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Project Summary

Treatment Alternatives for Controlling Chlorinated Organic Contaminants in Drinking Water

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A pilot plant study was conducted by the City of Thornton, CO, to evaluate techniques for controlling chlorinated organic compounds formed in drinking water as a result of breakpoint, or free, chlorination. The pilot plant was operated for 46 months using the raw water sources available to the City's 20-mgd Columbine Water Treatment Plant. The treatment techniques evaluated included conventional coagulation and sedimentation, adsorption of organic precursors on powdered activated carbon (PAC), adsorption of chlorinated organic compounds on granular activated carbon (GAC), and alternative methods of disinfection, including the use of chloramines and chlorine dioxide in addition to the present practice of breakpoint chlorination. The effectiveness of the alternatives were assessed with respect to formation or removal of total trihalomethane (TTHM) and total organic halogen (TOX). In addition, the alternative disinfectants were evaluated for biocidal effectiveness.

Based on the study findings, a process that employs chlorine dioxide in combination with chloramination was selected for full-scale evaluation. Neither GAC nor PAC was found to be capable of consistent or reliable control of TTHM or TOX. The method of chloramination affected the extent of TTHM and TOX formation and of bacteria inactivation. The method that resulted in the lowest concentration of these chlorinated organic compounds had the lowest biocidal efficiency as well and therefore was not considered acceptable.

A raw water monitoring program was conducted concurrently with the pilot plant program. Certain raw water sources exhibited a chlorine dosage dependency toward TTHM formation. Procedures were therefore instituted for determining the TTHM formation potential (TTHMFP) that should be considered when analyzing for TTHMFP.

This Program Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The City of Thornton, CO, located along the South Platte River downstream of the metropolitan Denver area, has historically experienced quality problems in their raw water supply. In 1978, nitrite (NO_2^-) concentrations approaching 2 mg/L as nitrogen were discovered within the distribution system. Based on data collected by the Thornton laboratory, the source of the nitrite was determined to be high concentrations of ammonia in the raw water. The ammonia was apparently being oxidized in the distribution system by nitrifying bacteria. This bacterial growth occurred despite the fact that bacteriological standards were being met in the finished

water. Because of the acute health effects associated with nitrite, Thornton immediately began breakpoint chlorination for nitrogen removal.

Once the immediate water quality problem was solved, evaluation of the breakpoint chlorination process proceeded. Although no specific data were available, the speculation was that high concentrations of chlorinated organics were being formed during the breakpoint chlorination process. Initial testing of the water following breakpoint chlorination confirmed this suspicion with instantaneous total trihalomethane (TTHM) exceeding 100 μg/L, total trihalomethane formulation potential (TTHMFP) exceeding 250 μg/L, and instantaneous total organic halogen (TOX) exceeding 250 μg/L, in the finished water from the Columbine Water Treatment Plant. As a result of these findings, a pilot plant study was recommended to evaluate the effectiveness of existing treatment processes as well as additional processes for treating the available raw water supplies.

The pilot plant was operated for 46 months using the raw water sources available to the City's 20-mgd Columbine Water Treatment Plant. Alternatives that were evaluated for controlling chlorinated organic compounds included adsorption of organics on granular activated carbon (GAC) and powdered activated carbon (PAC) and alternative methods of disinfection, including the use of chloramines and chlorine dioxide in addition to the present practice of breakpoint chlorination. The effectiveness of each alternative was assessed with respect to formation or removal of TTHM, formation or removal of TOX, and biocidal efficiency.

Procedures

Pilot Plant

A 10-gpm pilot plant used for this study consisted of a raw water rapid-mix chamber, a two-stage flocculation basin, a primary settling basin, a dual-media filter, and a treated water storage chamber. Carbon contactors used in conjunction with the pilot plant consisted of four 6-inch-diameter, 8-foot-tall glass columns with sample taps at six locations for monitoring organic breakthrough. Each column had 5.5 feet of coal-base GAC media. Two sets of two columns each were operated in series to provide a total empty bed contact time (EBCT) of 16 minutes for each set of columns.

Six different modes of operation were used for the pilot plant during the program. The first three modes used breakpoint chlorination as the means of disinfection. The Mode 1 configuration (control) was identical to the full-scale Columbine Treatment Plant, with chlorine added in the premix basin to achieve breakpoint. The Mode 2 configuration located the breakpoint chlorination downstream at the clarifier effluent to maximize the removal of precursor material before the addition of chlorine. The Mode 3 configuration was identical to Mode 2 except that no PAC was added. This mode allowed comparisons to determine the effectiveness of PAC on the removal of precursor material.

Modes 4 and 5 used two different forms of chloramination. In the Mode 4 configuration, chlorine was added to achieve breakpoint chlorination in the premix basin, after which ammonium sulfate was immediately added to form chloramines. The Mode 5 configuration included the addition of a preformed chloramine solution that was prepared off-line and added to the premix basin. Mode 6 consisted of a dual disinfection system using both chlorine dioxide and preformed chloramines added at the inflow to the plant.

Raw Water Monitoring

A total of 16 sample locations were selected for raw water monitoring. Included in the sampling were the four current raw water sources for the Columbine Treatment Plant, two possible future sources, and other locations within the watersheds to monitor impacts on the sources by wastewater treatment plant discharges.

Results and Discussion

Study results show the correlation between the pilot plant and the full-scale Columbine Water Treatment Plant, the ability of a process or process train to remove specific constituents, the different levels of chlorinated organic formation among alternative disinfection techniques, variations in bacteriological quality produced by alternative disinfectants, and variations in raw water quality.

Conventional Treatment

The average total organic carbon (TOC) concentration of the raw water entering the pilot plant was 5.2 mg/
TOC removal across the clarifier was a
proximately 11 percent and across th
filter approximately 8 percent.

With conventional treatment follov
ing breakpoint chlorination of the ra
water, approximately 40 percent of th
TTHMFP and 15 percent of the TOXF
was removed. By locating the point
chlorination at the clarifier effluent, co
ventional treatment consisting of flo
culation and sedimentation removed 5
percent of the TTHM precursors and 3
percent of the TOX precursors.

Pilot Plant Correlation

An important part of the pilot pla
program was to determine whether th
pilot plant results were representativ
of full-scale operation. Data were con
pared for the full-scale filter effluent an
the pilot plant filter effluent for the fo
lowing parameters: TOC, instantaneou
TTHM, TTHMFP, instantaneous TO
and TOX formation potential (TOXFP
Each of these analyses showed a goo
correlation between the performance
the full-scale plant and the pilot plant

Powdered Activated Carbon

During Mode 2 of the pilot plant ope
ation, PAC dosages of 5 to 10 mg/L we
added to the premix basin, with breal
point chlorination occurring after clarif
cation and before the filter. In Mode 3
the pilot plant operation, the proces
train remained identical to Mode 2 ope
ation except that the PAC was elim
nated to assess the effectiveness of PA
for removal of organic precursors.

Raw water quality was nearly equ
with respect to organic content, with a
erage TOC concentrations of 5.7 and 5
mg/L for Modes 2 and 3, respectivel
The data indicate that PAC at thos
dosages is only slightly effective for r
ducing TOC concentration in the filt
effluent. The filter effluent TOC concer
tration averaged 4.5 mg/L for Mode
and 4.7 mg/L for Mode 3. The averag
instantaneous TTHM concentration
the filter effluent is approximately th
same, regardless of whether PAC
used. The average TTHM concentr
tions were 33.7 μg/L for Mode 2 an
35.8 μg/L for Mode 3.

As with the TTHM data, the TOX co
centration is not significantly differe
with or without PAC addition. The da
showed a slightly higher average TO
concentration for Mode 2—189 μg
compared with 142 μg/L for Mode 3.

Granular Activated Carbon Performance

The performance of the GAC columns was analyzed using data from Modes 1 and 4. The methods of disinfection used were breakpoint chlorination in Mode 1 and breakpoint chlorination followed by ammoniation in Mode 4. The GAC columns were operated for 160 days during these modes to determine the breakthrough characteristics of the columns. Samples that were analyzed to determine GAC performance were the effluent from column 10-6 (which simulated a post-filtration GAC process), the effluent from column 11-6 (which simulated a retrofit of the existing filters), and the effluent from column 12-6 (which simulated replacing the filters with a GAC process). The carbon columns were filled with virgin carbon at the beginning of each mode and were backwashed weekly during operation.

The average TOC concentration of the GAC influent was 4.6 mg/L for the columns receiving clarifier effluent and 4.3 mg/L for the columns receiving filter effluent. The average TTHM concentrations during Mode 1 were 85 μg/L for clarifier effluent and 91 μg/L for filter effluent. The respective concentrations during Mode 4 were 23 and 26 μg/L. Thus the two sets of carbon columns in each mode received water with approximately the same TOC and TTHM.

Results from the pilot studies indicated that after a column was placed into service with virgin GAC, the TOC concentration in the effluent was low and increased almost immediately until it reached a steady state concentration. In all cases, this steady state concentration was reached in approximately 50 to 60 days. The effluent concentrations from Columns 10-6 and 12-6 were approximately equal (1 to 2 mg/L), whereas the effluent concentration from Column 11-6 was slightly higher (2 to 4 mg/L). The contact time through Column 11-6 (8 minutes) was only half the contact time through Columns 10-6 and 12-6 (16 minutes).

The GAC column performances for TTHM removal differed from those for TOC. The TTHM concentration in the effluent from the GAC columns remained below 5 μg/L for approximately 30 to 70 days, depending on the column. After that period, the TTHM concentration in the effluent began to increase and continued increasing for 30 to 50 days. The TTHM concentration then reached a longer-term steady state, during which a degree of removal could still be maintained.

TTHMFP is an important parameter for judging the performance of the GAC process. Since the water is dechlorinated during the GAC process, the effluent must be chlorinated before delivery to the customer. The TTHMFP concentration in the effluent from the GAC columns began below 50 μg/L and then increased to a quasi-steady state concentration after 30 to 50 days for Mode 1 and after 40 to 90 days for Mode 4. Because of the difference in contact time, TTHMFP in the effluent from column 11-6 began increasing sooner and reached a higher level (100 to 150 μg/L) than the effluents from columns 10-6 and 12-6 (50 to 90 μg/L).

Alternative Disinfectants

The water quality of the pilot plant filter effluent was used to determine the performance of the alternative disinfectants. Formation of chlorinated organic byproducts was determined using TTHM and TOX analyses. Bacteriological quality of the filter effluent was determined using both total coliform and standard plate count techniques. From these, the bactericidal efficiency of the alternative disinfectants could be determined.

Several batch studies were performed to evaluate critical characteristics with respect to disinfection and formation of chlorinated byproducts over a range of chlorination conditions. These studies were intended to supplement the pilot plant work by comparing different chlorination approaches on the same water sample. As such, the results from these evaluations yielded a direct comparison of these approaches. The batch experiments were performed by withdrawing 250-ml aliquots of a sample and placing each aliquot in a headspace-free bottle with a chlorine solution for a defined period of time. The pH was controlled in the range of 7.5 to 8.0 to match conditions normally encountered in the water distribution system. Temperature was controlled to match that of the finished water as an approximation of conditions found in the distribution system.

Chlorinated Organic Formation

The data evaluated were the TTHMFP of the full-scale raw blend, the instanteous TTHM of the pilot plant filter effluent, and the terminal TTHM of the pilot plant filter effluent. TTHMFP for the full-scale raw blend was determined by spiking the sample with chlorine at a dosage of 2 mg/L greater than the 1-hr demand. The sample was then stored for a 5-day period before analysis.

The average instantaneous TTHM concentration was approximately 80 μg/L for Mode 1 (free chlorination), 25 μg/L for Mode 4 (post-ammoniation), 15 μg/L for Mode 5 (preformed chloramines), and 10 μg/L for Mode 6 (dual disinfection). The average terminal TTHM concentration was approximately 190 μg/L for Mode 1 and 40 μg/L for Mode 4. The higher concentration for Mode 1 results from the free chlorine present during sample storage; Mode 4 had no free chlorine because of post-ammoniation. The data show no significant difference in the instantaneous and terminal TTHM values for Modes 5 and 6. The terminal values indicate the expected maximum concentration of TTHM in the distribution system for each mode of operation.

TOX is a nonspecific parameter for indication of chlorinated organics. The general trend for the TOX data is similar to that observed for the TTHM data. The average instantaneous TOX concentration in the pilot plant filter effluent was 270 μg/L for Mode 1, 130 μg/L for Mode 4, 120 μg/L for Mode 5, and 80 μg/L for Mode 6. The average terminal TOX concentration for the same four modes was 400, 400, 370, and 180 μg/L, respectively.

Bacterial Efficiency

Data for the pilot plant filter effluent show that total coliforms were reduced to levels below the detection limit in nearly all cases for each alternative disinfectant. Thus because of its greater sensitivity, the standard plate count (SPC) was used as a means for examining the bactericidal efficiency of the alternative disinfectants.

Probability distributions of the SPC data show that with breakpoint, or free, chlorination as practiced during Mode 1, an SPC of 10/mL was achieved approximately 98 percent of the time. When chloramination was practiced using the post-ammoniation method, as in Mode 4, an SPC of 10/mL was achieved only 87 percent of the time. With the use of a chloramine solution generated off-line, as practiced during Mode 5, an SPC of 10/mL was achieved only 76 percent of the time. When chlorine dioxide was used as the primary disinfectant in a dual disinfection system, as practiced during Mode 6, an

SPC of 10/mL was achieved approximately 97 percent of the time. The relative bactericidal efficiency of the alternative disinfectants is consistent with that found in the literature.

Batch Studies

The general approach used in all batch studies was to evaluate the characteristics of concern at different locations along a breakpoint chlorination curve. Those points located to the left of the classic breakpoint lie within regions where chloramines are the predominant form of total chlorine residual, and those points to the right of the breakpoint occur within the region of domination by free chlorine. Characteristics that were evaluated include the biocidal effectiveness of different methods of chlorination and the formation of chlorinated byproducts, such as TTHM, dichloroacetonitrile, TOX, and organic chloramines.

The use of breakpoint chlorination to achieve free chlorine results in the minimum bacteriological risk but maximizes the formation of chlorinated byproducts, as indicated by TTHM, dichloroacetonitrile, organic chloramines, and TOX. Conversely, the use of a preformed chloramine solution results in the formation of the lowest level of byproducts but results in the highest level of bacteriological risk. The use of other alternative chloramination methods results in mixed levels of risk for all parameters. The various chloramination modes result in a significant formation of chlorinated byproducts, particularly TOX, with the exception of the use of a preformed chloramine solution.

Raw Water Quality

Only those sources that are currently used as a raw water supply for the Columbine Water Treatment Plant or are readily available for use in the near future were considered for evaluation. The parameters that were evaluated included ammonia, nitrate plus nitrite, total Kjeldahl nitrogen, turbidity, coliform, TOC, TTHM, and TOX. Based on the data from these analyses, the raw water sources were ranked by their quality. This aided Thornton with their water treatment planning.

Conclusions

1. The quality of the Thornton, CO, raw water varies during the year and follows a fairly predictable annual cycle.
2. The raw water sources for the Columbine Water Treatment Plant exhibit a chlorine dosage dependency with respect to TTHM formation.
3. A literature review shows that TTHM formation can be related to algae concentrations in the raw water. A study conducted during the pilot plant program showed that TTHM produced by chlorination of proteins can be significant during summer months of high algae growth. TTHM is only one example of organohalogen compounds that can be produced by chlorination of proteins. Algae can be a significant source of these proteins.
4. Compared with a conventional coagulation and sedimentation process, PAC doses of 5 to 10 mg/L had a minimal effect on the removal of organics as measured by TOC. TOC removal was approximately 6 percent greater with PAC than without it. PAC addition did not effect the TTHM and TOX concentrations in the filter effluent.
5. GAC is capable of removing TTHM and TOX. These chlorinated organics reached a steady-state concentration in the effluent from the GAC columns, with breakthrough occurring at certain intervals. The interval of time to breakthrough was not long enough for GAC to be an economical alternative to using other disinfectants for controlling TTHM and TOX.
6. The conventional treatment processes could remove approximately 30 to 40 percent of the TTHMFP. By moving the point of chlorination downstream of conventional treatment, a decrease in TTHM formation was realized. However, the precursor removal by sedimentation was not adequate to consistently allow Thornton to produce water with less than 100 μg/L TTHMFP.
7. Alternative chlorination schemes can be characterized by the region in which the chlorine species occur along the breakpoint chlorination curve. Each chlorination scheme results in different water quality in terms of bacteria and chlorinated organic byproducts.
   The chloramination procedure affects the amount of disinfection and the byproduct formation even when the water following chlorar ination contains the same type ar concentration of chloramines.
8. Selection of the disinfectic scheme should be based on tv primary criteria: Disinfection c pabilities and disinfection b product formation. The goal is maximize disinfection (i.e., to k bacteria and other pathogen and to minimize the formation byproducts that have potentia adverse health effects.
9. None of the alternative chlorin tion schemes produced both fective disinfection and minim formation of chlorinated orgar byproducts, as indicated b TTHM and TOX, during the pil plant study. The chlorinatic schemes that maximized disi fection were those that result in higher byproduct concentr tions. Those schemes that mir mized byproduct formation hac smaller degree of bacteria kill.
10. The use of chlorine dioxide as disinfectant maximized bacter kill and minimized the formatic of chlorinated organic bypro ucts. However, because the chl rine dioxide residual is limited chlorite and chlorate formation chlorine or chloramine soluti must be added so that a disinfe tant residual can be maintained the distribution system.

Recommendations

1. The raw water monitoring pr gram should be continued to d velop the data base further. Th program will allow for evaluatio of water sources and provid data relating to the variability the supply on an annual basis.
2. The evaluation and eventual d sign of a full-scale chlorine dio ide generation and feed syste should be considered for th Columbine Water Treatmer Plant.
3. Alternative chlorination scheme should be evaluated for a wat supply containing a low ammonia concentration. The di infection and byproduct form tion results for a low-ammon water may be different than thos found during this pilot pla study.
4. When evaluating alternative di infectants, water utilities shou

consider more parameters than those currently regulated under the U.S. Environmental Protection Agency Primary Drinking Water Standards. Other parameters can provide a broader indication of disinfection byproducts and bacteriological quality. For example, when considering chloramines as an alternative to free chlorine, TOX should be used along with TTHM as a minimum indication of byproduct formation. A more sensitive indicator of bacteriological quality, such as heterotrophic plate count, should be used along with the total coliform count.

5. Because different waters have different characteristics in relation to TTHM formation, certain parameters should be monitored and reported when analyzing for TTHMFP. These parameters include free and total chlorine residuals, pH, temperature, and storage period. In addition, since some waters exhibit a dosage dependency toward TTHM formation, TTHMFP analyses should be conducted for at least two different chlorine dosages.

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The complete report, entitled "Treatment Alternatives for Controlling Chlorinated Organic Contaminants in Drinking Water," (Order No. PB 87-145 751/AS; Cost: $18.95, subject to change) will be available only from:
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