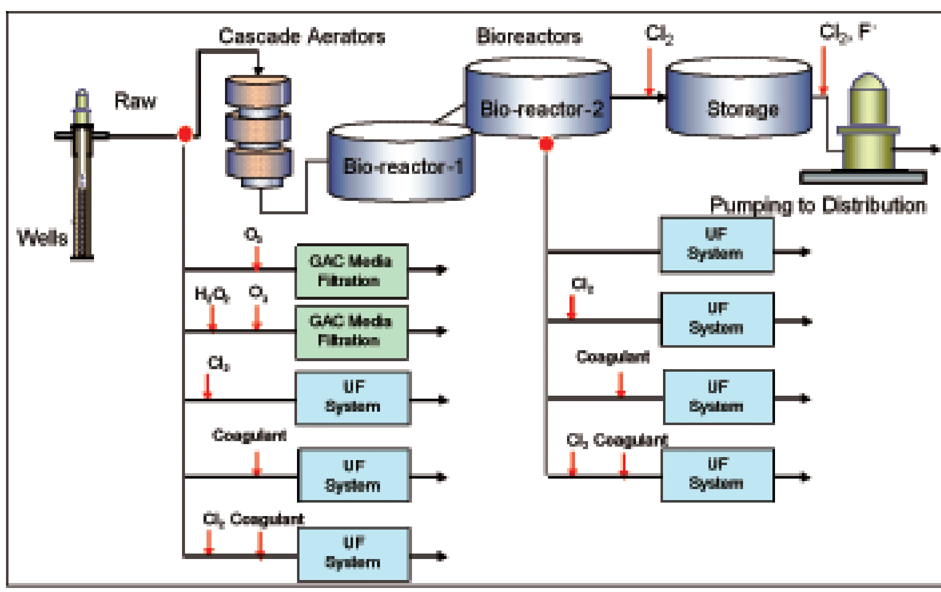

Figure 2

Table 1. Experimental Matrix for Ozone Screening and Long-Term Tests

Screening Tests	O_3 Dose (mg/L)	H_2O_2 Dose (mg/L)	H_2O_2/O_3	pH (SU)
Baseline	3.0	0.0	0.0	Ambient*
Test-1	3.0	0.0	0.0	6.5
Test-2	3.0	1.0	0.5	Ambient*
Test-3	3.0	1.0	0.5	6.5
Test-4	1.5	1.0	1.0	Ambient*
Test-5	1.5	1.0	1.0	6.5
Test-6	4.0	0.0	0.0	Ambient*
Long Term Tests				
Test-1	Optimal Dose			Optimal pH

*Ambient pH is 7.1 – 7.3

Scenario	Water	Cl_2 Dose (mg/L)	pH (SU)
Scenario-1	Bio-treated	0.0	7.1– 7.3
Scenario-2	Raw	8.0	7.1– 7.3

Table 2. UF Membrane Tests

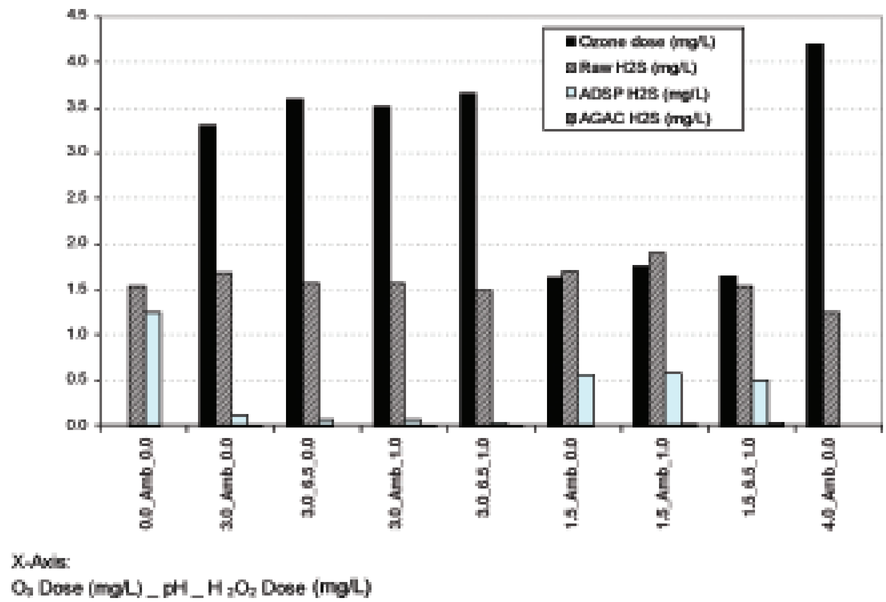

Figure 3

alone. Lower pH (6.5) conditions were also tested during the ozonation process.

Ozonation and AOP may decrease the biological stability of the process water. The purpose of the BAC filter is to biologically stabilize the water, if necessary. Assimilable organic carbon (AOC) is measured prior to and after the filter column to determine if the BAC filter can improve the biological stabiliy of the water. The filter is also used to evaluate the removal of particulates which may be formed through the oxidation of sulfide to sulfur during ozonation.

To evaluate the effectiveness of ozone and ozone with hydrogen peroxide, an orthogonal experimental design was developed. In this type of experimental design, a baseline condition is assumed and each independent variable is altered, one at a time, to isolate the effect of other parameters. Up to six sets of screening experiments (Table 1) were performed to determine the optimum conditions for the oxidation of hydrogen sulfide.

At the end of the screening tests, the optimal conditions (ozone dose, hydrogen peroxide dose, and pH) were selected and then tested for a longer duration. This longer duration test is currently ongoing at the pilot site and will be used to verify operation of the ozonation and filtration processes. This article

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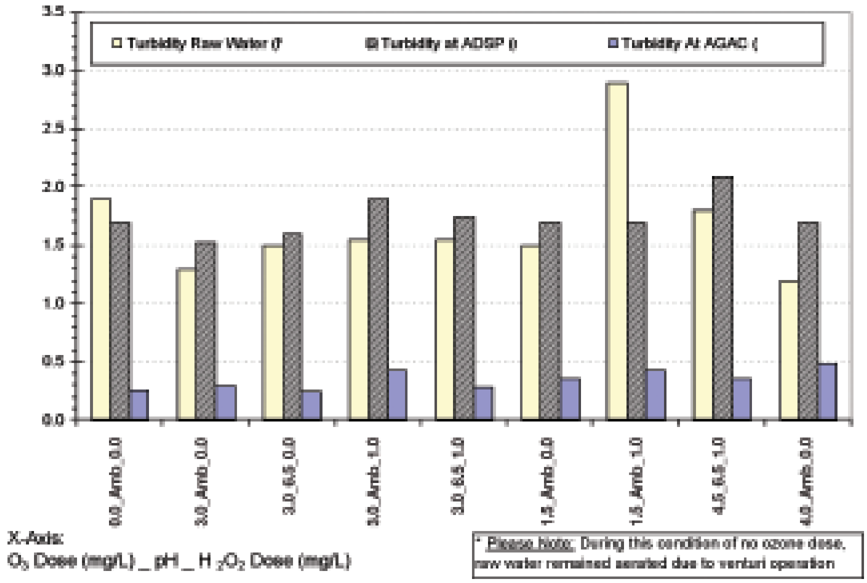

Figure 4

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includes only the screening test results which have then been used to determine the optimum dose for the long-term study. Further testing is underway to evaluate ozone with BAC under the pilot optimized conditions.

<u>Membrane System</u>

The performance of the submerged UF membrane system was evaluated with respect to its ability to treat raw groundwater or the full-scale plant bio-treated water (Figure 2). Two scenarios are presented in Table 2. Tests include using bio-treated or raw water with 8.0 mg/L chlorine addition prior to membrane filtration. The chlorine addition oxidizes sulfide to elemental sulfur and creates a filterable turbidity particle. The results of the initial tests of both membrane system alternatives warranted further evaluation and are ongoing.

<u>Field and Lab Measurements</u>

Water quality evaluated in support of these pilot efforts include both field and laboratory parameters. The field and/or onsite analyses include pH, temperature, turbidity, total sulfides, conductivity, color, dissolved oxygen, and chlorine residual.

Total organic carbon (TOC), sulfate, alkalinity, iron, *e. coli*, total coliform, HPC, HAAs, TTHMs, and bromate were analyzed by a certified laboratory. Analytical work has been performed by Hillsborough County staff, Tampa Bay Water staff or contract lab personnel. On-line instruments are also used to measure turbidity, total sulfides, chlorine residual, and dissolved ozone, which are verified daily by field measurements.

For the ozone-BAC system, samples are collected from three different locations prior to ozonation, after ozonation and before BAC, and after BAC filtration. For the UF membrane train, samples are collected prior to chlorine addition, after chlorine addition but prior to filtration (membrane feed), and after filtration (membrane permeate). Raw-water samples were collected prior to cascade aeration.

Results & Discussion

<u>Ozone-BAC System</u>

The initial ozone-BAC screening evaluation included varying ozone dose, the addition of hydrogen peroxide, and pH adjustment. Table 1 summarizes the experimental conditions. Ozone dose varied from 0 to 4 mg/L; hydrogen peroxide dose varied from 0 to 1.0 mg/L. Figure 3 summarizes the results of the ozone-BAC screening experiments.

In Figure 3, hydrogen sulfide concentrations for the raw, after-ozonation (ADSP H_2S), and after-GAC filtration (AGAC H_2S) waters are shown along with each ozone dose, pH, and hydrogen peroxide dose. Sulfide concentrations were measured in mg/L as hydrogen sulfide.

Increasing the ozone dose oxidized more hydrogen sulfide from the raw water (ADSP-after dissipation before GAC filter). A dose of 4.0 mg/L was found to be very effective for removing hydrogen sulfide from raw water. Peroxide or pH adjustment to 6.5 S.U. showed no additional benefit for sulfide removal. Sulfide was not detected after BAC filtration, independent of ozone dose, pH, or hydrogen peroxide dose. Thus, a dose of 3.5 - 4.0 mg/L without peroxide or pH adjustment was recommended for further evaluation.

Bromide and bromate were monitored during the ozone screening tests. The raw-water bromide level was low (0.06 mg/L), and after ozonation the amount of bromate formed was below the detection level (0.5 µg/L).

Turbidity was closely monitored in all locations. Figure 4 shows these results. The raw-water turbidity slightly increased after ozonation, but decreased significantly after BAC filtration.

<u>Membrane System</u>

Both raw and plant bio-treated waters were tested with and without chlorine addition for the submerged UF membrane system. In Scenario 1, full-scale, bio-treated water was used without chlorine addition.

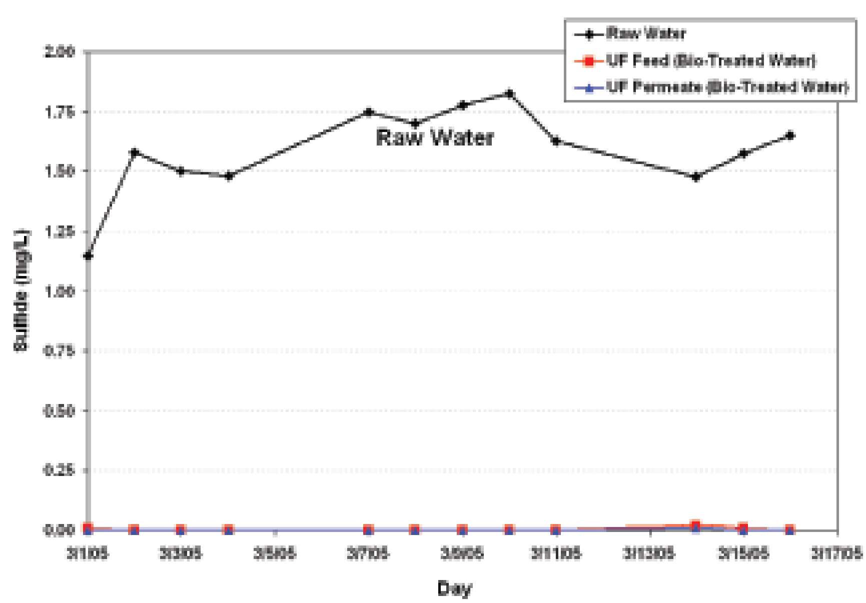

Figure 5

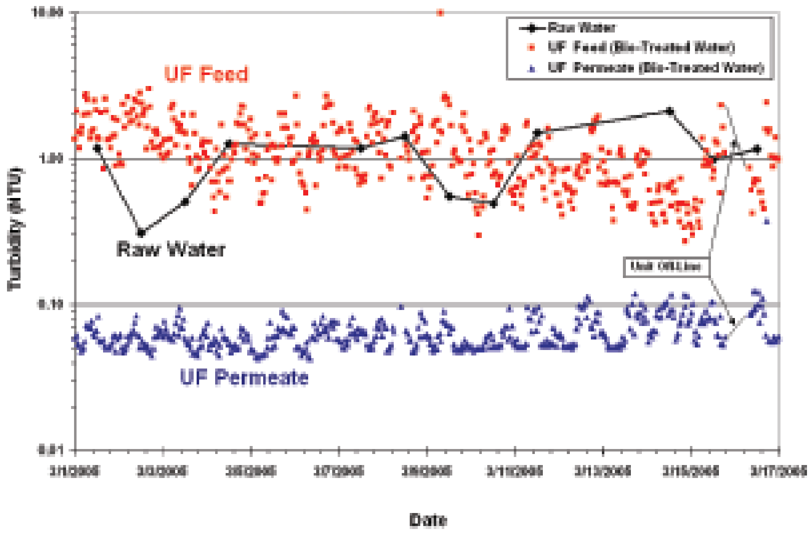

Figure 6. Turbidity removals for Bio-treated water followed by UF membrane filtration

The UF membranes were positioned downstream of the biological reactors to remove bacteria, particulate sulfur, and other particulate matter that may be carried over from the existing biological process. The UF membranes were introduced to provide a buffer against periodic water-quality upsets.

Scenario 2 utilized chlorine to oxidize sulfides in the raw water to elemental/precipitate sulfur, which could subsequently be removed by the UF membranes. A chlorine dose of 8.0 mg/L (determined by bench-scale testing) was added to oxidize sulfide to elemental sulfur prior to membrane filtration. Coagulation tests with ferric chloride, as described earlier and shown in Figure 2, are not reported here.

Coagulant addition was shown to have little or no benefit. In some instances, adverse effects on membrane performance were observed, including decreases in flux and increased transmembrane pressure.

Figure 5 shows results of Scenario 1 for bio-treated water without chlorine addition, before and after UF membrane filtration. This figure shows that full-scale bio-treatment is very effective in removing sulfide from the raw water.

Sulfide removal was essentially complete in the bio-treatment stage; membrane filtration did not provide any additional sulfide removal. Sulfide concentrations were measured in mg/L as total sulfides.

Figure 6 shows that UF was able to significantly reduce filtered water turbidity to less than 0.15 NTU. Overall, it appears that bio-treated water followed by membrane filtration does not provide additional hydrogen sulfide removal but does improve turbidity removal significantly.

In Scenario 2, raw water was chlorinated (8.0 mg/L dose) prior to UF membrane filtration. Figure 7 shows that chlorination followed by membrane filtration was very effective in removing hydrogen sulfide from the raw water. Sulfide concentrations were measured in mg/L as total sulfides.

Figure 8 shows a higher turbidity for the feed than the raw water. The increase in turbidity after chlorination is due to the forma-

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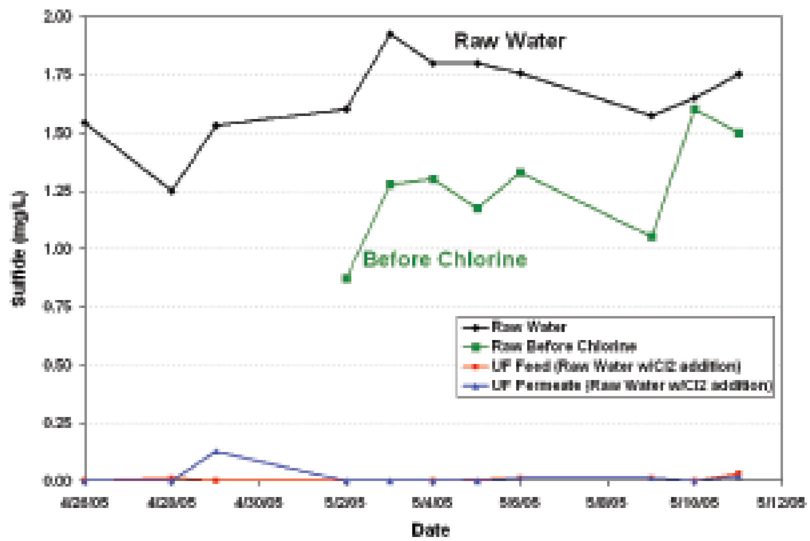

Figure 7. Sulfide removals for raw water followed by UF membrane filtration

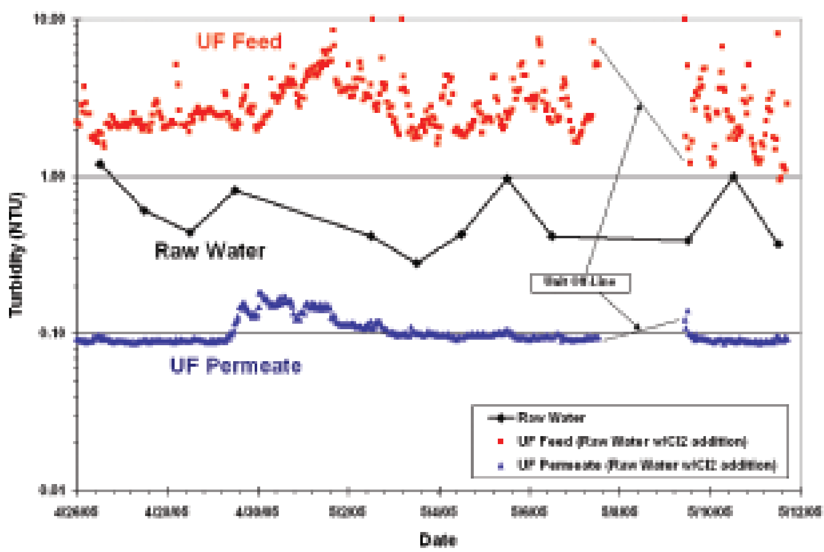

Figure 8. Turbidity removals for raw water followed by UF membrane filtration

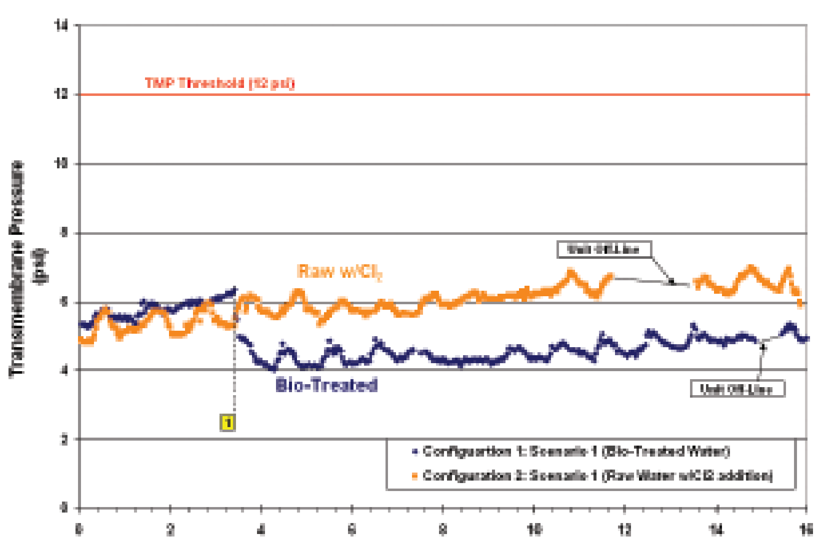

Figure 9

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tion of elemental/intermediate sulfur species. The turbidity significantly decreases after membrane filtration and is typically less than 0.10 NTU.

Raw-water chlorination followed by UF membrane filtration would be an effective means for removing hydrogen sulfide. Since the ambient TOC levels in this groundwater are low, managing disinfection byproduct formation is possible while removing hydrogen sulfide using this process.

Transmembrane pressure is used as an indicator of the need to perform a relatively aggressive cleaning on an UF membrane. Figure 9 shows the 16-day transmembrane pressure (TMP) measurements for the two scenarios investigated in the study. For both scenarios, the flux was held constant. The TMP drop at Point 1 (day 3.5) in Figure 9 is due to operational adjustments, not a change in flux.

In each condition (bio-treated water to the UF and chlorinated raw water to the UF), TMP remained much lower than the cleaning trigger of 12 psi. It is possible that the UF system could run for greater than 30 days between chemical cleanings. TMP for the bio-treated water train tends to be lower than the chlorinated raw water train. Current work is ongoing to evaluate these results more thoroughly.

Conclusion

The ozone-BAC screening tests and UF membrane filtration show that both of these alternative treatment technologies are effective for removing hydrogen sulfide from this groundwater. Ozone was found to be very effective for oxidizing hydrogen sulfide. The BAC filter would be effective for removing sulfide, as well as bio-stabilizing the water.

UF membrane filtration was also found to be effective for both bio-treated water (to control water-quality upsets) and raw water (to remove sulfide). A chlorine dose of 8.0 mg/L was effective for oxidizing sulfide to elemental/intermediate sulfur species, which was then effectively removed by membrane filtration.

Both technologies provide a possible means of lowering sulfide and turbidity. BAC filtration and UF membrane filtration both reduce filtered water turbidities to less than 1.0 NTU, but membrane filtration is more effective for turbidity removal. UF membrane filtration reduces filtered water turbidities to less than 0.15 NTU, whereas BAC filtration reduces turbidity below 0.5 NTU.

The ongoing, long-term ozone-BAC and UF membrane filtration experiments for the raw and bio-treated waters will provide additional information that may be helpful to compare each of these processes and to determine their effectiveness in lowering hydrogen sulfide from Lithia groundwater.