***N*-nitrosodimethylamine and trihalomethane formation and minimisation in Southeast Queensland drinking water**

Nicole Knight^{1*}, Kalinda Watson¹, Maria José Farré², Glen Shaw¹

¹*Smart Water Research Centre, Griffith University, Southport, 4215, Queensland, Australia*

²*Advanced Water Management Centre, University of Queensland, 4072, Queensland, Australia*

*Corresponding author: Ph: +61 7 5552 7817 F: +61 7 555 27831 E: n.knight@griffith.edu.au

Abstract

This study assesses the prevalence of disinfection by-product (DBPs) precursors in some Southeast Queensland drinking water sources by conducting formation potential experiments for the four regulated trihalomethanes (THMs), and the potent carcinogen, *N*-nitrosodimethylamine (NDMA). NDMA formation potentials were consistently low (<5 – 21 ng/L), and total THMs (tTHMs) formation potentials were consistently below the Australian Drinking Water Guideline (250 µg/L). NDMA concentration of finished drinking waters was also monitored, and found to be <5 ng/L in all cases.

The effect of coagulation and advanced oxidation on the formation of NDMA and THMs is also reported. UV/H₂O₂ pre-treatment was effective in producing water with very low THMs concentrations, and UV irradiation was an effective method for NDMA degradation. H₂O₂ was not required for the observed NDMA degradation to occur. Coagulation using alum, ferric chloride or poly(diallyldimethylammonium chloride) (polyDADMAC) was ineffective in removing DBPs precursors from the source water studied, irrespective of the low dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) attained. Rather, coagulation with polyDADMAC caused an increase in NDMA formation potential upon chloramination, and all coagulants led to an increased tTHMs formation potential upon chlorination, due to the high bromide concentration of the source water studied.

Keywords

Advanced oxidation, brominated THMs, coagulation, disinfection by-products, formation potential.

1.0 Introduction

The presence of NDMA in certain foods, beverages and other consumer products (for example; processed meats and beer) has been known for some time (Jakszyn and Gonzalez 2006) and it has also been identified as a contaminant in groundwater (from rocket fuel). However, more recently it has been identified as a by-product arising primarily from chloramination, although it can also be formed in chlorinated waters which contain an appropriate source of amine precursors (World Health Organisation 2006). The formation potential and prevalence of NDMA in Southeast Queensland drinking waters has not previously been reported.

The precursors for NDMA formation are still yet to be adequately defined. Dimethylamine, which is a known NDMA precursor, was found in a study investigating NDMA precursors in natural waters to account for only a small amount of the NDMA actually produced (Gerecke and Sedlak 2003). Natural organic matter (NOM) encompasses a significant portion of the remaining precursors, however, this source did not account for the total NDMA formed by chloramination of the waters studied (Gerecke and Sedlak 2003). Further sources of NDMA precursors may arise from organic polymeric coagulants such as polyDADMAC, which can be used in the water treatment process (Wilczak, Assadi-Rad *et al.* 2003) PolyDADMAC can form NDMA upon exposure to chloramines although much lower NDMA concentrations are formed by chlorination of this resin (Mitch, Sharp *et al.* 2003; Park, Wei *et al.* 2009).

THMs precursors are encompassed by NOM and halides available in the source water. While coagulation is utilised during water treatment to lower NOM in finished drinking waters, specific processes to remove halides is uncommon. While chloroform is often the most prevalent of all the THMs, it's brominated or iodinated counterparts can be formed under circumstances when these halides are present in the source water, often arising from salt water intrusion (Richardson, Plewa *et al.* 2007). The Australian context has potential for regions with increased Br-THMs and I-THMs concentrations, due to the often high salinity of source waters and low rainfall of many catchments.

The aim of this study is to monitor NDMA and THMs formation potentials for a number of Southeast Queensland drinking water sources, thereby understanding the concentrations and prevalence of the precursors to these DBPs present in this environment. In addition, this work investigates advanced oxidation and coagulation strategies in terms of their effect on NDMA and THMs formation in a prospective, salinity impacted, Southeast Queensland drinking water source.

2.0 Experimental

2.1 Sampling sites and frequency

A major focus of this study was on Teviot Brook and Logan River, in Southeast Queensland (figure 1). These waterways were chosen because of the recent development of the Wyaralong dam (under construction at the time of this study) on Teviot Brook. Water stored in this dam would be extracted for treatment after flowing into the Logan River. This dam would be expected to provide improved water supply to the inland region of Southeast Queensland, however, limited information on DBPs formation and minimisation arising from the various possible water disinfection

strategies is available. For this reason, Teviot Brook waters were chosen for all advanced oxidation and coagulation experiments. Sites sampled in this region are described as sites 1 to 4 (figure 1). Sites 1 and 2 are on Teviot Brook, with site 1 being inside the flood area of the dam, and site 2 being downstream of the dam's location. Sites 3 and 4 are on Logan River, with site 3 being the point at which water stored in Wyaralong dam will be extracted for treatment and distribution. Site 4 is downstream of this location.

In addition to the above four sampling sites, NDMA and THMs formation potential experiments and direct NDMA measurements were taken from five Southeast Queensland water treatment plants (WTPs); three chloramination plants (pre-chlorination followed by ammonia dosing) referred to as A-WTP, B-WTP and C-WTP, one chlorination plant, referred to as D-WTP, and one ozonation/chlorination plant, referred to as E-WTP. The actual WTP names are de-identified for confidentiality reasons.

These WTPs encompass the major drinking water supplies for the Brisbane region, as well as Brisbane's northern and southern coastal districts (Gold Coast and Sunshine Coast). A single sampling site on the Mary River at Traveston Crossing was also studied (site 5), because this site has been considered for inclusion of an additional dam for the fast-growing Southeast Queensland region. Each WTP was sampled at least 4 times, fortnightly, with the exception of E-WTP, which was sampled monthly, from June – September 2009. Sampling for A-WTP, B-WTP and C-WTPs was undertaken from February – April 2009, whereas sampling for D-WTP took place from October – December 2009. Sites 2 and 4 were sampled at least four times over the period from May - August 2009, with sites 1, 3 and 5 sampled twice over the same timeframe. Additional sampling took place at site 2 from September – November 2009 for use in all coagulation and advanced treatment experiments.

2.2 Sampling, preservation and storage

Grab samples were taken in all cases apart from A-WTP, in which case some 24 hr composite samples were taken. All samples for NDMA experiments were transported and stored in 1L amber glass bottles at 4 °C until use, and processed within two weeks of the sampling date. Samples for THMs experiments were transported and stored in 500 mL amber glass bottles at 4 °C, with Teflon lined screw-caps to protect against the loss of volatile THMs. Bottles were completely filled, leaving no headspace. Samples to be used for NDMA or THMs formation potential experiments were taken from before the disinfection stage of water treatment unless otherwise specified, and were not dosed with dechlorinating agent. All samples for direct NDMA or THMs analysis were dosed with 100 mg/L Na_2SO_3 or $\text{Na}_2\text{S}_2\text{O}_4$ to remove residual chlorine and prevent further DBPs formation. Sample bottles for NDMA and THMs analysis were detergent-washed, then rinsed with purified water and finally washed in acetone and dried prior to use. Samples for DON, DOC and total organic carbon (TOC) analyses were stored in high-density polyethylene (HDPE) bottles at -20 °C without preservative until such time as they were analysed.

2.3 Reagents

Chemicals were obtained from the following sources and used without further purification: Merck; KH_2PO_4 ($\geq 99\%$), Na_2HPO_4 ($\geq 99\%$), NH_4Cl ($\geq 99.8\%$), Na_2SO_3 ($\geq 95\%$), dichloromethane ($\geq 99.9\%$), methanol ($\geq 99.8\%$), acetone ($\geq 99\%$), Scharlau; anhydrous sodium sulphate ($\geq 99\%$), Novachem; Nitrosamine stock mixed standard (200 $\mu\text{g/mL}$ in the following nitrosamines; *N*-Nitrosodi-n-butylamine, *N*-Nitrosodi-n-propylamine, *N*-Nitrosodiethylamine, NDMA, *N*-Nitrosomethylethylamine, *N*-

Nitrosopiperidine, *N*-Nitrosopyrrolidine), NDMA-d₆ standard solution (1 mg/mL), LECO; SPE cartridges EPA-M521, Sigma-Aldrich; 1-decene ($\geq 99.5\%$), NaOCl ($\geq 4\%$), FeCl₃·6H₂O ($\geq 98\%$), polyDADMAC (20 % in H₂O), Al₂(SO₄)₃ (alum $\geq 98\%$), CaO ($\geq 98\%$) and H₂O₂ ($\geq 6\%$) K₂S₂O₈.

Purified water prepared by a Sartorius water purification system fitted with a UV light was used for all dilutions, solution preparation, and final glassware washing. Monochloramine and hypochlorite solutions were prepared fresh daily, and all stock solutions were stored at 4 °C. Free chlorine residual was quantified using the HACH, DPD powder pillows procedure, based on Standard Method 4500-Cl G for drinking water (Eaton 2005). Chloramine and free ammonia residual was determined using the HACH indophenol method (Harp 2001).

2.4 Water treatment procedures

THMs formation potentials were conducted under conditions attempting to replicate WTP conditions, while NDMA formation potentials were conducted using a large excess of disinfectant in all cases. This enabled measurement of a maximum NDMA formation potential (effectively a measurement of precursors present) and does not reflect what would be expected to occur under normal water treatment plant conditions (Mitch, Gerecke *et al.* 2003). This method was chosen because NDMA formation using simulated WTP conditions consistently formed NDMA concentrations of <5 ng/L.

2.4.1 Chlorination (for THMs formation potential)

Samples were thermally equilibrated to 22 °C then filtered through a GF/A filter paper. A final pH of 7.6 was attained by addition of 20 mM phosphate buffer into the 500 mL sample, as solid KH₂PO₄ and Na₂HPO₄. The final pH was measured using a Mettler Toledo pH meter. NaOCl solution was added at a dose of 3 mg/L and after mixing, the solution was allowed to react in sealed, amber glass bottles with no headspace for seven days. The temperature and disinfectant dose chosen was based on conditions at D-WTP. Water residence time is highly variable within the distribution system studied, ranging up to an expected maximum of 16 days. The seven day reaction time used here was chosen to reflect a moderate residence time experienced within this system. After this time, the free chlorine residual was measured then quenched by addition of 0.15 g Na₂SO₃. Free chlorine residuals were typically between 0.1 and 0.8 mg/L. Samples were stored at 4 °C in amber glass bottles with Teflon-lined screw caps, without headspace, until analysis. The conditions described here and in section 2.4.2 are intended to create simulated distribution system conditions (SDS), to the extent that it was possible.

2.4.2 Chloramination (for THMs formation potential)

Samples were treated as for section 2.4.1, however, rather than dosing with 3 mg/L chlorine, samples were dosed with 3.5 mg/L NaOCl followed by dosing with 0.95 mg/L NH₃ (2.99 mg/L NH₄Cl). The molar ratio of OCl⁻:NH₃ was approximately 1:1.2. Chloramine residual was measured prior to quenching with 0.15 g Na₂SO₃, and this was typically in the range 0.3 – 1.5 mg/L. The conditions of temperature, pH and disinfectant dose were modelled on conditions at C-WTP. As noted in section 2.4.1, the seven day reaction time was chosen to reflect a moderate residence time in the distribution system.

Monochloramine was formed *in situ* by adding ammonia to water dosed with hypochlorite, rather than pre-forming the monochloramine as for the NDMA formation potential experiments. This was also done to replicate conditions of chloramination at Southeast Queensland WTPs.

2.4.3 Chlorination (for maximum nitrosamine formation potential)

Samples were thermally equilibrated to 22 °C, then 20 mL was removed from each 1 L sample to give a volume of approximately 980 mL. Phosphate buffer was added as solid KH_2PO_4 and Na_2HPO_4 , to give a final concentration of 10 mM and a pH of 7. Once the buffer was dissolved, 20 mL of a 17 mM stock solution of NaOCl (made fresh by adding 3.46 mL of 36 000 mg/L NaOCl to pH 8 purified water in a volumetric flask to give a final volume of 100 mL) was added to each 980 mL sample to give a final concentration of 0.34 mM free chlorine. After mixing, these samples were reacted in sealed 1 L amber glass bottles at room temperature for seven days. After this time, the free chlorine residual was measured and each 1 L sample subsequently quenched with 2.5 g Na_2SO_3 (typical residual chlorine concentration was in the range 12 – 17 mg/L). Samples were stored at 4 °C in sealed, amber glass bottles until extraction and analysis. Stock hypochlorite solutions were regularly standardised to monitor degradation.

2.4.4 Chloramination (for maximum nitrosamine formation potential)

Samples were treated as for section 2.4.3, with the exception that rather than treating with NaOCl solution, each 980 mL sample was treated with 20 mL of 17 mM stock solution of monochloramine (made fresh daily by dissolving 107 mg solid NH_4Cl in pH 8 purified water, then slowly adding 3.46 mL of 36 000 mg/L NaOCl to the stirring solution and topping up with purified water in a volumetric flask to a final volume of 100 mL) giving a final monochloramine concentration of 0.34 mM. Chloramine residual was measured prior to quenching with 2.5 g Na_2SO_3 , and this was typically in the range 15 – 20 mg/L.

2.4.5 UV treatment

Filtered 1 L samples taken from site 2, with a known concentration of THMs (generated by chlorination of raw water) or nitrosamines (spiked into raw water) were subjected to a range of UV doses, and the change in DBPs concentration measured. UV irradiation doses used were: 5, 20, 40 and 60 mJ/cm^2 . This was achieved by circulating the sample through a sealed reactor past an Ultraviolet Technology of Australasia, LC 20 UV lamp, (operating pressure 552 kPa (80 psi)) emitting light at 254 nm for up to 6 minutes, after which the sample was stored in sealed amber glass at 4 °C until analysis. All experiments were undertaken in at least duplicate.

2.4.6 UV/ H_2O_2

Each advanced oxidation experiment included a primary step which was a H_2O_2 dose at a concentration in the range 0 - 30 mg/L, followed by a UV dose of 30 mJ/cm^2 (UV dose remained constant for all experiments). Filtered, 1 L samples from site 2 containing a known concentration of THMs (formed by chlorination) or nitrosamines (spiked into raw water) were subjected to this treatment at a number of H_2O_2 concentrations. Raw (not chlorinated) samples without THMs present were also treated as described, and the

effect of this treatment on their subsequent THMs formation potential examined. All advanced oxidation experiments were undertaken in at least duplicate.

2.4.7 Coagulation with lime softening

The three coagulants studied were $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (ferric chloride), $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (alum) and polyDADMAC. CaO (170 mg) was added to all 1 L samples to obtain a pH of 11, after which 30 mg/L of either ferric chloride or alum, or 3 mg/L polyDADMAC was added and the solution stirred for 2 minutes at 150 rpm, then stirred at 30 rpm for a further 30 mins. Site 2 source waters were used in all cases. The lime softening step described was necessitated by the high Ca^{2+} and Mg^{2+} concentration of this source water. The solution was then filtered through a GF/A glass fibre filter paper. After this procedure, aliquots of sample were taken for DOC and DON analysis. THMs and NDMA formation potential experiments were then conducted using the coagulant-treated water. THMs were formed by chlorinating as outlined in section 4.4.1, and NDMA was formed by chloraminating as outlined in section 4.4.4. All coagulation experiments were undertaken in at least duplicate.

2.5 Analytical methods and analysis

2.5.1 Nitrosamines

Nitrosamine analysis was conducted by first concentrating samples using solid phase extraction, then analysing by gas chromatography followed by chemical ionisation mass spectrometry (GCMS). The instrument used was a Finnigan Trace GC Ultra and Finnigan Trace DSQ mass spectrometer with ammonia chemical ionization, and the method employed was in accordance with USEPA method 521.1 (Munch and Bassett 2006). Each 1 L sample was concentrated 1000× to give a 1 mL extract. Two microlitre samples were splitless injected into the gas chromatograph at 250 °C. The column used was ZB-5MS (30 × 0.25 × 1.0). The initial temperature of the oven was 40 °C for 1 minute, then a ramp was programmed at 40 °C/minute to 265 °C. The final temperature was held for 5.4 minutes. Helium gas at 1 mL/minute was used as carrier gas. 99.99 % pure anhydrous ammonia gas was used in the mass spectrometer. Ammonia inlet pressure was 100 kPa and the reagent gas flow for chemical ionisation was 3.5 mL/minute. The method reporting limit was 5 ng/L, with the expanded uncertainty in the GCMS analysis being 2 ng/L, at a nitrosamine concentration of 10 ng/L. Expanded uncertainty was determined by injection of 111 replicates spiked with 10 ng/L nitrosamines, and calculating expanded uncertainty as two times the standard deviation between samples.

Quality controls employed were as outlined in USEPA method 521.1, and include extracting a blank (purified water), matrix blank (untreated source water), spike (purified water spiked with nitrosamine standard), and matrix spike (source water spiked with nitrosamine standard) with each batch of nitrosamine SPE extractions, as well as use of the internal standard method for determining analyte concentration, and use of the surrogate recovery method to ensure adequate extraction efficiency (≥ 70 %). Standard solutions were remade regularly.

2.5.2 Trihalomethanes

Trihalomethane analysis was conducted by purging the volatile organics directly from the aqueous sample and subjecting the volatilised component to gas chromatography-mass spectrometry, in accordance with USEPA method 524.2 revision 4.1 (Munch 1995). This was achieved using a Shimadzu QP2010 Plus GCMS with a Zebron ZB-624 column with dimensions 20m × 0.18 mm × 1.0 µM. The oven temperature was ramped from 40 °C (held for 2 minutes) to 200 °C at 10 °C/minute. The carrier gas (helium) pressure was programmed to maintain a constant velocity of 40 cm/second. Electron ionisation was employed at 70 V. The method reporting limit was 4 µg/L, and 1 µg/L for individual THMs. The uncertainty for the method was 10 %.

2.5.3 Nutrients and organic carbon

All nitrogen chemistries (ammonia, nitrogen oxides (NO_x) and total dissolved nitrogen (TDN)) were determined by a Lachat QC8000 Flow Injection Analyser, using methods described in Standard Methods for the Examination of Water and Wastewater (ammonia – section 4500-NH₃ H, nitrogen oxides – section 4500-NO₃ I and TDN section – 4500-P J) (Eaton 2005). DON was calculated by subtracting ammonia and NO_x from TDN. TOC (as non-purgeable organic carbon) was determined using a high temperature oxidation instrument (Elementar highTOC II). DOC was analysed as for TOC, with a pre-filtration step. TOC and DOC methods are as outlined in detail in Standard methods for the examination of water and wastewater, section 5310B (Eaton 2005). Ammonia, NO_x and TOC quality control samples were included in each run, (0.010, 0.070 and 0.80 mg/L as N for ammonia and NO_x, and 2.0 mg/L and 20 mg/L for TOC) and these remained within two standard deviations of the mean of >100 replicate quality control analyses at all times.

2.5.4 Hydrogen peroxide quantification

Residual H₂O₂ present after UV/H₂O₂ experiments was quantified spectrophotometrically using a Varian, Cary 50 UV-VIS spectrophotometer, by reacting the remaining hydrogen peroxide with metavanadate in acidic solution to give a coloured product with a maximum absorbance at 450 nm (Nogueira, Oliveira *et al.* 2005).

3.0 Results and discussion

3.1 NDMA and NDMA formation potential

Little information is available on NDMA concentrations and formation potentials in Australian drinking water, with no prior data having been collected for the Southeast Queensland region. NDMA formation potentials for all regions in this study remained between 5 – 21 ng/L in all cases (Table 1). In general, site 3 had a higher NDMA formation potential and DON concentration than site 4, and site 1 had a higher NDMA formation potential than site 2. The Teviot Brook sites (site 1 and site 2) often had a higher NDMA formation potential and DON than the Logan River sites (site 3 and site 4). The frequently observed decrease in NDMA formation potential as samples were taken

further downstream may reflect the dilution of NDMA precursors with increasing flow through the river system.

Dosing with high concentrations of free chlorine (as hypochlorite) did not give rise to NDMA concentrations > 5 ng/L in any case examined in this study. Therefore, all NDMA formation potentials reported here are based on reaction with monochloramine as disinfectant. Initial studies were based on treating source waters with the same disinfectant dose (chlorine or chloramine) and conditions as commonly employed in a typical Southeast Queensland water treatment plant (WTP), however, NDMA concentrations were consistently less than the method reporting limit (< 5 ng/L) for both chlorinated and chloraminated samples in this case. Therefore, the dose of monochloramine used for these experiments was a large excess compared to that which would actually be used within a WTP, and reported concentrations are in fact maximum formation potentials for these waters.

The actual NDMA concentrations leaving all WTPs studied here were < 5 ng/L at all times, as were the NDMA concentrations found in samples taken at the point of supply some distance down the distribution line, to allow time for NDMA formation to occur. One sample point at the point of supply was monitored for each WTP studied, and NDMA was not detected in any of these cases. Although NDMA was not detected in any 'real' treated drinking waters, the distribution system sampling was insufficient to thoroughly investigate NDMA formation throughout the entire system.

The increase in NDMA formation potential observed at site 2 (Table 1) correlates to an increase in DON concentration that occurred over the later part of the sampling period. This may reflect an increase in watershed runoff resulting from the higher rainfall that occurred in the catchment in the later months of sampling. This region had an approximate rainfall of 5 mm in the first month of sampling (August), followed by 22 mm and 38 mm in September and October respectively (Australian Government 2010). Teviot Brook is impacted by agricultural runoff, some industry discharge as well as wastewater effluent. During this study, DON at this site varied from 0.48 mg/L to 2.9 mg/L over the 6 months of monitoring, with the October samples having the highest concentrations of DON as well as the highest NDMA formation potentials (1.1 mg/L DON and 21 ng/L NDMA formation potential on 16/10/09 then 2.9 mg/L DON and 18 ng/L NDMA formation potential on 28/10/09).

An inverse relationship was found between the DOC/DON ratio and NDMA formation potential at site 2. Lee *et al.* have reported this relationship at a number of locations in the USA and France with the aim of correlating NDMA formation potential to the ratio between DOC/DON, based on the hypothesis that DON promotes the formation of nitrogenous DBPs (Lee, Westerhoff *et al.* 2007). It is suggested that DOC/DON ratios could be applied to estimate NDMA formation potential, however, while there was a loose relationship between these parameters in this case at site 2, it was not sufficient for use as a predictive indicator for NDMA formation potential due to the high error in the correlation. Lee *et al.* found similar margins of error in correlating these variables (Lee, Westerhoff *et al.* 2007). The relationship between DOC/DON ratio and NDMA formation potential for the other source waters studied was not applicable for regression analysis, due to the low correlation between parameters.

C-WTP provided an opportunity to examine the effect of pre-chlorination (prior to ammonia dosing) on NDMA formation potential. At the time of sampling, one bank of filters was pre-chlorinated, while a second bank of filters was not dosed with chlorine.

This enabled NDMA formation potentials to be measured for the same source water, under these different conditions. The NDMA formation potentials were lowered with pre-chlorination in this system (figure 2). This has been documented elsewhere (Schreiber and Mitch 2005), and may be attributed to chlorine oxidation of NDMA precursors prior to the addition of ammonia and subsequent formation of chloramines. This effect has been observed to be dependent on free chlorine contact time (Charrois and Hrudey 2007).

D-WTP uses polyDADMAC after alum dosing to attain low DOC levels in the finished water. The combination of polyDADMAC with other, inorganic coagulants such as alum can potentially lead to DOC and DON levels significantly lower than either coagulant is capable of delivering on its own at an equivalent dose (Lee and Westerhoff 2006). This has been suggested to be because the polymer can act as a bridge between the polar NOM molecules and the surface of the aluminium hydroxide formed upon dissolving alum in neutral or alkaline water, leading to easy precipitation (Montgomery 1985; Lurie and Rebhun 1997). Despite the improved coagulation efficiency possible through using this combination of primary coagulant and coagulant aid, there is a risk of forming NDMA during the disinfection process because polyDADMAC is known to contain NDMA precursors which may be leached into the water during treatment (Park, Wei *et al.* 2009)

D-WTP uses chlorination alone as the disinfectant, and this could be instrumental in their having NDMA levels < 5 ng/L in the finished water over the sampling period in this study. However, in order to examine the effect source water exposure to polyDADMAC had on NDMA formation potential, samples were taken immediately prior to polyDADMAC dosing (after alum dosing), as well as immediately after polyDADMAC dosing, and their formation potentials compared to that of the raw source water.

The raw water and water treated with alum consistently had comparable NDMA formation potentials across the four month sampling period, however, the water which had been exposed to polyDADMAC was found to have an approximately 3-fold increase in NDMA formation potential, relative to unexposed source water (figure 3). Although D-WTP uses chlorination, thereby minimising NDMA formation in the finished water, the introduction of the Southeast Queensland water grid potentially creates a situation in which polyDADMAC exposed water from D-WTP is transported through the grid, via disinfectant conversion stations, which convert the disinfectant residual from chlorine to chloramine. This scenario could enable significant NDMA formation.

3.2 THMs and THMs formation potential

In general, the tTHM formation potentials obtained indicated that chlorination gives rise to greater THM concentrations than chloramination (figure 4). This is well known, and has provided one of the motivations behind the move from chlorine to chloramine in modern water treatment (LeBel, Benoit *et al.* 1997; USEPA 2001). Regardless, chlorination of raw source waters still led to tTHM concentrations below the Australian Drinking Water Guidelines for all southeast Queensland regions examined in this study (note that the Australian Drinking Water Guidelines for THMs are comparatively high with respect to many other countries, at 250 µg/L). There was no discernable correlation between DOC and tTHM formation potential over the time studied (Table 2). This may be due to variability in the bromide ion concentration between the various source waters. That is, the observed Br-THM formation would be expected to be related to the Br:DOC ratio, rather than simply the DOC concentration alone, although this was not extensively monitored during this study.

The two sites on Logan River (sites 3 and 4) had tTHM formation potentials and DOC concentrations similar to each other throughout the sampling campaign. The tTHM formation potentials at the Teviot Brook sites were generally higher at site 1 than site 2. Sites 1 and 2 often had higher DOC concentrations than sites 3 and 4, and also tended to have higher tTHMs formation potentials from chloramination, although the tTHMs formation potentials from chlorination did not exhibit any clear trend. Again, tTHM formation potential and DOC concentration tended to decrease from sites 1 to 4, possibly due to increased dilution of solutes with increasing flow downstream.

The collated data for tTHMs formation potentials for all sites is presented in Table 2. Actual tTHMs concentrations in finished waters did not exceed the Australian Drinking Water Guidelines at any of the WTPs discussed here over the sampling period studied. The Teviot Brook, Logan River and Mary River sites (sites 1 – 5) are all unimpeded streams, therefore the observed variability in THMs formation potential as well as organic content is likely to be greater than what would be experienced in dams placed on these waterways. Some variation in THMs formation potential is inevitably observed due to changing seasonal conditions, particularly temperature and rainfall, although a comprehensive study of seasonal variability was outside the scope of the sampling campaign.

The mean distribution of the concentrations of the four regulated THMs for the sites studied are shown in figures 5 and 6. These graphs show the high concentration of THMs in chlorinated waters compared with chloraminated waters, as well as the relatively high concentration of brominated THMs formed from site 1 and 2 source waters. This is particularly evident in the chloraminated example (figure 6), in which the proportion of brominated THMs is much greater than for any of the remaining sites. This is a reflection of the high Br:DOC ratio of the source water (between 0.29 mg/L – 0.81 mg/L at site 2).

3.3 Degradation of NDMA and THMs by means of UV and UV/H₂O₂

3.3.1 NDMA

Samples were taken from site 2 on two different dates (two weeks apart) after which they were spiked with NDMA (120 ng/L) and subsequently exposed to variable doses of UV radiation, in the absence of any other oxidant. These duplicates provided reproducible results, and the resulting decay curve for NDMA degradation with increasing UV dose had an $R^2 = 0.96$ (figure 7). Notably, the UV dose range studied is comparable to that used for UV disinfection, and this dose range is also quite efficient in causing NDMA degradation. Specifically, a UV dose of 60 mJ/cm² degraded approximately 42 % of the NDMA present. Thus, for low concentrations of NDMA present as a drinking water contaminant, UV radiation may be an effective corrective measure. This observation is in agreement with previously reported findings (Mitch, Sharp *et al.* 2003).

Hydrogen peroxide is not required to achieve the observed NDMA degradation, nor does its presence improve the degree of NDMA degradation (figure 8). A significant decrease in NDMA concentration upon UV dosing was observed (30 mJ/cm² over 4 minutes) however, in this case, the UV dose was kept constant, and a variable hydrogen peroxide dose applied. Hydrogen peroxide doses from 0 mg/L to 30 mg/L did not have a measureable degradation affect on the NDMA present. Previously published work concluded that light-screening by H₂O₂ may in fact decrease the NDMA removal by UV

irradiation for optical path lengths typical of those found in UV reactors (Sharpless and Linden 2003).

3.3.2 THMs

Preliminary experiments were conducted in order to assess the effectiveness of UV/H₂O₂ in destroying THMs already formed in solution. Total THMs concentrations which were formed from chlorination or chloramination of site 2 raw water were not lowered by irradiating the sample with UV light up to a dose of 60 mJ/cm², either on its own or in conjunction with H₂O₂ up to a concentration of 30 mg/L (data not shown). That is, the doses of UV and H₂O₂ used in this study under the conditions described are not capable of destroying or degrading THMs themselves, and the concentration of tTHMs remained essentially constant between samples regardless of UV or H₂O₂ dose.

3.4 Reduction of THMs formation potential by UV and UV/H₂O₂

The destruction of THMs precursors by pre-treatment with UV/H₂O₂, followed by chlorination or chloramination was examined in order to assess the ability of these methods to lower THMs formation potential. A constant UV dose of 30 mJ/cm² was applied to the samples used for THMs analysis shown in figure 9, unless otherwise indicated. This UV dose was chosen to reflect typical UV doses employed for water disinfection (30 – 50 mJ/cm²) (Malcolm Pirnie 2003). These samples were taken from site 2, treated with either photolysis (UV) or advanced oxidation (UV/H₂O₂) with variable H₂O₂ concentration, then disinfected with chlorine or chloramine after the photolysis/advanced oxidation process, to determine the effect of these pre-treatment processes on removing THMs precursors and thus leading to lower THMs formation potential upon chlorination or chloramination.

UV irradiation alone removed some THMs precursors, and this was enhanced by addition of hydrogen peroxide (figure 9). A higher UV dose may be an alternative to the addition of hydrogen peroxide in attaining very low THMs formation potentials, however, this was not explored. These experiments illustrated a hydrogen peroxide dose of 5 mg/L was sufficient to reduce the THMs formation potential to < 10 µg/L. The reduction in tTHM formation potential ranged from 10.5 - 43.5% after UV irradiation pre-treatment. Dosing with H₂O₂ after UV irradiation lowered the tTHM formation potential further, with a >95% reduction after exposure to a 30 mg/L H₂O₂ dose.

3.5 Coagulation

The optimum pH for coagulation using alum is in the range 5.8 – 6.5, while ferric chloride is most effective at a higher pH (7.5 – 8.0) (Gebbie 2006). The organic coagulant PolyDADMAC operates well over a wide pH range (Gebbie 2006). The aim of these experiments was to determine the effectiveness of these commonly used coagulants under conditions of high pH, such as would be preferred in the treatment of water sourced from Teviot Brook (site 2 water was used for these experiments). The relationship between DON and DOC removal efficiency and the formation potential for both tTHMs and NDMA was then assessed.

Alum and FeCl₃ were shown to have very similar performance in lowering DOC and DON under these conditions (figure 10). Specifically, alum removed a mean of 55 % DOC and 80 % DON, while FeCl₃ removed a mean of 60 % of DOC and 82 % DON (duplicate samples taken two weeks apart). However, regardless of the highly effective removal of

organic nitrogen, there was no reduction in NDMA formation potential in samples having been exposed to coagulant (figure 11). This implies that the NDMA precursors present in the source water are not amenable to coagulation by these methods. A factor responsible for the lack of success in removing the organic DBPs precursors in these experiments may be their low molecular weight, which is understood to be the weight fraction least amenable to coagulation by traditional methods (Smith, Botica *et al.* 2001). FeCl_3 , alum and polyDADMAC tend to preferentially remove the highest molecular weight fraction of DOC and DON, and are less efficient at removing the low molecular weight fraction (Lee and Westerhoff 2006; Yan, Wang *et al.* 2006).

PolyDADMAC was found to lower DOC by a mean of 39 %, and lower DON by a mean of 75 % (duplicate samples taken two weeks apart). There was greater variability in the DON and DOC removal between replicates using polyDADMAC than was experienced with the other two coagulants (figure 10) however, the meaningfulness of this is unclear, given the small number of replicate samples measured. A much smaller dose of polyDADMAC is required relative to alum or FeCl_3 . PolyDADMAC has been shown previously to react in the presence of monochloramine to form NDMA (Park, Wei *et al.* 2009). The results of this work agree with this finding, with the NDMA formation potential of polyDADMAC exposed water increasing to approximately six times the NDMA formation potential of the untreated source water (figure 11). Despite the high efficiency of polyDADMAC in lowering DON and moderate efficiency in lowering DOC, this is not reflected in the measured NDMA or THMs formation potentials. Indeed, polyDADMAC is itself a significant source of NDMA precursors.

THMs formation potential (determined by chlorination) did not consistently decrease in samples which had been exposed to any of the coagulants tested, despite the large reduction in DOC achieved (figures 10 and 12). Total THMs formation potential generally increased with decreasing DOC over the duplicate analyses undertaken, in which site 2 waters sampled on two separate occasions were treated with coagulant to generate samples of variable DOC concentration, prior to chlorination (figures 13a and 13b). The tTHMs formation potential discussed here is expressed as a concentration by weight ($\mu\text{g/L}$), and in general this increases with decreasing DOC as the more highly brominated THMs increase in concentration. The tTHMs formation potential expressed as a molar concentration (sum of the molar concentration of the four THMs) also showed a general trend that the highest molar concentration of tTHMs tended to occur at the lowest concentrations of DOC (data not shown). This indicates that the increase in tTHMs formation potential is not simply a reflection of the higher molecular weight of bromine relative to chlorine, but represents, in general, an overall increase in molar concentration of tTHMs with coagulation, in this high bromide source water.

This data opposes the common research finding that tTHMs formation potential decreases with DOC (Uyak and Toroz 2005; Uyak, Yavuz *et al.* 2007), and is explained by the high bromide concentration present in the Teviot Brook source water (0.29 mg/L – 0.81 mg/L measured during this study, although this was not consistently monitored). This high bromide concentration allowed the formation of high concentrations of brominated THMs upon removal of organic material prior to oxidation (Rathbun 1996; Westerhoff, Song *et al.* 1998), due to the resultant increase in the Br:DOC ratio. Although a search of the literature found examples of Br-THMs concentrations increasing upon chlorination after coagulation (Black 1996), to the extent of the authors' knowledge, an overall increase in tTHMs concentration as a result of chlorination after coagulation has not previously been reported.

These experiments conclude that while coagulation using alum, FeCl_3 or polyDADMAC is effective at lowering DOC and DON, these coagulants had no effect on lowering the tTHMs or NDMA formation potential of the source water studied, and there was actually a general increase in tTHMs formation potential (from chlorination) as a result of coagulation (figure 12) arising from the high bromide concentration of the source water, as well as an increase in NDMA formation potential when polyDADMAC was used (figure 11).

Bromide concentrations tend to be higher in times of low flow (higher salinity). Conversely, DOC concentrations tend to be lower at times of low flow (decreased runoff). The combination of high bromide concentration and low DOC in this source water at times of low rainfall has the potential to form high concentrations of brominated DBPs upon disinfection, such as Br-THMs from chlorination and bromate from ozonation.

Oxidation of Br^- to the reactive species, BrO^- , is required for Br-THMs formation to occur. This is readily achieved by ozone or hypochlorite (ClO^-) during water disinfection (Pinkernell and von Gunten 2001; Buffle, Galli *et al.* 2004). However, DOC competes with Br^- for oxidant during disinfection, therefore higher DOC waters will form lower concentrations of BrO^- , and therefore lower Br-THMs, for a given Br^- concentration (Rathbun 1996; Westerhoff, Song *et al.* 1998; Ichihashi, Teranishi *et al.* 1999). When DOC concentration is lowered by coagulation, Br^- competes more effectively for oxidant, and therefore forms a higher concentration of BrO^- . Although BrO^- can react directly with DOC to form organobromine by-products including Br-THMs, ClO^- has a greater oxidation potential than BrO^- , while BrO^- has a greater rate of electrophilic substitution than ClO^- (Kristiana 2010). That is, Br-THMs formation is maximised by ClO^- oxidation of DOC to yield CHCl_3 , followed by sequential electrophilic substitution by BrO^- to form the Br-THMs. A higher BrO^- concentration will give rise to greater concentrations of the more highly brominated THMs. Given that BrO^- forms only to the extent that it can compete for oxidant with DOC, BrO^- formation will be inversely proportional to DOC concentration, therefore the more highly brominated THMs would also be expected to vary inversely with DOC (figures 13a and 13b).

Although more highly chlorinated THMs will tend to be lowered by lowering DOC concentration prior to addition of oxidant, Br-THMs tend to be increased. Consequently, an overall increase in tTHMs was often observed as a result of coagulation in this case, due to the more highly brominated THMs increasing in concentration to a greater extent than the more chlorinated THMs decrease in concentration (figures 13a and 13b). Thus, in low bromide waters a decrease in tTHMs with decreasing DOC is typically observed, and in high bromide waters an increase in tTHMs with decreasing DOC may occur.

4.0 Conclusions

NDMA was not found in any potable water samples taken during the one year of this study. Treated water leaving the WTPs consistently had NDMA < 5 ng/L. The prevalence of NDMA formation within the distribution system was not thoroughly addressed here, however, one sample point some distance down the distribution line of each WTP studied was monitored several times over the duration of the sampling campaign, and these consistently had NDMA concentrations < 5 ng/L.

NDMA formation potentials determined by excess chlorination of all raw source waters did not give rise to measureable NDMA concentrations (< 5 ng/L) in any case. NDMA formation potentials from excess chloramination of all source waters were consistently between 5 – 21 ng/L. These results suggest finished waters from Southeast Queensland WTPs are unlikely to require additional treatment to adhere to the proposed Australian Drinking Water Guideline value of 100 ng/L for NDMA. NDMA formation potentials were found to be lowered by longer free-chlorine contact times prior to the addition of ammonia.

THMs formation potential experiments confirmed that chlorination forms higher concentrations of THMs than chloramination, and that THMs formation potentials consistently adhered to the Australian Drinking Water Guideline value for tTHMs (250 μ g/L).

Photolysis experiments found that UV irradiation at a dose similar to that used for disinfection (UV dose of up to 60 mJ/cm^2) was effective in reducing existing NDMA concentrations in raw water. This outcome did not require H_2O_2 and the degree of NDMA destruction was not improved by the presence of H_2O_2 . Therefore, UV disinfection would be expected to be sufficient to remove low levels of NDMA present as a contaminant in treated waters.

THMs were not destroyed by either UV radiation or UV in conjunction with H_2O_2 . Their concentration remained essentially constant in chlorine or chloramine disinfected water irrespective of advanced treatment. However, application of advanced treatment (UV or UV/ H_2O_2) to raw waters prior to disinfection was very effective in removing THMs precursors, and subsequent THMs formation was low. Irrespective of whether the ensuing treatment was chlorination or chloramination, at H_2O_2 concentrations of 5 mg/L and UV dose of 30 mJ/cm^2 , the THMs formation potentials were similarly low (approximately 10 μ g/L). Pre-treatment by advanced oxidation may be an excellent means of reducing tTHMs levels in regions with particular difficulties minimizing these compounds.

DBPs minimization by coagulation using alum, ferric chloride or polyDADMAC proved to be ineffective using Teviot Brook source waters. Although a notable decrease in DOC and DON was achieved with these coagulants, the NDMA formation potential of the treated water remained constant with and without coagulation, except in the instance of coagulating with polyDADMAC, in which case the NDMA formation potential was dramatically increased. Importantly, polyDADMAC did not cause a detectable increase in NDMA formation potential when reacted with chlorine, rather, the increase in NDMA formation potential was exclusive to reaction with chloramine. In support of this, D-WTP, which uses polyDADMAC in the treatment process and chlorine as the disinfectant, had consistently undetectable NDMA in the finished water over the four month sampling period (< 5 ng/L).

Although it is commonly found that lowering DOC leads to lower tTHMs (Rathbun 1996; Westerhoff, Song *et al.* 1998; Ichihashi, Teranishi *et al.* 1999) this was not the case using site 2 waters due to its high bromide concentration. These high bromide waters exhibited an increased tTHMs formation potential from coagulation/chlorination despite a significantly lowered DOC concentration. This arises as a consequence of DOC and bromide competing for chlorine, therefore forming higher Br-THMs formation in lower DOC waters. When bromide levels are sufficiently high, coagulation will lead to an increase in tTHMs concentration upon chlorination.

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Fig. 1 Map showing sampling sites 1–4 surrounding the Wyaralong dam site. All sampling was undertaken prior to the completion of the construction of the dam; therefore, Teviot Brook was an unimpeded stream

Table 1 Maximum NDMA formation potentials (fp) arising from chloramination for all raw waters sampled during this study are shown, along with the DON concentration for each sample

<i>Sampling site</i>	<i>Parameters measured</i>	<i>Sampling events</i>				
		<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>
<i>Site 1</i>	NDMA fp (ng/L)	17	-	9	-	-
	DON (mg/L)	0.5		0.4		
<i>Site 2</i>	NDMA fp (ng/L)	7	5	6	21	18
	DON (mg/L)	0.3	0.5	0.6	1.1	2.6
<i>Site 3</i>	NDMA fp (ng/L)	6	-	13	-	-
	DON (mg/L)	0.6		0.5		
<i>Site 4</i>	NDMA fp (ng/L)	<5	5	9	12	6
	DON (mg/L)	0.2	0.3	0.3	0.4	0.5
<i>Site 5</i>	NDMA fp (ng/L)	-	-	-	11	11
	DON (mg/L)				0.5	0.3
<i>A-WTP</i>	NDMA fp (ng/L)	8	-	9	6	7
	DON (mg/L)	-	-	-	-	-
<i>B-WTP</i>	NDMA fp (ng/L)	-	12	18	11	12
	DON (mg/L)	-	-	-	-	-
<i>C-WTP</i>	NDMA fp (ng/L)	13	11	11	10	10
	DON (mg/L)	-	-	-	-	-
<i>D-WTP</i>	NDMA fp (ng/L)	-	16	8	9	10
	DON (mg/L)		0.2	0.3	0.2	0.3
<i>E-WTP</i>	NDMA fp (ng/L)	-	5	8	8	6
	DON (mg/L)		<0.1	0.2	0.1	0.2

Headings 1–5 indicate separate sampling events. Site 2, site 4, A-WTP, B-WTP, C-WTP and D-WTP were all sampled fortnightly, while all other sites listed were sampled monthly NA Data not available

Fig. 2 NDMA formation potentials for C-WTP are shown for pre-chlorinated and unchlorinated samples. Pre-formed monochloramine was added to pH 7 buffered samples at 22°C, giving a final concentration of 0.34 mM. The reaction was quenched after 7 days

Fig. 3 NDMA formation potential for D-WTP source water is shown, with and without prior exposure to polyDADMAC. Pre-formed monochloramine was added to pH 7 buffered samples at 22°C giving a final concentration of 0.34 mM. The reaction was quenched after 7 days

Fig. 4 tTHM formation potentials arising from chlorination or chloramination of D-WTP source water are shown. Chlorine dose was 3 mg/L, and chloramination was performed by dosing with 3.5 mg/L NaOCl, then adding 2.99 mg/L NH₄Cl. The pH was buffered to 7.6, and temperature was 22°C. The reaction was quenched after 7 days

Table 2 tTHM formation potentials (fp) from chlorination or chloramination of all raw source waters examined in this study are shown, along with the DOC concentration of each sample

<i>Sampling site</i>	<i>Parameters measured</i>	<i>Disinfection method</i>	<i>Sampling events</i>			
			<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>
<i>Site 1</i>	tTHM fp (µg/L)	Chlorination	87	-	82	-
		Chloramination	47	-	78	-
	DOC (mg/L)		5.9	-	7.1	-
<i>Site 2</i>	tTHM fp (µg/L)	Chlorination	50	147	41	43
		Chloramination	26	49	51	24
	DOC (mg/L)		6.9	3.2	5.1	7.4
<i>Site 3</i>	tTHM fp (µg/L)	Chlorination	62	-	108	-
		Chloramination	14		14	
	DOC (mg/L)		4.6	-	3.1	-
<i>Site 4</i>	tTHM fp (µg/L)	Chlorination	62	151	112	59
		Chloramination	7	44	13	9
	DOC (mg/L)		4.2	3.3	3.4	3.3
<i>Site 5</i>	tTHM fp (µg/L)	Chlorination	-	-	78	113
		Chloramination			14	15
	DOC (mg/L)		-	-	2.2	3.3
<i>D-WTP</i>	tTHM fp (µg/L)	Chlorination	140	106	118	114
		Chloramination	14	17	8	10
	DOC (mg/L)		3.9	3.4	4.2	3.8
<i>E-WTP</i>	tTHM fp (µg/L)	Chlorination	55	26	77	80
		Chloramination	2	6	7	5
	DOC (mg/L)		1.4	1.7	1.3	1.1

Headings 1–4 indicate separate sampling events. Sampling occurred fortnightly for sites 2 and 4, and D-WTP, while all other sites listed were sampled monthly

Fig. 5 Mean concentrations of each of the four regulated THMs arising from chlorination for a number of source waters. Each site was sampled four times excluding site 5 (sampled twice). Chlorine dose was 3 mg/L, and contact time was 7 days at a temperature of 22°C and pH of 7.6

Fig. 6 Mean concentrations of each of the four regulated THMs arising from chloramination for a number of source waters. Each site was sampled four times excluding site 5 (sampled twice). Chloramination was performed by dosing with 3.5 mg/L NaOCl, then adding 2.99 mg/L NH₄Cl, then allowing 7 days contact time. The pH was buffered to 7.6, and temperature was 22°C

Fig. 7 Decay curve showing decreasing NDMA concentration with increasing UV dose. The samples were taken from site 2 and spiked with a mixed standard of nitrosamines prior to photolysis at 22°C and neutral pH

Fig. 8 The change in NDMA concentration with advanced oxidation treatment is illustrated. Samples were taken from site 2, then spiked with NDMA and treated with increasing concentrations of [H₂O₂], while the UV dose was held constant at 30 mJ/cm² for all samples except the first (untreated) replicates. H₂O₂ did not improve NDMA degradation over the concentration range examined, and this was consistent over the duplicates analyses shown. Sample temperature was 22°C, and pH was neutral

Fig. 9 The variation in tTHM formation potential with UV irradiation and increasing [H₂O₂], as a pre-treatment before chlorination or chloramination, is illustrated. Samples were taken from site 2. UV or UV/H₂O₂ pre-treatment was undertaken at neutral pH at 22°C

Fig. 10 DOC and DON are lowered by coagulation using polyDADMAC, FeCl₃ or alum. All samples were taken from site 2 and dosed with 170 mg/L of CaO prior to coagulant addition. Inorganic coagulants were applied at a dose of 30 mg/L, and polyDADMAC was applied at a dose of 3 mg/L. The solution was stirred for 32 min, then filtered and analysed for DOC and DON

Fig. 11 NDMA precursors were unaffected by the coagulation process, although polyDADMAC exposure led to an increased NDMA formation potential. All samples were taken from site 2 and dosed with 170 mg/L of CaO prior to coagulant addition. Inorganic coagulants were applied at a dose of 30 mg/L, and polyDADMAC was applied at a dose of 3 mg/L. After stirring and filtering, pre-formed monochloramine was added to pH 7 buffered samples at 22°C giving a final concentration of 0.34 mM, and this was quenched after 7 days of contact time

Fig. 12 tTHM formation potential before and after coagulation treatment is shown. All samples were taken from site 2, then dosed with 170 mg/L of CaO, prior to addition of coagulant. Inorganic coagulants were applied at a dose of 30 mg/L, and polyDADMAC was applied at a dose of 3 mg/L. After stirring and filtering, 3 mg/L chlorine was added (as NaOCl) to pH 7 buffered samples at 22°C and allowed to react for 7 days, prior to quenching and analysis

a **b**

Fig. 13 a The formation potential of four THMs as their concentration varies with DOC concentration after coagulation. Data shown is for water from site 2 sampled 16/10/2009. All samples were initially dosed with 170 mg/L of CaO prior to coagulant dosing. After stirring and filtering, 3 mg/L NaOCl was added to pH 7 buffered samples at 22°C, and this was reacted for 7 days prior to quenching. **b** The formation potential of four THMs as their concentration varies with DOC concentration after coagulation. Data shown is for water from site 2 sampled 28/10/2009. All samples were initially dosed with 170 mg/L of CaO prior to coagulant dosing. After stirring and filtering, 3 mg/L NaOCl was added to pH 7 buffered samples at 22°C, and this was reacted for 7 days prior to quenching