

NOTICE: this is the author's version of a work that was accepted for publication in Chemosphere. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Chemosphere, 83, 5, 2011 DOI 10.1016/j.chemosphere.2011.02.017

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

4
5
6
7
8 Ina Kristiana, Cynthia Joll, and Anna Heitz

9
10 Curtin Water Quality Research Centre
11 Curtin University, Perth, Western Australia

12
13
14
15
16 Corresponding Author:

17 Ina Kristiana

18 Curtin Water Quality Research Centre

19 GPO Box 1987

20 Perth WA 6845

21 Phone : 61 08 9266 9389

22 Fax : 61 08 9266 3547

23 E-mail : I.Kristiana@curtin.edu.au

24

1 **Abstract**

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

20

21

22 **Keywords:** Powdered activated carbon; enhanced coagulation; disinfection by-products;
23 natural organic matter; trihalomethanes; haloacetic acids

24

25

1 **1. Introduction**

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

19

20 The formation of DBPs can be controlled and minimised using one, or a combination of, the
21 following approach: removal of DBP precursors prior to disinfection, change of disinfectant,
22 and removal of DBPs following disinfection (Karanfil *et al.*, 2008). The removal of organic
23 precursors of DBPs *i.e.* natural organic matter (NOM) prior to disinfection and distribution is
24 considered to be the most effective approach to minimise the formation of DBPs. Due to the
25 increasingly stringent DBP regulations, advanced precursor removal technologies are being

1 used to maximise NOM removal. These include membrane filtration (microfiltration,
2 nanofiltration, reverse osmosis), activated carbon (granular activated carbon (GAC),
3 powdered activated carbon (PAC)), and ion exchange (MIEX[®] resin).

4
5 In Australia, many source waters contain particularly high concentrations of NOM by
6 international standards (up to 40 mg L⁻¹ as dissolved organic carbon (DOC)), and sources in
7 coastal locations may contain elevated levels of bromide ion (up to 2 mg L⁻¹). This poses
8 challenges to Australian water utilities to produce drinking water which meets the ADWG.

9 An important source water that presents a particularly difficult treatment process challenge is
10 a reservoir in the southwest of Western Australia (WA) (referred to here as SW reservoir).

11 The water from this reservoir contains elevated concentrations of DOC (ranging from 20 – 40
12 mg L⁻¹) and the bromide ion concentration is also high (300 – 600 µg L⁻¹). Water from this
13 reservoir is treated at a nearby water treatment plant (SW WTP) for the removal of DOC.

14 Historically, the treatment process has used enhanced coagulation (alum) and flocculation,
15 followed by sedimentation and sand filtration, and disinfection with chlorine. This

16 conventional treatment removed 80 – 90% of DOC from the raw water. However, since the
17 initial DOC concentration was so high, the residual DOC in the treated water was still

18 typically around 4-5 mg L⁻¹, which led to excessive chlorine consumption and the production
19 of elevated concentrations of DBPs in the disinfected water. Occasionally, when disinfection

20 levels needed to be increased to ensure residual throughout the distribution system, the

21 concentrations of total THMs in the distribution system exceeded the ADWG value of 250 µg

22 L⁻¹. In such cases, aeration was employed to volatilise the THMs formed, in order to reduce

23 the concentrations of THMs in the distribution system. However, it was found that some of

24 the chlorine residual was also lost during the aeration process.

25

1 After consideration of the best available technologies to manage the formation of THMs at the
2 treatment plant and in the distribution system, PAC treatment was selected by the local water
3 utility as the preferred technology to enhance NOM removal, and thus reduce the formation of
4 THMs, at this particular treatment plant. In drinking water treatment, PAC is traditionally
5 used for the removal of organic compounds that cause taste and odour (Najm *et al.*, 1991).
6 However, PAC has also been reported to be an effective adsorbent for organic precursors of
7 DBPs, *i.e.* NOM (*e.g.* Najm *et al.*, 1990; Amy *et al.*, 1991; Jacangelo *et al.*, 1995; Najm *et al.*,
8 1998; Fabris *et al.*, 2004). The extent of NOM removal by PAC has been found to largely
9 depend on the type of PAC, as well as the quality of the source water which determines the
10 dose of PAC required to achieve the desired NOM removal (Najm *et al.*, 1991; Jacangelo *et*
11 *al.*, 1995). PAC treatment has also been used in conjunction with coagulation, enhanced
12 coagulation, or ultrafiltration to improve the removal of NOM (*e.g.* Jacangelo *et al.*, 1995;
13 Najm *et al.*, 1998; Uyak *et al.*, 2007). In a pilot-scale study, Jacangelo *et al.* (1995) reported
14 12 to 80% removal of NOM from a US river water, depending on PAC dose, when PAC is
15 added as a pre-treatment to ultrafiltration. Based on the results from a series of laboratory-
16 scale jar test experiments, Najm *et al.* (1998) claimed that the combination of enhanced
17 coagulation and PAC provides a more cost-effective treatment process than enhanced
18 coagulation only, in order to produce drinking water that meets US water quality regulations.
19 In another laboratory-scale study, Uyak *et al.* (2007) demonstrated that supplementing
20 enhanced coagulation with PAC in the treatment of a Turkish lake water resulted in an
21 increased DOC removal from 45 to 76% at an optimum PAC dose of 40 mg L⁻¹. Recently, in
22 a laboratory-scale study on the effect of PAC addition on the removal of NOM, Alvarez-
23 Uriarte *et al.* (2010) reported that the addition of small amounts (up to 50 mg L⁻¹) of PAC
24 during coagulation increased the removal of THM precursors from 40 to 70%. However,
25 Carrière *et al.* (2009) found that the application of PAC (11 mg L⁻¹) combined with enhanced

1 coagulation at a WTP in Canada only resulted in a small increase (7%) in the reduction of
2 DOC and did not improve the removal of THM precursors.

3

4 Preliminary laboratory-scale experiments using varying PAC types (Acticarb PS1000 and
5 Acticarb PS1300), PAC dose rates and contact times were conducted by the local water utility
6 to evaluate the effectiveness of PAC added into the enhanced coagulation step for

7 enhancement of the removal of THM precursors in the source water from the SW reservoir.

8 The laboratory-scale trials showed that Acticarb PS1300 performed better than Acticarb

9 PS1000 for removal of THM precursors. Using Acticarb PS1300, a dose of 150 mg L^{-1} was

10 sufficient to reduce the concentration of THMs in the treated water to well below the

11 guideline value. Following successful plant trials, PAC treatment was added to the existing

12 WTP through addition of PAC into the enhanced alum coagulation step. The SW WTP is the

13 only WTP in Australia that uses the combination of PAC and enhanced coagulation for the

14 removal of NOM.

15

16 Here, we report the first study of the efficacy of plant-scale PAC combined with enhanced

17 coagulation for DBP minimisation from the humic-rich surface waters of South Western

18 Australia. South Western Australia has been undergoing long-term drought since the 1970s

19 and waters of more marginal quality have become important drinking water sources. This

20 study investigated the efficiency of NOM removal, the changes in the disinfection behaviour

21 of the treated water, and the variations in distribution system water quality, as a result of the

22 addition of PAC treatment at the WTP. The efficiency of NOM removal before and after the

23 use of PAC at the WTP was evaluated by comparison of the characteristics of NOM in the

24 treated waters. The disinfection behaviour of waters treated with and without PAC was

25 studied through bench-scale evaluation of the DBP formation potential of the treated waters.

1 The variations in distribution system water quality were assessed by analyses of selected
2 water quality parameters in samples collected at selected sampling sites, before and after the
3 application of PAC treatment at the WTP. To our knowledge, there has only been one other
4 published report on the plant-scale application of PAC combined with enhanced coagulation
5 to improve the removal of NOM. This is the first comprehensive assessment of the impact of
6 plant-scale application of PAC combined with enhanced coagulation on the removal of NOM
7 and the formation potential of DBPs from an Australian source water.

8

9 **2. Materials and Methods**

10 **2.1 Sample Collection**

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

16

17 **2.2 Chemicals and Reagents**

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

20

21 **2.3 Water Quality Analysis**

22 Water samples were filtered through a 0.45 μ m glass membrane filter prior to DOC and UV₂₅₄
23 measurements. The UV₂₅₄ absorbance of the water samples was determined using a HP
24 8452A Diode Array Spectrophotometer with a 5 cm quartz cell. The DOC concentration of
25 the water samples was determined by the UV/persulfate oxidation method, using a Shimadzu

1 TOC Analyser. The concentration of bromide ions in the water samples was determined using
2 ion chromatography with conductivity detection.

3

4 **2.4 Chlorination Experiments**

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

13

14 **2.5 Analysis of DBPs**

15 Water samples were analysed for THMs (four species of THMs: chloroform,
16 bromodichloromethane, chlorodibromomethane, and bromoform), HAAs (nine species of
17 HAAs: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic
18 acid, dibromoacetic acid, tribromoacetic acid, bromochloroacetic acid, bromodichloroacetic
19 acid, chlorodibromoacetic acid), and HANs (six species of HANs: monochloroacetonitrile,
20 dichloroacetonitrile, trichloroacetonitrile, monobromoacetonitrile, dibromoacetonitrile,
21 bromochloroacetonitrile). THMs and HANs were extracted from the samples using solid-
22 phase microextraction in the headspace mode, and analysed using gas chromatography with
23 mass spectrometric detection (HS SPME/GC-MS). HAAs were analysed using a modified
24 EPA Method 552.3, which involves liquid-liquid extraction of the acids with methyl *tert*-butyl
25 ether (MTBE) as solvent, followed by derivatisation of the acids into their corresponding

1 methyl esters using acidic methanol, and subsequent analysis of the HAA methyl esters by
2 GC-MS. The GC-MS system used for the analysis of these DBPs was a Hewlett Packard
3 6980N GC interfaced to Hewlett Packard 5973 Network Mass Selective Detector, equipped
4 with a 60 m x 0.25 mm ID ZB-5 (Phenomenex) column with a film thickness of 1 μm .

5

6 **2.6 Size Exclusion Chromatography**

7 High performance size exclusion chromatography (HPSEC) was carried out using a TSK
8 G3000SW_{xl} column and a Hewlett-Packard 1090 Series II HPLC instrument with filter
9 photometric UV detection at $\lambda = 254 \text{ nm}$ (HPSEC-UV₂₅₄), following the method described by
10 Allpike *et al.* (2005). The samples were filtered through a 0.45 μm glass membrane filter prior
11 to SEC analysis.

12

13 **3 Results and Discussion**

14 **3.1 Water Treatment Plant Process**

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

1

2 **3.2 Characteristics of the Source Water**

3 Before (sampling event #1) and after (sampling event #2) the introduction of PAC treatment
4 at the WTP, samples of the raw and treated (but not chlorinated) water were collected, as well
5 as a series of samples from the distribution system. The raw water samples from the SW
6 reservoir had very high DOC concentrations (approximately 20 mg L⁻¹), as well as high UV₂₅₄
7 and SUVA₂₅₄ values, on both sampling occasions (Table 1). Source water from this reservoir
8 is known to be highly coloured and to contain the highest DOC concentrations in this region,
9 due to the influence of the runoff from the highly vegetated catchment area surrounding the
10 reservoir. The raw water samples also had relatively high concentrations of bromide ion. The
11 water samples collected at sampling event #2 contained significantly higher concentrations of
12 bromide ion than those collected in sampling event #1. This indicates an increased input of
13 bromide ion into the reservoir, possibly through runoff from saline areas at the extremities of
14 the catchment (Garbin *et al.*, 2010); or an increased concentration of bromide ion in the
15 reservoir due to reduced rainfall experienced by the region prior to sampling event #2.

16

17 The treatment process at the SW WTP was able to significantly reduce the DOC
18 concentration of the source water. The reduction in the DOC concentration upon treatment at
19 the SW WTP was accompanied by significant decreases in UV₂₅₄ and SUVA₂₅₄ values,
20 indicating that the treatment process had preferentially removed the fraction of NOM that
21 contributed to UV absorbance at 254 nm, NOM which is generally associated with DBP
22 formation (Croué *et al.*, 2000). Using the conventional enhanced coagulation (EC) treatment
23 process (sampling event #1), the SW WTP removed 73% of DOC in the raw water and
24 decreased the UV₂₅₄ absorbance of the water by 90%. With the addition of PAC (sampling
25 event #2), these % removals increased to 93% and 98%, respectively, demonstrating the

1 effectiveness of PAC treatment in enhancing the removal of NOM. There was little difference
2 between bromide ion concentrations in raw and treated water samples, demonstrating that
3 bromide ion concentration was unaffected by the treatment processes at the SW WTP.

4
5 The characteristics of the NOM in the water samples were also evaluated using HPSEC with
6 UV₂₅₄ detection. Figure 2 shows the HPSEC-UV₂₅₄ chromatograms of the raw waters from
7 SW reservoir (SW Raw #1 and SW Raw #2) and the treated waters from SW WTP (SW-EC:
8 conventional enhanced coagulation treatment; SW-PAC: enhanced coagulation with PAC
9 treatment). The retention times in these chromatograms relate to the apparent molecular
10 weight (AMW) of the UV₂₅₄-active organic matter, with the higher AMW compounds eluting
11 prior to the lower AMW compounds, since smaller compounds are retained more in the pores
12 of the SEC column (Pelekani *et al.*, 1999). The chromatograms in Fig. 2 demonstrate that the
13 treatment processes at the SW WTP preferentially removed high AMW UV₂₅₄-active NOM,
14 giving treated waters that contained mostly lower AMW NOM.

15
16 Figure 2 confirms that there was a higher removal of UV₂₅₄-active organic matter in the
17 treatment process during the second sampling event, which reflects the modification in the
18 treatment process (PAC addition) applied at the SW WTP between the two sampling events.
19 As a result of the PAC addition, DOC removal was improved by 70%, as demonstrated by the
20 lower DOC concentration in the treated water, and illustrated by the lower responses of the
21 chromatogram of SW-PAC compared to that of SW-EC. The HPSEC-UV₂₅₄ chromatograms
22 (Fig. 2) also show that the addition of PAC into this process did not seem to result in
23 preferential removal of a specific AMW fraction of UV₂₅₄-active NOM.

24
25

1 **3.3 The Effect of PAC Addition on the Disinfection Behaviour of the Treated Waters**

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

13
14 Significantly lower concentrations of DBPs were measured in the chlorinated samples of SW-
15 PAC, demonstrating the effectiveness of PAC for removal of DBP precursors, thus
16 minimising the formation of DBPs. In this study, the production of THMs, HAAs, and HANs
17 decreased by 80%, 85%, and 95%, respectively, as a result of the addition of PAC treatment
18 at the SW WTP. This compares well with some previously reported studies. Jacangelo *et al.*
19 (1995) reported a reduction of 97% in the formation of THMs when PAC was used at a high
20 dose (90 mg L⁻¹). Najm *et al.* (1991) reported a 50% reduction in THM formation potential
21 (THMFP) when using a PAC dose of 100 mg L⁻¹ in a pilot scale study in the US. In a bench
22 scale study, a 90% reduction in THMFP was achieved when a PAC dose of 500 mg L⁻¹ was
23 used (Najm *et al.*, 1991). Interestingly, other studies have reported lower reductions in the
24 formation of DBPs at similarly high doses of PAC (*e.g.* Amy *et al.*, 1991; Fabris *et al.*, 2004),
25 as well as at lower doses of PAC (*e.g.* Uyak *et al.*, 2007; Alvarez-Uriarte *et al.*, 2010). This

1 demonstrates that the removal efficiency of DBP precursors does not correlate with PAC
2 dose, but rather depends on other factors such as the type of PAC and the quality of the source
3 water.

4
5 As reported in Section 3.2, the removal of DOC was improved by 70% with the addition of
6 PAC, and this corresponds to reductions in the production of THMs, HAAs, and HANs of
7 80%, 85%, and 95%, respectively. The higher reduction in DBP formation compared to DOC
8 removal suggests that, in this case, PAC preferentially removed DBP precursors from the
9 water. Najm *et al.* (1991) also reported a substantially greater reduction in THMFP than DOC
10 with the addition of PAC for some US source waters. However, a reduction in DOC
11 concentration with an insignificant reduction in the concentration of THMs upon the
12 application of PAC was also observed in other source waters (Fabris *et al.*, 2004; Najm *et al.*,
13 1991). This demonstrates that the characteristics of the source water play an important role in
14 the effectiveness of PAC treatment for DOC removal and DBP control. In this study, the
15 results showed that the characteristics of the raw water from the SW reservoir allowed for an
16 effective removal of DBP precursors by PAC adsorption.

17
18 Among the three groups of DBPs measured in the chlorinated samples, THMs were formed at
19 highest mass concentration, followed by HAAs and HANs. On a mass basis, the
20 concentrations of HANs were only 1 – 10% of the concentrations of THMs. Similar
21 observations have been reported by other researchers. THMs and HAAs have often been
22 reported to be the two largest classes of DBPs detected (on a mass concentration basis) in
23 chlorinated waters (*e.g.* Karanfil *et al.*, 2008; Obolensky and Singer, 2005). HAN precursors
24 have been reported to be associated with organic nitrogen compounds contained in
25 proteinaceous materials and other nitrogen-containing species (Reckhow *et al.*, 2001). The

1 low concentration of HANs was consistent with the comparatively low proportion of organic
2 nitrogen in aquatic NOM (1 – 5%), significantly lower than that of organic carbon (~ 50%)
3 (Croué *et al.*, 2000). In fact, the nitrogen vs. organic carbon content in water from the SW
4 reservoir was previously reported to be extremely low in comparison to other WA surface
5 waters (*e.g.* C/N = 32 for SW reservoir *cf.* C/N = 6.7 for a reservoir in the north-west of
6 Western Australia (Allpike *et al.*, 2008)).

7
8 The species distribution of DBPs and the halogen incorporation in the chlorinated SW-EC and
9 SW-PAC water samples were found to be different and reflected the concentration of bromide
10 ion in the respective water samples. In chlorination, the ratio of $\text{DOC}:\text{Br}^-:\text{Cl}_2$ influences the
11 species distribution of DBPs (Amy *et al.*, 1991). As shown in Table 1, the bromide ion
12 concentrations in the water samples collected in the second sampling event were significantly
13 higher. Consequently, in the chlorinated SW-PAC water sample, the most abundant THMs
14 and HAAs were bromoform and dibromoacetic acid, respectively, while the corresponding
15 species in the chlorinated SW-EC water were bromodichloromethane and dichloroacetic acid.
16 Table 2 presents the ratios of the number of moles of bromine to the number of moles
17 chlorine incorporated into the overall measured DBPs (THMs, HAAs, and HANs) in the
18 chlorinated samples. As a result of the higher initial bromide ion concentration in the SW-
19 PAC sample, a significantly higher Br/Cl ratio was obtained for SW-PAC compared to SW-
20 EC. Moreover, the total number of moles of chlorine incorporated into DBPs in the
21 chlorinated SW-PAC sample was less than that of bromine, indicating a preferential
22 incorporation of bromine into DBP precursors in this water sample. In the presence of
23 chlorine, bromide ion is readily oxidised to bromine (HOBr). In reactions with NOM,
24 bromine is more reactive than chlorine, and kinetic studies have demonstrated that chlorine
25 acts preferentially as an oxidant, whereas bromine is a more effective substituting agent

1 (Westerhoff *et al.*, 2004). In the case of the SW-PAC water sample, the high concentration of
2 bromide ion in the sample led to an abundance of bromine in the sample through the oxidation
3 of bromide by chlorine. The generated bromine reacted faster with DBP precursors than
4 chlorine to form brominated DBPs, resulting in a higher incorporation of bromine than
5 chlorine into DBP precursors.

6
7 Further evaluation of the incorporation of bromine into NOM can be made using the
8 'Bromine Incorporation Factor' (BIF) parameter. The BIF was introduced by Obolensky and
9 Singer (2005) and is a measure of the extent of bromine substitution in a DBP class,
10 characterised by the bromine fraction of the total molar halogen in the class. Figure 3 shows
11 the BIF (THMs) with respect to that of dihaloacetic acids (BIF (X₂AAs)) after 7-day
12 chlorination of the treated waters. The results from all sampling times in each chlorination
13 experiment were included. The solid line in the figure corresponds to the theoretical 1:1 line
14 (*i.e.* $x = y$ line), if bromine incorporation was the same for both DBP classes. Figure 3 shows
15 that the BIF (THMs) correlated relatively well with the BIF (X₂AAs), indicated by the
16 majority of data points lying close to the $x = y$ line, suggesting that bromine substitutes into
17 THMs and X₂AAs to similar extents. A cluster of data points which lie below the $x = y$ line
18 correspond to data points from the SW-PAC water sample. In this sample, slightly greater
19 bromine substitution in THMs than X₂AAs was observed, likely to be related to the high
20 initial bromide ion concentration in this water sample. In addition, HOBr has been reported to
21 be more reactive towards aliphatic precursors and the hydrophilic fraction of NOM than
22 aromatic precursors and the hydrophobic fraction (Liang and Singer, 2003). Previous studies
23 have also reported that aliphatic precursors play a more important role in THM formation than
24 in HAA formation; and that THM precursors tend to come from the hydrophilic fraction of
25 NOM (Kanokkantapong *et al.*, 2006; Liang and Singer, 2003). The greater bromine

1 substitution into THMs than HAAs observed for the SW-PAC water sample may indicate that
2 the NOM remaining in this particular water sample contained a higher proportion of aliphatic
3 precursors and hydrophilic NOM than the other water samples.

4
5 It is important to note that the treatment process of PAC combined with enhanced coagulation
6 did not affect the bromide ion concentration in the water (Table 1). This is consistent with the
7 reported observation that PAC removes NOM 'intact' by adsorption and has little effect on
8 any bromide ions that are present in the water (Amy *et al.*, 1991). The inability of PAC and
9 enhanced coagulation to remove bromide ion leads to an increased ratio of bromide to DOC
10 in the treated water, which in turn results in an increase in the proportion of brominated DBPs
11 upon chlorination. This may be of a concern and need to be evaluated, since a number of
12 studies have demonstrated that brominated DBPs are significantly more toxic and
13 carcinogenic than their chlorinated analogues.

15 **3.4 Water Quality and DBP Concentration in Distribution System**

16 On the same day as the samples were collected from the SW reservoir and WTP, four samples
17 were also collected from the distribution system. These sampling points were located at
18 increasing distances from the SW WTP: post-chlorination sampling point at the SW treatment
19 plant (SW-A), a reservoir outlet (SW-B), a mid point at the distribution system (SW-C), and a
20 sampling point at the extremity of the distribution system (SW-D). Some water quality
21 parameters (DOC concentration, UV₂₅₄ absorbance, and bromide ion concentration (after
22 quenching of the disinfectant residual)) of these samples are presented in Table 3. The use of
23 PAC in the treatment process at the SW WTP significantly reduced the DOC concentration in
24 the distribution system in the second sampling event. There was little difference in the UV₂₅₄
25 absorbance and the DOC and bromide ion concentrations along the distribution system at

1 each sampling event. Significant decreases were observed in the disinfectant residual
2 concentrations along the distribution system, as expected. During the first sampling event,
3 maintenance of disinfectant residual at the extremity of the system was clearly an operational
4 issue, with the free chlorine equivalent residual concentration of sample SW-D being less than
5 0.1 mg L^{-1} . During the second sampling event, however, the maintenance of disinfectant
6 residual was significantly improved, with the free chlorine equivalent residual concentration
7 greater than 0.6 mg L^{-1} at the extremity of the distribution system (sample SW-D). This
8 demonstrates that the addition of the PAC treatment process at the SW WTP has produced
9 treated water with significantly lower DOC concentration and chlorine demand, allowing
10 improved maintenance of water quality in the distribution system.

11

12 The distribution system samples were also analysed for THMs, HAAs, and HANs, after
13 quenching of the disinfectant residual. Figure 4 shows the variations in the concentrations of
14 THMs, HAAs, and HANs in the SW distribution system at the two sampling events. In the
15 second sampling event, the concentrations of THMs and HAAs were clearly lower, however,
16 higher concentrations of HANs were measured. Although the concentrations of DBPs
17 measured in the two sampling events could not be compared directly due to differences in
18 WTP conditions and the quality of the source waters, these changes can be attributed to the
19 addition of PAC treatment at the SW WTP which significantly reduced the DOC
20 concentration in the treated water. Interestingly, the DOC concentration was improved by
21 70%, however, the corresponding improvement in the concentrations of THMs was only 15 –
22 40%, while a higher reduction in the formation of HAAs was observed (65 – 90%) and higher
23 concentrations of HANs were observed in the second sampling event. These trends were
24 found to be different than those observed in the laboratory scale experiments, and were likely

1 due to differences in the WTP conditions including chlorine dose, which could not be kept
2 constant, unlike experimental conditions in a laboratory.
3

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

17 Biodegradation of some HAA species, caused by microorganisms present in distribution
18 system pipes, has been observed in the absence of chlorine residual and in waters with low
19 levels of chlorine residual, with dichloroacetic acid usually being more affected than
20 trichloroacetic acid (Baribeau *et al.*, 2005). With regards to HANs, several studies have
21 shown that HANs are chemically unstable, readily hydrolysing into haloacetamides or
22 trihaloacetic acids depending on the pH of the system, and that their degradation is
23 accelerated by the presence of free chlorine (Reckhow *et al.*, 2001; Glezer *et al.*, 1999). These
24 processes may have caused the observed variability in HAAs and HANs concentrations in the
25 present study.

1
2 The bromine incorporation factors (BIF) for THMs and X₂AA formed in the field samples
3 were also calculated. Figure 3 shows the BIF (THMs) with respect to the BIF (X₂AAs) in the
4 field samples. As in the case of water samples from the laboratory-scale study, the data points
5 lie relatively close to the $x = y$ line, indicating that bromine substituted into THMs and
6 X₂AAs to similar extents. Comparing the BIF (THMs) and BIF (X₂AAs) for the samples
7 collected in the first sampling event to those collected in the second sampling event, a similar
8 trend to that observed in the laboratory-scale study was noted. There was also a slight
9 tendency for bromine to be incorporated more into THM precursors than HAA precursors in
10 samples collected in the second sampling event. This demonstrates that disinfection by-
11 product formation from the laboratory-scale study compared well to the formation found in
12 the field system, despite the fact that distribution system variables, such as biofilms, pipewall
13 deposits, and hydraulics, were not taken into consideration in the laboratory-scale study.

14

15 **4 Conclusions**

16 The characteristics of the source water from the SW reservoir allowed PAC combined with
17 enhanced coagulation to effectively remove the NOM which was not removed through
18 enhanced coagulation alone. As a result of the addition of PAC to the treatment process,
19 NOM removal was improved by 70%, which led to a significant reduction (80 – 95%) in the
20 formation of DBPs upon laboratory chlorination of the treated, unchlorinated water. The
21 water quality in the distribution system was also improved, indicated by the lower
22 concentrations of DBPs in the distribution system and a better maintenance of disinfectant
23 residual at the extremity of the distribution system. The concentrations of DBPs in samples
24 collected from the distribution system showed that the concentrations of THMs increased with
25 increasing residence time in the distribution system, while those of HAAs and HANs were

1 found to be variable, with increasing residence time. The behaviour of DBP species in
2 distribution systems is of significant importance to the selection of sampling points for
3 regulatory measurements of DBPs, and for the management of the distribution system to
4 minimise further DBP formation. Recommendations from this study include that THM
5 species should not only be measured at the treatment plant outlet, but also at the extremities of
6 the distribution system, and that HAAs and HANs should be measured at a number of
7 locations in the distribution system, in order to provide a better indication of the
8 concentrations of DBPs for exposure assessment. PAC combined with enhanced coagulation
9 has been shown to be very effective for NOM removal, however, this process does not have
10 the capacity to remove bromide ion, which is also an important precursor to DBPs. Following
11 addition of PAC to an enhanced coagulation process, an increase in the ratio of bromide ion to
12 DOC is expected, which will lead to the formation of more brominated DBPs. When the
13 concentration of bromide in the source water is high, the increased health risk associated with
14 brominated DBPs should be considered alongside the improvements in water quality
15 associated with this treatment process.

16

17

18

19 **Acknowledgements**

20 The authors would like to thank the Water Corporation of Western Australia, the Cooperative
21 Research Centre for Water Quality and Treatment, and Curtin University for funding the
22 project.

23

24

25

1 **References**

2 Allpike, B.P., Heitz, A., Joll, C.A., Kagi, R.I., Abbt-Braun, G., Frimmel, F.H., Brinkmann, T.,
3 Her, N., Amy, G.L., 2005. Size exclusion chromatography to characterise DOC removal in
4 drinking water treatment. *Environ. Sci. Technol.* 39, 2334-2342.

5

6 Allpike, B.P., Joll, C.A., Heitz, A., Kagi, R.I., 2008. Hydrous Pyrolysis as a NOM
7 Characterisation Tool. Proceedings of NOM2008 Conference Natural Organic Matter: from
8 Source to Tap, Bath, U.K., 2-4 September.

9

10 Álvarez-Uriarte, J.I, Iriarte-Velasco, U., Chimeno-Alanís, N., Gonzáles-Velasco, J.R., 2010.
11 The effect of mixed oxidants and powdered activated carbon on the removal of natural
12 organic matter. *J. Hazard. Mater.* 181, 426-431.

13

14 Amy, G.L., Tan, L., Davis, M.K., 1991. The effects of ozonation and activated carbon
15 adsorption on trihalomethane speciation. *Water Res.* 25, 191-202.

16

17 Baribeau, H., Krasner, S.W., Chinn, R., Singer, P.C., 2005. Impact of biomass on the stability
18 of HAAs and THMs in a simulated distribution system. *J.- Am. Water Works Assoc.* 97, 69-
19 81.

20

21 Carrière, A., Vachon, M., Bélisle, J-L., Barbeau, B., 2009. Supplementing coagulation with
22 powdered activated carbon as a control strategy for trihalomethanes: application to an existing
23 utility. *J. Water Supply: Res. Technol – AQUA*, 58, 363-371.

24

1 Croué, J-P., Korshin, G.V., Benjamin, M., 2000. Characterisation of Natural Organic Matter
2 in Drinking Water (Report #159), American Water Works Association Research Foundation,
3 Denver, Colorado, USA.

4

5 Garbin, S., McDonald, S., von Eckstaedt, S.V., Joll, C.A., Heitz, A., Harris, J.E., Antenucci,
6 J.P., 2010. Characterisation of Natural Organic Matter in Highly Coloured Surface Waters
7 (Research Report #82), Water Quality Research Australia Ltd., Adelaide, Australia.

8

9 Glezer, V., Harris, B., Tal, N., Iosefzon, B., Lev, O., 1999. Hydrolysis of haloacetonitriles:
10 Linear free energy relationship, kinetics, and products. *Water Res.* 33, 1938-1948.

11

12 Jacangelo, J.G., Laîné, J-M., Cummings, E.W., Adham, S.S., 1995. UF with pretreatment for
13 removing DBP precursors. *J.- Am. Water Works Assoc.* 87, 100-112.

14

15 Kanokkantapong, V., Marhaba, T.F., Panyapinyophol, B., Pavasant, P., 2006. FTIR
16 evaluation of functional groups involved in the formation of haloacetic acids during the
17 chlorination of raw water. *J. Hazard. Mater.* 136, 188-196.

18

19 Karanfil, T., Krasner, S.W., Westerhoff, P., Xie, Y., 2008. Recent advances in disinfection
20 by-product formation, occurrence, control, health effects, and regulations, in: Karanfil, T.,
21 Krasner, S.W., Westerhoff, P., Xie, Y. (Eds.), *Disinfection By-Products in Drinking Water*.
22 American Chemical Society, Washington DC, pp. 2-19.

23

1 LeBel, G.L., Benoit, F.M., Williams, D.T., 1997. A one-year survey of halogenated
2 disinfection by-products in the distribution system of treatment plants using three different
3 disinfection processes. *Chemosphere*, 34, 2301-2317.
4
5 Liang, L., Singer, P.C., 2003. Factors influencing the formation and relative distribution of
6 haloacetic acids and trihalomethanes in drinking water. *Environ. Sci. Technol.* 37, 2920-2928.
7
8 Najm, I., Tate, C., Selby, D., 1998. Optimizing enhanced coagulation with PAC: a case study.
9 *J.- Am. Water Works Assoc.* 90, 88-95.
10
11 Najm, I., Snoeyink, V.L., Lykins Jr., B.W., Adams, J.Q., 1991. Using powdered activated
12 carbon: A critical review. *J.- Am. Water Works Assoc.* 83, 65-76.
13
14 Najm, I., Snoeyink, V.L., Suidan, M.T., Lee, C.H., Richard, Y., 1990. Effect of particle size
15 and background natural organics on the adsorption efficiency of PAC. *J.- Am. Water Works*
16 *Assoc.* 82, 65-72.
17
18 Obolensky, A., Singer, P.C., 2005. Halogen substitution patterns among disinfection
19 byproducts in the Information Collection Rule database. *Environ. Sci. Technol.* 39, 2719-
20 2730.
21
22 Pelekani, C., Newcombe, G., Snoeyink, V.L., Hepplewhite, C., Asemi, S., Beckett, R., 1999.
23 Characterisation of natural organic matter using high performance size exclusion
24 chromatography. *Environ. Sci. Technol.* 33, 2807-2813.
25

1 Reckhow, D.A., Platt, T.L., MacNeill, A.L., McClellan, J.N., 2001. Formation and
2 degradation of dichloroacetonitrile in drinking waters. *J. Water Supply: Res. Technol –*
3 *AQUA*, 50, 1-13.
4
5 Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007.
6 Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-
7 products in drinking water: A review and roadmap for research. *Mutat. Res.* 636, 178-242.
8
9 Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S., Genceli, E.A., 2007. Disinfection by-products
10 precursors removal by enhanced coagulation and PAC adsorption. *Desalination*, 216, 334-
11 344.
12
13 Westerhoff, P., Chao, P., Mash, H., 2004. Reactivity of natural organic matter with aqueous
14 chlorine and bromine. *Water Res.* 38, 1502-1513.
15