Powdered activated carbon coupled with enhanced coagulation for natural organic matter removal and disinfection by-product control: Application in a Western Australian water treatment plant

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Abstract

The removal of organic precursors of disinfection by-products (DBPs), i.e. natural organic matter (NOM), prior to disinfection and distribution is considered as the most effective approach to minimise the formation of DBPs. This study investigated the impact of the addition of powdered activated carbon (PAC) to an enhanced coagulation treatment process at an existing water treatment plant on the efficiency of NOM removal, the disinfection behaviour of the treated water, and the water quality in the distribution system. This is the first comprehensive assessment of the efficacy of plant-scale application of PAC combined with enhanced coagulation on an Australian source water. As a result of the PAC addition, the removal of NOM improved by 70%, which led to a significant reduction (80 – 95%) in the formation of DBPs. The water quality in the distribution system also improved, indicated by lower concentrations of DBPs in the distribution system and better maintenance of disinfectant residual at the extremities of the distribution system. The efficacy of the PAC treatment for NOM removal was shown to be a function of the characteristics of the NOM and the quality of the source water, as well as the PAC dose. PAC treatment did not have the capacity to remove bromide ion, resulting in the formation of more brominated DBPs. Since brominated DBPs have been found to be more toxic than their chlorinated analogues, their preferential formation upon PAC addition must be considered, especially in source waters containing high concentrations of bromide.

Keywords: Powdered activated carbon; enhanced coagulation; disinfection by-products; natural organic matter; trihalomethanes; haloacetic acids
1. Introduction

Since the beginning of the 20th century, disinfection has been an integral part of drinking water treatment due to its crucial role in preventing the spread of waterborne diseases. While disinfectants are effective in inactivating harmful microorganisms, as powerful oxidants, they also react with organic and inorganic materials in treated waters, leading to the formation of disinfection by-products (DBPs). Through epidemiological studies, some DBPs have been associated with a number of adverse human health effects e.g. cancers of the urinary and digestive tracts, bladder and colon cancers, low birth weight, intrauterine growth retardation, and spontaneous abortion (Richardson et al., 2007), although some of these effects are still somewhat controversial and require further studies. Due to the potential adverse health effects associated with DBPs, in many countries the concentrations of DBPs in drinking waters are regulated. For example, the maximum contaminant level (MCL) of THMs (the total concentrations of four species of THMs: chloroform, bromodichloroacetic acid, chlorodibromoacetic acid, and bromoform) in the US is currently 80 µg L⁻¹, while the Australian Drinking Water Guidelines (ADWG) set the guideline value for the concentration of total THMs at 250 µg L⁻¹. Water utilities are therefore required to ensure that drinking water treatment processes are in place and adequate, such that the concentrations of DBPs in the distributed drinking water do not exceed the specified regulations and guidelines.

The formation of DBPs can be controlled and minimised using one, or a combination of, the following approach: removal of DBP precursors prior to disinfection, change of disinfectant, and removal of DBPs following disinfection (Karanfil et al., 2008). The removal of organic precursors of DBPs i.e. natural organic matter (NOM) prior to disinfection and distribution is considered to be the most effective approach to minimise the formation of DBPs. Due to the increasingly stringent DBP regulations, advanced precursor removal technologies are being
used to maximise NOM removal. These include membrane filtration (microfiltration, nanofiltration, reverse osmosis), activated carbon (granular activated carbon (GAC), powdered activated carbon (PAC)), and ion exchange (MIEX® resin).

In Australia, many source waters contain particularly high concentrations of NOM by international standards (up to 40 mg L\(^{-1}\) as dissolved organic carbon (DOC)), and sources in coastal locations may contain elevated levels of bromide ion (up to 2 mg L\(^{-1}\)). This poses challenges to Australian water utilities to produce drinking water which meets the ADWG. An important source water that presents a particularly difficult treatment process challenge is a reservoir in the southwest of Western Australia (WA) (referred to here as SW reservoir). The water from this reservoir contains elevated concentrations of DOC (ranging from 20 – 40 mg L\(^{-1}\)) and the bromide ion concentration is also high (300 – 600 µg L\(^{-1}\)). Water from this reservoir is treated at a nearby water treatment plant (SW WTP) for the removal of DOC. Historically, the treatment process has used enhanced coagulation (alum) and flocculation, followed by sedimentation and sand filtration, and disinfection with chlorine. This conventional treatment removed 80 – 90% of DOC from the raw water. However, since the initial DOC concentration was so high, the residual DOC in the treated water was still typically around 4-5 mg L\(^{-1}\), which led to excessive chlorine consumption and the production of elevated concentrations of DBPs in the disinfected water. Occasionally, when disinfection levels needed to be increased to ensure residual throughout the distribution system, the concentrations of total THMs in the distribution system exceeded the ADWG value of 250 µg L\(^{-1}\). In such cases, aeration was employed to volatilise the THMs formed, in order to reduce the concentrations of THMs in the distribution system. However, it was found that some of the chlorine residual was also lost during the aeration process.
After consideration of the best available technologies to manage the formation of THMs at the treatment plant and in the distribution system, PAC treatment was selected by the local water utility as the preferred technology to enhance NOM removal, and thus reduce the formation of THMs, at this particular treatment plant. In drinking water treatment, PAC is traditionally used for the removal of organic compounds that cause taste and odour (Najm et al., 1991). However, PAC has also been reported to be an effective adsorbent for organic precursors of DBPs, *i.e.* NOM (e.g. Najm et al., 1990; Amy et al., 1991; Jacangelo et al., 1995; Najm et al., 1998; Fabris et al., 2004). The extent of NOM removal by PAC has been found to largely depend on the type of PAC, as well as the quality of the source water which determines the dose of PAC required to achieve the desired NOM removal (Najm et al., 1991; Jacangelo et al., 1995). PAC treatment has also been used in conjunction with coagulation, enhanced coagulation, or ultrafiltration to improve the removal of NOM (*e.g.* Jacangelo et al., 1995; Najm et al., 1998; Uyak et al., 2007). In a pilot-scale study, Jacangelo *et al.* (1995) reported 12 to 80% removal of NOM from a US river water, depending on PAC dose, when PAC is added as a pre-treatment to ultrafiltration. Based on the results from a series of laboratory-scale jar test experiments, Najm *et al.* (1998) claimed that the combination of enhanced coagulation and PAC provides a more cost-effective treatment process than enhanced coagulation only, in order to produce drinking water that meets US water quality regulations. In another laboratory-scale study, Uyak *et al.* (2007) demonstrated that supplementing enhanced coagulation with PAC in the treatment of a Turkish lake water resulted in an increased DOC removal from 45 to 76% at an optimum PAC dose of 40 mg L$^{-1}$. Recently, in a laboratory-scale study on the effect of PAC addition on the removal of NOM, Alvarez-Uriarte *et al.* (2010) reported that the addition of small amounts (up to 50 mg L$^{-1}$) of PAC during coagulation increased the removal of THM precursors from 40 to 70%. However, Carrière *et al.* (2009) found that the application of PAC (11 mg L$^{-1}$) combined with enhanced
coagulation at a WTP in Canada only resulted in a small increase (7%) in the reduction of
DOC and did not improve the removal of THM precursors.

Preliminary laboratory-scale experiments using varying PAC types (Acticarb PS1000 and
Acticarb PS1300), PAC dose rates and contact times were conducted by the local water utility
to evaluate the effectiveness of PAC added into the enhanced coagulation step for
enhancement of the removal of THM precursors in the source water from the SW reservoir.
The laboratory-scale trials showed that Acticarb PS1300 performed better than Acticarb
PS1000 for removal of THM precursors. Using Acticarb PS1300, a dose of 150 mg L\(^{-1}\) was
sufficient to reduce the concentration of THMs in the treated water to well below the
guideline value. Following successful plant trials, PAC treatment was added to the existing
WTP through addition of PAC into the enhanced alum coagulation step. The SW WTP is the
only WTP in Australia that uses the combination of PAC and enhanced coagulation for the
removal of NOM.

Here, we report the first study of the efficacy of plant-scale PAC combined with enhanced
coagulation for DBP minimisation from the humic-rich surface waters of South Western
Australia. South Western Australia has been undergoing long-term drought since the 1970s
and waters of more marginal quality have become important drinking water sources. This
study investigated the efficiency of NOM removal, the changes in the disinfection behaviour
of the treated water, and the variations in distribution system water quality, as a result of the
addition of PAC treatment at the WTP. The efficiency of NOM removal before and after the
use of PAC at the WTP was evaluated by comparison of the characteristics of NOM in the
treated waters. The disinfection behaviour of waters treated with and without PAC was
studied through bench-scale evaluation of the DBP formation potential of the treated waters.
The variations in distribution system water quality were assessed by analyses of selected water quality parameters in samples collected at selected sampling sites, before and after the application of PAC treatment at the WTP. To our knowledge, there has only been one other published report on the plant-scale application of PAC combined with enhanced coagulation to improve the removal of NOM. This is the first comprehensive assessment of the impact of plant-scale application of PAC combined with enhanced coagulation on the removal of NOM and the formation potential of DBPs from an Australian source water.

2. Materials and Methods

2.1 Sample Collection

Two sampling events were carried out, before and after the application of PAC treatment at the WTP treating water from the SW reservoir. At each sampling event, raw and treated (after filtration and prior to disinfection) water samples, and samples from distribution system sampling points were collected. Disinfectant residual in the samples from the distribution system was quenched with either sodium sulfite or ascorbic acid solution.

2.2 Chemicals and Reagents

All chemicals, reagents, and organic solvents used in this study were of analytical grade purity (AR grade ≥ 99% pure) or better, and were used without further purification.

2.3 Water Quality Analysis

Water samples were filtered through a 0.45 μm glass membrane filter prior to DOC and UV$_{254}$ measurements. The UV$_{254}$ absorbance of the water samples was determined using a HP 8452A Diode Array Spectrophotometer with a 5 cm quartz cell. The DOC concentration of the water samples was determined by the UV/persulfate oxidation method, using a Shimadzu
TOC Analyser. The concentration of bromide ions in the water samples was determined using ion chromatography with conductivity detection.

2.4 Chlorination Experiments

The treated water samples were subjected to chlorination using aqueous sodium hypochlorite solution. The target chlorine residual was determined to be 0.5 – 1 mg L\(^{-1}\), to represent residual concentrations in distribution systems. The chlorination experiments were carried out at 22\(^\circ\)C, for 168 hours, at pH 7 (buffered using phosphate buffer). At various time intervals up to 168 hours, the residual chlorine in a subsample of the reaction solution was quenched with aqueous sodium sulfite or ascorbic acid solution, and the sample was then analysed for DBPs. The residual chlorine concentration at the end of the experimental period in each sample was measured using the DPD colorimetric method.

2.5 Analysis of DBPs

Water samples were analysed for THMs (four species of THMs: chloroform, bromodichloromethane, chlorodibromomethane, and bromoform), HAAs (nine species of HAAs: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid, tribromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, chlorodibromoacetic acid), and HANs (six species of HANs: monochloroacetonitrile, dichloroacetonitrile, monobromoacetonitrile, dibromoacetonitrile, bromochloroacetonitrile). THMs and HANs were extracted from the samples using solid-phase microextraction in the headspace mode, and analysed using gas chromatography with mass spectrometric detection (HS SPME/GC-MS). HAAs were analysed using a modified EPA Method 552.3, which involves liquid-liquid extraction of the acids with methyl tert-butyl ether (MTBE) as solvent, followed by derivatisation of the acids into their corresponding
methyl esters using acidic methanol, and subsequent analysis of the HAA methyl esters by GC-MS. The GC-MS system used for the analysis of these DBPs was a Hewlett Packard 6980N GC interfaced to Hewlett Packard 5973 Network Mass Selective Detector, equipped with a 60 m x 0.25 mm ID ZB-5 (Phenomenex) column with a film thickness of 1 µm.

2.6 Size Exclusion Chromatography

High performance size exclusion chromatography (HPSEC) was carried out using a TSK G3000SWxl column and a Hewlett-Packard 1090 Series II HPLC instrument with filter photometric UV detection at $\lambda = 254$ nm (HPSEC-UV254), following the method described by Allpike et al. (2005). The samples were filtered through a 0.45 µm glass membrane filter prior to SEC analysis.

3 Results and Discussion

3.1 Water Treatment Plant Process

Water from the SW reservoir is treated at the SW WTP to provide drinking water to approximately 5000 local residents, as well as seasonal tourists. Initially, the process consisted of conventional water treatment utilising enhanced coagulation and sand filtration for the removal of organic matter in the water. Following successful laboratory-scale and plant-scale trials, PAC treatment was added to the conventional treatment process to maximise the removal of NOM, thus minimising the formation of DBPs. Figure 1 shows the current treatment train at the SW WTP. PAC is dosed at 150 mg L$^{-1}$ and is added to the water at the same time as alum. Laboratory-scale tests showed that this dosing regime resulted in higher removal of DOC from the water than other regimes (i.e. prior to alum addition and post coagulation-flocculation). This translated to adding PAC at the same point of application as alum in the plant, which was fortuitously the simplest modification option at the plant.
3.2 Characteristics of the Source Water

Before (sampling event #1) and after (sampling event #2) the introduction of PAC treatment at the WTP, samples of the raw and treated (but not chlorinated) water were collected, as well as a series of samples from the distribution system. The raw water samples from the SW reservoir had very high DOC concentrations (approximately 20 mg L\(^{-1}\)), as well as high UV\(_{254}\) and SUVA\(_{254}\) values, on both sampling occasions (Table 1). Source water from this reservoir is known to be highly coloured and to contain the highest DOC concentrations in this region, due to the influence of the runoff from the highly vegetated catchment area surrounding the reservoir. The raw water samples also had relatively high concentrations of bromide ion. The water samples collected at sampling event #2 contained significantly higher concentrations of bromide ion than those collected in sampling event #1. This indicates an increased input of bromide ion into the reservoir, possibly through runoff from saline areas at the extremities of the catchment (Garbin et al., 2010); or an increased concentration of bromide ion in the reservoir due to reduced rainfall experienced by the region prior to sampling event #2.

The treatment process at the SW WTP was able to significantly reduce the DOC concentration of the source water. The reduction in the DOC concentration upon treatment at the SW WTP was accompanied by significant decreases in UV\(_{254}\) and SUVA\(_{254}\) values, indicating that the treatment process had preferentially removed the fraction of NOM that contributed to UV absorbance at 254 nm, NOM which is generally associated with DBP formation (Croué et al., 2000). Using the conventional enhanced coagulation (EC) treatment process (sampling event #1), the SW WTP removed 73% of DOC in the raw water and decreased the UV\(_{254}\) absorbance of the water by 90%. With the addition of PAC (sampling event #2), these % removals increased to 93% and 98%, respectively, demonstrating the
effectiveness of PAC treatment in enhancing the removal of NOM. There was little difference
between bromide ion concentrations in raw and treated water samples, demonstrating that
bromide ion concentration was unaffected by the treatment processes at the SW WTP.

The characteristics of the NOM in the water samples were also evaluated using HPSEC with
UV$_{254}$ detection. Figure 2 shows the HPSEC-UV$_{254}$ chromatograms of the raw waters from
SW reservoir (SW Raw #1 and SW Raw #2) and the treated waters from SW WTP (SW-EC:
conventional enhanced coagulation treatment; SW-PAC: enhanced coagulation with PAC
treatment). The retention times in these chromatograms relate to the apparent molecular
weight (AMW) of the UV$_{254}$-active organic matter, with the higher AMW compounds eluting
prior to the lower AMW compounds, since smaller compounds are retained more in the pores
of the SEC column (Pelekani et al., 1999). The chromatograms in Fig. 2 demonstrate that the
treatment processes at the SW WTP preferentially removed high AMW UV$_{254}$-active NOM,
giving treated waters that contained mostly lower AMW NOM.

Figure 2 confirms that there was a higher removal of UV$_{254}$-active organic matter in the
treatment process during the second sampling event, which reflects the modification in the
treatment process (PAC addition) applied at the SW WTP between the two sampling events.
As a result of the PAC addition, DOC removal was improved by 70%, as demonstrated by the
lower DOC concentration in the treated water, and illustrated by the lower responses of the
chromatogram of SW-PAC compared to that of SW-EC. The HPSEC-UV$_{254}$ chromatograms
(Fig. 2) also show that the addition of PAC into this process did not seem to result in
preferential removal of a specific AMW fraction of UV$_{254}$-active NOM.
3.3 The Effect of PAC Addition on the Disinfection Behaviour of the Treated Waters

The treated water samples were chlorinated at pH 7 and the residual chlorine equivalent concentration and disinfection by-product concentrations were measured at various times over a 7 day period. The chlorine demand and the concentrations of THMs, HAAs, and HANs in the chlorinated samples after 7 days are shown in Table 2. The concentrations of THMs, HAAs, and HANs presented in Table 2 are the sums of the concentrations of the individual species, with the exclusion of species that were present at concentrations below their detection limits. As expected, the sample with the higher DOC concentration, SW-EC, had a higher chlorine demand than that with the lower DOC concentration. However, both water samples had similar specific chlorine demands, indicating that the chlorine demand in these waters was largely due to NOM. As a consequence of its higher DOC concentration, SW-EC also produced significantly higher concentrations of DBPs than SW-PAC.

Significantly lower concentrations of DBPs were measured in the chlorinated samples of SW-PAC, demonstrating the effectiveness of PAC for removal of DBP precursors, thus minimising the formation of DBPs. In this study, the production of THMs, HAAs, and HANs decreased by 80%, 85%, and 95%, respectively, as a result of the addition of PAC treatment at the SW WTP. This compares well with some previously reported studies. Jacangelo et al. (1995) reported a reduction of 97% in the formation of THMs when PAC was used at a high dose (90 mg L\(^{-1}\)). Najm et al. (1991) reported a 50% reduction in THM formation potential (THMFP) when using a PAC dose of 100 mg L\(^{-1}\) in a pilot scale study in the US. In a bench scale study, a 90% reduction in THMFP was achieved when a PAC dose of 500 mg L\(^{-1}\) was used (Najm et al., 1991). Interestingly, other studies have reported lower reductions in the formation of DBPs at similarly high doses of PAC (e.g. Amy et al., 1991; Fabris et al., 2004), as well as at lower doses of PAC (e.g. Uyak et al., 2007; Alvarez-Uriarte et al., 2010). This
demonstrates that the removal efficiency of DBP precursors does not correlate with PAC dose, but rather depends on other factors such as the type of PAC and the quality of the source water.

As reported in Section 3.2, the removal of DOC was improved by 70% with the addition of PAC, and this corresponds to reductions in the production of THMs, HAAs, and HANs of 80%, 85%, and 95%, respectively. The higher reduction in DBP formation compared to DOC removal suggests that, in this case, PAC preferentially removed DBP precursors from the water. Najm et al. (1991) also reported a substantially greater reduction in THMFP than DOC with the addition of PAC for some US source waters. However, a reduction in DOC concentration with an insignificant reduction in the concentration of THMs upon the application of PAC was also observed in other source waters (Fabris et al., 2004; Najm et al., 1991). This demonstrates that the characteristics of the source water play an important role in the effectiveness of PAC treatment for DOC removal and DBP control. In this study, the results showed that the characteristics of the raw water from the SW reservoir allowed for an effective removal of DBP precursors by PAC adsorption.

Among the three groups of DBPs measured in the chlorinated samples, THMs were formed at highest mass concentration, followed by HAAs and HANs. On a mass basis, the concentrations of HANs were only 1 – 10% of the concentrations of THMs. Similar observations have been reported by other researchers. THMs and HAAs have often been reported to be the two largest classes of DBPs detected (on a mass concentration basis) in chlorinated waters (e.g. Karanfil et al., 2008; Obolensky and Singer, 2005). HAN precursors have been reported to be associated with organic nitrogen compounds contained in proteinaceous materials and other nitrogen-containing species (Reckhow et al., 2001). The
low concentration of HANs was consistent with the comparatively low proportion of organic nitrogen in aquatic NOM (1 – 5%), significantly lower than that of organic carbon (~ 50%) (Croué et al., 2000). In fact, the nitrogen vs. organic carbon content in water from the SW reservoir was previously reported to be extremely low in comparison to other WA surface waters (e.g. C/N = 32 for SW reservoir cf. C/N = 6.7 for a reservoir in the north-west of Western Australia (Allpike et al., 2008)).

The species distribution of DBPs and the halogen incorporation in the chlorinated SW-EC and SW-PAC water samples were found to be different and reflected the concentration of bromide ion in the respective water samples. In chlorination, the ratio of DOC:Br⁻:Cl₂ influences the species distribution of DBPs (Amy et al., 1991). As shown in Table 1, the bromide ion concentrations in the water samples collected in the second sampling event were significantly higher. Consequently, in the chlorinated SW-PAC water sample, the most abundant THMs and HAAs were bromoform and dibromoacetic acid, respectively, while the corresponding species in the chlorinated SW-EC water were bromodichloromethane and dichloroacetic acid. Table 2 presents the ratios of the number of moles of bromine to the number of moles chlorine incorporated into the overall measured DBPs (THMs, HAAs, and HANs) in the chlorinated samples. As a result of the higher initial bromide ion concentration in the SW-PAC sample, a significantly higher Br/Cl ratio was obtained for SW-PAC compared to SW-EC. Moreover, the total number of moles of chlorine incorporated into DBPs in the chlorinated SW-PAC sample was less than that of bromine, indicating a preferential incorporation of bromine into DBP precursors in this water sample. In the presence of chlorine, bromide ion is readily oxidised to bromine (HOBr). In reactions with NOM, bromine is more reactive than chlorine, and kinetic studies have demonstrated that chlorine acts preferentially as an oxidant, whereas bromine is a more effective substituting agent.
(Westerhoff et al., 2004). In the case of the SW-PAC water sample, the high concentration of bromide ion in the sample led to an abundance of bromine in the sample through the oxidation of bromide by chlorine. The generated bromine reacted faster with DBP precursors than chlorine to form brominated DBPs, resulting in a higher incorporation of bromine than chlorine into DBP precursors.

Further evaluation of the incorporation of bromine into NOM can be made using the ‘Bromine Incorporation Factor’ (BIF) parameter. The BIF was introduced by Obolensky and Singer (2005) and is a measure of the extent of bromine substitution in a DBP class, characterised by the bromine fraction of the total molar halogen in the class. Figure 3 shows the BIF (THMs) with respect to that of dihaloacetic acids (BIF (X₂As)) after 7-day chlorination of the treated waters. The results from all sampling times in each chlorination experiment were included. The solid line in the figure corresponds to the theoretical 1:1 line (i.e. \( x = y \) line), if bromine incorporation was the same for both DBP classes. Figure 3 shows that the BIF (THMs) correlated relatively well with the BIF (X₂As), indicated by the majority of data points lying close to the \( x = y \) line, suggesting that bromine substitutes into THMs and X₂As to similar extents. A cluster of data points which lie below the \( x = y \) line correspond to data points from the SW-PAC water sample. In this sample, slightly greater bromine substitution in THMs than X₂As was observed, likely to be related to the high initial bromide ion concentration in this water sample. In addition, HOBr has been reported to be more reactive towards aliphatic precursors and the hydrophilic fraction of NOM than aromatic precursors and the hydrophobic fraction (Liang and Singer, 2003). Previous studies have also reported that aliphatic precursors play a more important role in THM formation than in HAA formation; and that THM precursors tend to come from the hydrophilic fraction of NOM (Kanokkantapong et al., 2006; Liang and Singer, 2003). The greater bromine
substitution into THMs than HAAs observed for the SW-PAC water sample may indicate that the NOM remaining in this particular water sample contained a higher proportion of aliphatic precursors and hydrophilic NOM than the other water samples.

It is important to note that the treatment process of PAC combined with enhanced coagulation did not affect the bromide ion concentration in the water (Table 1). This is consistent with the reported observation that PAC removes NOM ‘intact’ by adsorption and has little effect on any bromide ions that are present in the water (Amy et al., 1991). The inability of PAC and enhanced coagulation to remove bromide ion leads to an increased ratio of bromide to DOC in the treated water, which in turn results in an increase in the proportion of brominated DBPs upon chlorination. This may be of a concern and need to be evaluated, since a number of studies have demonstrated that brominated DBPs are significantly more toxic and carcinogenic than their chlorinated analogues.

### 3.4 Water Quality and DBP Concentration in Distribution System

On the same day as the samples were collected from the SW reservoir and WTP, four samples were also collected from the distribution system. These sampling points were located at increasing distances from the SW WTP: post-chlorination sampling point at the SW treatment plant (SW-A), a reservoir outlet (SW-B), a mid point at the distribution system (SW-C), and a sampling point at the extremity of the distribution system (SW-D). Some water quality parameters (DOC concentration, UV$_{254}$ absorbance, and bromide ion concentration (after quenching of the disinfectant residual)) of these samples are presented in Table 3. The use of PAC in the treatment process at the SW WTP significantly reduced the DOC concentration in the distribution system in the second sampling event. There was little difference in the UV$_{254}$ absorbance and the DOC and bromide ion concentrations along the distribution system at
each sampling event. Significant decreases were observed in the disinfectant residual concentrations along the distribution system, as expected. During the first sampling event, maintenance of disinfectant residual at the extremity of the system was clearly an operational issue, with the free chlorine equivalent residual concentration of sample SW-D being less than 0.1 mg L$^{-1}$. During the second sampling event, however, the maintenance of disinfectant residual was significantly improved, with the free chlorine equivalent residual concentration greater than 0.6 mg L$^{-1}$ at the extremity of the distribution system (sample SW-D). This demonstrates that the addition of the PAC treatment process at the SW WTP has produced treated water with significantly lower DOC concentration and chlorine demand, allowing improved maintenance of water quality in the distribution system.

The distribution system samples were also analysed for THMs, HAAs, and HANs, after quenching of the disinfectant residual. Figure 4 shows the variations in the concentrations of THMs, HAAs, and HANs in the SW distribution system at the two sampling events. In the second sampling event, the concentrations of THMs and HAAs were clearly lower, however, higher concentrations of HANs were measured. Although the concentrations of DBPs measured in the two sampling events could not be compared directly due to differences in WTP conditions and the quality of the source waters, these changes can be attributed to the addition of PAC treatment at the SW WTP which significantly reduced the DOC concentration in the treated water. Interestingly, the DOC concentration was improved by 70%, however, the corresponding improvement in the concentrations of THMs was only 15 – 40%, while a higher reduction in the formation of HAAs was observed (65 – 90%) and higher concentrations of HANs were observed in the second sampling event. These trends were found to be different than those observed in the laboratory scale experiments, and were likely
due to differences in the WTP conditions including chlorine dose, which could not be kept
constant, unlike experimental conditions in a laboratory.

Spatial and temporal variations in the concentrations of DBPs have been reported to occur in
distribution systems, influenced by factors such as the temperature and the hydraulics of the
system, disinfectant residual concentrations, residence time, and the presence of biofilms
(Karanfil et al., 2008; LeBel et al., 1997). The concentrations of THMs in the SW distribution
system increased as the residence time of the water increased for both sampling events. The
concentration of THMs was higher by 50 – 60% at the extremity of the distribution system
(SW-D sampling point) relative to the first sampling point nearest to the WTP. This shows
that THMs continued to be formed along the distribution system, which is in agreement with
other studies (e.g. Baribeau et al., 2005; LeBel et al., 1997). THMs will apparently continue
to form in the distribution system as long as NOM and disinfectant (chlorine equivalent)
residual are present in the distributed water. There was no clear trend in the concentrations of
HAAs and HANs along the distribution system in both sampling times. Some studies have
reported that HAAs and HANs are more susceptible to degradation than THMs.

Biodegradation of some HAA species, caused by microorganisms present in distribution
system pipes, has been observed in the absence of chlorine residual and in waters with low
levels of chlorine residual, with dichloroacetic acid usually being more affected than
trichloroacetic acid (Baribeau et al., 2005). With regards to HANs, several studies have
shown that HANs are chemically unstable, readily hydrolysing into haloacetamides or
trihaloacetic acids depending on the pH of the system, and that their degradation is
accelerated by the presence of free chlorine (Reckhow et al., 2001; Glezer et al., 1999). These
processes may have caused the observed variability in HAAs and HANs concentrations in the
present study.
The bromine incorporation factors (BIF) for THMs and $X_2$AAs formed in the field samples were also calculated. Figure 3 shows the BIF (THMs) with respect to the BIF ($X_2$AAs) in the field samples. As in the case of water samples from the laboratory-scale study, the data points lie relatively close to the $x = y$ line, indicating that bromine substituted into THMs and $X_2$AAs to similar extents. Comparing the BIF (THMs) and BIF ($X_2$AAs) for the samples collected in the first sampling event to those collected in the second sampling event, a similar trend to that observed in the laboratory-scale study was noted. There was also a slight tendency for bromine to be incorporated more into THM precursors than HAA precursors in samples collected in the second sampling event. This demonstrates that disinfection by-product formation from the laboratory-scale study compared well to the formation found in the field system, despite the fact that distribution system variables, such as biofilms, pipewall deposits, and hydraulics, were not taken into consideration in the laboratory-scale study.

4 Conclusions

The characteristics of the source water from the SW reservoir allowed PAC combined with enhanced coagulation to effectively remove the NOM which was not removed through enhanced coagulation alone. As a result of the addition of PAC to the treatment process, NOM removal was improved by 70%, which led to a significant reduction (80 – 95%) in the formation of DBPs upon laboratory chlorination of the treated, unchlorinated water. The water quality in the distribution system was also improved, indicated by the lower concentrations of DBPs in the distribution system and a better maintenance of disinfectant residual at the extremity of the distribution system. The concentrations of DBPs in samples collected from the distribution system showed that the concentrations of THMs increased with increasing residence time in the distribution system, while those of HAAs and HANs were
found to be variable, with increasing residence time. The behaviour of DBP species in
distribution systems is of significant importance to the selection of sampling points for
regulatory measurements of DBPs, and for the management of the distribution system to
minimise further DBP formation. Recommendations from this study include that THM
species should not only be measured at the treatment plant outlet, but also at the extremities of
the distribution system, and that HAAs and HANs should be measured at a number of
locations in the distribution system, in order to provide a better indication of the
concentrations of DBPs for exposure assessment. PAC combined with enhanced coagulation
has been shown to be very effective for NOM removal, however, this process does not have
the capacity to remove bromide ion, which is also an important precursor to DBPs. Following
addition of PAC to an enhanced coagulation process, an increase in the ratio of bromide ion to
DOC is expected, which will lead to the formation of more brominated DBPs. When the
concentration of bromide in the source water is high, the increased health risk associated with
brominated DBPs should be considered alongside the improvements in water quality
associated with this treatment process.

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References


