

## Comparing methods to remove emerging contaminants and disinfection by-product precursors at pilot scale

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### ABSTRACT

The removal of selected pharmaceuticals and personal care products, atrazine, and disinfection by-product precursors, was evaluated during a pilot-scale study conducted at the Bollman Water Treatment Plant in Concord, California, USA. Treatment alternatives included ozonation followed by biologically active filtration (BAF), and nanofiltration. Both technologies exhibited excellent broad-spectrum removal of the spiked target contaminants. The ozone/BAF system in particular showed a high degree of effectiveness despite relatively low ozone doses corresponding to a low disinfection target (0.5-log *Giardia* reduction). The BAF system was observed to remove several contaminants that were relatively unreactive with ozone, demonstrating an important synergy between the ozone and BAF.

**Key words** | biologically active filtration, disinfection by-product, nanofiltration, ozone, personal care product, pharmaceutical

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### INTRODUCTION

The Sacramento-San Joaquin River Delta, in California, USA, is a source of drinking water to over 23 million people. The water quality in the Delta is potentially at risk of deteriorating in the future due to input from agriculture drains and other surface water discharges, increased fresh water diversions, and the possibility of severe drought. The Contra Costa Water District (District) provides untreated and treated water to approximately 500,000 people in the Contra Costa County and obtains its water supply exclusively from the Delta. To prepare itself and other Delta utilities for anticipated future water quality challenges and regulations, the District conducted a pilot study at its Bollman Water Treatment Plant (WTP) to explore methods to

enhance the removal of organic contaminants in the source water, including trace organics that are often classified as PPCPs (pharmaceuticals and personal care products), the herbicide atrazine, and bulk organics that serve as disinfection by-product (DBP) precursors. The contaminants selected for this study were spiked into the water to represent a simulation of possible future contamination, and are therefore not representative of actual water quality currently produced at the plant.

The Bollman WTP treats drinking water by prechlorination, pH depression, alum coagulation and flocculation, conventional sedimentation, intermediate ozonation, and dual media biologically active filtration (BAF – granular

activated carbon operating in a biological mode, and sand). An alternative treatment option being examined is nanofiltration. The ability of ozone/BAF and nanofiltration to remove many PPCPs, pesticides, and DBP precursors has already been reported by others (for example, Huber *et al.* 2003; Ternes *et al.* 2003; Westerhoff *et al.* 2005; Snyder *et al.* 2006; Reungoat *et al.* 2011). The current work is useful, however, in that it allows a side-by-side comparison of ozone/BAF and nanofiltration when treating the same source of water, and when applying ozone doses of relevance to drinking water disinfection. This work also adds to the database of the performance of these technologies in a unique estuarine natural water, thereby expanding the range of water matrices that have been evaluated using these treatment processes for PPCP, atrazine, and DBP precursor removal.

## MATERIALS AND METHODS

### Experimental plan and pilot facilities

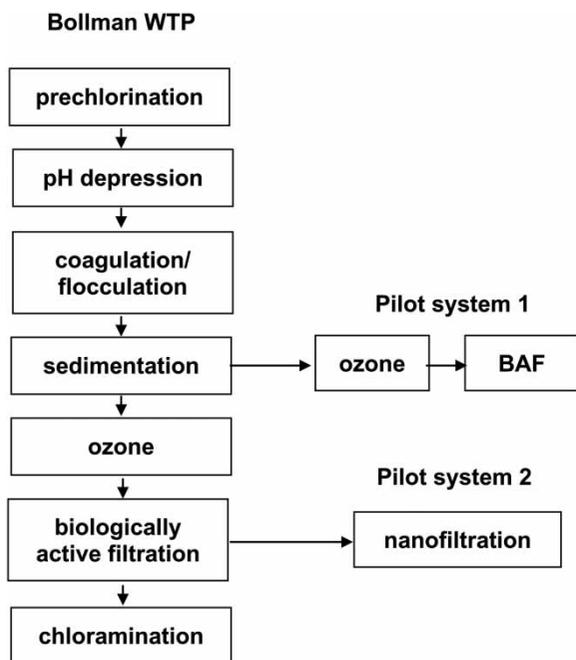
This project began with a survey of PPCPs and pesticides in the source water for the Bollman WTP. Samples were drawn from the Old River (near one of the District's intakes) in both October and February to explore potential seasonal variability. A list of the survey compounds is given in Table 1, with the maximum concentration detected given in parentheses. The selection of priority compounds for the pilot-scale testing (identified in Table 1 with asterisks) was based on this survey information, together with a review of PPCPs and pesticides commonly found in other surveys (Kolpin *et al.* 2002; USGS 2002; Snyder *et al.* 2007), and a strategy to select compounds that represent a broad spectrum of chemical classes.

The pilot plant included an ozone/BAF system drawing water from the full-scale plant following the coagulation/flocculation and sedimentation process, and a parallel nanofiltration system drawing water following the full-scale plant's BAF step (Figure 1). The pilot systems were operated for a period of over two months, with the first month used to establish baseline performance and to confirm system stability, and the second month devoted to monitoring organic contaminant removal. Because of the low ambient

**Table 1** | Compounds included in the preliminary survey of source water and in the pilot tests. The maximum concentrations (ng/L) detected are shown in parenthesis and the compounds selected for study in the pilot-scale tests are indicated with an asterisk. ND = not detected

|                                      |   |
|--------------------------------------|---|
| <b>Acidic drugs</b>                  | <b>Antibacterial agents</b>                 |
| Gemfibrozil (20)*                    | Triclosan (35)*                             |
| Acetaminophen (41)                   | Triclocarban (ND)                           |
| Ibuprofen (11)*                      | <b>Sulfonamide antibiotics</b>              |
| Naproxen (ND)                        | Sulfamethoxazole (18)*                      |
| <b>Neutral drugs</b>                 | Sulfapyridine (ND)                          |
| Carbamazepine (4)*                   | <b>Synthetic musks</b>                      |
| Caffeine (28)*                       | HHCB (Galaxolide) (17)                      |
| Cotinine (9)                         | AHTN (Tonalide) (ND)                        |
| Trimethoprim (5)                     | DPMI (Cashmeran) (ND)                       |
| <b>Estrogens &amp; xenoestrogens</b> | ATII (Traseolide) (ND)                      |
| 17 $\alpha$ -ethinylestradiol (ND)   | ADBI (Celestolide) (ND)                     |
| 17 $\beta$ -estradiol (ND)           | AHMI (Phantolide) (ND)                      |
| Estrone (16)                         | Musk xylene (ND)                            |
| Bisphenol A (3,485)*                 | Musk ambrette (ND)                          |
| 4-nonylphenol (6)*                   | Musk moskene (ND)                           |
| <b>Beta blockers</b>                 | Musk tibetene (ND)                          |
| Propranolol (ND)                     | Musk ketone (ND)                            |
| Metoprolol (5)                       | <b>Antidepressants</b>                      |
| Atenolol (23)*                       | Fluoxetine and norfluoxetine (ND)           |
| Sotalol (ND)                         | Venlafaxine/O-desmethyl<br>venlafaxine (ND) |
| <b>Pesticides</b>                    | Citalopram and desmethyl<br>citalopram (ND) |
| Atrazine (ND)*                       | Sertraline and desmethyl<br>sertraline (ND) |
| Simazine (60)                        | Bupropion (ND)                              |
| <b>X-ray contrast chemical</b>       | Paroxetine (ND)                             |
| Iopromide (ND)*                      |   |

concentrations of the target compounds in untreated water and the need for high enough concentrations to allow for measurement of percentage removals, PPCPs and atrazine were spiked following a holding tank and blended with the influent water to achieve low ppb ( $\mu\text{g/L}$ ) initial concentrations. The spiking solution was applied at least 4 h (approximately 8 retention times) prior to sampling to ensure complete mixing through the pilot processes. The PPCPs and atrazine were added in an acetone carrier solvent to yield concentrations of approximately 0.5–1  $\mu\text{g/L}$  when blended with the main flow. This is several orders of magnitude greater than the ng/L concentrations in natural



**Figure 1** | Schematic of the ozone/BAF and nanofiltration treatment trains.

raw waters reported elsewhere. Tests confirmed that the added acetone had no observed impact on ozone stability, and calculations indicated that any hydroxyl radical scavenging due to the acetone would be negligible compared to the background organic matter and inorganic carbon. The spiking solution also included salts to increase the background bromide concentration by 0.4 mg/L, chloride by 119 mg/L, and iodide by 0.04 mg/L. This salt addition simulates a potential future increase in source water salinity, and addresses several other research objectives that are not included in this paper.

The ozone system was an Ozone Module Z100 (Intutech, Salt Lake City, Utah) and was operated to simulate the treatment plant that applies ozone to achieve a 0.5-log *Giardia* and 2-log virus inactivation, which at the time of the pilot study required 0.5 to 1.6 mg/L of applied ozone, with a 0.2 to 0.3 mg/L residual after 8 min of contact time. The GAC/sand filter skid was provided by Carollo Engineers and included three filter columns, each 4 inches (10 cm) in diameter. GAC was obtained from the full-scale BAF filters and had more than 6 years of service life. It was therefore assumed that all adsorptive capacity of the GAC was exhausted and that it would operate

solely as a biological filter, however biological activity was not specifically monitored. The filters contained approximately 4 feet (1.2 m) of GAC overlying 10 inches (25 cm) of sand and were operated at a filter loading rate of 0.8 ft/min (0.25 m/min) to deliver an empty bed contact time in the GAC phase of 6.1 min, and a total EBCT of 7.4 min in both GAC/sand media. The nanofiltration (NF) system was an NF-4040 spiral wound Filmtec membrane from Dow (Chicago, IL), mounted on a skid provided by Harn R/O systems (Venice, Florida). The membrane had a nominal 200 Da molecular weight cutoff, and was operated in a two-stage single pass mode, with the reject from the first stage passing through the second stage to yield an overall 80% recovery. Applied flow rates for the first and second stage were 20 and 11 gallons per minute respectively (76 and 42 L/min), at pressures of approximately 95 pounds per square inch (655 kPa). The membrane fluxes in the first and second stages averaged 48 and 29 gallons per day per square foot, respectively (2,000 and 1,180 L/m<sup>2</sup>/day).

## Analytical

For the initial survey of PPCPs and triazine herbicides in the Old River, 1 L samples of water were analyzed at the Water Quality Centre at Trent University (Ontario, Canada), using methods described by Hua *et al.* (2006) for triazine herbicides, Yang & Metcalfe (2006) for synthetic musks, Metcalfe *et al.* (2010) for antidepressants, Scheurer *et al.* (2010) for beta-blockers, Topp *et al.* (2008) for acidic and neutral drugs and sulfonamide antibiotics, and Li *et al.* (2010) for bisphenol A (BPA), 4-nonylphenol (4-NP), estrogen hormones and triclosan. Following the initial survey, the list of target compounds was reduced to the herbicide atrazine, selected acidic and neutral drugs, BPA, 4-NP and triclosan, the beta-blocker drug, atenolol, the X-ray contrast agent iopromide, and the sulfonamide antibiotic, sulfamethoxazole (SMX). All of these compounds were extracted from water samples of 100 mL using solid phase extraction (SPE) with either Oasis HLB or MCX extraction cartridges purchased from Waters (Mississauga, ON, Canada). The extracts were analyzed by high pressure liquid chromatography and tandem mass spectrometry (LC-MS/MS)

using either electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) as the ionization source. Stable isotope surrogates for all target analytes were spiked into the water samples as internal standards prior to extraction to aid with sample quantitation. The relative standard deviation for the analysis of all of these compounds in the study's water matrix was determined to be less than 20–30%.

One field blank and two matrix spikes were processed with each test of the pilot trains. The field blanks were deionized water, with 1 g/L sodium azide added for preservation (or hydrochloric acid in the case of the atrazine sample), and were exposed to ambient conditions while the samples were collected from the pilot trains. The matrix spikes were prepared by extracting a known volume of the spiking solution and adding it to water collected from the pilot influent. The matrix spikes were also preserved with 1 g/L sodium azide or hydrochloric acid.

Trihalomethanes and haloacetic acids were measured according to Standard Method 6231B and 6251B, respectively (APHA/AWWA/WEF 2005), using a Hewlett Packard 5890 II gas chromatograph with an electron capture detector. Difficulty was experienced in measuring monochloroacetic acid and monobromoacetic acid, with unknown interfering compounds co-eluting with these two HAAs. Methods to try to resolve the problem were

unsuccessful. As such, we are only able to report the other seven chlorinated/brominated HAAs, and denote this as HAA<sub>7</sub> in this paper. The authors suggest that since many surveys have demonstrated monochloro- and monobromoacetic acid concentrations to typically contribute less than several percent to the sum of the nine chlorinated/brominated HAAs, the lack of these two compounds does not significantly detract from the results of this work.

Total organic carbon was measured with an OI Analytical 1010 TOC analyzer according to Standard Method 531 °C (APHA/AWWA/WEF 2005). Ultraviolet light absorbance was recorded using a Hewlett Packard 8452A diode array spectrophotometer according to Standard Method 5910B (APHA/AWWA/WEF 2005). THM and HAA formation potential tests were conducted at pH 7.0, 22 °C, by chlorinating samples at a chlorine concentration that yielded a 3–5 mg/L residual after 7 days.

## RESULTS AND DISCUSSION

### Removal of PPCPs and atrazine by ozone and BAF

The concentrations of PPCPs and atrazine were measured upstream and downstream of the pilot-scale ozone contactor and BAF processes. The results are shown in Table 2 in

**Table 2** | PPCP and pesticide removal across the pilot treatment processes. CBZ = carbamazepine, SMX = sulfamethoxazole, BPA = bisphenol A, 4-NP = 4-nonylphenol

| Compound    | Concentration (ng/L)<br>Ozone-BAF system<br>1.0 mg/L ozone dose |                     |          |                     |                     |          | Nanofiltration system |          |             |          |          |             |
|-------------|---|---------------------|----------|---------------------|---------------------|----------|-----------------------|----------|-------------|----------|----------|-------------|
|             | 0.5 mg/L ozone dose   |                     |          | 0.5 mg/L ozone dose |                     |          | Week 1                |          |             | Week 2   |          |             |
|             | Influent  | Post-O <sub>3</sub> | Post-BAF | Influent            | Post-O <sub>3</sub> | Post-BAF | Influent              | Permeate | Concentrate | Influent | Permeate | Concentrate |
| BPA         | 1,324   | 102                 | 58       | 818                 | 389                 | 16       | 223                   | 31       | 1,329       | 987      | 201      | 3,320       |
| 4-NP        | 106   | 10                  | 10       | 191                 | 10                  | 10       | 15                    | 10       | 263         | 14       | 10       | 67          |
| Atenolol    | 907   | 75                  | 12       | 990                 | 604                 | 107      | 880                   | 75       | 4,890       | 1,310    | 93       | 4,613       |
| Triclosan   | 590   | 10                  | 10       | 522                 | 10                  | 10       | 294                   | 10       | 495         | 268      | 10       | 484         |
| Caffeine    | 855   | 62                  | 31       | 1,022               | 419                 | 98       | 373                   | 76       | 1,818       | 1,242    | 97       | 3,852       |
| CBZ         | 690   | 10                  | 10       | 652                 | 12                  | 12       | 760                   | 20       | 3,660       | 982      | 26       | 4,245       |
| Ibuprofen   | 1,010   | 612                 | 274      | 964                 | 695                 | 387      | 1,228                 | 17       | 4,903       | 2,022    | 10       | 5,222       |
| Gemfibrozil | 1,439   | 26                  | 23       | 1,478               | 39                  | 39       | 1,727                 | 33       | 6,803       | 1,889    | 39       | 10,871      |
| Iopromide   | 263   | 131                 | 90       | 359                 | 254                 | 255      | 255                   | 10       | 604         | 341      | 10       | 911         |
| SMX         | 787   | 10                  | 10       | 875                 | 32                  | 18       | 947                   | 10       | 4,543       | 998      | 35       | 5,367       |
| Atrazine    | 500   | 400                 | 100      | 500                 | NA                  | 200      | 600                   | 50       | 1,275       | 700      | 50       | 1,425       |

terms of absolute concentrations, while the normalized fractional reductions are illustrated in Figure 2. Due to laboratory constraints, only single water samples could be analyzed for each set of experimental conditions.

The experiment was conducted at two ozone doses (1.0 and 0.5 mg/L) which allowed for the impact of ozone concentration to be observed. It is presumed that this water matrix would tend to be moderately unfavourable for hydroxyl radical reactions (pH 7.2, alkalinity of 55 mg/L as CaCO<sub>3</sub> and 3.3 mg/L TOC), but measurement of the relative contributions of molecular ozone and hydroxyl radical reaction pathways – such as by determining the  $R_{CT}$  (Elovitz & von Gunten 1999) – was beyond the scope of the study.

The results indicate that most of the compounds were very effectively removed by a 1.0 mg/L initial ozone dose over the 8 min of contact time. When the ozone dose was lowered to 0.5 mg/L, a 20–50% reduction in the removal of atenolol, caffeine, and BPA was observed, indicating

some resistance to ozone. Removal of iopromide, ibuprofen, and atrazine by ozone was poor (20–50%) at even the 1.0 mg/L ozone dose. These results reflect the known ozone reaction rate coefficients reported by Zimmermann *et al.* (2011), Huber *et al.* (2003), Beltran *et al.* (2000), and Snyder *et al.* (2007). The ‘fast’ reacting compounds in this study (bisphenol A, 4-nonylphenol, triclosan, carbamazepine, sulfamethoxazole) have ozone reaction rate coefficients of greater than  $10^5 \text{ M}^{-1} \text{ s}^{-1}$ , while the compounds exhibiting less than 50% removal (ibuprofen, iopromide, atrazine) have reaction rate coefficients of less than  $10 \text{ M}^{-1} \text{ s}^{-1}$ . From a practical perspective, this study demonstrated that at the ozone dose of 1 mg/L, corresponding to 0.5-log *Giardia* inactivation, all compounds with ozone reaction rate coefficients of greater than  $10^3 \text{ M}^{-1} \text{ s}^{-1}$  were reduced by more than 90%.

Table 2 and Figure 2 also show the contaminant removals attributable to the biologically active filtration. In most cases, since ozone had effectively removed most of

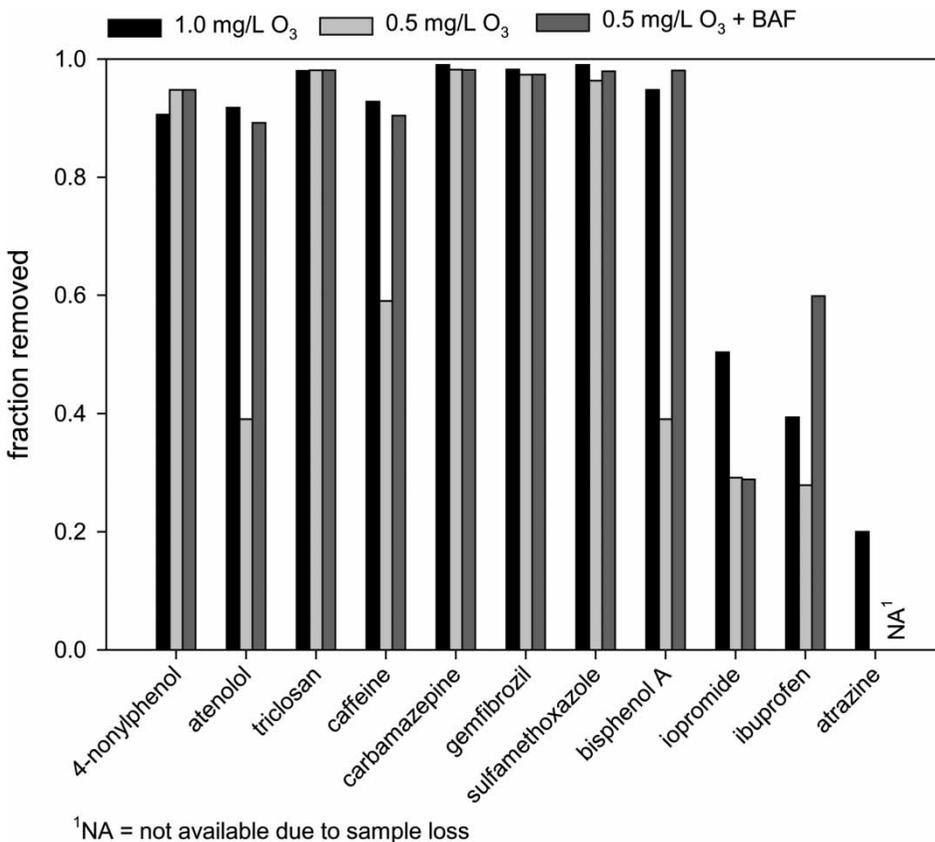


Figure 2 | Fraction removal of contaminants across ozone, and ozone + BAF.

the contaminant, the removal via BAF could not be observed. However, atenolol, caffeine, BPA and ibuprofen were all poorly removed at an ozone dose of 0.5 mg/L, but there was significant additional removal through the BAF process (i.e. a 20–40% increase in removal). The activated carbon in the pilot system had been taken from the BAF bed in the full-scale plant and was presumed to have an exhausted adsorptive capacity, so it is assumed that the removal across the BAF was due to biological activity. Of all of the compounds monitored, only iopromide appears to be resistant to both ozone, with only a 30–50% destruction at doses of 0.5 to 1 mg/L, and BAF, with no observed additional removal across the filter. These results are similar to those reported by Lee (2011), where wastewater from a membrane bioreactor was subsequently treated by ozone + BAF, with the BAF observed to result in greater than 90% removal of atenolol and caffeine when an ozone dose of 4 mg/L was applied, but iopromide was reportedly more recalcitrant, with only 40% removal across the BAF. Interestingly, Lee (2011) reported that an 8 mg/L ozone dose resulted in 89% removal of iopromide across the BAF, presumably by enhanced biological activity, suggesting that iopromide may be biodegradable, but only under very favourable conditions.

An important interpretation of these results is that the ozone dose that was used for a moderate level of disinfection (0.5-log *Giardia* inactivation), combined with subsequent BAF achieved more than 90% reduction of 8 out of the 11 compounds monitored, and about 50% reduction of two of the remaining three compounds. There is a growing interest in ozone + BAF treatment for enhanced organic DBP precursor removal, improved taste and odor control, and reduced distribution system biofilm. This work demonstrates that an added benefit to ozone + BAF is broad-spectrum control of PPCPs and atrazine.

### Removal of PPCPs and atrazine by nanofiltration

Nanofiltration has previously been reported to be very effective at removing various PPCPs and pesticides, although it is difficult to generalize about performance due to the wide variety of types of nanofiltration, and associated operating conditions. Yoon *et al.* (2006, 2007)

reported 50–80% removal of a suite of pharmaceuticals and personal care products across a laboratory-scale dead-end nanofilter with a molecular weight cutoff (MWCO) of 600 Daltons when evaluating different surface water matrices. Flyborg *et al.* (2010) reported reduction of more than 70 out of 95 pharmaceuticals in treated wastewater to below quantitation limits when using a pilot-scale nanofilter with a MWCO of 150 Daltons.

In this study, the 200 Dalton MWCO nanofiltration pilot system removed most compounds to levels below detection limits (Figure 3). Caffeine and BPA exhibited the lowest removal, but the removals were still at 80 and 86%, respectively. Snyder *et al.* (2007) reported some destruction of steroids following addition of anti-scalant chemicals for a reverse osmosis system. A proprietary anti-scalant was applied in this work, but compound concentrations were not monitored between addition of the anti-scalant and post-membrane. As such, the observed reductions could be due to the combination of reaction with anti-scalant and removal by the membrane.

### DBP precursor removal

The total organic carbon (TOC) concentration remained constant across the ozone contactor (Table 3). This is expected because ozone generally leads to very little mineralization of organics at typical doses (Carr & Baird 2000). In

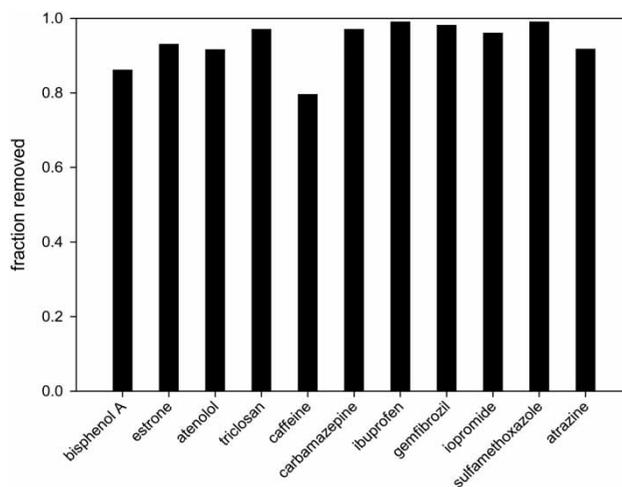


Figure 3 | Fraction removal of contaminants across nanofiltration.

**Table 3** | Percentage removal of TOC, UV<sub>254</sub>, and THMFP and HAA<sub>7</sub>FP across treatment processes

|                     | Across the ozone            |                             | Across the BAF              |                             | Across the NF |            |
|---------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|---------------|------------|
|                     | 1.0 mg/L O <sub>3</sub> (%) | 0.5 mg/L O <sub>3</sub> (%) | 1.0 mg/L O <sub>3</sub> (%) | 0.5 mg/L O <sub>3</sub> (%) | Week 1 (%)    | Week 2 (%) |
| TOC                 | 0                           | 0                           | 18                          | 10                          | 78            | 78         |
| UV <sub>254</sub>   | 33                          | 20                          | 9                           | 10                          | 100           | 91         |
| THMFP               | 11                          | 11                          | 28                          | 15                          | 51            | 38         |
| HAA <sub>7</sub> FP | 21                          | 19                          | 30                          | 29                          | 87            | 78         |

contrast, the ozone reduced the UV<sub>254</sub> absorbance significantly by 20–30%, with the higher UV<sub>254</sub> reduction associated with the higher ozone dose of 1.0 mg/L. Ozone is known to react with carbon-carbon double bonds, which are responsible for UV absorbance, and which are also major contributors to chlorinated DBP formation and chlorine demand.

About 10% of the TOC was removed across the BAF filters when a 0.5 mg/L ozone dose was applied, with the TOC removal increasing to 18% at the higher 1.0 mg/L ozone dose. This demonstrates the synergy between ozone and BAF, with higher ozone doses enhancing the biodegradability of the organics. The BAF system also removed 9–10% of the UV<sub>254</sub>, independent of the ozone dose.

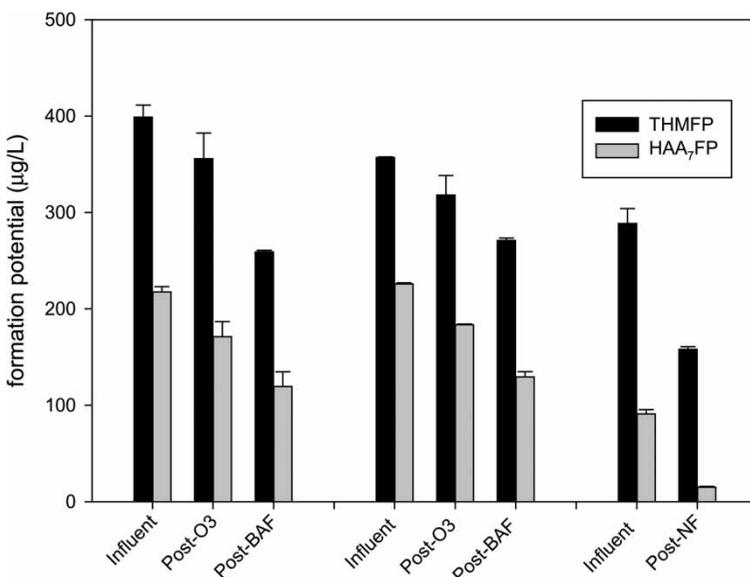
TOC and UV<sub>254</sub> removal were superior in the nanofiltration system compared to the ozone/BAF system. TOC

removal across the membrane was 78%, while UV<sub>254</sub> removal exceeded 90%.

THM and HAA formation potential tests were undertaken on water collected from the pilot plant to better understand the DBP precursor removal by ozone + BAF or nanofiltration. Ozone reduced the THM formation potential (THMFP) by 11%, regardless of the ozone dose, while the HAA<sub>7</sub>FP was reduced by approximately 20% at both ozone doses (Table 3 and Figure 4).

The BAF reduced the THMFP by 15 and 28% when preceded by ozone doses of 0.5 and 1.0 mg/L, respectively, demonstrating that the lower ozone dose had not completely maximized conversion of the organic matter to a biodegradable form. In contrast, HAA<sub>7</sub>FP was reduced by approximately 30% across the BAF system at both ozone doses. These reductions in DBP formation potential across the BAF are considerably higher than the TOC removal, suggesting that the BAF process may have been selectively removing THM and HAA precursors. It is unknown, however, to what extent the biological mechanism contributed to the reduction in DBPFP relative to simple filtration, since there was no non-biological control filter during the study.

Of the treatments tested, nanofiltration was found to be the most effective for reducing the DBP formation potential. The THMFP was reduced by 45% in nanofilter permeate

**Figure 4** | DBP formation potential reduction.

relative to the influent, while the HAA<sub>7</sub>FP decreased by 83%. Since the TOC reduction across the nanofilter was 82%, these results suggest that HAA<sub>7</sub> precursor removal across the nanofilter was proportional to TOC removal, but that THM precursors were less well controlled than bulk TOC by the system.

## CONCLUSIONS

Both the pilot-scale ozone/BAF treatment train and the nanofiltration system demonstrated excellent removals of trace organic contaminants, as well as DBP precursors. Of particular interest was the ability of ozone at relatively low disinfection doses consistent with 0.5-log *Giardia* inactivation, in combination with BAF, to provide a very high degree of trace organic contaminant removal for the broad spectrum of contaminants tested. This, coupled with THMFP and HAA<sub>7</sub>FP removal rates of 30–40%, shows the excellent capabilities of an ozone/BAF treatment train.

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